The Enzyme List
Class 4 — Lyases

Nomenclature Committee
of the
International Union of Biochemistry and Molecular Biology
(NC-IUBMB)

LaTeX version prepared by Andrew McDonald,
School of Biochemistry and Immunology, Trinity College Dublin, Ireland

Generated from the ExplorEnz database, May 2023

Contents

EC 4.1 Carbon-carbon lyases

This subclass contains the decarboxylases (carboxy-lyases; EC 4.1.1), the aldehyde-lyases, which catalyse the reversal of an aldol condensation (EC 4.1.2), the oxo-acid-lyases, which catalyse the cleavage of a 3-hydroxy acid (EC 4.1.3) and other carbon-carbon lyases (EC 4.1.99), or the reverse reactions.

EC 4.1.1 Carboxy-lyases

EC 4.1.1.1

Accepted name: pyruvate decarboxylase
Reaction: a 2-oxo carboxylate = an aldehyde + CO_2
Other name(s): α-carboxylase (ambiguous); pyruvic decarboxylase; α-ketoacid carboxylase; 2-oxo-acid carboxy-lyase
Systematic name: 2-oxo-acid carboxy-lyase (aldehyde-forming)
Comments: A thiamine-diphosphate protein. Also catalyses acyloin formation.
References: [1279]

[EC 4.1.1.1 created 1961]

EC 4.1.1.2

Accepted name: oxalate decarboxylase
Reaction: oxalate + H^+ = formate + CO_2
Other name(s): oxalate carboxy-lyase
Systematic name: oxalate carboxy-lyase (formate-forming)
Comments: The enzyme from *Bacillus subtilis* contains manganese and requires O_2 for activity, even though there is no net redox change.
References: [618, 1354, 1355]

[EC 4.1.1.2 created 1961]

[4.1.1.3 Transferred entry. oxaloacetate decarboxylase. Now recognized to be two enzymes EC 7.2.4.2 [oxaloacetate decarboxylase (Na$^+$ extruding)] and EC 4.1.1.112 (oxaloacetate decarboxylase).]

[EC 4.1.1.3 created 1961 as EC 4.1.1.3, modified 1986, modified 2000, deleted 2018]

EC 4.1.1.4

Accepted name: acetoacetate decarboxylase
Reaction: acetoacetate + H^+ = acetone + CO_2
Other name(s): acetoacetic acid decarboxylase; acetoacetate carboxy-lyase
Systematic name: acetoacetate carboxy-lyase (acetone-forming)
References: [293, 1548, 561]

[EC 4.1.1.4 created 1961]

EC 4.1.1.5

Accepted name: acetolactate decarboxylase
Reaction: (2*S*)-2-hydroxy-2-methyl-3-oxobutanoate = (3*R*)-3-hydroxybutan-2-one + CO_2
Other name(s): α-acetolactate decarboxylase; (*S*)-2-hydroxy-2-methyl-3-oxobutanoate carboxy-lyase; (*S*)-2-hydroxy-2-methyl-3-oxobutanoate carboxy-lyase [(*R*)-2-acetoin-forming]; (*S*)-2-hydroxy-2-methyl-3-oxobutanoate carboxy-lyase [(3*R*)-3-hydroxybutan-2-one-forming]
Systematic name: (2*S*)-2-hydroxy-2-methyl-3-oxobutanoate carboxy-lyase [(3*R*)-3-hydroxybutan-2-one-forming]
References: [553, 1309]

[EC 4.1.1.5 created 1961]

EC 4.1.1.6

Accepted name: *cis*-aconitate decarboxylase
Reaction: *cis*-aconitate = itaconate + CO_2
Other name(s): *cis*-aconitic decarboxylase; *cis*-aconitate carboxy-lyase; CAD1 (gene name); IRG1 (gene name)
Systematic name: *cis*-aconitate carboxy-lyase (itaconate-forming)
Comments: The enzyme has been characterized from the fungus *Aspergillus terreus* and from human macrophages. *cf.* EC 4.1.1.113, *trans*-aconitate decarboxylase.
References: [89, 343, 659, 937]

[EC 4.1.1.6 created 1961, modified 2018]

EC 4.1.1.7

Accepted name: benzoylformate decarboxylase
Reaction: phenylglyoxylate = benzaldehyde + CO_2
Other name(s): phenylglyoxylate decarboxylase; benzoylformate carboxy-lyase; benzoylformate carboxy-lyase (benzaldehyde-forming)
Systematic name: phenylglyoxylate carboxy-lyase (benzaldehyde-forming)
Comments: A thiamine-diphosphate protein.
References: [476]

[EC 4.1.1.7 created 1961]

EC 4.1.1.8

Accepted name: oxalyl-CoA decarboxylase
Reaction: oxalyl-CoA = formyl-CoA + CO_2
Other name(s): oxalyl coenzyme A decarboxylase; oxalyl-CoA carboxy-lyase
Systematic name: oxalyl-CoA carboxy-lyase (formyl-CoA-forming)
Comments: A thiamine-diphosphate protein.
References: [1112]

[EC 4.1.1.8 created 1961]

EC 4.1.1.9

Accepted name: malonyl-CoA decarboxylase
Reaction: malonyl-CoA = acetyl-CoA + CO_2
Other name(s): malonyl coenzyme A decarboxylase; malonyl-CoA carboxy-lyase
Systematic name: malonyl-CoA carboxy-lyase (acetyl-CoA-forming)
Comments: Specific for malonyl-CoA. The enzyme from *Pseudomonas ovalis* also catalyses the reaction of EC 2.8.3.3 malonate CoA-transferase.
References: [153, 1343]

[EC 4.1.1.9 created 1961, deleted 1972, reinstated 1978]

[4.1.1.10 Deleted entry. aminomalonate decarboxylase. Now included with EC 4.1.1.12, aspartate 4-decarboxylase]

[EC 4.1.1.10 created 1961, deleted 1972]

EC 4.1.1.11

Accepted name: aspartate 1-decarboxylase
Reaction: L-aspartate = β-alanine + CO_2
Other name(s): aspartate α-decarboxylase; L-aspartate α-decarboxylase; aspartic α-decarboxylase; L-aspartate 1-carboxy-lyase
Systematic name: L-aspartate 1-carboxy-lyase (β-alanine-forming)
Comments: The *Escherichia coli* enzyme contains a pyruvoyl group.
References: [1469]

[EC 4.1.1.11 created 1961, deleted 1972, reinstated 1984]

EC 4.1.1.12

Accepted name: aspartate 4-decarboxylase
Reaction: L-aspartate = L-alanine + CO_2
Other name(s): desulfinase; aminomalonic decarboxylase; aspartate β-decarboxylase; aspartate ω-decarboxylase; aspartic ω-decarboxylase; aspartic β-decarboxylase; L-aspartate β-decarboxylase; cysteine sulfinic desulfinase; L-cysteine sulfinate acid desulfinase; L-aspartate 4-carboxy-lyase
Systematic name: L-aspartate 4-carboxy-lyase (L-alanine-forming)
Comments: A pyridoxal-phosphate protein. Also catalyses the decarboxylation of aminomalonate (formerly listed as EC 4.1.1.10), and the desulfination of 3-sulfino-L-alanine to sulfite and alanine.
References: [653, 1016, 1048, 1470]

[EC 4.1.1.12 created 1961, modified 1976 (EC 4.1.1.10 created 1961, incorporated 1972)]

[4.1.1.13 Deleted entry. carbamoylaspartate decarboxylase]

[EC 4.1.1.13 created 1961, deleted 1972]

EC 4.1.1.14

Accepted name: valine decarboxylase
Reaction: L-valine = 2-methylpropanamine + CO_2
Other name(s): leucine decarboxylase; L-valine carboxy-lyase
Systematic name: L-valine carboxy-lyase (2-methylpropanamine-forming)
Comments: A pyridoxal-phosphate protein. Also acts on L-leucine.
References: [1324]

[EC 4.1.1.14 created 1961]

EC 4.1.1.15

Accepted name: glutamate decarboxylase
Reaction: L-glutamate = 4-aminobutanoate + CO_2
Other name(s): L-glutamic acid decarboxylase; L-glutamic decarboxylase; cysteic acid decarboxylase; L-glutamate α-decarboxylase; aspartate 1-decarboxylase; aspartic α-decarboxylase; L-aspartate-α-decarboxylase; γ-glutamate decarboxylase; L-glutamate 1-carboxy-lyase
Systematic name: L-glutamate 1-carboxy-lyase (4-aminobutanoate-forming)
Comments: A pyridoxal-phosphate protein. The brain enzyme also acts on L-cysteate, 3-sulfino-L-alanine and L-aspartate.
References: [22, 989, 1163]

[EC 4.1.1.15 created 1961]

EC 4.1.1.16

Accepted name: hydroxyglutamate decarboxylase

Reaction: 3-hydroxy-L-glutamate = 4-amino-3-hydroxybutanoate + CO_2

Other name(s): 3-hydroxy-L-glutamate 1-carboxy-lyase

Systematic name: 3-hydroxy-L-glutamate 1-carboxy-lyase (4-amino-3-hydroxybutanoate-forming)

Comments: A pyridoxal-phosphate protein.

References: [1410]

[EC 4.1.1.16 created 1961]

EC 4.1.1.17

Accepted name: ornithine decarboxylase

Reaction: L-ornithine = putrescine + CO_2

Other name(s): SpeC; L-ornithine carboxy-lyase

Systematic name: L-ornithine carboxy-lyase (putrescine-forming)

Comments: A pyridoxal-phosphate protein.

References: [1034, 1360]

[EC 4.1.1.17 created 1961]

EC 4.1.1.18

Accepted name: lysine decarboxylase

Reaction: L-lysine = cadaverine + CO_2

Other name(s): L-lysine carboxy-lyase

Systematic name: L-lysine carboxy-lyase (cadaverine-forming)

Comments: A pyridoxal-phosphate protein. Also acts on 5-hydroxy-L-lysine.

References: [422, 1288]

[EC 4.1.1.18 created 1961]

EC 4.1.1.19

Accepted name: arginine decarboxylase

Reaction: L-arginine = agmatine + CO_2

Other name(s): SpeA; L-arginine carboxy-lyase

Systematic name: L-arginine carboxy-lyase (agmatine-forming)

Comments: A pyridoxal-phosphate protein.

References: [102, 1126, 1360]

[EC 4.1.1.19 created 1961]

EC 4.1.1.20

Accepted name: diaminopimelate decarboxylase

Reaction: *meso*-2,6-diaminoheptanedioate = L-lysine + CO_2

Other name(s): diaminopimelic acid decarboxylase; *meso*-diaminopimelate decarboxylase; DAP-decarboxylase; *meso*-2,6-diaminoheptanedioate carboxy-lyase

Systematic name: *meso*-2,6-diaminoheptanedioate carboxy-lyase (L-lysine-forming)

Comments: A pyridoxal-phosphate protein.

References: [315]

[EC 4.1.1.20 created 1961]

EC 4.1.1.21

Accepted name: phosphoribosylaminoimidazole carboxylase

Reaction: 5-amino-1-(5-phospho-D-ribosyl)imidazole-4-carboxylate = 5-amino-1-(5-phospho-D-ribosyl)imidazole + CO_2

Other name(s): 5-phosphoribosyl-5-aminoimidazole carboxylase; 5-amino-1-ribosylimidazole 5-phosphate carboxylase; AIR carboxylase; 1-(5-phosphoribosyl)-5-amino-4-imidazolecarboxylate carboxy-lyase; ADE2; class II PurE; 5-amino-1-(5-phospho-D-ribosyl)imidazole-4-carboxylate carboxy-lyase

Systematic name: 5-amino-1-(5-phospho-D-ribosyl)imidazole-4-carboxylate carboxy-lyase [5-amino-1-(5-phospho-D-ribosyl)imidazole-forming]

Comments: While this is the reaction that occurs in vertebrates during purine biosynthesis, two enzymes are required to carry out the same reaction in *Escherichia coli*, namely EC 6.3.4.18, 5-(carboxyamino)imidazole ribonucleotide synthase and EC 5.4.99.18, 5-(carboxyamino)imidazole ribonucleotide mutase [384]. 5-Carboxyamino-1-(5-phospho-D-ribosyl)imidazole is not a substrate.

References: [856, 385, 384]

[EC 4.1.1.21 created 1961, modified 2000, modified 2006]

EC 4.1.1.22

Accepted name: histidine decarboxylase

Reaction: L-histidine = histamine + CO_2

Other name(s): L-histidine decarboxylase; L-histidine carboxy-lyase

Systematic name: L-histidine carboxy-lyase (histamine-forming)

Comments: A pyridoxal-phosphate protein (in animal tissues). The bacterial enzyme has a pyruvoyl residue as prosthetic group.

References: [363, 1152, 1169]

[EC 4.1.1.22 created 1961]

EC 4.1.1.23

Accepted name: orotidine-5′-phosphate decarboxylase

Reaction: orotidine 5′-phosphate = UMP + CO_2

Other name(s): orotidine-5′-monophosphate decarboxylase; orotodylate decarboxylase; orotidine phosphate decarboxylase; OMP decarboxylase; orotate monophosphate decarboxylase; orotidine monophosphate decarboxylase; orotidine phosphate decarboxylase; OMP-DC; orotate decarboxylase; orotidine 5′-phosphate decarboxylase; orotidylic decarboxylase; orotidylic acid decarboxylase; orotodylate decarboxylase; ODCase; orotic decarboxylase; orotidine-5′-phosphate carboxy-lyase

Systematic name: orotidine-5′-phosphate carboxy-lyase (UMP-forming)

Comments: The enzyme from higher eukaryotes is identical with EC 2.4.2.10 orotate phosphoribosyltransferase .

References: [646, 813, 907]

[EC 4.1.1.23 created 1961, modified 1986]

EC 4.1.1.24

Accepted name: aminobenzoate decarboxylase

Reaction: 4(or 2)-aminobenzoate = aniline + CO_2

Systematic name: aminobenzoate carboxy-lyase (aniline-forming)

Comments: A pyridoxal-phosphate protein.

References: [909]

[EC 4.1.1.24 created 1961]

EC 4.1.1.25

Accepted name: tyrosine decarboxylase

Reaction: L-tyrosine = tyramine + CO_2
Other name(s): L-tyrosine decarboxylase; L-(-)-tyrosine apodecarboxylase; L-tyrosine carboxy-lyase
Systematic name: L-tyrosine carboxy-lyase (tyramine-forming)
Comments: A pyridoxal-phosphate protein. The bacterial enzyme also acts on 3-hydroxytyrosine and, more slowly, on 3-hydroxyphenylalanine.
References: [911]

[EC 4.1.1.25 created 1961]

[4.1.1.26 Deleted entry. DOPA decarboxylase. Now included with EC 4.1.1.28 aromatic-L-amino-acid decarboxylase]

[EC 4.1.1.26 created 1961, deleted 1972]

[4.1.1.27 Deleted entry. tryptophan decarboxylase. Now included with EC 4.1.1.28 aromatic-L-amino-acid decarboxylase]

[EC 4.1.1.27 created 1961, deleted 1972]

EC 4.1.1.28

Accepted name: aromatic-L-amino-acid decarboxylase
Reaction: (1) L-dopa = dopamine + CO_2
(2) 5-hydroxy-L-tryptophan = 5-hydroxytryptamine + CO_2
Other name(s): DOPA decarboxylase; tryptophan decarboxylase; hydroxytryptophan decarboxylase; L-DOPA decarboxylase; aromatic amino acid decarboxylase; 5-hydroxytryptophan decarboxylase; aromatic-L-amino-acid carboxy-lyase (tryptamine-forming)
Systematic name: aromatic-L-amino-acid carboxy-lyase
Comments: A pyridoxal-phosphate protein. The enzyme also acts on some other aromatic L-amino acids, including L-tryptophan, L-tyrosine and L-phenylalanine.
References: [231, 847, 911, 1249, 1459]

[EC 4.1.1.28 created 1961 (EC 4.1.1.26 and EC 4.1.1.27 both created 1961 and incorporated 1972)]

EC 4.1.1.29

Accepted name: sulfinoalanine decarboxylase
Reaction: 3-sulfino-L-alanine = hypotaurine + CO_2
Other name(s): cysteine-sulfinate decarboxylase; L-cysteinesulfinic acid decarboxylase; cysteine-sulfinate decarboxylase; CADCase/CSADCase; CSAD; cysteic decarboxylase; cysteinesulfinic acid decarboxylase; cysteinesulfinate decarboxylase; sulfoalanine decarboxylase; 3-sulfino-L-alanine carboxy-lyase
Systematic name: 3-sulfino-L-alanine carboxy-lyase (hypotaurine-forming)
Comments: A pyridoxal-phosphate protein. Also acts on L-cysteate. The 1992 edition of the Enzyme List erroneously gave the name sulfoalanine decarboxylase to this enzyme.
References: [471, 611]

[EC 4.1.1.29 created 1961, deleted 1972, reinstated 1976, modified 1983, modified 1999]

EC 4.1.1.30

Accepted name: pantothenoylcysteine decarboxylase
Reaction: *N*-[(*R*)-pantothenoyl]-L-cysteine = pantetheine + CO_2
Other name(s): pantothenylcysteine decarboxylase; *N*-[(*R*)-pantothenoyl]-L-cysteine carboxy-lyase
Systematic name: *N*-[(*R*)-pantothenoyl]-L-cysteine carboxy-lyase (pantetheine-forming)
References: [143]

[EC 4.1.1.30 created 1961]

EC 4.1.1.31

Accepted name: phospho*enol*pyruvate carboxylase

Reaction: phosphate + oxaloacetate = phospho*enol*pyruvate + HCO_3^-

Other name(s): phosphopyruvate (phosphate) carboxylase; PEP carboxylase; phospho*enol*pyruvic carboxylase; PEPC; PEPCase; phosphate:oxaloacetate carboxy-lyase (phosphorylating)

Systematic name: phosphate:oxaloacetate carboxy-lyase (adding phosphate, phospho*enol*pyruvate-forming)

Comments: This enzyme replenishes oxaloacetate in the tricarboxylic acid cycle when operating in the reverse direction. The reaction proceeds in two steps: formation of carboxyphosphate and the enolate form of pyruvate, followed by carboxylation of the enolate and release of phosphate.

References: [217, 903, 1383]

[EC 4.1.1.31 created 1961, modified 2011]

EC 4.1.1.32

Accepted name: phospho*enol*pyruvate carboxykinase (GTP)

Reaction: GTP + oxaloacetate = GDP + phospho*enol*pyruvate + CO_2

Other name(s): phospho*enol*pyruvate carboxylase (ambiguous); phosphopyruvate carboxylase (ambiguous); phosphopyruvate (guanosine triphosphate) carboxykinase; phospho*enol*pyruvic carboxykinase (GTP); phosphopyruvate carboxylase (GTP); phospho*enol*pyruvic carboxylase (GTP); phospho*enol*pyruvic carboxykinase (ambiguous); phospho*enol*pyruvate carboxykinase (ambiguous); PEP carboxylase (ambiguous); GTP:oxaloacetate carboxy-lyase (transphosphorylating)

Systematic name: GTP:oxaloacetate carboxy-lyase (adding GTP; phospho*enol*pyruvate-forming)

Comments: ITP can act as phosphate donor.

References: [210, 767]

[EC 4.1.1.32 created 1961]

EC 4.1.1.33

Accepted name: diphosphomevalonate decarboxylase

Reaction: ATP + (*R*)-5-diphosphomevalonate = ADP + phosphate + isopentenyl diphosphate + CO_2

Other name(s): pyrophosphomevalonate decarboxylase; mevalonate-5-pyrophosphate decarboxylase; pyrophosphomevalonic acid decarboxylase; 5-pyrophosphomevalonate decarboxylase; mevalonate 5-diphosphate decarboxylase; ATP:(*R*)-5-diphosphomevalonate carboxy-lyase (dehydrating)

Systematic name: ATP:(*R*)-5-diphosphomevalonate carboxy-lyase (adding ATP; isopentenyl-diphosphate-forming)

References: [104]

[EC 4.1.1.33 created 1961]

EC 4.1.1.34

Accepted name: dehydro-L-gulonate decarboxylase

Reaction: 3-dehydro-L-gulonate = L-xylulose + CO_2

Other name(s): keto-L-gulonate decarboxylase; 3-keto-L-gulonate decarboxylase; 3-dehydro-L-gulonate carboxy-lyase

Systematic name: 3-dehydro-L-gulonate carboxy-lyase (L-xylulose-forming)

References: [1282]

[EC 4.1.1.34 created 1965]

EC 4.1.1.35

Accepted name: UDP-glucuronate decarboxylase

Reaction: UDP-D-glucuronate = UDP-D-xylose + CO_2

Other name(s): uridine-diphosphoglucuronate decarboxylase; UDP-D-glucuronate carboxy-lyase

Systematic name: UDP-D-glucuronate carboxy-lyase (UDP-D-xylose-forming)

Comments: Requires NAD$^+$.
References: [32]

[EC 4.1.1.35 created 1965]

EC 4.1.1.36

Accepted name: phosphopantothenoylcysteine decarboxylase
Reaction: *N*-[(*R*)-4′-phosphopantothenoyl]-L-cysteine = pantotheine 4′-phosphate + CO_2
Other name(s): 4-phosphopantotheoylcysteine decarboxylase; 4-phosphopantothenoyl-L-cysteine decarboxylase; PPC-decarboxylase; *N*-[(*R*)-4′-phosphopantothenoyl]-L-cysteine carboxy-lyase
Systematic name: *N*-[(*R*)-4′-phosphopantothenoyl]-L-cysteine carboxy-lyase (pantotheine-4′-phosphate-forming)
References: [144, 145]

[EC 4.1.1.36 created 1965]

EC 4.1.1.37

Accepted name: uroporphyrinogen decarboxylase
Reaction: uroporphyrinogen III = coproporphyrinogen III + **4** CO_2
Other name(s): uroporphyrinogen III decarboxylase; porphyrinogen carboxy-lyase; porphyrinogen decarboxylase; uroporphyrinogen-III carboxy-lyase
Systematic name: uroporphyrinogen-III carboxy-lyase (coproporphyrinogen-III-forming)
Comments: Acts on a number of porphyrinogens.
References: [901, 1378]

[EC 4.1.1.37 created 1965]

EC 4.1.1.38

Accepted name: phospho*enol*pyruvate carboxykinase (diphosphate)
Reaction: diphosphate + oxaloacetate = phosphate + phospho*enol*pyruvate + CO_2
Other name(s): phosphopyruvate carboxylase (ambiguous); PEP carboxyphosphotransferase (ambiguous); PEP carboxykinase (ambiguous); phosphopyruvate carboxykinase (pyrophosphate); PEP carboxylase (ambiguous); phosphopyruvate carboxykinase (ambiguous); phospho*enol*pyruvic carboxykinase (ambiguous); phospho*enol*pyruvic carboxylase (ambiguous); phospho*enol*pyruvate carboxytransphosphorylase (ambiguous); phospho*enol*pyruvate carboxykinase (ambiguous); phospho*enol*pyruvic carboxykinase; phospho*enol*pyruvic carboxylase; PEPCTrP; phospho*enol*pyruvic carboxykinase (pyrophosphate); phospho*enol*pyruvic carboxylase (pyrophosphate); phospho*enol*pyruvate carboxylase (ambiguous); phospho*enol*pyruvate carboxyphosphotransferase (ambiguous); phospho*enol*pyruvic carboxytransphosphorylase (ambiguous); phospho*enol*pyruvate carboxylase (pyrophosphate); phosphopyruvate carboxylase (pyrophosphate); diphosphate:oxaloacetate carboxy-lyase (transphosphorylating)
Systematic name: diphosphate:oxaloacetate carboxy-lyase (transphosphorylating; phospho*enol*pyruvate-forming)
Comments: Also catalyses the reaction: phospho*enol*pyruvate + phosphate = pyruvate + diphosphate.
References: [840]

[EC 4.1.1.38 created 1965]

EC 4.1.1.39

Accepted name: ribulose-bisphosphate carboxylase
Reaction: **2** 3-phospho-D-glycerate + **2** H$^+$ = D-ribulose 1,5-bisphosphate + CO_2 + H_2O

Other name(s): D-ribulose 1,5-diphosphate carboxylase; D-ribulose-1,5-bisphosphate carboxylase; RuBP carboxylase; carboxydismutase; diphosphoribulose carboxylase; ribulose 1,5-bisphosphate carboxylase; ribulose 1,5-bisphosphate carboxylase/oxygenase; ribulose 1,5-diphosphate carboxylase; ribulose 1,5-diphosphate carboxylase/oxygenase; ribulose bisphosphate carboxylase/oxygenase; ribulose diphosphate carboxylase; ribulose diphosphate carboxylase/oxygenase; rubisco; 3-phospho-D-glycerate carboxy-lyase (dimerizing)
Systematic name: 3-phospho-D-glycerate carboxy-lyase (dimerizing; D-ribulose-1,5-bisphosphate-forming)
Comments: Will utilize O_2 instead of CO_2, forming 3-phospho-D-glycerate and 2-phosphoglycolate.
References: [124, 1473]

[EC 4.1.1.39 created 1965, modified 2001, modified 2003]

EC 4.1.1.40
Accepted name: hydroxypyruvate decarboxylase
Reaction: hydroxypyruvate = glycolaldehyde + CO_2
Other name(s): hydroxypyruvate carboxy-lyase
Systematic name: hydroxypyruvate carboxy-lyase (glycolaldehyde-forming)
References: [533]

[EC 4.1.1.40 created 1972]

[4.1.1.41 Transferred entry. (S)-methylmalonyl-CoA decarboxylase. Now EC 7.2.4.3, (S)-methylmalonyl-CoA decarboxylase]

[EC 4.1.1.41 created 1972, modified 1983, modified 1986, deleted 2018]

EC 4.1.1.42
Accepted name: carnitine decarboxylase
Reaction: carnitine = 2-methylcholine + CO_2
Other name(s): carnitine carboxy-lyase
Systematic name: carnitine carboxy-lyase (2-methylcholine-forming)
Comments: Requires ATP.
References: [692]

[EC 4.1.1.42 created 1972]

EC 4.1.1.43
Accepted name: phenylpyruvate decarboxylase
Reaction: phenylpyruvate = phenylacetaldehyde + CO_2
Other name(s): phenylpyruvate carboxy-lyase; phenylpyruvate carboxy-lyase (phenylacetaldehyde-forming)
Systematic name: 3-phenyl-2-oxopropanoate carboxy-lyase (phenylacetaldehyde-forming)
Comments: The enzyme from the bacterium *Azospirillum brasilense* also acts on some other substrates, including (indol-3-yl)pyruvate, with much lower efficiency. However, it only possesses classical Michaelis-Menten kinetics with phenylpyruvate. Aliphatic 2-oxo acids longer that 2-oxohexanoate are not substrates. *cf.* EC 4.1.1.74, indolepyruvate decarboxylase.
References: [41, 1292]

[EC 4.1.1.43 created 1972]

EC 4.1.1.44
Accepted name: 4-carboxymuconolactone decarboxylase
Reaction: (*R*)-2-carboxy-2,5-dihydro-5-oxofuran-2-acetate = 4,5-dihydro-5-oxofuran-2-acetate + CO_2

Other name(s): γ-4-carboxymuconolactone decarboxylase; 4-carboxymuconolactone carboxy-lyase; 2-carboxy-2,5-dihydro-5-oxofuran-2-acetate carboxy-lyase (4,5-dihydro-5-oxofuran-2-acetate-forming)
Systematic name: (*R*)-2-carboxy-2,5-dihydro-5-oxofuran-2-acetate carboxy-lyase (4,5-dihydro-5-oxofuran-2-acetate-forming)
References: [1039, 1040]

[EC 4.1.1.44 created 1972]

EC 4.1.1.45

Accepted name: aminocarboxymuconate-semialdehyde decarboxylase
Reaction: 2-amino-3-(3-oxoprop-1-en-1-yl)but-2-enedioate = 2-aminomuconate semialdehyde + CO_2
Other name(s): picolinic acid carboxylase; picolinic acid decarboxylase; α-amino-β-carboxymuconate-ε-semialdehade decarboxylase; α-amino-β-carboxymuconate-ε-semialdehyde β-decarboxylase; 2-amino-3-(3-oxoprop-2-enyl)but-2-enedioate carboxy-lyase; 2-amino-3-(3-oxoprop-1-en-1-yl)but-2-enedioate carboxy-lyase
Systematic name: 2-amino-3-(3-oxoprop-1-en-1-yl)but-2-enedioate carboxy-lyase (2-aminomuconate-semialdehyde-forming)
Comments: Product rearranges non-enzymically to picolinate.
References: [594]

[EC 4.1.1.45 created 1972]

EC 4.1.1.46

Accepted name: *o*-pyrocatechuate decarboxylase
Reaction: 2,3-dihydroxybenzoate = catechol + CO_2
Other name(s): 2,3-dihydroxybenzoate carboxy-lyase
Systematic name: 2,3-dihydroxybenzoate carboxy-lyase (catechol-forming)
References: [1132]

[EC 4.1.1.46 created 1972]

EC 4.1.1.47

Accepted name: tartronate-semialdehyde synthase
Reaction: **2** glyoxylate = 2-hydroxy-3-oxopropanoate + CO_2
Other name(s): tartronate semialdehyde carboxylase; glyoxylate carbo-ligase; glyoxylic carbo-ligase; hydroxymalonic semialdehyde carboxylase; tartronic semialdehyde carboxylase; glyoxalate carboligase; glyoxylate carboxy-lyase (dimerizing); glyoxylate carboxy-lyase (dimerizing; tartronate-semialdehyde-forming)
Systematic name: glyoxylate carboxy-lyase (dimerizing; 2-hydroxy-3-oxopropanoate-forming)
Comments: A flavoprotein.
References: [480, 737]

[EC 4.1.1.47 created 1972]

EC 4.1.1.48

Accepted name: indole-3-glycerol-phosphate synthase
Reaction: 1-(2-carboxyphenylamino)-1-deoxy-D-ribulose 5-phosphate = 1-*C*-(indol-3-yl)glycerol 3-phosphate + CO_2 + H_2O
Other name(s): indoleglycerol phosphate synthetase; indoleglycerol phosphate synthase; indole-3-glycerophosphate synthase; 1-(2-carboxyphenylamino)-1-deoxy-D-ribulose-5-phosphate carboxy-lyase (cyclizing)
Systematic name: 1-(2-carboxyphenylamino)-1-deoxy-D-ribulose-5-phosphate carboxy-lyase [cyclizing; 1-*C*-(indol-3-yl)glycerol-3-phosphate-forming]

Comments: In some organisms, this enzyme is part of a multifunctional protein, together with one or more other components of the system for the biosynthesis of tryptophan [EC 2.4.2.18 (anthranilate phosphoribosyltransferase), EC 4.1.3.27 (anthranilate synthase), EC 4.2.1.20 (tryptophan synthase) and EC 5.3.1.24 (phosphoribosylanthranilate isomerase)].

References: [260, 261, 590]

[EC 4.1.1.48 created 1972]

EC 4.1.1.49

Accepted name: phospho*enol*pyruvate carboxykinase (ATP)

Reaction: ATP + oxaloacetate = ADP + phospho*enol*pyruvate + CO$_2$

Other name(s): phosphopyruvate carboxylase (ATP); phospho*enol*pyruvate carboxylase (ambiguous); phospho*enol*pyruvate carboxykinase (ambiguous); phosphopyruvate carboxykinase (adenosine triphosphate); PEP carboxylase (ambiguous); PEP carboxykinase (ambiguous); PEPCK (ATP); PEPK; PEPCK; phospho*enol*pyruvic carboxylase (ambiguous); phospho*enol*pyruvic carboxykinase (ambiguous); phospho*enol*pyruvate carboxylase (ATP); phosphopyruvate carboxykinase (ambiguous); ATP:oxaloacetate carboxy-lyase (transphosphorylating)

Systematic name: ATP:oxaloacetate carboxy-lyase (transphosphorylating; phospho*enol*pyruvate-forming)

References: [185, 186, 187]

[EC 4.1.1.49 created 1972]

EC 4.1.1.50

Accepted name: adenosylmethionine decarboxylase

Reaction: *S*-adenosyl-L-methionine = *S*-adenosyl 3-(methylsulfanyl)propylamine + CO$_2$

Other name(s): *S*-adenosylmethionine decarboxylase; *S*-adenosyl-L-methionine decarboxylase; *S*-adenosyl-L-methionine carboxy-lyase; *S*-adenosyl-L-methionine carboxy-lyase [(5-deoxy-5-adenosyl)(3-aminopropyl)methylsulfonium-salt-forming]

Systematic name: *S*-adenosyl-L-methionine carboxy-lyase [*S*-adenosyl 3-(methylsulfanyl)propylamine-forming]

Comments: The *Escherichia coli* enzyme contains a pyruvoyl group.

References: [33, 1335]

[EC 4.1.1.50 created 1972]

EC 4.1.1.51

Accepted name: 3-hydroxy-2-methylpyridine-4,5-dicarboxylate 4-decarboxylase

Reaction: 3-hydroxy-2-methylpyridine-4,5-dicarboxylate = 3-hydroxy-2-methylpyridine-5-carboxylate + CO$_2$

Other name(s): 3-hydroxy-2-methylpyridine-4,5-dicarboxylate 4-carboxy-lyase

Systematic name: 3-hydroxy-2-methylpyridine-4,5-dicarboxylate 4-carboxy-lyase (3-hydroxy-2-methylpyridine-5-carboxylate-forming)

References: [1287]

[EC 4.1.1.51 created 1972]

EC 4.1.1.52

Accepted name: 6-methylsalicylate decarboxylase

Reaction: 6-methylsalicylate = 3-methylphenol + CO$_2$

Other name(s): 6-methylsalicylic acid (2,6-cresotic acid) decarboxylase; 6-MSA decarboxylase; 6-methylsalicylate carboxy-lyase

Systematic name: 6-methylsalicylate carboxy-lyase (3-methylphenol-forming)

References: [814, 1425]

[EC 4.1.1.52 created 1972, modified 2011]

EC 4.1.1.53

Accepted name: phenylalanine decarboxylase

Reaction: L-phenylalanine = phenylethylamine + CO_2

Other name(s): L-phenylalanine decarboxylase; aromatic L-amino acid decarboxylase (ambiguous); L-phenylalanine carboxy-lyase

Systematic name: L-phenylalanine carboxy-lyase (phenylethylamine-forming)

Comments: A pyridoxal-phosphate protein. Also acts on tyrosine and other aromatic amino acids.

References: [847, 1237]

[EC 4.1.1.53 created 1972]

EC 4.1.1.54

Accepted name: dihydroxyfumarate decarboxylase

Reaction: dihydroxyfumarate = 2-hydroxy-3-oxopropanoate + CO_2

Other name(s): dihydroxyfumarate carboxy-lyase; dihydroxyfumarate carboxy-lyase (tartronate-semialdehyde-forming)

Systematic name: dihydroxyfumarate carboxy-lyase (2-hydroxy-3-oxopropanoate-forming)

References: [415]

[EC 4.1.1.54 created 1972]

EC 4.1.1.55

Accepted name: 4,5-dihydroxyphthalate decarboxylase

Reaction: 4,5-dihydroxyphthalate = 3,4-dihydroxybenzoate + CO_2

Other name(s): 4,5-dihydroxyphthalate carboxy-lyase

Systematic name: 4,5-dihydroxyphthalate carboxy-lyase (3,4-dihydroxybenzoate-forming)

References: [1148]

[EC 4.1.1.55 created 1972]

EC 4.1.1.56

Accepted name: 3-oxolaurate decarboxylase

Reaction: 3-oxododecanoate = 2-undecanone + CO_2

Other name(s): β-ketolaurate decarboxylase; β-ketoacyl decarboxylase; 3-oxododecanoate carboxy-lyase

Systematic name: 3-oxododecanoate carboxy-lyase (2-undecanone-forming)

Comments: Also decarboxylates other C_{14} to C_{16} oxo acids.

References: [402]

[EC 4.1.1.56 created 1972]

EC 4.1.1.57

Accepted name: methionine decarboxylase

Reaction: L-methionine = 3-(methylsulfanyl)propanamine + CO_2

Other name(s): L-methionine decarboxylase; L-methionine carboxy-lyase; L-methionine carboxy-lyase (3-methylthiopropanamine-forming)

Systematic name: L-methionine carboxy-lyase [3-(methylsulfanyl)propanamine-forming]

References: [486]

[EC 4.1.1.57 created 1972]

EC 4.1.1.58

Accepted name: orsellinate decarboxylase

Reaction: orsellinate = orcinol + CO_2
Other name(s): orsellinate carboxy-lyase
Systematic name: 2,4-dihydroxy-6-methylbenzoate carboxy-lyase (orcinol-forming)
References: [1073]

[EC 4.1.1.58 created 1972]

EC 4.1.1.59

Accepted name: gallate decarboxylase
Reaction: 3,4,5-trihydroxybenzoate = 1,2,3-trihydroxybenzene + CO_2
Other name(s): gallic acid decarboxylase; gallate carboxy-lyase; 3,4,5-trihydroxybenzoate carboxy-lyase (pyrogallol-forming)
Systematic name: 3,4,5-trihydroxybenzoate carboxy-lyase (1,2,3-trihydroxybenzene-forming)
References: [463, 1544, 634]

[EC 4.1.1.59 created 1972]

EC 4.1.1.60

Accepted name: stipitatonate decarboxylase
Reaction: stipitatonate = stipitatate + CO_2
Other name(s): stipitatonate carboxy-lyase (decyclizing); stipitatonate carboxy-lyase (decyclizing, stipitatate-forming)
Systematic name: stipitatonate carboxy-lyase (ring-opening, stipitatate-forming)
References: [90]

[EC 4.1.1.60 created 1972]

EC 4.1.1.61

Accepted name: 4-hydroxybenzoate decarboxylase
Reaction: 4-hydroxybenzoate = phenol + CO_2
Other name(s): *p*-hydroxybenzoate decarboxylase; 4-hydroxybenzoate carboxy-lyase
Systematic name: 4-hydroxybenzoate carboxy-lyase (phenol-forming)
References: [463, 1395]

[EC 4.1.1.61 created 1972]

EC 4.1.1.62

Accepted name: gentisate decarboxylase
Reaction: 2,5-dihydroxybenzoate = hydroquinone + CO_2
Other name(s): 2,5-dihydroxybenzoate decarboxylase; gentisate carboxy-lyase
Systematic name: 2,5-dihydroxybenzoate carboxy-lyase (hydroquinone-forming)
References: [463]

[EC 4.1.1.62 created 1972]

EC 4.1.1.63

Accepted name: protocatechuate decarboxylase
Reaction: 3,4-dihydroxybenzoate = catechol + CO_2
Other name(s): 3,4-dihydrobenzoate decarboxylase; protocatechuate carboxy-lyase
Systematic name: 3,4-dihydroxybenzoate carboxy-lyase (catechol-forming)
References: [463]

[EC 4.1.1.63 created 1972]

EC 4.1.1.64

Accepted name: 2,2-dialkylglycine decarboxylase (pyruvate)

Reaction: 2,2-dialkylglycine + pyruvate = dialkyl ketone + CO_2 + L-alanine

Other name(s): dialkyl amino acid (pyruvate) decarboxylase; α-dialkyl amino acid transaminase; 2,2-dialkyl-2-amino acid-pyruvate aminotransferase; L-alanine-α-ketobutyrate aminotransferase; dialkylamino-acid decarboxylase (pyruvate); 2,2-dialkylglycine carboxy-lyase (amino-transferring)

Systematic name: 2,2-dialkylglycine carboxy-lyase (amino-transferring; L-alanine-forming)

Comments: A pyridoxal-phosphate protein. Acts on 2-amino-2-methylpropanoate (i.e. 2-methylalanine), 2-amino-2-methylbutanoate and 1-aminocyclopentanecarboxylate.

References: [60]

[EC 4.1.1.64 created 1972]

EC 4.1.1.65

Accepted name: phosphatidylserine decarboxylase

Reaction: phosphatidyl-L-serine = phosphatidylethanolamine + CO_2

Other name(s): PS decarboxylase; phosphatidyl-L-serine carboxy-lyase

Systematic name: phosphatidyl-L-serine carboxy-lyase (phosphatidylethanolamine-forming)

Comments: A pyridoxal-phosphate protein. In *Escherichia coli*, the prosthetic group is a pyruvoyl group.

References: [662, 1197]

[EC 4.1.1.65 created 1976]

EC 4.1.1.66

Accepted name: uracil-5-carboxylate decarboxylase

Reaction: uracil 5-carboxylate = uracil + CO_2

Other name(s): uracil-5-carboxylic acid decarboxylase; uracil-5-carboxylate carboxy-lyase

Systematic name: uracil-5-carboxylate carboxy-lyase (uracil-forming)

References: [1050]

[EC 4.1.1.66 created 1976]

EC 4.1.1.67

Accepted name: UDP-galacturonate decarboxylase

Reaction: UDP-D-galacturonate = UDP-L-arabinose + CO_2

Other name(s): UDP-galacturonic acid decarboxylase; UDPGalUA carboxy lyase; UDP-D-galacturonate carboxy-lyase

Systematic name: UDP-D-galacturonate carboxy-lyase (UDP-L-arabinose-forming)

References: [376]

[EC 4.1.1.67 created 1984]

EC 4.1.1.68

Accepted name: 5-oxopent-3-ene-1,2,5-tricarboxylate decarboxylase

Reaction: (3*E*,5*R*)-5-carboxy-2-oxohept-3-enedioate = (4*Z*)-2-oxohept-4-enedioate + CO_2 (overall reaction)
(1a) (3*E*,5*R*)-5-carboxy-2-oxohept-3-enedioate = (2*Z*,4*Z*)-2-hydroxyhepta-2,4-dienedioate + CO_2
(1b) (2*Z*,4*Z*)-2-hydroxyhepta-2,4-dienedioate = (4*Z*)-2-oxohept-4-enedioate

Other name(s): 5-carboxymethyl-2-oxo-hex-3-ene-1,6-dioate decarboxylase; 5-oxopent-3-ene-1,2,5-tricarboxylate carboxy-lyase; 5-oxopent-3-ene-1,2,5-tricarboxylate carboxy-lyase (2-oxohept-3-enedioate-forming)

Systematic name: (3*E*,5*R*)-5-carboxy-2-oxohept-3-enedioate carboxy-lyase [(4*Z*)-2-oxohept-4-enedioate-forming]

Comments: Requires Mg^{2+} [640, 641]. Part of the 4-hydroxyphenylacetate degradation pathway in *Escherichia coli*.

References: [427, 640, 641]

[EC 4.1.1.68 created 1984]

EC 4.1.1.69

Accepted name: 3,4-dihydroxyphthalate decarboxylase
Reaction: 3,4-dihydroxyphthalate = 3,4-dihydroxybenzoate + CO$_2$
Other name(s): 3,4-dihydroxyphthalate carboxy-lyase
Systematic name: 3,4-dihydroxyphthalate carboxy-lyase (3,4-dihydroxybenzoate-forming)
References: [347]

[EC 4.1.1.69 created 1986]

[4.1.1.70 Transferred entry. glutaconyl-CoA decarboxylase. Now EC 7.2.4.5, glutaconyl-CoA decarboxylase]

[EC 4.1.1.70 created 1986, modified 2003, deleted 2019]

EC 4.1.1.71

Accepted name: 2-oxoglutarate decarboxylase
Reaction: 2-oxoglutarate = succinate semialdehyde + CO$_2$
Other name(s): oxoglutarate decarboxylase; α-ketoglutarate decarboxylase; α-ketoglutaric decarboxylase; pre-2-oxoglutarate decarboxylase; 2-oxoglutarate carboxy-lyase
Systematic name: 2-oxoglutarate carboxy-lyase (succinate-semialdehyde-forming)
Comments: Requires thiamine diphosphate. Highly specific.
References: [1263]

[EC 4.1.1.71 created 1989]

EC 4.1.1.72

Accepted name: branched-chain-2-oxoacid decarboxylase
Reaction: (3*S*)-3-methyl-2-oxopentanoate = 2-methylbutanal + CO$_2$
Other name(s): branched-chain oxo acid decarboxylase; branched-chain α-keto acid decarboxylase; branched-chain keto acid decarboxylase; BCKA; (3*S*)-3-methyl-2-oxopentanoate carboxy-lyase
Systematic name: (3*S*)-3-methyl-2-oxopentanoate carboxy-lyase (2-methylbutanal-forming)
Comments: Acts on a number of 2-oxo acids, with a high affinity towards branched-chain substrates. The aldehyde formed may be enzyme-bound, and may be an intermediate in the bacterial system for the biosynthesis of branched-chain fatty acids.
References: [1028, 303, 1284]

[EC 4.1.1.72 created 1990]

EC 4.1.1.73

Accepted name: tartrate decarboxylase
Reaction: (*R*,*R*)-tartrate = D-glycerate + CO$_2$
Other name(s): (*R*,*R*)-tartrate carboxy-lyase
Systematic name: (*R*,*R*)-tartrate carboxy-lyase (D-glycerate-forming)
References: [418]

[EC 4.1.1.73 created 1992]

EC 4.1.1.74

Accepted name: indolepyruvate decarboxylase
Reaction: 3-(indol-3-yl)pyruvate = 2-(indol-3-yl)acetaldehyde + CO$_2$
Other name(s): indol-3-yl-pyruvate carboxy-lyase; 3-(indol-3-yl)pyruvate carboxy-lyase
Systematic name: 3-(indol-3-yl)pyruvate carboxy-lyase [(2-indol-3-yl)acetaldehyde-forming]

Comments: Thiamine diphosphate- and Mg^{2+}-dependent. More specific than EC 4.1.1.1 pyruvate decarboxylase
References: [721]

[EC 4.1.1.74 created 1999]

EC 4.1.1.75

Accepted name: 5-guanidino-2-oxopentanoate decarboxylase
Reaction: 5-guanidino-2-oxopentanoate = 4-guanidinobutanal + CO$_2$
Other name(s): α-ketoarginine decarboxylase; 2-oxo-5-guanidinopentanoate carboxy-lyase
Systematic name: 5-guanidino-2-oxopentanoate carboxy-lyase (4-guanidinobutanal-forming)
Comments: Enzyme activity is dependent on the presence of thiamine diphosphate and a divalent cation.
References: [1416]

[EC 4.1.1.75 created 1999]

EC 4.1.1.76

Accepted name: arylmalonate decarboxylase
Reaction: 2-aryl-2-methylmalonate = 2-arylpropanoate + CO$_2$
Other name(s): AMDASE; 2-aryl-2-methylmalonate carboxy-lyase; 2-aryl-2-methylmalonate carboxy-lyase (2-arylpropionate-forming)
Systematic name: 2-aryl-2-methylmalonate carboxy-lyase (2-arylpropanoate-forming)
References: [948]

[EC 4.1.1.76 created 1999]

EC 4.1.1.77

Accepted name: 2-oxo-3-hexenedioate decarboxylase
Reaction: (3*E*)-2-oxohex-3-enedioate = 2-oxopent-4-enoate + CO$_2$
Other name(s): 4-oxalocrotonate carboxy-lyase (misleading); 4-oxalocrotonate decarboxylase (misleading); *cnbF* (gene name); *praD* (gene name); *amnE* (gene name); *nbaG* (gene name); *xylI* (gene name)
Systematic name: (3*E*)-2-oxohex-3-enedioate carboxy-lyase (2-oxopent-4-enoate-forming)
Comments: Involved in the meta-cleavage pathway for the degradation of phenols, modified phenols and catechols. The enzyme has been reported to accept multiple tautomeric forms [1267, 1344, 1297, 1445]. However, careful analysis of the stability of the different tautomers, as well as characterization of the enzyme that produces its substrate, EC 5.3.2.6, 2-hydroxymuconate tautomerase, showed that the actual substrate for the enzyme is (3*E*)-2-oxohex-3-enedioate [1445].
References: [1267, 1344, 1297, 1445, 670]

[EC 4.1.1.77 created 1999, modified 2011, modified 2012]

EC 4.1.1.78

Accepted name: acetylenedicarboxylate decarboxylase
Reaction: acetylenedicarboxylate + H$_2$O = pyruvate + CO$_2$
Other name(s): acetylenedicarboxylate hydratase; acetylenedicarboxylate hydrase; acetylenedicarboxylate carboxy-lyase
Systematic name: acetylenedicarboxylate carboxy-lyase (pyruvate-forming)
Comments: The mechanism appears to involve hydration of the acetylene and decarboxylation of the oxaloacetic acid formed, although free oxaloacetate is not an intermediate. It is thus analogous to EC 4.2.1.27 (acetylenecarboxylate hydratase) in its mechanism.
References: [1488]

[EC 4.1.1.78 created 1978 as EC 4.2.1.72, transferred 2000 to EC 4.1.1.78]

EC 4.1.1.79

Accepted name: sulfopyruvate decarboxylase

Reaction: 3-sulfopyruvate = 2-sulfoacetaldehyde + CO_2

Other name(s): sulfopyruvate carboxy-lyase

Systematic name: 3-sulfopyruvate carboxy-lyase (2-sulfoacetaldehyde-forming)

Comments: Requires thiamine diphosphate. Does not decarboxylate pyruvate or phosphonopyruvate. The enzyme appears to be oxygen-sensitive.

References: [464]

[EC 4.1.1.79 created 2002]

EC 4.1.1.80

Accepted name: 4-hydroxyphenylpyruvate decarboxylase

Reaction: 4-hydroxyphenylpyruvate = 4-hydroxyphenylacetaldehyde + CO_2

Other name(s): 4-hydroxyphenylpyruvate carboxy-lyase

Systematic name: 4-hydroxyphenylpyruvate carboxy-lyase (4-hydroxyphenylacetaldehyde-forming)

Comments: Reacts with dopamine to give the benzylisoquinoline alkaloid skeleton.

References: [1173]

[EC 4.1.1.80 created 2002]

EC 4.1.1.81

Accepted name: threonine-phosphate decarboxylase

Reaction: L-threonine *O*-3-phosphate = (*R*)-1-aminopropan-2-yl phosphate + CO_2

Other name(s): L-threonine-*O*-3-phosphate decarboxylase; CobD; L-threonine-*O*-3-phosphate carboxy-lyase

Systematic name: L-threonine-*O*-3-phosphate carboxy-lyase [(*R*)-1-aminopropan-2-yl-phosphate-forming]

Comments: A pyridoxal-phosphate protein. This enzyme is unable to decarboxylate the D-isomer of threonine *O*-3-phosphate. The product of this reaction, (*R*)-1-aminopropan-2-yl phosphate, is the substrate of EC 6.3.1.10, adenosylcobinamide-phosphate synthase, which converts adenosylcobyric acid into adenosylcobinamide phosphate in the anaerobic cobalamin biosynthesis pathway.

References: [221, 150, 1453]

[EC 4.1.1.81 created 2004]

EC 4.1.1.82

Accepted name: phosphonopyruvate decarboxylase

Reaction: 3-phosphonopyruvate = 2-phosphonoacetaldehyde + CO_2

Other name(s): 3-phosphonopyruvate carboxy-lyase

Systematic name: 3-phosphonopyruvate carboxy-lyase (2-phosphonoacetaldehyde-forming)

Comments: The enzyme catalyses a step in the biosynthetic pathway of 2-aminoethylphosphonate, a component of the capsular polysaccharide complex of *Bacteroides fragilis*. Requires thiamine diphosphate and Mg^{2+} as cofactors. The enzyme is activated by the divalent cations Mg^{2+}, Ca^{2+} and Mn^{2+}. Pyruvate and sulfopyruvate can also act as substrates, but more slowly. This enzyme drives the reaction catalysed by EC 5.4.2.9, phospho*enol*pyruvate mutase, in the thermodynamically unfavourable direction of 3-phosphonopyruvate formation [1247]. It is the initial step in all of the major biosynthetic pathways of phosphonate natural products [990].

References: [1550, 1247, 990]

[EC 4.1.1.82 created 2005]

EC 4.1.1.83

Accepted name: 4-hydroxyphenylacetate decarboxylase

Reaction: (4-hydroxyphenyl)acetate + H^+ = 4-methylphenol + CO_2

Other name(s): *p*-hydroxyphenylacetate decarboxylase; *p*-Hpd; 4-Hpd; 4-hydroxyphenylacetate carboxy-lyase
Systematic name: (4-hydroxyphenyl)acetate carboxy-lyase (4-methylphenol-forming)
Comments: The enzyme, from the strict anaerobe *Clostridium difficile*, can also use (3,4-dihydroxyphenyl)acetate as a substrate, yielding 4-methylcatechol as a product. The enzyme is a glycyl radical enzyme.
References: [289, 1252, 31]

[EC 4.1.1.83 created 2005]

EC 4.1.1.84

Accepted name: D-dopachrome decarboxylase
Reaction: D-dopachrome = 5,6-dihydroxyindole + CO_2
Other name(s): phenylpyruvate tautomerase II; D-tautomerase; D-dopachrome tautomerase; D-dopachrome carboxy-lyase
Systematic name: D-dopachrome carboxy-lyase (5,6-dihydroxyindole-forming)
Comments: This enzyme is specific for D-dopachrome as substrate and belongs to the MIF (macrophage migration inhibitory factor) family of proteins. L-Dopachrome, L- or D-α-methyldopachrome and dopaminochrome do not act as substrates (see also EC 5.3.3.12, L-dopachrome isomerase)
References: [1024, 1512, 1320, 1007]

[EC 4.1.1.84 created 2005]

EC 4.1.1.85

Accepted name: 3-dehydro-L-gulonate-6-phosphate decarboxylase
Reaction: 3-dehydro-L-gulonate 6-phosphate + H^+ = L-xylulose 5-phosphate + CO_2
Other name(s): 3-keto-L-gulonate 6-phosphate decarboxylase; UlaD; SgaH; SgbH; KGPDC; 3-dehydro-L-gulonate-6-phosphate carboxy-lyase
Systematic name: 3-dehydro-L-gulonate-6-phosphate carboxy-lyase (L-xylulose-5-phosphate-forming)
Comments: Requires Mg^{2+}. Along with EC 5.1.3.22, L-ribulose-5-phosphate 3-epimerase, this enzyme is involved in a pathway for the utilization of L-ascorbate by *Escherichia coli*.
References: [1510, 1471]

[EC 4.1.1.85 created 2005]

EC 4.1.1.86

Accepted name: diaminobutyrate decarboxylase
Reaction: L-2,4-diaminobutanoate = propane-1,3-diamine + CO_2
Other name(s): DABA DC; L-2,4-diaminobutyrate decarboxylase; L-2,4-diaminobutanoate carboxy-lyase
Systematic name: L-2,4-diaminobutanoate carboxy-lyase (propane-1,3-diamine-forming)
Comments: A pyridoxal-phosphate protein that requires a divalent cation for activity [1497]. N^4-Acetyl-L-2,4-diaminobutanoate, 2,3-diaminopropanoate, ornithine and lysine are not substrates. Found in the proteobacteria *Haemophilus influenzae* and *Acinetobacter baumannii*. In the latter, this enzyme is cotranscribed with the *dat* gene that encodes EC 2.6.1.76, diaminobutyrate—2-oxoglutarate transaminase, which can supply the substrate for this enzyme.
References: [1497, 596, 597]

[EC 4.1.1.86 created 2006]

EC 4.1.1.87

Accepted name: malonyl-*S*-ACP decarboxylase
Reaction: a malonyl-[acyl-carrier protein] + H^+ = an acetyl-[acyl-carrier protein] + CO_2
Other name(s): malonyl-*S*-acyl-carrier protein decarboxylase; MdcD/MdcE; MdcD,E
Systematic name: malonyl-[acyl-carrier-protein] carboxy-lyase

Comments: This enzyme comprises the β and γ subunits of EC 4.1.1.88, biotin-independent malonate decarboxylase but is not present in EC 7.2.4.4, biotin-dependent malonate decarboxylase. It follows on from EC 2.3.1.187, acetyl-*S*-ACP:malonate ACP transferase, and results in the regeneration of the acetylated form of the acyl-carrier-protein subunit of malonate decarboxylase [323]. The carboxy group is lost with retention of configuration [499].
References: [1214, 731, 499, 227, 323]

[EC 4.1.1.87 created 2008]

EC 4.1.1.88
Accepted name: biotin-independent malonate decarboxylase
Reaction: malonate + H^+ = acetate + CO_2
Other name(s): malonate decarboxylase (without biotin); malonate decarboxylase (ambiguous); MDC
Systematic name: malonate carboxy-lyase (biotin-independent)
Comments: Two types of malonate decarboxylase are currently known, both of which form multienzyme complexes. This enzyme is a cytosolic protein that is biotin-independent. The other type is a biotin-dependent, Na^+-translocating enzyme that includes both soluble and membrane-bound components (*cf.* EC 7.2.4.4, biotin-dependent malonate decarboxylase). As free malonate is chemically rather inert, it has to be activated prior to decarboxylation. In both enzymes, this is achieved by exchanging malonate with an acetyl group bound to an acyl-carrier protiein (ACP), to form malonyl-ACP and acetate, with subsequent decarboxylation regenerating the acetyl-ACP. The ACP subunit of both enzymes differs from that found in fatty-acid biosynthesis by having phosphopantethine attached to a serine side-chain as 2-(5-triphosphoribosyl)-3-dephospho-CoA rather than as phosphopantetheine 4′-phosphate. The individual enzymes involved in carrying out the reaction of this enzyme complex are EC 2.3.1.187 (acetyl-*S*-ACP:malonate ACP transferase), EC 2.3.1.39 ([acyl-carrier-protein] *S*-malonyltransferase) and EC 4.1.1.87 (malonyl-*S*-ACP decarboxylase). The carboxy group is lost with retention of configuration [499].
References: [1214, 165, 562, 228, 563, 499, 731, 704, 323]

[EC 4.1.1.88 created 2008, modified 2018]

[4.1.1.89 Transferred entry. biotin-dependent malonate decarboxylase. Now EC 7.2.4.4, biotin-dependent malonate decarboxylase]

[EC 4.1.1.89 created 2008, deleted 2018]

EC 4.1.1.90
Accepted name: peptidyl-glutamate 4-carboxylase
Reaction: peptidyl-4-carboxyglutamate + 2,3-epoxyphylloquinone + H_2O = peptidyl-glutamate + CO_2 + O_2 + phylloquinol
Other name(s): vitamin K-dependent carboxylase; γ-glutamyl carboxylase; peptidyl-glutamate 4-carboxylase (2-methyl-3-phytyl-1,4-naphthoquinone-epoxidizing)
Systematic name: peptidyl-glutamate 4-carboxylase (2-methyl-3-phytyl-1,4-naphthoquinol-epoxidizing)
Comments: The enzyme can use various vitamin-K derivatives, including menaquinol, but does not contain iron. The mechanism appears to involve the generation of a strong base by oxygenation of vitamin K. It catalyses the post-translational carboxylation of glutamate residues of several proteins of the blood-clotting system. 9–12 glutamate residues are converted to 4-carboxyglutamate (Gla) in a specific domain of the target protein. The 4-*pro-S* hydrogen of the glutamate residue is removed [876] and there is an inversion of stereochemistry at this position [336].
References: [330, 417, 1157, 1274, 876, 336, 1156]

[EC 4.1.1.90 created 2009, modified 2011]

EC 4.1.1.91

Accepted name: salicylate decarboxylase

Reaction: salicylate = phenol + CO_2

Other name(s): salicylic acid decarboxylase; Scd

Systematic name: salicylate carboxy-lyase

Comments: In the reverse direction the enzyme catalyses the regioselective carboxylation of phenol into stoichiometric amounts of salicylate. The enzyme also catalyses the reversible decarboxylation of 2,4-dihydroxybenzoate, 2,6-dihydroxybenzoate, 2,3-dihydroxybenzoate and 4-aminosalicylate [706].

References: [706]

[EC 4.1.1.91 created 2011]

EC 4.1.1.92

Accepted name: indole-3-carboxylate decarboxylase

Reaction: indole-3-carboxylate = indole + CO_2

Systematic name: indole-3-carboxylate carboxy-lyase

Comments: Activated by Zn^{2+}, Mn^{2+} or Mg^{2+}.

References: [1514]

[EC 4.1.1.92 created 2011]

EC 4.1.1.93

Accepted name: pyrrole-2-carboxylate decarboxylase

Reaction: (1) pyrrole-2-carboxylate = pyrrole + CO_2
(2) pyrrole-2-carboxylate + H_2O = pyrrole + HCO_3^-

Systematic name: pyrrole-2-carboxylate carboxy-lyase

Comments: The enzyme catalyses both the carboxylation and decarboxylation reactions. However, while bicarbonate is the preferred substrate for the carboxylation reaction, decarboxylation produces carbon dioxide. The enzyme is activated by carboxylic acids.

References: [1464, 1032, 1465]

[EC 4.1.1.93 created 2011]

EC 4.1.1.94

Accepted name: ethylmalonyl-CoA decarboxylase

Reaction: (*S*)-ethylmalonyl-CoA = butanoyl-CoA + CO_2

Systematic name: (*S*)-ethylmalonyl-CoA carboxy-lyase (butanoyl-CoA-forming)

Comments: The enzyme, which exists in all vertebrates, decarboxylates ethylmalonyl-CoA, a potentially toxic compound that is formed in low amounts by the activity of EC 6.4.1.2, acetyl-CoA carboxylase and EC 6.4.1.3, propanoyl-CoA carboxylase. It prefers the *S* isomer, and can decarboxylate (*R*)-ethylmalonyl-CoA with lower efficiency. *cf.* EC 7.2.4.1, (*S*)-methylmalonyl-CoA decarboxylase (sodium-transporting).

References: [823]

[EC 4.1.1.94 created 2012]

EC 4.1.1.95

Accepted name: L-glutamyl-[BtrI acyl-carrier protein] decarboxylase

Reaction: L-glutamyl-[BtrI acyl-carrier protein] = 4-amino butanoyl-[BtrI acyl-carrier protein] + CO_2

Other name(s): *btrK* (gene name)

Systematic name: L-glutamyl-[BtrI acyl-carrier protein] carboxy-lyase

Comments: Binds pyridoxal 5′-phosphate. Catalyses a step in the biosynthesis of the side chain of the aminoglycoside antibiotics of the butirosin family. Has very low activity with substrates not bound to an acyl-carrier protein.

References: [806]

[EC 4.1.1.95 created 2012]

EC 4.1.1.96

Accepted name: carboxynorspermidine decarboxylase

Reaction: (1) carboxynorspermidine = bis(3-aminopropyl)amine + CO$_2$
(2) carboxyspermidine = spermidine + CO$_2$

Other name(s): carboxyspermidine decarboxylase; CANSDC; VC1623 (gene name)

Systematic name: carboxynorspermidine carboxy-lyase (bis(3-aminopropyl)amine-forming)

Comments: A pyridoxal 5′-phosphate enzyme. Part of a bacterial polyamine biosynthesis pathway. The enzyme is essential for biofilm formation in the bacterium *Vibrio cholerae* [790]. The enzyme from *Campylobacter jejuni* only produces spermidine *in vivo* even though it shows activity with carboxynorspermidine *in vitro* [503].

References: [790, 311, 503]

[EC 4.1.1.96 created 2012]

EC 4.1.1.97

Accepted name: 2-oxo-4-hydroxy-4-carboxy-5-ureidoimidazoline decarboxylase

Reaction: 5-hydroxy-2-oxo-4-ureido-2,5-dihydro-1*H*-imidazole-5-carboxylate = (*S*)-allantoin + CO$_2$

Other name(s): OHCU decarboxylase; *hpxQ* (gene name); PRHOXNB (gene name)

Systematic name: 5-hydroxy-2-oxo-4-ureido-2,5-dihydro-1*H*-imidazole-5-carboxylate carboxy-lyase [(*S*)-allantoin-forming]

Comments: This enzyme is part of the pathway from urate to (*S*)-allantoin, which is present in bacteria, plants and animals (but not in humans).

References: [1128, 201, 702, 403]

[EC 4.1.1.97 created 2014]

EC 4.1.1.98

Accepted name: 4-hydroxy-3-polyprenylbenzoate decarboxylase

Reaction: a 4-hydroxy-3-polyprenylbenzoate = a 2-polyprenylphenol + CO$_2$

Other name(s): *ubiD* (gene name); 4-hydroxy-3-solanesylbenzoate decarboxylase; 3-octaprenyl-4-hydroxybenzoate decarboxylase

Systematic name: 4-hydroxy-3-polyprenylbenzoate carboxy-lyase

Comments: The enzyme catalyses a step in prokaryotic ubiquinone biosynthesis, as well as in plastoquinone biosynthesis in cyanobacteria. The enzyme can accept substrates with different polyprenyl tail lengths *in vitro*, but uses a specific length *in vivo*, which is determined by the polyprenyl diphosphate synthase that exists in the specific organism. It requires a prenylated flavin cofactor that is produced by EC 2.5.1.129, flavin prenyltransferase.

References: [796, 473, 1074, 817, 1059]

[EC 4.1.1.98 created 2014, modified 2015]

EC 4.1.1.99

Accepted name: phosphomevalonate decarboxylase

Reaction: ATP + (*R*)-5-phosphomevalonate = ADP + phosphate + isopentenyl phosphate + CO$_2$

Systematic name: ATP:(*R*)-5-phosphomevalonate carboxy-lyase (adding ATP; isopentenyl-phosphate-forming)

Comments: The enzyme participates in a mevalonate pathway that occurs in halophilic archaea. The activity is also present in eubacteria of the Chloroflexi phylum. *cf.* EC 4.1.1.33, diphosphomevalonate decarboxylase, and EC 4.1.1.110, bisphosphomevalonate decarboxylase.

References: [309, 1417, 1366]

[EC 4.1.1.99 created 2014, modified 2018]

EC 4.1.1.100

Accepted name: prephenate decarboxylase

Reaction: prephenate = 3-[(4*R*)-4-hydroxycyclohexa-1,5-dien-1-yl]-2-oxopropanoate + CO_2

Other name(s): BacA; AerD; SalX; non-aromatizing prephenate decarboxylase

Systematic name: prephenate carboxy-lyase (3-[(4*R*)-4-hydroxycyclohexa-1,5-dien-1-yl]-2-oxopropanoate-forming)

Comments: The enzyme, characterized from the bacterium *Bacillus subtilis*, is involved in the biosynthesis of the nonribosomally synthesized dipeptide antibiotic bacilysin, composed of L-alanine and L-anticapsin. The enzyme isomerizes only the *pro-R* double bond in prephenate.

References: [866, 865, 1054]

[EC 4.1.1.100 created 2015]

EC 4.1.1.101

Accepted name: malolactic enzyme

Reaction: (*S*)-malate = (*S*)-lactate + CO_2

Other name(s): *mleA* (gene name); *mleS* (gene name)

Systematic name: (*S*)-malate carboxy-lyase

Comments: The enzyme is involved in the malolactic fermentation of wine, which results in a natural decrease in acidity and favorable changes in wine flavors. It has been purified from several lactic acid bacteria, including *Leuconostoc mesenteroides* [841], *Lactobacillus plantarum* [195], and *Oenococcus oeni* [992, 1239]. The enzyme contains a tightly bound NAD^+ cofactor and requires Mn^{2+}.

References: [841, 195, 992, 1239]

[EC 4.1.1.101 created 2015]

EC 4.1.1.102

Accepted name: phenacrylate decarboxylase

Reaction: (1) 4-coumarate = 4-vinylphenol + CO_2
(2) *trans*-cinnamate = styrene + CO_2
(3) ferulate = 4-vinylguaiacol + CO_2

Other name(s): FDC1 (gene name); ferulic acid decarboxylase

Systematic name: 3-phenylprop-2-enoate carboxy-lyase

Comments: The enzyme, found in fungi, catalyses the decarboxylation of phenacrylic acids present in plant cell walls. It requires a prenylated flavin cofactor that is produced by EC 2.5.1.129, flavin prenyltransferase.

References: [967, 96, 1059]

[EC 4.1.1.102 created 2015]

EC 4.1.1.103

Accepted name: γ-resorcylate decarboxylase

Reaction: 2,6-dihydroxybenzoate = 1,3-dihydroxybenzene + CO_2

Other name(s): *graF* (gene name); *tsdA* (gene name)

Systematic name: 2,6-dihydroxybenzoate carboxy-lyase

Comments: The enzyme, characterized from several bacterial strains, is involved in the degradation of γ-resorcylate. It contains a zinc ion and a water molecule at the active site. The reaction is reversible, but equilibrium greatly favors the decarboxylation reaction.

References: [1513, 603, 895, 455, 669]

[EC 4.1.1.103 created 2016]

EC 4.1.1.104

Accepted name: 3-dehydro-4-phosphotetronate decarboxylase

Reaction: (1) 3-dehydro-4-phospho-L-erythronate = glycerone phosphate + CO_2
(2) 3-dehydro-4-phospho-D-erythronate = glycerone phosphate + CO_2

Other name(s): *otnC* (gene name)

Systematic name: 3-dehydro-4-phosphotetronate carboxy-lyase

Comments: The enzyme, characterized from bacteria, is involved in D-erythronate and L-threonate catabolism.

References: [1553]

[EC 4.1.1.104 created 2017]

EC 4.1.1.105

Accepted name: L-tryptophan decarboxylase

Reaction: L-tryptophan = tryptamine + CO_2

Other name(s): *psiD* (gene name); TDC (gene name)

Systematic name: L-tryptophan carboxy-lyase

Comments: The enzyme has been characterized from bacteria, plants, and fungi. Unlike EC 4.1.1.28, aromatic-L-amino-acid decarboxylase, this enzyme is specific for L-tryptophan.

References: [1010, 156, 991, 844, 406]

[EC 4.1.1.105 created 2017]

EC 4.1.1.106

Accepted name: fatty acid photodecarboxylase

Reaction: a long-chain fatty acid + $h\nu$ = a long-chain alkane + CO_2

Other name(s): FAP (gene name)

Systematic name: fatty acid carboxy-lyase (light-dependent, alkane-forming)

Comments: This algal enzyme, characterized from the green algae *Chlorella variabilis* and *Chlamydomonas reinhardtii*, is dependent on blue light, which photooxidizes its FAD cofactor. The enzyme acts on fatty acids in the range of C_{12} to C_{22}, with a higher efficiency for C_{16} to C_{17} chains, and forms an alkane product that is one carbon shorter than the substrate. The enzyme can also act on unsaturated fatty acids, forming the respective alkenes, but does not generate a new double bond.

References: [1291]

[EC 4.1.1.106 created 2017]

EC 4.1.1.107

Accepted name: 3,4-dihydroxyphenylacetaldehyde synthase

Reaction: L-dopa + O_2 + H_2O = 3,4-dihydroxyphenylacetaldehyde + CO_2 + NH_3 + H_2O_2

Other name(s): DHPAA synthase

Systematic name: L-dopa carboxy-lyase (oxidative-deaminating)

Comments: A pyridoxal 5′-phosphate protein. The enzyme, isolated from the mosquito *Aedes aegypti*, catalyses the production of 3,4-dihydroxylphenylacetaldehyde directly from L-dopa. Dopamine is not formed as an intermediate (*cf.* EC 4.1.1.28, aromatic-L-amino-acid decarboxylase). The enzyme is specific for L-dopa and does not react with other aromatic amino acids with the exception of a low activity with α-methyl-L-dopa.

References: [1420]

[EC 4.1.1.107 created 2017]

EC 4.1.1.108

Accepted name: 4-hydroxyphenylacetaldehyde synthase

Reaction: L-tyrosine + O_2 + H_2O = (4-hydroxyphenyl)acetaldehyde + CO_2 + NH_3 + H_2O_2

Other name(s): TYRD*C*-2 (gene name)
Systematic name: L-tyrosine carboxy-lyase (oxidative-deaminating)
Comments: A pyridoxal $5'$-phosphate protein. The enzyme, isolated from the the plant *Petroselinum crispum* (parsley), catalyses the production of 4-hydroxyphenylacetaldehyde directly from L-tyrosine. Tyramine is not formed as an intermediate. The enzyme has a low activity with L-dopa (*cf.* EC 4.1.1.107, 3,4-dihydroxyphenylacetaldehyde synthase).
References: [1381, 1382]

[EC 4.1.1.108 created 2017]

EC 4.1.1.109

Accepted name: phenylacetaldehyde synthase
Reaction: L-phenylalanine + O_2 + H_2O = phenylacetaldehyde + CO_2 + NH_3 + H_2O_2
Other name(s): PAAS (gene name)
Systematic name: L-phenylalanine carboxy-lyase (oxidative-deaminating)
Comments: A pyridoxal $5'$-phosphate protein. The enzyme, isolated from the the plants *Petunia hybrida* and a *Rosa* hybrid, catalyses the production of phenylacetaldehyde directly from L-phenylalanine. The enzyme is specific for L-phenylalanine and does not accept other aromatic amino acids as substrates.
References: [656]

[EC 4.1.1.109 created 2017]

EC 4.1.1.110

Accepted name: bisphosphomevalonate decarboxylase
Reaction: (*R*)-3,5-bisphosphomevalonate = isopentenyl phosphate + CO_2 + phosphate
Other name(s): mevalonate 3,5-bisphosphate decarboxylase
Systematic name: (*R*)-3,5-bisphosphomevalonate carboxy-lyase (isopentenyl-phosphate-forming)
Comments: The enzyme participates in an alternative mevalonate pathway that takes place in extreme acidophiles of the Thermoplasmatales order. *cf.* EC 4.1.1.99, phosphomevalonate decarboxylase.
References: [1423]

[EC 4.1.1.110 created 2018]

EC 4.1.1.111

Accepted name: siroheme decarboxylase
Reaction: siroheme = 12,18-didecarboxysiroheme + **2** CO_2
Other name(s): sirohaem decarboxylase; nirDLHG (gene name); *ahbAB* (gene name)
Systematic name: siroheme carboxy-lyase
Comments: The enzyme from archaea is involved in an alternative heme biosynthesis pathway. The enzyme from denitrifying bacteria is involved in the heme d1 biosynthesis pathway.
References: [70, 753, 1051, 525]

[EC 4.1.1.111 created 2018]

EC 4.1.1.112

Accepted name: oxaloacetate decarboxylase
Reaction: oxaloacetate = pyruvate + CO_2
Other name(s): oxaloacetate β-decarboxylase; oxalacetic acid decarboxylase; oxalate β-decarboxylase; oxaloacetate carboxy-lyase
Systematic name: oxaloacetate carboxy-lyase (pyruvate-forming)

Comments: Requires a divalent metal cation. The enzymes from the fish *Gadus morhua* (Atlantic cod) and the bacterium *Micrococcus luteus* prefer Mn^{2+}, while those from the bacteria *Pseudomonas putida* and *Pseudomonas aeruginosa* prefer Mg^{2+}. Unlike EC 7.2.4.2 [oxaloacetate decarboxylase (Na^{+} extruding)], there is no evidence of the enzyme's involvement in Na^{+} transport.

References: [1223, 542, 576, 1254, 993]

[EC 4.1.1.112 created 1961 as EC 4.1.1.3, modified 1986, modified 2000, part transferred 2018 to EC 4.1.1.112]

EC 4.1.1.113

Accepted name: *trans*-aconitate decarboxylase

Reaction: *trans*-aconitate = itaconate + CO_2

Other name(s): TAD1 (gene name)

Systematic name: *trans*-aconitate carboxy-lyase (itaconate-forming)

Comments: The enzyme, characterized from the smut fungus *Ustilago maydis*, is involved in an alternative pathway for the biosynthesis of itaconate. *cf.* EC 4.1.1.6, *cis*-aconitate decarboxylase.

References: [432]

[EC 4.1.1.113 created 2018]

EC 4.1.1.114

Accepted name: *cis*-3-alkyl-4-alkyloxetan-2-one decarboxylase

Reaction: a *cis*-3-alkyl-4-alkyloxetan-2-one = a *cis*-alkene + CO_2

Other name(s): *oleB* (gene name)

Systematic name: *cis*-3-alkyl-4-alkyloxetan-2-one carboxy-lyase (*cis*-alkene-forming)

Comments: The enzyme, found in certain bacterial species, catalyses the last step in a pathway for the production of olefins.

References: [233, 232]

[EC 4.1.1.114 created 2018]

EC 4.1.1.115

Accepted name: indoleacetate decarboxylase

Reaction: (1*H*-indol-3-yl)acetate = skatole + CO_2

Other name(s): IAD

Systematic name: (1*H*-indol-3-yl)acetate carboxy-lyase (skatole-forming)

Comments: This glycyl radical enzyme has been isolate from a number of bacterial species. Skatole contributes to the characteristic smell of animal faeces.

References: [827]

[EC 4.1.1.115 created 2019]

EC 4.1.1.116

Accepted name: D-ornithine/D-lysine decarboxylase

Reaction: (1) D-ornithine = putrescine + CO_2
(2) D-lysine = cadaverine + CO_2

Other name(s): *dokD* (gene name); DOKDC

Systematic name: D-ornithine/D-lysine carboxy-lyase

Comments: The enzyme, characterized from the bacterium *Salmonella typhimurium* LT2, is specific for D-ornithine and D-lysine. Requires pyridoxal $5'$-phosphate.

References: [1079]

[EC 4.1.1.116 created 2019]

EC 4.1.1.117

Accepted name: 2-[(L-alanin-3-ylcarbamoyl)methyl]-2-hydroxybutanedioate decarboxylase

Reaction: 2-[(L-alanin-3-ylcarbamoyl)methyl]-2-hydroxybutanedioate = 2-[(2-aminoethylcarbamoyl)methyl]-2-hydroxybutanedioate + CO_2

Other name(s): *sbnH* (gene name)

Systematic name: 2-[(L-alanin-3-ylcarbamoyl)methyl]-2-hydroxybutanedioate carboxy-lyase (2-[(2-aminoethylcarbamoyl)methyl]-2-hydroxybutanedioate-forming)

Comments: The enzyme, characterized from the bacterium *Staphylococcus aureus*, participates in the biosynthesis of the siderophore staphyloferrin B.

References: [223]

[EC 4.1.1.117 created 2019]

EC 4.1.1.118

Accepted name: isophthalyl-CoA decarboxylase

Reaction: isophthalyl-CoA = benzoyl-CoA + CO_2

Other name(s): IPCD

Systematic name: isophthalyl-CoA carboxy-lyase

Comments: The enzyme, characterized from the bacterium *Syntrophorhabdus aromaticivorans*, participates in an anaerobic isophthalate degradation pathway. The enzyme requires a prenylated flavin mononucleotide cofactor.

References: [651]

[EC 4.1.1.118 created 2019]

EC 4.1.1.119

Accepted name: phenylacetate decarboxylase

Reaction: phenylacetate = toluene + CO_2

Other name(s): *phdB* (gene name)

Systematic name: phenylacetate carboxy-lyase

Comments: This bacterial enzyme, isolated from anoxic, toluene-producing microbial communities, is a glycyl radical enzyme. It needs to be activated by a dedicated activating enzyme (PhdA). The activase catalyses the reductive cleavage of AdoMet, producing a $5'$-deoxyadenosyl radical that leads to the production of the glycyl radical in PhdB.

References: [1541, 84, 1167]

[EC 4.1.1.119 created 2019]

EC 4.1.1.120

Accepted name: 3-oxoisoapionate decarboxylase

Reaction: 3-oxoisoapionate = L-erythrulose + CO_2

Other name(s): *oiaC* (gene name)

Systematic name: 3-oxoisoapionate carboxy-lyase

Comments: The enzyme, characterized from several bacterial species, is involved in the degradation of D-apionate. Stereospecificity of 3-oxoisoapionate has not been determined.

References: [194]

[EC 4.1.1.120 created 2020]

EC 4.1.1.121

Accepted name: 3-oxoisoapionate-4-phosphate decarboxylase

Reaction: 3-oxoisoapionate 4-phosphate = L-erythrulose 1-phosphate + CO_2

Other name(s): *oiaX* (gene name)

Systematic name: 3-oxoisoapionate 4-phosphate carboxy-lyase
Comments: The enzyme, characterized from several bacterial species, participates in the degradation of D-apionate. It belongs to the RuBisCO-like-protein (RLP) superfamily. Stereospecificity of 3-oxoisoapionate 4-phosphate has not been determined.
References: [194]

[EC 4.1.1.121 created 2020]

EC 4.1.1.122

Accepted name: L-cysteate decarboxylase
Reaction: L-cysteate = taurine + CO_2
Other name(s): CAD
Systematic name: L-cysteate carboxy-lyase (taurine-forming)
Comments: Requires pyridoxal $5'$-phosphate. The enzyme, characterized from chicken, is specific for L-cysteate and has poor activity with 3-sulfino-L-alanine. *cf.* EC 4.1.1.29, sulfinoalanine decarboxylase.
References: [867]

[EC 4.1.1.122 created 2022]

EC 4.1.1.123

Accepted name: phenyl-phosphate phosphatase/carboxylase
Reaction: 4-hydroxybenzoate + phosphate = phenyl phosphate + CO_2 + H_2O
Other name(s): phenyl phosphate carboxylase
Systematic name: 4-hydroxybenzoate carboxy-lyase (phenyl phosphate-forming)
Comments: The enzyme, characterized from the bacterium *Thauera aromatica*, participates in an anaerobic phenol degradation pathway. It catalyses the *para* dephosphorylation and carboxylation of phenylphosphate to 4-hydroxybenzoate. The enzyme from *Thauera aromatica* consists of four different subunits and requires K^+ and a divalent metal cation (Mg^{2+} or Mn^{2+}) for activity. It is strongly inhibited by oxygen.
References: [1236]

[EC 4.1.1.123 created 2022]

EC 4.1.2 Aldehyde-lyases

[4.1.2.1 Deleted entry. hydroxyoxobutyrate aldolase. Now included with EC 4.1.3.16 4-hydroxy-2-oxoglutarate aldolase]

[EC 4.1.2.1 created 1961, deleted 1972]

EC 4.1.2.2

Accepted name: ketotetrose-phosphate aldolase
Reaction: erythrulose 1-phosphate = glycerone phosphate + formaldehyde
Other name(s): phosphoketotetrose aldolase; erythrulose-1-phosphate synthetase; erythrose-1-phosphate synthase; erythrulose-1-phosphate formaldehyde-lyase
Systematic name: erythrulose-1-phosphate formaldehyde-lyase (glycerone-phosphate-forming)
References: [211]

[EC 4.1.2.2 created 1961]

[4.1.2.3 Deleted entry. pentosealdolase]

[EC 4.1.2.3 created 1961, deleted 1972]

EC 4.1.2.4

Accepted name: deoxyribose-phosphate aldolase

Reaction: 2-deoxy-D-ribose 5-phosphate = D-glyceraldehyde 3-phosphate + acetaldehyde

Other name(s): phosphodeoxyriboaldolase; deoxyriboaldolase; deoxyribose-5-phosphate aldolase; 2-deoxyribose-5-phosphate aldolase; 2-deoxy-D-ribose-5-phosphate acetaldehyde-lyase

Systematic name: 2-deoxy-D-ribose-5-phosphate acetaldehyde-lyase (D-glyceraldehyde-3-phosphate-forming)

References: [565, 623, 1123, 564]

[EC 4.1.2.4 created 1961]

EC 4.1.2.5

Accepted name: L-threonine aldolase

Reaction: L-threonine = glycine + acetaldehyde

Other name(s): L-threonine acetaldehyde-lyase

Systematic name: L-threonine acetaldehyde-lyase (glycine-forming)

Comments: A pyridoxal-phosphate protein. This enzyme is specific for L-threonine and can not utilize L-*allo*-threonine. Different from EC 4.1.2.49, L-*allo*-threonine aldolase, and EC 4.1.2.48, low-specificity L-threonine aldolase.

References: [287, 667]

[EC 4.1.2.5 created 1961, deleted 1972, reinstated 1976, modified 2011]

[4.1.2.6 Deleted entry. allothreonine aldolase. Reaction is due to EC 2.1.2.1, glycine hydroxymethyltransferase]

[EC 4.1.2.6 created 1961, deleted 1972]

[4.1.2.7 Deleted entry. ketose-1-phosphate aldolase. Now included with EC 4.1.2.13 fructose-bisphosphate aldolase]

[EC 4.1.2.7 created 1961, deleted 1972]

EC 4.1.2.8

Accepted name: indole-3-glycerol-phosphate lyase

Reaction: (1*S*,2*R*)-1-*C*-(indol-3-yl)glycerol 3-phosphate = indole + D-glyceraldehyde 3-phosphate

Other name(s): tryptophan synthase α; TSA; indoleglycerolphosphate aldolase; indole glycerol phosphate hydrolase; indole synthase; indole-3-glycerolphosphate D-glyceraldehyde-3-phosphate-lyase; indole-3-glycerol phosphate lyase; IGL; BX1; (1*S*,2*R*)-1-*C*-(indol-3-yl)glycerol 3-phosphate D-glyceraldehyde-3-phosphate-lyase

Systematic name: (1*S*,2*R*)-1-*C*-(indol-3-yl)glycerol-3-phosphate D-glyceraldehyde-3-phosphate-lyase (indole-forming)

Comments: Forms part of the defence mechanism against insects and microbial pathogens in the grass family, Gramineae, where it catalyses the first committed step in the formation of the cyclic hydroxamic acids 2,4-dihydroxy-2*H*-1,4-benzoxazin-3(4*H*)-one (DIBOA) and 2,4-dihydroxy-7-methoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (DIMBOA) [1505]. This enzyme resembles the α-subunit of EC 4.2.1.20, tryptophan synthase [405], for which, (1*S*,2*R*)-1-*C*-(indol-3-yl)glycerol 3-phosphate is also a substrate, but, unlike tryptophan synthase, its activity is independent of the β-subunit and free indole is released [404].

References: [1505, 404, 405, 924]

[EC 4.1.2.8 created 1961, deleted 1972, reinstated 2006]

EC 4.1.2.9

Accepted name: phosphoketolase

Reaction: D-xylulose 5-phosphate + phosphate = acetyl phosphate + D-glyceraldehyde 3-phosphate + H_2O

Other name(s): D-xylulose-5-phosphate D-glyceraldehyde-3-phosphate-lyase (phosphate-acetylating)

Systematic name: D-xylulose-5-phosphate D-glyceraldehyde-3-phosphate-lyase (adding phosphate; acetyl-phosphate-forming)

Comments: A thiamine-diphosphate protein.
References: [531, 1233]

[EC 4.1.2.9 created 1961]

EC 4.1.2.10

Accepted name: (*R*)-mandelonitrile lyase
Reaction: (*R*)-mandelonitrile = cyanide + benzaldehyde
Other name(s): (*R*)-oxynitrilase; oxynitrilase; D-oxynitrilase; D-α-hydroxynitrile lyase; mandelonitrile benzaldehyde-lyase; PaHNL; AtHNL; PhaMDL; (*R*)-HNL; (*R*)-PeHNL; (*R*)-hydroxynitrile lyase; *R*-selective hydroxynitrile lyase; *R*-selective HNL; (*R*)-(+)-mandelonitrile lyase
Systematic name: (*R*)-mandelonitrile benzaldehyde-lyase (cyanide-forming)
Comments: A variety of enzymes from different sources and with different properties. Some are flavoproteins, others are not. Active towards a number of aromatic and aliphatic hydroxynitriles (cyanohydrins).
References: [1404, 818, 301, 1405, 28, 482]

[EC 4.1.2.10 created 1961, modified 1999, modified 2011]

EC 4.1.2.11

Accepted name: hydroxymandelonitrile lyase
Reaction: (*S*)-4-hydroxymandelonitrile = cyanide + 4-hydroxybenzaldehyde
Other name(s): hydroxynitrile lyase; oxynitrilase; *Sorghum* hydroxynitrile lyase; (*S*)-4-hydroxymandelonitrile hydroxybenzaldehyde-lyase
Systematic name: (*S*)-4-hydroxymandelonitrile 4-hydroxybenzaldehyde-lyase (cyanide-forming)
Comments: Does not accept aliphatic hydroxynitriles, unlike EC 4.1.2.10 (mandelonitrile lyase), EC 4.1.2.46 [aliphatic (*R*)-hydroxynitrile lyase] and EC 4.1.2.47 [(*S*)-hydroxynitrile ketone-lyase (cyanide forming)].
References: [123, 1245]

[EC 4.1.2.11 created 1965, modified 1999]

EC 4.1.2.12

Accepted name: 2-dehydropantoate aldolase
Reaction: 2-dehydropantoate = 3-methyl-2-oxobutanoate + formaldehyde
Other name(s): ketopantoaldolase; 2-dehydropantoate formaldehyde-lyase
Systematic name: 2-dehydropantoate formaldehyde-lyase (3-methyl-2-oxobutanoate-forming)
References: [913]

[EC 4.1.2.12 created 1965, modified 2002]

EC 4.1.2.13

Accepted name: fructose-bisphosphate aldolase
Reaction: D-fructose 1,6-bisphosphate = glycerone phosphate + D-glyceraldehyde 3-phosphate
Other name(s): aldolase; fructose-1,6-bisphosphate triosephosphate-lyase; fructose diphosphate aldolase; diphosphofructose aldolase; fructose 1,6-diphosphate aldolase; ketose 1-phosphate aldolase; phosphofructoaldolase; zymohexase; fructoaldolase; fructose 1-phosphate aldolase; fructose 1-monophosphate aldolase; 1,6-diphosphofructose aldolase; SMALDO; D-fructose-1,6-bisphosphate D-glyceraldehyde-3-phosphate-lyase
Systematic name: D-fructose-1,6-bisphosphate D-glyceraldehyde-3-phosphate-lyase (glycerone-phosphate-forming)
Comments: Also acts on (3*S*,4*R*)-ketose 1-phosphates. The yeast and bacterial enzymes are zinc proteins. The enzymes increase electron-attraction by the carbonyl group, some (Class I) forming a protonated imine with it, others (Class II), mainly of microbial origin, polarizing it with a metal ion, e.g. zinc.
References: [574, 17]

[EC 4.1.2.13 created 1965, modified 1999 (EC 4.1.2.7 created 1961, incorporated 1972)]

EC 4.1.2.14

Accepted name: 2-dehydro-3-deoxy-phosphogluconate aldolase

Reaction: 2-dehydro-3-deoxy-6-phospho-D-gluconate = pyruvate + D-glyceraldehyde 3-phosphate

Other name(s): phospho-2-keto-3-deoxygluconate aldolase; KDPG aldolase; phospho-2-keto-3-deoxygluconic aldolase; 2-keto-3-deoxy-6-phosphogluconic aldolase; 2-keto-3-deoxy-6-phosphogluconate aldolase; 6-phospho-2-keto-3-deoxygluconate aldolase; ODPG aldolase; 2-oxo-3-deoxy-6-phosphogluconate aldolase; 2-keto-3-deoxygluconate-6-*P*-aldolase; 2-keto-3-deoxygluconate-6-phosphate aldolase; 2-dehydro-3-deoxy-D-gluconate-6-phosphate D-glyceraldehyde-3-phosphate-lyase; 2-dehydro-3-deoxy-D-gluconate-6-phosphate D-glyceraldehyde-3-phosphate-lyase (pyruvate-forming)

Systematic name: 2-dehydro-3-deoxy-6-phospho-D-gluconate D-glyceraldehyde-3-phosphate-lyase (pyruvate-forming)

Comments: The enzyme shows no activity with 2-dehydro-3-deoxy-6-phosphate-D-galactonate. *cf.* EC 4.1.2.55, 2-dehydro-3-deoxy-phosphogluconate/2-dehydro-3-deoxy-6-phosphogalactonate aldolase [77]. Also acts on 2-oxobutanoate [926].

References: [926, 77]

[EC 4.1.2.14 created 1965, modified 1976, modified 2014]

[4.1.2.15 Transferred entry. 2-dehydro-3-deoxy-phosphoheptonate aldolase. Now EC 2.5.1.54, 3-deoxy-7-phosphoheptulonate synthase]

[EC 4.1.2.15 created 1965, modified 1976, deleted 2002]

[4.1.2.16 Transferred entry. 2-dehydro-3-deoxy-phosphooctonate aldolase. Now EC 2.5.1.55, 3-deoxy-8-phosphooctulonate synthase]

[EC 4.1.2.16 created 1965, deleted 2002]

EC 4.1.2.17

Accepted name: L-fuculose-phosphate aldolase

Reaction: L-fuculose 1-phosphate = glycerone phosphate + (*S*)-lactaldehyde

Other name(s): L-fuculose 1-phosphate aldolase; fuculose aldolase; L-fuculose-1-phosphate lactaldehyde-lyase

Systematic name: L-fuculose-1-phosphate (*S*)-lactaldehyde-lyase (glycerone-phosphate-forming)

References: [434, 333, 334]

[EC 4.1.2.17 created 1965]

EC 4.1.2.18

Accepted name: 2-dehydro-3-deoxy-L-pentonate aldolase

Reaction: 2-dehydro-3-deoxy-L-pentonate = pyruvate + glycolaldehyde

Other name(s): 2-keto-3-deoxy-L-pentonate aldolase; 2-keto-3-deoxy-L-arabonate aldolase; 2-keto-3-deoxy-D-xylonate aldolase; 3-deoxy-D-pentulosonic acid aldolase; 2-dehydro-3-deoxy-L-pentonate glycolaldehyde-lyase

Systematic name: 2-dehydro-3-deoxy-L-pentonate glycolaldehyde-lyase (pyruvate-forming)

References: [282]

[EC 4.1.2.18 created 1972, modified 1976]

EC 4.1.2.19

Accepted name: rhamnulose-1-phosphate aldolase

Reaction: L-rhamnulose 1-phosphate = glycerone phosphate + (*S*)-lactaldehyde

Other name(s): rhamnulose phosphate aldolase; L-rhamnulose 1-phosphate aldolase; L-rhamnulose-phosphate aldolase; L-rhamnulose-1-phosphate lactaldehyde-lyase

Systematic name: L-rhamnulose-1-phosphate (*S*)-lactaldehyde-lyase (glycerone-phosphate-forming)
References: [225, 1202]

[EC 4.1.2.19 created 1972]

EC 4.1.2.20

Accepted name: 2-dehydro-3-deoxyglucarate aldolase
Reaction: 2-dehydro-3-deoxy-D-glucarate = pyruvate + 2-hydroxy-3-oxopropanoate
Other name(s): 2-keto-3-deoxyglucarate aldolase; α-keto-β-deoxy-D-glucarate aldolase; 2-dehydro-3-deoxy-D-glucarate tartronate-semialdehyde-lyase; 2-dehydro-3-deoxy-D-glucarate tartronate-semialdehyde-lyase (pyruvate-forming)
Systematic name: 2-dehydro-3-deoxy-D-glucarate 2-hydroxy-3-oxopropanoate-lyase (pyruvate-forming)
References: [388]

[EC 4.1.2.20 created 1961 as EC 4.1.2.8, transferred 1972 to EC 4.1.2.20]

EC 4.1.2.21

Accepted name: 2-dehydro-3-deoxy-6-phosphogalactonate aldolase
Reaction: 2-dehydro-3-deoxy-6-phospho-D-galactonate = pyruvate + D-glyceraldehyde 3-phosphate
Other name(s): 6-phospho-2-keto-3-deoxygalactonate aldolase; phospho-2-keto-3-deoxygalactonate aldolase; 2-keto-3-deoxy-6-phosphogalactonic aldolase; phospho-2-keto-3-deoxygalactonic aldolase; 2-keto-3-deoxy-6-phosphogalactonic acid aldolase; (KDPGal)aldolase; 2-dehydro-3-deoxy-D-galactonate-6-phosphate D-glyceraldehyde-3-phosphate-lyase; 2-dehydro-3-deoxy-D-galactonate-6-phosphate D-glyceraldehyde-3-phosphate-lyase (pyruvate-forming)
Systematic name: 2-dehydro-3-deoxy-6-phospho-D-galactonate D-glyceraldehyde-3-phospho-lyase (pyruvate-forming)
Comments: The enzyme catalyses the last reaction in a D-galactose degradation pathway. *cf.* EC 4.1.2.55, 2-dehydro-3-deoxy-phosphogluconate/2-dehydro-3-deoxy-6-phosphogalactonate aldolase.
References: [1269]

[EC 4.1.2.21 created 1972, modified 2014]

EC 4.1.2.22

Accepted name: fructose-6-phosphate phosphoketolase
Reaction: D-fructose 6-phosphate + phosphate = acetyl phosphate + D-erythrose 4-phosphate + H_2O
Other name(s): D-fructose-6-phosphate D-erythrose-4-phosphate-lyase (phosphate-acetylating)
Systematic name: D-fructose-6-phosphate D-erythrose-4-phosphate-lyase (adding phosphate; acetyl-phosphate-forming)
Comments: Also acts on D-xylulose 5-phosphate.
References: [1233]

[EC 4.1.2.22 created 1972]

EC 4.1.2.23

Accepted name: 3-deoxy-D-*manno*-octulosonate aldolase
Reaction: 3-deoxy-D-*manno*-octulosonate = pyruvate + D-arabinose
Other name(s): 2-keto-3-deoxyoctonate aldolase; KDOaldolase; 3-deoxyoctulosonic aldolase; 2-keto-3-deoxyoctonic aldolase; 3-deoxy-D-*manno*-octulosonic aldolase; 3-deoxy-D-*manno*-octulosonate D-arabinose-lyase
Systematic name: 3-deoxy-D-*manno*-octulosonate D-arabinose-lyase (pyruvate-forming)
References: [435]

[EC 4.1.2.23 created 1972]

EC 4.1.2.24

Accepted name: dimethylaniline-*N*-oxide aldolase

Reaction: *N*,*N*-dimethylaniline *N*-oxide = *N*-methylaniline + formaldehyde

Other name(s): microsomal oxidase II; microsomal *N*-oxide dealkylase; *N*,*N*-dimethylaniline-*N*-oxide formaldehyde-lyase

Systematic name: *N*,*N*-dimethylaniline-*N*-oxide formaldehyde-lyase (*N*-methylaniline-forming)

Comments: Acts on various *N*,*N*-dialkylarylamides.

References: [858]

[EC 4.1.2.24 created 1972]

EC 4.1.2.25

Accepted name: dihydroneopterin aldolase

Reaction: 7,8-dihydroneopterin = 6-(hydroxymethyl)-7,8-dihydropterin + glycolaldehyde

Other name(s): 7,8-dihydroneopterin aldolase; 2-amino-4-hydroxy-6-(D-*erythro*-1,2,3-trihydroxypropyl)-7,8-dihydropteridine glycolaldehyde-lyase; 2-amino-4-hydroxy-6-(D-*erythro*-1,2,3-trihydroxypropyl)-7,8-dihydropteridine glycolaldehyde-lyase (2-amino-4-hydroxy-6-hydroxymethyl-7,8-dihydropteridine-forming); DHNA; *mptD* (gene name); *folB* (gene name)

Systematic name: 7,8-dihydroneopterin glycolaldehyde-lyase [6-(hydroxymethyl)-7,8-dihydropterin-forming]

Comments: The enzyme participates in folate (in bacteria, plants and fungi) and methanopterin (in archaea) biosynthesis. The enzymes from the bacterium *Escherichia coli* and the plant *Arabidopsis thaliana* also catalyse the epimerisation of the $2'$ hydroxy-group (EC 5.1.99.8, 7,8-dihydroneopterin epimerase) [527, 459]. The enzyme from the bacterium *Mycobacterium tuberculosis* is trifunctional and also catalyses EC 5.1.99.8 and EC 1.13.11.81, 7,8-dihydroneopterin oxygenase [1451]. The enzyme from the yeast *Saccharomyces cerevisiae* also catalyses the two subsequent steps in the folate biosynthesis pathway - EC 2.7.6.3, 2-amino-4-hydroxy-6-(hydroxymethyl)dihydropteridine diphosphokinase, and EC 2.5.1.15, dihydropteroate synthase [472].

References: [891, 527, 459, 472, 277, 1451, 99]

[EC 4.1.2.25 created 1972, modified 2015]

EC 4.1.2.26

Accepted name: phenylserine aldolase

Reaction: L-*threo*-3-phenylserine = glycine + benzaldehyde

Other name(s): L-*threo*-3-phenylserine benzaldehyde-lyase

Systematic name: L-*threo*-3-phenylserine benzaldehyde-lyase (glycine-forming)

Comments: A pyridoxal-phosphate protein.

References: [149]

[EC 4.1.2.26 created 1972]

EC 4.1.2.27

Accepted name: sphinganine-1-phosphate aldolase

Reaction: sphinganine 1-phosphate = phosphoethanolamine + palmitaldehyde

Other name(s): dihydrosphingosine 1-phosphate aldolase; sphinganine-1-phosphate alkanal-lyase; sphinganine-1-phosphate lyase; sphinganine-1-phosphate palmitaldehyde-lyase

Systematic name: sphinganine-1-phosphate palmitaldehyde-lyase (phosphoethanolamine-forming)

Comments: A pyridoxal-phosphate protein.

References: [1306]

[EC 4.1.2.27 created 1972]

EC 4.1.2.28

Accepted name: 2-dehydro-3-deoxy-D-pentonate aldolase
Reaction: 2-dehydro-3-deoxy-D-pentonate = pyruvate + glycolaldehyde
Other name(s): 2-keto-3-deoxy-D-pentonate aldolase; 3-deoxy-D-pentulosonic acid aldolase; 2-dehydro-3-deoxy-D-pentonate glycolaldehyde-lyase
Systematic name: 2-dehydro-3-deoxy-D-pentonate glycolaldehyde-lyase (pyruvate-forming)
References: [281, 284]

[EC 4.1.2.28 created 1976]

EC 4.1.2.29

Accepted name: 5-dehydro-2-deoxyphosphogluconate aldolase
Reaction: 5-dehydro-2-deoxy-D-gluconate 6-phosphate = glycerone phosphate + malonate semialdehyde
Other name(s): phospho-5-keto-2-deoxygluconate aldolase; 5-dehydro-2-deoxy-D-gluconate-6-phosphate malonate-semialdehyde-lyase
Systematic name: 5-dehydro-2-deoxy-D-gluconate-6-phosphate malonate-semialdehyde-lyase (glycerone-phosphate-forming)
References: [27]

[EC 4.1.2.29 created 1976]

[4.1.2.30 Transferred entry. 17α-hydroxyprogesterone aldolase. Now EC 1.14.14.32, 17α-hydroxyprogesterone deacetylase]

[EC 4.1.2.30 created 1976, deleted 2016]

[4.1.2.31 Deleted entry. 2-oxo-4-hydroxyglutarate aldolase. Now included with EC 4.1.3.16 4-hydroxy-2-oxoglutarate aldolase]

[EC 4.1.2.31 created 1978, deleted 1982]

EC 4.1.2.32

Accepted name: trimethylamine-oxide aldolase
Reaction: trimethylamine *N*-oxide = dimethylamine + formaldehyde
Other name(s): trimethylamine *N*-oxide formaldehyde-lyase; trimethylamine *N*-oxide aldolase; trimethylamine *N*-oxide demethylase; trimethylamine-*N*-oxide formaldehyde-lyase
Systematic name: trimethylamine-*N*-oxide formaldehyde-lyase (dimethylamine-forming)
References: [786, 977]

[EC 4.1.2.32 created 1978]

EC 4.1.2.33

Accepted name: fucosterol-epoxide lyase
Reaction: $(24R,24^{1}R)$-fucosterol epoxide = desmosterol + acetaldehyde
Other name(s): $(24R,24'R)$-fucosterol-epoxide acetaldehyde-lyase; $(24R,24'R)$-fucosterol-epoxide acetaldehyde-lyase (desmosterol-forming)
Systematic name: $(24R,24^{1}R)$-fucosterol-epoxide acetaldehyde-lyase (desmosterol-forming)
Comments: The insect enzyme is involved in the conversion of sitosterol into cholesterol.
References: [1101]

[EC 4.1.2.33 created 1989, modified 2013]

EC 4.1.2.34

Accepted name: 4-(2-carboxyphenyl)-2-oxobut-3-enoate aldolase
Reaction: (3*Z*)-4-(2-carboxyphenyl)-2-oxobut-3-enoate + H_2O = 2-formylbenzoate + pyruvate

Other name(s): 2′-carboxybenzalpyruvate aldolase; (3*E*)-4-(2-carboxyphenyl)-2-oxobut-3-enoate 2-carboxybenzaldehyde-lyase; (3*Z*)-4-(2-carboxyphenyl)-2-oxobut-3-enoate 2-formylbenzoate-lyase
Systematic name: (3*Z*)-4-(2-carboxyphenyl)-2-oxobut-3-enoate 2-formylbenzoate-lyase (pyruvate-forming)
Comments: Involved, with EC 1.13.11.38 (1-hydroxy-2-naphthoate 1,2-dioxygenase), in the metabolism of phenanthrene in bacteria.
References: [76]

[EC 4.1.2.34 created 1989]

EC 4.1.2.35

Accepted name: propioin synthase
Reaction: 4-hydroxy-3-hexanone = **2** propanal
Other name(s): 4-hydroxy-3-hexanone aldolase; 4-hydroxy-3-hexanone propanal-lyase
Systematic name: 4-hydroxy-3-hexanone propanal-lyase (propanal-forming)
References: [958]

[EC 4.1.2.35 created 1990]

EC 4.1.2.36

Accepted name: lactate aldolase
Reaction: (*S*)-lactate = formate + acetaldehyde
Other name(s): lactate synthase; (*S*)-lactate acetaldehyde-lyase
Systematic name: (*S*)-lactate acetaldehyde-lyase (formate-forming)
References: [474]

[EC 4.1.2.36 created 1990]

[4.1.2.37 Deleted entry. hydroxynitrilase. Now covered by EC 4.1.2.46 [aliphatic (R)-hydroxynitrile lyase] and EC 4.1.2.47 [(S)-hydroxynitrile ketone-lyase (cyanide forming)]]

[EC 4.1.2.37 created 1992 (EC 4.1.2.39 created 1999, incorporated 2007), deleted 2011]

EC 4.1.2.38

Accepted name: benzoin aldolase
Reaction: 2-hydroxy-1,2-diphenylethanone = **2** benzaldehyde
Other name(s): benzaldehyde lyase; 2-hydroxy-1,2-diphenylethanone benzaldehyde-lyase
Systematic name: 2-hydroxy-1,2-diphenylethanone benzaldehyde-lyase (benzaldehyde-forming)
Comments: A thiamine-diphosphate protein.
References: [451]

[EC 4.1.2.38 created 1992]

[4.1.2.39 Deleted entry. hydroxynitrilase. The enzyme is identical to EC 4.1.2.37, hydroxynitrilase]

[EC 4.1.2.39 created 1999, deleted 2007]

EC 4.1.2.40

Accepted name: tagatose-bisphosphate aldolase
Reaction: D-tagatose 1,6-bisphosphate = glycerone phosphate + D-glyceraldehyde 3-phosphate
Other name(s): D-tagatose-1,6-bisphosphate triosephosphate lyase
Systematic name: D-tagatose 1,6-bisphosphate D-glyceraldehyde-3-phosphate-lyase (glycerone-phosphate-forming)
Comments: Enzyme activity is stimulated by certain divalent cations. It is involved in the tagatose 6-phosphate pathway of lactose catabolism in bacteria.
References: [26, 1168]

[EC 4.1.2.40 created 1999]

[4.1.2.41 Transferred entry. vanillin synthase. Now included with EC 4.1.2.61, feruloyl-CoA hydratase/lyase]

[EC 4.1.2.41 created 2000, deleted 2019]

EC 4.1.2.42

Accepted name: D-threonine aldolase

Reaction: (1) D-threonine = glycine + acetaldehyde
(2) D-allothreonine = glycine + acetaldehyde

Other name(s): D-TA; DTA; low specificity D-TA; low specificity D-threonine aldolase

Systematic name: D-threonine acetaldehyde-lyase (glycine-forming)

Comments: A pyridoxal-phosphate protein that is activated by divalent metal cations (e.g. Co^{2+}, Ni^{2+}, Mn^{2+} or Mg^{2+}) [672, 830]. The reaction is reversible, which can lead to the interconversion of D-threonine and D-allothreonine [672]. Several other D-β-hydroxy-α-amino acids, such as D-β-phenylserine, D-β-hydroxy-α-aminovaleric acid and D-β-3,4-dihydroxyphenylserine, can also act as substrate [672].

References: [672, 830, 834, 835, 832, 1047]

[EC 4.1.2.42 created 2007]

EC 4.1.2.43

Accepted name: 3-hexulose-6-phosphate synthase

Reaction: D-*arabino*-hex-3-ulose 6-phosphate = D-ribulose 5-phosphate + formaldehyde

Other name(s): D-*arabino*-3-hexulose 6-phosphate formaldehyde-lyase; 3-hexulosephosphate synthase; 3-hexulose phosphate synthase; HPS

Systematic name: D-*arabino*-hex-3-ulose-6-phosphate formaldehyde-lyase (D-ribulose-5-phosphate-forming)

Comments: Requires Mg^{2+} or Mn^{2+} for maximal activity [381]. The enzyme is specific for D-ribulose 5-phosphate as substrate as ribose 5-phosphate, xylulose 5-phosphate, allulose 6-phosphate and fructose 6-phosphate cannot act as substrate. In addition to formaldehyde, the enzyme can also use glycolaldehyde and methylglyoxal [675]. This enzyme, along with EC 5.3.1.27, 6-phospho-3-hexuloisomerase, plays a key role in the ribulose-monophosphate cycle of formaldehyde fixation, which is present in many microorganisms that are capable of utilizing C1-compounds [381]. The hyperthermophilic and anaerobic archaeon *Pyrococcus horikoshii* OT3 constitutively produces a bifunctional enzyme that sequentially catalyses the reactions of this enzyme and EC 5.3.1.27, 6-phospho-3-hexuloisomerase [1037]. This enzyme is a member of the orotidine $5'$-monophosphate decarboxylase (OMPDC) suprafamily [677].

References: [381, 676, 1501, 1537, 677, 1037, 675]

[EC 4.1.2.43 created 2008]

EC 4.1.2.44

Accepted name: 2,3-epoxybenzoyl-CoA dihydrolase

Reaction: 2,3-epoxy-2,3-dihydrobenzoyl-CoA + **2** H$_2$O = (3*Z*)-6-oxohex-3-enoyl-CoA + formate

Other name(s): 2,3-dihydro-2,3-dihydroxybenzoyl-CoA lyase/hydrolase (deformylating); BoxC; dihydrodiol transforming enzyme; benzoyl-CoA oxidation component C; 2,3-dihydro-2,3-dihydroxybenzoyl-CoA 3,4-didehydroadipyl-CoA semialdehyde-lyase (formate-forming); benzoyl-CoA-dihydrodiol lyase (incorrect); 2,3-dihydro-2,3-dihydroxybenzoyl-CoA 3,4-didehydroadipyl-CoA-semialdehyde-lyase (formate-forming)

Systematic name: 2,3-epoxy-2,3-dihydrobenzoyl-CoA (3*Z*)-6-oxohex-3-enoyl-CoA-lyase (formate-forming)

Comments: The enzyme is involved in the aerobic benzoyl-CoA catabolic pathway of the bacterium *Azoarcus evansii*. The enzyme converts 2,3-epoxy-2,3-dihydrobenzoyl-CoA to its oxepin form prior to the ring-opening and the formation of a dialdehyde intermediate.

References: [433, 1135]

[EC 4.1.2.44 created 2010, modified 2015]

EC 4.1.2.45

Accepted name: *trans*-*o*-hydroxybenzylidenepyruvate hydratase-aldolase

Reaction: (3*E*)-4-(2-hydroxyphenyl)-2-oxobut-3-enoate + H_2O = salicylaldehyde + pyruvate

Other name(s): $2'$-hydroxybenzalpyruvate aldolase; NsaE; tHBPA hydratase-aldolase

Systematic name: (3*E*)-4-(2-hydroxyphenyl)-2-oxobut-3-enoate hydro-lyase

Comments: This enzyme is involved in naphthalene degradation. The enzyme catalyses a retro-aldol reaction *in vitro*, and it accepts a broad range of aldehydes and 4-substituted 2-oxobut-3-enoates as substrates [346].

References: [752, 684, 345, 346]

[EC 4.1.2.45 created 2010, modified 2011]

EC 4.1.2.46

Accepted name: aliphatic (*R*)-hydroxynitrile lyase

Reaction: (2*R*)-2-hydroxy-2-methylbutanenitrile = cyanide + butan-2-one

Other name(s): (*R*)-HNL; (*R*)-oxynitrilase; (*R*)-hydroxynitrile lyase; *LuHNL*

Systematic name: (2*R*)-2-hydroxy-2-methylbutanenitrile butan-2-one-lyase (cyanide-forming)

Comments: The enzyme contains Zn^{2+} [1391]. The enzyme catalyses the stereoselective synthesis of aliphatic (*R*)-cyanohydrins [1391]. No activity towards mandelonitrile and 4-hydroxymandelonitrile [167]. Natural substrates for the (*R*)-oxynitrilase from *Linum usitatissimum* are acetone and butan-2-one, which are the building blocks of the cyanogen glycosides in *Linum*, linamarin and lotaustralin, or linustatin and neolinustatin, respectively [1484].

References: [1391, 1392, 16, 1484, 167, 134]

[EC 4.1.2.46 created 2011]

EC 4.1.2.47

Accepted name: (*S*)-hydroxynitrile lyase

Reaction: (1) an aliphatic (*S*)-hydroxynitrile = cyanide + an aliphatic aldehyde or ketone
(2) an aromatic (*S*)-hydroxynitrile = cyanide + an aromatic aldehyde

Other name(s): (*S*)-cyanohydrin producing hydroxynitrile lyase; (*S*)-oxynitrilase; (*S*)-HbHNL; (*S*)-MeHNL; hydroxynitrile lyase; oxynitrilase; HbHNL; MeHNL; (*S*)-selective hydroxynitrile lyase; (*S*)-cyanohydrin carbonyl-lyase (cyanide forming)

Systematic name: (*S*)-cyanohydrin lyase (cyanide-forming)

Comments: Hydroxynitrile lyases catalyses the the cleavage of hydroxynitriles into cyanide and the corresponding aldehyde or ketone. In nature the liberation of cyanide serves as a defense mechanism against herbivores and microbial attack in plants. *In vitro* the enzymes from *Manihot esculenta* and *Hevea brasiliensis* accept a broad range of aliphatic and aromatic carbonyl compounds as substrates and catalyse the formation of (*S*)-hydroxynitriles [396, 711].

References: [396, 154, 1253, 49, 1428, 1217, 428, 1432, 1221, 711]

[EC 4.1.2.47 created 2011]

EC 4.1.2.48

Accepted name: low-specificity L-threonine aldolase

Reaction: (1) L-threonine = glycine + acetaldehyde
(2) L-*allo*-threonine = glycine + acetaldehyde

Other name(s): LtaE

Systematic name: L-threonine/L-*allo*-threonine acetaldehyde-lyase (glycine-forming)

Comments: Requires pyridoxal phosphate. The low-specificity L-threonine aldolase can act on both L-threonine and L-*allo*-threonine [1490, 754]. The enzyme from *Escherichia coli* can also act on L-*threo*-phenylserine and L-*erythro*-phenylserine [831]. The enzyme can also catalyse the aldol condensation of glycolaldehyde and glycine to form 4-hydroxy-L-threonine, an intermediate of pyridoxal phosphate biosynthesis [833]. Different from EC 4.1.2.5, L-threonine aldolase, and EC 4.1.2.49, L-*allo*-threonine aldolase.

References: [1490, 754, 833, 831, 701]

[EC 4.1.2.48 created 2011]

EC 4.1.2.49

Accepted name: L-*allo*-threonine aldolase

Reaction: L-*allo*-threonine = glycine + acetaldehyde

Systematic name: L-*allo*-threonine acetaldehyde-lyase (glycine-forming)

Comments: Requires pyridoxal phosphate. This enzyme, characterized from the bacterium *Aeromonas jandaei*, is specific for L-*allo*-threonine and can not act on either L-threonine or L-serine. Different from EC 4.1.2.5, L-threonine aldolase, and EC 4.1.2.48, low-specificity L-threonine aldolase. A previously listed enzyme with this name, EC 4.1.2.6, was deleted in 1971 after it was found to be identical to EC 2.1.2.1, glycine hydroxymethyltransferase.

References: [673]

[EC 4.1.2.49 created 2011]

EC 4.1.2.50

Accepted name: 6-carboxytetrahydropterin synthase

Reaction: 7,8-dihydroneopterin 3′-triphosphate + H_2O = 6-carboxy-5,6,7,8-tetrahydropterin + acetaldehyde + triphosphate

Other name(s): CPH4 synthase; *queD* (gene name); ToyB; *ykvK* (gene name)

Systematic name: 7,8-dihydroneopterin 3′-triphosphate acetaldehyde-lyase (6-carboxy-5,6,7,8-tetrahydropterin and triphosphate-forming)

Comments: Binds Zn^{2+}. Isolated from the bacteria *Bacillus subtilis* and *Escherichia coli*. The reaction is part of the biosynthesis pathway of queuosine.The enzyme from *Escherichia coli* can also convert 6-pyruvoyl-5,6,7,8-tetrahydropterin and sepiapterin to 6-carboxy-5,6,7,8-tetrahydropterin [905].

References: [236, 905]

[EC 4.1.2.50 created 2012]

EC 4.1.2.51

Accepted name: 2-dehydro-3-deoxy-D-gluconate aldolase

Reaction: 2-dehydro-3-deoxy-D-gluconate = pyruvate + D-glyceraldehyde

Other name(s): Pto1279 (gene name); KDGA; KDG-specific aldolase

Systematic name: 2-dehydro-3-deoxy-D-gluconate D-glyceraldehyde-lyase (pyruvate-forming)

Comments: The enzyme from the archaeon *Picrophilus torridus* is involved in D-glucose and D-galactose catabolism via the nonphosphorylative variant of the Entner-Doudoroff pathway. In the direction of aldol synthesis the enzyme catalyses the formation of 2-dehydro-3-deoxy-D-gluconate and 2-dehydro-3-deoxy-D-galactonate at a similar ratio. It shows no activity with 2-dehydro-3-deoxy-D-gluconate 6-phosphate. *cf.* EC 4.1.2.14, 2-dehydro-3-deoxy-phosphogluconate aldolase.

References: [1142]

[EC 4.1.2.51 created 2013]

EC 4.1.2.52

Accepted name: 4-hydroxy-2-oxoheptanedioate aldolase

Reaction: 4-hydroxy-2-oxoheptanedioate = pyruvate + succinate semialdehyde

Other name(s): 2,4-dihydroxyhept-2-enedioate aldolase; HHED aldolase; 4-hydroxy-2-ketoheptanedioate aldolase; HKHD aldolase; HpcH; *Hpa*I; 4-hydroxy-2-oxoheptanedioate succinate semialdehyde lyase (pyruvate-forming)

Systematic name: 4-hydroxy-2-oxoheptanedioate succinate-semialdehyde-lyase (pyruvate-forming)

Comments: Requires Co^{2+} or Mn^{2+} for activity. The enzyme is also able to catalyse the aldol cleavage of 4-hydroxy-2-oxopentanoate and 4-hydroxy-2-oxohexanoate, and can use 2-oxobutanoate as carbonyl donor, with lower efficiency. In the reverse direction, is able to condense a range of aldehyde acceptors with pyruvate. The enzyme from the bacterium *Escherichia coli* produces a racemic mixture of (4*R*)- and (4*S*)-hydroxy-2-oxoheptanedioate [1447].

References: [1448, 1139, 1449, 1447]

[EC 4.1.2.52 created 2013]

EC 4.1.2.53

Accepted name: 2-keto-3-deoxy-L-rhamnonate aldolase

Reaction: 2-dehydro-3-deoxy-L-rhamnonate = pyruvate + (*S*)-lactaldehyde

Other name(s): KDR aldolase; 2-dehydro-3-deoxyrhamnonate aldolase; 2-keto-3-deoxy acid sugar aldolase; YfaU; 2-dehydro-3-deoxy-L-rhamnonate (*S*)-lactaldehyde lyase (pyruvate-forming); 2-dehydro-3-deoxy-L-rhamnonate (*R*)-lactaldehyde lyase (pyruvate-forming)

Systematic name: 2-dehydro-3-deoxy-L-rhamnonate (*S*)-lactaldehyde-lyase (pyruvate-forming)

Comments: Requires Mg^{2+} for activity. The enzyme can also use 2-oxo-3-deoxy-L-mannonate, 2-oxo-3-deoxy-L-lyxonate and 4-hydroxy-2-ketoheptane-1,7-dioate (HKHD) as substrates [1140].

References: [1124, 1140]

[EC 4.1.2.53 created 2013]

EC 4.1.2.54

Accepted name: L-*threo*-3-deoxy-hexylosonate aldolase

Reaction: 2-dehydro-3-deoxy-L-galactonate = pyruvate + L-glyceraldehyde

Other name(s): GAAC; LGA1

Systematic name: 2-dehydro-3-deoxy-L-galactonate L-glyceraldehyde-lyase (pyruvate-forming)

Comments: The enzyme takes part in a D-galacturonate degradation pathway in the fungi *Aspergillus niger* and *Trichoderma reesei* (*Hypocrea jecorina*).

References: [552, 878]

[EC 4.1.2.54 created 2013]

EC 4.1.2.55

Accepted name: 2-dehydro-3-deoxy-phosphogluconate/2-dehydro-3-deoxy-6-phosphogalactonate aldolase

Reaction: (1) 2-dehydro-3-deoxy-6-phospho-D-gluconate = pyruvate + D-glyceraldehyde 3-phosphate
(2) 2-dehydro-3-deoxy-6-phospho-D-galactonate = pyruvate + D-glyceraldehyde 3-phosphate

Other name(s): 2-keto-3-deoxygluconate aldolase (ambiguous); KDGA (ambiguous)

Systematic name: 2-dehydro-3-deoxy-6-phospho-D-gluconate/2-dehydro-3-deoxy-6-phospho-D-galactonate D-glyceraldehyde-3-phosphate-lyase (pyruvate-forming)

Comments: In the archaeon *Sulfolobus solfataricus* the enzyme is involved in glucose and galactose catabolism via the branched variant of the Entner-Doudoroff pathway. It utilizes 2-dehydro-3-deoxy-6-phosphate-D-gluconate and 2-dehydro-3-deoxy-6-phosphate-D-galactonate with similar catalytic efficiency. *In vitro* the enzyme can also catalyse the cleavage of the non-phosphorylated forms 2-dehydro-3-deoxy-D-gluconate and 2-dehydro-3-deoxy-D-galactonate with much lower catalytic efficiency. *cf.* EC 4.1.2.21, 2-dehydro-3-deoxy-6-phosphogalactonate aldolase, and EC 4.1.2.14, 2-dehydro-3-deoxy-phosphogluconate aldolase.

References: [151, 780, 1415]

[EC 4.1.2.55 created 2014]

EC 4.1.2.56

Accepted name: 2-amino-4,5-dihydroxy-6-oxo-7-(phosphooxy)heptanoate synthase

Reaction: 2-amino-4,5-dihydroxy-6-oxo-7-(phosphooxy)heptanoate = glycerone phosphate + L-aspartate 4-semialdehyde

Other name(s): *griI* (gene name)

Systematic name: 2-amino-4,5-dihydroxy-6-oxo-7-(phosphooxy)heptanoate L-aspartate 4-semialdehyde-lyase (glycerone phosphate-forming)

Comments: Part of the pathway for the biosynthesis of grixazone, a mixture of yellow pigments produced by the bacterium *Streptomyces griseus*.

References: [1325]

[EC 4.1.2.56 created 2014]

EC 4.1.2.57

Accepted name: sulfofructosephosphate aldolase

Reaction: 6-deoxy-6-sulfo-D-fructose 1-phosphate = glycerone phosphate + (2*S*)-3-sulfolactaldehyde

Other name(s): *yihT* (gene name)

Systematic name: 6-deoxy-6-sulfofructose-1-phosphate (2*S*)-3-sulfolactaldehyde-lyase (glycerone-phosphate-forming)

Comments: The enzyme, characterized from the bacterium *Escherichia coli*, is involved in the degradation pathway of sulfoquinovose, the polar headgroup of sulfolipids found in the photosynthetic membranes of all higher plants, mosses, ferns, algae, and most photosynthetic bacteria, as well as the surface layer of some archaea.

References: [314]

[EC 4.1.2.57 created 2014]

EC 4.1.2.58

Accepted name: 2-dehydro-3,6-dideoxy-6-sulfogluconate aldolase

Reaction: 2-dehydro-3,6-dideoxy-6-sulfo-D-gluconate = (2*S*)-3-sulfolactaldehyde + pyruvate

Other name(s): KDSG aldolase

Systematic name: 2-dehydro-3,6-dideoxy-6-sulfo-D-gluconate (2*S*)-3-sulfolactaldehyde-lyase (pyruvate-forming)

Comments: The enzyme, characterized from the bacterium *Pseudomonas putida* SQ1, participates in a sulfoquinovose degradation pathway.

References: [380]

[EC 4.1.2.58 created 2016]

EC 4.1.2.59

Accepted name: dihydroneopterin phosphate aldolase

Reaction: 7,8-dihydroneopterin $3'$-phosphate = 6-(hydroxymethyl)-7,8-dihydropterin + glycolaldehyde phosphate

Other name(s): H_2NMP aldolase

Systematic name: 7,8-dihydroneopterin $3'$-phosphate glycolaldehyde phosphate-lyase [6-(hydroxymethyl)-7,8-dihydropterin-forming]

Comments: The enzyme participates in methanopterin biosynthesis the archaeon *Pyrococcus furiosus*. The enzyme is specific for 7,8-dihydroneopterin $3'$-phosphate. *cf.* EC 4.1.2.25, dihydroneopterin aldolase and EC 4.1.2.60, dihydroneopterin triphosphate aldolase.

References: [300]

[EC 4.1.2.59 created 2017]

EC 4.1.2.60

Accepted name: dihydroneopterin triphosphate aldolase

Reaction: 7,8-dihydroneopterin $3'$-triphosphate = 6-(hydroxymethyl)-7,8-dihydropterin + glycolaldehyde triphosphate

Other name(s): PTPS-III

Systematic name: 7,8-dihydroneopterin $3'$-triphosphate glycolaldehyde phosphate-lyase [6-(hydroxymethyl)-7,8-dihydropterin-forming]

Comments: The enzyme, which participates in a pathway for folate biosynthesis, is found in the Stramenopiles, a large group that includes oomycetes, various microalgae and brown algae, as well as in several bacterial phyla. It provides a bypass mechanism compensating for the lack of EC 4.1.2.25, dihydroneopterin aldolase. In the malaria parasite *Plasmodium falciparum* the enzyme is bifunctional and also catalyses the activity of EC 4.2.3.12, 6-pyruvoyltetrahydropterin synthase. *cf.* EC 4.1.2.59, dihydroneopterin phosphate aldolase.

References: [325, 593, 1103]

[EC 4.1.2.60 created 2017]

EC 4.1.2.61

Accepted name: feruloyl-CoA hydratase/lyase

Reaction: feruloyl-CoA + H_2O = vanillin + acetyl-CoA (overall reaction)
(1a) feruloyl-CoA + H_2O = 3-hydroxy-3-(4-hydroxy-3-methoxyphenyl)propanoyl-CoA
(1b) 3-hydroxy-3-(4-hydroxy-3-methoxyphenyl)propanoyl-CoA = vanillin + acetyl-CoA

Other name(s): hydroxycinnamoyl-CoA hydratase lyase; enoyl-CoA hydratase/aldolase; HCHL; *ferB* (gene name); *couA* (gene name)

Systematic name: feruloyl-CoA hydro-lyase/vanillin-lyase (acetyl-CoA-forming)

Comments: The enzyme is a member of the enoyl-CoA hydratase/isomerase superfamily. It catalyses a two-step process involving first the hydration of the double bond of feruloyl-CoA and then the cleavage of the resultant β-hydroxy thioester by retro-aldol reaction. (*E*)-caffeoyl-CoA and (*E*)-4-coumaroyl-CoA are also substrates.

References: [1093, 994, 430, 1045, 88, 556, 1502]

[EC 4.1.2.61 created 2020 (EC 4.1.2.41 created 2000, incorporated 2020, EC 4.2.1.101 created 2000, incorporated 2020)]

EC 4.1.2.62

Accepted name: 5-deoxyribulose 1-phosphate aldolase

Reaction: (1) 5-deoxy-D-ribulose 1-phosphate = glycerone phosphate + acetaldehyde
(2) *S*-methyl-5-thio-D-ribulose 1-phosphate = glycerone phosphate + (2-methylsulfanyl)acetaldehyde

Other name(s): 5-(methylthio)ribulose-1-phosphate aldolase; *ald2* (gene name)

Systematic name: 5-deoxy-D-ribulose 1-phosphate acetaldehyde-lyase (glycerone-phosphate-forming)

Comments: The enzyme, originally characterized from the bacterium *Rhodospirillum rubrum*, is involved in degradation pathways for $5'$-deoxyadenosine and *S*-methyl-$5'$-thioadenosine, which are formed from *S*-adenosyl-L-methionine (SAM, AdoMet) by radical SAM enzymes and other types of SAM-dependent enzymes, respectively. The enzyme requires a divalent metal cation, with Co^{2+} producing the highest activity.

References: [1014, 1015]

[EC 4.1.2.62 created 2020]

EC 4.1.2.63

Accepted name: 2-hydroxyacyl-CoA lyase

Reaction: (1) a 2-hydroxy-3-methyl-C_n-fatty-acyl-CoA = a 2-methyl-branched C_{n-1}-fatty aldehyde + formyl-CoA
(2) a (2*R*)-2-hydroxy-C_n-long-chain fatty acyl-CoA = a C_{n-1}-long-chain fatty aldehyde + formyl-CoA

Other name(s): HACL1 (gene name); 2-hydroxyphytanoyl-CoA lyase; 2-HPCL
Systematic name: 2-hydroxy-3-methyl fatty-CoA formyl-CoA lyase (2-methyl branched fatty aldehyde-forming)
Comments: Requires Mg^{2+} and thiamine diphosphate. This peroxisomal enzyme, found in animals, is involved in the α-oxidation of 3-methyl-branched fatty acids like phytanic acid and the shortening of 2-hydroxy long-chain fatty acids.
References: [397, 398, 196]

[EC 4.1.2.63 created 2021]

EC 4.1.3 Oxo-acid-lyases

EC 4.1.3.1
Accepted name: isocitrate lyase
Reaction: isocitrate = succinate + glyoxylate
Other name(s): isocitrase; isocitritase; isocitratase; *threo*-D_s-isocitrate glyoxylate-lyase; isocitrate glyoxylate-lyase
Systematic name: isocitrate glyoxylate-lyase (succinate-forming)
Comments: The isomer of isocitrate involved is (1*R*,2*S*)-1-hydroxypropane-1,2,3-tricarboxylate [1422].
References: [910, 1264, 1422]

[EC 4.1.3.1 created 1961]

[4.1.3.2 Transferred entry. malate synthase. Now EC 2.3.3.9, malate synthase]

[EC 4.1.3.2 created 1961, deleted 2002]

EC 4.1.3.3
Accepted name: *N*-acetylneuraminate lyase
Reaction: aceneuramate = *N*-acetyl-D-mannosamine + pyruvate
Other name(s): *N*-acetylneuraminic acid aldolase; acetylneuraminate lyase; sialic aldolase; sialic acid aldolase; sialate lyase; *N*-acetylneuraminic aldolase; neuraminic aldolase; *N*-acetylneuraminate aldolase; neuraminic acid aldolase; neuraminate aldolase; *N*-acetylneuraminic lyase; *N*-acetylneuraminic acid lyase; NPL; NALase; NANA lyase; acetylneuraminate pyruvate-lyase; *N*-acetylneuraminate pyruvate-lyase; NanA; *N*-acetylneuraminate pyruvate-lyase (*N*-acetyl-D-mannosamine-forming)
Systematic name: aceneuramate pyruvate-lyase (*N*-acetyl-D-mannosamine-forming)
Comments: This enzyme is involved in the degradation of *N*-acetylneuraminate. It is specific for the open form of the sugar. It also acts on *N*-glycoloylneuraminate and on *O*-acetylated sialic acids, other than 4-*O*-acetylated derivatives.
References: [246, 1203, 688]

[EC 4.1.3.3 created 1961, modified 2021]

EC 4.1.3.4
Accepted name: hydroxymethylglutaryl-CoA lyase
Reaction: (*S*)-3-hydroxy-3-methylglutaryl-CoA = acetyl-CoA + acetoacetate
Other name(s): hydroxymethylglutaryl coenzyme A-cleaving enzyme; hydroxymethylglutaryl coenzyme A lyase; 3-hydroxy-3-methylglutaryl coenzyme A lyase; 3-hydroxy-3-methylglutaryl CoA cleaving enzyme; 3-hydroxy-3-methylglutaryl-CoA lyase; (*S*)-3-hydroxy-3-methylglutaryl-CoA acetoacetate-lyase
Systematic name: (*S*)-3-hydroxy-3-methylglutaryl-CoA acetoacetate-lyase (acetyl-CoA-forming)
References: [54]

[EC 4.1.3.4 created 1961]

[4.1.3.5 Transferred entry. hydroxymethylglutaryl-CoA synthase. Now EC 2.3.3.10, hydroxymethylglutaryl-CoA synthase]

[EC 4.1.3.5 created 1961, deleted 2002]

EC 4.1.3.6

Accepted name: citrate (*pro*-3*S*)-lyase
Reaction: citrate = acetate + oxaloacetate
Other name(s): citrase; citratase; citritase; citridesmolase; citrate aldolase; citric aldolase; citrate lyase; citrate oxaloacetate-lyase; citrate oxaloacetate-lyase [(*pro*-3*S*)-CH$_2$COO$^-$→acetate]
Systematic name: citrate oxaloacetate-lyase (forming acetate from the *pro-S* carboxymethyl group of citrate)
Comments: The enzyme can be dissociated into components, two of which are identical with EC 2.8.3.10 (citrate CoA-transferase) and EC 4.1.3.34 (citryl-CoA lyase). EC 3.1.2.16, citrate lyase deacetylase, deacetylates and inactivates the enzyme.
References: [280, 324]

[EC 4.1.3.6 created 1961]

[4.1.3.7 Transferred entry. citrate (Si)-synthase. Now EC 2.3.3.1, citrate (Si)-synthase]

[EC 4.1.3.7 created 1961, deleted 2002]

[4.1.3.8 Transferred entry. ATP citrate (pro-S)-lyase. Now EC 2.3.3.8, ATP citrate synthase]

[EC 4.1.3.8 created 1965, modified 1986, deleted 2002]

[4.1.3.9 Transferred entry. 2-hydroxyglutarate synthase. Now EC 2.3.3.11, 2-hydroxyglutarate synthase]

[EC 4.1.3.9 created 1965, deleted 2002]

[4.1.3.10 Transferred entry. 3-ethylmalate synthase. Now EC 2.3.3.7, 3-ethylmalate synthase]

[EC 4.1.3.10 created 1965, modified 1983, deleted 2002]

[4.1.3.11 Transferred entry. 3-propylmalate synthase. Now EC 2.3.3.12, 3-propylmalate synthase]

[EC 4.1.3.11 created 1972, deleted 2002]

[4.1.3.12 Transferred entry. 2-isopropylmalate synthase. Now EC 2.3.3.13, 2-isopropylmalate synthase]

[EC 4.1.3.12 created 1972, deleted 2002]

EC 4.1.3.13

Accepted name: oxalomalate lyase
Reaction: 3-oxalomalate = oxaloacetate + glyoxylate
Other name(s): 3-oxalomalate glyoxylate-lyase
Systematic name: 3-oxalomalate glyoxylate-lyase (oxaloacetate-forming)
References: [1251]

[EC 4.1.3.13 created 1972]

EC 4.1.3.14

Accepted name: L-*erythro*-3-hydroxyaspartate aldolase
Reaction: L-*erythro*-3-hydroxy-aspartate = glycine + glyoxylate
Other name(s): L-*erythro*-β-hydroxyaspartate aldolase; L-*erythro*-β-hydroxyaspartate glycine-lyase; *erythro*-3-hydroxy-L$_s$-aspartate glyoxylate-lyase
Systematic name: L-*erythro*-3-hydroxy-aspartate glyoxylate-lyase (glycine-forming)
Comments: A pyridoxal-phosphate protein. The enzyme, purified from the bacterium *Paracoccus denitrificans* NCIMB 8944, is strictly specific for the L-*erythro* stereoisomer of 3-hydroxyaspartate. Different from EC 4.1.3.41, *erythro*-3-hydroxy-D-aspartate aldolase. Requires a divalent cation.
References: [437]

[EC 4.1.3.14 created 1972, modified 2011]

[4.1.3.15 Transferred entry. 2-hydroxy-3-oxoadipate synthase. Now EC 2.2.1.5, 2-hydroxy-3-oxoadipate synthase]

[EC 4.1.3.15 created 1972, deleted 2002]

EC 4.1.3.16

Accepted name: 4-hydroxy-2-oxoglutarate aldolase

Reaction: 4-hydroxy-2-oxoglutarate = pyruvate + glyoxylate

Other name(s): 2-oxo-4-hydroxyglutarate aldolase; hydroxyketoglutaric aldolase; 4-hydroxy-2-ketoglutaric aldolase; 2-keto-4-hydroxyglutaric aldolase; 4-hydroxy-2-ketoglutarate aldolase; 2-keto-4-hydroxyglutarate aldolase; 2-oxo-4-hydroxyglutaric aldolase; DL-4-hydroxy-2-ketoglutarate aldolase; hydroxyketoglutarate aldolase; 2-keto-4-hydroxybutyrate aldolase; 4-hydroxy-2-oxoglutarate glyoxylate-lyase; KHGA

Systematic name: 4-hydroxy-2-oxoglutarate glyoxylate-lyase (pyruvate-forming)

Comments: The enzymes from rat liver and bovine liver act on both enantiomers of 4-hydroxy-2-oxoglutarate. *cf.* EC 4.1.3.42, (4*S*)-4-hydroxy-2-oxoglutarate aldolase.

References: [768, 718, 784, 1232]

[EC 4.1.3.16 created 1972 (EC 4.1.2.1 created 1961, incorporated 1972, EC 4.1.2.31 created 1978, incorporated 1982)]

EC 4.1.3.17

Accepted name: 4-hydroxy-4-methyl-2-oxoglutarate aldolase

Reaction: (1) 4-hydroxy-4-methyl-2-oxoglutarate = **2** pyruvate
(2) 2-hydroxy-4-oxobutane-1,2,4-tricarboxylate = oxaloacetate + pyruvate

Other name(s): pyruvate aldolase; γ-methyl-γ-hydroxy-α-ketoglutaric aldolase; 4-hydroxy-4-methyl-2-ketoglutarate aldolase; 4-hydroxy-4-methyl-2-oxoglutarate pyruvate-lyase; HMG aldolase; CHA aldolase; 4-carboxy-4-hydroxy-2-oxoadipate aldolase

Systematic name: 4-hydroxy-4-methyl-2-oxoglutarate pyruvate-lyase (pyruvate-forming)

Comments: Requires a divalent metal ion [888]. This enzyme participates in the degradation of 3,4-dihydroxybenzoate (via the *meta*-cleavage pathway), phthalate, syringate and 3,4,5-trihydroxybenzoate [1339, 1475, 888]. The enzyme from *Pseudomonas straminea* can also catalyse the activity of EC 4.1.3.16, 4-hydroxy-2-oxoglutarate aldolase, and the decarboxylation of oxaloacetate [888].

References: [1339, 1475, 888, 1011]

[EC 4.1.3.17 created 1972, modified 2012]

[4.1.3.18 Transferred entry. acetolactate synthase. Now EC 2.2.1.6, acetolactate synthase]

[EC 4.1.3.18 created 1972, deleted 2002]

[4.1.3.19 Transferred entry. N-acetylneuraminate synthase. Now EC 2.5.1.56, N-acetylneuraminate synthase]

[EC 4.1.3.19 created 1972, deleted 2002]

[4.1.3.20 Transferred entry. N-acylneuraminate-9-phosphate synthase. Now EC 2.5.1.57, N-acylneuraminate-9-phosphate synthase]

[EC 4.1.3.20 created 1972, deleted 2002]

[4.1.3.21 Transferred entry. homocitrate synthase. Now EC 2.3.3.14, homocitrate synthase]

[EC 4.1.3.21 created 1972, deleted 2002]

EC 4.1.3.22

Accepted name: citramalate lyase
Reaction: (2*S*)-2-hydroxy-2-methylbutanedioate = acetate + pyruvate
Other name(s): citramalate pyruvate-lyase; citramalate synthase; citramalic-condensing enzyme; citramalate synthetase; citramalic synthase; (*S*)-citramalate lyase; (+)-citramalate pyruvate-lyase; citramalate pyruvate lyase; (3*S*)-citramalate pyruvate-lyase; (2*S*)-2-hydroxy-2-methylbutanedioate pyruvate-lyase
Systematic name: (2*S*)-2-hydroxy-2-methylbutanedioate pyruvate-lyase (acetate-forming)
Comments: The enzyme can be dissociated into components, two of which are identical with EC 2.8.3.11 (citramalate CoA-transferase) and EC 4.1.3.25 (citramalyl-CoA lyase).
References: [73, 322]

[EC 4.1.3.22 created 1972]

[4.1.3.23 Transferred entry. decylcitrate synthase. Now EC 2.3.3.2, decylcitrate synthase]

[EC 4.1.3.23 created 1972, deleted 2002]

EC 4.1.3.24

Accepted name: malyl-CoA lyase
Reaction: (1) (*S*)-malyl-CoA = acetyl-CoA + glyoxylate
(2) (2*R*,3*S*)-2-methylmalyl-CoA = propanoyl-CoA + glyoxylate
Other name(s): malyl-coenzyme A lyase; (3*S*)-3-carboxy-3-hydroxypropanoyl-CoA glyoxylate-lyase; *mclA* (gene name); mcl1 (gene name); (3*S*)-3-carboxy-3-hydroxypropanoyl-CoA glyoxylate-lyase (acetyl-CoA-forming); L-malyl-CoA lyase
Systematic name: (*S*)-malyl-CoA glyoxylate-lyase (acetyl-CoA-forming)
Comments: The enzymes from *Rhodobacter* species catalyse a step in the ethylmalonyl-CoA pathway for acetate assimilation [923, 364]. The enzyme from halophilic bacteria participate in the methylaspartate cycle and catalyse the reaction in the direction of malyl-CoA formation [116]. The enzyme from the bacterium *Chloroflexus aurantiacus*, which participates in the 3-hydroxypropanoate cycle for carbon assimilation, also has the activity of EC 4.1.3.25, (3*S*)-citramalyl-CoA lyase [545, 408].
References: [1397, 545, 923, 408, 364, 116]

[EC 4.1.3.24 created 1972, modified 2014]

EC 4.1.3.25

Accepted name: (*S*)-citramalyl-CoA lyase
Reaction: (3*S*)-citramalyl-CoA = acetyl-CoA + pyruvate
Other name(s): citramalyl coenzyme A lyase (ambiguous); (+)-CMA-CoA lyase; (3*S*)-citramalyl-CoA pyruvate-lyase; Mcl (ambiguous); citramalyl-CoA lyase (ambiguous)
Systematic name: (3*S*)-citramalyl-CoA pyruvate-lyase (acetyl-CoA-forming)
Comments: Requires Mg^{2+} ions for activity [408]. The enzyme from the bacterium *Clostridium tetanomorphum* is a component of EC 4.1.3.22, citramalate lyase [322]. It also acts on (3*S*)-citramalyl thioacyl-carrier protein [322]. The enzyme from the bacterium *Chloroflexus aurantiacus* also has the activity of EC 4.1.3.24, malyl-CoA lyase [408]. It has no activity with (3*R*)-citramalyl-CoA (*cf.* EC 4.1.3.46, (*R*)-citramalyl-CoA lyase) [408].
References: [253, 322, 408]

[EC 4.1.3.25 created 1972, modified 2014]

EC 4.1.3.26

Accepted name: 3-hydroxy-3-isohexenylglutaryl-CoA lyase
Reaction: 3-hydroxy-3-(4-methylpent-3-en-1-yl)glutaryl-CoA = 7-methyl-3-oxooct-6-enoyl-CoA + acetate

Other name(s): β-hydroxy-β-isohexenylglutaryl CoA-lyase; hydroxyisohexenylglutaryl-CoA:acetatelyase; 3-hydroxy-3-isohexenylglutaryl coenzyme A lyase; 3-hydroxy-3-isohexenylglutaryl-CoA isopentenylacetoacetyl-CoA-lyase; 3-hydroxy-3-(4-methylpent-3-en-1-yl)glutaryl-CoA acetate-lyase

Systematic name: 3-hydroxy-3-(4-methylpent-3-en-1-yl)glutaryl-CoA acetate-lyase (7-methyl-3-oxooct-6-enoyl-CoA-forming)

Comments: Also acts on the hydroxy derivative of farnesoyl-CoA.

References: [1257]

[EC 4.1.3.26 created 1972]

EC 4.1.3.27

Accepted name: anthranilate synthase

Reaction: chorismate + L-glutamine = anthranilate + pyruvate + L-glutamate (overall reaction)
(1a) L-glutamine + H_2O = L-glutamate + NH_3
(1b) chorismate + NH_3 = (2*S*)-2-amino-4-deoxychorismate + H_2O
(1c) (2*S*)-2-amino-4-deoxychorismate = anthranilate + pyruvate

Other name(s): anthranilate synthetase; chorismate lyase; chorismate pyruvate-lyase (amino-accepting); TrpDE

Systematic name: chorismate pyruvate-lyase (amino-accepting; anthranilate-forming)

Comments: The enzyme, found in plants, fungi and bacteria is composed of two parts, a glutaminase subunit and a lyase subunit. The glutaminase produces ammonia that is channeled to the lyase subunit. In the absence of the glutaminase, the lyase can convert ammonia and chorismate into anthranilate. In some organisms, this enzyme is part of a multifunctional protein, together with one or more other components of the system for the biosynthesis of tryptophan [EC 2.4.2.18 (anthranilate phosphoribosyltransferase), EC 4.1.1.48 (indole-3-glycerol-phosphate synthase), EC 4.2.1.20 (tryptophan synthase) and EC 5.3.1.24 (phosphoribosylanthranilate isomerase)].

References: [68, 261, 590, 605, 1539, 959, 664]

[EC 4.1.3.27 created 1972, modified 2022]

[4.1.3.28 Transferred entry. citrate (Re)-synthase. Now EC 2.3.3.3, citrate (Re)-synthase]

[EC 4.1.3.28 created 1972, deleted 2002]

[4.1.3.29 Transferred entry. decylhomocitrate synthase. Now EC 2.3.3.4, decylhomocitrate synthase]

[EC 4.1.3.29 created 1976, deleted 2002]

EC 4.1.3.30

Accepted name: methylisocitrate lyase

Reaction: (2*S*,3*R*)-3-hydroxybutane-1,2,3-tricarboxylate = succinate + pyruvate

Other name(s): 2-methylisocitrate lyase; MICL; (2*S*,3*R*)-3-hydroxybutane-1,2,3-tricarboxylate pyruvate-lyase

Systematic name: (2*S*,3*R*)-3-hydroxybutane-1,2,3-tricarboxylate pyruvate-lyase (succinate-forming)

Comments: The enzyme acts on *threo*-D$_s$-2-methylisocitrate, but not on *threo*-D$_s$-isocitrate, *threo*-DL-isocitrate or *erythro*-L$_s$-isocitrate.

References: [1336, 1337]

[EC 4.1.3.30 created 1978]

[4.1.3.31 Transferred entry. 2-methylcitrate synthase. Now EC 2.3.3.5, 2-methylcitrate synthase]

[EC 4.1.3.31 created 1978, deleted 2002]

EC 4.1.3.32

Accepted name: 2,3-dimethylmalate lyase

Reaction: (2*R*,3*S*)-2,3-dimethylmalate = propanoate + pyruvate

Other name(s): 2,3-dimethylmalate pyruvate-lyase; (2*R*,3*S*)-2,3-dimethylmalate pyruvate-lyase

Systematic name: (2*R*,3*S*)-2,3-dimethylmalate pyruvate-lyase (propanoate-forming)

References: [1088, 18]

[EC 4.1.3.32 created 1981]

[4.1.3.33 Transferred entry. 2-ethylmalate synthase. Now EC 2.3.3.6, 2-ethylmalate synthase]

[EC 4.1.3.33 created 1983, deleted 2002]

EC 4.1.3.34

Accepted name: citryl-CoA lyase

Reaction: (3*S*)-citryl-CoA = acetyl-CoA + oxaloacetate

Other name(s): (3*S*)-citryl-CoA oxaloacetate-lyase

Systematic name: (3*S*)-citryl-CoA oxaloacetate-lyase (acetyl-CoA-forming)

Comments: The enzyme is a component of EC 4.1.3.6 [citrate (*pro*-3*S*)-lyase]and EC 2.3.3.8 [ATP citrate synthase]. Also acts on (3*S*)-citryl thioacyl-carrier protein.

References: [324, 815]

[EC 4.1.3.34 created 1984, modified 1986]

EC 4.1.3.35

Accepted name: (1-hydroxycyclohexan-1-yl)acetyl-CoA lyase

Reaction: (1-hydroxycyclohexan-1-yl)acetyl-CoA = acetyl-CoA + cyclohexanone

Other name(s): (1-hydroxycyclohexan-1-yl)acetyl-CoA cyclohexanone-lyase

Systematic name: (1-hydroxycyclohexan-1-yl)acetyl-CoA cyclohexanone-lyase (acetyl-CoA-forming)

References: [1044]

[EC 4.1.3.35 created 1986]

EC 4.1.3.36

Accepted name: 1,4-dihydroxy-2-naphthoyl-CoA synthase

Reaction: 4-(2-carboxyphenyl)-4-oxobutanoyl-CoA = 1,4-dihydroxy-2-naphthoyl-CoA + H_2O

Other name(s): naphthoate synthase; 1,4-dihydroxy-2-naphthoate synthase; dihydroxynaphthoate synthase; *o*-succinylbenzoyl-CoA 1,4-dihydroxy-2-naphthoate-lyase (cyclizing); MenB; *o*-succinylbenzoyl-CoA dehydratase (cyclizing)

Systematic name: 4-(2-carboxyphenyl)-4-oxobutanoyl-CoA dehydratase (cyclizing)

Comments: This enzyme is involved in the synthesis of 1,4-dihydroxy-2-naphthoate, a branch point metabolite leading to the biosynthesis of menaquinone (vitamin K_2, in bacteria), phylloquinone (vitamin K_1 in plants), and many plant pigments. The coenzyme A group is subsequently removed from the product by EC 3.1.2.28, 1,4-dihydroxy-2-naphthoyl-CoA hydrolase.

References: [916, 724, 639, 1390]

[EC 4.1.3.36 created 1992, modified 2010]

*[4.1.3.37 Transferred entry. 1-deoxy-*D*-xylulose 5-phosphate synthase. Now EC 2.2.1.7, 1-deoxy-*D*-xylulose 5-phosphate synthase]*

[EC 4.1.3.37 created 2001, deleted 2002]

EC 4.1.3.38

Accepted name: aminodeoxychorismate lyase

Reaction: 4-amino-4-deoxychorismate = 4-aminobenzoate + pyruvate

Other name(s): enzyme X; 4-amino-4-deoxychorismate lyase; 4-amino-4-deoxychorismate pyruvate-lyase

Systematic name: 4-amino-4-deoxychorismate pyruvate-lyase (4-aminobenzoate-forming)

Comments: A pyridoxal-phosphate protein. Forms part of the folate biosynthesis pathway. Acts on 4-amino-4-deoxychorismate, the product of EC 2.6.1.85, aminodeoxychorismate synthase, to form *p*-aminobenzoate.

References: [1506, 465, 987]

[EC 4.1.3.38 created 2003]

EC 4.1.3.39

Accepted name: 4-hydroxy-2-oxovalerate aldolase

Reaction: (*S*)-4-hydroxy-2-oxopentanoate = acetaldehyde + pyruvate

Other name(s): 4-hydroxy-2-ketovalerate aldolase; HOA; DmpG; 4-hydroxy-2-oxovalerate pyruvate-lyase; 4-hydroxy-2-oxopentanoate pyruvate-lyase; BphI; 4-hydroxy-2-oxopentanoate pyruvate-lyase (acetaldehyde-forming)

Systematic name: (*S*)-4-hydroxy-2-oxopentanoate pyruvate-lyase (acetaldehyde-forming)

Comments: Requires Mn^{2+} for maximal activity [871]. The enzyme from the bacterium *Pseudomonas putida* is also stimulated by NADH [871]. In some bacterial species the enzyme forms a bifunctional complex with EC 1.2.1.10, acetaldehyde dehydrogenase (acetylating). The enzymes from the bacteria *Burkholderia xenovorans* and *Thermus thermophilus* also perform the reaction of EC 4.1.3.43, 4-hydroxy-2-oxohexanoate aldolase [64, 65].

References: [871, 1099, 870, 64, 65, 67]

[EC 4.1.3.39 created 2006, modified 2011]

EC 4.1.3.40

Accepted name: chorismate lyase

Reaction: chorismate = 4-hydroxybenzoate + pyruvate

Other name(s): CL; CPL; UbiC

Systematic name: chorismate pyruvate-lyase (4-hydroxybenzoate-forming)

Comments: This enzyme catalyses the first step in the biosynthesis of ubiquinone in *Escherichia coli* and other Gram-negative bacteria [1003]. The yeast *Saccharomyces cerevisiae* can synthesize ubiquinone from either chorismate or tyrosine [915].

References: [1003, 1270, 915]

[EC 4.1.3.40 created 2007]

EC 4.1.3.41

Accepted name: 3-hydroxy-D-aspartate aldolase

Reaction: (1) *threo*-3-hydroxy-D-aspartate = glycine + glyoxylate
(2) D-*erythro*-3-hydroxyaspartate = glycine + glyoxylate

Other name(s): D-3-hydroxyaspartate aldolase

Systematic name: 3-hydroxy-D-aspartate glyoxylate-lyase (glycine-forming)

Comments: A pyridoxal-phosphate protein. The enzyme, purified from the bacterium *Paracoccus denitrificans* IFO 13301, is strictly D-specific as to the α-position of the substrate, but accepts both the *threo* and *erythro* forms at the β-position. The *erythro* form is a far better substrate (about 100-fold). The enzyme can also accept D-allothreonine, D-threonine, *erythro*-3-phenyl-D-serine and *threo*-3-phenyl-D-serine. Different from EC 4.1.3.14, *erythro*-3-hydroxy-L-aspartate aldolase. Requires a divalent cation, such as Mg^{2+}, Mn^{2+} or Co^{2+}.

References: [829]

[EC 4.1.3.41 created 2011]

EC 4.1.3.42

Accepted name: (4*S*)-4-hydroxy-2-oxoglutarate aldolase

Reaction: (4*S*)-4-hydroxy-2-oxoglutarate = pyruvate + glyoxylate

Other name(s): 2-oxo-4-hydroxyglutarate aldolase (ambiguous); hydroxyketoglutaric aldolase (ambiguous); 4-hydroxy-2-ketoglutaric aldolase (ambiguous); 2-keto-4-hydroxyglutaric aldolase (ambiguous); 4-hydroxy-2-ketoglutarate aldolase (ambiguous); 2-keto-4-hydroxyglutarate aldolase (ambiguous); 2-oxo-4-hydroxyglutaric aldolase (ambiguous); hydroxyketoglutarate aldolase (ambiguous); 2-keto-4-hydroxybutyrate aldolase (ambiguous); 4-hydroxy-2-oxoglutarate glyoxylate-lyase (ambiguous); *eda* (gene name)

Systematic name: (4*S*)-4-hydroxy-2-oxoglutarate glyoxylate-lyase (pyruvate-forming)

Comments: The enzyme from the bacterium *Escherichia coli*, which is specific for the (*S*)-enantiomer, is trifunctional, and also catalyses the reaction of EC 4.1.2.14, 2-dehydro-3-deoxy-phosphogluconate aldolase, and the β-decarboxylation of oxaloacetate. *cf.* EC 4.1.3.16, 4-hydroxy-2-oxoglutarate aldolase.

References: [1006, 1057]

[EC 4.1.3.42 created 2013]

EC 4.1.3.43

Accepted name: 4-hydroxy-2-oxohexanoate aldolase

Reaction: (*S*)-4-hydroxy-2-oxohexanoate = propanal + pyruvate

Other name(s): BphI

Systematic name: (*S*)-4-hydroxy-2-oxohexanoate pyruvate-lyase (propanal-forming)

Comments: Requires Mn^{2+} for maximal activity [66, 1447]. The enzymes from the bacteria *Burkholderia xenovorans* and *Thermus thermophilus* also perform the reaction of EC 4.1.3.39, 4-hydroxy-2-oxovalerate aldolase [1,2,6]. The enzyme forms a bifunctional complex with EC 1.2.1.87, propanal dehydrogenase (CoA-propanoylating), with a tight channel connecting the two subunits [3,4,6].

References: [66, 1447, 64, 190, 67, 65]

[EC 4.1.3.43 created 2013]

EC 4.1.3.44

Accepted name: tRNA 4-demethylwyosine synthase (AdoMet-dependent)

Reaction: N^1-methylguanine^{37} in tRNA^{Phe} + pyruvate + *S*-adenosyl-L-methionine = 4-demethylwyosine^{37} in tRNA^{Phe} + L-methionine + 5′-deoxyadenosine + CO_2 + H_2O

Other name(s): TYW1

Systematic name: tRNA^{Phe} N^1-methylguanine,pyruvate acetaldehyde-lyase (tRNA^{Phe} 4-demethylwyosine-forming, decarboxylating, dehydrating)

Comments: This enzyme, which is a member of the superfamily of *S*-adenosyl-L-methionine-dependent radical (radical AdoMet) enzymes, binds two [4Fe-4S] clusters [1516, 1065]. Carbons C_2 and C_3 from pyruvate are incorporated into 4-demethylwyosine [1516]. The enzyme is found in eukaryotes where it is part of the pathway for wybutosine synthesis, and in archaea, where it is involved in the biosynthesis of archaeal wye bases, such as wyosine, isowyosine, and methylwyosine.

References: [456, 1330, 1516, 1065]

[EC 4.1.3.44 created 2013]

EC 4.1.3.45

Accepted name: 3-hydroxybenzoate synthase

Reaction: chorismate = 3-hydroxybenzoate + pyruvate

Other name(s): chorismatase/3-hydroxybenzoate synthase; hyg5 (gene name); bra8 (gene name); XanB2

Systematic name: chorismate pyruvate-lyase (3-hydroxybenzoate-forming)

Comments: The enzyme, found in several bacterial species is involved in biosynthesis of secondary products. The enzyme from the bacterium *Xanthomonas campestris* pv. *campestris* also has the activity of EC 4.1.3.40, chorismate lyase [1568].

References: [29, 633, 1568]

[EC 4.1.3.45 created 2013]

EC 4.1.3.46

Accepted name: (*R*)-citramalyl-CoA lyase

Reaction: (3*R*)-citramalyl-CoA = acetyl-CoA + pyruvate

Other name(s): Ccl

Systematic name: (3*R*)-citramalyl-CoA pyruvate-lyase (acetyl-CoA-forming)

Comments: Requires Mn^{2+} ions for activity. The enzyme, purified from the bacterium *Chloroflexus aurantiacus*, has no activity with (3*S*)-citramalyl-CoA (*cf.* EC 4.1.3.25, (*S*)-citramalyl-CoA lyase).

References: [408]

[EC 4.1.3.46 created 2014]

EC 4.1.99 Other carbon-carbon lyases

EC 4.1.99.1

Accepted name: tryptophanase

Reaction: L-tryptophan + H_2O = indole + pyruvate + NH_3 (overall reaction)
(1a) L-tryptophan = indole + 2-aminoprop-2-enoate
(1b) 2-aminoprop-2-enoate = 2-iminopropanoate (spontaneous)
(1c) 2-iminopropanoate + H_2O = pyruvate + NH_3 (spontaneous)

Other name(s): L-tryptophanase; L-tryptophan indole-lyase (deaminating); TNase

Systematic name: L-tryptophan indole-lyase (deaminating; pyruvate-forming)

Comments: A pyridoxal-phosphate protein, requiring K^+. The enzyme cleaves a carbon-carbon bond, releasing indole and an unstable enamine product that tautomerizes to an imine form, which undergoes a hydrolytic deamination to form pyruvate and ammonia. The latter reaction, which can occur spontaneously, can also be catalysed by EC 3.5.99.10, 2-iminobutanoate/2-iminopropanoate deaminase. Also catalyses 2,3-elimination and β-replacement reactions of some indole-substituted tryptophan analogues of L-cysteine, L-serine and other 3-substituted amino acids.

References: [161, 1002, 257, 1286]

[EC 4.1.99.1 created 1972]

EC 4.1.99.2

Accepted name: tyrosine phenol-lyase

Reaction: L-tyrosine + H_2O = phenol + pyruvate + NH_3 (overall reaction)
(1a) L-tyrosine = phenol + 2-aminoprop-2-enoate
(1b) 2-aminoprop-2-enoate = 2-iminopropanoate (spontaneous)
(1c) 2-iminopropanoate + H_2O = pyruvate + NH_3 (spontaneous)

Other name(s): β-tyrosinase; L-tyrosine phenol-lyase (deaminating)

Systematic name: L-tyrosine phenol-lyase (deaminating; pyruvate-forming)

Comments: A pyridoxal-phosphate protein. The enzyme cleaves a carbon-carbon bond, releasing phenol and an unstable enamine product that tautomerizes to an imine form, which undergoes a hydrolytic deamination to form pyruvate and ammonia. The latter reaction, which can occur spontaneously, can also be catalysed by EC 3.5.99.10, 2-iminobutanoate/2-iminopropanoate deaminase. The enzyme also slowly catalyses similar reactions with D-tyrosine, *S*-methyl-L-cysteine, L-cysteine, L-serine and D-serine.

References: [756, 757]

[EC 4.1.99.2 created 1972]

EC 4.1.99.3

Accepted name: deoxyribodipyrimidine photo-lyase

Reaction: cyclobutadipyrimidine (in DNA) = **2** pyrimidine residues (in DNA)

Other name(s): photoreactivating enzyme; DNA photolyase; DNA-photoreactivating enzyme; DNA cyclobutane dipyrimidine photolyase; DNA photolyase; deoxyribonucleic photolyase; deoxyribodipyrimidine photolyase; photolyase; PRE; PhrB photolyase; deoxyribonucleic cyclobutane dipyrimidine photolyase; phr A photolyase; dipyrimidine photolyase (photosensitive); deoxyribonucleate pyrimidine dimer lyase (photosensitive)

Systematic name: deoxyribocyclobutadipyrimidine pyrimidine-lyase

Comments: A flavoprotein (FAD), containing a second chromophore group. The enzyme catalyses the reactivation by light of irradiated DNA. A similar reactivation of irradiated RNA is probably due to a separate enzyme.

References: [353, 1191, 1256]

[EC 4.1.99.3 created 1972]

[4.1.99.4 Transferred entry. 1-aminocyclopropane-1-carboxylate deaminase. Now EC 3.5.99.7, 1-aminocyclopropane-1-carboxylate deaminase]

[EC 4.1.99.4 created 1981, deleted 2002]

EC 4.1.99.5

Accepted name: aldehyde oxygenase (deformylating)

Reaction: a long-chain aldehyde + O_2 + **2** NADPH + **2** H^+ = an alkane + formate + H_2O + **2** $NADP^+$

Other name(s): decarbonylase; aldehyde decarbonylase; octadecanal decarbonylase; octadecanal alkane-lyase

Systematic name: a long-chain aldehyde alkane-lyase

Comments: Contains a diiron center. Involved in the biosynthesis of alkanes. The enzyme from the cyanobacterium *Nostoc punctiforme* PCC 73102 is only active *in vitro* in the presence of ferredoxin, ferredoxin reductase and NADPH, and produces mostly C_{15} and C_{17} alkanes [1211, 1454]. The enzyme from pea (*Pisum sativum*) produces alkanes of chain length C_{18} to C_{32} and is inhibited by metal-chelating agents [1376]. The substrate for this enzyme is formed by EC 1.2.1.80, acyl-[acyl-carrier protein] reductase.

References: [1376, 1211, 1454, 804]

[EC 4.1.99.5 created 1989, modified 2011, modified 2013]

[4.1.99.6 Transferred entry. trichodiene synthase. Now EC 4.2.3.6, trichodiene synthase]

[EC 4.1.99.6 created 1989, deleted 2000]

[4.1.99.7 Transferred entry. aristolochene synthase. Now EC 4.2.3.9, aristolochene synthase]

[EC 4.1.99.7 created 1992 as EC 2.5.1.40, transferred 1999 to EC 4.1.99.7, deleted 2000]

[4.1.99.8 Transferred entry. pinene synthase. Now EC 4.2.3.14, pinene synthase]

[EC 4.1.99.8 created 2000, deleted 2000]

[4.1.99.9 Transferred entry. myrcene synthase. Now EC 4.2.3.15, myrcene synthase]

[EC 4.1.99.9 created 2000, deleted 2000]

[4.1.99.10 Transferred entry. (-)-(4S)-limonene synthase. Now EC 4.2.3.16, (4S)-limonene synthase]

[EC 4.1.99.10 created 2000, deleted 2000]

EC 4.1.99.11

Accepted name: benzylsuccinate synthase
Reaction: benzylsuccinate = toluene + fumarate
Other name(s): benzylsuccinate fumarate-lyase
Systematic name: benzylsuccinate fumarate-lyase (toluene-forming)
Comments: A glycyl radical enzyme that is inhibited by benzyl alcohol, benzaldehyde, phenylhydrazine and is inactivated by oxygen.
References: [85, 798]

[EC 4.1.99.11 created 2000]

EC 4.1.99.12

Accepted name: 3,4-dihydroxy-2-butanone-4-phosphate synthase
Reaction: D-ribulose 5-phosphate = formate + L-3,4-dihydroxybutan-2-one 4-phosphate
Other name(s): DHBP synthase; L-3,4-dihydroxybutan-2-one-4-phosphate synthase
Systematic name: D-ribulose 5-phosphate formate-lyase (L-3,4-dihydroxybutan-2-one 4-phosphate-forming)
Comments: Requires a divalent cation, preferably Mg^{2+}, for activity [1426]. The reaction involves an intramolecular skeletal rearrangement, with the bonds in D-ribulose 5-phosphate that connect C-3 and C-5 to C-4 being broken, C-4 being removed as formate and reconnection of C-3 and C-5 [1426]. The phosphorylated four-carbon product (L-3,4-dihydroxybutan-2-one 4-phosphate) is an intermediate in the biosynthesis of riboflavin [1426].
References: [1426, 810, 687, 811, 386, 1302, 1301, 348]

[EC 4.1.99.12 created 2007]

EC 4.1.99.13

Accepted name: (6-4)DNA photolyase
Reaction: (6-4) photoproduct (in DNA) = **2** pyrimidine residues (in DNA)
Other name(s): DNA photolyase; H64PRH; NF-10; phr (6-4); PL-(6-4); OtCPF1; (6-4) PHR; *At*64PHR
Systematic name: (6-4) photoproduct pyrimidine-lyase
Comments: A flavoprotein (FAD). The overall repair reaction consists of two distinct steps, one of which is light-independent and the other one light-dependent. In the initial light-independent step, a 6-iminium ion is thought to be generated via proton transfer induced by two histidines highly conserved among the (6-4) photolyases. This intermediate spontaneously rearranges to form an oxetane intermediate by intramolecular nucleophilic attack. In the subsequent light-driven reaction, one electron is believed to be transferred from the fully reduced FAD cofactor (FADH^{-}) to the oxetane intermediate thus forming a neutral FADH radical and an anionic oxetane radical, which spontaneously fractures. The excess electron is then back-transferred to the flavin radical restoring the fully reduced flavin cofactor and a pair of pyrimidine bases [1212].
References: [560, 1212]

[EC 4.1.99.13 created 2009]

EC 4.1.99.14

Accepted name: spore photoproduct lyase
Reaction: (5*R*)-5,6-dihydro-5-(thymidin-7-yl)thymidine (in double-helical DNA) = thymidylyl-$(3'\rightarrow5')$-thymidylate (in double-helical DNA)
Other name(s): SAM; SP lyase; SPL; SplB; SplG
Systematic name: spore photoproduct pyrimidine-lyase

Comments: This enzyme is a member of the ‘AdoMet radical’ (radical SAM) family. The enzyme binds a [4Fe-4S] cluster. The cluster is coordinated by 3 cysteines and an exchangeable SAM molecule [155]. The 5′-deoxy-adenosine radical formed after electron transfer from the [4Fe-4S] cluster to the *S*-adenosyl-L-methionine, initiates the repair by abstracting the C-6 hydrogen of the spore photoproduct lesion. During the second part of the repair process the SAM molecule is regenerated [155].

References: [206, 1086, 155, 874, 1277]

[EC 4.1.99.14 created 2009, modified 2010]

[4.1.99.15 Deleted entry. S-specific spore photoproduct lyase. This enzyme was classified on the basis of an incorrect reaction. The activity is covered by EC 4.1.99.14, spore photoproduct lyase]

[EC 4.1.99.15 created 2009, deleted 2010]

EC 4.1.99.16

Accepted name: geosmin synthase

Reaction: (1*E*,4*S*,5*E*,7*R*)-germacra-1(10),5-dien-11-ol + H_2O = (–)-geosmin + acetone

Systematic name: germacradienol geosmin-lyase (acetone-forming)

Comments: Requires Mg^{2+}. Geosmin is the cause of the characteristic smell of moist soil. It is a bifunctional enzyme. The N-terminal part of the enzyme is EC 4.2.3.22, germacradienol synthase, and forms germacradienol from FPP. The C-terminal part of the enzyme catalyses the conversion of germacradienol to geosmin via (1*S*,4a*S*,8a*S*)-1,4a-dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalene.

References: [629, 175, 630]

[EC 4.1.99.16 created 2011]

EC 4.1.99.17

Accepted name: phosphomethylpyrimidine synthase

Reaction: 5-amino-1-(5-phospho-D-ribosyl)imidazole + *S*-adenosyl-L-methionine = 4-amino-2-methyl-5-(phosphooxymethyl)pyrimidine + 5′-deoxyadenosine + L-methionine + formate + CO

Other name(s): *thiC* (gene name)

Systematic name: 5-amino-1-(5-phospho-D-ribosyl)imidazole formate-lyase (decarboxylating, 4-amino-2-methyl-5-(phosphooxymethyl)pyrimidine-forming)

Comments: Binds a [4Fe-4S] cluster that is coordinated by 3 cysteines and an exchangeable *S*-adenosyl-L-methionine molecule. The first stage of catalysis is reduction of the *S*-adenosyl-L-methionine to produce L-methionine and a 5′-deoxyadenosin-5′-yl radical that is crucial for the conversion of the substrate. Part of the pathway for thiamine biosynthesis.

References: [213, 884, 212]

[EC 4.1.99.17 created 2011]

[4.1.99.18 Transferred entry. cyclic pyranopterin phosphate synthase. Now known to be catalysed by the combined effort of EC 4.1.99.22, GTP 3,8-cyclase, and EC 4.6.1.17, cyclic pyranopterin monophosphate synthase]

[EC 4.1.99.18 created 2011, deleted 2016]

EC 4.1.99.19

Accepted name: 2-iminoacetate synthase

Reaction: L-tyrosine + *S*-adenosyl-L-methionine + NADPH = 2-iminoacetate + 4-methylphenol + 5′-deoxyadenosine + L-methionine + $NADP^+$ + H^+

Other name(s): *thiH* (gene name)

Systematic name: L-tyrosine 4-methylphenol-lyase (2-iminoacetate-forming)

Comments: Binds a [4Fe-4S] cluster that is coordinated by 3 cysteines and an exchangeable *S*-adenosyl-L-methionine molecule. The first stage of catalysis is reduction of the *S*-adenosyl-L-methionine to produce methionine and a 5-deoxyadenosin-5-yl radical that is crucial for the conversion of the substrate. The reductant is assumed to be NADPH, which is provided by a flavoprotein:NADPH oxidoreductase system [204]. Part of the pathway for thiamine biosynthesis.

References: [795, 739, 740, 204]

[EC 4.1.99.19 created 2011, modified 2014]

EC 4.1.99.20

Accepted name: 3-amino-4-hydroxybenzoate synthase

Reaction: 2-amino-4,5-dihydroxy-6-oxo-7-(phosphooxy)heptanoate = 3-amino-4-hydroxybenzoate + phosphate + **2** H_2O

Other name(s): 3,4-AHBA synthase; *griH* (gene name)

Systematic name: 2-amino-4,5-dihydroxy-6-oxo-7-(phosphooxy)heptanoate hydro-lyase (cyclizing, 3-amino-4-hydroxybenzoate-forming)

Comments: Requires Mn^{2+} for maximum activity. The reaction is suggested to take place in several steps. Schiff base formation, double bond migration and dephosphorylation followed by ring opening and closing to form a pyrrolidine ring, and finally dehydration to form the product 3-amino-4-hydroxybenzoate. In the bacterium *Streptomyces griseus* the enzyme is involved in biosynthesis of grixazone, a yellow pigment that contains a phenoxazinone chromophore.

References: [1325]

[EC 4.1.99.20 created 2013, modified 2016]

[4.1.99.21 Transferred entry. (5-formylfuran-3-yl)methyl phosphate synthase. Now EC 4.2.3.153 (5-formylfuran-3-yl)methyl phosphate synthase.]

[EC 4.1.99.21 created 2015, deleted 2015]

EC 4.1.99.22

Accepted name: GTP 3′,8-cyclase

Reaction: GTP + *S*-adenosyl-L-methionine + reduced electron acceptor = (8*S*)-3′,8-cyclo-7,8-dihydroguanosine 5′-triphosphate + 5′-deoxyadenosine + L-methionine + oxidized electron acceptor

Other name(s): MOCS1A (gene name); *moaA* (gene name); cnx2 (gene name)

Systematic name: GTP 3′,8-cyclase [(8*S*)-3′,8-cyclo-7,8-dihydroguanosine 5′-triphosphate-forming]

Comments: The enzyme catalyses an early step in the biosynthesis of the molybdenum cofactor (MoCo). In bacteria and plants the reaction is catalysed by MoaA and Cnx2, respectively. In mammals it is catalysed by the MOCS1A domain of the bifunctional MOCS1 protein, which also catalyses EC 4.6.1.17, cyclic pyranopterin monophosphate synthase. The enzyme belongs to the superfamily of radical *S*-adenosyl-L-methionine (radical SAM) enzymes, and contains two oxygen-sensitive FeS clusters.

References: [507, 508, 509, 794, 578, 580, 579]

[EC 4.1.99.22 created 2011 as EC 4.1.99.18, part transferred 2016 to EC 4.1.99.22]

EC 4.1.99.23

Accepted name: 5-hydroxybenzimidazole synthase

Reaction: 5-amino-1-(5-phospho-β-D-ribosyl)imidazole + *S*-adenosyl-L-methionine + reduced acceptor = 5-hydroxybenzimidazole + 5′-deoxyadenosine + L-methionine + formate + NH_3 + phosphate + oxidized acceptor

Other name(s): *bzaF* (gene name); HBI synthase

Systematic name: 5-amino-1-(5-phospho-β-D-ribosyl)imidazole formate-lyase (5-hydroxybenzimidazole-forming)

Comments: The enzyme, purified from bacteria, is part of the anaerobic pathway for cobalamin biosynthesis. It binds a [4Fe-4S] cluster that is coordinated by 3 cysteines and an exchangeable *S*-adenosyl-L-methionine molecule. The first stage of catalysis is reduction of the *S*-adenosyl-L-methionine to produce L-methionine and a 5′-deoxyadenosin-5′-yl radical that is crucial for the conversion of the substrate.

References: [920, 529]

[EC 4.1.99.23 created 2017]

EC 4.1.99.24

Accepted name: L-tyrosine isonitrile synthase

Reaction: L-tyrosine + D-ribulose 5-phosphate = (2*S*)-3-(4-hydroxyphenyl)-2-isocyanopropanoate + hydroxyacetone + formaldehyde + phosphate + H_2O

Other name(s): *pvcA* (gene name)

Systematic name: L-tyrosine:D-ribulose-5-phosphate lyase (isonitrile-forming)

Comments: The enzymes from the bacteria *Pseudomonas aeruginosa* and *Xenorhabdus nematophila* are involved in the biosynthesis of paerucumarin and rhabduscin, respectively. According to the proposed mechanism, the enzyme forms an imine intermediate composed of linked L-tyrosine and D-ribulose 5-phosphate, followed by loss of the phosphate group and formation of a β-keto imine and keto-enol tautomerization. This is followed by a C-C bond cleavage, the release of hydroxyacetone, and a retro aldol type reaction that releases formaldehyde and forms the final product [207]. *cf.* EC 4.1.99.25, L-tryptophan isonitrile synthase.

References: [239, 331, 207]

[EC 4.1.99.24 created 2018]

EC 4.1.99.25

Accepted name: L-tryptophan isonitrile synthase

Reaction: L-tryptophan + D-ribulose 5-phosphate = (2*S*)-3-(1*H*-indol-3-yl)-2-isocyanopropanoate + hydroxyacetone + formaldehyde + phosphate + H_2O

Other name(s): *isnA* (gene name); *ambI1* (gene name); *welI1* (gene name)

Systematic name: L-tryptophan:D-ribulose-5-phosphate lyase (isonitrile-forming)

Comments: The enzymes from cyanobacteria that belong to the Nostocales order participate in the biosynthesis of hapalindole-type alkaloids. According to the proposed mechanism, the enzyme forms an imine intermediate composed of linked L-tryptophan and D-ribulose 5-phosphate, followed by loss of the phosphate group and formation of a β-keto imine and keto-enol tautomerization. This is followed by a C-C bond cleavage, the release of hydroxyacetone, and a retro aldol type reaction that releases formaldehyde and forms the final product [554]. *cf.* EC 4.1.99.24, L-tyrosine isonitrile synthase.

References: [129, 130, 554, 207]

[EC 4.1.99.25 created 2018]

EC 4.1.99.26

Accepted name: 3-amino-5-[(4-hydroxyphenyl)methyl]-4,4-dimethylpyrrolidin-2-one synthase

Reaction: C-terminal [mycofactocin precursor peptide]-glycyl-3-amino-5-[(4-hydroxyphenyl)methyl]-4,4-dimethylpyrrolidin-2-one + 5′-deoxyadenosine + L-methionine + A = C-terminal [mycofactocin precursor peptide]-glycyl-L-valyl-4-[2-aminoethenyl]phenol + *S*-adenosyl-L-methionine + AH_2

Other name(s): *mftC* (gene name)

Systematic name: C-terminal [mycofactocin precursor peptide]-glycyl-3-amino-5-[(4-hydroxyphenyl)methyl]-4,4-dimethylpyrrolidin-2-one lyase (C-terminal [mycofactocin precursor peptide]-glycyl-L-valyl-4-[2-aminoethenyl]phenol-forming)

Comments: This is a bifunctional radical AdoMet (radical SAM) enzyme that catalyses the first two steps in the biosynthesis of the enzyme cofactor mycofactocin. Activity requires the presence of the MftB chaperone. The reaction occurs in the right-to-left direction. The other activity of the enzyme is EC 1.3.98.7, [mycofactocin precursor peptide]-tyrosine decarboxylase.

References: [484, 148, 693, 50]

[EC 4.1.99.26 created 2021]

EC 4.1.99.27

Accepted name: cyclopenase

Reaction: (–)-cyclopenine = viridicatin + methyl isocyanate

Other name(s): *asqI* (gene name)

Systematic name: (–)-cyclopenine methyl-isocyanate lyase (viridicatin-forming)

Comments: This fungal enzyme catalyses a key reaction in the biosynthesis of quinolone compounds, converting the benzodiazepine structure into a quinolone structure. The enzyme is also active with (–)-4′-methoxycyclopenine.

References: [707]

[EC 4.1.99.27 created 2022]

EC 4.2 Carbon-oxygen lyases

This subclass contains enzymes that catalyse the breakage of a carbon-oxygen bond. Sub-subclasses are based on the group that is eliminated: water (hydro-lyases; EC 4.2.1), an alcohol from a polysaccharide (EC 4.2.2), a phosphate (EC 4.2.3), or some other group (EC 4.2.99).

EC 4.2.1 Hydro-lyases

EC 4.2.1.1

Accepted name: carbonic anhydrase

Reaction: $H_2CO_3 = CO_2 + H_2O$

Other name(s): carbonate dehydratase; anhydrase; carbonate anhydrase; carbonic acid anhydrase; carboxyanhydrase; carbonic anhydrase A; carbonate hydro-lyase; carbonate hydro-lyase (carbon-dioxide-forming)

Systematic name: carbonic acid hydro-lyase (carbon-dioxide-forming)

Comments: The enzyme catalyses the reversible hydration of dissolved CO_2 to carbonic acid, which dissociates to give hydrogencarbonate above neutral pH. It is widespread and found in archaea, bacteria, and eukaryotes. Three distinct classes exist, and appear to have evolved independently. Contains zinc.

References: [685, 663, 971, 607, 1285, 265, 930]

[EC 4.2.1.1 created 1961, modified 2016]

EC 4.2.1.2

Accepted name: fumarate hydratase

Reaction: (*S*)-malate = fumarate + H_2O

Other name(s): fumarase; L-malate hydro-lyase; (*S*)-malate hydro-lyase

Systematic name: (*S*)-malate hydro-lyase (fumarate-forming)

References: [15, 661]

[EC 4.2.1.2 created 1961]

EC 4.2.1.3

Accepted name: aconitate hydratase

Reaction: citrate = isocitrate (overall reaction)
(1a) citrate = *cis*-aconitate + H_2O
(1b) *cis*-aconitate + H_2O = isocitrate

Other name(s): *cis*-aconitase; aconitase; AcnB; 2-methylaconitate hydratase; citrate(isocitrate) hydro-lyase

Systematic name: citrate(isocitrate) hydro-lyase (*cis*-aconitate-forming)

Comments: Besides interconverting citrate and *cis*-aconitate, it also interconverts *cis*-aconitate with isocitrate and, hence, interconverts citrate and isocitrate. The equilibrium mixture is 91% citrate, 6% isocitrate and 3% aconitate. *cis*-Aconitate is used to designate the isomer (*Z*)-prop-1-ene-1,2,3-tricarboxylate. An iron-sulfur protein, containing a [4Fe-4S] cluster to which the substrate binds.

References: [321, 960, 787]

[EC 4.2.1.3 created 1961, modified 2003]

[4.2.1.4] Deleted entry. citrate dehydratase. Now known to be a partial reaction catalysed by EC 4.2.1.3, aconitate hydratase.

[EC 4.2.1.4 created 1961, deleted 2013]

EC 4.2.1.5

Accepted name: arabinonate dehydratase

Reaction: D-arabinonate = 2-dehydro-3-deoxy-D-arabinonate + H_2O

Other name(s): D-arabinonate hydro-lyase

Systematic name: D-arabinonate hydro-lyase (2-dehydro-3-deoxy-D-arabinonate-forming)

References: [1049]

[EC 4.2.1.5 created 1961]

EC 4.2.1.6

Accepted name: galactonate dehydratase

Reaction: D-galactonate = 2-dehydro-3-deoxy-D-galactonate + H_2O

Other name(s): D-galactonate dehydrase; D-galactonate dehydratase; D-galactonate hydro-lyase

Systematic name: D-galactonate hydro-lyase (2-dehydro-3-deoxy-D-galactonate-forming)

Comments: The enzyme shows no activity with D-gluconate [328]. *cf.* EC 4.2.1.140, gluconate/galactonate dehydratase.

References: [802, 328]

[EC 4.2.1.6 created 1961]

EC 4.2.1.7

Accepted name: altronate dehydratase

Reaction: D-altronate = 2-dehydro-3-deoxy-D-gluconate + H_2O

Other name(s): D-altronate hydro-lyase

Systematic name: D-altronate hydro-lyase (2-dehydro-3-deoxy-D-gluconate-forming)

References: [1281]

[EC 4.2.1.7 created 1961, deleted 1972, reinstated 1976]

EC 4.2.1.8

Accepted name: mannonate dehydratase

Reaction: D-mannonate = 2-dehydro-3-deoxy-D-gluconate + H_2O

Other name(s): mannonic hydrolase; mannonate hydrolyase; altronic hydro-lyase; altronate hydrolase; D-mannonate hydrolyase; D-mannonate hydro-lyase

Systematic name: D-mannonate hydro-lyase (2-dehydro-3-deoxy-D-gluconate-forming)

References: [45, 1162]

[EC 4.2.1.8 created 1961, modified 1976]

EC 4.2.1.9

Accepted name: dihydroxy-acid dehydratase

Reaction: 2,3-dihydroxy-3-methylbutanoate = 3-methyl-2-oxobutanoate + H_2O

Other name(s): acetohydroxyacid dehydratase; α,β-dihydroxyacid dehydratase; 2,3-dihydroxyisovalerate dehydratase; α,β-dihydroxyisovalerate dehydratase; dihydroxy acid dehydrase; DHAD; 2,3-dihydroxy-acid hydro-lyase

Systematic name: 2,3-dihydroxy-3-methylbutanoate hydro-lyase (3-methyl-2-oxobutanoate-forming)

References: [660, 976]

[EC 4.2.1.9 created 1961]

EC 4.2.1.10

Accepted name: 3-dehydroquinate dehydratase

Reaction: 3-dehydroquinate = 3-dehydroshikimate + H_2O

Other name(s): 3-dehydroquinate hydrolase; DHQase; dehydroquinate dehydratase; 3-dehydroquinase; 5-dehydroquinase; dehydroquinase; 5-dehydroquinate dehydratase; 5-dehydroquinate hydro-lyase; 3-dehydroquinate hydro-lyase

Systematic name: 3-dehydroquinate hydro-lyase (3-dehydroshikimate-forming)

References: [945, 946]

[EC 4.2.1.10 created 1961, modified 1976]

EC 4.2.1.11

Accepted name: phosphopyruvate hydratase

Reaction: 2-phospho-D-glycerate = phospho*enol*pyruvate + H_2O

Other name(s): enolase; 2-phosphoglycerate dehydratase; 14-3-2-protein; nervous-system specific enolase; phospho*enol*pyruvate hydratase; 2-phosphoglycerate dehydratase; 2-phosphoglyceric dehydratase; 2-phosphoglycerate enolase; γ-enolase; 2-phospho-D-glycerate hydro-lyase

Systematic name: 2-phospho-D-glycerate hydro-lyase (phospho*enol*pyruvate-forming)

Comments: Also acts on 3-phospho-D-erythronate.

References: [570, 869, 1462]

[EC 4.2.1.11 created 1961]

EC 4.2.1.12

Accepted name: phosphogluconate dehydratase

Reaction: 6-phospho-D-gluconate = 2-dehydro-3-deoxy-6-phospho-D-gluconate + H_2O

Other name(s): 6-phosphogluconate dehydratase; 6-phosphogluconic dehydrase; gluconate-6-phosphate dehydratase; gluconate 6-phosphate dehydratase; 6-phosphogluconate dehydrase; 6-phospho-D-gluconate hydro-lyase

Systematic name: 6-phospho-D-gluconate hydro-lyase (2-dehydro-3-deoxy-6-phospho-D-gluconate-forming)

References: [927]

[EC 4.2.1.12 created 1961]

[4.2.1.13 Transferred entry. L*-serine dehydratase. Now EC 4.3.1.17,* L*-serine ammonia-lyase]*

[EC 4.2.1.13 created 1961, deleted 2001]

[4.2.1.14 Transferred entry. D-serine dehydratase. Now EC 4.3.1.18, D-serine ammonia-lyase]

[EC 4.2.1.14 created 1961, deleted 2001]

[4.2.1.15 Deleted entry. homoserine dehydratase. Identical with EC 4.4.1.1 cystathionine γ-lyase]

[EC 4.2.1.15 created 1961, deleted 1972]

[4.2.1.16 Transferred entry. threonine dehydratase. Now EC 4.3.1.19, threonine ammonia-lyase]

[EC 4.2.1.16 created 1961, deleted 2001]

EC 4.2.1.17

Accepted name: enoyl-CoA hydratase

Reaction: (3*S*)-3-hydroxyacyl-CoA = *trans*-2(or 3)-enoyl-CoA + H_2O

Other name(s): enoyl hydrase; unsaturated acyl-CoA hydratase; β-hydroxyacyl-CoA dehydrase; β-hydroxyacid dehydrase; acyl coenzyme A hydrase; crotonase; crotonyl hydrase; 2-octenoyl coenzyme A hydrase; enoyl coenzyme A hydratase; 2-enoyl-CoA hydratase; short-chain enoyl-CoA hydratase; ECH; *trans*-2-enoyl-CoA hydratase; enoyl coenzyme A hydrase (D); enoyl coenzyme A hydrase (L); short chain enoyl coenzyme A hydratase; D-3-hydroxyacyl-CoA dehydratase; enol-CoA hydratase

Systematic name: (3*S*)-3-hydroxyacyl-CoA hydro-lyase

Comments: Acts in the reverse direction. With *cis*-compounds, yields (3*R*)-3-hydroxyacyl-CoA. *cf.* EC 4.2.1.74 long-chain-enoyl-CoA hydratase.

References: [963, 1303]

[EC 4.2.1.17 created 1961]

EC 4.2.1.18

Accepted name: methylglutaconyl-CoA hydratase

Reaction: (*S*)-3-hydroxy-3-methylglutaryl-CoA = *trans*-3-methylglutaconyl-CoA + H_2O

Other name(s): methylglutaconyl coenzyme A hydratase; 3-methylglutaconyl CoA hydratase; methylglutaconase; (*S*)-3-hydroxy-3-methylglutaryl-CoA hydro-lyase

Systematic name: (*S*)-3-hydroxy-3-methylglutaryl-CoA hydro-lyase (*trans*-3-methylglutaconyl-CoA-forming)

References: [555]

[EC 4.2.1.18 created 1961]

EC 4.2.1.19

Accepted name: imidazoleglycerol-phosphate dehydratase

Reaction: D-*erythro*-1-(imidazol-4-yl)glycerol 3-phosphate = 3-(imidazol-4-yl)-2-oxopropyl phosphate + H_2O

Other name(s): IGP dehydratase; D-*erythro*-1-(imidazol-4-yl)glycerol 3-phosphate hydro-lyase

Systematic name: D-*erythro*-1-(imidazol-4-yl)glycerol-3-phosphate hydro-lyase [3-(imidazol-4-yl)-2-oxopropyl-phosphate-forming]

References: [23]

[EC 4.2.1.19 created 1961]

EC 4.2.1.20

Accepted name: tryptophan synthase

Reaction: L-serine + 1-*C*-(indol-3-yl)glycerol 3-phosphate = L-tryptophan + D-glyceraldehyde 3-phosphate + H_2O (overall reaction)
(1a) 1-*C*-(indol-3-yl)glycerol 3-phosphate = indole + D-glyceraldehyde 3-phosphate
(1b) L-serine + indole = L-tryptophan + H_2O

Other name(s): L-tryptophan synthetase; indoleglycerol phosphate aldolase; tryptophan desmolase; tryptophan synthetase; L-serine hydro-lyase (adding indoleglycerol-phosphate); L-serine hydro-lyase [adding 1-*C*-(indol-3-yl)glycerol 3-phosphate, L-tryptophan and glyceraldehyde-3-phosphate-forming]

Systematic name: L-serine hydro-lyase [adding 1-*C*-(indol-3-yl)glycerol 3-phosphate, L-tryptophan and D-glyceraldehyde-3-phosphate-forming]

Comments: A pyridoxal-phosphate protein. The α-subunit catalyses the conversion of 1-*C*-(indol-3-yl)glycerol 3-phosphate to indole and D-glyceraldehyde 3-phosphate (this reaction was included formerly under EC 4.1.2.8). The indole migrates to the β-subunit where, in the presence of pyridoxal 5′-phosphate, it is combined with L-serine to form L-tryptophan. In some organisms this enzyme is part of a multifunctional protein that also includes one or more of the enzymes EC 2.4.2.18 (anthranilate phosphoribosyltransferase), EC 4.1.1.48 (indole-3-glycerol-phosphate synthase), EC 4.1.3.27 (anthranilate synthase) and EC 5.3.1.24 (phosphoribosylanthranilate isomerase). In thermophilic organisms, where the high temperature enhances diffusion and causes the loss of indole, a protein similar to the β subunit can be found (EC 4.2.1.122). That enzyme cannot combine with the α unit of EC 4.2.1.20 to form a complex.

References: [259, 261, 590, 592, 1474]

[EC 4.2.1.20 created 1961, modified 1976, modified 2002, modified 2011]

[4.2.1.21 Deleted entry. cystathionine β-synthase. Now EC 4.2.1.22 cystathionine β-synthase]

[EC 4.2.1.21 created 1961, deleted 1964]

EC 4.2.1.22

Accepted name: cystathionine β-synthase

Reaction: L-serine + L-homocysteine = L-cystathionine + H_2O

Other name(s): serine sulfhydrase; β-thionase; methylcysteine synthase; cysteine synthase (incorrect); serine sulfhydrylase; L-serine hydro-lyase (adding homocysteine)

Systematic name: L-serine hydro-lyase (adding homocysteine; L-cystathionine-forming)

Comments: A pyridoxal-phosphate protein. A multifunctional enzyme: catalyses β-replacement reactions between L-serine, L-cysteine, cysteine thioethers, or some other β-substituted α-L-amino acids, and a variety of mercaptans.

References: [133, 986, 1213]

[EC 4.2.1.22 created 1961 (EC 4.2.1.21 created 1961, incorporated 1964, EC 4.2.1.23 created 1961, incorporated 1972)]

[4.2.1.23 Deleted entry. methylcysteine synthase. The reaction was due to a side-reaction of EC 4.2.1.22 cystathionine β-synthase]

[EC 4.2.1.23 created 1961, deleted 1972]

EC 4.2.1.24

Accepted name: porphobilinogen synthase

Reaction: **2** 5-aminolevulinate = porphobilinogen + **2** H_2O

Other name(s): aminolevulinate dehydratase; δ-aminolevulinate dehydratase; δ-aminolevulinic acid dehydrase; δ-aminolevulinic acid dehydratase; aminolevulinic dehydratase; δ-aminolevulinic dehydratase; 5-levulinic acid dehydratase; 5-aminolevulinate hydro-lyase (adding 5-aminolevulinate and cyclizing); *hemB* (gene name)

Systematic name: 5-aminolevulinate hydro-lyase (adding 5-aminolevulinate and cyclizing; porphobilinogen-forming)

Comments: The enzyme catalyses the asymmetric condensation and cyclization of two 5-aminolevulinate molecules, which is the first common step in the biosynthesis of tetrapyrrole pigments such as porphyrin, chlorophyll, vitamin B_{12}, siroheme, phycobilin, and cofactor F_{430}. The enzyme is widespread, being essential in organisms that carry out respiration, photosynthesis, or methanogenesis. The enzymes from most organisms utilize metal ions (Zn^{2+}, Mg^{2+}, K^{+}, and Na^{+}) as cofactors that reside at multiple sites, including the active site and allosteric sites. Enzymes from archaea, yeast, and metazoa (including human) contain Zn^{2+} at the active site. In humans, the enzyme is a primary target for the environmental toxin Pb. The enzymes from some organisms utilize a dynamic equilibrium between architecturally distinct multimeric assemblies as a means for allosteric regulation.
References: [439, 728, 1498, 944, 615, 1452, 616, 1374]

[EC 4.2.1.24 created 1961]

EC 4.2.1.25

Accepted name: L-arabinonate dehydratase
Reaction: L-arabinonate = 2-dehydro-3-deoxy-L-arabinonate + H_2O
Other name(s): L-arabonate dehydrase; L-arabonate dehydratase; L-arabinonate hydro-lyase
Systematic name: L-arabinonate hydro-lyase (2-dehydro-3-deoxy-L-arabinonate-forming)
References: [1458]

[EC 4.2.1.25 created 1965]

[4.2.1.26 Deleted entry. aminodeoxygluconate dehydratase. This enzyme was transferred to EC 4.3.1.21, aminodeoxygluconate ammonia-lyase, which has since been deleted. The enzyme is identical to EC 4.3.1.9, glucosaminate ammonia-lyase]

[EC 4.2.1.26 created 1965, deleted 2002]

EC 4.2.1.27

Accepted name: acetylenecarboxylate hydratase
Reaction: 3-oxopropanoate = propynoate + H_2O
Other name(s): acetylenemonocarboxylate hydratase; alkynoate hydratase; acetylenemonocarboxylate hydrase; acetylenemonocarboxylic acid hydrase; malonate-semialdehyde dehydratase; 3-oxopropanoate hydro-lyase
Systematic name: 3-oxopropanoate hydro-lyase (propynoate-forming)
Comments: The reaction is effectively irreversible, favouring oxopropanoate (malonic semialdehyde) and its tautomers. Also acts on but-3-ynoate forming acetoacetate. The mechanism appears to involve hydration of the acetylene to 3-hydroxypropenoate, which will spontaneously tautomerize to 3-oxopropanoate. It is thus analogous to EC 4.1.1.78, acetylenedicarboxylate decarboxylase, in its mechanism.
References: [310, 1489]

[EC 4.2.1.27 created 1965, (EC 4.2.1.71 created 1978, modified 1989, modified 2000, incorporated 2004) modified 2004]

EC 4.2.1.28

Accepted name: propanediol dehydratase
Reaction: propane-1,2-diol = propanal + H_2O
Other name(s): *meso*-2,3-butanediol dehydrase; diol dehydratase; DL-1,2-propanediol hydro-lyase; diol dehydrase; adenosylcobalamin-dependent diol dehydratase; propanediol dehydrase; coenzyme B_{12}-dependent diol dehydrase; 1,2-propanediol dehydratase; dioldehydratase; propane-1,2-diol hydro-lyase; RiDD
Systematic name: propane-1,2-diol hydro-lyase (propanal-forming)
Comments: Two different forms of the enzyme have been described. One form requires a cobamide coenzyme, while the other is a glycyl radical enzyme. The cobamide-dependent enzyme has been shown to also dehydrate ethylene glycol to acetaldehyde.
References: [1147, 789, 395, 778]

[EC 4.2.1.28 created 1965]

[4.2.1.29 Transferred entry. indoleacetaldoxime dehydratase. Now EC 4.99.1.6, indoleacetaldoxime dehydratase. The enzyme was classified incorrectly as a C-O lyase when the bond broken is a N-O bond]

[EC 4.2.1.29 created 1965, deleted 2004]

EC 4.2.1.30

Accepted name: glycerol dehydratase

Reaction: glycerol = 3-hydroxypropanal + H_2O

Other name(s): glycerol dehydrase; glycerol hydro-lyase; *dhaB* (gene name)

Systematic name: glycerol hydro-lyase (3-hydroxypropanal-forming)

Comments: Two different forms of the enzyme have been described. One form requires a cobamide coenzyme, while the other is a glycyl radical enzyme.

References: [1283, 1227, 1226, 395, 1019]

[EC 4.2.1.30 created 1972]

EC 4.2.1.31

Accepted name: maleate hydratase

Reaction: (*R*)-malate = maleate + H_2O

Other name(s): D-malate hydro-lyase; malease; (*R*)-malate hydro-lyase

Systematic name: (*R*)-malate hydro-lyase (maleate-forming)

References: [137, 1180]

[EC 4.2.1.31 created 1972]

EC 4.2.1.32

Accepted name: L(+)-tartrate dehydratase

Reaction: (*R*,*R*)-tartrate = oxaloacetate + H_2O

Other name(s): tartrate dehydratase; tartaric acid dehydrase; L-tartrate dehydratase; L-(+)-tartaric acid dehydratase; (*R*,*R*)-tartrate hydro-lyase

Systematic name: (*R*,*R*)-tartrate hydro-lyase (oxaloacetate-forming)

Comments: The enzyme exists in an inactive low-molecular-mass form, which is converted into active enzyme in the presence of Fe^{2+} and thiol. *cf.* EC 4.2.1.81 D(-)-tartrate dehydratase.

References: [589]

[EC 4.2.1.32 created 1972, modified 1986]

EC 4.2.1.33

Accepted name: 3-isopropylmalate dehydratase

Reaction: (2*R*,3*S*)-3-isopropylmalate = (2*S*)-2-isopropylmalate (overall reaction)
(1a) (2*R*,3*S*)-3-isopropylmalate = 2-isopropylmaleate + H_2O
(1b) 2-isopropylmaleate + H_2O = (2*S*)-2-isopropylmalate

Other name(s): (2*R*,3*S*)-3-isopropylmalate hydro-lyase; β-isopropylmalate dehydratase; isopropylmalate isomerase; α-isopropylmalate isomerase; 3-isopropylmalate hydro-lyase

Systematic name: (2*R*,3*S*)-3-isopropylmalate hydro-lyase (2-isopropylmaleate-forming)

Comments: Forms part of the leucine biosynthesis pathway. The enzyme brings about the interconversion of the two isomers of isopropylmalate. It contains an iron-sulfur cluster.

References: [469, 171, 243, 620]

[EC 4.2.1.33 created 1972, modified 1976, modified 2012]

EC 4.2.1.34

Accepted name: (*S*)-2-methylmalate dehydratase

Reaction: (*S*)-2-methylmalate = 2-methylfumarate + H_2O

Other name(s): mesaconate hydratase; (+)-citramalate hydro-lyase; L-citramalate hydrolase; citramalate dehydratase; (+)-citramalic hydro-lyase; mesaconate mesaconase; mesaconase; (*S*)-2-methylmalate hydro-lyase

Systematic name: (*S*)-2-methylmalate hydro-lyase (2-methylfumarate-forming)

Comments: Also hydrates fumarate to (*S*)-malate.

References: [98, 1438]

[EC 4.2.1.34 created 1972]

EC 4.2.1.35

Accepted name: (*R*)-2-methylmalate dehydratase

Reaction: (*R*)-2-methylmalate = 2-methylmaleate + H_2O

Other name(s): citraconate hydratase; citraconase; citramalate hydro-lyase; (-)-citramalate hydro-lyase; (*R*)-2-methylmalate hydro-lyase

Systematic name: (*R*)-2-methylmalate hydro-lyase (2-methylmaleate-forming)

Comments: Requires Fe^{2+}.

References: [1316, 1131]

[EC 4.2.1.35 created 1972]

EC 4.2.1.36

Accepted name: homoaconitate hydratase

Reaction: (1*R*,2*S*)-1-hydroxybutane-1,2,4-tricarboxylate = (*Z*)-but-1-ene-1,2,4-tricarboxylate + H_2O

Other name(s): homoaconitase; *cis*-homoaconitase; HACN; Lys^4; LysF; 2-hydroxybutane-1,2,4-tricarboxylate hydro-lyase (incorrect)

Systematic name: (1*R*,2*S*)-1-hydroxybutane-1,2,4-tricarboxylate hydro-lyase [(*Z*)-but-1-ene-1,2,4-tricarboxylate-forming]

Comments: Requires a [4Fe-4S] cluster for activity. The enzyme from the hyperthermophilic eubacterium *Thermus thermophilus* can catalyse the reaction shown above but cannot catalyse the previously described reaction, i.e. formation of (*R*)-homocitrate by hydration of *cis*-homoaconitate. The enzyme responsible for the conversion of *cis*-homoaconitate into (*R*)-homocitrate in *T. thermophilus* is unknown at present but the reaction can be catalysed *in vitro* using aconitate hydratase from pig (EC 4.2.1.3) [628].

References: [1311, 628, 1538]

[EC 4.2.1.36 created 1972, modified 2007]

[4.2.1.37 Transferred entry. trans-epoxysuccinate hydratase. Now EC 3.3.2.4, trans-epoxysuccinate hydrolase]

[EC 4.2.1.37 created 1972, deleted 1992]

[4.2.1.38 Transferred entry. erythro-3-hydroxyaspartate dehydratase. Now EC 4.3.1.20, erythro-3-hydroxyaspartate ammonia-lyase]

[EC 4.2.1.38 created 1972, deleted 2001]

EC 4.2.1.39

Accepted name: gluconate dehydratase

Reaction: D-gluconate = 2-dehydro-3-deoxy-D-gluconate + H_2O

Other name(s): D-gluconate dehydratase; D-gluconate hydro-lyase

Systematic name: D-gluconate hydro-lyase (2-dehydro-3-deoxy-D-gluconate-forming)

Comments: The enzyme shows no activity with D-galactonate [86]. *cf.* EC 4.2.1.140, gluconate/galactonate dehydratase.

References: [30, 86]

[EC 4.2.1.39 created 1972]

EC 4.2.1.40

Accepted name: glucarate dehydratase
Reaction: D-glucarate = 5-dehydro-4-deoxy-D-glucarate + H_2O
Other name(s): D-glucarate dehydratase; D-glucarate hydro-lyase
Systematic name: D-glucarate hydro-lyase (5-dehydro-4-deoxy-D-glucarate-forming)
References: [107]

[EC 4.2.1.40 created 1972]

EC 4.2.1.41

Accepted name: 5-dehydro-4-deoxyglucarate dehydratase
Reaction: 5-dehydro-4-deoxy-D-glucarate = 2,5-dioxopentanoate + H_2O + CO_2
Other name(s): 5-keto-4-deoxy-glucarate dehydratase; 5-keto-4-deoxy-glucarate dehydratase; deoxyketoglucarate dehydratase; D-4-deoxy-5-ketoglucarate hydro-lyase; 5-dehydro-4-deoxy-D-glucarate hydro-lyase (decarboxylating)
Systematic name: 5-dehydro-4-deoxy-D-glucarate hydro-lyase (decarboxylating; 2,5-dioxopentanoate-forming)
References: [624]

[EC 4.2.1.41 created 1972]

EC 4.2.1.42

Accepted name: galactarate dehydratase
Reaction: galactarate = (2*R*,3*S*)-2,3-dihydroxy-5-oxohexanedioate + H_2O
Other name(s): D-galactarate hydro-lyase; D-galactarate hydro-lyase (5-dehydro-4-deoxy-D-glucarate-forming); *talrD* (gene name)/galrD (gene name); galactarate dehydratase (L-*threo*-forming)
Systematic name: galactarate hydro-lyase (5-dehydro-4-deoxy-D-glucarate-forming)
Comments: The enzyme from the bacterium *Escherichia coli* is specific for galactarate [586], while the enzyme from *Salmonella typhimurium* also has activity with L-talarate (*cf.* EC 4.2.1.156, L-talarate dehydratase) [1509]. *cf.* EC 4.2.1.158, galactarate dehydratase (D-*threo*-forming).
References: [108, 586, 1509, 1125]

[EC 4.2.1.42 created 1972, modified 2015]

EC 4.2.1.43

Accepted name: 2-dehydro-3-deoxy-L-arabinonate dehydratase
Reaction: 2-dehydro-3-deoxy-L-arabinonate = 2,5-dioxopentanoate + H_2O
Other name(s): 2-keto-3-deoxy-L-arabinonate dehydratase; 2-dehydro-3-deoxy-L-arabinonate hydro-lyase
Systematic name: 2-dehydro-3-deoxy-L-arabinonate hydro-lyase (2,5-dioxopentanoate-forming)
References: [1307]

[EC 4.2.1.43 created 1972]

EC 4.2.1.44

Accepted name: *myo*-inosose-2 dehydratase
Reaction: 2,4,6/3,5-pentahydroxycyclohexanone = 3,5/4-trihydroxycyclohexa-1,2-dione + H_2O
Other name(s): inosose 2,3-dehydratase; ketoinositol dehydratase; 2,4,6/3,5-pentahydroxycyclohexanone hydro-lyase
Systematic name: 2,4,6/3,5-pentahydroxycyclohexanone hydro-lyase (3,5/4-trihydroxycyclohexa-1,2-dione-forming)
Comments: Requires Co^{2+} or Mn^{2+}.

References: [93]

[EC 4.2.1.44 created 1972]

EC 4.2.1.45

Accepted name: CDP-glucose 4,6-dehydratase

Reaction: CDP-glucose = CDP-4-dehydro-6-deoxy-D-glucose + H_2O

Other name(s): cytidine diphosphoglucose oxidoreductase; CDP-glucose 4,6-hydro-lyase

Systematic name: CDP-glucose 4,6-hydro-lyase (CDP-4-dehydro-6-deoxy-D-glucose-forming)

Comments: Requires bound NAD^+.

References: [549, 894, 925]

[EC 4.2.1.45 created 1972]

EC 4.2.1.46

Accepted name: dTDP-glucose 4,6-dehydratase

Reaction: dTDP-α-D-glucose = dTDP-4-dehydro-6-deoxy-α-D-glucose + H_2O

Other name(s): thymidine diphosphoglucose oxidoreductase; TDP-glucose oxidoreductase; dTDP-glucose 4,6-hydro-lyase; dTDP-glucose 4,6-hydro-lyase (dTDP-4-dehydro-6-deoxy-α-D-glucose-forming)

Systematic name: dTDP-α-D-glucose 4,6-hydro-lyase (dTDP-4-dehydro-6-deoxy-α-D-glucose-forming)

Comments: Requires bound NAD^+.

References: [442, 925, 1444, 534, 468]

[EC 4.2.1.46 created 1972]

EC 4.2.1.47

Accepted name: GDP-mannose 4,6-dehydratase

Reaction: GDP-α-D-mannose = GDP-4-dehydro-α-D-rhamnose + H_2O

Other name(s): guanosine 5′-diphosphate-D-mannose oxidoreductase; guanosine diphosphomannose oxidoreductase; guanosine diphosphomannose 4,6-dehydratase; GDP-D-mannose dehydratase; GDP-D-mannose 4,6-dehydratase; Gmd; GDP-mannose 4,6-hydro-lyase; GDP-mannose 4,6-hydro-lyase (GDP-4-dehydro-6-deoxy-D-mannose-forming)

Systematic name: GDP-α-D-mannose 4,6-hydro-lyase (GDP-4-dehydro-α-D-rhamnose-forming)

Comments: The bacterial enzyme requires bound NAD^+. This enzyme forms the first step in the biosynthesis of GDP-α-D-rhamnose and GDP-β-L-fucose. In *Aneurinibacillus thermoaerophilus* L420-91^T, this enzyme acts as a bifunctional enzyme, catalysing the above reaction as well as the reaction catalysed by EC 1.1.1.281, GDP-4-dehydro-6-deoxy-D-mannose reductase [715]. Belongs to the short-chain dehydrogenase/reductase enzyme family, having homologous structures and a conserved catalytic triad of Lys, Tyr and Ser/Thr residues [968].

References: [355, 812, 925, 1321, 715, 968]

[EC 4.2.1.47 created 1972, modified 2004]

EC 4.2.1.48

Accepted name: D-glutamate cyclase

Reaction: D-glutamate = 5-oxo-D-proline + H_2O

Other name(s): D-glutamate hydro-lyase (cyclizing)

Systematic name: D-glutamate hydro-lyase (cyclizing; 5-oxo-D-proline-forming)

Comments: Also acts on various derivatives of D-glutamate.

References: [922]

[EC 4.2.1.48 created 1972]

EC 4.2.1.49

Accepted name: urocanate hydratase

Reaction: 3-(5-oxo-4,5-dihydro-3*H*-imidazol-4-yl)propanoate = urocanate + H_2O

Other name(s): urocanase; 3-(5-oxo-4,5-dihydro-3*H*-imidazol-4-yl)propanoate hydro-lyase

Systematic name: 3-(5-oxo-4,5-dihydro-3*H*-imidazol-4-yl)propanoate hydro-lyase (urocanate-forming)

Comments: Contains tightly bound NAD^+.

References: [1146, 521, 657, 1332]

[EC 4.2.1.49 created 1972, modified 2001]

EC 4.2.1.50

Accepted name: pyrazolylalanine synthase

Reaction: L-serine + pyrazole = 3-(pyrazol-1-yl)-L-alanine + H_2O

Other name(s): β-pyrazolylalaninase; β-(1-pyrazolyl)alanine synthase; L-serine hydro-lyase (adding pyrazole)

Systematic name: L-serine hydro-lyase [adding pyrazole; 3-(pyrazol-1-yl)-L-alanine-forming]

Comments: A pyridoxal-phosphate protein.

References: [340]

[EC 4.2.1.50 created 1972]

EC 4.2.1.51

Accepted name: prephenate dehydratase

Reaction: prephenate = phenylpyruvate + H_2O + CO_2

Other name(s): prephenate hydro-lyase (decarboxylating)

Systematic name: prephenate hydro-lyase (decarboxylating; phenylpyruvate-forming)

Comments: This enzyme in the enteric bacteria also possesses chorismate mutase (EC 5.4.99.5) activity, and converts chorismate into prephenate.

References: [203, 256, 1220]

[EC 4.2.1.51 created 1972]

[4.2.1.52 Transferred entry. dihydrodipicolinate synthase. Now EC 4.3.3.7, 4-hydroxy-2,3,4,5-tetrahydrodipicolinate synthase.]

[EC 4.2.1.52 created 1972, deleted 2012]

EC 4.2.1.53

Accepted name: oleate hydratase

Reaction: (*R*)-10-hydroxystearate = oleate + H_2O

Other name(s): (*R*)-10-hydroxystearate 10-hydro-lyase

Systematic name: (*R*)-10-hydroxystearate 10-hydro-lyase (oleate-forming)

Comments: Acts on a number of 10-hydroxy acids.

References: [295, 457, 1004]

[EC 4.2.1.53 created 1972]

EC 4.2.1.54

Accepted name: lactoyl-CoA dehydratase

Reaction: (*R*)-lactoyl-CoA = acryloyl-CoA + H_2O

Other name(s): lactoyl coenzyme A dehydratase; lactyl-coenzyme A dehydrase; lactyl CoA dehydratase; acrylyl coenzyme A hydratase; lactoyl-CoA hydro-lyase

Systematic name: (*R*)-lactoyl-CoA hydro-lyase (acryloyl-CoA-forming)

Comments: A bacterial enzyme that is involved in propanoate fermentation (also known as the acrylate pathway).

References: [69, 1241, 745, 746, 566]

[EC 4.2.1.54 created 1972, modified 2012]

EC 4.2.1.55

Accepted name: 3-hydroxybutyryl-CoA dehydratase
Reaction: (3*R*)-3-hydroxybutanoyl-CoA = crotonoyl-CoA + H_2O
Other name(s): D-3-hydroxybutyryl coenzyme A dehydratase; D-3-hydroxybutyryl-CoA dehydratase; enoyl coenzyme A hydrase (D); (3*R*)-3-hydroxybutanoyl-CoA hydro-lyase
Systematic name: (3*R*)-3-hydroxybutanoyl-CoA hydro-lyase (crotonoyl-CoA-forming)
Comments: Also acts on crotonoyl thioesters of pantetheine and acyl-carrier protein.
References: [963]

[EC 4.2.1.55 created 1972]

EC 4.2.1.56

Accepted name: itaconyl-CoA hydratase
Reaction: citramalyl-CoA = itaconyl-CoA + H_2O
Other name(s): itaconyl coenzyme A hydratase; citramalyl-CoA hydro-lyase
Systematic name: citramalyl-CoA hydro-lyase (itaconyl-CoA-forming)
References: [253]

[EC 4.2.1.56 created 1972]

EC 4.2.1.57

Accepted name: isohexenylglutaconyl-CoA hydratase
Reaction: 3-hydroxy-3-(4-methylpent-3-en-1-yl)glutaryl-CoA = 3-(4-methylpent-3-en-1-yl)pent-2-enedioyl-CoA + H_2O
Other name(s): 3-hydroxy-3-isohexenylglutaryl-CoA-hydrolase; isohexenylglutaconyl coenzyme A hydratase; β-isohexenylglutaconyl-CoA-hydratase; 3-hydroxy-3-(4-methylpent-3-en-1-yl)glutaryl-CoA hydro-lyase
Systematic name: 3-hydroxy-3-(4-methylpent-3-en-1-yl)glutaryl-CoA hydro-lyase [3-(4-methylpent-3-en-1-yl)pent-2-enedioyl-CoA-forming]
Comments: Also acts on dimethylacryloyl-CoA and farnesoyl-CoA.
References: [1257]

[EC 4.2.1.57 created 1972]

[4.2.1.58 Deleted entry. crotonoyl-[acyl-carrier-protein] hydratase. The reaction described is covered by EC 4.2.1.59.]

[EC 4.2.1.58 created 1972, deleted 2012]

EC 4.2.1.59

Accepted name: 3-hydroxyacyl-[acyl-carrier-protein] dehydratase
Reaction: a (3*R*)-3-hydroxyacyl-[acyl-carrier protein] = a *trans*-2-enoyl-[acyl-carrier protein] + H_2O
Other name(s): *fabZ* (gene name); *fabA* (gene name); D-3-hydroxyoctanoyl-[acyl carrier protein] dehydratase; D-3-hydroxyoctanoyl-acyl carrier protein dehydratase; β-hydroxyoctanoyl-acyl carrier protein dehydrase; β-hydroxyoctanoyl thioester dehydratase; β-hydroxyoctanoyl-ACP-dehydrase; (3*R*)-3-hydroxyoctanoyl-[acyl-carrier-protein] hydro-lyase; (3*R*)-3-hydroxyoctanoyl-[acyl-carrier-protein] hydro-lyase (oct-2-enoyl-[acyl-carrier protein]-forming); 3-hydroxyoctanoyl-[acyl-carrier-protein] dehydratase
Systematic name: (3*R*)-3-hydroxyacyl-[acyl-carrier protein] hydro-lyase (*trans*-2-enoyl-[acyl-carrier protein]-forming)

Comments: This enzyme is responsible for the dehydration step of the dissociated (type II) fatty-acid biosynthesis system that occurs in plants and bacteria. The enzyme uses fatty acyl thioesters of ACP *in vivo*. Different forms of the enzyme may have preferences for substrates with different chain length. For example, the activity of FabZ, the ubiquitous enzyme in bacteria, decreases with increasing chain length. Gram-negative bacteria that produce unsaturated fatty acids, such as *Escherichia coli*, have another form (FabA) that prefers intermediate chain length, and also catalyses EC 5.3.3.14, *trans*-2-decenoyl-[acyl-carrier protein] isomerase. Despite the differences both forms can catalyse all steps leading to the synthesis of palmitate (C16:0). FabZ, but not FabA, can also accept unsaturated substrates [532].
References: [949, 1258, 952, 532]

[EC 4.2.1.59 created 1972, modified 2012]

[4.2.1.60 Deleted entry. 3-hydroxydecanoyl-[acyl-carrier-protein] dehydratase. The reaction described is covered by EC 4.2.1.59.]

[EC 4.2.1.60 created 1972, modified 2006, deleted 2012]

[4.2.1.61 Deleted entry. 3-hydroxypalmitoyl-[acyl-carrier-protein] dehydratase. The reaction described is covered by EC 4.2.1.59.]

[EC 4.2.1.61 created 1972, deleted 2012]

EC 4.2.1.62

Accepted name: 5α-hydroxysteroid dehydratase
Reaction: 5α-ergosta-7,22-diene-3β,5-diol = ergosterol + H_2O
Other name(s): 5α-ergosta-7,22-diene-3β,5-diol 5,6-hydro-lyase
Systematic name: 5α-ergosta-7,22-diene-3β,5-diol 5,6-hydro-lyase (ergosterol-forming)
References: [1380]

[EC 4.2.1.62 created 1972]

[4.2.1.63 Transferred entry. epoxide hydratase. Now known to comprise two enzymes, microsomal epoxide hydrolase (EC 3.3.2.9) and soluble epoxide hydrolase (EC 3.3.2.10)]

[EC 4.2.1.63 created 1972, deleted 1978]

[4.2.1.64 Transferred entry. arene-oxide hydratase. Now known to comprise two enzymes, microsomal epoxide hydrolase (EC 3.3.2.9) and soluble epoxide hydrolase (EC 3.3.2.10)]

[EC 4.2.1.64 created 1972, deleted 1978]

EC 4.2.1.65

Accepted name: 3-cyanoalanine hydratase
Reaction: L-asparagine = 3-cyanoalanine + H_2O
Other name(s): β-cyanoalanine hydrolase; β-cyanoalanine hydratase; β-CNAla hydrolase; β-CNA nitrilase; L-asparagine hydro-lyase
Systematic name: L-asparagine hydro-lyase (3-cyanoalanine-forming)
References: [198]

[EC 4.2.1.65 created 1976]

EC 4.2.1.66

Accepted name: cyanide hydratase
Reaction: formamide = cyanide + H_2O
Other name(s): formamide dehydratase; formamide hydro-lyase
Systematic name: formamide hydro-lyase (cyanide-forming)

References: [410]

[EC 4.2.1.66 created 1976]

EC 4.2.1.67

Accepted name: D-fuconate dehydratase
Reaction: D-fuconate = 2-dehydro-3-deoxy-D-fuconate + H_2O
Other name(s): D-fuconate hydro-lyase
Systematic name: D-fuconate hydro-lyase (2-dehydro-3-deoxy-D-fuconate-forming)
Comments: Also acts on L-arabinonate.
References: [283]

[EC 4.2.1.67 created 1976]

EC 4.2.1.68

Accepted name: L-fuconate dehydratase
Reaction: L-fuconate = 2-dehydro-3-deoxy-L-fuconate + H_2O
Other name(s): L-fuconate hydro-lyase
Systematic name: L-fuconate hydro-lyase (2-dehydro-3-deoxy-L-fuconate-forming)
Comments: Also acts, slowly, on D-arabinonate.
References: [1535]

[EC 4.2.1.68 created 1976]

EC 4.2.1.69

Accepted name: cyanamide hydratase
Reaction: urea = cyanamide + H_2O
Other name(s): urea hydro-lyase
Systematic name: urea hydro-lyase (cyanamide-forming)
References: [1310]

[EC 4.2.1.69 created 1976]

EC 4.2.1.70

Accepted name: pseudouridylate synthase
Reaction: uracil + D-ribose 5-phosphate = pseudouridine 5′-phosphate + H_2O
Other name(s): pseudouridylic acid synthetase; pseudouridine monophosphate synthetase; 5-ribosyluracil 5-phosphate synthetase; pseudouridylate synthetase; upsilonUMP synthetase; uracil hydro-lyase (adding D-ribose 5-phosphate); YeiN; pseudouridine-5′-phosphate glycosidase
Systematic name: uracil hydro-lyase (adding D-ribose 5-phosphate; pseudouridine-5′-phosphate-forming)
Comments: The reaction it readily reversible. While the enzymes from *Tetrahymena pyriformis* and *Agrobacterium tumefaciens* produce pseudouridine 5′-phosphate the enzyme from *Escherichia coli* functions as a pseudouridine-5′-phosphate glycosidase *in vivo* [1102].
References: [535, 898, 1145, 1328, 1102]

[EC 4.2.1.70 created 1978]

[4.2.1.71 Deleted entry. acetylenecarboxylate hydratase. This enzyme is identical to EC 4.2.1.27, acetylenecarboxylate hydratase]

[EC 4.2.1.71 created 1978, modified 1989, modified 2000, deleted 2004]

[4.2.1.72 Transferred entry. acetylenedicarboxylate hydratase. Now EC 4.1.1.78, acetylenedicarboxylate decarboxylase]

[EC 4.2.1.72 created 1978, deleted 2000]

EC 4.2.1.73

Accepted name: protoaphin-aglucone dehydratase (cyclizing)
Reaction: protoaphin aglucone = xanthoaphin + H_2O
Other name(s): protoaphin dehydratase; protoaphin dehydratase (cyclizing); protoaphin-aglucone hydro-lyase (cyclizing)
Systematic name: protoaphin-aglucone hydro-lyase (cyclizing; xanthoaphin-forming)
Comments: The product is converted non-enzymically to erythroaphin, an aphid pigment.
References: [172]

[EC 4.2.1.73 created 1978]

EC 4.2.1.74

Accepted name: medium-chain-enoyl-CoA hydratase
Reaction: a medium-chain (3*S*)-3-hydroxyacyl-CoA = a medium-chain *trans*-2-enoyl-CoA + H_2O
Other name(s): long-chain enoyl coenzyme A hydratase (incorrect); long-chain-enoyl-CoA hydratase (incorrect); long-chain-(3*S*)-3-hydroxyacyl-CoA hydro-lyase (incorrect)
Systematic name: medium-chain-(3*S*)-3-hydroxyacyl-CoA hydro-lyase
Comments: Acts in the reverse direction. The best substrate for the porcine enzyme is oct-2-enoyl-CoA. Unlike EC 4.2.1.17 enoyl-CoA hydratase, it does not act on crotonoyl-CoA.
References: [394, 1238, 37]

[EC 4.2.1.74 created 1981, modified 2022]

EC 4.2.1.75

Accepted name: uroporphyrinogen-III synthase
Reaction: hydroxymethylbilane = uroporphyrinogen III + H_2O
Other name(s): porphobilinogenase; uroporphyrinogen isomerase; uroporphyrinogen III cosynthase; URO-synthase; hydroxymethylbilane hydro-lyase (cyclizing)
Systematic name: hydroxymethylbilane hydro-lyase (cyclizing; uroporphyrinogen-III-forming)
Comments: In the presence of EC 2.5.1.61, hydroxymethylbilane synthase, the enzyme forms uroporphyrinogen III from porphobilinogen.
References: [79, 1394]

[EC 4.2.1.75 created 1982]

EC 4.2.1.76

Accepted name: UDP-glucose 4,6-dehydratase
Reaction: UDP-α-D-glucose = UDP-4-dehydro-6-deoxy-α-D-glucose + H_2O
Other name(s): UDP-D-glucose-4,6-hydrolyase; UDP-D-glucose oxidoreductase; UDP-glucose 4,6-hydro-lyase
Systematic name: UDP-α-D-glucose 4,6-hydro-lyase (UDP-4-dehydro-6-deoxy-α-D-glucose-forming)
References: [658]

[EC 4.2.1.76 created 1984]

EC 4.2.1.77

Accepted name: *trans*-L-3-hydroxyproline dehydratase
Reaction: *trans*-3-hydroxy-L-proline = 1-pyrroline 2-carboxylate + H_2O
Other name(s): *trans*-L-3-hydroxyproline hydro-lyase
Systematic name: *trans*-3-hydroxy-L-proline hydro-lyase (1-pyrroline-2-carboxylate-forming)
Comments: Highly specific.
References: [1127, 1424]

[EC 4.2.1.77 created 1984]

EC 4.2.1.78

Accepted name: (*S*)-norcoclaurine synthase

Reaction: 4-hydroxyphenylacetaldehyde + dopamine = (*S*)-norcoclaurine + H_2O

Other name(s): (*S*)-norlaudanosoline synthase; 4-hydroxyphenylacetaldehyde hydro-lyase (adding dopamine)

Systematic name: 4-hydroxyphenylacetaldehyde hydro-lyase [adding dopamine; (*S*)-norcoclaurine-forming]

Comments: The reaction makes a six-membered ring by forming a bond between C-6 of the 3,4-dihydroxyphenyl group of the dopamine and C-1 of the aldehyde in the imine formed between the substrates. The product is the precursor of the benzylisoquinoline alkaloids in plants. The enzyme, formerly known as (*S*)-norlaudanosoline synthase, will also catalyse the reaction of 4-(2-aminoethyl)benzene-1,2-diol + (3,4-dihydroxyphenyl)acetaldehyde to form (*S*)-norlaudanosoline, but this alkaloid has not been found to occur in plants.

References: [1294, 1295, 1190]

[EC 4.2.1.78 created 1984, modified 1999]

EC 4.2.1.79

Accepted name: 2-methylcitrate dehydratase

Reaction: (2*S*,3*S*)-2-hydroxybutane-1,2,3-tricarboxylate = (*Z*)-but-2-ene-1,2,3-tricarboxylate + H_2O

Other name(s): 2-methylcitrate hydro-lyase; PrpD; 2-hydroxybutane-1,2,3-tricarboxylate hydro-lyase

Systematic name: (2*S*,3*S*)-2-hydroxybutane-1,2,3-tricarboxylate hydro-lyase [(*Z*)-but-2-ene-1,2,3-tricarboxylate-forming]

Comments: The enzyme is specific for (2*S*,3*S*)-methylcitrate, showing no activity with (2*R*,3*S*)-methylcitrate [139]. The enzyme can also use *cis*-aconitate as a substrate but more slowly [139]. Both this enzyme and EC 4.2.1.3, aconitate hydratase, are required to complete the isomerization of (2*S*,3*S*)-methylcitrate to (2*R*,3*S*)-2-methylisocitrate [139].

References: [34, 139]

[EC 4.2.1.79 created 1984]

EC 4.2.1.80

Accepted name: 2-oxopent-4-enoate hydratase

Reaction: (*S*)-4-hydroxy-2-oxopentanoate = (2*Z*)-2-hydroxypenta-2,4-dienoate + H_2O

Other name(s): 2-keto-4-pentenoate hydratase; OEH; 2-keto-4-pentenoate (vinylpyruvate)hydratase; 4-hydroxy-2-oxopentanoate hydro-lyase; 4-hydroxy-2-oxopentanoate hydro-lyase (2-oxopent-4-enoate-forming); *mhpD* (gene name); *ahdF* (gene name); *todG* (gene name); *cmtF* (gene name); *xylJ* (gene name); *cnbE* (gene name)

Systematic name: (*S*)-4-hydroxy-2-oxopentanoate hydro-lyase ((2*Z*)-2-hydroxypenta-2,4-dienoate-forming)

Comments: The enzyme is involved in the catechol *meta*-cleavage pathway, a major mechanism for degradation of aromatic compounds. Also acts, more slowly, on *cis*-2-oxohex-4-enoate, but not on the *trans*-isomer. The enzyme was named when it was thought that the substrate is 2-oxopent-4-enoate. However, it was later found that the actual substrate is its tautomer (2*Z*)-2-hydroxypenta-2,4-dienoate. In some organisms the enzyme forms a complex with EC 4.1.1.77, 2-oxo-3-hexenedioate decarboxylase (previously named 4-oxalocrotonate decarboxylase).

References: [764, 512, 1092]

[EC 4.2.1.80 created 1984]

EC 4.2.1.81

Accepted name: D(-)-tartrate dehydratase

Reaction: (*S*,*S*)-tartrate = oxaloacetate + H_2O

Other name(s): D-tartrate dehydratase; (*S*,*S*)-tartrate hydro-lyase

Systematic name: (*S*,*S*)-tartrate hydro-lyase (oxaloacetate-forming)

Comments: Requires Fe^{2+} or Mn^{2+}. *cf.* EC 4.2.1.32 L(+)-tartrate dehydratase.

References: [1165, 1166]

[EC 4.2.1.81 created 1986]

EC 4.2.1.82

Accepted name: xylonate dehydratase

Reaction: D-xylonate = 2-dehydro-3-deoxy-D-arabinonate + H_2O

Other name(s): D-xylo-aldonate dehydratase; D-xylonate dehydratase; D-xylonate hydro-lyase

Systematic name: D-xylonate hydro-lyase (2-dehydro-3-deoxy-D-arabinonate-forming)

References: [285, 328]

[EC 4.2.1.82 created 1986]

EC 4.2.1.83

Accepted name: 4-oxalomesaconate hydratase

Reaction: 2-hydroxy-4-oxobutane-1,2,4-tricarboxylate = (1*E*,3*E*)-4-hydroxybuta-1,3-diene-1,2,4-tricarboxylate + H_2O

Other name(s): 4-oxalmesaconate hydratase; 4-carboxy-2-oxohexenedioate hydratase; 4-carboxy-2-oxobutane-1,2,4-tricarboxylate 2,3-hydro-lyase; oxalmesaconate hydratase; γ-oxalmesaconate hydratase; 2-hydroxy-4-oxobutane-1,2,4-tricarboxylate 2,3-hydro-lyase; LigJ; GalB

Systematic name: (1*E*,3*E*)-4-hydroxybuta-1,3-diene-1,2,4-tricarboxylate 1,2-hydro-lyase (2-hydroxy-4-oxobutane-1,2,4-tricarboxylate-forming)

Comments: This enzyme participates in the degradation of 3,4-dihydroxybenzoate (via the *meta*-cleavage pathway), syringate and 3,4,5-trihydroxybenzoate, catalysing the reaction in the opposite direction [886, 887, 510]. It accepts the enol-form of 4-oxalomesaconate, 2-hydroxy-4-carboxy-hexa-2,4-dienedioate [1011].

References: [886, 887, 510, 1011]

[EC 4.2.1.83 created 1986, modified 2011]

EC 4.2.1.84

Accepted name: nitrile hydratase

Reaction: an aliphatic amide = a nitrile + H_2O

Other name(s): nitrilase (ambiguous); 3-cyanopyridine hydratase; NHase; L-NHase; *H*-NHase; acrylonitrile hydratase; aliphatic nitrile hydratase; nitrile hydro-lyase

Systematic name: aliphatic-amide hydro-lyase (nitrile-forming)

Comments: Acts on short-chain aliphatic nitriles, converting them into the corresponding amides. Does not act on these amides or on aromatic nitriles. *cf.* EC 3.5.5.1 nitrilase.

References: [44]

[EC 4.2.1.84 created 1989]

EC 4.2.1.85

Accepted name: dimethylmaleate hydratase

Reaction: (2*R*,3*S*)-2,3-dimethylmalate = dimethylmaleate + H_2O

Other name(s): (2*R*,3*S*)-2,3-dimethylmalate hydro-lyase

Systematic name: (2*R*,3*S*)-2,3-dimethylmalate hydro-lyase (dimethylmaleate-forming)

Comments: Requires Fe^{2+}. Inhibited by oxygen.

References: [725]

[EC 4.2.1.85 created 1989]

[4.2.1.86 Deleted entry. 16-dehydroprogesterone hydratase (reaction is identical to that of EC 4.2.1.98, 16α-hydroxyprogesterone dehydratase)]

[EC 4.2.1.86 created 1989, deleted 2004]

EC 4.2.1.87

Accepted name: octopamine dehydratase

Reaction: 1-(4-hydroxyphenyl)-2-aminoethanol = (4-hydroxyphenyl)acetaldehyde + NH_3

Other name(s): octopamine hydrolyase; octopamine hydro-lyase (deaminating)

Systematic name: 1-(4-hydroxyphenyl)-2-aminoethanol hydro-lyase [deaminating; (4-hydroxyphenyl)acetaldehyde-forming]

Comments: The enzyme-catalysed reaction is believed to be dehydration to an enamine, which is spontaneously hydrolysed to an aldehyde and ammonia.

References: [276]

[EC 4.2.1.87 created 1989]

EC 4.2.1.88

Accepted name: synephrine dehydratase

Reaction: (*R*)-synephrine = (4-hydroxyphenyl)acetaldehyde + methylamine

Other name(s): syringinase

Systematic name: (*R*)-synephrine hydro-lyase (methylamine-forming)

Comments: Removal of H_2O from (*R*)-synephrine produces a 2,3-enamine, which hydrolyses to the products shown in the reaction above. The enzyme from *Arthrobacter synephrinum* is highly specific [1421].

References: [1421, 872]

[EC 4.2.1.88 created 1989, modified 2012]

[4.2.1.89 Deleted entry. carnitine dehydratase. The activity has now been shown to be due to EC 2.8.3.21, L-carnitine CoA-transferase and EC 4.2.1.149, crotonobetainyl-CoA hydratase.]

[EC 4.2.1.89 created 1989, deleted 2014]

EC 4.2.1.90

Accepted name: L-rhamnonate dehydratase

Reaction: L-rhamnonate = 2-dehydro-3-deoxy-L-rhamnonate + H_2O

Other name(s): L-rhamnonate hydro-lyase

Systematic name: L-rhamnonate hydro-lyase (2-dehydro-3-deoxy-L-rhamnonate-forming)

References: [1151]

[EC 4.2.1.90 created 1989]

EC 4.2.1.91

Accepted name: arogenate dehydratase

Reaction: L-arogenate = L-phenylalanine + H_2O + CO_2

Other name(s): carboxycyclohexadienyl dehydratase; L-arogenate hydro-lyase (decarboxylating)

Systematic name: L-arogenate hydro-lyase (decarboxylating; L-phenylalanine-forming)

Comments: Also acts on prephenate and D-prephenyllactate. *cf.* EC 4.2.1.51, prephenate dehydratase.

References: [387, 1540, 1271]

[EC 4.2.1.91 created 1992, modified 2005]

EC 4.2.1.92

Accepted name: hydroperoxide dehydratase

Reaction: (9*Z*,11*E*,15*Z*)-(13*S*)-hydroperoxyoctadeca-9,11,15-trienoate = (9*Z*,15*Z*)-(13*S*)-12,13-epoxyoctadeca-9,11,15-trienoate + H_2O

Other name(s): hydroperoxide isomerase; linoleate hydroperoxide isomerase; linoleic acid hydroperoxide isomerase; HPI; (9*Z*,11*E*,14*Z*)-(13*S*)-hydroperoxyoctadeca-9,11,14-trienoate 12,13-hydro-lyase; (9*Z*,11*E*,14*Z*)-(13*S*)-hydroperoxyoctadeca-9,11,14-trienoate 12,13-hydro-lyase [(9*Z*)-(13*S*)-12,13-epoxyoctadeca-9,11-dienoate-forming]; allene oxide synthase; AOS

Systematic name: (9*Z*,11*E*,15*Z*)-(13*S*)-hydroperoxyoctadeca-9,11,15-trienoate 12,13-hydro-lyase [(9*Z*,15*Z*)-(13*S*)-12,13-epoxyoctadeca-9,11,15-trienoate-forming]

Comments: Acts on a number of unsaturated fatty-acid hydroperoxides, forming the corresponding allene oxides. The product of the above reaction is unstable and is acted upon by EC 5.3.99.6, allene-oxide cyclase, to form the cyclopentenone derivative (15*Z*)-12-oxophyto-10,15-dienoate (OPDA), which is the first cyclic and biologically active metabolite in the jasmonate biosynthesis pathway [495]. The enzyme from many plants belongs to the CYP-74 family of *P*-450 monooxygenases [788].

References: [367, 494, 495, 788]

[EC 4.2.1.92 created 1992, modified 2008]

EC 4.2.1.93

Accepted name: ATP-dependent NAD(P)H-hydrate dehydratase

Reaction: (1) ATP + (6*S*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine dinucleotide = ADP + phosphate + NADH

(2) ATP + (6*S*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine dinucleotide phosphate = ADP + phosphate + NADPH

Other name(s): reduced nicotinamide adenine dinucleotide hydrate dehydratase; ATP-dependent $H_4NAD(P)^+OH$ dehydratase; (6*S*)-β-6-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine-dinucleotide hydro-lyase(ATP-hydrolysing); (6*S*)-6-β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine-dinucleotide hydro-lyase (ATP-hydrolysing; NADH-forming)

Systematic name: (6*S*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine-dinucleotide hydro-lyase (ATP-hydrolysing; NADH-forming)

Comments: Acts equally well on hydrated NADH and hydrated NADPH. NAD(P)H spontaneously hydrates to both the (6*S*)- and (6*R*)- isomers, and these are interconverted by EC 5.1.99.6, NAD(P)H-hydrate epimerase, to a 60:40 ratio [875]. Hence EC 4.2.1.93 together with EC 5.1.99.6 can restore the mixture of hydrates into NAD(P)H [2, 875]. The enzyme from eukaryotes has no activity with ADP, contrary to the enzyme from bacteria (*cf.* EC 4.2.1.136, ADP-dependent NAD(P)H-hydrate dehydratase) [875].

References: [921, 1418, 2, 875]

[EC 4.2.1.93 created 1992, modified 2012]

EC 4.2.1.94

Accepted name: scytalone dehydratase

Reaction: scytalone = 1,3,8-trihydroxynaphthalene + H_2O

Other name(s): scytalone 7,8-hydro-lyase

Systematic name: scytalone 7,8-hydro-lyase (1,3,8-trihydroxynaphthalene-forming)

Comments: Involved, with EC 1.1.1.252 tetrahydroxynaphthalene reductase, in the biosynthesis of melanin in pathogenic fungi.

References: [164, 1340, 1463]

[EC 4.2.1.94 created 1992]

EC 4.2.1.95

Accepted name: kievitone hydratase

Reaction: kievitone hydrate = kievitone + H_2O

Other name(s): KHase; kievitone-hydrate hydro-lyase

Systematic name: kievitone-hydrate hydro-lyase (kievitone-forming)

Comments: The enzyme from *Fusarium* sp. hydrates the methylbutenyl sidechain of the isoflavonoid phytoalexins, thus reducing their toxicity.
References: [1398]

[EC 4.2.1.95 created 1992]

EC 4.2.1.96

Accepted name: 4a-hydroxytetrahydrobiopterin dehydratase
Reaction: 4a-hydroxytetrahydrobiopterin = 6,7-dihydrobiopterin + H_2O
Other name(s): 4α-hydroxy-tetrahydropterin dehydratase; 4a-carbinolamine dehydratase; pterin-4α-carbinolamine dehydratase; 4a-hydroxytetrahydrobiopterin hydro-lyase
Systematic name: 4a-hydroxytetrahydrobiopterin hydro-lyase (6,7-dihydrobiopterin-forming)
Comments: In concert with EC 1.5.1.34, 6,7-dihydropteridine reductase, the enzyme recycles 4a-hydroxytetrahydrobiopterin back to tetrahydrobiopterin, a cosubstrate for several enzymes, including aromatic amino acid hydroxylases. The enzyme is bifunctional, and also acts as a dimerization cofactor of hepatocyte nuclear factor-1α (HNF-1).
References: [238, 524, 1372, 358, 264]

[EC 4.2.1.96 created 1999, modified 2020]

EC 4.2.1.97

Accepted name: phaseollidin hydratase
Reaction: phaseollidin hydrate = phaseollidin + H_2O
Other name(s): phaseollidin-hydrate hydro-lyase
Systematic name: phaseollidin-hydrate hydro-lyase (phaseollidin-forming)
Comments: The enzyme from *Fusarium solani*, which is distinct from kievitone hydratase (EC 4.2.1.95), hydrates the methylbutenyl side-chain of the isoflavonoid phytoalexin, phaseollidin.
References: [1399]

[EC 4.2.1.97 created 1999]

EC 4.2.1.98

Accepted name: 16α-hydroxyprogesterone dehydratase
Reaction: 16α-hydroxyprogesterone = 16,17-didehydroprogesterone + H_2O
Other name(s): hydroxyprogesterone dehydroxylase; 16α-hydroxyprogesterone dehydroxylase; 16α-dehydroxylase; 16α-hydroxyprogesterone hydro-lyase
Systematic name: 16α-hydroxyprogesterone hydro-lyase (16,17-didehydroprogesterone-forming)
Comments: 16α-Hydroxypregnenolone is also a substrate.
References: [444]

[EC 4.2.1.98 created 1999, modified 2004 (EC 4.2.1.86 created 1989, incorporated 2004)]

EC 4.2.1.99

Accepted name: 2-methylisocitrate dehydratase
Reaction: (2*S*,3*R*)-3-hydroxybutane-1,2,3-tricarboxylate = (*Z*)-but-2-ene-1,2,3-tricarboxylate + H_2O
Other name(s): (2*S*,3*R*)-3-hydroxybutane-1,2,3-tricarboxylate hydro-lyase
Systematic name: (2*S*,3*R*)-3-hydroxybutane-1,2,3-tricarboxylate hydro-lyase [(*Z*)-but-2-ene-1,2,3-tricarboxylate-forming]
Comments: The enzyme from the fungus *Yarrowia lipolytica* (Saccharomycopsis) does not act on isocitrate.
References: [35, 1338]

[EC 4.2.1.99 created 1999]

EC 4.2.1.100

Accepted name: cyclohexa-1,5-dienecarbonyl-CoA hydratase
Reaction: 6-hydroxycyclohex-1-ene-1-carbonyl-CoA = cyclohexa-1,5-diene-1-carbonyl-CoA + H_2O
Other name(s): cyclohexa-1,5-diene-1-carbonyl-CoA hydratase; dienoyl-CoA hydratase; cyclohexa-1,5-dienecarbonyl-CoA hydro-lyase (incorrect); 6-hydroxycyclohex-1-enecarbonyl-CoA hydro-lyase (cyclohexa-1,5-dienecarbonyl-CoA-forming)
Systematic name: 6-hydroxycyclohex-1-ene-1-carbonyl-CoA hydro-lyase (cyclohexa-1,5-diene-1-carbonyl-CoA-forming)
Comments: Forms part of the anaerobic benzoate degradation pathway, which also includes EC 1.3.8.6 [glutaryl-CoA dehydrogenase (ETF)], EC 1.3.7.8 (benzoyl-CoA reductase) and EC 4.2.1.55 (3-hydroyxbutyryl-CoA dehydratase).
References: [775, 516, 719]

[EC 4.2.1.100 created 2000, modified 2001]

[4.2.1.101 Transferred entry. trans-feruloyl-CoA hydratase. Now included with EC 4.1.2.61, feruloyl-CoA hydratase/lyase]

[EC 4.2.1.101 created 2000, deleted 2020]

[4.2.1.102 Transferred entry. cyclohexa-1,5-dienecarbonyl-CoA hydratase. Now EC 4.2.1.100, cyclohexa-1,5-dienecarbonyl-CoA hydratase]

[EC 4.2.1.102 created 2001, deleted 2001]

EC 4.2.1.103

Accepted name: cyclohexyl-isocyanide hydratase
Reaction: *N*-cyclohexylformamide = cyclohexyl isocyanide + H_2O
Other name(s): isonitrile hydratase; *N*-cyclohexylformamide hydro-lyase
Systematic name: *N*-cyclohexylformamide hydro-lyase (cyclohexyl-isocyanide-forming)
Comments: The enzyme from *Pseudomonas putida* strain N19-2 can also catalyse the hydration of other isonitriles to the corresponding *N*-substituted formamides. The enzyme has no metal requirements.
References: [447]

[EC 4.2.1.103 created 2001]

EC 4.2.1.104

Accepted name: cyanase
Reaction: cyanate + hydrogencarbonate + **2** H^+ = NH_3 + **2** CO_2 (overall reaction)
(1a) cyanate + hydrogencarbonate + H^+ = carbamate + CO_2
(1b) carbamate + H^+ = NH_3 + CO_2 (spontaneous)
Other name(s): cyanate lyase; cyanate hydrolase; cyanate aminohydrolase; cyanate C-N-lyase; cyanate hydratase
Systematic name: carbamate hydro-lyase
Comments: This enzyme, which is found in bacteria and plants, is used to decompose cyanate, which can be used as the sole source of nitrogen [736, 1437]. Reaction (1a) can be considered an equivalent of ‘cyanate + H_2O = carbamate’, where the water molecule is provided by the dehydration of bicarbonate to carbon dioxide [642], and hence the enzyme is classified as a hydrolase.
References: [24, 642, 1358, 1359, 25, 736, 1437]

[EC 4.2.1.104 created 1972 as EC 3.5.5.3, transferred 1990 to EC 4.3.99.1, transferred 2001 to EC 4.2.1.104, modified 2007]

EC 4.2.1.105

Accepted name: 2-hydroxyisoflavanone dehydratase
Reaction: (1) 2,4′,7-trihydroxyisoflavanone = daidzein + H_2O
(2) 2,4′,5,7-tetrahydroxyisoflavanone = genistein + H_2O

Other name(s): 2,7,4′-trihydroxyisoflavanone hydro-lyase; 2,7,4′-trihydroxyisoflavanone hydro-lyase (daidzein-forming)
Systematic name: 2,4′,7-trihydroxyisoflavanone hydro-lyase (daidzein-forming)
Comments: Catalyses the final step in the formation of the isoflavonoid skeleton. The reaction also occurs spontaneously.
References: [487]

[EC 4.2.1.105 created 2004, modified 2013]

EC 4.2.1.106

Accepted name: bile-acid 7α-dehydratase
Reaction: 7α,12α-dihydroxy-3-oxochol-4-en-24-oyl-CoA = 12α-hydroxy-3-oxochola-4,6-dien-24-oyl-CoA + H_2O
Other name(s): *baiE* (gene name); 7α,12α-dihydroxy-3-oxochol-4-enoate hydro-lyase; 7α,12α-dihydroxy-3-oxochol-4-enoate hydro-lyase (12α-hydroxy-3-oxochola-4,6-dienoate-forming); BA7 α dehydratase
Systematic name: 7α,12α-dihydroxy-3-oxochol-4-enoyl-CoA hydro-lyase (12α-hydroxy-3-oxochola-4,6-dienoyl-CoA-forming)
Comments: This enzyme, characterized from the gut bacterium *Clostridium scindens* (previously known as *Eubacterium* sp. strain VPI 12708), participates in the 7-dehydroxylation process associated with bile acid degradation.
References: [868, 298, 95]

[EC 4.2.1.106 created 2005, modified 2016]

EC 4.2.1.107

Accepted name: 3α,7α,12α-trihydroxy-5β-cholest-24-enoyl-CoA hydratase
Reaction: (24*R*,25*R*)-3α,7α,12α,24-tetrahydroxy-5β-cholestanoyl-CoA = (24*E*)-3α,7α,12α-trihydroxy-5β-cholest-24-enoyl-CoA + H_2O
Other name(s): 46 kDa hydratase 2; (24*R*,25*R*)-3α,7α,12α,24-tetrahydroxy-5β-cholestanoyl-CoA hydro-lyase
Systematic name: (24*R*,25*R*)-3α,7α,12α,24-tetrahydroxy-5β-cholestanoyl-CoA hydro-lyase [(24*E*)-3α,7α,12α-trihydroxy-5β-cholest-24-enoyl-CoA-forming]
Comments: This enzyme forms part of the rat peroxisomal multifunctional enzyme perMFE-2, which also exhibits a dehydrogenase activity. The enzyme is involved in the β-oxidation of the cholesterol side chain in the cholic-acid-biosynthesis pathway.
References: [1111, 1487, 705, 412, 769, 1175]

[EC 4.2.1.107 created 2005]

EC 4.2.1.108

Accepted name: ectoine synthase
Reaction: (2*S*)-4-acetamido-2-aminobutanoate = L-ectoine + H_2O
Other name(s): *ectC* (gene name); *N*-acetyldiaminobutyrate dehydratase; *N*-acetyldiaminobutanoate dehydratase; L-ectoine synthase; 4-*N*-acetyl-L-2,4-diaminobutanoate hydro-lyase (L-ectoine-forming); N^4-acetyl-L-2,4-diaminobutanoate hydro-lyase (L-ectoine-forming)
Systematic name: (2*S*)-4-acetamido-2-aminobutanoate (L-ectoine-forming)
Comments: Ectoine is an osmoprotectant that is found in halophilic eubacteria. This enzyme is part of the ectoine biosynthesis pathway and only acts in the direction of ectoine formation. *cf.* EC 3.5.4.44, ectoine hydrolase.
References: [1066, 1033, 751, 846, 1243]

[EC 4.2.1.108 created 2006, modified 2017]

EC 4.2.1.109

Accepted name: methylthioribulose 1-phosphate dehydratase

Reaction: 5-(methylsulfanyl)-D-ribulose 1-phosphate = 5-(methylsulfanyl)-2,3-dioxopentyl phosphate + H_2O

Other name(s): 1-PMT-ribulose dehydratase; *S*-methyl-5-thio-D-ribulose-1-phosphate hydro-lyase; *S*-methyl-5-thio-D-ribulose-1-phosphate 4-hydro-lyase [5-(methylthio)-2,3-dioxopentyl-phosphate-forming]

Systematic name: 5-(methylsulfanyl)-D-ribulose-1-phosphate 4-hydro-lyase [5-(methylsulfanyl)-2,3-dioxopentyl-phosphate-forming]

Comments: This enzyme forms part of the methionine-salvage pathway.

References: [416, 1476]

[EC 4.2.1.109 created 2006]

EC 4.2.1.110

Accepted name: aldos-2-ulose dehydratase

Reaction: 1,5-anhydro-D-fructose = 2-hydroxy-2-(hydroxymethyl)-2*H*-pyran-3(6*H*)-one + H_2O (overall reaction)
(1a) 1,5-anhydro-D-fructose = 1,5-anhydro-4-deoxy-D-*glycero*-hex-3-en-2-ulose + H_2O
(1b) 1,5-anhydro-4-deoxy-D-*glycero*-hex-3-en-2-ulose = 2-hydroxy-2-(hydroxymethyl)-2*H*-pyran-3(6*H*)-one

Other name(s): pyranosone dehydratase; AUDH; 1,5-anhydro-D-fructose dehydratase (microthecin-forming)

Systematic name: 1,5-anhydro-D-fructose hydro-lyase (microthecin-forming)

Comments: This enzyme catalyses two of the steps in the anhydrofructose pathway, which leads to the degradation of glycogen and starch via 1,5-anhydro-D-fructose [1525, 1521]. Aldose-2-uloses such as 2-dehydroglucose can also act as substrates, but more slowly [1,2,4]. This is a bifunctional enzyme that acts as both a lyase and as an isomerase [1521]. Differs from EC 4.2.1.111, which can carry out only reaction (1a), is inhibited by its product and requires metal ions for activity [1525].

References: [1525, 1521, 138, 419, 1527]

[EC 4.2.1.110 created 2006]

EC 4.2.1.111

Accepted name: 1,5-anhydro-D-fructose dehydratase

Reaction: 1,5-anhydro-D-fructose = 1,5-anhydro-4-deoxy-D-*glycero*-hex-3-en-2-ulose + H_2O

Other name(s): 1,5-anhydro-D-fructose 4-dehydratase; 1,5-anhydro-D-fructose hydrolyase; 1,5-anhydro-D-*arabino*-hex-2-ulose dehydratase; AFDH; AF dehydratase; 1,5-anhydro-D-fructose hydro-lyase

Systematic name: 1,5-anhydro-D-fructose hydro-lyase (ascopyrone-M-forming)

Comments: This enzyme catalyses one of the steps in the anhydrofructose pathway, which leads to the degradation of glycogen and starch via 1,5-anhydro-D-fructose [1527, 1525]. The other enzymes involved in this pathway are EC 4.2.1.110 (aldos-2-ulose dehydratase), EC 4.2.2.13 [exo-(1→4)-α-D-glucan lyase] and EC 5.3.2.7 (ascopyrone tautomerase). Requires divalent (Ca^{2+} or Mg^{2+}) or monovalent cations (Na^+) for optimal activity. Unlike EC 4.2.1.110, the enzyme is specific for 1,5-anhydro-D-fructose as substrate and shows no activity towards aldose-2-uloses such as 2-dehydroglucose [1,2,3]. In addition, it is inhibited by its end-product ascopyrone M [1525] and it cannot convert ascopyrone M into microthecin, as can EC 4.2.1.110.

References: [1527, 1525, 1521]

[EC 4.2.1.111 created 2006]

EC 4.2.1.112

Accepted name: acetylene hydratase

Reaction: acetaldehyde = acetylene + H_2O

Other name(s): AH; acetaldehyde hydro-lyase

Systematic name: acetaldehyde hydro-lyase (acetylene-forming)

Comments: This is a non-redox-active enzyme that contains two molybdopterin guanine dinucleotide (MGD) cofactors, a tungsten centre and a cubane type [4Fe-4S] cluster [1248].The tungsten centre binds a water molecule that is activated by an adjacent aspartate residue, enabling it to attack acetylene bound in a distinct hydrophobic pocket [1248]. Ethylene cannot act as a substrate [1171].
References: [1171, 1248]

[EC 4.2.1.112 created 2007]

EC 4.2.1.113

Accepted name: *o*-succinylbenzoate synthase
Reaction: (1*R*,6*R*)-6-hydroxy-2-succinylcyclohexa-2,4-diene-1-carboxylate = 2-succinylbenzoate + H_2O
Other name(s): *o*-succinylbenzoic acid synthase; OSB synthase; OSBS; 2-succinylbenzoate synthase; MenC
Systematic name: (1*R*,6*R*)-6-hydroxy-2-succinylcyclohexa-2,4-diene-1-carboxylate hydro-lyase (2-succinylbenzoate-forming)
Comments: Belongs to the enolase superfamily and requires divalent cations, preferably Mg^{2+} or Mn^{2+}, for activity. Forms part of the vitamin-K-biosynthesis pathway.
References: [1259, 712, 1052, 1369, 1153]

[EC 4.2.1.113 created 2007]

EC 4.2.1.114

Accepted name: methanogen homoaconitase
Reaction: (*R*)-2-hydroxybutane-1,2,4-tricarboxylate = (1*R*,2*S*)-1-hydroxybutane-1,2,4-tricarboxylate (overall reaction)
(1a) (*R*)-2-hydroxybutane-1,2,4-tricarboxylate = (*Z*)-but-1-ene-1,2,4-tricarboxylate + H_2O
(1b) (*Z*)-but-1-ene-1,2,4-tricarboxylate + H_2O = (1*R*,2*S*)-1-hydroxybutane-1,2,4-tricarboxylate
Other name(s): methanogen HACN
Systematic name: (*R*)-2-hydroxybutane-1,2,4-tricarboxylate hydro-lyase [(1*R*,2*S*)-1-hydroxybutane-1,2,4-tricarboxylate-forming]
Comments: This enzyme catalyses several reactions in the pathway of coenzyme-B biosynthesis in methanogenic archaea. Requires a [4Fe-4S] cluster for activity. In contrast to EC 4.2.1.36, homoaconitate hydratase, this enzyme can catalyse both the dehydration of (*R*)-homocitrate to form *cis*-homoaconitate and the subsequent hydration reaction that forms homoisocitrate. In addition to *cis*-homoaconitate, the enzyme can also catalyse the hydration of the physiological substrates dihomoaconitate and trihomoaconitate as well as the non-physiological substrate tetrahomoaconitate. *cis*-Aconitate and *threo*-DL-isocitrate cannot act as substrates, and (*S*)-homocitrate and *trans*-homoaconitate act as inhibitors of the enzyme.
References: [332]

[EC 4.2.1.114 created 2009]

EC 4.2.1.115

Accepted name: UDP-*N*-acetylglucosamine 4,6-dehydratase (configuration-inverting)
Reaction: UDP-*N*-acetyl-α-D-glucosamine = UDP-2-acetamido-2,6-dideoxy-β-L-*arabino*-hex-4-ulose + H_2O
Other name(s): FlaA1; UDP-*N*-acetylglucosamine 5-inverting 4,6-dehydratase; PseB; UDP-*N*-acetylglucosamine hydro-lyase (inverting; UDP-2-acetamido-2,6-dideoxy-β-L-*arabino*-hex-4-ulose-forming)
Systematic name: UDP-*N*-acetyl-α-D-glucosamine hydro-lyase (inverting; UDP-2-acetamido-2,6-dideoxy-β-L-*arabino*-hex-4-ulose-forming)

Comments: Contains NADP$^+$ as a cofactor. This is the first enzyme in the biosynthetic pathway of pseudaminic acid [1230], a sialic-acid-like sugar that is unique to bacteria and is used by *Helicobacter pylori* to modify its flagellin. This enzyme plays a critical role in *H. pylori*'s pathogenesis, being involved in the synthesis of both functional flagella and lipopolysaccharides [604, 1210]. It is completely inhibited by UDP-α-D-galactose. The reaction results in the chirality of the C-5 atom being inverted. It is thought that Lys-133 acts sequentially as a catalytic acid, protonating the C-6 hydroxy group and as a catalytic base, abstracting the C-5 proton, resulting in the elimination of water. This enzyme belongs to the short-chain dehydrogenase/reductase family of enzymes.

References: [604, 1210, 1230]

[EC 4.2.1.115 created 2009]

EC 4.2.1.116

Accepted name: 3-hydroxypropionyl-CoA dehydratase

Reaction: 3-hydroxypropanoyl-CoA = acryloyl-CoA + H_2O

Other name(s): 3-hydroxypropionyl-CoA hydro-lyase; 3-hydroxypropanoyl-CoA dehydratase

Systematic name: 3-hydroxypropanoyl-CoA hydro-lyase

Comments: Catalyses a step in the 3-hydroxypropanoate/4-hydroxybutanoate cycle, an autotrophic CO_2 fixation pathway found in some thermoacidophilic archaea [92]. The enzyme from *Metallosphaera sedula* acts nearly equally as well on (*S*)-3-hydroxybutanoyl-CoA but not (*R*)-3-hydroxybutanoyl-CoA [1362].

References: [92, 1362]

[EC 4.2.1.116 created 2009]

EC 4.2.1.117

Accepted name: 2-methylcitrate dehydratase (2-methyl-*trans*-aconitate forming)

Reaction: (2*S*,3*S*)-2-methylcitrate = 2-methyl-*trans*-aconitate + H_2O

Systematic name: (2*S*,3*S*)-2-hydroxybutane-1,2,3-tricarboxylate hydro-lyase (2-methyl-*trans*-aconitate-forming)

Comments: Catalyses the dehydration of (2*S*,3*S*)-2-methylcitrate, forming the *trans* isomer of 2-methyl-aconitate (unlike EC 4.2.1.79, which forms only the *cis* isomer). Part of a propionate degradation pathway. The enzyme from *Shewanella oneidensis* can also accept citrate and *cis*-aconitate, but activity with (2*S*,3*S*)-2-methylcitrate was approximately 2.5-fold higher. 2-methylisocitrate and isocitrate were not substrates [467]. An iron-sulfur protein.

References: [467]

[EC 4.2.1.117 created 2009]

EC 4.2.1.118

Accepted name: 3-dehydroshikimate dehydratase

Reaction: 3-dehydro-shikimate = 3,4-dihydroxybenzoate + H_2O

Systematic name: 3-dehydroshikimate hydro-lyase

Comments: Catalyses an early step in the biosynthesis of petrobactin, a siderophore produced by many bacteria, including the human pathogen *Bacillus anthracis*. Requires divalent ions, with a preference for Mn^{2+}.

References: [399, 1075]

[EC 4.2.1.118 created 2009]

EC 4.2.1.119

Accepted name: enoyl-CoA hydratase 2

Reaction: (3*R*)-3-hydroxyacyl-CoA = (2*E*)-2-enoyl-CoA + H_2O

Other name(s): 2-enoyl-CoA hydratase 2; AtECH2; ECH2; MaoC; MFE-2; PhaJAc; D-3-hydroxyacyl-CoA hydro-lyase; D-specific 2-*trans*-enoyl-CoA hydratase

Systematic name: (3*R*)-3-hydroxyacyl-CoA hydro-lyase

Comments: This enzyme catalyses a hydration step in peroxisomal β-oxidation. The human multifunctional enzyme type 2 (MFE-2) is a 79000 Da enzyme composed of three functional units: (3*R*)-hydroxyacyl-CoA dehydrogenase, 2-enoyl-CoA hydratase 2 and sterol carrier protein 2-like units [733]. The enzymes from *Aeromonas caviae* [558] and *Arabidopsis thaliana* [449] are monofunctional enzymes. 2-Enoyl-CoA hydratase 3 from *Candida tropicalis* is a part from multifunctional enzyme type 2 [734].

References: [733, 414, 734, 558, 449, 359]

[EC 4.2.1.119 created 2009]

EC 4.2.1.120

Accepted name: 4-hydroxybutanoyl-CoA dehydratase

Reaction: 4-hydroxybutanoyl-CoA = (*E*)-but-2-enoyl-CoA + H_2O

Systematic name: 4-hydroxybutanoyl-CoA hydro-lyase

Comments: Contains FAD and a [4Fe-4S] iron-sulfur cluster. The enzyme has been characterized from several microorganisms, including *Clostridium kluyveri*, where it participates in succinate fermentation [78, 1206], *Clostridium aminobutyricum*, where it participates in 4-aminobutyrate degradation [1205, 966], and *Metallosphaera sedula*, where it participates in the 3-hydroxypropionate/4-hydroxybutyrate cycle, an autotrophic CO_2 fixation pathway found in some thermoacidophilic archaea [92].

References: [78, 1206, 1205, 966, 92]

[EC 4.2.1.120 created 2009]

EC 4.2.1.121

Accepted name: colneleate synthase

Reaction: (9*S*,10*E*,12*Z*)-9-hydroperoxyoctadeca-10,12-dienoate = (8*E*)-9-[(1*E*,3*Z*)-nona-1,3-dien-1-yloxy]non-8-enoate + H_2O

Other name(s): 9-divinyl ether synthase; 9-DES; CYP74D; CYP74D1; CYP74 cytochrome *P*-450; DES1; (8*E*)-9-[(1*E*,3*E*)-nona-1,3-dien-1-yloxy]non-8-enoate synthase

Systematic name: (9*S*,10*E*,12*Z*)-9-hydroperoxyoctadeca-10,12-dienoate hydro-lyase

Comments: A heme-thiolate protein (*P*-450) [606]. It catalyses the selective removal of *pro-R* hydrogen at C-8 in the biosynthesis of colneleic acid [496]. It forms also (8*E*)-9-[(1*E*,3*Z*,6*Z*)-nona-1,3,6-trien-1-yloxy]non-8-enoic acid (i.e. colnelenate) from (9*S*,10*E*,12*Z*,15*Z*)-9-hydroperoxy-10,12,15-octadecatrienoate. The corresponding 13-hydroperoxides are poor substrates [1315, 375]. The divinyl ethers colneleate and colnelenate have antimicrobial activity.

References: [1315, 606, 375, 496]

[EC 4.2.1.121 created 2011, modified 2014]

EC 4.2.1.122

Accepted name: tryptophan synthase (indole-salvaging)

Reaction: L-serine + indole = L-tryptophan + H_2O

Other name(s): tryptophan synthase β2

Systematic name: L-serine hydro-lyase [adding indole, L-tryptophan-forming]

Comments: Most mesophilic bacteria have a multimeric tryptophan synthase complex (EC 4.2.1.20) that forms L-tryptophan from L-serine and 1-*C*-(indol-3-yl)glycerol 3-phosphate via an indole intermediate. This intermediate, which is formed by the α subunits, is transferred in an internal tunnel to the β units, which convert it to tryptophan. In thermophilic organisms the high temperature enhances diffusion and causes the loss of indole. This enzyme, which does not combine with the α unit to form a complex, salvages the lost indole back to L-tryptophan. It has a much lower K_m for indole than the β subunit of EC 4.2.1.20.

References: [548]

[EC 4.2.1.122 created 2011]

EC 4.2.1.123

Accepted name: tetrahymanol synthase
Reaction: tetrahymanol = squalene + H_2O
Systematic name: squalene hydro-lyase (tetrahymanol-forming)
Comments: The reaction occurs in the reverse direction.
References: [1179, 443]

[EC 4.2.1.123 created 2011]

EC 4.2.1.124

Accepted name: arabidiol synthase
Reaction: arabidiol = (3*S*)-2,3-epoxy-2,3-dihydrosqualene + H_2O
Other name(s): PEN1 (gene name); (*S*)-squalene-2,3-epoxide hydro-lyase (arabidiol forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene hydro-lyase (arabidiol-forming)
Comments: The reaction occurs in the reverse direction.
References: [1480]

[EC 4.2.1.124 created 2011]

EC 4.2.1.125

Accepted name: dammarenediol II synthase
Reaction: dammarenediol II = (3*S*)-2,3-epoxy-2,3-dihydrosqualene + H_2O
Other name(s): dammarenediol synthase; 2,3-oxidosqualene (20*S*)-dammarenediol cyclase; DDS; (*S*)-squalene-2,3-epoxide hydro-lyase (dammarenediol-II forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene hydro-lyase (dammarenediol-II-forming)
Comments: The reaction occurs in the reverse direction.
References: [1356, 498]

[EC 4.2.1.125 created 2011]

EC 4.2.1.126

Accepted name: *N*-acetylmuramic acid 6-phosphate etherase
Reaction: (*R*)-lactate + *N*-acetyl-D-glucosamine 6-phosphate = *N*-acetylmuramate 6-phosphate + H_2O
Other name(s): MurNAc-6-*P* etherase; MurQ
Systematic name: (*R*)-lactate hydro-lyase (adding *N*-acetyl-D-glucosamine 6-phosphate; *N*-acetylmuramate 6-phosphate-forming)
Comments: This enzyme, along with EC 2.7.1.170, anhydro-*N*-acetylmuramic acid kinase, is required for the utilization of anhydro-*N*-acetylmuramic acid in proteobacteria. The substrate is either imported from the medium or derived from the bacterium’s own cell wall murein during cell wall recycling.
References: [613, 1408, 1407, 483, 614]

[EC 4.2.1.126 created 2011]

EC 4.2.1.127

Accepted name: linalool dehydratase
Reaction: (3*S*)-linalool = myrcene + H_2O
Other name(s): linalool hydro-lyase (myrcene-forming)
Systematic name: (3*S*)-linalool hydro-lyase (myrcene-forming)

Comments: In absence of oxygen the bifunctional linalool dehydratase-isomerase can catalyse *in vitro* two reactions, the hydration of myrcene to (3*S*)-linalool and the isomerization of (3*S*)-linalool to geraniol, the latter activity being classified as EC 5.4.4.4, geraniol isomerase.
References: [140, 854]

[EC 4.2.1.127 created 2011, modified 2012]

EC 4.2.1.128

Accepted name: lupan-3β,20-diol synthase
Reaction: lupan-3β,20-diol = (3*S*)-2,3-epoxy-2,3-dihydrosqualene + H_2O
Other name(s): LUP1 (gene name)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene hydro-lyase (lupan-3β,20-diol-forming)
Comments: The reaction occurs in the reverse direction. The recombinant enzyme from *Arabidopsis thaliana* gives a 1:1 mixture of lupeol and lupan-3β,20-diol with small amounts of β-amyrin, germanicol, taraxasterol and ψ-taraxasterol. See EC 5.4.99.41 (lupeol synthase).
References: [1246, 770]

[EC 4.2.1.128 created 2011]

EC 4.2.1.129

Accepted name: squalene—hopanol cyclase
Reaction: hopan-22-ol = squalene + H_2O
Other name(s): squalene—hopene cyclase (ambiguous)
Systematic name: hopan-22-ol hydro-lyase
Comments: The enzyme produces the cyclization products hopene (*cf.* EC 5.4.99.17) and hopanol from squalene at a constant ratio of 5:1.
References: [577, 1194]

[EC 4.2.1.129 created 2011]

EC 4.2.1.130

Accepted name: D-lactate dehydratase
Reaction: (*R*)-lactate = 2-oxopropanal + H_2O
Other name(s): glyoxylase III; GLO3
Systematic name: (*R*)-lactate hydro-lyase
Comments: The enzyme, described from the fungi *Candida albicans* and *Schizosaccharomyces pombe*, converts 2-oxopropanal to (*R*)-lactate in a single glutathione (GSH)-independent step. The other known route for this conversion is the two-step GSH-dependent pathway catalysed by EC 4.4.1.5 (lactoylglutathione lyase) and EC 3.1.2.6 (hydroxyacylglutathione hydrolase).
References: [520, 1564]

[EC 4.2.1.130 created 2011]

EC 4.2.1.131

Accepted name: carotenoid 1,2-hydratase
Reaction: (1) 1-hydroxy-1,2-dihydrolycopene = lycopene + H_2O
(2) 1,1′-dihydroxy-1,1′,2,2′-tetrahydrolycopene = 1-hydroxy-1,2-dihydrolycopene + H_2O
Other name(s): CrtC
Systematic name: lycopene hydro-lyase (1-hydroxy-1,2-dihydrolycopene-forming)
Comments: In *Rubrivivax gelatinosus* [1300] and *Thiocapsa roseopersicina* [559] both products are formed, whereas *Rhodobacter capsulatus* [1300] only gives 1-hydroxy-1,2-dihydrolycopene. Also acts on neurosporene giving 1-hydroxy-1,2-dihydroneurosporene with both organism but 1,1′-dihydroxy-1,1′,2,2′-tetrahydroneurosporene only with *Rubrivivax gelatinosus*.

References: [1300, 559]

[EC 4.2.1.131 created 2011]

EC 4.2.1.132

Accepted name: 2-hydroxyhexa-2,4-dienoate hydratase

Reaction: 4-hydroxy-2-oxohexanoate = (2*Z*,4*Z*)-2-hydroxyhexa-2,4-dienoate + H_2O

Other name(s): *tesE* (gene name); *hsaE* (gene name)

Systematic name: 4-hydroxy-2-oxohexanoate hydro-lyase [(2*Z*,4*Z*)-2-hydroxyhexa-2,4-dienoate-forming]

Comments: This enzyme catalyses a late step in the bacterial steroid degradation pathway. The product, 4-hydroxy-2-oxohexanoate, forms a 2-hydroxy-4-hex-2-enolactone under acidic conditions.

References: [575]

[EC 4.2.1.132 created 2012]

EC 4.2.1.133

Accepted name: copal-8-ol diphosphate hydratase

Reaction: (13*E*)-8α-hydroxylabd-13-en-15-yl diphosphate = geranylgeranyl diphosphate + H_2O

Other name(s): CcCLS

Systematic name: geranylgeranyl-diphosphate hydro-lyase [(13*E*)-8α-hydroxylabd-13-en-15-yl diphosphate-forming]

Comments: Requires Mg^{2+}. The enzyme was characterized from the plant *Cistus creticus* subsp. *creticus*.

References: [371]

[EC 4.2.1.133 created 2012]

EC 4.2.1.134

Accepted name: very-long-chain (3*R*)-3-hydroxyacyl-CoA dehydratase

Reaction: a very-long-chain (3*R*)-3-hydroxyacyl-CoA = a very-long-chain *trans*-2,3-dehydroacyl-CoA + H_2O

Other name(s): PHS1 (gene name); PAS2 (gene name)

Systematic name: very-long-chain (3*R*)-3-hydroxyacyl-CoA hydro-lyase

Comments: This is the third component of the elongase, a microsomal protein complex responsible for extending palmitoyl-CoA and stearoyl-CoA (and modified forms thereof) to very-long chain acyl CoAs. *cf.* EC 2.3.1.199, very-long-chain 3-oxoacyl-CoA synthase, EC 1.1.1.330, very-long-chain 3-oxoacyl-CoA reductase, and EC 1.3.1.93, very-long-chain enoyl-CoA reductase.

References: [52, 695]

[EC 4.2.1.134 created 2012, modified 2014]

EC 4.2.1.135

Accepted name: UDP-*N*-acetylglucosamine 4,6-dehydratase (configuration-retaining)

Reaction: UDP-*N*-acetyl-α-D-glucosamine = UDP-2-acetamido-2,6-dideoxy-α-D-*xylo*-hex-4-ulose + H_2O

Other name(s): PglF

Systematic name: UDP-*N*-acetyl-α-D-glucosamine hydro-lyase (configuration-retaining; UDP-2-acetamido-2,6-dideoxy-α-D-*xylo*-hex-4-ulose-forming)

Comments: Contains NAD^+ as a cofactor [1029]. This is the first enzyme in the biosynthetic pathway of *N*,*N*′-diacetylbacillosamine [1231], the first carbohydrate in the glycoprotein N-linked heptasaccharide in *Campylobacter jejuni*. This enzyme belongs to the short-chain dehydrogenase/reductase family of enzymes.

References: [1231, 1029]

[EC 4.2.1.135 created 2012]

EC 4.2.1.136

Accepted name: ADP-dependent NAD(P)H-hydrate dehydratase

Reaction: (1) ADP + (6*S*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine dinucleotide = AMP + phosphate + NADH
(2) ADP + (6*S*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine dinucleotide phosphate = AMP + phosphate + NADPH

Other name(s): (6*S*)-β-6-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine-dinucleotide hydro-lyase(ADP-hydrolysing); (6*S*)-6-β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine-dinucleotide hydro-lyase (ADP-hydrolysing; NADH-forming)

Systematic name: (6*S*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine-dinucleotide hydro-lyase (ADP-hydrolysing; NADH-forming)

Comments: Acts equally well on hydrated NADH and hydrated NADPH. NAD(P)H spontaneously hydrates to both the (6*S*)- and (6*R*)- isomers. The enzyme from bacteria consists of two domains, one of which acts as an NAD(P)H-hydrate epimerase that interconverts the two isomers to a 60:40 ratio (*cf.* EC 5.1.99.6), while the other catalyses the dehydration. Hence the enzyme can restore the complete mixture of isomers into NAD(P)H. The enzyme has no activity with ATP, contrary to the enzyme from eukaryotes (*cf.* EC 4.2.1.93, ATP-dependent NAD(P)H-hydrate dehydratase).

References: [875]

[EC 4.2.1.136 created 2012]

EC 4.2.1.137

Accepted name: sporulenol synthase

Reaction: sporulenol = tetraprenyl-β-curcumene + H_2O

Other name(s): *sqhC* (gene name)

Systematic name: tetraprenyl-β-curcumene—sporulenol cyclase

Comments: The reaction occurs in the reverse direction. Isolated from *Bacillus subtilis*. Similar sesquarterpenoids are present in a number of *Bacillus* species.

References: [1196]

[EC 4.2.1.137 created 2012]

EC 4.2.1.138

Accepted name: (+)-caryolan-1-ol synthase

Reaction: (+)-β-caryophyllene + H_2O = (+)-caryolan-1-ol

Other name(s): GcoA

Systematic name: (+)-β-caryophyllene hydrolase [cyclizing, (+)-caryolan-1-ol-forming]

Comments: A multifunctional enzyme which also forms (+)-β-caryophyllene from farnesyl diphosphate [EC 4.2.3.89, (+)-β-caryophyllene synthase].

References: [988]

[EC 4.2.1.138 created 2011 as EC 3.7.1.15, transferred 2013 to EC 4.2.1.138]

EC 4.2.1.139

Accepted name: pterocarpan synthase

Reaction: a (4*R*)-4,2′-dihydroxyisoflavan = a pterocarpan + H_2O

Other name(s): medicarpin synthase; medicarpan synthase; 7,2′-dihydroxy-4′-methoxyisoflavanol dehydratase; 2′,7-dihydroxy-4′-methoxyisoflavanol dehydratase; DMI dehydratase; DMID; 2′-hydroxyisoflavanol 4,2′-dehydratase; PTS (gene name); 4′-methoxyisoflavan-2′,4,7-triol hydro-lyase [(–)-medicarpin-forming]

Systematic name: (4*R*)-4,2′-dihydroxyisoflavan hydro-lyase (pterocarpan-forming)

Comments: The enzyme catalyses the formation of the additional ring in pterocarpan, the basic structure of phytoalexins produced by leguminous plants, including (–)-medicarpin, (+)-medicarpin, (–)-maackiain and (+)-maackiain. The enzyme requires that the hydroxyl group at C-4 of the substrate is in the (4*R*) configuration. The configuration of the hydrogen atom at C-3 determines whether the pterocarpan is the (+)- or (–)-enantiomer. The enzyme contains amino acid motifs characteristic of dirigent proteins.
References: [478, 477, 1401]

[EC 4.2.1.139 created 2013, modified 2019]

EC 4.2.1.140

Accepted name: gluconate/galactonate dehydratase
Reaction: (1) D-gluconate = 2-dehydro-3-deoxy-D-gluconate + H_2O
(2) D-galactonate = 2-dehydro-3-deoxy-D-galactonate + H_2O
Other name(s): gluconate dehydratase (ambiguous); Sso3198 (gene name); Pto0485 (gene name)
Systematic name: D-gluconate/D-galactonate hydro-lyase
Comments: The enzyme is involved in glucose and galactose catabolism via the nonphosphorylative variant of the Entner-Doudoroff pathway in *Picrophilus torridus* [1142] and via the branched variant of the Entner-Doudoroff pathway in *Sulfolobus solfataricus* [779, 8]. *In vitro* it utilizes D-gluconate with 6-10 fold higher catalytic efficiency than D-galactonate [779, 1142]. It requires Mg^{2+} for activity [779, 8]. *cf.* EC 4.2.1.6, galactonate dehydratase, and EC 4.2.1.39, gluconate dehydratase.
References: [779, 8, 1142]

[EC 4.2.1.140 created 2013]

EC 4.2.1.141

Accepted name: 2-dehydro-3-deoxy-D-arabinonate dehydratase
Reaction: 2-dehydro-3-deoxy-D-arabinonate = 2,5-dioxopentanoate + H_2O
Systematic name: 2-dehydro-3-deoxy-D-arabinonate hydro-lyase (2,5-dioxopentanoate-forming)
Comments: The enzyme participates in pentose oxidation pathways that convert pentose sugars to the tricarboxylic acid cycle intermediate 2-oxoglutarate.
References: [142, 141, 638]

[EC 4.2.1.141 created 2013]

EC 4.2.1.142

Accepted name: 5′-oxoaverantin cyclase
Reaction: 5′-oxoaverantin = (1′*S*,5′*S*)-averufin + H_2O
Other name(s): OAVN cyclase; 5′-oxoaverantin hydro-lyase [(2′*S*,5′*S*)-averufin forming]
Systematic name: 5′-oxoaverantin hydro-lyase [(1′*S*,5′*S*)-averufin-forming]
Comments: Isolated from the aflatoxin-producing mold *Aspergillus parasiticus*. The enzyme also catalyses the conversion of versiconal to versicolorin B (EC 4.2.1.143, versicolorin B synthase). Involved in aflatoxin biosynthesis.
References: [1187, 1186]

[EC 4.2.1.142 created 2013]

EC 4.2.1.143

Accepted name: versicolorin B synthase
Reaction: versiconal = versicolorin B + H_2O
Other name(s): versiconal cyclase; VBS
Systematic name: versiconal hydro-lyase (versicolorin-B-forming)
Comments: Isolated from the aflatoxin-producing mold *Aspergillus parasiticus*. Involved in aflatoxin biosynthesis.

References: [816, 912, 1272, 1273]

[EC 4.2.1.143 created 2013]

EC 4.2.1.144

Accepted name: 3-amino-5-hydroxybenzoate synthase
Reaction: 5-amino-5-deoxy-3-dehydroshikimate = 3-amino-5-hydroxybenzoate + H_2O
Other name(s): AHBA synthase; *rifK* (gene name)
Systematic name: 5-amino-5-deoxy-3-dehydroshikimate hydro-lyase (3-amino-5-hydroxybenzoate-forming)
Comments: A pyridoxal $5'$-phosphate enzyme. The enzyme from the bacterium *Amycolatopsis mediterranei* participates in the pathway for rifamycin B biosynthesis. The enzyme also functions as a transaminase earlier in the pathway, producing UDP-α-D-kanosamine [393].
References: [696, 344, 393]

[EC 4.2.1.144 created 2013]

EC 4.2.1.145

Accepted name: capreomycidine synthase
Reaction: (2*S*,3*S*)-3-hydroxyarginine = (2*S*,3*R*)-capreomycidine + H_2O
Other name(s): VioD (ambiguous)
Systematic name: (2*S*,3*S*)-3-hydroxyarginine hydro-lyase (cyclizing, (2*S*,3*R*)-capreomycidine-forming)
Comments: A pyridoxal $5'$-phosphate protein. The enzyme is involved in the biosynthesis of the cyclic pentapeptide antibiotic viomycin.
References: [1511, 648]

[EC 4.2.1.145 created 2013]

EC 4.2.1.146

Accepted name: L-galactonate dehydratase
Reaction: L-galactonate = 2-dehydro-3-deoxy-L-galactonate + H_2O
Other name(s): LGD1
Systematic name: L-galactonate hydro-lyase (2-dehydro-3-deoxy-L-galactonate-forming)
Comments: The enzyme takes part in a D-galacturonate degradation pathway in the fungi *Trichoderma reesei* (*Hypocrea jecorina*) and *Aspergillus niger*.
References: [765, 878]

[EC 4.2.1.146 created 2013]

EC 4.2.1.147

Accepted name: 5,6,7,8-tetrahydromethanopterin hydro-lyase
Reaction: 5,6,7,8-tetrahydromethanopterin + formaldehyde = 5,10-methylenetetrahydromethanopterin + H_2O
Other name(s): formaldehyde-activating enzyme
Systematic name: 5,6,7,8-tetrahydromethanopterin hydro-lyase (formaldehyde-adding, tetrahydromethanopterin-forming)
Comments: Found in methylotrophic bacteria and methanogenic archaea.
References: [1430, 1]

[EC 4.2.1.147 created 2014]

EC 4.2.1.148

Accepted name: 2-methylfumaryl-CoA hydratase
Reaction: (2*R*,3*S*)-2-methylmalyl-CoA = 2-methylfumaryl-CoA + H_2O

Other name(s): Mcd; *erythro*-β-methylmalonyl-CoA hydrolyase; mesaconyl-coenzyme A hydratase (ambiguous); mesaconyl-C_1-CoA hydratase
Systematic name: (2*R*,3*S*)-2-methylmalyl-CoA hydro-lyase (2-methylfumaryl-CoA-forming)
Comments: The enzyme from the bacterium *Chloroflexus aurantiacus* is part of the 3-hydroxypropanoate cycle for carbon assimilation.
References: [1543]

[EC 4.2.1.148 created 2014]

EC 4.2.1.149

Accepted name: crotonobetainyl-CoA hydratase
Reaction: L-carnitinyl-CoA = (*E*)-4-(trimethylammonio)but-2-enoyl-CoA + H_2O
Other name(s): CaiD; L-carnityl-CoA dehydratase
Systematic name: L-carnitinyl-CoA hydro-lyase [(*E*)-4-(trimethylammonio)but-2-enoyl-CoA-forming]
Comments: The enzyme is also able to use crotonyl-CoA as substrate, with low efficiency [357].
References: [361, 357, 362]

[EC 4.2.1.149 created 2014]

EC 4.2.1.150

Accepted name: short-chain-enoyl-CoA hydratase
Reaction: a short-chain (3*S*)-3-hydroxyacyl-CoA = a short-chain *trans*-2-enoyl-CoA + H_2O
Other name(s): 3-hydroxybutyryl-CoA dehydratase; crotonase; *crt* (gene name)
Systematic name: short-chain-(3*S*)-3-hydroxyacyl-CoA hydro-lyase
Comments: The enzyme from the bacterium *Clostridium acetobutylicum* is part of the central fermentation pathway and plays a key role in the production of both acids and solvents. It is specific for short, C_4-C_6, chain length substrates and exhibits an extremely high turnover number for crotonyl-CoA. *cf.* EC 4.2.1.17, enoyl-CoA hydratase and EC 4.2.1.74, long-chain-enoyl-CoA hydratase.
References: [1455, 1456, 126]

[EC 4.2.1.150 created 2014]

EC 4.2.1.151

Accepted name: chorismate dehydratase
Reaction: chorismate = 3-[(1-carboxyvinyl)oxy]benzoate + H_2O
Other name(s): MqnA
Systematic name: chorismate hydro-lyase (3-[(1-carboxyvinyl)oxy]benzoate-forming)
Comments: The enzyme, found in several bacterial species, is part of the futalosine pathway for menaquinone biosynthesis.
References: [864]

[EC 4.2.1.151 created 2014]

EC 4.2.1.152

Accepted name: hydroperoxy icosatetraenoate dehydratase
Reaction: a hydroperoxyicosatetraenoate = an oxoicosatetraenoate + H_2O
Other name(s): epidermal lipoxygenase-3 (ambiguous); eLOX3 (ambiguous)
Systematic name: hydroperoxyicosatetraenoate hydro-lyase (oxoicosatetraenoate-forming)

Comments: Binds Fe^{2+}. The mammalian enzymes accept a range of hydroperoxyicosatetraenoates (HPETE). The human enzyme has highest activity with (12*R*)-HPETE, followed by (12*S*)-HPETE and (15*R*)-HPETE with much lower efficiency. The murine enzyme has highest activity with (8*R*)-HPETE followed by (8*S*)-HPETE. All HPETE isoforms are converted to the corresponding oxoicosatetraenoate forms (KETE) [1532]. The enzymes also catalyse the reaction of EC 5.4.4.7, hydroperoxy icosatetraenoate isomerase.

References: [1533, 1532, 1566]

[EC 4.2.1.152 created 2014]

EC 4.2.1.153

Accepted name: 3-methylfumaryl-CoA hydratase

Reaction: (*S*)-citramalyl-CoA = 3-methylfumaryl-CoA + H_2O

Other name(s): Meh; mesaconyl-C_4-CoA hydratase; mesaconyl-coenzyme A hydratase (ambiguous)

Systematic name: (*S*)-citramalyl-CoA hydro-lyase (3-methylfumaryl-CoA-forming)

Comments: The enzyme from the bacterium *Chloroflexus aurantiacus* is part of the 3-hydroxypropanoate cycle for carbon assimilation.

References: [1542]

[EC 4.2.1.153 created 2014]

EC 4.2.1.154

Accepted name: tetracenomycin F2 cyclase

Reaction: tetracenomycin F2 = tetracenomycin F1 + H_2O

Other name(s): *tcmI* (gene name)

Systematic name: tetracenomycin F2 hydro-lyase (tetracenomycin-F1-forming)

Comments: The enzyme is involved in biosynthesis of the anthracycline antibiotic tetracenomycin C by the bacterium *Streptomyces glaucescens*.

References: [1260, 1370]

[EC 4.2.1.154 created 2014]

EC 4.2.1.155

Accepted name: (methylthio)acryloyl-CoA hydratase

Reaction: 3-(methylsulfanyl)acryloyl-CoA + **2** H_2O = acetaldehyde + methanethiol + CoA + CO_2 (overall reaction)
(1a) 3-(methylsulfanyl)acryloyl-CoA + H_2O = 3-hydroxy-3-(methylsulfanyl)propanoyl-CoA
(1b) 3-hydroxy-3-(methylsulfanyl)propanoyl-CoA = 3-oxopropanoyl-CoA + methanethiol
(1c) 3-oxopropanoyl-CoA + H_2O = 3-oxopropanoate + CoA
(1d) 3-oxopropanoate = acetaldehyde + CO_2

Other name(s): DmdD

Systematic name: 3-(methylsulfanyl)prop-2-enoyl-CoA hydro-lyase (acetaldehyde-forming)

Comments: The enzyme is involved in the degradation of 3-(dimethylsulfonio)propanoate, an osmolyte produced by marine phytoplankton. Isolated from the bacterium *Ruegeria pomeroyi*.

References: [1350]

[EC 4.2.1.155 created 2015]

EC 4.2.1.156

Accepted name: L-talarate dehydratase

Reaction: L-altarate = 5-dehydro-4-deoxy-D-glucarate + H_2O

Other name(s): L-talarate hydro-lyase

Systematic name: L-altarate hydro-lyase (5-dehydro-4-deoxy-D-glucarate-forming)

Comments: Requires Mg^{2+}. The enzyme, isolated from the bacteria *Salmonella typhimurium* and Polaromonas sp. JS666, also has activity with galactarate (*cf.* EC 4.2.1.42, galactarate dehydratase).

References: [1509]

[EC 4.2.1.156 created 2015]

EC 4.2.1.157

Accepted name: (*R*)-2-hydroxyisocaproyl-CoA dehydratase

Reaction: (*R*)-2-hydroxy-4-methylpentanoyl-CoA = 4-methylpent-2-enoyl-CoA + H_2O

Other name(s): 2-hydroxyisocaproyl-CoA dehydratase; HadBC

Systematic name: (*R*)-2-hydroxy-4-methylpentanoyl-CoA hydro-lyase

Comments: The enzyme, isolated from the bacterium *Peptoclostridium difficile*, is involved in the reductive branch of L-leucine fermentation. It catalyses an α/β-dehydration, which depends on the reductive formation of ketyl radicals on the substrate generated by injection of a single electron from the ATP-dependent activator protein HadI.

References: [698, 714]

[EC 4.2.1.157 created 2015]

EC 4.2.1.158

Accepted name: galactarate dehydratase (D-*threo*-forming)

Reaction: galactarate = (2*S*,3*R*)-2,3-dihydroxy-5-oxohexanedioate + H_2O

Systematic name: galactarate hydro-lyase (3-deoxy-D-*threo*-hex-2-ulosarate-forming)

Comments: The enzyme has been characterized from the bacterium *Oceanobacillus iheyensis*. *cf.* EC 4.2.1.42, galactarate dehydratase.

References: [1125]

[EC 4.2.1.158 created 2015]

EC 4.2.1.159

Accepted name: dTDP-4-dehydro-6-deoxy-α-D-glucopyranose 2,3-dehydratase

Reaction: dTDP-4-dehydro-6-deoxy-α-D-glucopyranose = dTDP-3,4-didehydro-2,6-dideoxy-α-D-glucose + H_2O (overall reaction)

(1a) dTDP-4-dehydro-6-deoxy-α-D-glucopyranose = dTDP-2,6-dideoxy-D-*glycero*-hex-2-enos-4-ulose + H_2O

(1b) dTDP-2,6-dideoxy-D-*glycero*-hex-2-enos-4-ulose = dTDP-3,4-didehydro-2,6-dideoxy-α-D-glucose (spontaneous)

Other name(s): *jadO* (gene name); *evaA* (gene name); megBVI (gene name); *eryBV* (gene name); *mtmV* (gene name); *oleV* (gene name); *spnO* (gene name); TDP-4-keto-6-deoxy-D-glucose 2,3-dehydratase; dTDP-4-dehydro-6-deoxy-α-D-glucopyranose hydro-lyase (dTDP-(2*R*,6*S*)-2,4-dihydroxy-6-methyl-2,6-dihydropyran-3-one-forming)

Systematic name: dTDP-4-dehydro-6-deoxy-α-D-glucopyranose hydro-lyase (dTDP-2,6-dideoxy-D-*glycero*-hex-2-enos-4-ulose-forming)

Comments: The enzyme participates in the biosynthesis of several deoxysugars, including β-L-4-*epi*-vancosamine, α-L-megosamine, L- and D-olivose, D-oliose, D-mycarose, forosamine and β-L-digitoxose. *In vitro* the intermediate can undergo a spontaneous decomposition to maltol [216, 450].

References: [6, 216, 450, 1442, 572, 1411]

[EC 4.2.1.159 created 2015]

EC 4.2.1.160

Accepted name: 2,5-diamino-6-(5-phospho-D-ribosylamino)pyrimidin-4(3*H*)-one isomerase/dehydratase

Reaction: 2,5-diamino-6-(5-phospho-D-ribosylamino)pyrimidin-4(3*H*)-one = 7,8-dihydroneopterin 3′-phosphate + H_2O
Systematic name: 2,5-diamino-6-(5-phospho-D-ribosylamino)pyrimidin-4(3*H*)-one cyclohydrolase
Comments: The enzyme participates in a folate biosynthesis pathway in *Chlamydia*.
References: [3]

[EC 4.2.1.160 created 2015]

EC 4.2.1.161

Accepted name: bisanhydrobacterioruberin hydratase
Reaction: bacterioruberin = bisanhydrobacterioruberin + **2** H_2O (overall reaction)
(1a) bacterioruberin = monoanhydrobacterioruberin + H_2O
(1b) monoanhydrobacterioruberin = bisanhydrobacterioruberin + H_2O
Other name(s): CruF; C_{50} carotenoid 2″,3″-hydratase
Systematic name: bacterioruberin hydro-lyase (bisanhydrobacterioruberin-forming)
Comments: The enzyme, isolated from the archaeon *Haloarcula japonica*, is involved in the biosynthesis of the C_{50} carotenoid bacterioruberin. In this pathway it catalyses the introduction of hydroxyl groups to C3″ and C3‴ of bisanhydrobacterioruberin to generate bacterioruberin.
References: [1503]

[EC 4.2.1.161 created 2015]

EC 4.2.1.162

Accepted name: 6-deoxy-6-sulfo-D-gluconate dehydratase
Reaction: 6-deoxy-6-sulfo-D-gluconate = 2-dehydro-3,6-dideoxy-6-sulfo-D-gluconate + H_2O
Other name(s): SG dehydratase
Systematic name: 6-deoxy-6-sulfo-D-gluconate hydro-lyase (2-dehydro-3,6-dideoxy-6-sulfo-D-gluconate-forming)
Comments: The enzyme, characterized from the bacterium *Pseudomonas putida* SQ1, participates in a sulfoquinovose degradation pathway.
References: [380]

[EC 4.2.1.162 created 2016]

EC 4.2.1.163

Accepted name: 2-oxo-hept-4-ene-1,7-dioate hydratase
Reaction: (4*Z*)-2-oxohept-4-enedioate + H_2O = (4*S*)-4-hydroxy-2-oxoheptanedioate
Other name(s): HpcG
Systematic name: (4*S*)-4-hydroxy-2-oxoheptanedioate hydro-lyase [(4*Z*)-2-oxohept-4-enedioate-forming]
Comments: Requires Mg^{2+} [610]. Part of a 4-hydroxyphenylacetate degradation pathway in *Escherichia coli* C.
References: [159, 610]

[EC 4.2.1.163 created 2016]

EC 4.2.1.164

Accepted name: dTDP-4-dehydro-2,6-dideoxy-D-glucose 3-dehydratase
Reaction: dTDP-4-dehydro-2,6-dideoxy-α-D-glucose + **2** reduced ferredoxin [iron-sulfur] cluster + **2** H^+ = dTDP-4-dehydro-2,3,6-trideoxy-α-D-hexopyranose + H_2O + **2** oxidized ferredoxin [iron-sulfur] cluster
Other name(s): SpnQ; TDP-4-keto-2,6-dideoxy-D-glucose 3-dehydrase
Systematic name: dTDP-4-dehydro-2,6-dideoxy-α-D-glucose hydro-lyase (dTDP-2,3,6-trideoxy-α-D-hexopyranose-forming)

Comments: A pyridoxal $5'$-phosphate protein. The enzyme, isolated from the bacterium *Saccharopolyspora spinosa*, participates in the biosynthesis of forosamine. Requires ferredoxin/ferredoxin reductase or flavodoxin/flavodoxin reductase [571].

References: [571, 572]

[EC 4.2.1.164 created 2016]

EC 4.2.1.165

Accepted name: chlorophyllide *a* 3^1-hydratase

Reaction: (1) 3-devinyl-3-(1-hydroxyethyl)chlorophyllide *a* = chlorophyllide *a* + H_2O
(2) 3-deacetyl-3-(1-hydroxyethyl)bacteriochlorophyllide *a* = 3-deacetyl-3-vinylbacteriochlorophyllide *a* + H_2O

Other name(s): *bchF* (gene name)

Systematic name: chlorophyllide-*a* 3^1-hydro-lyase

Comments: The enzyme, together with EC 1.3.7.15, chlorophyllide-*a* reductase, and EC 1.1.1.396, bacteriochlorophyllide-*a* dehydrogenase, is involved in the conversion of chlorophyllide *a* to bacteriochlorophyllide *a*. The enzymes can act in multiple orders, resulting in the formation of different intermediates, but the final product of the cumulative action of the three enzymes is always bacteriochlorophyllide *a*. The enzyme catalyses the hydration of a vinyl group on ring A, converting it to a hydroxyethyl group.

References: [1108, 157, 785, 511]

[EC 4.2.1.165 created 2016]

EC 4.2.1.166

Accepted name: phosphinomethylmalate isomerase

Reaction: 2-(hydroxyphosphonoylmethyl)malate = 3-(hydroxyphosphonoylmethyl)malate (overall reaction)
(1a) 2-(hydroxyphosphonoylmethyl)malate = 2-(phosphinatomethylidene)butanedioate + H_2O
(1b) 2-(phosphinatomethylidene)butanedioate + H_2O = 3-(hydroxyphosphonoylmethyl)malate

Other name(s): *pmi* (gene name)

Systematic name: 2-(phosphinomethyl)malate hydro-lyase [3-(phosphinomethyl)malate-forming]

Comments: The enzyme, characterized from the bacterium *Streptomyces viridochromogenes*, is involved in bialaphos biosynthesis. The enzyme from the bacterium *Kitasatospora phosalacinea* participates in the biosynthesis of the related compound phosalacine. Both compounds contain the nonproteinogenic amino acid L-phosphinothricin that acts as a potent inhibitor of EC 6.3.1.2, glutamine synthetase. The similar enzyme EC 4.2.1.3, aconitate hydratase, cannot catalyse this reaction.

References: [536]

[EC 4.2.1.166 created 2016]

EC 4.2.1.167

Accepted name: (*R*)-2-hydroxyglutaryl-CoA dehydratase

Reaction: (*R*)-2-hydroxyglutaryl-CoA = (*E*)-glutaconyl-CoA + H_2O

Other name(s): *hgdAB* (gene names)

Systematic name: (*R*)-2-hydroxyglutaryl-CoA hydro-lyase ((*E*)-glutaconyl-CoA-forming)

Comments: The enzymes from the bacteria *Acidaminococcus fermentans* and *Clostridium symbiosum* are involved in the fermentation of L-glutamate. The enzyme contains [4Fe-4S] clusters, $FMNH_2$ and riboflavin. It must be activated by an activator protein. Once activated, it can catalyse many turnovers.

References: [152, 1242, 969, 504, 839, 1055]

[EC 4.2.1.167 created 2016]

EC 4.2.1.168

Accepted name: GDP-4-dehydro-6-deoxy-α-D-mannose 3-dehydratase

Reaction: GDP-4-dehydro-α-D-rhamnose + L-glutamate = GDP-4-dehydro-3,6-dideoxy-α-D-mannose + 2-oxoglutarate + NH_3 (overall reaction)
(1a) GDP-4-dehydro-α-D-rhamnose + L-glutamate = 2-GDP-[(2*S*,3*S*,6*R*)-5-amino-6-methyl-3,6-dihydro-2*H*-pyran-3-ol] + 2-oxoglutarate + H_2O
(1b) 2-GDP-[(2*S*,3*S*,6*R*)-5-amino-6-methyl-3,6-dihydro-2*H*-pyran-3-ol] = 2-GDP-[(2*S*,3*S*,6*R*)-5-imino-6-methyloxan-3-ol] (spontaneous)
(1c) GDP-2-[(2*S*,3*S*,6*R*)-5-imino-6-methyloxan-3-ol] + H_2O = GDP-4-dehydro-3,6-dideoxy-α-D-mannose + NH_3 (spontaneous)

Other name(s): *colD* (gene name)

Systematic name: GDP-4-dehydro-α-D-rhamnose 3-hydro-lyase

Comments: This enzyme, involved in β-L-colitose biosynthesis, is a unique vitamin-B6-dependent enzyme. In the first step of catalysis, the bound pyridoxal phosphate (PLP) cafactor is transaminated to the pyridoxamine $5'$-phosphate (PMP) form of vitamin B_6, using L-glutamate as the amino group donor. The PMP cofactor then forms a Schiff base with the sugar substrate and the resulting adduct undergoes a 1,4-dehydration to eliminate the 3-OH group. Hydrolysis of the product from the enzyme restores the PLP cofactor and results in the release of an unstable enamine intermediate. This intermediate tautomerizes to form an imine form, which hydrolyses spontaneously, releasing ammonia and forming the final product.

References: [11, 247]

[EC 4.2.1.168 created 2016]

EC 4.2.1.169

Accepted name: 3-vinyl bacteriochlorophyllide *d* 3^1-hydratase

Reaction: a 3-(1-hydroxyethyl) bacteriochlorophyllide *d* = a 3-vinyl bacteriochlorophyllide *d* + H_2O

Other name(s): *bchV* (gene name)

Systematic name: 3-vinylbacteriochlorophyllide-*d* 3^1-hydro-lyase

Comments: This enzyme, found in green sulfur bacteria (Chlorobiaceae) and green flimentous bacteria (Chloroflexaceae), is involved in the biosynthesis of bacteriochlorophylls *c*, *d* and *e*. It acts in the direction of hydration, and the hydroxyl group that is formed is essential for the ability of the resulting bacteriochlorophylls to self-aggregate in the chlorosomes, unique light-harvesting antenna structures found in these organisms. The product is formed preferentially in the (*R*)-configuration.

References: [409, 511]

[EC 4.2.1.169 created 2016]

EC 4.2.1.170

Accepted name: 2-(ω-methylthio)alkylmalate dehydratase

Reaction: (1) a 2-[(ω-methylsulfanyl)alkyl]malate = a 2-[(ω-methylsulfanyl)alkyl]maleate + H_2O
(2) a 3-[(ω-methylsulfanyl)alkyl]malate = a 2-[(ω-methylsulfanyl)alkyl]maleate + H_2O

Other name(s): IPMI (gene name); 2-[(ω-methylthio)alkyl]malate hydro-lyase (2-[(ω-methylthio)alkyl]maleate-forming)

Systematic name: 2-[(ω-methylsulfanyl)alkyl]malate hydro-lyase (2-[(ω-methylsulfanyl)alkyl]maleate-forming)

Comments: The enzyme, characterized from the plant *Arabidopsis thaliana*, is involved in the L-methionine side-chain elongation pathway, forming substrates for the biosynthesis of aliphatic glucosinolates. By catalysing a dehydration of a 2-[(ω-methylsulfanyl)alkyl]maleate, followed by a hydration at a different position, the enzyme achieves the isomerization of its substrates. The enzyme is a heterodimer comprising a large and a small subunits. The large subunit can also bind to an alternative small subunit, forming EC 4.2.1.33, 3-isopropylmalate dehydratase, which participates in L-leucine biosynthesis.

References: [716]

[EC 4.2.1.170 created 2016]

EC 4.2.1.171

Accepted name: *cis*-L-3-hydroxyproline dehydratase
Reaction: *cis*-3-hydroxy-L-proline = 1-pyrroline-2-carboxylate + H_2O
Other name(s): *cis*-L-3-hydroxyproline hydro-lyase; c3LHypD
Systematic name: *cis*-3-hydroxy-L-proline hydro-lyase (1-pyrroline-2-carboxylate-forming)
References: [1554]

[EC 4.2.1.171 created 2017]

EC 4.2.1.172

Accepted name: *trans*-4-hydroxy-L-proline dehydratase
Reaction: *trans*-4-hydroxy-L-proline = (*S*)-1-pyrroline-5-carboxylate + H_2O
Systematic name: *trans*-4-hydroxy-L-proline hydro-lyase
Comments: The enzyme has been characterized from the bacterium *Peptoclostridium difficile*. The active form contains a glycyl radical that is generated by a dedicated activating enzyme via chemistry involving *S*-adenosyl-L-methionine (SAM) and a [4Fe-4S] cluster.
References: [799]

[EC 4.2.1.172 created 2017]

EC 4.2.1.173

Accepted name: *ent*-8α-hydroxylabd-13-en-15-yl diphosphate synthase
Reaction: *ent*-8α-hydroxylabd-13-en-15-yl diphosphate = geranylgeranyl diphosphate + H_2O
Other name(s): SmCPS4
Systematic name: geranylgeranyl-diphosphate hydro-lyase (*ent*-8α-hydroxylabd-13-en-15-yl diphosphate-forming)
Comments: Isolated from the plant *Salvia miltiorrhiza* (red sage).
References: [275]

[EC 4.2.1.173 created 2017]

EC 4.2.1.174

Accepted name: peregrinol diphosphate synthase
Reaction: peregrinol diphosphate = geranylgeranyl diphosphate + H_2O
Other name(s): MvCPS1
Systematic name: geranylgeranyl-diphosphate hydro-lyase (peregrinol-diphosphate-forming)
Comments: Isolated from the plant *Marrubium vulgare* (white horehound). Involved in marrubiin biosynthesis.
References: [1545]

[EC 4.2.1.174 created 2017]

EC 4.2.1.175

Accepted name: (*R*)-3-(aryl)lactoyl-CoA dehydratase
Reaction: (1) (*R*)-3-(phenyl)lactoyl-CoA = (*E*)-cinnamoyl-CoA + H_2O
(2) (*R*)-3-(4-hydroxyphenyl)lactoyl-CoA = (*E*)-4-coumaroyl-CoA + H_2O
(3) (*R*)-3-(indol-3-yl)lactoyl-CoA = 3-(indol-3-yl)acryloyl-CoA + H_2O
Other name(s): *fldBC* (gene names); (*R*)-phenyllactoyl-CoA dehydratase; aryllactyl-CoA dehydratase
Systematic name: (*R*)-3-(aryl)lactoyl-CoA hydro-lyase

Comments: The enzyme, found in some amino acid-fermenting anaerobic bacteria, participates in the fermentation pathways of L-phenylalanine, L-tyrosine, and L-tryptophan. It is a heterodimeric protein consisting of the FldB and FldC polypeptides, both of which contain an [4Fe-4S] cluster, and forms a complex with EC 2.8.3.17, 3-(aryl)acryloyl-CoA:(*R*)-3-(aryl)lactate CoA-transferase (FldA). In order to catalyse the reaction, the enzyme requires one high-energy electron that transiently reduces the electrophilic thiol ester carbonyl of the substrate to a nucleophilic ketyl radical anion, facilitating the elimination of the hydroxyl group. This electron, which is provided by by EC 5.6.1.9, (*R*)-2-hydroxyacyl-CoA dehydratase activating ATPase, needs to be supplied only once, before the first reaction takes place, as it is regenerated at the end of each reaction cycle. The enzyme acts on (*R*)-3-(aryl)lactoyl-CoAs produced by FldA, and regenerates the CoA donors used by that enzyme.

References: [320, 319, 700, 699, 326]

[EC 4.2.1.175 created 2019]

EC 4.2.1.176

Accepted name: L-lyxonate dehydratase

Reaction: L-lyxonate = 2-dehydro-3-deoxy-L-arabinonate + H_2O

Other name(s): *lyxD* (gene name)

Systematic name: L-lyxonate hydro-lyase

Comments: The enzyme, characterized from several bacterial species, is involved in an L-lyxonate degradation pathway.

References: [436]

[EC 4.2.1.176 created 2021]

EC 4.2.1.177

Accepted name: (2*S*)-3-sulfopropanediol dehydratase

Reaction: (2*S*)-2,3-dihydroxypropane-1-sulfonate = 3-oxopropane-1-sulfonate + H_2O

Other name(s): *hpfG* (gene name); (*S*)-DHPS dehydratase

Systematic name: (2*S*)-2,3-dihydroxypropane-1-sulfonate hydro-lyase

Comments: The enzyme, characterized from the bacterium *Klebsiella oxytoca*, participates in (2*S*)-2,3-dihydroxypropane-1-sulfonate degradation. The active form of the enzyme contains a glycyl radical that is generated by a dedicated activating enzyme via chemistry involving *S*-adenosyl-L-methionine (AdoMet) and a [4Fe-4S] cluster.

References: [828]

[EC 4.2.1.177 created 2021]

EC 4.2.1.178

Accepted name: difructose-dianhydride-III synthase

Reaction: inulobiose = α-D-fructofuranose-β-D-fructofuranose 2′,1:2,3′-dianhydride + H_2O

Other name(s): DFA-IIIase; difructose anhydride III hydrolase

Systematic name: inulobiose hydro-lyase (α-D-fructofuranose-β-D-fructofuranose 2′,1:2,3′-dianhydride-forming)

Comments: The enzyme participates in an inulin degradation pathway, in which it forms inulobiose from difructose anhydride III. A conformational change in the enzyme from the bacterium *Pseudarthrobacter chlorophenolicus* results in it also catalysing the activity of EC 4.2.2.18, inulin fructotransferase (DFA-III-forming).

References: [1351, 1000, 1184, 1529, 1528]

[EC 4.2.1.178 created 2021]

EC 4.2.1.179

Accepted name: difructose-anhydride-I synthase

Reaction: inulobiose = bis-D-fructose 2′,1:2,1′-dianhydride + H_2O
Other name(s): DFAIase; inulobiose hydrolase; bis-D-fructose 2′,1:2,1′-dianhydride fructohydrolase
Systematic name: inulobiose hydro-lyase (α-D-fructofuranose-β-D-fructofuranose 2′,1:2,1′-dianhydride-forming)
Comments: The enzyme, studied in the fungus *Aspergillus fumigatus*, may participate in an inulin degradation pathway in which it converts the product of EC 4.2.2.17, inulin fructotransferase (DFA-I-forming), to inulobiose, though *in vitro* activity was higher in the direction of DFA-I formation.
References: [899, 900]

[EC 4.2.1.179 created 1992 as EC 3.2.1.134, transferred to EC 4.2.1.179 2021]

EC 4.2.1.180

Accepted name: (*E*)-benzylidenesuccinyl-CoA hydratase
Reaction: (*R*,*S*)-2-(α-hydroxybenzyl)succinyl-CoA = (*E*)-benzylidenesuccinyl-CoA + H_2O
Other name(s): *bbsH* (gene name)
Systematic name: (*R*,*S*)-2-(α-hydroxybenzyl)succinyl-CoA hydro-lyase
Comments: The enzyme, purified from the bacterium *Thauera aromatica*, is involved in an anaerobic toluene degradation pathway in which it catalyses the hydration of (*E*)-benzylidenesuccinyl-CoA.
References: [1427]

[EC 4.2.1.180 created 2022]

EC 4.2.2 Acting on polysaccharides

EC 4.2.2.1

Accepted name: hyaluronate lyase
Reaction: Cleaves hyaluronate chains at a β-D-GlcNAc-(1→4)-β-D-GlcA bond, ultimately breaking the polysaccharide down to 3-(4-deoxy-β-D-gluc-4-enuronosyl)-*N*-acetyl-D-glucosamine.
Other name(s): hyaluronidase (ambiguous); glucuronoglycosaminoglycan lyase (ambiguous); spreading factor; mucinase (ambiguous)
Systematic name: hyaluronate lyase
Comments: The enzyme catalyses the degradation of hyaluronan by a β-elimination reaction. Also acts on chondroitin. The product is more systematically known as 3-(4-deoxy-α-L-*threo*-hex-4-enopyranosyluronic acid)-2-acetamido-2-deoxy-D-glucose
References: [822, 933, 954]

[EC 4.2.2.1 created 1961 as EC 4.2.99.1, transferred 1972 to EC 4.2.2.1, modified 2001]

EC 4.2.2.2

Accepted name: pectate lyase
Reaction: Eliminative cleavage of (1→4)-α-D-galacturonan to give oligosaccharides with 4-deoxy-α-D-galact-4-enuronosyl groups at their non-reducing ends
Other name(s): polygalacturonic transeliminase; pectic acid transeliminase; polygalacturonate lyase; endopectin methyltranseliminase; pectate transeliminase; endogalacturonate transeliminase; pectic acid lyase; pectic lyase; α-1,4-D-endopolygalacturonic acid lyase; PGA lyase; PPase-N; endo-α-1,4-polygalacturonic acid lyase; polygalacturonic acid lyase; pectin *trans*-eliminase; Polygalacturonic acid *trans*-eliminase
Systematic name: (1→4)-α-D-galacturonan lyase
Comments: Favours pectate, the anion, over pectin, the methyl ester (which is the preferred substrate of EC 4.2.2.10, pectin lyase).
References: [13, 350, 349, 983, 995, 902]

[EC 4.2.2.2 created 1965 as EC 4.2.99.3, transferred 1972 to EC 4.2.2.2, modified 2002]

EC 4.2.2.3

Accepted name: mannuronate-specific alginate lyase

Reaction: Eliminative cleavage of alginate to give oligosaccharides with 4-deoxy-α-L-*erythro*-hex-4-enuronosyl groups at their non-reducing ends and β-D-mannuronate at their reducing end.

Other name(s): alginate lyase I; alginate lyase; alginase I; alginase II; alginase; poly(β-D-1,4-mannuronide) lyase; poly(β-D-mannuronate) lyase; *aly* (gene name) (ambiguous); poly[(1→4)-β-D-mannuronide] lyase

Systematic name: alginate β-D-mannuronate—uronate lyase

Comments: The enzyme catalyses the degradation of alginate by a β-elimination reaction. It cleaves the (1→4) bond between β-D-mannuronate and either α-L-guluronate or β-D-mannuronate, generating oligosaccharides with 4-deoxy-α-L-*erythro*-hex-4-enuronosyl groups at their non-reducing ends and β-D-mannuronate at the reducing end. Depending on the composition of the substrate, the enzyme produces oligosaccharides ranging from two to four residues, with preference for shorter products. *cf.* EC 4.2.2.11, guluronate-specific alginate lyase.

References: [291, 984, 1100]

[EC 4.2.2.3 created 1965 as EC 4.2.99.4, transferred 1972 to EC 4.2.2.3, modified 1990, modified 2015]

[4.2.2.4 Transferred entry. chondroitin ABC lyase. Now known to comprise two enzymes: EC 4.2.2.20, chondroitin-sulfate-ABC endolyase and EC 4.2.2.21, chondroitin-sulfate-ABC exolyase]

[EC 4.2.2.4 created 1972 (EC 4.2.99.6 created 1965, part incorporated 1976), deleted 2006]

EC 4.2.2.5

Accepted name: chondroitin AC lyase

Reaction: Eliminative degradation of polysaccharides containing 1,4-β-D-hexosaminyl and 1,3-β-D-glucuronosyl linkages to disaccharides containing 4-deoxy-β-D-gluc-4-enuronosyl groups

Other name(s): chondroitinase (ambiguous); chondroitin sulfate lyase; chondroitin AC eliminase; chondroitinase AC; ChnAC

Systematic name: chondroitin AC lyase

Comments: Acts on chondroitin 4-sulfate and chondroitin 6-sulfate, but less well on hyaluronate. In general, chondroitin sulfate (CS) and dermatan sulfate (DS) chains comprise a linkage region, a chain cap and a repeat region. The repeat region of CS is a repeating disaccharide of glucuronic acid (GlcA) and *N*-acetylgalactosamine (GalNAc) [-4)GlcA(β1-3)GalNAc(β1-]$_n$, which may be *O*-sulfated on the C-4 and/or C-6 of GalNAc and C-2 of GlcA. GlcA residues of CS may be epimerized to iduronic acid (IdoA) forming the repeating disaccharide [-4)IdoA(α1-3)GalNAc(β1-]$_n$ of DS. Both the concentrations and locations of sulfate-ester substituents vary with glucosaminoglycan source [588].

References: [985, 1091, 382, 588]

[EC 4.2.2.5 created 1972 (EC 4.2.99.6 created 1965, part incorporated 1976)]

EC 4.2.2.6

Accepted name: oligogalacturonide lyase

Reaction: 4-(4-deoxy-α-D-galact-4-enuronosyl)-D-galacturonate = **2** 5-dehydro-4-deoxy-D-glucuronate

Other name(s): oligogalacturonate lyase; unsaturated oligogalacturonate transeliminase; OGTE

Systematic name: oligogalacturonide lyase

Comments: Also catalyses eliminative removal of unsaturated terminal residues from oligosaccharides of D-galacturonate.

References: [955]

[EC 4.2.2.6 created 1972, modified 2010]

EC 4.2.2.7

Accepted name: heparin lyase

Reaction: Eliminative cleavage of polysaccharides containing (1→4)-linked D-glucuronate or L-iduronate residues and (1→4)-α-linked 2-sulfoamino-2-deoxy-6-sulfo-D-glucose residues to give oligosaccharides with terminal 4-deoxy-α-D-gluc-4-enuronosyl groups at their non-reducing ends

Other name(s): heparin eliminase; heparinase

Systematic name: heparin lyase

References: [581]

[EC 4.2.2.7 created 1972]

EC 4.2.2.8

Accepted name: heparin-sulfate lyase

Reaction: Elimination of sulfate; appears to act on linkages between *N*-acetyl-D-glucosamine and uronate. Product is an unsaturated sugar.

Other name(s): heparin-sulfate eliminase; heparitin-sulfate lyase; heparitinase I; heparitinase II

Systematic name: heparin-sulfate lyase

Comments: Does not act on *N,O*-desulfated glucosamine or *N*-acetyl-*O*-sulfated glucosamine linkages.

References: [581]

[EC 4.2.2.8 created 1972]

EC 4.2.2.9

Accepted name: pectate disaccharide-lyase

Reaction: (1,4-α-D-galacturonosyl)$_n$ = (1,4-α-D-galacturonosyl)$_{n-2}$ + 4-(4-deoxy-α-D-galact-4-enuronosyl)-D-galacturonate

Other name(s): pectate exo-lyase; exopectic acid transeliminase; exopectate lyase; exopolygalacturonic acid-*trans*-eliminase; PATE; exo-PATE; exo-PGL; exopolygalacturonate lyase (ambiguous); *pelW* (gene name); *pelX* (gene name)

Systematic name: (1→4)-α-D-galacturonan reducing-end-disaccharide-lyase

Comments: The enzyme catalyses the eliminative cleavage of an unsaturated disaccharide from the reducing end of homogalacturonan (the backbone of smooth regions of pectate, also known as de-esterified pectin).

References: [859, 1262, 1261]

[EC 4.2.2.9 created 1972, modified 2002]

EC 4.2.2.10

Accepted name: pectin lyase

Reaction: Eliminative cleavage of (1→4)-α-D-galacturonan methyl ester to give oligosaccharides with 4-deoxy-6-*O*-methyl-α-D-galact-4-enuronosyl groups at their non-reducing ends

Other name(s): pectin *trans*-eliminase; endo-pectin lyase; polymethylgalacturonic transeliminase; pectin methyltranseliminase; pectolyase; PL; PNL; PMGL

Systematic name: (1→4)-6-*O*-methyl-α-D-galacturonan lyase

Comments: Favours pectin, the methyl ester, over pectate, the anion (which is the preferred substrate of EC 4.2.2.2, pectate lyase). Demethylation progressively slows its action; it can nevertheless cleave on either side of a demethylated residue if the residue at the other end of the scissile bond is methylated.

References: [14, 902, 690, 972]

[EC 4.2.2.10 created 1972, modified 2002]

EC 4.2.2.11

Accepted name: guluronate-specific alginate lyase

Reaction: Eliminative cleavage of alginate to give oligosaccharides with 4-deoxy-α-L-*erythro*-hex-4-enuronosyl groups at their non-reducing ends and α-L-guluronate at their reducing end.

Other name(s): alginase II; guluronate lyase; L-guluronan lyase; L-guluronate lyase; poly-α-L-guluronate lyase; polyguluronate-specific alginate lyase; poly(α-L-1,4-guluronide) exo-lyase; poly(α-L-guluronate) lyase; poly[(1→4)-α-L-guluronide] exo-lyase

Systematic name: alginate α-L-guluronate—uronate lyase

Comments: The enzyme catalyses the degradation of alginate by a β-elimination reaction. It cleaves the (1→4) bond between α-L-guluronate and either α-L-guluronate or β-D-mannuronate, generating oligosaccharides with 4-deoxy-α-L-*erythro*-hex-4-enuronosyl groups at their non-reducing ends and α-L-guluronate at the reducing end. Depending on the composition of the substrate, the enzyme produces oligosaccharides ranging from two to six residues, with preference for shorter products. *cf.* EC 4.2.2.3, mannuronate-specific alginate lyase.

References: [125, 292]

[EC 4.2.2.11 created 1990, modified 2015]

EC 4.2.2.12

Accepted name: xanthan lyase

Reaction: Eliminative cleavage of the terminal β-D-mannosyl-(1→4)-β-D-glucuronosyl linkage of the side-chain of the polysaccharide xanthan, leaving a 4-deoxy-α-L-*threo*-hex-4-enuronosyl group at the terminus of the side-chain

Systematic name: xanthan lyase

References: [1323]

[EC 4.2.2.12 created 1990]

EC 4.2.2.13

Accepted name: exo-(1→4)-α-D-glucan lyase

Reaction: linear α-glucan = (***n*-1**) 1,5-anhydro-D-fructose + D-glucose

Other name(s): α-(1→4)-glucan 1,5-anhydro-D-fructose eliminase; α-1,4-glucan exo-lyase; α-1,4-glucan lyase; GLase

Systematic name: (1→4)-α-D-glucan exo-4-lyase (1,5-anhydro-D-fructose-forming)

Comments: The enzyme catalyses the sequential degradation of (1→4)-α-D-glucans from the non-reducing end with the release of 1,5-anhydro-D-fructose. Thus, for an α-glucan containing *n* (1→4)-linked glucose units, the final products are 1 glucose plus (*n*-1) 1,5-anhydro-D-fructose. Maltose, maltosaccharides and amylose are all completely degraded. It does not degrade (1→6)-α-glucosidic bonds and thus the degradation of a branched glucan, such as amylopectin or glycogen, will result in the formation of 1,5-anhydro-D-fructose plus a limit dextrin. Other enzymes involved in the anhydrofructose pathway are EC 4.2.1.110 (aldos-2-ulose dehydratase), EC 4.2.1.111 (1,5-anhydro-D-fructose dehydratase) and EC 5.3.2.7 (ascopyrone tautomerase).

References: [1526, 1520, 1522, 1524, 1523, 792, 793]

[EC 4.2.2.13 created 1999]

EC 4.2.2.14

Accepted name: glucuronan lyase

Reaction: Eliminative cleavage of (1→4)-β-D-glucuronans to give oligosaccharides with 4-deoxy-β-D-gluc-4-enuronosyl groups at their non-reducing ends. Complete degradation of glucuronans results in the formation of tetrasaccharides.

Other name(s): (1,4)-β-D-glucuronan lyase

Systematic name: (1→4)-β-D-glucuronan lyase

References: [934]

[EC 4.2.2.14 created 2000]

EC 4.2.2.15

Accepted name: anhydrosialidase

Reaction: Elimination of α-sialyl groups in *N*-acetylneuraminic acid glycosides, releasing 2,7-anhydro-α-*N*-acetylneuraminate

Other name(s): anhydroneuraminidase; sialglycoconjugate *N*-acylneuraminylhydrolase (2,7-cyclizing); sialidase L

Systematic name: glycoconjugate sialyl-lyase (2,7-cyclizing)

Comments: Also acts on *N*-glycolylneuraminate glycosides. *cf.* EC 3.2.1.18 (exo-α-sialidase) and EC 3.2.1.129 (endo-α-sialidase).

References: [808]

[EC 4.2.2.15 created 1992 as EC 3.2.1.138, transferred 2003 to EC 4.2.2.15]

EC 4.2.2.16

Accepted name: levan fructotransferase (DFA-IV-forming)

Reaction: Produces di-β-D-fructofuranose 2,6′:2′,6-dianhydride (DFA IV) by successively eliminating the diminishing (2→6)-β-D-fructan (levan) chain from the terminal D-fructosyl-D-fructosyl disaccharide

Other name(s): 2,6-β-D-fructan D-fructosyl-D-fructosyltransferase (forming di-β-D-fructofuranose 2,6′:2′,6-dianhydride); levan fructotransferase; 2,6-β-D-fructan lyase (di-β-D-fructofuranose-2,6′:2′,6-dianhydride-forming)

Systematic name: (2→6)-β-D-fructan lyase (di-β-D-fructofuranose-2,6′:2′,6-dianhydride-forming)

Comments: This enzyme, like EC 4.2.2.17 [inulin fructotransferase (DFA-I-forming)] and EC 4.2.2.18 [inulin fructotransferase (DFA-III-forming)] eliminates the fructan chain from the terminal disaccharide leaving a difructose dianhydride. These enzymes have long been known as fructotransferases, so this is retained in the accepted name. Since the transfer is intramolecular, the reaction is an elimination and, hence, the enzyme is a lyase, belonging in EC 4.

References: [1290, 619, 1185]

[EC 4.2.2.16 created 2004]

EC 4.2.2.17

Accepted name: inulin fructotransferase (DFA-I-forming)

Reaction: Produces α-D-fructofuranose β-D-fructofuranose 1,2′:2,1′-dianhydride (DFA I) by successively eliminating the diminishing (2→1)-β-D-fructan (inulin) chain from the terminal D-fructosyl-D-fructosyl disaccharide.

Other name(s): inulin fructotransferase (DFA-I-producing); inulin fructotransferase (depolymerizing, difructofuranose-1,2′:2′,1-dianhydride-forming); inulin D-fructosyl-D-fructosyltransferase (1,2′:1′,2-dianhydride-forming); inulin D-fructosyl-D-fructosyltransferase (forming α-D-fructofuranose β-D-fructofuranose 1,2′:1′,2-dianhydride); 2,1-β-D-fructan lyase (α-D-fructofuranose-β-D-fructofuranose-1,2′:2,1′-dianhydride-forming)

Systematic name: (2→1)-β-D-fructan lyase (α-D-fructofuranose-β-D-fructofuranose-1,2′:2,1′-dianhydride-forming)

Comments: This enzyme, like EC 4.2.2.16 [levan fructotransferase (DFA-IV-forming)] and EC 4.2.2.18 [inulin fructotransferase (DFA-III-forming)] eliminates the fructan chain from the terminal disaccharide leaving a difructose dianhydride. These enzymes have long been known as fructotransferases, so this is retained in the accepted name. Since the transfer is intramolecular, the reaction is an elimination and, hence, the enzyme is a lyase, belonging in EC 4.

References: [1250]

[EC 4.2.2.17 created 1992 as EC 2.4.1.200, transferred 2004 to EC 4.2.2.17]

EC 4.2.2.18

Accepted name: inulin fructotransferase (DFA-III-forming)

Reaction: Produces α-D-fructofuranose β-D-fructofuranose 1,2′:2,3′-dianhydride (DFA III) by successively eliminating the diminishing (2→1)-β-D-fructan (inulin) chain from the terminal D-fructosyl-D-fructosyl disaccharide.

Other name(s): inulin fructotransferase (DFA-III-producing); inulin fructotransferase (depolymerizing); inulase II; inulinase II; inulin fructotransferase (depolymerizing, difructofuranose-1,2′:2,3′-dianhydride-forming); inulin D-fructosyl-D-fructosyltransferase (1,2′:2,3′-dianhydride-forming); inulin D-fructosyl-D-fructosyltransferase (forming α-D-fructofuranose β-D-fructofuranose 1,2′:2,3′-dianhydride); 2,1-β-D-fructan lyase (α-D-fructofuranose-β-D-fructofuranose-1,2′:2,3′-dianhydride-forming)

Systematic name: (2→1)-β-D-fructan lyase (α-D-fructofuranose-β-D-fructofuranose-1,2′:2,3′-dianhydride-forming)

Comments: This enzyme, like EC 4.2.2.16 [levan fructotransferase (DFA-IV-forming)] and EC 4.2.2.17 [inulin fructotransferase (DFA-I-forming)] eliminates the fructan chain from the terminal disaccharide leaving a difructose dianhydride. These enzymes have long been known as fructotransferases, so this is retained in the accepted name. Since the transfer is intramolecular, the reaction is an elimination and, hence, the enzyme is a lyase, belonging in EC 4.

References: [1402, 1403]

[EC 4.2.2.18 created 1976 as EC 2.4.1.93, transferred 2004 to EC 4.2.2.18]

EC 4.2.2.19

Accepted name: chondroitin B lyase

Reaction: Eliminative cleavage of dermatan sulfate containing (1→4)-β-D-hexosaminyl and (1→3)-β-D-glucurosonyl or (1→3)-α-L-iduronosyl linkages to disaccharides containing 4-deoxy-β-D-gluc-4-enuronosyl groups to yield a 4,5-unsaturated dermatan-sulfate disaccharide (ΔUA-GalNAc-4S).

Other name(s): chondroitinase B; ChonB; ChnB

Systematic name: chondroitin B lyase

Comments: This is the only lyase that is known to be specific for dermatan sulfate as substrate. The minimum substrate length required for catalysis is a tetrasaccharide [1090]. In general, chondroitin sulfate (CS) and dermatan sulfate (DS) chains comprise a linkage region, a chain cap and a repeat region. The repeat region of CS is a repeating disaccharide of glucuronic acid (GlcA) and *N*-acetylgalactosamine (GalNAc) [-4)GlcA(β1-3)GalNAc(β1-]$_n$, which may be *O*-sulfated on the C-4 and/or C-6 of GalNAc and C-2 of GlcA. GlcA residues of CS may be epimerized to iduronic acid (IdoA) forming the repeating disaccharide [-4)IdoA(α1-3)GalNAc(β1-]$_n$ of DS. Both the concentrations and locations of sulfate-ester substituents vary with glucosaminoglycan source [1043].

References: [470, 1090, 1091, 1326, 1043, 1375, 935, 807, 584, 588]

[EC 4.2.2.19 created 2005]

EC 4.2.2.20

Accepted name: chondroitin-sulfate-ABC endolyase

Reaction: Endolytic cleavage of (1→4)-β-galactosaminic bonds between *N*-acetylgalactosamine and either D-glucuronic acid or L-iduronic acid to produce a mixture of Δ^4-unsaturated oligosaccharides of different sizes that are ultimately degraded to Δ^4-unsaturated tetra- and disaccharides

Other name(s): chondroitinase (ambiguous); chondroitin ABC eliminase (ambiguous); chondroitinase ABC (ambiguous); chondroitin ABC lyase (ambiguous); chondroitin sulfate ABC lyase (ambiguous); ChS ABC lyase (ambiguous); chondroitin sulfate ABC endoeliminase; chondroitin sulfate ABC endolyase; ChS ABC lyase I

Systematic name: chondroitin-sulfate-ABC endolyase

Comments: This enzyme degrades a variety of glycosaminoglycans of the chondroitin-sulfate- and dermatan-sulfate type. Chondroitin sulfate, chondroitin-sulfate proteoglycan and dermatan sulfate are the best substrates but the enzyme can also act on hyaluronan at a much lower rate. Keratan sulfate, heparan sulfate and heparin are not substrates. In general, chondroitin sulfate (CS) and dermatan sulfate (DS) chains comprise a linkage region, a chain cap and a repeat region. The repeat region of CS is a repeating disaccharide of glucuronic acid (GlcA) and *N*-acetylgalactosamine (GalNAc) [-4)GlcA(β1-3)GalNAc(β1-]$_n$, which may be *O*-sulfated on the C-4 and/or C-6 of GalNAc and C-2 of GlcA. GlcA residues of CS may be epimerized to iduronic acid (IdoA) forming the repeating disaccharide [-4)IdoA(α1-3)GalNAc(β1-]$_n$ of DS. Both the concentrations and locations of sulfate-ester substituents vary with glucosaminoglycan source [588]. The related enzyme EC 4.2.2.21, chondroitin-sulfate-ABC exolyase, has the same substrate specificity but removes disaccharide residues from the non-reducing ends of both polymeric chondroitin sulfates and their oligosaccharide fragments produced by EC 4.2.2.20 [492].

References: [1495, 1183, 1327, 492, 588]

[EC 4.2.2.20 created 2006 (EC 4.2.2.4 created 1972, part-incorporated 2006 (EC 4.2.99.6 created 1965, part incorporated 1976))]

EC 4.2.2.21

Accepted name: chondroitin-sulfate-ABC exolyase

Reaction: Exolytic removal of Δ^4-unsaturated disaccharide residues from the non-reducing ends of both polymeric chondroitin/dermatan sulfates and their oligosaccharide fragments.

Other name(s): chondroitinase (ambiguous); chondroitin ABC eliminase (ambiguous); chondroitinase ABC (ambiguous); chondroitin ABC lyase (ambiguous); chondroitin sulfate ABC lyase (ambiguous); ChS ABC lyase (ambiguous); chondroitin sulfate ABC exoeliminase; chondroitin sulfate ABC exolyase; ChS ABC lyase II

Systematic name: chondroitin-sulfate-ABC exolyase

Comments: This enzyme degrades a variety of glycosaminoglycans of the chondroitin-sulfate- and dermatan-sulfate type. Chondroitin sulfate, chondroitin-sulfate proteoglycan and dermatan sulfate are the best substrates but the enzyme can also act on hyaluronan at a much lower rate. Keratan sulfate, heparan sulfate and heparin are not substrates. The related enzyme EC 4.2.2.20, chondroitin-sulfate-ABC endolyase, has the same substrate specificity but produces a mixture of oligosaccharides of different sizes that are ultimately degraded to tetra- and disaccharides [492]. Both enzymes act by the removal of a relatively acidic C-5 proton of the uronic acid followed by the elimination of a 4-linked hexosamine, resulting in the formation of an unsaturated C^4—C^5 bond on the hexuronic acid moiety of the products [492, 1556].

References: [1495, 1183, 1327, 492, 588, 1556]

[EC 4.2.2.21 created 2006 (EC 4.2.2.4 created 1972, part-incorporated 2006 (EC 4.2.99.6 created 1965, part incorporated 1976)), modified 2010]

EC 4.2.2.22

Accepted name: pectate trisaccharide-lyase

Reaction: eliminative cleavage of unsaturated trigalacturonate as the major product from the reducing end of polygalacturonic acid/pectate

Other name(s): exopectate-lyase; pectate lyase A; PelA

Systematic name: (1→4)-α-D-galacturonan reducing-end-trisaccharide-lyase

Comments: Differs in specificity from EC 4.2.2.9, pectate disaccharide-lyase, as the predominant action is removal of a trisaccharide rather than a disaccharide from the reducing end. Disaccharides and tetrasaccharides may also be removed [1347].

References: [713, 1347, 91]

[EC 4.2.2.22 created 2007]

EC 4.2.2.23

Accepted name: rhamnogalacturonan endolyase

Reaction: Endotype eliminative cleavage of L-α-rhamnopyranosyl-(1→4)-α-D-galactopyranosyluronic acid bonds of rhamnogalacturonan I domains in ramified hairy regions of pectin leaving L-rhamnopyranose at the reducing end and 4-deoxy-4,5-unsaturated D-galactopyranosyluronic acid at the non-reducing end.

Other name(s): rhamnogalacturonase B; α-L-rhamnopyranosyl-(1→4)-α-D-galactopyranosyluronide lyase; Rgase B; rhamnogalacturonan α-L-rhamnopyranosyl-(1,4)-α-D-galactopyranosyluronide lyase; RG-lyase; YesW; RGL4; Rgl11A; Rgl11Y; RhiE

Systematic name: α-L-rhamnopyranosyl-(1→4)-α-D-galactopyranosyluronate endolyase

Comments: The enzyme is part of the degradation system for rhamnogalacturonan I in *Bacillus subtilis* strain 168 and *Aspergillus aculeatus*.

References: [975, 51, 974, 652, 773, 1046, 1022, 626]

[EC 4.2.2.23 created 2011]

EC 4.2.2.24

Accepted name: rhamnogalacturonan exolyase

Reaction: Exotype eliminative cleavage of α-L-rhamnopyranosyl-(1→4)-α-D-galactopyranosyluronic acid bonds of rhamnogalacturonan I oligosaccharides containing α-L-rhamnopyranose at the reducing end and 4-deoxy-4,5-unsaturated D-galactopyranosyluronic acid at the non-reducing end. The products are the disaccharide 2-*O*-(4-deoxy-β-L-*threo*-hex-4-enopyranuronosyl)-α-L-rhamnopyranose and the shortened rhamnogalacturonan oligosaccharide containing one 4-deoxy-4,5-unsaturated D-galactopyranosyluronic acid at the non-reducing end.

Other name(s): YesX

Systematic name: α-L-rhamnopyranosyl-(1→4)-α-D-galactopyranosyluronate exolyase

Comments: The enzyme is part of the degradation system for rhamnogalacturonan I in *Bacillus subtilis* strain 168.

References: [1021, 1020]

[EC 4.2.2.24 created 2011]

EC 4.2.2.25

Accepted name: gellan lyase

Reaction: Eliminative cleavage of β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyluronate bonds of gellan backbone releasing tetrasaccharides containing a 4-deoxy-4,5-unsaturated D-glucopyranosyluronic acid at the non-reducing end. The tetrasaccharide produced from deacetylated gellan is β-D-4-deoxy-Δ^4-GlcA*p*-(1→4)-β-D-Glc*p*-(1→4)-α-L-Rha*p*-(1→3)-β-D-Glc*p*.

Systematic name: gellan β-D-glucopyranosyl-(1→4)-D-glucopyranosyluronate lyase

Comments: The enzyme is highly specific to gellan, especially deacetylated gellan.

References: [517, 519, 947]

[EC 4.2.2.25 created 2011]

EC 4.2.2.26

Accepted name: oligo-alginate lyase

Reaction: Cleavage of poly(4-deoxy-α-L-*erythro*-hexopyranuronoside) oligosaccharides with 4-deoxy-α-L-*erythro*-hex-4-enopyranuronosyl groups at their non-reducing ends into 4-deoxy-α-L-*erythro*-hex-4-enopyranuronate monosaccharides.

Other name(s): *aly* (gene name) (ambiguous); *oalS*17 (gene name); oligoalginate lyase; exo-oligoalginate lyase

Systematic name: alginate oligosaccharide 4-deoxy-α-L-*erythro*-hex-4-enopyranuronate-(1→4)-hexananopyranuronate lyase

Comments: The enzyme degrades unsaturated oligosaccharides produced by the action of alginate lyases (EC 4.2.2.3 and EC 4.2.2.11) on alginate, by repeatedly removing the unsaturated residue from the non-reducing end until only unsaturated monosaccharides are left. The enzyme catalyses a β-elimination reaction, generating a new unsaturated non-reducing end after removal of the pre-existing one.
References: [518, 697, 617, 1441]

[EC 4.2.2.26 created 2015]

EC 4.2.2.27

Accepted name: pectin monosaccharide-lyase
Reaction: (1,4-α-D-galacturonosyl methyl ester)$_n$ = (1,4-α-D-galacturonosyl methyl ester)$_{n-1}$ + 4-deoxy-6-*O*-methyl-L-*threo*-hex-4-enopyranuronate
Other name(s): exo-pectin lyase; PLIII
Systematic name: poly(1,4-α-D-galacturonosyl methyl ester) non-reducing-end-monosaccharide-lyase
Comments: The enzyme, isolated from the fungus *Aspergillus giganteus*, acts on the non-reducing end of methyl-esterified polygalacturonan, releasing either 4-deoxy$^-$-L-*threo*-hex-4-enopyranuronate or 4-deoxy-6-*O*-methyl-L-*threo*-hex-4-enopyranuronate. The enzyme is stimulated by divalent cations, with Co^{2+} having the strongest effect. It is able to act on substrates as short as a disaccharide, and was active on substrates with degrees of methyl esterification ranging between 34% and 90%.
References: [1062]

[EC 4.2.2.27 created 2020]

EC 4.2.2.28

Accepted name: α-L-rhamnosyl-(1→4)-β-D-glucuronate lyase
Reaction: an α-L-rhamnose-(1→4)-β-D-glucuronide = α-L-rhamnopyranose + a 4-deoxy-α-L-*threo*-hex-4-enopyranuronoside
Other name(s): L-rhamnose-α-1,4-D-glucuronate lyase; FoRham (gene name)
Systematic name: α-L-rhamnosyl-(1→4)-β-D-glucuronate lyase
Comments: The enzyme, characterized from the phytopathogenic fungus *Fusarium oxysporum*, removes the rhamnosyl residue from α-L-rhamnosyl-(1→4)-β-D-glucuronate or from oligosaccharides that contain this motif at the non-reducing end, leaving an unsaturated glucuronate residue. Among its natural substrates is the type II arabinogalactan component of gum arabic.
References: [730]

[EC 4.2.2.28 created 2022]

EC 4.2.3 Acting on phosphates

EC 4.2.3.1

Accepted name: threonine synthase
Reaction: *O*-phospho-L-homoserine + H_2O = L-threonine + phosphate
Other name(s): threonine synthetase; *O*-phospho-L-homoserine phospho-lyase (adding water)
Systematic name: *O*-phospho-L-homoserine phosphate-lyase (adding water; L-threonine-forming)
Comments: A pyridoxal-phosphate protein.
References: [390]

[EC 4.2.3.1 created 1961 as EC 4.2.99.2, transferred 2000 to EC 4.2.3.1]

EC 4.2.3.2

Accepted name: ethanolamine-phosphate phospho-lyase
Reaction: ethanolamine phosphate + H_2O = acetaldehyde + NH_3 + phosphate

Other name(s): *O*-phosphoethanolamine-phospholyase; amino alcohol *O*-phosphate phospholyase; *O*-phosphorylethanol-amine phospho-lyase; ethanolamine-phosphate phospho-lyase (deaminating)
Systematic name: ethanolamine-phosphate phosphate-lyase (deaminating; acetaldehyde-forming)
Comments: A pyridoxal-phosphate protein. Also acts on D(or L)-1-aminopropan-2-ol *O*-phosphate.
References: [392, 643]

[EC 4.2.3.2 created 1972 as EC 4.2.99.7, transferred 2000 to EC 4.2.3.2]

EC 4.2.3.3

Accepted name: methylglyoxal synthase
Reaction: glycerone phosphate = 2-oxopropanal + phosphate
Other name(s): methylglyoxal synthetase; glycerone-phosphate phospho-lyase
Systematic name: glycerone-phosphate phosphate-lyase (methylglyoxal-forming)
Comments: Does not act on D-glyceraldehyde 3-phosphate.
References: [252, 573, 1138]

[EC 4.2.3.3 created 1972 as EC 4.2.99.11, transferred 2000 to EC 4.2.3.3]

EC 4.2.3.4

Accepted name: 3-dehydroquinate synthase
Reaction: 3-deoxy-D-*arabino*-hept-2-ulosonate 7-phosphate = 3-dehydroquinate + phosphate
Other name(s): 5-dehydroquinate synthase; 5-dehydroquinic acid synthetase; dehydroquinate synthase; 3-dehydroquinate synthetase; 3-deoxy-*arabino*-heptulosonate-7-phosphate phosphate-lyase (cyclizing); 3-deoxy-*arabino*-heptulonate-7-phosphate phosphate-lyase (cyclizing); 3-deoxy-*arabino*-heptulonate-7-phosphate phosphate-lyase (cyclizing; 3-dehydroquinate-forming)
Systematic name: 3-deoxy-D-*arabino*-hept-2-ulosonate-7-phosphate phosphate-lyase (cyclizing; 3-dehydroquinate-forming)
Comments: Requires Co^{2+} and bound NAD^{+}. The hydrogen atoms on C-7 of the substrate are retained on C-2 of the product.
References: [1172, 1293, 87, 192]

[EC 4.2.3.4 created 1978 as EC 4.6.1.3, transferred 2000 to EC 4.2.3.4, modified 2002]

EC 4.2.3.5

Accepted name: chorismate synthase
Reaction: 5-*O*-(1-carboxyvinyl)-3-phosphoshikimate = chorismate + phosphate
Other name(s): 5-*O*-(1-carboxyvinyl)-3-phosphoshikimate phosphate-lyase
Systematic name: 5-*O*-(1-carboxyvinyl)-3-phosphoshikimate phosphate-lyase (chorismate-forming)
Comments: Requires FMN. The reaction goes via a radical mechanism that involves reduced FMN and its semiquinone (FMNH·). Shikimate is numbered so that the double-bond is between C-1 and C-2, but some earlier papers numbered the ring in the reverse direction.
References: [420, 956, 1460, 117, 118, 1041]

[EC 4.2.3.5 created 1978 as EC 4.6.1.4, modified 1983, transferred 2000 to EC 4.2.3.5, modified 2002]

EC 4.2.3.6

Accepted name: trichodiene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = trichodiene + diphosphate
Other name(s): trichodiene synthetase; sesquiterpene cyclase; *trans*,*trans*-farnesyl-diphosphate sesquiterpenoid-lyase
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, trichodiene-forming)
References: [569, 567, 1178]

[EC 4.2.3.6 created 1989 as EC 4.1.99.6, transferred 2000 to EC 4.2.3.6]

EC 4.2.3.7

Accepted name: pentalenene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = pentalenene + diphosphate
Other name(s): pentalenene synthetase
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, pentalenene-forming)
Comments: Isolated from *Streptomyces avermitilis*. The enzyme is involved in the biosynthesis of pentalenolactone and related antibiotics. The 9*si* hydrogen of farnesyl diphosphate undergoes a 1,2-hydride shift where it becomes the 1α hydrogen of pentalenene.
References: [173, 182, 178, 174, 797, 1572]

[EC 4.2.3.7 created 1989 as EC 4.6.1.5, transferred 2000 to EC 4.2.3.7]

EC 4.2.3.8

Accepted name: casbene synthase
Reaction: geranylgeranyl diphosphate = casbene + diphosphate
Other name(s): casbene synthetase; geranylgeranyl-diphosphate diphosphate-lyase (cyclizing)
Systematic name: geranylgeranyl-diphosphate diphosphate-lyase (cyclizing, casbene-forming)
Comments: The enzyme from castor bean (*Ricinus communis*) produces the antifungal diterpene casbene.
References: [950]

[EC 4.2.3.8 created 1989 as EC 4.6.1.7, transferred 2000 to EC 4.2.3.8]

EC 4.2.3.9

Accepted name: aristolochene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = aristolochene + diphosphate
Other name(s): sesquiterpene cyclase; *trans*,*trans*-farnesyl diphosphate aristolochene-lyase; *trans*,*trans*-farnesyl-diphosphate diphosphate-lyase (cyclizing, aristolochene-forming)
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, aristolochene-forming)
Comments: The initial internal cyclization produces the monocyclic intermediate germacrene A; further cyclization and methyl transfer converts the intermediate into aristolochene. While in some species germacrene A remains as an enzyme-bound intermediate, it has been shown to be a minor product of the reaction in *Penicillium roqueforti* [170] (see also EC 4.2.3.23, germacrene-A synthase). The enzyme from *Penicillium roqueforti* requires Mg^{2+}. Mn^{2+} can partially substitute, at low concentrations. Aristolochene is the likely parent compound for a number of sesquiterpenes produced by filamentous fungi.
References: [176, 177, 568, 1104, 170]

[EC 4.2.3.9 created 1992 as EC 2.5.1.40, transferred 1999 to EC 4.1.99.7, transferred 2000 to EC 4.2.3.9, modified 2006]

EC 4.2.3.10

Accepted name: (-)-*endo*-fenchol synthase
Reaction: geranyl diphosphate + H_2O = (-)-*endo*-fenchol + diphosphate
Other name(s): (-)-*endo*-fenchol cyclase; geranyl pyrophosphate:(-)-*endo*-fenchol cyclase
Systematic name: geranyl-diphosphate diphosphate-lyase [cyclizing, (-)-*endo*-fenchol-forming]
Comments: (3*R*)-Linalyl diphosphate is an intermediate in the reaction
References: [267, 271]

[EC 4.2.3.10 created 1992 as EC 4.6.1.8, transferred 2000 to EC 4.2.3.10]

EC 4.2.3.11

Accepted name: sabinene-hydrate synthase
Reaction: geranyl diphosphate + H_2O = sabinene hydrate + diphosphate
Other name(s): sabinene hydrate cyclase

Systematic name: geranyl-diphosphate diphosphate-lyase (cyclizing, sabinene-hydrate-forming)
Comments: Both *cis*- and *trans*- isomers of sabinene hydrate are formed. (3*R*)-Linalyl diphosphate is an intermediate in the reaction
References: [490, 491]

[EC 4.2.3.11 created 1992 as EC 4.6.1.9, transferred 2000 to EC 4.2.3.11]

EC 4.2.3.12

Accepted name: 6-pyruvoyltetrahydropterin synthase
Reaction: 7,8-dihydroneopterin $3'$-triphosphate = 6-pyruvoyl-5,6,7,8-tetrahydropterin + triphosphate
Other name(s): 2-amino-4-oxo-6-[(1*S*,2*R*)-1,2-dihydroxy-3-triphosphooxypropyl]-7,8-dihydroxypteridine triphosphate lyase; 6-[(1*S*,2*R*)-1,2-dihydroxy-3-triphosphooxypropyl]-7,8-dihydropterin triphosphate-lyase (6-pyruvoyl-5,6,7,8-tetrahydropterin-forming)
Systematic name: 7,8-dihydroneopterin $3'$-triphosphate triphosphate-lyase (6-pyruvoyl-5,6,7,8-tetrahydropterin-forming)
Comments: Catalyses triphosphate elimination and an intramolecular redox reaction in the presence of Mg^{2+}. It has been identified in human liver. This enzyme is involved in the de novo synthesis of tetrahydrobiopterin from GTP, with the other enzymes involved being EC 1.1.1.153 (sepiapterin reductase) and EC 3.5.4.16 (GTP cyclohydrolase I) [1322].
References: [943, 1371, 1322]

[EC 4.2.3.12 created 1999 as EC 4.6.1.10, transferred 2000 to EC 4.2.3.12, modified 2001]

EC 4.2.3.13

Accepted name: (+)-δ-cadinene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-δ-cadinene + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, (+)-δ-cadinene-forming)
Comments: The sesquiterpenoid (+)-δ-cadinene is an intermediate in phytoalexin biosynthesis. Mg^{2+} is required for activity.
References: [220, 294, 296]

[EC 4.2.3.13 created 1999 as EC 4.6.1.11, transferred 2000 to EC 4.2.3.13, modified 2011]

[4.2.3.14 Deleted entry. pinene synthase. Now covered by EC 4.2.3.119, (-)-α-pinene synthase, and EC 4.2.3.120, (-)-β-pinene synthase]

[EC 4.2.3.14 created 2000 as EC 4.1.99.8, transferred 2000 to EC 4.2.3.14, deleted 2012]

EC 4.2.3.15

Accepted name: myrcene synthase
Reaction: geranyl diphosphate = myrcene + diphosphate
Systematic name: geranyl-diphosphate diphosphate-lyase (myrcene-forming)
Comments: A recombinant enzyme (also known as a monoterpene synthase or cyclase) from the grand fir (*Abies grandis*) requires Mn^{2+} and K^+ for activity. Mg^{2+} is essentially ineffective as the divalent metal ion cofactor.
References: [114]

[EC 4.2.3.15 created 2000 as EC 4.1.99.9, transferred 2000 to EC 4.2.3.15]

EC 4.2.3.16

Accepted name: (4*S*)-limonene synthase
Reaction: geranyl diphosphate = (*S*)-limonene + diphosphate

Other name(s): (-)-(4*S*)-limonene synthase; 4*S*-(-)-limonene synthase; geranyldiphosphate diphosphate lyase (limonene forming); geranyldiphosphate diphosphate lyase [cyclizing, (4*S*)-limonene-forming]; geranyl-diphosphate diphosphate-lyase [cyclizing; (-)-(4*S*)-limonene-forming]
Systematic name: geranyl-diphosphate diphosphate-lyase [cyclizing; (*S*)-limonene-forming]
Comments: A recombinant enzyme (also known as a monoterpene synthase or cyclase) from the grand fir (*Abies grandis*) requires Mn^{2+} and K^{+} for activity. Mg^{2+} is essentially ineffective as the divalent metal ion cofactor.
References: [114, 245, 1534]

[EC 4.2.3.16 created 2000 as EC 4.1.99.10, transferred 2000 to EC 4.2.3.16, modified 2003]

EC 4.2.3.17

Accepted name: taxadiene synthase
Reaction: geranylgeranyl diphosphate = taxa-4,11-diene + diphosphate
Other name(s): geranylgeranyl-diphosphate diphosphate-lyase (cyclizing, taxadiene-forming)
Systematic name: geranylgeranyl-diphosphate diphosphate-lyase (cyclizing; taxa-4,11-diene-forming)
Comments: This is the committed step in the biosynthesis of the diterpenoid antineoplastic drug Taxol (paclitaxel). The cyclization involves a 1,5-hydride shift.
References: [720, 551, 820, 550, 1468]

[EC 4.2.3.17 created 2002]

EC 4.2.3.18

Accepted name: abieta-7,13-diene synthase
Reaction: (+)-copalyl diphosphate = abieta-7,13-diene + diphosphate
Other name(s): copalyl-diphosphate diphosphate-lyase (cyclizing) (ambiguous); abietadiene synthase (ambiguous)
Systematic name: (+)-copalyl-diphosphate diphosphate-lyase [cyclizing, abieta-7,13-diene-forming]
Comments: Part of a bifunctional enzyme involved in the biosynthesis of abietadiene. See also EC 5.5.1.12, copalyl diphosphate synthase. Requires Mg^{2+}.
References: [1070, 1071, 1068, 1067, 1137]

[EC 4.2.3.18 created 2002, modified 2012]

EC 4.2.3.19

Accepted name: *ent*-kaurene synthase
Reaction: *ent*-copalyl diphosphate = *ent*-kaurene + diphosphate
Other name(s): *ent*-kaurene synthase B; *ent*-kaurene synthetase B, *ent*-copalyl-diphosphate diphosphate-lyase (cyclizing)
Systematic name: *ent*-copalyl-diphosphate diphosphate-lyase (cyclizing, *ent*-kaurene-forming)
Comments: Part of a bifunctional enzyme involved in the biosynthesis of *ent*-kaurene. See also EC 5.5.1.13 (*ent*-copalyl diphosphate synthase)
References: [374, 1496, 682, 1384]

[EC 4.2.3.19 created 2002]

EC 4.2.3.20

Accepted name: (*R*)-limonene synthase
Reaction: geranyl diphosphate = (*R*)-limonene + diphosphate
Other name(s): (+)-limonene synthase; geranyldiphosphate diphosphate lyase [(+)-(*R*)-limonene-forming]; geranyl-diphosphate diphosphate-lyase [cyclizing, (+)-(4*R*)-limonene-forming]
Systematic name: geranyl-diphosphate diphosphate-lyase [cyclizing, (*R*)-limonene-forming]

Comments: Forms the first step of carvone biosynthesis in caraway. The enzyme from *Carum carvi* (caraway) seeds requires a divalent metal ion (preferably Mn^{2+}) for catalysis. This enzyme occurs in *Citrus*, *Carum* (caraway) and *Anethum* (dill); (-)-limonene, however, is made in the fir, *Abies*, and mint, *Mentha*, by EC 4.2.3.16, (4*S*)-limonene synthase.

References: [119, 853, 890]

[EC 4.2.3.20 created 2003]

EC 4.2.3.21

Accepted name: vetispiradiene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = vetispiradiene + diphosphate

Other name(s): vetispiradiene-forming farnesyl pyrophosphate cyclase; pemnaspirodiene synthase; HVS; vetispiradiene cyclase

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, vetispiradiene-forming)

Comments: The initial internal cyclization produces the monocyclic intermediate germacrene A.

References: [55, 686, 892, 1515, 883]

[EC 4.2.3.21 created 2004, modified 2011]

EC 4.2.3.22

Accepted name: germacradienol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = (1*E*,4*S*,5*E*,7*R*)-germacra-1(10),5-dien-11-ol + diphosphate

Other name(s): germacradienol/germacrene-D synthase; 2-*trans*,6-*trans*-farnesyl-diphosphate diphosphate-lyase [(1*E*,4*S*,5*E*,7*R*)-germacra-1(10),5-dien-11-ol-forming]

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(1*E*,4*S*,5*E*,7*R*)-germacra-1(10),5-dien-11-ol-forming]

Comments: Requires Mg^{2+} for activity. *H*-1*si* of farnesyl diphosphate is lost in the formation of (1*E*,4*S*,5*E*,7*R*)-germacra-1(10),5-dien-11-ol. Formation of (-)-germacrene D involves a stereospecific 1,3-hydride shift of *H*-1*si* of farnesyl diphosphate. Both products are formed from a common intermediate [530]. Other enzymes produce germacrene D as the sole product using a different mechanism. The enzyme mediates a key step in the biosynthesis of geosmin (see EC 4.1.99.16 geosmin synthase), a widely occurring metabolite of many streptomycetes, bacteria and fungi [530]. Also catalyses the reaction of EC 4.2.3.75, (-)-germacrene D synthase.

References: [183, 530, 481]

[EC 4.2.3.22 created 2006, modified 2011]

EC 4.2.3.23

Accepted name: germacrene-A synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-(*R*)-gemacrene A + diphosphate

Other name(s): germacrene A synthase; (+)-germacrene A synthase; (+)-(10*R*)-germacrene A synthase; GAS; 2-*trans*,6-*trans*-farnesyl-diphosphate diphosphate-lyase (germacrene-A-forming)

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(+)-(*R*)-germacrene-A-forming]

Comments: Requires Mg^{2+} for activity. While germacrene A is an enzyme-bound intermediate in the biosynthesis of a number of phytoalexins, e.g. EC 4.2.3.9 (aristolochene synthase) from some species and EC 4.2.3.21 (vetispiradiene synthase), it is the sole sesquiterpenoid product formed in chicory [120].

References: [120, 1106, 302, 170, 208]

[EC 4.2.3.23 created 2006]

EC 4.2.3.24

Accepted name: amorpha-4,11-diene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = amorpha-4,11-diene + diphosphate

Other name(s): amorphadiene synthase

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (amorpha-4,11-diene-forming)

Comments: Requires Mg^{2+} and Mn^{2+} for activity. This is a key enzyme in the biosynthesis of the antimalarial endoperoxide artemisinin [122]. Catalyses the formation of both olefinic [e.g. amorpha-4,11-diene, amorpha-4,7(11)-diene, γ-humulene and β-sesquiphellandrene] and oxygenated (e.g. amorpha-4-en-7-ol) sesquiterpenes, with amorpha-4,11-diene being the major product. When geranyl diphosphate is used as a substrate, no monoterpenes are produced [928].

References: [1435, 928, 122, 209, 882, 1082]

[EC 4.2.3.24 created 2006]

EC 4.2.3.25

Accepted name: *S*-linalool synthase

Reaction: geranyl diphosphate + H_2O = (3*S*)-linalool + diphosphate

Other name(s): LIS; Lis; 3*S*-linalool synthase

Systematic name: geranyl-diphosphate diphosphate-lyase [(3*S*)-linalool-forming]

Comments: Requires Mn^{2+} or Mg^{2+} for activity. Neither (*S*)- nor (*R*)-linalyl diphosphate can act as substrate for the enzyme from the flower *Clarkia breweri* [1084]. Unlike many other monoterpene synthases, only a single product, (3*S*)-linalool, is formed.

References: [1084, 851, 337]

[EC 4.2.3.25 created 2006]

EC 4.2.3.26

Accepted name: R-linalool synthase

Reaction: geranyl diphosphate + H_2O = (3*R*)-linalool + diphosphate

Other name(s): (3*R*)-linalool synthase; (–)-3*R*-linalool synthase

Systematic name: geranyl-diphosphate diphosphate-lyase [(3*R*)-linalool-forming]

Comments: Geranyl diphosphate cannot be replaced by isopentenyl diphosphate (3-methylbut-3-en-1-yl diphosphate), prenyl diphosphate, farnesyl diphosphate or geranylgeranyl diphosphate as substrate [627]. Requires Mg^{2+} or Mn^{2+} for activity. Unlike many other monoterpene synthases, only a single product, (3*R*)-linalool, is formed.

References: [627, 273]

[EC 4.2.3.26 created 2006]

EC 4.2.3.27

Accepted name: isoprene synthase

Reaction: prenyl diphosphate = isoprene + diphosphate

Other name(s): ISPC; ISPS; dimethylallyl-diphosphate diphosphate-lyase (isoprene-forming)

Systematic name: prenyl-diphosphate diphosphate-lyase (isoprene-forming)

Comments: Requires Mg^{2+} or Mn^{2+} for activity. This enzyme is located in the chloroplast of isoprene-emitting plants, such as poplar and aspen, and may be activitated by light-dependent changes in chloroplast pH and Mg^{2+} concentration [1276, 1228].

References: [1275, 1276, 1467, 1229, 939, 1280, 1193, 1228]

[EC 4.2.3.27 created 2007]

EC 4.2.3.28

Accepted name: *ent*-cassa-12,15-diene synthase

Reaction: *ent*-copalyl diphosphate = *ent*-cassa-12,15-diene + diphosphate

Other name(s): OsDTC1; OsKS7

Systematic name: *ent*-copalyl-diphosphate diphosphate-lyase (*ent*-cassa-12,15-diene-forming)

Comments: This class I diterpene cyclase produces *ent*-cassa-12,15-diene, a precursor of the rice phytoalexins (-)-phytocassanes A-E. Phytoalexins are diterpenoid secondary metabolites that are involved in the defense mechanism of the plant, and are produced in response to pathogen attack through the perception of elicitor signal molecules such as chitin oligosaccharide, or after exposure to UV irradiation.

References: [226]

[EC 4.2.3.28 created 2008]

EC 4.2.3.29

Accepted name: *ent*-sandaracopimaradiene synthase

Reaction: *ent*-copalyl diphosphate = *ent*-sandaracopimara-8(14),15-diene + diphosphate

Other name(s): OsKS10; *ent*-sandaracopimara-8(14),15-diene synthase

Systematic name: *ent*-copalyl-diphosphate diphosphate-lyase [*ent*-sandaracopimara-8(14),15-diene-forming]

Comments: *ent*-Sandaracopimaradiene is a precursor of the rice oryzalexins A-F. Phytoalexins are diterpenoid secondary metabolites that are involved in the defense mechanism of the plant, and are produced in response to pathogen attack through the perception of elicitor signal molecules such as chitin oligosaccharide, or after exposure to UV irradiation. As a minor product, this enzyme also forms *ent*-pimara-8(14),15-diene, which is the sole product of EC 4.2.3.30, *ent*-pimara-8(14),15-diene synthase. *ent*-Pimara-8(14),15-diene is not a precursor in the biosynthesis of either gibberellins or phytoalexins [665].

References: [1042, 665]

[EC 4.2.3.29 created 2008]

EC 4.2.3.30

Accepted name: *ent*-pimara-8(14),15-diene synthase

Reaction: *ent*-copalyl diphosphate = *ent*-pimara-8(14),15-diene + diphosphate

Other name(s): OsKS5

Systematic name: *ent*-copalyl-diphosphate diphosphate-lyase [*ent*-pimara-8(14),15-diene-forming]

Comments: Unlike EC 4.2.3.29, *ent*-sandaracopimaradiene synthase, which can produce both *ent*-sandaracopimaradiene and *ent*-pimara-8(14),15-diene, this diterpene cyclase produces only *ent*-pimara-8(14),15-diene. *ent*-Pimara-8(14),15-diene is not a precursor in the biosynthesis of either gibberellins or phytoalexins.

References: [665]

[EC 4.2.3.30 created 2008]

EC 4.2.3.31

Accepted name: *ent*-pimara-9(11),15-diene synthase

Reaction: *ent*-copalyl diphosphate = *ent*-pimara-9(11),15-diene + diphosphate

Other name(s): PMD synthase

Systematic name: *ent*-copalyl-diphosphate diphosphate-lyase [*ent*-pimara-9(11),15-diene-forming]

Comments: This enzyme is involved in the biosynthesis of the diterpenoid viguiepinol and requires Mg^{2+}, Co^{2+}, Zn^{2+} or Ni^{2+} for activity.

References: [598]

[EC 4.2.3.31 created 2008]

EC 4.2.3.32

Accepted name: levopimaradiene synthase

Reaction: (+)-copalyl diphosphate = abieta-8(14),12-diene + diphosphate

Other name(s): PtTPS-LAS; LPS; copalyl-diphosphate diphosphate-lyase [abieta-8(14),12-diene-forming]
Systematic name: (+)-copalyl-diphosphate diphosphate-lyase [abieta-8(14),12-diene-forming]
Comments: In *Ginkgo*, the enzyme catalyses the initial cyclization step in the biosynthesis of ginkgolides, a structurally unique family of diterpenoids that are highly specific platelet-activating-factor receptor antagonists [1204]. Levopimaradiene is widely distributed in higher plants. In some species the enzyme also forms abietadiene, palustradiene, and neoabietadiene [1160].
References: [1204, 1160]

[EC 4.2.3.32 created 2008, modified 2012]

EC 4.2.3.33

Accepted name: stemar-13-ene synthase
Reaction: 9α-copalyl diphosphate = stemar-13-ene + diphosphate
Other name(s): OsDTC2; OsK8; OsKL8; OsKS8; stemarene synthase; *syn*-stemar-13-ene synthase
Systematic name: 9α-copalyl-diphosphate diphosphate-lyase (stemar-13-ene-forming)
Comments: This diterpene cyclase produces stemar-13-ene, a putative precursor of the rice phytoalexin oryzalexin S. Phytoalexins are diterpenoid secondary metabolites that are involved in the defense mechanism of the plant, and are produced in response to pathogen attack through the perception of elicitor signal molecules such as chitin oligosaccharide, or after exposure to UV irradiation.
References: [951, 999]

[EC 4.2.3.33 created 2008]

EC 4.2.3.34

Accepted name: stemod-13(17)-ene synthase
Reaction: 9α-copalyl diphosphate = stemod-13(17)-ene + diphosphate
Other name(s): OsKSL11; stemodene synthase
Systematic name: 9α-copalyl-diphosphate diphosphate-lyase [stemod-13(17)-ene-forming]
Comments: This enzyme catalyses the committed step in the biosynthesis of the stemodane family of diterpenoid secondary metabolites, some of which possess mild antiviral activity. The enzyme also produces stemod-12-ene and stemar-13-ene as minor products.
References: [962]

[EC 4.2.3.34 created 2008]

EC 4.2.3.35

Accepted name: *syn*-pimara-7,15-diene synthase
Reaction: 9α-copalyl diphosphate = 9β-pimara-7,15-diene + diphosphate
Other name(s): 9β-pimara-7,15-diene synthase; OsDTS2; OsKS4
Systematic name: 9α-copalyl-diphosphate diphosphate-lyase (9β-pimara-7,15-diene-forming)
Comments: This enzyme is a class I terpene synthase [1466]. 9β-Pimara-7,15-diene is a precursor of momilactones A and B, rice diterpenoid phytoalexins that are produced in response to attack (by a pathogen, elicitor or UV irradiation) and are involved in the defense mechanism of the plant. Momilactone B can also act as an allochemical, being constitutively produced in the root of the plant and secreted to the rhizosphere where it suppresses the growth of neighbouring plants and soil microorganisms [1466].
References: [1466, 1042]

[EC 4.2.3.35 created 2008]

EC 4.2.3.36

Accepted name: terpentetriene synthase
Reaction: terpentedienyl diphosphate = terpentetriene + diphosphate

Other name(s): Cyc2 (ambiguous)
Systematic name: terpentedienyl-diphosphate diphosphate-lyase (terpentetriene-forming)
Comments: Requires Mg^{2+} for maximal activity but can use Mn^{2+}, Fe^{2+} or Co^{2+} to a lesser extent [493]. Following on from EC 5.5.1.15, terpentedienyl-diphosphate synthase, this enzyme completes the transformation of geranylgeranyl diphosphate (GGDP) into terpentetriene, which is a precursor of the diterpenoid antibiotic terpentecin. Farnesyl diphosphate can also act as a substrate.
References: [288, 493, 351]

[EC 4.2.3.36 created 2008]

EC 4.2.3.37

Accepted name: *epi*-isozizaene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-*epi*-isozizaene + diphosphate
Other name(s): SCO5222 protein
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(+)-*epi*-isozizaene-forming]
Comments: Requires Mg^{2+} for activity. The displacement of the diphosphate group of farnesyl diphosphate occurs with retention of configuration [821]. In the soil-dwelling bacterium *Streptomyces coelicolor* A3(2), the product of this reaction is used by EC 1.14.13.106, *epi*-isozizaene 5-monooxygenase, to produce the sesquiterpene antibiotic albaflavenone [1558].
References: [821, 1558]

[EC 4.2.3.37 created 2008]

EC 4.2.3.38

Accepted name: α-bisabolene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (*E*)-α-bisabolene + diphosphate
Other name(s): bisabolene synthase
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(*E*)-α-bisabolene-forming]
Comments: This cytosolic sesquiterpenoid synthase requires a divalent cation cofactor (Mg^{2+} or, to a lesser extent, Mn^{2+}) to neutralize the negative charge of the diphosphate leaving group. While unlikely to encounter geranyl diphosphate (GDP) *in vivo* as it is localized to plastids, the enzyme can use GDP as a substrate *in vitro* to produce (+)-(4*R*)-limonene [*cf.* EC 4.2.3.20, (*R*)-limonene synthase]. The enzyme is induced as part of a defense mechanism in the grand fir *Abies grandis* as a response to stem wounding.
References: [111]

[EC 4.2.3.38 created 2009]

EC 4.2.3.39

Accepted name: *epi*-cedrol synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = 8-*epi*-cedrol + diphosphate
Other name(s): 8-epicedrol synthase; epicedrol synthase
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (8-*epi*-cedrol-forming)
Comments: The enzyme is activated by Mg^{2+} [583]. Similar to many other plant terpenoid synthases, this enzyme produces many products from a single substrate. The predominant product is the cyclic sesquiterpenoid alcohol, 8-*epi*-cedrol, with minor products including cedrol and the olefins α-cedrene, β-cedrene, (*E*)-β-farnesene and (*E*)-α-bisabolene [929].
References: [929, 583]

[EC 4.2.3.39 created 2009]

EC 4.2.3.40

Accepted name: (*Z*)-γ-bisabolene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (*Z*)-γ-bisabolene + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(*Z*)-γ-bisabolene-forming]
Comments: This sesquiterpenoid enzyme is constitutively expressed in the root, hydathodes and stigma of the plant *Arabidopsis thaliana*. If the leaves of the plant are wounded, e.g. by cutting, the enzyme is also induced close to the wound site. The sesquiterpenoids (*E*)-nerolidol and α-bisabolol are also produced by this enzyme as minor products.
References: [1161]

[EC 4.2.3.40 created 2009]

EC 4.2.3.41

Accepted name: elisabethatriene synthase
Reaction: geranylgeranyl diphosphate = elisabethatriene + diphosphate
Other name(s): elisabethatriene cyclase
Systematic name: geranylgeranyl-diphosphate diphosphate-lyase (elisabethatriene-forming)
Comments: Requires Mg^{2+} or less efficiently Mn^{2+}. The enzyme is also able to use farnesyl diphosphate and geranyl diphosphate.
References: [722, 146]

[EC 4.2.3.41 created 2009]

EC 4.2.3.42

Accepted name: aphidicolan-16β-ol synthase
Reaction: 9α-copalyl diphosphate + H_2O = aphidicolan-16β-ol + diphosphate
Other name(s): PbACS
Systematic name: 9α-copalyl-diphosphate diphosphate-lyase (aphidicolan-16β-ol-forming)
Comments: This is a bifunctional enzyme which also has EC 5.5.1.14 *syn*-copalyl diphosphate synthase activity. Aphidicolan-16β-ol is a precursor of aphidicolin, a specific inhibitor of DNA polymerase α (EC 2.7.7.7).
References: [1026, 1385]

[EC 4.2.3.42 created 2009]

EC 4.2.3.43

Accepted name: fusicocca-2,10(14)-diene synthase
Reaction: geranylgeranyl diphosphate = fusicocca-2,10(14)-diene + diphosphate
Other name(s): fusicoccadiene synthase; PaFS; PaDC4
Systematic name: geranylgeranyl diphosphate-lyase (fusicocca-2,10(14)-diene-forming)
Comments: A multifunctional enzyme with EC 2.5.1.29 farnesyl*trans*transferase activity.
References: [1387]

[EC 4.2.3.43 created 2009]

EC 4.2.3.44

Accepted name: isopimara-7,15-diene synthase
Reaction: (+)-copalyl diphosphate = isopimara-7,15-diene + diphosphate
Other name(s): PaTPS-Iso; copalyl diphosphate-lyase (isopimara-7,15-diene-forming)
Systematic name: (+)-copalyl diphosphate-lyase (isopimara-7,15-diene-forming)
Comments: The enzyme only gave isopimara-7,15-diene.
References: [880]

[EC 4.2.3.44 created 2009]

EC 4.2.3.45

Accepted name: phyllocladan-16α-ol synthase

Reaction: (+)-copalyl diphosphate + H_2O = phyllocladan-16α-ol + diphosphate

Other name(s): PaDC1

Systematic name: (+)-copalyl-diphosphate diphosphate-lyase (phyllocladan-16α-ol-forming)

Comments: The adjacent gene *PaDC2* codes EC 5.5.1.12 copalyl diphosphate synthase.

References: [1386]

[EC 4.2.3.45 created 2009]

EC 4.2.3.46

Accepted name: α-farnesene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = (3*E*,6*E*)-α-farnesene + diphosphate

Other name(s): (*E*,*E*)-α-farnesene synthase; AFS1; MdAFS1

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate lyase [(3*E*,6*E*)-α-farnesene-forming]

References: [1060, 466, 1005]

[EC 4.2.3.46 created 2010]

EC 4.2.3.47

Accepted name: β-farnesene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = (*E*)-β-farnesene + diphosphate

Other name(s): farnesene synthase; terpene synthase 10; terpene synthase 10-B73; TPS10

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(*E*)-β-farnesene-forming]

References: [1557, 1081, 726, 1225, 889, 262, 1224, 587]

[EC 4.2.3.47 created 2010]

EC 4.2.3.48

Accepted name: (3*S*,6*E*)-nerolidol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = (3*S*,6*E*)-nerolidol + diphosphate

Other name(s): (*E*)-nerolidol synthase; nerolidol synthase; (3*S*)-(*E*)-nerolidol synthase; FaNES1

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(3*S*,6*E*)-nerolidol-forming]

Comments: The enzyme catalyses a step in the formation of (3*E*)-4,8-dimethylnona-1,3,7-triene, a key signal molecule in induced plant defense mediated by the attraction of enemies of herbivores [121]. Nerolidol is a naturally occurring sesquiterpene found in the essential oils of many types of plants.

References: [7, 121, 307, 38]

[EC 4.2.3.48 created 2010]

EC 4.2.3.49

Accepted name: (3*R*,6*E*)-nerolidol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = (3*R*,6*E*)-nerolidol + diphosphate

Other name(s): terpene synthase 1

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(3*R*,6*E*)-nerolidol-forming]

Comments: The enzyme catalyses a step in the formation of (3*E*)-4,8-dimethylnona-1,3,7-triene, a key signal molecule in induced plant defense mediated by the attraction of enemies of herbivores [1224]. Nerolidol is a naturally occurring sesquiterpene found in the essential oils of many types of plants.

References: [1224]

[EC 4.2.3.49 created 2010]

EC 4.2.3.50

Accepted name: (+)-α-santalene synthase [(2*Z*,6*Z*)-farnesyl diphosphate cyclizing]
Reaction: (2*Z*,6*Z*)-farnesyl diphosphate = (+)-α-santalene + diphosphate
Other name(s): SBS (ambiguous)
Systematic name: (2*Z*,6*Z*)-farnesyl diphosphate lyase [cyclizing; (+)-α-santalene-forming]
Comments: The enzyme synthesizes a mixture of sesquiterpenoids from (2*Z*,6*Z*)-farnesyl diphosphate. Following dephosphorylation of (2*Z*,6*Z*)-farnesyl diphosphate, the (2*Z*,6*Z*)-farnesyl carbocation is converted to either the (6*R*)- or the (6*S*)-bisabolyl cations depending on the stereochemistry of the 6,1 closure. The (6*R*)-bisabolyl cation will then lead to the formation of (+)-α-santalene (EC 4.2.3.50), while the (6*S*)-bisabolyl cation will give rise to (+)-*endo*-β-bergamotene (see EC 4.2.3.53) as well as (-)-*endo*-α-bergamotene (see EC 4.2.3.54). Small amounts of (-)-*epi*-β-santalene are also formed from the (6*R*)-bisabolyl cation and small amounts of (-)-*exo*-α-bergamotene are formed from the (6*S*)-bisabolyl cation [1189].
References: [1189]

[EC 4.2.3.50 created 2010]

EC 4.2.3.51

Accepted name: β-phellandrene synthase (neryl-diphosphate-cyclizing)
Reaction: neryl diphosphate = β-phellandrene + diphosphate
Other name(s): phellandrene synthase 1; PHS1; monoterpene synthase PHS1
Systematic name: neryl-diphosphate diphosphate-lyase [cyclizing; β-phellandrene-forming]
Comments: The enzyme from *Solanum lycopersicum* has very poor affinity with geranyl diphosphate as substrate. Catalyses the formation of the acyclic myrcene and ocimene as major products in addition to β-phellandrene [1209].
References: [1209]

[EC 4.2.3.51 created 2010]

EC 4.2.3.52

Accepted name: (4*S*)-β-phellandrene synthase (geranyl-diphosphate-cyclizing)
Reaction: geranyl diphosphate = (4*S*)-β-phellandrene + diphosphate
Other name(s): phellandrene synthase; (-)-β-phellandrene synthase; (-)-(4*S*)-β-phellandrene synthase
Systematic name: geranyl-diphosphate diphosphate-lyase [cyclizing; (4*S*)-β-phellandrene-forming]
Comments: Requires Mn^{2+}. Mg^{2+} is not effective [1200]. Some (-)-α-phellandrene is also formed [1433]. The reaction involves a 1,3-hydride shift [776].
References: [1200, 112, 1433, 776]

[EC 4.2.3.52 created 2010]

EC 4.2.3.53

Accepted name: (+)-*endo*-β-bergamotene synthase [(2*Z*,6*Z*)-farnesyl diphosphate cyclizing]
Reaction: (2*Z*,6*Z*)-farnesyl diphosphate = (+)-*endo*-β-bergamotene + diphosphate
Other name(s): SBS (ambiguous)
Systematic name: (2*Z*,6*Z*)-farnesyl diphosphate lyase (cyclizing; (+)-*endo*-β-bergamotene-forming)
Comments: The enzyme synthesizes a mixture of sesquiterpenoids from (2*Z*,6*Z*)-farnesyl diphosphate. Following dephosphorylation of (2*Z*,6*Z*)-farnesyl diphosphate, the (2*Z*,6*Z*)-farnesyl carbocation is converted to either the (6*R*)- or the (6*S*)-bisabolyl cations depending on the stereochemistry of the 6,1 closure. The (6*R*)-bisabolyl cation will then lead to the formation of (+)-α-santalene (see EC 4.2.3.50), while the (6*S*)-bisabolyl cation will give rise to (-)-*endo*-α-bergamotene (see EC 4.2.3.54), as well as (+)-*endo*-β-bergamotene. Small amounts of (-)-*epi*-β-santalene are also formed from the (6*R*)-bisabolyl cation and small amounts of (-)-*exo*-α-bergamotene are formed from the (6*S*)-bisabolyl cation [1189].
References: [1189]

[EC 4.2.3.53 created 2010]

EC 4.2.3.54

Accepted name: (-)-*endo*-α-bergamotene synthase [(2Z,6*Z*)-farnesyl diphosphate cyclizing]

Reaction: (2Z,6*Z*)-farnesyl diphosphate = (-)-*endo*-α-bergamotene + diphosphate

Other name(s): SBS (ambiguous)

Systematic name: (2Z,6*Z*)-farnesyl diphosphate lyase [cyclizing; (-)-*endo*-α-bergamotene-forming]

Comments: The enzyme synthesizes a mixture of sesquiterpenoids from (2Z,6*Z*)-farnesyl diphosphate. Following dephosphorylation of (2Z,6*Z*)-farnesyl diphosphate, the (2Z,6*Z*)-farnesyl carbocation is converted to either the (6*R*)- or the (6*S*)-bisabolyl cations depending on the stereochemistry of the 6,1 closure. The (6*R*)-bisabolyl cation will then lead to the formation of (+)-α-santalene (see EC 4.2.3.50), while the (6*S*)-bisabolyl cation will give rise to (+)-*endo*-β-bergamotene (EC 4.2.3.53) as well as (-)-*endo*-α-bergamotene. Small amounts of (-)-*epi*-β-santalene are also formed from the (6*R*)-bisabolyl cation and small amounts of (-)-*exo*-α-bergamotene are formed from the (6*S*)-bisabolyl cation [1189].

References: [1189]

[EC 4.2.3.54 created 2010]

EC 4.2.3.55

Accepted name: (*S*)-β-bisabolene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = (*S*)-β-bisabolene + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(*S*)-β-bisabolene-forming]

Comments: The synthesis of (*S*)-β-macrocarpene from (2*E*,6*E*)-farnesyl diphosphate proceeds in two steps. The first step is the cyclization to (*S*)-β-bisabolene. The second step is the isomerization to (*S*)-β-macrocarpene (*cf.* EC 5.5.1.17, (*S*)-β-macrocarpene synthase). The enzyme requires Mg^{2+} or Mn^{2+} for activity.

References: [413]

[EC 4.2.3.55 created 2011]

EC 4.2.3.56

Accepted name: γ-humulene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = γ-humulene + diphosphate

Other name(s): humulene cyclase

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (γ-humulene-forming)

References: [1299, 826]

[EC 4.2.3.56 created 2011]

EC 4.2.3.57

Accepted name: (-)-β-caryophyllene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = (-)-β-caryophyllene + diphosphate

Other name(s): β-caryophyllene synthase; (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (caryophyllene-forming)

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(-)-β-caryophyllene-forming]

Comments: Widely distributed in higher plants, *cf.* EC 4.2.3.89 (+)-β-caryophyllene synthase.

References: [168]

[EC 4.2.3.57 created 2011, modified 2011]

EC 4.2.3.58

Accepted name: longifolene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = longifolene + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (longifolene-forming)
Comments: As well as 61% longifolene the enzyme gives 15% of α-longipinene, 6% longicyclene and traces of other sesquiterpenoids.
References: [880]

[EC 4.2.3.58 created 2011]

EC 4.2.3.59

Accepted name: (*E*)-γ-bisabolene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (*E*)-γ-bisabolene + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(*E*)-γ-bisabolene-forming]
References: [587]

[EC 4.2.3.59 created 2011]

EC 4.2.3.60

Accepted name: germacrene C synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = germacrene C + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (germacrene-C-forming)
References: [242]

[EC 4.2.3.60 created 2011]

EC 4.2.3.61

Accepted name: 5-epiaristolochene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-5-epiaristolochene + diphosphate
Other name(s): 5-*epi*-aristolochene synthase; tobacco epiaristolochene synthase; farnesyl pyrophosphate cyclase (ambiguous); EAS; TEAS
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(+)-5-epiaristolochene-forming]
Comments: Initial cyclization gives (+)-germacrene A in an enzyme bound form which is not released to the medium.
References: [57, 1298, 56, 1158, 113, 1030]

[EC 4.2.3.61 created 2011]

EC 4.2.3.62

Accepted name: (-)-γ-cadinene synthase [(2*Z*,6*E*)-farnesyl diphosphate cyclizing]
Reaction: (2*Z*,6*E*)-farnesyl diphosphate = (-)-γ-cadinene + diphosphate
Other name(s): (-)-γ-cadinene cyclase
Systematic name: (2*Z*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(-)-γ-cadinene-forming]
Comments: Isolated from the liverwort *Heteroscyphus planus*. cf EC 4.2.3.92 (+)-γ-cadinene synthase.
References: [978]

[EC 4.2.3.62 created 2011, modified 2011]

EC 4.2.3.63

Accepted name: (+)-cubenene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-cubenene + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(+)-cubenene-forming]
Comments: Requires Mg^{2+}.
References: [979, 978]

[EC 4.2.3.63 created 2011]

EC 4.2.3.64

Accepted name: (+)-epicubenol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = (+)-epicubenol + diphosphate

Other name(s): farnesyl pyrophosphate cyclase (ambiguous)

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(+)-epicubenol-forming]

Comments: Requires Mg^{2+}. In the bacteria *Streptomyces* and the liverwort Heteroscyphus the (+)-isomer is formed in contrast to higher plants where the (-)-isomer is formed.

References: [179, 180, 181, 979, 978]

[EC 4.2.3.64 created 2011]

EC 4.2.3.65

Accepted name: zingiberene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = zingiberene + diphosphate

Other name(s): α-zingiberene synthase; ZIS

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (zingiberene-forming)

References: [290]

[EC 4.2.3.65 created 2011]

EC 4.2.3.66

Accepted name: β-selinene cyclase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = β-selinene + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (β-selinene-forming)

Comments: Initial cyclization gives (+)-germacrene A in an enzyme bound form which is not released to the medium.

References: [82]

[EC 4.2.3.66 created 2011]

EC 4.2.3.67

Accepted name: *cis*-muuroladiene synthase

Reaction: (1) (2*E*,6*E*)-farnesyl diphosphate = *cis*-muurola-3,5-diene + diphosphate
(2) (2*E*,6*E*)-farnesyl diphosphate = *cis*-muurola-4(14),5-diene + diphosphate

Other name(s): MxpSS1

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (*cis*-muuroladiene-forming)

Comments: The recombinant enzyme from black peppermint (*Mentha* x *piperita*) gave a mixture of *cis*-muurola-3,5-diene (45%) and *cis*-muurola-4(14),5-diene (43%).

References: [1107]

[EC 4.2.3.67 created 2011]

EC 4.2.3.68

Accepted name: β-eudesmol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = β-eudesmol + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (β-eudesmol-forming)

Comments: The recombinant enzyme from ginger (*Zingiber zerumbet*) gives 62.6% β-eudesmol, 16.8% 10-*epi*-γ-eudesmol (*cf.* EC 4.2.3.84, 10-*epi*-γ-eudesmol synthase), 10% α-eudesmol (*cf.* EC 4.2.3.85, α-eudesmol synthase), and 5.6% aristolene.

References: [1518]

[EC 4.2.3.68 created 2011, modified 2011, modified 2012]

EC 4.2.3.69

Accepted name: (+)-α-barbatene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-α-barbatene + diphosphate
Other name(s): AtBS
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(+)-α-barbatene-forming]
Comments: The recombinant enzyme from the plant *Arabidopsis thaliana* produces 27.3% α-barbatene, 17.8% thujopsene (*cf.* EC 4.2.3.79, thujopsene synthase) and 9.9% β-chamigrene (*cf.* EC 4.2.3.78, β-chamigrene synthase) [1477] plus traces of other sesquiterpenoids [1364].
References: [1477, 1364]

[EC 4.2.3.69 created 2011, modified 2012]

EC 4.2.3.70

Accepted name: patchoulol synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = patchoulol + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (patchoulol-forming)
References: [268, 970, 378]

[EC 4.2.3.70 created 2011]

EC 4.2.3.71

Accepted name: (*E*,*E*)-germacrene B synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (*E*,*E*)-germacrene B + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(*E*,*E*)-germacrene-B-forming]
References: [1412]

[EC 4.2.3.71 created 2011]

EC 4.2.3.72

Accepted name: α-gurjunene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (-)-α-gurjunene + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(-)-α-gurjunene-forming]
Comments: Initial cyclization probably gives biyclogermacrene in an enzyme bound form which is not released to the medium. The enzyme from *Solidago canadensis* also forms a small amount of (+)-γ-gurjunene [1218].
References: [1218]

[EC 4.2.3.72 created 2011]

EC 4.2.3.73

Accepted name: valencene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-valencene + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (valencene-forming)
Comments: The recombinant enzyme from *Vitis vinifera* gave 49.5% (+)-valencene and 35.5% (-)-7-*epi*-α-selinene. Initial cyclization gives (+)-germacrene A in an enzyme bound form which is not released to the medium.
References: [852]

[EC 4.2.3.73 created 2011]

EC 4.2.3.74

Accepted name: presilphiperfolanol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = presilphiperfolan-8β-ol + diphosphate
Other name(s): BcBOT2; CND15
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphohydrolase (presilphiperfolan-8β-ol-forming)
Comments: Requires Mg^{2+}. Presilphiperfolan-8β-ol is the precursor of botrydial, a phytotoxic sesquiterpene metabolite secreted by the fungus *Botryotinia fuckeliana* (*Botrytis cinerea*), the causal agent of gray mold disease in plants.
References: [1087, 1440]

[EC 4.2.3.74 created 2011]

EC 4.2.3.75

Accepted name: (-)-germacrene D synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (-)-germacrene D + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(-)-germacrene-D-forming]
Comments: In *Solidago canadensis* the biosynthesis results in the *pro-R* hydrogen at C-1 of the farnesy diphosphate ending up at C-11 of the (-)-germacrene D [1219]. With *Streptomyces coelicolor* the *pro-S* hydrogen at C-1 ends up at C-11 of the (-)-germacrene D [530].
References: [1219, 530, 852, 1105]

[EC 4.2.3.75 created 2011]

EC 4.2.3.76

Accepted name: (+)-δ-selinene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-δ-selinene + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(+)-δ-selinene-forming]
Comments: Initial cyclization gives germacrene C in an enzyme bound form which is not released to the medium.
References: [1299, 826]

[EC 4.2.3.76 created 2011]

EC 4.2.3.77

Accepted name: (+)-germacrene D synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-germacrene D + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(+)-germacrene-D-forming]
Comments: Requires Mg^{2+}, Mn^{2+}, Ni^{2+} or Co^{2+}. The formation of (+)-germacrene D involves a 1,2-hydride shift whereas for (-)-germacrene D there is a 1,3-hydride shift (see EC 4.2.3.75).
References: [1083]

[EC 4.2.3.77 created 2011]

EC 4.2.3.78

Accepted name: β-chamigrene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-β-chamigrene + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl diphosphate lyase (cyclizing, (+)-β-chamigrene-forming)
Comments: The recombinant enzyme from the plant *Arabidopsis thaliana* produces 27.3% (+)-α-barbatene, 17.8% (+)-thujopsene and 9.9% (+)-β-chamigrene [1477] plus traces of other sesquiterpenoids [1364]. See EC 4.2.3.69 (+)-α-barbatene synthase, and EC 4.2.3.79 thujopsene synthase.
References: [1477, 1364]

[EC 4.2.3.78 created 2011]

EC 4.2.3.79

Accepted name: thujopsene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-thujopsene + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl diphosphate lyase (cyclizing, (+)-thujopsene-forming)

Comments: The recombinant enzyme from the plant *Arabidopsis thaliana* produces 27.3% (+)-α-barbatene, 17.8% (+)-thujopsene and 9.9% (+)-β-chamigrene [1477] plus traces of other sesquiterpenoids [1364]. See EC 4.2.3.69 (+)-α-barbatene synthase, and EC 4.2.3.78 β-chamigrene synthase.

References: [1477, 1364]

[EC 4.2.3.79 created 2011]

EC 4.2.3.80

Accepted name: α-longipinene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = α-longipinene + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (α-longipinene-forming)

Comments: The enzyme from Norway spruce produces longifolene as the main product (*cf*. EC 4.2.3.58, longifolene synthase). α-Longipinene constitutes about 15% of the total products.

References: [880, 732]

[EC 4.2.3.80 created 2011]

EC 4.2.3.81

Accepted name: *exo*-α-bergamotene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = (-)-*exo*-α-bergamotene + diphosphate

Other name(s): *trans*-α-bergamotene synthase; LaBERS (gene name)

Systematic name: (2*E*,6*E*)-farnesyl diphosphate lyase (cyclizing, (-)-*exo*-α-bergamotene-forming)

Comments: The enzyme synthesizes a mixture of sesquiterpenoids from (2*E*,6*E*)-farnesyl diphosphate. As well as (-)-*exo*-α-bergamotene (74%) there were (*E*)-nerolidol (10%), (*Z*)-α-bisabolene (6%), (*E*)-β-farnesene (5%) and β-sesquiphellandrene (1%).

References: [1225, 783]

[EC 4.2.3.81 created 2011]

EC 4.2.3.82

Accepted name: α-santalene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-α-santalene + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl diphosphate lyase (cyclizing, (+)-α-santalene-forming)

Comments: The enzyme synthesizes a mixture of sesquiterpenoids from (2*E*,6*E*)-farnesyl diphosphate. As well as (+)-α-santalene, (-)-β-santalene and (-)-*exo*-α-bergamotene are formed with traces of (+)-*epi*-β-santalene. See EC 4.2.3.83 [(-)-β-santalene synthase], and EC 4.2.3.81 [(-)-*exo*-α-bergamotene synthase]. *cf*. EC 4.2.3.50 α-santalene synthase [(2Z,6*Z*)-farnesyl diphosphate cyclizing]

References: [645]

[EC 4.2.3.82 created 2011]

EC 4.2.3.83

Accepted name: β-santalene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = (-)-β-santalene + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl diphosphate lyase (cyclizing, (-)-β-santalene-forming)

Comments: The enzyme synthesizes a mixture of sesquiterpenoids from (2*E*,6*E*)-farnesyl diphosphate. As well as (-)-β-santalene (+)-α-santalene and (-)-*exo*-α-bergamotene are formed with traces of (+)-*epi*-β-santalene. See EC 4.2.3.82 [(+)-α-santalene synthase], and EC 4.2.3.81 [(-)-*exo*-α-bergamotene synthase].

References: [645]

[EC 4.2.3.83 created 2011]

EC 4.2.3.84

Accepted name: 10-*epi*-γ-eudesmol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = 10-*epi*-γ-eudesmol + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (10-*epi*-γ-eudesmol-forming)

Comments: The recombinant enzyme from ginger (*Zingiber zerumbet*) gives 62.6% β-eudesmol, 16.8% 10-*epi*-γ-eudesmol, 10% α-eudesmol, and 5.6% aristolene. *cf.* EC 4.2.3.68 (β-eudesmol synthase) and EC 4.2.3.85 (α-eudesmol synthase)

References: [1518]

[EC 4.2.3.84 created 2011]

EC 4.2.3.85

Accepted name: α-eudesmol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = α-eudesmol + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (α-eudesmol-forming)

Comments: The recombinant enzyme from ginger (*Zingiber zerumbet*) gives 62.6% β-eudesmol, 16.8% 10-*epi*-γ-eudesmol, 10% α-eudesmol, and 5.6% aristolene. *cf.* EC 4.2.3.68 (β-eudesmol synthase) and EC 4.2.3.84 (10-*epi*-γ-eudesmol synthase)

References: [1518]

[EC 4.2.3.85 created 2011]

EC 4.2.3.86

Accepted name: 7-*epi*-α-selinene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = 7-*epi*-α-selinene + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (7-*epi*-α-selinene-forming)

Comments: The recombinant enzyme from *Vitis vinifera* forms 49.5% (+)-valencene (*cf.* EC 4.2.3.73, valencene synthase) and 35.5% (-)-7-*epi*-α-selinene. Initial cyclization gives (+)-germacrene A in an enzyme bound form which is not released to the medium.

References: [852, 881]

[EC 4.2.3.86 created 2011]

EC 4.2.3.87

Accepted name: α-guaiene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = α-guaiene + diphosphate

Other name(s): PatTps177 (gene name)

Systematic name: (2*Z*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, α-guaiene-forming)

Comments: Requires Mg^{2+}. The enzyme from *Pogostemon cablin* gives 13% α-guaiene as well as 37% (-)-patchoulol (see EC 4.2.3.70), 13% δ-guaiene (see EC 4.2.3.93), and traces of at least ten other sesquiterpenoids [308]. In *Aquilaria crassna* three clones of the enzyme gave about 80% δ-guaiene and 20% α-guaiene, with traces of α-humulene. A fourth clone gave 54% δ-guaiene and 45% α-guaiene [762].

References: [308, 762]

[EC 4.2.3.87 created 2011]

EC 4.2.3.88

Accepted name: viridiflorene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = viridiflorene + diphosphate
Other name(s): TPS31
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (viridiflorene-forming)
Comments: Viridiflorene is the only product of this enzyme from *Solanum lycopersicum*.
References: [101]

[EC 4.2.3.88 created 2011]

EC 4.2.3.89

Accepted name: (+)-β-caryophyllene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-β-caryophyllene + diphosphate
Other name(s): GcoA
Systematic name: (2*Z*,6*E*)-farnesyl-diphosphate diphosphate-lyase [cyclizing, (+)-β-caryophyllene-forming]
Comments: A multifunctional enzyme which also converts the (+)-β-caryophyllene to (+)-caryolan-1-ol (see EC 4.2.1.138, (+)-caryolan-1-ol synthase). *cf.* EC 4.2.3.57 (–)-β-caryophyllene synthase.
References: [988]

[EC 4.2.3.89 created 2011]

EC 4.2.3.90

Accepted name: 5-*epi*-α-selinene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = 5-*epi*-α-selinene + diphosphate
Other name(s): 8a-*epi*-α-selinene synthase; NP1
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, 5-*epi*-α-selinene-forming)
Comments: Requires Mg^{2+}. The enzyme forms 5-*epi*-α-selinene possibly via germecrene A or a 1,6-hydride shift mechanism.
References: [5]

[EC 4.2.3.90 created 2011]

EC 4.2.3.91

Accepted name: cubebol synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = cubebol + diphosphate
Other name(s): Cop4
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, cubebol-forming)
Comments: Requires Mg^{2+}. The enzyme gives 28% cubebol, 29% (-)-germacrene D, 10% (+)-δ-cadinene and traces of several other sesquiterpenoids. See also EC 4.2.3.75 (–)-germacrene D synthase and EC 4.2.3.13 (+)-δ-cadinene synthase.
References: [842]

[EC 4.2.3.91 created 2011]

EC 4.2.3.92

Accepted name: (+)-γ-cadinene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-γ-cadinene + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(+)-γ-cadinene-forming]
Comments: The cloned enzyme from the melon, *Cucumis melo*, gave mainly δ- and γ-cadinene with traces of several other sesquiterpenoids *cf.* EC 4.2.3.62 (-)-γ-cadinene synthase [(2*Z*,6*E*)-farnesyl diphosphate cyclizing]; EC 4.2.3.13 (+)-δ-cadinene synthase.
References: [595, 1097]

[EC 4.2.3.92 created 2011]

EC 4.2.3.93

Accepted name: δ-guaiene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = δ-guaiene + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, δ-guaiene-forming)

Comments: Requires Mg^{2+}. In *Aquilaria crassna* three clones of the enzyme gave about 80% δ-guaiene and 20% α-guaiene (see also EC 4.2.3.87). A fourth clone gave 54% δ-guaiene and 45% α-guaiene [762]. The enzyme from *Pogostemon cablin* gives 13% δ-guaiene as well as 37% (-)-patchoulol (see EC 4.2.3.70), 13% α-guaiene (see EC 4.2.3.87), and traces of at least ten other sesquiterpenoids [308].

References: [308, 762]

[EC 4.2.3.93 created 2011]

EC 4.2.3.94

Accepted name: γ-curcumene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = γ-curcumene + diphosphate

Other name(s): PatTpsA (gene name)

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, γ-curcumene-forming)

Comments: One of five sesquiterpenoid synthases in *Pogostemon cablin* (patchouli).

References: [308]

[EC 4.2.3.94 created 2012]

EC 4.2.3.95

Accepted name: (-)-α-cuprenene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = (-)-α-cuprenene + diphosphate

Other name(s): Cop6

Systematic name: (-)-α-cuprenene hydrolase [cyclizing, (-)-α-cuprenene-forming]

Comments: The enzyme from the fungus Coprinopsis cinerea produces (-)-α-cuprenene with high selectivity.

References: [842]

[EC 4.2.3.95 created 2012]

EC 4.2.3.96

Accepted name: avermitilol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = avermitilol + diphosphate

Systematic name: avermitilol hydrolase (cyclizing, avermitilol-forming)

Comments: Requires Mg^{2+}. The recombinent enzyme gives avermitilol (85%) plus traces of germacrene A, germacrene B and viridiflorol. The (1*S*)-hydrogen of farnesyl diphosphate is retained.

References: [230]

[EC 4.2.3.96 created 2012]

EC 4.2.3.97

Accepted name: (-)-δ-cadinene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = (-)-δ-cadinene + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, (-)-δ-cadinene-forming)

Comments: The cyclization mechanism involves an intermediate nerolidyl diphosphate leading to a helminthogermacradienyl cation. Following a 1,3-hydride shift of the original 1-*pro-S* hydrogen of (2*E*,6*E*)-farnesyl diphosphate, cyclization and deprotonation gives (-)-δ-cadinene.

References: [582]

[EC 4.2.3.97 created 2012]

EC 4.2.3.98

Accepted name:	(+)-T-muurolol synthase
Reaction:	(2*E*,6*E*)-farnesyl diphosphate + H_2O = (+)-T-muurolol + diphosphate
Systematic name:	(2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, (+)-T-muurolol-forming)
Comments:	The cyclization mechanism involves an intermediate nerolidyl diphosphate leading to a helminthogermacradienyl cation. After a 1,3-hydride shift of the original 1-*pro-S* hydrogen of farnesyl diphosphate, cyclization and deprotonation result in (+)-T-muurolol.
References:	[582]

[EC 4.2.3.98 created 2012]

EC 4.2.3.99

Accepted name:	labdatriene synthase
Reaction:	9α-copalyl diphosphate = (12*E*)-9α-labda-8(17),12,14-triene + diphosphate
Other name(s):	OsKSL10 (gene name)
Systematic name:	9α-copalyl-diphosphate diphosphate-lyase [(12*E*)-9α-labda-8(17),12,14-triene-forming]
Comments:	The enzyme from rice (*Oryza sativa*), expressed in *Escherichia coli*, also produces *ent*-sandaracopimara-8(14),15-diene from *ent*-copalyl diphosphate, another naturally occuring copalyl isomer in rice (*cf.* *ent*-sandaracopimaradiene synthase, EC 4.2.3.29).
References:	[961]

[EC 4.2.3.99 created 2012]

EC 4.2.3.100

Accepted name:	bicyclogermacrene synthase
Reaction:	(2*E*,6*E*)-farnesyl diphosphate = bicyclogermacrene + diphosphate
Other name(s):	Ov-TPS4
Systematic name:	(2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (bicyclogermacrene-forming)
Comments:	The enzyme from oregano (*Origanum vulgare*) gives mainly bicyclogermacrene with Mn^{2+} as a cofactor. With Mg^{2+} a more complex mixture is produced.
References:	[263]

[EC 4.2.3.100 created 2012]

EC 4.2.3.101

Accepted name:	7-*epi*-sesquithujene synthase
Reaction:	(2*E*,6*E*)-farnesyl diphosphate = 7-*epi*-sesquithujene + diphosphate
Other name(s):	TP*S*4-B73
Systematic name:	(2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (7-*epi*-sesquithujene-forming)
Comments:	The enzyme from *Zea mays*, variety B73, gives mainly 7-*epi*-sesquithujene with (*S*)-β-bisabolene and traces of other sesquiterpenoids, *cf.* EC 4.2.3.55 (*S*)-β-bisabolene synthase. It requires Mg^{2+} or Mn^{2+}. The product ratio is dependent on which metal ion is present. 7-*epi*-Sesquithujene is an attractant for the emerald ash borer beetle.
References:	[727]

[EC 4.2.3.101 created 2012]

EC 4.2.3.102

Accepted name:	sesquithujene synthase
Reaction:	(2*E*,6*E*)-farnesyl diphosphate = sesquithujene + diphosphate

Other name(s): TP*S*5-Del1
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (sesquithujene-forming)
Comments: The enzyme from *Zea mays*, variety Delprim, gives mainly sesquithujene with (*S*)-β-bisabolene and (*E*)-β-farnesene plus traces of other sesquiterpenoids, *cf.* EC 4.2.3.55 [(*S*)-β-bisabolene synthase] and EC 4.2.3.47 (β-farnesene synthase). It requires Mg^{2+} or Mn^{2+}. The exact product ratio is dependent on which metal ion is present.
References: [727]

[EC 4.2.3.102 created 2012]

EC 4.2.3.103

Accepted name: *ent*-isokaurene synthase
Reaction: *ent*-copalyl diphosphate = *ent*-isokaurene + diphosphate
Other name(s): OsKSL5i; OsKSL6
Systematic name: *ent*-copalyl-diphosphate diphosphate-lyase (cyclizing, *ent*-isokaurene-forming)
Comments: Two enzymes of the rice sub-species *Oryza sativa* ssp. *indica*, OsKSL5 and OsKSL6, produce *ent*-isokaurene. A variant of OsKSL5 from the sub-species *Oryza sativa* ssp. japonica produces *ent*-pimara-8(14),15-diene instead [*cf.* EC 4.2.3.30, *ent*-pimara-8(14),15-diene synthase].
References: [1485, 1486]

[EC 4.2.3.103 created 2012]

EC 4.2.3.104

Accepted name: α-humulene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = α-humulene + diphosphate
Other name(s): ZSS1
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (α-humulene-forming)
Comments: The enzyme from *Zingiber zerumbet*, shampoo ginger, also gives traces of β-caryophyllene.
References: [1519]

[EC 4.2.3.104 created 2012]

EC 4.2.3.105

Accepted name: tricyclene synthase
Reaction: geranyl diphosphate = tricyclene + diphosphate
Other name(s): TPS3
Systematic name: geranyl-diphosphate diphosphate-lyase (cyclizing; tricyclene-forming)
Comments: The enzyme from *Solanum lycopersicum* (tomato) gives a mixture of tricyclene, camphene, β-myrcene, limonene, and traces of several other monoterpenoids. See EC 4.2.3.117. (-)-camphene synthase, EC 4.2.3.15, myrcene synthase and EC 4.2.3.16, (4*S*)-limonene synthase.
References: [370]

[EC 4.2.3.105 created 2012]

EC 4.2.3.106

Accepted name: (*E*)-β-ocimene synthase
Reaction: geranyl diphosphate = (*E*)-β-ocimene + diphosphate
Other name(s): β-ocimene synthase; AtTPS03; ama0a23; LjEβOS; MtEBOS
Systematic name: geranyl-diphosphate diphosphate-lyase [(*E*)-β-ocimene-forming]
Comments: Widely distributed in plants, which release β-ocimene when attacked by herbivorous insects.
References: [372, 338, 39, 997]

[EC 4.2.3.106 created 2012]

EC 4.2.3.107

Accepted name: (+)-car-3-ene synthase

Reaction: geranyl diphosphate = (+)-car-3-ene + diphosphate

Other name(s): 3-carene cyclase; 3-carene synthase; 3CAR; (+)-3-carene synthase

Systematic name: geranyl-diphosphate diphosphate-lyase [cyclizing, (+)-car-3-ene-forming]

Comments: The enzyme reacts with (3*S*)-linalyl diphosphate twice as rapidly as geranyl diphosphate, but 25 times as rapidly as (3*R*)-linalyl diphosphate. It is assumed that (3*S*)-linalyl diphosphate is normally formed as an enzyme bound intermediate in the reaction. In the reaction the 5-*pro-R* hydrogen of geranyl diphosphate is eliminated during cyclopropane ring formation [1199, 1201]. In *Picea abies* (Norway spruce) and *Picea sitchensis* (Sitka spruce) terpinolene is also formed [373, 488]. See EC 4.2.3.113 terpinolene synthase. (+)-Car-3-ene is associated with resistance of *Picea sitchensis* (Sitka spruce) to white pine weevil [488].

References: [1199, 1201, 1200, 373, 497, 488]

[EC 4.2.3.107 created 2012]

EC 4.2.3.108

Accepted name: 1,8-cineole synthase

Reaction: geranyl diphosphate + H_2O = 1,8-cineole + diphosphate

Other name(s): 1,8-cineole cyclase; geranyl pyrophoshate:1,8-cineole cyclase; 1,8-cineole synthetase

Systematic name: geranyl-diphosphate diphosphate-lyase (cyclizing, 1,8-cineole-forming)

Comments: Requires Mn^{2+} or Zn^{2+}. Mg^{2+} is less effective than either. 1,8-Cineole is the main product from the enzyme with just traces of other monoterpenoids. The oxygen atom is derived from water. The reaction proceeds via linalyl diphosphate and α-terpineol, the stereochemistry of both depends on the organism. However neither intermediate can substitute for geranyl diphosphate. The reaction in *Salvia officinalis* (sage) proceeds via (–)-(3*R*)-linalyl diphosphate [266, 1472, 1069] while that in *Arabidopsis* (rock cress) proceeds via (+)-(3*S*)-linalyl diphosphate [215].

References: [266, 1472, 1069, 215, 691]

[EC 4.2.3.108 created 2012]

EC 4.2.3.109

Accepted name: (-)-sabinene synthase

Reaction: geranyl diphosphate = (-)-sabinene + diphosphate

Systematic name: geranyl-diphosphate diphosphate-lyase [cyclizing, (-)-sabinene-forming]

Comments: Requires Mg^{2+}. Isolated from *Pinus contorta* (lodgepole pine) as cyclase I [1200] and from *Conocephalum conicum* (liverwort) [1069].

References: [1200, 1069]

[EC 4.2.3.109 created 2012]

EC 4.2.3.110

Accepted name: (+)-sabinene synthase

Reaction: geranyl diphosphate = (+)-sabinene + diphosphate

Other name(s): SS

Systematic name: geranyl-diphosphate diphosphate-lyase [cyclizing, (+)-sabinene-forming]

Comments: Isolated from *Salvia officinalis* (sage). The recombinant enzyme gave 63% (+)-sabinene, 21% γ-terpinene, and traces of other monoterpenoids. See EC 4.2.3.114 γ-terpinene synthase.

References: [1472, 1069]

[EC 4.2.3.110 created 2012]

EC 4.2.3.111

Accepted name: (-)-α-terpineol synthase
Reaction: geranyl diphosphate + H_2O = (-)-α-terpineol + diphosphate
Systematic name: geranyl-diphosphate diphosphate-lyase [cyclizing, (-)-α-terpineol-forming]
Comments: The enzyme has been characterized from *Vitis vinifera* (grape). Also forms some 1,8-cineole and traces of other monoterpenoids.
References: [879, 852]

[EC 4.2.3.111 created 2012]

EC 4.2.3.112

Accepted name: (+)-α-terpineol synthase
Reaction: geranyl diphosphate + H_2O = (+)-α-terpineol + diphosphate
Systematic name: geranyl-diphosphate diphosphate-lyase [cyclizing, (+)-α-terpineol-forming]
Comments: The enzyme has been characterized from *Santalum album* (sandalwood). Also forms some (-)-limonene and traces of other monoterpenoids. See EC 4.2.3.16 (4*S*)-limonene synthase.
References: [644]

[EC 4.2.3.112 created 2012]

EC 4.2.3.113

Accepted name: terpinolene synthase
Reaction: geranyl diphosphate = terpinolene + diphosphate
Other name(s): ag9; PmeTPS2; LaLIMS_RR
Systematic name: geranyl-diphosphate diphosphate-lyase (cyclizing, terpinolene-forming)
Comments: Requires Mg^{2+}. Mn^{2+} is less effective and product ratio changes. Forms traces of other monoterpenoids.
References: [269, 112, 373, 587, 783]

[EC 4.2.3.113 created 2012]

EC 4.2.3.114

Accepted name: γ-terpinene synthase
Reaction: geranyl diphosphate = γ-terpinene + diphosphate
Other name(s): OvTPS2; ClcTS
Systematic name: geranyl-diphosphate diphosphate-lyase (cyclizing, γ-terpinene-forming)
Comments: Isolated from *Thymus vulgaris* (thyme) [21, 776], *Citrus limon* (lemon) [853], *Citrus unshiu* (satsuma) [1331] and *Origanum vulgare* (oregano) [263]. Requires Mg^{2+}. Mn^{2+} less effective. The reaction involves a 1,2-hydride shift. The 5-*pro-S* hydrogen of geranyl diphosphate is lost. Traces of several other monoterpenoids are formed in addition to γ-terpinene.
References: [21, 776, 853, 1331, 263]

[EC 4.2.3.114 created 2012]

EC 4.2.3.115

Accepted name: α-terpinene synthase
Reaction: geranyl diphosphate = α-terpinene + diphosphate
Systematic name: geranyl-diphosphate diphosphate-lyase (cyclizing, α-terpinene-forming)
Comments: The enzyme has been characterized from *Dysphania ambrosioides* (American wormseed). Requires Mg^{2+}. Mn^{2+} is less effective. The enzyme will also use (3*R*)-linalyl diphosphate. The reaction involves a 1,2-hydride shift. The 1-*pro-S* hydrogen of geranyl diphosphate is lost.
References: [1098, 776]

[EC 4.2.3.115 created 2012]

EC 4.2.3.116

Accepted name: (+)-camphene synthase

Reaction: geranyl diphosphate = (+)-camphene + diphosphate

Systematic name: geranyl-diphosphate diphosphate-lyase [cyclizing, (+)-camphene-forming]

Comments: Cyclase I of *Salvia officinalis* (sage) gives about equal parts (+)-camphene and (+)-α-pinene. (3*R*)-Linalyl diphosphate can also be used by the enzyme in preference to (3*S*)-linalyl diphosphate. Requires Mg^{2+} (preferred to Mn^{2+}). See also EC 4.2.3.121 (+)-α-pinene synthase.

References: [423, 270, 1434, 1110]

[EC 4.2.3.116 created 2012]

EC 4.2.3.117

Accepted name: (-)-camphene synthase

Reaction: geranyl diphosphate = (-)-camphene + diphosphate

Other name(s): CS

Systematic name: geranyl-diphosphate diphosphate-lyase [cyclizing, (-)-camphene-forming]

Comments: (-)-Camphene is the major product in *Abies grandis* (grand fir) with traces of other monoterpenoids [112]. In *Pseudotsuga menziesii* (Douglas-fir) there are about equal parts of (-)-camphene and (-)-α-pinene with traces of four other monoterpenoids [587, 591]. In *Solanum lycopersicum* (tomato) tricyclene, β-myrcene, limonene, and traces of several other monoterpenoids are also formed [370]. See also EC 4.2.3.15 myrcene synthase, EC 4.2.3.16 (4*S*)-limonene synthase, EC 4.2.3.119 (-)-α-pinene synthase and EC 4.2.3.105 tricyclene synthase.

References: [112, 587, 591, 370]

[EC 4.2.3.117 created 2012]

EC 4.2.3.118

Accepted name: 2-methylisoborneol synthase

Reaction: (*E*)-2-methylgeranyl diphosphate + H_2O = 2-methylisoborneol + diphosphate

Other name(s): sco7700; 2-MIB cyclase; MIB synthase; MIBS

Systematic name: (*E*)-2-methylgeranyl-diphosphate diphosphate-lyase (cyclizing, 2-methylisoborneol-forming)

Comments: The product, 2-methylisoborneol, is a characteristc odiferous compound with a musty smell produced by soil microorganisms.

References: [1439, 729, 440]

[EC 4.2.3.118 created 2012]

EC 4.2.3.119

Accepted name: (-)-α-pinene synthase

Reaction: geranyl diphosphate = (-)-α-pinene + diphosphate

Other name(s): (-)-α-pinene/(-)-camphene synthase; (-)-α-pinene cyclase

Systematic name: geranyl-diphosphate diphosphate-lyase [cyclizing, (-)-α-pinene-forming]

Comments: Cyclase II of *Salvia officinalis* (sage) gives about equal parts (-)-α-pinene, (-)-β-pinene and (-)-camphene, plus traces of other monoterpenoids. (3*S*)-Linalyl diphosphate can also be used by the enzyme in preference to (3*R*)-linalyl diphosphate. The 4-pro-*S*-hydrogen of geranyl diphosphate is lost. Requires Mg^{2+} (preferred to Mn^{2+}) [423, 272, 270, 269, 1110, 850]. The enzyme from *Abies grandis* (grand fir) gives roughly equal parts (-)-α-pinene and (-)-β-pinene. However the clone ag11 gave 35% (-)-limonene, 24% (-)-α-pinene and 20% (-)-β-phellandrene. It requires Mn^{2+} and K^{+} (Mg^{2+} is ineffective) [801, 114, 112, 591]. Synthase I from *Pinus taeda* (loblolly pine) produces (-)-α-pinene with traces of (-)-β-pinene and requires Mn^{2+} (preferred to Mg^{2+}) [1077, 1078]. The enzyme from *Picea sitchensis* (Sika spruce) forms 70% (-)-α-pinene and 30% (-)-β-pinene [914]. The recombinant PmeTPS1 enzyme from *Pseudotsuga menziesii* (Douglas fir) gave roughly equal proportions of (-)-α-pinene and (-)-camphene plus traces of other monoterpenoids [587]. See also EC 4.2.3.120, (-)-β-pinene synthase; EC 4.2.3.117, (-)-camphene synthase; EC 4.2.3.16, (-)-limonene synthase; and EC 4.2.3.52, (-)-β-phellandrene synthase.

References: [423, 272, 270, 269, 1110, 850, 801, 114, 112, 591, 1077, 1078, 914, 587]

[EC 4.2.3.119 created 2012]

EC 4.2.3.120

Accepted name: (-)-β-pinene synthase

Reaction: geranyl diphosphate = (-)-β-pinene + diphosphate

Other name(s): β-geraniolene synthase; (-)-(1*S*,5*S*)-pinene synthase; geranyldiphosphate diphosphate lyase (pinene forming)

Systematic name: geranyl-diphosphate diphosphate-lyase [cyclizing, (-)-β-pinene-forming]

Comments: Cyclase II of *Salvia officinalis* (sage) produces about equal parts (-)-α-pinene, (-)-β-pinene and (-)-camphene, plus traces of other monoterpenoids. The enzyme, which requires Mg^{2+} (preferred to Mn^{2+}), can also use (3*S*)-Linalyl diphosphate (preferred to (3*R*)-linalyl diphosphate) [272, 269, 270, 1110]. The enzyme from *Abies grandis* (grand fir) produces roughly equal parts of (-)-α-pinene and (-)-β-pinene [441, 801, 114, 591]. Cyclase IV from *Pinus contorta* (lodgepole pine) produces 63% (-)-β-pinene, 26% 3-carene, and traces of α-pinene [1201]. Synthase III from *Pinus taeda* (loblolly pine) forms (-)-β-pinene with traces of α-pinene and requires Mn^{2+} and K^{+} (Mg^{2+} is ineffective) [1077]. A cloned enzyme from *Artemisia annua* (sweet wormwood) gave (-)-β-pinene with traces of (-)-α-pinene [850]. The enzyme from Picea sitchensis (Sika spruce) forms 30% (-)-β-pinene and 70% (-)-α-pinene [914]. See also EC 4.2.3.119, (-)-α-pinene synthase, EC 4.2.3.117, (-)-camphene synthase, and EC 4.2.3.107 (+)-3-carene synthase.

References: [272, 269, 270, 1110, 850, 441, 801, 114, 591, 1201, 1077, 914]

[EC 4.2.3.120 created 2012]

EC 4.2.3.121

Accepted name: (+)-α-pinene synthase

Reaction: geranyl diphosphate = (+)-α-pinene + diphosphate

Other name(s): (+)-α-pinene cyclase; cyclase I

Systematic name: geranyl-diphosphate diphosphate-lyase [cyclizing, (+)-α-pinene-forming]

Comments: Cyclase I of *Salvia officinalis* (sage) gives about equal parts (+)-α-pinene and (+)-camphene, whereas cyclase III gives about equal parts of (+)-α-pinene and (+)-β-pinene. (3*R*)-Linalyl diphosphate can also be used by the enzyme in preference to (3*S*)-linalyl diphosphate. The 4-*pro*-*R*-hydrogen of geranyl diphosphate is lost. Requires Mg^{2+} (preferred to Mn^{2+}) [423, 270, 1434, 1110]. With synthase II of *Pinus taeda* (loblolly pine) (+)-α-pinene was the only product [1077, 1078]. Requires Mn^{2+} (preferred to Mg^{2+}). See also EC 4.2.3.122, (+)-β-pinene synthase, and EC 4.2.3.116, (+)-camphene synthase.

References: [423, 270, 1434, 1110, 1077, 1078]

[EC 4.2.3.121 created 2012]

EC 4.2.3.122

Accepted name: (+)-β-pinene synthase

Reaction: geranyl diphosphate = (+)-β-pinene + diphosphate

Other name(s): (+)-pinene cyclase; cyclase III

Systematic name: geranyl-diphosphate diphosphate-lyase [(+)-β-pinene-forming]

Comments: Cyclase III from *Salvia officinalis* (sage) gives roughly equal parts of (+)-β-pinene and (+)-α-pinene. See EC 4.2.3.121, (+)-α-pinene synthase.

References: [1434, 1110]

[EC 4.2.3.122 created 2012]

EC 4.2.3.123

Accepted name: β-sesquiphellandrene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = β-sesquiphellandrene + diphosphate

Other name(s): Tps1; Os08g07100 (gene name)

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, β-sesquiphellandrene-forming)

References: [1571]

[EC 4.2.3.123 created 2012]

EC 4.2.3.124

Accepted name: 2-deoxy-*scyllo*-inosose synthase

Reaction: D-glucose 6-phosphate = 2-deoxy-L-*scyllo*-inosose + phosphate

Other name(s): *btrC* (gene name); *neoC* (gene name); *kanC* (gene name)

Systematic name: D-glucose-6-phosphate phosphate-lyase (2-deoxy-L-*scyllo*-inosose-forming)

Comments: Requires Co^{2+} [747]. Involved in the biosynthetic pathways of several clinically important aminocyclitol antibiotics, including kanamycin, butirosin, neomycin and ribostamycin. Requires an NAD$^+$ cofactor, which is transiently reduced during the reaction [750, 585]. The enzyme from the bacterium *Bacillus circulans* forms a complex with the glutamine amidotransferase subunit of pyridoxal 5′-phosphate synthase (EC 4.3.3.6), which appears to stabilize the complex [1348, 1349].

References: [750, 747, 749, 585, 1373, 1348, 1349]

[EC 4.2.3.124 created 2012]

EC 4.2.3.125

Accepted name: α-muurolene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = α-muurolene + diphosphate

Other name(s): Cop3

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, α-muurolene-forming)

Comments: The enzyme has been characterized from the fungus *Coprinus cinereus*. Also gives germacrene A and γ-muurolene, see EC 4.2.3.23, germacrene-A synthase and EC 4.2.3.126, γ-muurolene synthase.

References: [4, 843]

[EC 4.2.3.125 created 2012]

EC 4.2.3.126

Accepted name: γ-muurolene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = γ-muurolene + diphosphate

Other name(s): Cop3

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lase (cyclizing, γ-muurolene-forming)

Comments: The enzyme has been characterized from the fungus *Coprinus cinereus*. Also gives germacrene A and α-muurolene, see EC 4.2.3.23, germacrene-A synthase and EC 4.2.3.125, α-muurolene synthase.

References: [4, 843]

[EC 4.2.3.126 created 2012]

EC 4.2.3.127

Accepted name: β-copaene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = β-copaene + diphosphate
Other name(s): cop4
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, β-copaene-forming)
Comments: Isolated from the fungus *Coprinus cinereus*. The enzyme also forms (+)-δ-cadinene, β-cubebene, (+)-sativene and traces of several other sequiterpenoids [4, 842, 843]. β-Copaene is formed in the presence of Mg^{2+} but not Mn^{2+} [842]. See EC 4.2.3.13, (+)-δ-cadinene synthase, EC 4.2.3.128, β-cubebene synthase, and EC 4.2.3.129, (+)-sativene synthase.
References: [4, 842, 843]

[EC 4.2.3.127 created 2012]

EC 4.2.3.128

Accepted name: β-cubebene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = β-cubebene + diphosphate
Other name(s): cop4; Mg25
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, β-cubebene-forming)
Comments: Isolated from the fungus *Coprinus cinereus*. The enzyme also forms (+)-δ-cadinene, β-copaene, (+)-sativene and traces of several other sequiterpenoids [4, 842, 843]. It is found in many higher plants such as *Magnolia grandiflora* (Southern Magnolia) together with germacrene A [791]. See EC 4.2.3.13, (+)-δ-cadinene synthase, EC 4.2.3.127, β-copaene synthase, EC 4.2.3.129, (+)-sativene synthase, and EC 4.2.3.23, germacrene A synthase.
References: [791, 4, 842, 843]

[EC 4.2.3.128 created 2012]

EC 4.2.3.129

Accepted name: (+)-sativene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-sativene + diphosphate
Other name(s): cop4
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, (+)-sativene-forming)
Comments: Isolated from the fungus *Coprinus cinereus*. The enzyme also forms (+)-δ-cadinene, β-copaene, β-cubebene, and traces of several other sequiterpenoids. See EC 4.2.3.13, (+)-δ-cadinene synthase, EC 4.2.3.127, β-copaene synthase, and EC 4.2.3.128, β-cubebene synthase.
References: [4, 842, 843]

[EC 4.2.3.129 created 2012]

EC 4.2.3.130

Accepted name: tetraprenyl-β-curcumene synthase
Reaction: *all-trans*-heptaprenyl diphosphate = tetraprenyl-β-curcumene + diphosphate
Other name(s): *ytpB* (gene name)
Systematic name: *all-trans*-heptaprenyl-diphosphate diphosphate-lyase (cyclizing, tetraprenyl-β-curcumene-forming)
Comments: Isolated from *Bacillus subtilis*. This sesquarterpene is present in a number of *Bacillus* species.
References: [1196]

[EC 4.2.3.130 created 2012]

EC 4.2.3.131

Accepted name: miltiradiene synthase
Reaction: (+)-copalyl diphosphate = miltiradiene + diphosphate
Other name(s): SmMDS; SmiKSL; *RoKSL*
Systematic name: (+)-copalyl-diphosphate diphosphate-lyase (cyclizing, miltiradiene-forming)
Comments: Isolated from the plants *Rosmarinus officinalis* (rosemary) and *Salvia miltiorrhiza*. The enzyme from the plant *Selaginella moellendorffii* is mutifunctional and also catalyses EC 5.5.1.12, copalyl diphosphate synthase [1319].
References: [424, 1319, 147]

[EC 4.2.3.131 created 2012]

EC 4.2.3.132

Accepted name: neoabietadiene synthase
Reaction: (+)-copalyl diphosphate = neoabietadiene + diphosphate
Other name(s): TPS-LAS
Systematic name: (+)-copaly-diphosphate diphosphate-lyase (cyclizing, neoabietadiene-forming)
Comments: Isolated from *Abies grandis* (grand fir) [1070]. This class I enzyme forms about equal proportions of abietadiene, levopimaradiene and neoabietadiene. See also EC 4.2.3.18, abieta-7,13-diene synthase and EC 4.2.3.32, levopimaradiene synthase. An X-ray study of this multifunctional enzyme showed that the class I activity is in the α domain, while (+)-copalyl diphosphate synthase activity (EC 5.5.1.12, a class II activity) is in the β and γ domains [1567]. In *Pinus taeda* (loblolly pine) the major product is levopimaradiene, with less abietadiene and neoabietadiene [1160].
References: [1070, 1567, 1160]

[EC 4.2.3.132 created 2012]

EC 4.2.3.133

Accepted name: α-copaene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (-)-α-copaene + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, α-copaene-forming)
Comments: Isolated from *Helianthus annuus* (sunflower). The enzyme also produces β-caryophyllene, δ-cadinene and traces of other sesquiterpenoids. See EC 4.2.3.13 (+)-δ-cadinene synthase, EC 4.2.3.57 (-)-β-caryophyllene synthase.
References: [453, 1482]

[EC 4.2.3.133 created 2012]

EC 4.2.3.134

Accepted name: 5-phosphooxy-L-lysine phospho-lyase
Reaction: (5*R*)-5-phosphooxy-L-lysine + H_2O = (*S*)-2-amino-6-oxohexanoate + NH_3 + phosphate
Other name(s): 5-phosphohydroxy-L-lysine ammoniophospholyase; AGXT2L2 (gene name); (5*R*)-5-phosphonooxy-L-lysine phosphate-lyase (deaminating; (*S*)-2-amino-6-oxohexanoate-forming); 5-phosphonooxy-L-lysine phospho-lyase
Systematic name: (5*R*)-5-phosphooxy-L-lysine phosphate-lyase (deaminating; (*S*)-2-amino-6-oxohexanoate-forming)
Comments: A pyridoxal-phosphate protein. Has no activity with phosphoethanolamine (*cf.* EC 4.2.3.2, ethanolamine-phosphate phospho-lyase).
References: [1393, 279]

[EC 4.2.3.134 created 2012]

EC 4.2.3.135

Accepted name: Δ^6-protoilludene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = Δ^6-protoilludene + diphosphate
Other name(s): 6-protoilludene synthase
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, Δ^6-protoilludene-forming)
Comments: Isolated from the fungus *Armillaria gallica*. Δ^6-Protoilludene is the first step in the biosynthesis of the melleolides.
References: [360]

[EC 4.2.3.135 created 2012]

EC 4.2.3.136

Accepted name: α-isocomene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (-)-α-isocomene + diphosphate
Other name(s): MrTPS2
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, (-)-α-isocomene-forming)
Comments: Isolated from the roots of the plant *Matricaria chamomilla* var. recutita (chamomile). The enzyme also produced traces of five other sesquiterpenoids.
References: [601]

[EC 4.2.3.136 created 2012]

EC 4.2.3.137

Accepted name: (*E*)-2-*epi*-β-caryophyllene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (*E*)-2-*epi*-β-caryophyllene + diphosphate
Other name(s): 2-*epi*-(*E*)-β-caryophyllene synthase; SmMTPSL26
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, (*E*)-2-*epi*-β-caryophyllene-forming)
Comments: Isolated from the plant *Selaginella moellendorfii*. The enzyme also gives two other sesquiterpenoids.
References: [803]

[EC 4.2.3.137 created 2012]

EC 4.2.3.138

Accepted name: (+)-*epi*-α-bisabolol synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = (+)-*epi*-α-bisabolol + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, (+)-*epi*-α-bisabolol-forming)
Comments: Isolated from the plant *Phyla dulcis* (Aztec sweet herb). (+)-*epi*-α-Bisabolol is the precursor of the sweetener hernandulcin.
References: [48]

[EC 4.2.3.138 created 2012]

EC 4.2.3.139

Accepted name: valerena-4,7(11)-diene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = valerena-4,7(11)-diene + diphosphate
Other name(s): VoTPS2; VoTPS7
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, valerena-4,7(11)-diene-forming)
Comments: Isolated from the plant *Valeriana officinalis* (valerian). Note that due to a different numbering system the product is also known as valerena-1,10-diene.
References: [1109, 1508]

[EC 4.2.3.139 created 2012]

EC 4.2.3.140

Accepted name: *cis*-abienol synthase

Reaction: (13*E*)-8α-hydroxylabd-13-en-15-yl diphosphate = *cis*-abienol + diphosphate

Other name(s): *Z*-abienol synthase; CAS; ABS

Systematic name: (13*E*)-8α-hydroxylabd-13-en-15-yl-diphosphate-lyase (*cis*-abienol-forming)

Comments: Isolated from the plants *Abies balsamea* (balsam fir) [1546] and *Nicotiana tabacum* (tobacco) [1188].

References: [1546, 1188]

[EC 4.2.3.140 created 2012]

EC 4.2.3.141

Accepted name: sclareol synthase

Reaction: (13*E*)-8α-hydroxylabd-13-en-15-yl diphosphate + H_2O = sclareol + diphosphate

Other name(s): SS

Systematic name: (13*E*)-8α-hydroxylabd-13-en-15-yl-diphosphate-lyase (sclareol-forming)

Comments: Isolated from the plant *Salvia sclarea* (clary sage). Originally thought to be synthesized in one step from geranylgeranyl diphosphate it is now known to require two enzymes, EC 4.2.1.133, copal-8-ol diphosphate synthase and EC 4.2.3.141, sclareol synthase. Sclareol is used in perfumery.

References: [184]

[EC 4.2.3.141 created 2013, modified 2017]

EC 4.2.3.142

Accepted name: 7-epizingiberene synthase [(2Z,6*Z*)-farnesyl diphosphate cyclizing]

Reaction: (2*Z*,6*Z*)-farnesyl diphosphate = 7-epizingiberene + diphosphate

Other name(s): *ShZIS* (gene name)

Systematic name: (2Z,6*Z*)-farnesyl-diphosphate lyase (cyclizing; 7-epizingiberene-forming)

Comments: Isolated from the plant *Solanum habrochaites*. 7-Epizingiberene is a whitefly repellant.

References: [100]

[EC 4.2.3.142 created 2013]

EC 4.2.3.143

Accepted name: kunzeaol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = kunzeaol + diphosphate

Other name(s): TgTPS2 (gene name)

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (kunzeaol-forming)

Comments: Isolated from the root of the plant *Thapsia garganica*. The enzyme also produces germacrene D, bicyclogermacrene and traces of other sesquiterpenoids. See EC 4.2.3.77, (+)-germacrene D synthase and EC 4.2.3.100, bicyclogermacrene synthase.

References: [1085]

[EC 4.2.3.143 created 2013]

EC 4.2.3.144

Accepted name: geranyllinalool synthase

Reaction: geranylgeranyl diphosphate + H_2O = (6*E*,10*E*)-geranyllinalool + diphosphate

Other name(s): TPS04/GES; GES

Systematic name: geranylgeranyl-diphosphate diphosphate-lyase [(*E*,*E*)-geranyllinalool-forming]

Comments: The enzyme is a component of the herbivore-induced indirect defense system. The product, (*E*,*E*)-geranyllinalool, is a precursor to the volatile compound 4,8,12-trimethyl-1,3,7,11-tridecatetraene (TMTT), which is released by many plants in response to damage.

References: [543, 46]

[EC 4.2.3.144 created 2013]

EC 4.2.3.145

Accepted name: ophiobolin F synthase

Reaction: (2*E*,6*E*,10*E*,14*E*)-geranylfarnesyl diphosphate + H_2O = ophiobolin F + diphosphate

Systematic name: (2*E*,6*E*,10*E*,14*E*)-geranylfarnesyl-diphosphate diphosphate-lyase (cyclizing, ophiobolin-F-forming)

Comments: Isolated from the fungus *Aspergillus clavatus*. The product is a sesterterpenoid (C_{25} terpenoid).

References: [224]

[EC 4.2.3.145 created 2014]

EC 4.2.3.146

Accepted name: cyclooctat-9-en-7-ol synthase

Reaction: geranylgeranyl diphosphate + H_2O = cyclooctat-9-en-7-ol + diphosphate

Other name(s): *cotB*2

Systematic name: geranylgeranyl-diphosphate diphosphate-lyase (cyclooctat-9-en-7-ol-forming)

Comments: Requires Mg^{2+}. Isolated from the bacterium *Streptomyces melanosporofaciens*, where it is part of the biosynthesis of cyclooctatin, a potent inhibitor of lysophospholipase.

References: [703, 1555, 622, 917, 1379]

[EC 4.2.3.146 created 2014]

EC 4.2.3.147

Accepted name: pimaradiene synthase

Reaction: (+)-copalyl diphosphate = pimara-8(14),15-diene + diphosphate

Other name(s): PbmPIM1; PcmPIM1

Systematic name: (+)-copalyl diphosphate-lyase (pimara-8(14),15-diene-forming)

Comments: Isolated from the plants *Pinus banksiana* (jack pine) and *Pinus contorta* (lodgepole pine).

References: [489]

[EC 4.2.3.147 created 2014]

EC 4.2.3.148

Accepted name: cembrene C synthase

Reaction: geranylgeranyl diphosphate = cembrene C + diphosphate

Other name(s): DtcycA (gene name)

Systematic name: geranylgeranyl-diphosphate diphosphate-lyase (cembrene-C-forming)

Comments: Requires Mg^{2+}. Isolated from the bacterium *Streptomyces* sp. SANK 60404. This bifunctional enzyme also produces (*R*)-nephthenol. See EC 4.2.3.149, nephthenol synthase.

References: [918]

[EC 4.2.3.148 created 2014]

EC 4.2.3.149

Accepted name: nephthenol synthase

Reaction: geranylgeranyl diphosphate + H_2O = (*R*)-nephthenol + diphosphate

Other name(s): DtcycA (gene name); DtcycB (gene name)

Systematic name: geranylgeranyl-diphosphate diphosphate-lyase [(*R*)-nephthenol-forming]

Comments: Requires Mg^{2+}. Two isozymes with this activity were isolated from the bacterium *Streptomyces* sp. SANK 60404. The enzyme encoded by the DtcycA gene also produces cembrene C (see EC 4.2.3.148, cembrene C synthase), while the enzyme encoded by the DtcycB gene also produces (*R*)-cembrene A and (1*S*,4*E*,8*E*,12*E*)-2,2,5,9,13-pentamethylcyclopentadeca-4,8,12-trien-1-ol (see EC 4.2.3.150, cembrene A synthase, and EC 4.2.3.151, pentamethylcyclopentadecatrienol synthase).

References: [918]

[EC 4.2.3.149 created 2014]

EC 4.2.3.150

Accepted name: cembrene A synthase

Reaction: geranylgeranyl diphosphate = (*R*)-cembrene A + diphosphate

Other name(s): DtcycB (gene name)

Systematic name: geranylgeranyl-diphosphate diphosphate-lyase [(*R*)-cembrene-A-forming]

Comments: Requires Mg^{2+}. Isolated from the bacterium *Streptomyces* sp. SANK 60404. This trifunctional enzyme, which contains a [4Fe-4S] cluster, also produces (*R*)-nephthenol and (1*S*,4*E*,8*E*,12*E*)-2,2,5,9,13-pentamethylcyclopentadeca-4,8,12-trien-1-ol. See EC 4.2.3.149, nephthenol synthase and EC 4.2.3.151, pentamethylcyclopentadecatrienol synthase.

References: [918]

[EC 4.2.3.150 created 2014]

EC 4.2.3.151

Accepted name: pentamethylcyclopentadecatrienol synthase

Reaction: geranylgeranyl diphosphate + H_2O = (1*S*,4*E*,8*E*,12*E*)-2,2,5,9,13-pentamethylcyclopentadeca-4,8,12-trien-1-ol + diphosphate

Other name(s): DtcycB (gene name)

Systematic name: geranylgeranyl-diphosphate diphosphate-lyase [(1*S*,4*E*,8*E*,12*E*)-2,2,5,9,13-pentamethylcyclopentadeca-4,8,12-trien-1-ol-forming]

Comments: Requires Mg^{2+}. Isolated from the bacterium *Streptomyces* sp. SANK 60404. This trifunctional enzyme, which contains a [4Fe-4S] cluster, also produces (*R*)-nephthenol and (*R*)-cembrene A. See EC 4.2.3.150, cembrene A synthase and EC 4.2.3.149, nephthenol synthase.

References: [918]

[EC 4.2.3.151 created 2014]

EC 4.2.3.152

Accepted name: 2-*epi*-5-*epi*-valiolone synthase

Reaction: α-D-sedoheptulopyranose 7-phosphate = 2-*epi*-5-*epi*-valiolone + phosphate

Other name(s): AcbC; ValA; CetA; SalQ; C_7-cyclitol synthase

Systematic name: α-D-sedoheptulopyranose-7-phosphate phosphate-lyase (cyclizing; 2-*epi*-5-*epi*-valiolone-forming)

Comments: The enzyme is highly specific for α-D-sedoheptulopyranose 7-phosphate. It requires a divalent metal ion (Zn^{2+} or Co^{2+}) and an NAD^+ cofactor, which is transiently reduced during the reaction. The enzyme is involved in the biosynthesis of C_7N-aminocyclitol natural products, such as the valienamine moiety of the antidiabetic drug acarbose and the crop protectant validamycin A. *cf.* EC 4.2.3.155, 2-*epi*-valiolone synthase and EC 4.2.3.154, demethyl-4-deoxygadusol synthase.

References: [1312, 1530, 1478, 229, 683]

[EC 4.2.3.152 created 2015, modified 2016]

EC 4.2.3.153

Accepted name: (5-formylfuran-3-yl)methyl phosphate synthase

Reaction: **2** D-glyceraldehyde 3-phosphate = (5-formylfuran-3-yl)methyl phosphate + phosphate + **2** H_2O

Other name(s): *mfnB* (gene name); 4-HFC-*P* synthase; 4-(hydroxymethyl)-2-furaldehyde phosphate synthase

Systematic name: D-glyceraldehyde-3-phosphate phosphate-lyase [D-glyceraldehyde-3-phosphate-adding; (5-formylfuran-3-yl)methyl-phosphate-forming]

Comments: The enzyme catalyses the reaction in the direction of producing (5-formylfuran-3-yl)methyl phosphate, an intermediate in the biosynthesis of methanofuran. The sequence of events starts with the removal of a phosphate group, followed by aldol condensation and cyclization. Methanofuran is a carbon-carrier cofactor involved in the first step of the methanogenic reduction of carbon dioxide by methanogenic archaea.

References: [940, 109, 1450]

[EC 4.2.3.153 created 2015 as EC 4.1.99.21, transferred 2015 to EC 4.2.3.153]

EC 4.2.3.154

Accepted name: demethyl-4-deoxygadusol synthase

Reaction: D-sedoheptulose 7-phosphate = demethyl-4-deoxygadusol + phosphate + H_2O

Other name(s): Nos2 (gene name); Anb2 (gene name)

Systematic name: D-sedoheptulose-7-phosphate phosphate-lyase (cyclizing; demethyl-4-deoxygadusol-forming)

Comments: The enzyme, characterized from the cyanobacterium *Nostoc punctiforme* PCC 73102, is involved in the biosynthesis of the sunscreen compound shinorine. It requires a divalent metal ion (Zn^{2+} or Co^{2+}) and an NAD^+ cofactor, which is transiently reduced during the reaction. *cf.* EC 4.2.3.152, 2-*epi*-5-*epi*-valiolone synthase and EC 4.2.3.155, 2-*epi*-valiolone synthase.

References: [71, 42]

[EC 4.2.3.154 created 2016]

EC 4.2.3.155

Accepted name: 2-*epi*-valiolone synthase

Reaction: D-sedoheptulose 7-phosphate = 2-*epi*-valiolone + phosphate

Systematic name: D-sedoheptulose-7-phosphate phosphate-lyase (cyclizing; 2-*epi*-valiolone-forming)

Comments: The enzyme, characterized from the bacteria *Actinosynnema mirum* and *Stigmatella aurantiaca* DW4/3-1, produces 2-*epi*-valiolone, which is believed to function as a precursor in aminocyclitol biosynthesis. It requires a divalent metal ion (Zn^{2+} or Co^{2+}) and an NAD^+ cofactor, which is transiently reduced during the reaction. *cf.* EC 4.2.3.152, 2-*epi*-5-*epi*-valiolone synthase and EC 4.2.3.154, demethyl-4-deoxygadusol synthase.

References: [42]

[EC 4.2.3.155 created 2016]

EC 4.2.3.156

Accepted name: hydroxysqualene synthase

Reaction: presqualene diphosphate + H_2O = hydroxysqualene + diphosphate

Other name(s): *hpnC* (gene name)

Systematic name: presqualene diphosphate diphosphate-lyase (adding water; hydroxyasqualene-forming)

Comments: This enzyme, isolated from the bacteria *Rhodopseudomonas palustris* and *Zymomonas mobilis*, participates, along with EC 2.5.1.103, presqualene diphosphate synthase, and EC 1.17.8.1, hydroxysqualene dehydroxylase, in the conversion of *all-trans*-farnesyl diphosphate to squalene. Eukaryotes achieve the same goal in a single step, catalysed by EC 2.5.1.21, squalene synthase.

References: [1053]

[EC 4.2.3.156 created 2016]

EC 4.2.3.157

Accepted name: (+)-isoafricanol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = (+)-isoafricanol + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [cyclizing, (+)-isoafricanol-forming]

Comments: (+)-Isoafricanol is a sesquiterpene alcohol. Its synthesis has been shown to occur in the bacteria *Streptomyces violaceusniger* and *Streptomyces malaysiensis*.

References: [1149, 1119]

[EC 4.2.3.157 created 2017]

EC 4.2.3.158

Accepted name: (–)-spiroviolene synthase

Reaction: geranylgeranyl diphosphate = (–)-spiroviolene + diphosphate

Systematic name: geranylgeranyl-diphosphate diphosphate-lyase [cyclizing, (–)-spiroviolene-forming]

Comments: The enzyme, which forms the diterpene (–)-spiroviolene, has been characterized from the bacterium *Streptomyces violens*.

References: [1117]

[EC 4.2.3.158 created 2017]

EC 4.2.3.159

Accepted name: tsukubadiene synthase

Reaction: geranylgeranyl diphosphate = tsukubadiene + diphosphate

Systematic name: geranylgeranyl-diphosphate diphosphate-lyase (cyclizing, tsukubadiene-forming)

Comments: The synthesis of the diterpene tsukubadiene has been shown to occur in the Actinobacterium *Streptomyces tsukubaensis*.

References: [1493, 1117]

[EC 4.2.3.159 created 2017]

EC 4.2.3.160

Accepted name: (2*S*,3*R*,6*S*,9*S*)-(–)-protoillud-7-ene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = (2*S*,3*R*,6*S*,9*S*)-(–)-protoillud-7-ene + diphosphate

Other name(s): TPS6 (gene name)

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [cyclizing, (2*S*,3*R*,6*S*,9*S*)-(–)-protoillud-7-ene-forming]

Comments: The enzyme has been described from the slime-mould *Dictyostelium discoideum*. It is specific for (2*E*,6*E*)-farnesyl diphosphate. While the major product is the sequiterpene (2*S*,3*R*,6*S*,9*S*)-(–)-protoillud-7-ene, traces of pentalenene are also formed.

References: [219, 1118]

[EC 4.2.3.160 created 2017]

EC 4.2.3.161

Accepted name: (3*S*)-(+)-asterisca-2(9),6-diene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = (3*S*)-(+)-asterisca-2(9),6-diene + diphosphate

Other name(s): TPS2 (gene name)

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [cyclizing, (3*S*)-(+)-asterisca-2(9),6-diene-forming]

Comments: The sequiterpene (3*S*)-(+)-asterisca-2(9),6-diene has been shown to be synthezised in the slime-mould *Dictyostelium discoideum*. The enzyme is specific for (2*E*,6*E*)-farnesyl diphosphate.

References: [219, 1118]

[EC 4.2.3.161 created 2017]

EC 4.2.3.162

Accepted name: (–)-α-amorphene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (–)-α-amorphene + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [cyclizing, (–)-α-amorphene-forming]
Comments: The enzyme, found in the bacterium *Streptomyces viridochromogenes*, is specific for (2*E*,6*E*)-farnesyl diphosphate and produces only (–)-α-amorphene.
References: [1114, 1155, 1120]

[EC 4.2.3.162 created 2017]

EC 4.2.3.163

Accepted name: (+)-corvol ether B synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = (+)-corvol ether B + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [cyclizing, (+)-corvol ether B-forming]
Comments: The enzyme, which forms the sesquiterpene (+)-corvol ether B, has been reported from the bacterium *Kitasatospora setae*.
References: [1116, 1115, 1155]

[EC 4.2.3.163 created 2017]

EC 4.2.3.164

Accepted name: (+)-eremophilene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-eremophilene + diphosphate
Other name(s): STC3 (gene name); *geoA* (gene name)
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [cyclizing, (+)-eremophilene-forming]
Comments: The enzyme has been identified in the myxobacterium *Sorangium cellulosum* and in the fungus *Fusarium fujikuroi*.
References: [1208, 158]

[EC 4.2.3.164 created 2017]

EC 4.2.3.165

Accepted name: (1*R*,4*R*,5*S*)-(–)-guaia-6,10(14)-diene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (1*R*,4*R*,5*S*)-(–)-guaia-6,10(14)-diene + diphosphate
Other name(s): STC5 (gene name)
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [cyclizing, (1*R*,4*R*,5*S*)-(–)-guaia-6,10(14)-diene-forming]
Comments: The original enzyme (STC5) from the fungus *Fusarium fujikuroi* is inactive because of a critically naturally occuring mutation that leads to an asparagine to lysine exchange in the NSE (Asn-Ser-Glu) triad, a highly conserved motif of type I terpene cyclases. Sequence correction by site-directed mutagenesis (K288N) restores activity.
References: [158]

[EC 4.2.3.165 created 2017]

EC 4.2.3.166

Accepted name: (+)-(1*E*,4*E*,6*S*,7*R*)-germacra-1(10),4-dien-6-ol synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = (+)-(1*E*,4*E*,6*S*,7*R*)-germacra-1(10),4-dien-6-ol + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [cyclizing, (+)-(1*E*,4*E*,6*S*,7*R*)-germacra-1(10),4-dien-6-ol-forming]
Comments: The enzyme has been identified in the bacterium *Streptomyces pratensis*. It is specific for (2*E*,6*E*)-farnesyl diphosphate.
References: [1113]

[EC 4.2.3.166 created 2017]

EC 4.2.3.167

Accepted name: dolabella-3,7-dien-18-ol synthase

Reaction: geranylgeranyl diphosphate + H_2O = (3*E*,7*E*)-dolabella-3,7-dien-18-ol + diphosphate

Other name(s): TPS20 (gene name)

Systematic name: geranylgeranyl-diphosphate diphosphate-lyase [cyclizing, (3*E*,7*E*)-dolabella-3,7-dien-18-ol-forming]

Comments: Isolated from an ecotype of the plant *Arabidopsis thaliana* from Cape Verde Islands. The enzyme also gives (3*E*,7*E*)-dolathalia-3,7,11-triene and traces of other terpenoids. *cf.* EC 4.2.3.168 dolathalia-3,7,11-triene synthase.

References: [1443]

[EC 4.2.3.167 created 2017]

EC 4.2.3.168

Accepted name: dolathalia-3,7,11-triene synthase

Reaction: geranylgeranyl diphosphate = (3*E*,7*E*)-dolathalia-3,7,11-triene + diphosphate

Other name(s): TPS20 (gene name)

Systematic name: geranylgeranyl-diphosphate diphosphate-lyase [cyclizing, (3*E*,7*E*)-dolathalia-3,7,11-triene-forming]

Comments: Isolated from an ecotype of the plant *Arabidopsis thaliana* from Cape Verde Islands. The enzyme also gives (3*E*,7*E*)-dolabella-3,7-dien-18-ol and traces of other terpenoids. *cf.* EC 4.2.3.167 dolabella-3,7-dien-18-ol synthase.

References: [1443]

[EC 4.2.3.168 created 2017]

EC 4.2.3.169

Accepted name: 7-*epi*-α-eudesmol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = 7-*epi*-α-eudesmol + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, 7-*epi*-α-eudesmol-forming)

Comments: The enzyme, found in the bacterium *Streptomyces viridochromogenes*, is specific for (2*E*,6*E*)-farnesyl diphosphate.

References: [1120]

[EC 4.2.3.169 created 2017]

EC 4.2.3.170

Accepted name: 4-*epi*-cubebol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = 4-*epi*-cubebol + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, 4-*epi*-cubebol-forming)

Comments: The enzyme, found in the bacterium *Streptosporangium roseum*, is specific for (2*E*,6*E*)-farnesyl diphosphate.

References: [1120]

[EC 4.2.3.170 created 2017]

EC 4.2.3.171

Accepted name: (+)-corvol ether A synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = (+)-corvol ether A + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [cyclizing, (+)-corvol ether A-forming]

Comments: The enzyme, which forms the sesquiterpene (+)-corvol ether A, has been reported from the bacterium *Kitasatospora setae*.

References: [1116, 1115, 1155]

[EC 4.2.3.171 created 2017]

EC 4.2.3.172

Accepted name: 10-*epi*-juneol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = 10-*epi*-juneol + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, 10-*epi*-juneol-forming)

Comments: Isolated from the plant *Inula hupehensis*. The enzyme also gives gives τ-cadinol and traces of other terpenoids, see EC 4.2.3.173, τ-cadinol synthase.

References: [458]

[EC 4.2.3.172 created 2017]

EC 4.2.3.173

Accepted name: τ-cadinol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = τ-cadinol + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, τ-cadinol-forming)

Comments: Isolated from the plant *Inula hupehensis*. The enzyme also gives 10-*epi*-juneol and traces of other terpenoids, see EC 4.2.3.172, 10-*epi*-juneol synthase. It has also been isolated from the plants maize (*Zea mays*) and lavender (*Lavandula angustifolia*).

References: [458, 649, 1144]

[EC 4.2.3.173 created 2017]

EC 4.2.3.174

Accepted name: (2*E*,6*E*)-hedycaryol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = (2*E*,6*E*)-hedycaryol + diphosphate

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [cyclizing, (2*E*,6*E*)-hedycaryol-forming]

Comments: Isolated from the plant *Camellia brevistyla*. See also EC 4.2.3.187, (2*Z*,6*E*)-hedycaryol synthase.

References: [522]

[EC 4.2.3.174 created 2017]

EC 4.2.3.175

Accepted name: 10-*epi*-cubebol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = 10-*epi*-cubebol + diphosphate

Other name(s): sce6369

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, 10-*epi*-cubebol-forming)

Comments: Isolated from the bacterium *Sorangium cellulosum* So ce56. The enzyme is also responsible for the formation of trace amounts of many other sesquiterpenes, mainly cadinanes and cubebanes.

References: [1207]

[EC 4.2.3.175 created 2017]

EC 4.2.3.176

Accepted name: sesterfisherol synthase

Reaction: (2*E*,6*E*,10*E*,14*E*)-geranylfarnesyl diphosphate + H_2O = sesterfisherol + diphosphate

Other name(s): NfSS

Systematic name: (2*E*,6*E*,10*E*,14*E*)-geranylfarnesyl-diphosphate diphosphate-lyase (cyclizing, sesterfisherol-forming)

Comments: Isolated from the fungus *Neosartorya fischeri*.

References: [1507]

[EC 4.2.3.176 created 2017]

EC 4.2.3.177

Accepted name: β-thujene synthase

Reaction: geranyl diphosphate = β-thujene + diphosphate

Other name(s): CoTPS1

Systematic name: geranyl-diphosphate diphosphate-lyase (cyclizing, β-thujene-forming)

Comments: Isolated from the plant *Cananga odorata* var. *fruticosa* (ylang ylang). The enzyme forms roughly equal proportions of β-thujene, sabinene, β-pinene and α-terpinene see EC 4.2.3.109/EC 4.2.3.110 sabinene synthase, EC 4.2.3.120/EC 4.2.3.122 β-pinene synthase, EC 4.2.3.115 α-terpinene synthase.

References: [636]

[EC 4.2.3.177 created 2017]

EC 4.2.3.178

Accepted name: stellata-2,6,19-triene synthase

Reaction: (2*E*,6*E*,10*E*,14*E*)-geranylfarnesyl diphosphate = stellata-2,6,19-triene + diphosphate

Systematic name: (2*E*,6*E*,10*E*,14*E*)-geranylfarnesyl-diphosphate diphosphate-lyase (cylizing, stellata-2,6,19-triene-forming)

Comments: Isolated from the fungus *Aspergillus stellatus*.

References: [893]

[EC 4.2.3.178 created 2017]

EC 4.2.3.179

Accepted name: guaia-4,6-diene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = guaia-4,6-diene + diphosphate

Other name(s): XsTPS2

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, guaia-4,6-diene-forming)

Comments: Isolated from the plant *Xanthium strumarium* (rough cocklebur).

References: [805]

[EC 4.2.3.179 created 2017]

EC 4.2.3.180

Accepted name: pseudolaratriene synthase

Reaction: geranylgeranyl diphosphate = pseudolaratriene + diphosphate

Other name(s): PxaTPS8

Systematic name: geranylgeranyl-diphosphate diphosphate-lyase (cyclizing, pseudolaradiene-forming)

Comments: Isolated from the plant *Pseudolarix amabilis* (golden larch). The product is oxidized to pseudolaric acid B, a microtubule-destabilizing agent.

References: [862]

[EC 4.2.3.180 created 2017]

EC 4.2.3.181

Accepted name: selina-4(15),7(11)-diene synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate = selina-4(15),7(11)-diene + diphosphate

Other name(s): SdS

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, selina-4(15),7(11)-diene-forming)

Comments: Isolated from the bacteria *Streptomyces pristinaespiralis* and *S. somaliensis*.

References: [1114, 59]

[EC 4.2.3.181 created 2017]

EC 4.2.3.182

Accepted name: pristinol synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = (+)-(2*S*,3*R*,9*R*)-pristinol + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [cyclizing, (+)-(2*S*,3*R*,9*R*)-pristinol-forming]
Comments: Isolated from the bacterium *Streptomyces pristinaespiralis*.
References: [709]

[EC 4.2.3.182 created 2017]

EC 4.2.3.183

Accepted name: nezukol synthase
Reaction: (+)-copalyl diphosphate + H_2O = nezukol + diphosphate
Other name(s): TPS2
Systematic name: (+)-copalyl-diphosphate diphosphate-lyase (cyclizing, nezukol-forming)
Comments: Isolated from the plant *Isodon rubescens*.
References: [1064]

[EC 4.2.3.183 created 2017]

EC 4.2.3.184

Accepted name: 5-hydroxy-α-gurjunene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = 5-hydroxy-α-gurjunene + diphosphate
Other name(s): MpMTPSL4
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, 5-hydroxy-α-gurjunene-forming)
Comments: Isolated from the liverwort *Marchantia polymorpha*.
References: [759]

[EC 4.2.3.184 created 2017]

EC 4.2.3.185

Accepted name: *ent*-atiserene synthase
Reaction: *ent*-copalyl diphosphate = *ent*-atiserene + diphosphate
Other name(s): IrKSL4
Systematic name: *ent*-copalyl-diphosphate diphosphate-lyase (cyclizing, *ent*-atiserine-forming)
Comments: Isolated from the plant *Isodon rubescens*.
References: [635]

[EC 4.2.3.185 created 2017]

EC 4.2.3.186

Accepted name: *ent*-13-*epi*-manoyl oxide synthase
Reaction: *ent*-8α-hydroxylabd-13-en-15-yl diphosphate = *ent*-13-*epi*-manoyl oxide + diphosphate
Other name(s): SmKSL2; *ent*-LDPP synthase
Systematic name: *ent*-8α-hydroxylabd-13-en-15-yl-diphosphate diphosphate-lyase (cyclizing, *ent*-13-*epi*-manoyl-oxide-forming)
Comments: Isolated from the plant *Salvia miltiorrhiza* (red sage).
References: [275]

[EC 4.2.3.186 created 2017]

EC 4.2.3.187

Accepted name: (2*Z*,6*E*)-hedycaryol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = (2*Z*,6*E*)-hedycaryol + diphosphate

Other name(s): HcS

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [cyclizing, (2*Z*,6*E*)-hedycaryol-forming]

Comments: Isolated from the bacterium *Kitasatospora setae*. The stereochemistry suggests the farnesyl diphosphate rearranges to nerolidyl diphosphate or an equivalent intermediate before cyclization. See also EC 4.2.3.174 (2*E*,6*E*)-hedycaryol synthase.

References: [58]

[EC 4.2.3.187 created 2017]

EC 4.2.3.188

Accepted name: β-geranylfarnesene synthase

Reaction: (1) *all-trans*-geranylfarnesyl diphosphate = β-geranylfarnesene + diphosphate
(2) *all-trans*-hexaprenyl diphosphate = β-hexaprene + diphosphate
(3) *all-trans*-heptaprenyl diphosphate = β-heptaprene + diphosphate

Other name(s): Bcl-TS

Systematic name: *all-trans*-geranylfarnesyl-diphosphate diphosphate-lyase (β-geranylfarnesene-forming)

Comments: Isolated from the bacterium *Bacillus clausii*. The enzyme acts on a range of polyprenyl diphosphates.

References: [1195, 1406]

[EC 4.2.3.188 created 2017]

EC 4.2.3.189

Accepted name: 9,13-epoxylabd-14-ene synthase

Reaction: peregrinol diphosphate = (13*R*)-9,13-epoxylabd-14-ene + diphosphate

Other name(s): ELS (gene name); TPS2 (gene name) (ambiguous); peregrinol-diphosphate diphosphate-lyase (9,13-epoxylabd-14-ene-forming)

Systematic name: peregrinol-diphosphate diphosphate-lyase [(13*R*)-9,13-epoxylabd-14-ene-forming]

Comments: Isolated from the plants *Marrubium vulgare* (white horehound) and *Vitex agnus-castus* (chaste tree). Involved in marrubiin biosynthesis.

References: [1545, 547]

[EC 4.2.3.189 created 2017]

EC 4.2.3.190

Accepted name: manoyl oxide synthase

Reaction: (13*E*)-8α-hydroxylabd-13-en-15-yl diphosphate = manoyl oxide + diphosphate

Other name(s): GrTPS6; CfTPS3; CfTPS4; *MvELS*

Systematic name: (13*E*)-8α-hydroxylabd-13-en-15-yl-diphosphate diphosphate-lyase (manoyl-oxide-forming)

Comments: Manoyl oxide is found in many plants. This enzyme has been isolated from the plants, *Grindelia hirsutula* (gum weed), *Plectranthus barbatus* (forskohlii) and *Marrubium vulgare* (white horehound).

References: [1547, 1056, 1545]

[EC 4.2.3.190 created 2017]

EC 4.2.3.191

Accepted name: cycloaraneosene synthase

Reaction: geranylgeranyl diphosphate = cycloaraneosene + diphosphate

Other name(s): SdnA

Systematic name: geranylgeranyl-diphosphate diphosphate-lyase (cycloaraneosene-forming)

Comments: Isolated from the fungus *Sordaria araneosa*. Cycloaraneosene is a precursor of the antibiotic sordarin.

References: [748]

[EC 4.2.3.191 created 2017]

EC 4.2.3.192

Accepted name: labda-7,13(16),14-triene synthase

Reaction: (13*E*)-labda-7,13-dienyl diphosphate = labda-7,13(16),14-triene + diphosphate

Other name(s): SCLAV_p0491

Systematic name: (13*E*)-labda-7,13-dienyl-diphosphate diphosphate-lyase (labda-7,13(16),14-triene-forming)

Comments: Isolated from the bacterium *Streptomyces clavuligerus*.

References: [1494]

[EC 4.2.3.192 created 2017]

EC 4.2.3.193

Accepted name: (12*E*)-labda-8(17),12,14-triene synthase

Reaction: (+)-copalyl diphosphate = (12*E*)-labda-8(17),12,14-triene + diphosphate

Other name(s): CldD

Systematic name: (+)-copalyl-diphosphate diphosphate-lyase [(12*E*)-labda-8(17),12,14-triene-forming]

Comments: Isolated from the bacterium *Streptomyces cyslabdanicus*.

References: [1494]

[EC 4.2.3.193 created 2017]

EC 4.2.3.194

Accepted name: (–)-drimenol synthase

Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = (–)-drimenol + diphosphate

Other name(s): PhDS; VoTPS3; farnesyl pyrophosphate:drimenol cyclase; drimenol cyclase; (2*E*,6*E*)-farnesyl-diphosphate diphosphohydrolase (drimenol-forming)

Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphospho-lyase [cyclising, (–)-drimenol-forming]

Comments: Isolated from the plants *Valeriana officinalis* (valerian) and *Persicaria hydropiper* (water pepper). The enzyme does not act on farnesol or drimenol diphosphate. Using 18-oxygen labelled water 18-oxygen was incorporated suggesting involvement of a stabilised carbocation or an equivalent species.

References: [72, 772, 540]

[EC 4.2.3.194 created 2011 as EC 3.1.7.7, transferred 2017 to EC 4.2.3.194]

EC 4.2.3.195

Accepted name: rhizathalene A synthase

Reaction: geranylgeranyl diphosphate = rhizathalene A + diphosphate

Other name(s): TPS08 (gene name)

Systematic name: geranygeranyl-diphosphate diphosphate-lyase (rhizathalene A-forming)

Comments: The enzyme was identified in the roots of the plant *Arabidopsis thaliana* (thale cress). The product is a semivolatile diterpene that acts as a local antifeedant in belowground direct defense against root-feeding insects.

References: [1419]

[EC 4.2.3.195 created 2017]

EC 4.2.3.196

Accepted name: dolabradiene synthase

Reaction: *ent*-copalyl diphosphate = dolabradiene + diphosphate

Other name(s): KSL4 (gene name)
Systematic name: *ent*-copalyl-diphosphate diphosphate-lyase (dolabradiene-forming)
Comments: The enzyme, which has been characterized from maize, is involved in the biosynthesis of dolabralexins (type of antifungal phytoalexins).
References: [861]

[EC 4.2.3.196 created 2018]

EC 4.2.3.197

Accepted name: eudesmane-5,11-diol synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate + **2** H_2O = 7-*epi*-*ent*-eudesmane-5,11-diol + diphosphate
Other name(s): *ZmEDS* (gene name)
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, 7-*epi*-*ent*-eudesmane-5,11-diol-forming)
Comments: Isolated from the plant *Zea mays* (maize). The product is named in the reference using a different numbering scheme for eudesmane.
References: [809]

[EC 4.2.3.197 created 2018]

EC 4.2.3.198

Accepted name: α-selinene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = α-selinene + diphosphate
Other name(s): LfTPS2 (gene name)
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (cyclizing, α-selinene-forming)
Comments: The enzyme from the plant *Ocimum basilicum* (sweet basil) also produces β-selinene while that from *Liquidambar formosana* (Formosan sweet gum) also produces traces of aromadendrene.
References: [595, 235]

[EC 4.2.3.198 created 2018]

EC 4.2.3.199

Accepted name: (–)-5-epieremophilene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (–)-5-epieremophilene + diphosphate
Other name(s): STPS1 (gene name); STP2 (gene name); STP3 (gene name)
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [cyclizing, (–)-epieremophilene-forming]
Comments: The plant *Salvia miltiorrhiza* (danshen) produces three different forms of the enzyme, encoded by paralogous genes, that exhibit different spacial expression patterns and respond differently to hormone treatment.
References: [377]

[EC 4.2.3.199 created 2018]

EC 4.2.3.200

Accepted name: β-pinacene synthase
Reaction: geranylgeranyl diphosphate = β-pinacene + diphosphate
Other name(s): PcS
Systematic name: geranylgeranyl-diphosphate diphosphate-lyase (cyclizing, β-pinacene-forming)
Comments: Isolated from the slime mould *Dictyostelium discoideum*. The 1-*proR* hydrogen atom of geranylgeranyl diphosphate is lost in the reaction.
References: [1154]

[EC 4.2.3.200 created 2018]

EC 4.2.3.201

Accepted name: hydropyrene synthase
Reaction: geranylgeranyl diphosphate = hydropyrene + diphosphate
Other name(s): HpS
Systematic name: geranylgeranyl-diphosphate diphosphate-lyase (cyclizing, hydropyrene-forming)
Comments: Isolated from the bacterium *Streptomyces clavuligerus*. The 1-*proR* hydrogen atom of geranylgeranyl diphosphate is lost in the reaction. The enzyme also produces hydropyrenol, isoelisabethatriene and traces of other diterpenoids. *cf.* EC 4.2.3.202, hydropyrenol synthase, and EC 4.2.3.203, isoelisabethatriene synthase.
References: [1154]

[EC 4.2.3.201 created 2019]

EC 4.2.3.202

Accepted name: hydropyrenol synthase
Reaction: geranylgeranyl diphosphate + H_2O = hydropyrenol + diphosphate
Other name(s): HpS
Systematic name: geranylgeranyl-diphosphate diphosphate-lyase (cyclizing, hydropyrenol-forming)
Comments: Isolated from the bacterium *Streptomyces clavuligerus*. The 1-*proR* hydrogen atom of geranylgeranyl diphosphate is lost in the reaction. The enzyme also produces hydropyrene, isoelisabethatriene and traces of other diterpenoids. *cf.* EC 4.2.3.201, hydropyrene synthase, and EC 4.2.3.203, isoelisabethatriene synthase.
References: [1154]

[EC 4.2.3.202 created 2019]

EC 4.2.3.203

Accepted name: isoelisabethatriene synthase
Reaction: geranylgeranyl diphosphate = isoelisabethatriene + diphosphate
Other name(s): HpS (ambiguous)
Systematic name: geranylgeranyl-diphosphate diphosphate-lyase (cyclizing, isoelisabethatriene-forming)
Comments: Isolated from the bacterium *Streptomyces clavuligerus*. The 1-*proR* hydrogen atom of geranylgeranyl diphosphate is involved in a 1,3-hydride shift to the side-chain. The enzyme also produces hydropyrene, hydropyrenol, and traces of other diterpenoids. *cf.* EC 4.2.3.201, hydropyrene synthase, and EC 4.2.3.202, hydropyrenol synthase.
References: [1154]

[EC 4.2.3.203 created 2019]

EC 4.2.3.204

Accepted name: valerianol synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate + H_2O = valerianol + diphosphate
Other name(s): ChTPS1 (gene name); CsiTPS8 (gene name)
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase (valerianol-forming)
Comments: The enzyme was characterized from the trees *Camellia hiemalis* and *Camellia sinensis* (black tea). The enzyme from *Camellia hiemalis* produces (2*Z*,6*E*)-hedycaryol as a minor product.
References: [523]

[EC 4.2.3.204 created 2019]

EC 4.2.3.205

Accepted name: sodorifen synthase
Reaction: pre-sodorifen diphosphate = sodorifen + diphosphate

Other name(s): *sodD* (gene name)
Systematic name: pre-sodorifen diphosphate-lyase [sodorifen-forming]
Comments: The enzyme has been characterized from the bacterium *Serratia plymuthica*.
References: [327, 1222, 1429]

[EC 4.2.3.205 created 2019]

EC 4.2.3.206

Accepted name: (–)-cyatha-3,12-diene synthase
Reaction: geranylgeranyl diphosphate = (–)-cyatha-3,12-diene + diphosphate
Other name(s): *eriG* (gene name); CyaTC
Systematic name: geranylgeranyl diphosphate-lyase [(–)-cyatha-3,12-diene-forming]
Comments: The enzyme, characterized from the fungi *Hericium erinaceus* and *Cyathus africanus*, requires Mg^{2+} for activity.
References: [1504]

[EC 4.2.3.206 created 2022]

EC 4.2.3.207

Accepted name: neoverrucosan-5β-ol synthase
Reaction: geranylgeranyl diphosphate + H_2O = neoverrucosan-5β-ol + diphosphate
Other name(s): SapTC1
Systematic name: geranylgeranyl- diphosphate diphosphate-lyase (neoverrucosan-5β-ol-forming)
Comments: Requires Mg^{2+}. Characterized from the marine bacterium *Saprospira grandis*.
References: [1504]

[EC 4.2.3.207 created 2022]

EC 4.2.3.208

Accepted name: verrucosan-2β-ol synthase
Reaction: geranylgeranyl diphosphate + H_2O = verrucosan-2β-ol + diphosphate
Other name(s): ChlTC2
Systematic name: geranylgeranyl-diphosphate diphosphate-lyase (verrucosan-2β-ol-forming)
Comments: Requires Mg^{2+}. Characterized from the bacterium *Chloroflexus aurantiacus*.
References: [1504]

[EC 4.2.3.208 created 2022]

EC 4.2.3.209

Accepted name: (*R*)-axinyssene synthase
Reaction: geranylgeranyl diphosphate = (*R*)-axinyssene + diphosphate
Other name(s): CysTC2
Systematic name: geranylgeranyl-diphosphate diphosphate-lyase [(*R*)-axinyssene-forming]
Comments: Requires Mg^{2+}. Characterized from the bacterium *Archangium violaceum*.
References: [1504]

[EC 4.2.3.209 created 2022]

EC 4.2.3.210

Accepted name: lydicene synthase
Reaction: geranylgeranyl diphosphate = lydicene + diphosphate
Other name(s): StlTC

Systematic name: geranylgerany-diphosphate diphosphate-lyase (lydicene-forming)
Comments: Requires Mg^{2+}. Characterized from the bacterium *Streptomyces lydicus*.
References: [1504]

[EC 4.2.3.210 created 2022]

EC 4.2.3.211
Accepted name: (+)-*exo*-β-bergamotene synthase
Reaction: (2*E*,6*E*)-farnesyl diphosphate = (+)-*exo*-β-bergamotene + diphosphate
Systematic name: (2*E*,6*E*)-farnesyl-diphosphate diphosphate-lyase [(+)-*exo*-β-bergamotene-forming]
Comments: The enzyme, characterized from the mold *Aspergillus fumigatus*, participates in the biosynthesis of the meroterpenoid fumagillin.
References: [819]

[EC 4.2.3.211 created 2022]

EC 4.2.99 Other carbon-oxygen lyases

[4.2.99.1 Transferred entry. hyaluronate lyase. Now EC 4.2.2.1, hyaluronate lyase]

[EC 4.2.99.1 created 1961, deleted 1972]

[4.2.99.2 Transferred entry. threonine synthase. Now EC 4.2.3.1, threonine synthase]

[EC 4.2.99.2 created 1961, deleted 2000]

[4.2.99.3 Transferred entry. pectate lyase. Now EC 4.2.2.2, pectate lyase]

[EC 4.2.99.3 created 1965, deleted 1972]

[4.2.99.4 Transferred entry. alginate lyase. Now EC 4.2.2.3, poly(β-D-mannuronate) lyase]

[EC 4.2.99.4 created 1965, deleted 1972]

[4.2.99.5 Deleted entry. polyglucuronide lyase]

[EC 4.2.99.5 created 1965, deleted 1972]

[4.2.99.6 Deleted entry. chondroitin sulfate lyase. Now included with EC 4.2.2.4 (chondroitin ABC lyase) and EC 4.2.2.5 (chondroitin AC lyase)]

[EC 4.2.99.6 created 1965, deleted 1972]

[4.2.99.7 Transferred entry. ethanolamine-phosphate phospho-lyase. Now EC 4.2.3.2, ethanolamine-phosphate phospho-lyase]

[EC 4.2.99.7 created 1972, deleted 2000]

[4.2.99.8 Transferred entry. cysteine synthase. Now EC 2.5.1.47, cysteine synthase]

[EC 4.2.99.8 created 1972, modified 1976, modified 1990, deleted 2002]

[4.2.99.9 Transferred entry. O-succinylhomoserine (thiol)-lyase. Now EC 2.5.1.48, cystathionine γ-synthase]

[EC 4.2.99.9 created 1972, deleted 2002]

[4.2.99.10 Transferred entry. O-acetylhomoserine (thiol)-lyase. Now EC 2.5.1.49, O-acetylhomoserine aminocarboxypropyltransferase]

[EC 4.2.99.10 created 1972, deleted 2002]

[4.2.99.11 Transferred entry. methylglyoxal synthase. Now EC 4.2.3.3, methylglyoxal synthase]

[EC 4.2.99.11 created 1972, deleted 2000]

EC 4.2.99.12

Accepted name: carboxymethyloxysuccinate lyase
Reaction: carboxymethyloxysuccinate = fumarate + glycolate
Other name(s): carbon-oxygen lyase; carboxymethyloxysuccinate glycolate-lyase
Systematic name: carboxymethyloxysuccinate glycolate-lyase (fumarate-forming)
References: [1072]

[EC 4.2.99.12 created 1976]

[4.2.99.13 Transferred entry. β-(9-cytokinin)-alanine synthase. Now EC 2.5.1.50, zeatin 9-aminocarboxyethyltransferase]

[EC 4.2.99.13 created 1984, deleted 2002]

[4.2.99.14 Transferred entry. β-pyrazolylalanine synthase (acetylserine). Now EC 2.5.1.51, β-pyrazolylalanine synthase]

[EC 4.2.99.14 created 1989 (EC 4.2.99.17 incorporated 1992), deleted 2002]

[4.2.99.15 Transferred entry. L-mimosine synthase. Now EC 2.5.1.52, L-mimosine synthase]

[EC 4.2.99.15 created 1989, deleted 2002]

[4.2.99.16 Transferred entry. uracilylalanine synthase. Now EC 2.5.1.53, uracilylalanine synthase]

[EC 4.2.99.16 created 1990, deleted 2002]

[4.2.99.17 Deleted entry. thermopsin. Listed as EC 2.5.1.51, β-pyrazolylalanine synthase]

[EC 4.2.99.17 created 1992, deleted 1992]

EC 4.2.99.18

Accepted name: DNA-(apurinic or apyrimidinic site) lyase
Reaction: The C-*O*-P bond $3'$ to the apurinic or apyrimidinic site in DNA is broken by a β-elimination reaction, leaving a $3'$-terminal unsaturated sugar and a product with a terminal $5'$-phosphate
Other name(s): AP lyase; AP endonuclease class I; endodeoxyribonuclease (apurinic or apyrimidinic); deoxyribonuclease (apurinic or apyrimidinic); *E. coli* endonuclease III; phage-T4 UV endonuclease; *Micrococcus luteus* UV endonuclease; AP site-DNA $5'$-phosphomonoester-lyase; X-ray endonuclease III
Systematic name: DNA-(apurinic or apyrimidinic site) $5'$-phosphomonoester-lyase
Comments: ‘Nicking’ of the phosphodiester bond is due to a lyase-type reaction, not hydrolysis. This group of enzymes was previously listed as endonucleases, under EC 3.1.25.2.
References: [61, 62, 63, 873]

[EC 4.2.99.18 created 1978 as EC 3.1.25.2, transferred 1992 to EC 4.2.99.18]

[4.2.99.19 Transferred entry. 2-hydroxypropyl-CoM lyase. Now EC 4.4.1.23, 2-hydroxypropyl-CoM lyase. The enzyme was incorrectly classified as acting on a C-O bond rather than a C-S bond]

[EC 4.2.99.19 created 2001, deleted 2005]

EC 4.2.99.20

Accepted name: 2-succinyl-6-hydroxy-2,4-cyclohexadiene-1-carboxylate synthase
Reaction: 5-enolpyruvoyl-6-hydroxy-2-succinylcyclohex-3-ene-1-carboxylate = (1*R*,6*R*)-6-hydroxy-2-succinylcyclohexa-2,4-diene-1-carboxylate + pyruvate
Other name(s): 2-succinyl-6-hydroxy-2,4-cyclohexadiene-1-carboxylic acid synthase; 6-hydroxy-2-succinylcyclohexa-2,4-diene-1-carboxylate synthase; SHCHC synthase; MenH; YfbB
Systematic name: 5-enolpyruvoyl-6-hydroxy-2-succinylcyclohex-3-ene-1-carboxylate pyruvate-lyase [(1*R*,6*R*)-6-hydroxy-2-succinylcyclohexa-2,4-diene-1-carboxylate-forming]

Comments: This enzyme is involved in the biosynthesis of vitamin K_2 (menaquinone). In most anaerobes and all Gram-positive aerobes, menaquinone is the sole electron transporter in the respiratory chain and is essential for their survival. It had previously been thought that the reactions carried out by this enzyme and EC 2.2.1.9, 2-succinyl-5-enolpyruvyl-6-hydroxy-3-cyclohexene-1-carboxylic-acid synthase, were carried out by a single enzyme but this has since been disproved [631].

References: [632, 631]

[EC 4.2.99.20 created 2008 (EC 2.5.1.64 created 2003, part-incorporated 2008)]

EC 4.2.99.21

Accepted name: isochorismate lyase

Reaction: isochorismate = salicylate + pyruvate

Other name(s): salicylate biosynthesis protein *pchB*; pyochelin biosynthetic protein PchB; isochorismate pyruvate lyase

Systematic name: isochorismate pyruvate-lyase (salicylate-forming)

Comments: This enzyme is part of the pathway of salicylate formation from chorismate, and forms an integral part of pathways that produce salicylate-derived siderophores, such as pyochelin and yersiniabactin.

References: [1255, 689]

[EC 4.2.99.21 created 2010]

EC 4.2.99.22

Accepted name: tuliposide A-converting enzyme

Reaction: 6-tuliposide A = tulipalin A + D-glucose

Other name(s): tuliposide-converting enzyme; 6-*O*-(4′-hydroxy-2′-methylenebutyryl)-D-glucose acyltransferase (lactone-forming); TCA; TCEA

Systematic name: 6-tuliposide A D-glucose-lyase (tulipalin-A-forming)

Comments: Isolated from the plant *Tulipa gesneriana* (tulip). The reaction is an intramolecular transesterification producing the lactone. The enzyme also has a weak activity with 6-tuliposide B and 6-*O*-benzoyl-D-glucose.

References: [679, 1013]

[EC 4.2.99.22 created 2013]

EC 4.2.99.23

Accepted name: tuliposide B-converting enzyme

Reaction: 6-tuliposide B = tulipalin B + D-glucose

Systematic name: 6-tuliposide B D-glucose-lyase (tulipalin B-forming)

Comments: The enzyme, characterized from pollen of the plant *Tulipa gesneriana* (tulip), catalyses the intramolecular transesterification of 6-tuliposide B to form the antibiotic aglycon tulipalin B as a sole product. It does not catalyse the hydrolysis of 6-tuliposide B to form a hydroxy acid. The enzyme has marginal activity with 6-tuliposide A. *cf.* EC 4.2.99.22, tuliposide A-converting enzyme.

References: [1012]

[EC 4.2.99.23 created 2016]

EC 4.2.99.24

Accepted name: thebaine synthase

Reaction: salutaridinol 7-*O*-acetate = thebaine + acetate

Other name(s): THS

Systematic name: salutaridinol 7-*O*-acetate acetate-lyase (thebaine-forming)

Comments: Isolated from the plant *Papaver somniferum* (opium poppy). The reaction occurs spontaneously when the pH is between 8-9, but the enzyme is required at the physiological pH, which is close to 7.

References: [218]

[EC 4.2.99.24 created 2019]

EC 4.3 Carbon-nitrogen lyases

This subclass contains the enzymes that release ammonia or one of its derivatives, with the formation of a double bond or ring. Some catalyse the actual elimination of the ammonia, amine or amide, e.g. ¡p¿

¿CH-CH(-NH-R)- → ¿C=CH- + NH_2-R¡P¿

Others, however, catalyse elimination of another component, e.g. water, which is followed by spontaneous reactions that lead to breakage of the C-N bond, e.g. as in EC 4.3.1.17 (L-serine ammonia-lyase), so that the overall reaction is:¡p¿

¡img src="images/EZgif/EC43.gif"¿¡/p¿

i.e., an elimination with rearrangement. The sub-subclasses of EC 4.3 are the ammonia-lyases (EC 4.3.1), lyases acting on amides, amidines, etc. (amidine-lyases; EC 4.3.2) and the amine-lyases (EC 4.3.3).

EC 4.3.1 Ammonia-lyases

EC 4.3.1.1

Accepted name: aspartate ammonia-lyase
Reaction: L-aspartate = fumarate + NH_3
Other name(s): aspartase; fumaric aminase; L-aspartase; L-aspartate ammonia-lyase
Systematic name: L-aspartate ammonia-lyase (fumarate-forming)
References: [356]

[EC 4.3.1.1 created 1961]

EC 4.3.1.2

Accepted name: methylaspartate ammonia-lyase
Reaction: L-*threo*-3-methylaspartate = mesaconate + NH_3
Other name(s): β-methylaspartase; 3-methylaspartase; L-*threo*-3-methylaspartate ammonia-lyase
Systematic name: L-*threo*-3-methylaspartate ammonia-lyase (mesaconate-forming)
Comments: A cobalamin protein.
References: [75, 135]

[EC 4.3.1.2 created 1961]

EC 4.3.1.3

Accepted name: histidine ammonia-lyase
Reaction: L-histidine = urocanate + NH_3
Other name(s): histidase; histidinase; histidine α-deaminase; L-histidine ammonia-lyase
Systematic name: L-histidine ammonia-lyase (urocanate-forming)
Comments: This enzyme is a member of the aromatic amino acid lyase family, other members of which are EC 4.3.1.23 (tyrosine ammonia-lyase), EC 4.3.1.24 (phenylalanine ammonia-lyase) and EC 4.3.1.25 (phenylalanine/tyrosine ammonia-lyase). The enzyme contains the cofactor 3,5-dihydro-5-methylidene-4*H*-imidazol-4-one (MIO), which is common to this family [845]. This unique cofactor is formed autocatalytically by cyclization and dehydration of the three amino-acid residues alanine, serine and glycine [1240]. This enzyme catalyses the first step in the degradation of histidine and the product, urocanic acid, is further metabolized to glutamate [1457, 1094].
References: [919, 1457, 1094, 845, 1240]

[EC 4.3.1.3 created 1961, modified 2008]

EC 4.3.1.4

Accepted name: formimidoyltetrahydrofolate cyclodeaminase

Reaction: 5-formimidoyltetrahydrofolate = 5,10-methenyltetrahydrofolate + NH_3

Other name(s): forminotetrahydrofolate cyclodeaminase; 5-formimidoyltetrahydrofolate ammonia-lyase (cyclizing)

Systematic name: 5-formimidoyltetrahydrofolate ammonia-lyase (cyclizing; 5,10-methenyltetrahydrofolate-forming)

Comments: In eukaroytes, occurs as a bifunctional enzyme that also has glutamate formimidoyltransferase (EC 2.1.2.5) activity.

References: [1121]

[EC 4.3.1.4 created 1961, modified 2000]

[4.3.1.5 Transferred entry. phenylalanine ammonia-lyase. Now divided into EC 4.3.1.23 (tyrosine ammonia-lyase), EC 4.3.1.24 (phenylalanine ammonia-lyase) and EC 4.3.1.25 (phenylalanine/tyrosine ammonia-lyase)]

[EC 4.3.1.5 created 1965, deleted 2008]

EC 4.3.1.6

Accepted name: β-alanyl-CoA ammonia-lyase

Reaction: β-alanyl-CoA = acryloyl-CoA + NH_3

Other name(s): β-alanyl coenzyme A ammonia-lyase

Systematic name: β-alanyl-CoA ammonia-lyase (acryloyl-CoA-forming)

Comments: The reaction has only been demonstrated in the direction of addition of ammonia.

References: [1296]

[EC 4.3.1.6 created 1965]

EC 4.3.1.7

Accepted name: ethanolamine ammonia-lyase

Reaction: ethanolamine = acetaldehyde + NH_3

Other name(s): ethanolamine deaminase

Systematic name: ethanolamine ammonia-lyase (acetaldehyde-forming)

Comments: A cobalamin protein.

References: [127, 128, 666]

[EC 4.3.1.7 created 1972]

[4.3.1.8 Transferred entry. hydroxymethylbilane synthase. Now EC 2.5.1.61, hydroxymethylbilane synthase]

[EC 4.3.1.8 created 1972, modified 1982, modified 1989, deleted 2003]

EC 4.3.1.9

Accepted name: glucosaminate ammonia-lyase

Reaction: 2-amino-2-deoxy-D-gluconate = 2-dehydro-3-deoxy-D-gluconate + NH_3 (overall reaction)
(1a) 2-amino-2-deoxy-D-gluconate = (2*Z*,4*S*,5*R*)-2-amino-4,5,6-trihydroxyhex-2-enoate + H_2O
(1b) (2*Z*,4*S*,5*R*)-2-amino-4,5,6-trihydroxyhex-2-enoate = (4*S*,5*R*)-4,5,6-trihydroxy-2-iminohexanoate (spontaneous)
(1c) (4*S*,5*R*)-4,5,6-trihydroxy-2-iminohexanoate + H_2O = 2-dehydro-3-deoxy-D-gluconate + NH_3 (spontaneous)

Other name(s): glucosaminic dehydrase; D-glucosaminate dehydratase; D-glucosaminic acid dehydrase; aminodeoxygluconate dehydratase; 2-amino-2-deoxy-D-gluconate hydro-lyase (deaminating); aminodeoxygluconate ammonia-lyase; 2-amino-2-deoxy-D-gluconate ammonia-lyase; D-glucosaminate ammonia-lyase; D-glucosaminate ammonia-lyase (isomerizing; 2-dehydro-3-deoxy-D-gluconate-forming)

Systematic name: 2-amino-2-deoxy-D-gluconate ammonia-lyase (isomerizing; 2-dehydro-3-deoxy-D-gluconate-forming)
Comments: Contains pyridoxal phosphate. The enzyme releases an unstable enamine product that tautomerizes to an imine form, which undergoes spontaneous hydrolytic deamination to form the final product.
References: [599, 931, 608, 609]

[EC 4.3.1.9 created 1972, (EC 4.3.1.21 created 1965 as EC 4.2.1.26, transferred 2002 to EC 4.3.1.21, incorporated 2004) modified 2004]

EC 4.3.1.10

Accepted name: serine-sulfate ammonia-lyase
Reaction: L-serine *O*-sulfate + H_2O = pyruvate + NH_3 + sulfate
Other name(s): (L-SOS)lyase
Systematic name: L-serine-*O*-sulfate ammonia-lyase (pyruvate-forming)
References: [1365]

[EC 4.3.1.10 created 1972]

[4.3.1.11 Deleted entry. dihydroxyphenylalanine ammonia-lyase. The entry had been drafted on the basis of a single abstract that did not provide experimental evidence of the enzyme-catalysed reaction]

[EC 4.3.1.11 created 1972, deleted 2007]

EC 4.3.1.12

Accepted name: ornithine cyclodeaminase
Reaction: L-ornithine = L-proline + NH_3
Other name(s): ornithine cyclase; ornithine cyclase (deaminating); L-ornithine ammonia-lyase (cyclizing)
Systematic name: L-ornithine ammonia-lyase (cyclizing; L-proline-forming)
Comments: Requires NAD^+. The enzyme is a member of the μ-crystallin protein family [452]. The reaction is stimulated by the presence of ADP or ATP and is inhibited by O_2 [973].
References: [255, 973, 366, 452, 12]

[EC 4.3.1.12 created 1976]

EC 4.3.1.13

Accepted name: carbamoyl-serine ammonia-lyase
Reaction: *O*-carbamoyl-L-serine + H_2O = pyruvate + **2** NH_3 + CO_2 (overall reaction)
(1a) *O*-carbamoyl-L-serine = CO_2 + NH_3 + 2-aminoprop-2-enoate
(1b) 2-aminoprop-2-enoate = 2-iminopropanoate (spontaneous)
(1c) 2-iminopropanoate + H_2O = pyruvate + NH_3 (spontaneous)
Other name(s): *O*-carbamoyl-L-serine deaminase; carbamoylserine deaminase; *O*-carbamoyl-L-serine ammonia-lyase (pyruvate-forming)
Systematic name: *O*-carbamoyl-L-serine ammonia-lyase (decarboxylating; pyruvate-forming)
Comments: A pyridoxal-phosphate protein. The enzyme cleaves a carbon-oxygen bond, releasing CO_2, ammonia, and an unstable enamine product that tautomerizes to an imine form, which undergoes a hydrolytic deamination to form pyruvate and a second ammonia molecule. The latter reaction, which can occur spontaneously, can also be catalysed by EC 3.5.99.10, 2-iminobutanoate/2-iminopropanoate deaminase.
References: [251]

[EC 4.3.1.13 created 1976]

EC 4.3.1.14

Accepted name: 3-aminobutyryl-CoA ammonia-lyase

Reaction: L-3-aminobutyryl-CoA = crotonoyl-CoA + NH_3
Other name(s): L-3-aminobutyryl-CoA deaminase; L-3-aminobutyryl-CoA ammonia-lyase
Systematic name: L-3-aminobutyryl-CoA ammonia-lyase (crotonoyl-CoA-forming)
Comments: Hydroxylamine can replace ammonia as a substrate. Crotonoyl-pantetheine can replace crotonoyl-CoA but it is a poorer substrate.
References: [625, 74]

[EC 4.3.1.14 created 1999]

EC 4.3.1.15

Accepted name: diaminopropionate ammonia-lyase
Reaction: 2,3-diaminopropanoate + H_2O = pyruvate + **2** NH_3
Other name(s): diaminopropionatase; α,β-diaminopropionate ammonia-lyase; 2,3-diaminopropionate ammonia-lyase; 2,3-diaminopropanoate ammonia-lyase; 2,3-diaminopropanoate ammonia-lyase (adding H_2O; pyruvate-forming)
Systematic name: 2,3-diaminopropanoate ammonia-lyase (adding water; pyruvate-forming)
Comments: A pyridoxal phosphate enzyme. Active towards both D- and L-diaminopropanoate. D- and L-serine are poor substrates.
References: [982]

[EC 4.3.1.15 created 1999]

EC 4.3.1.16

Accepted name: *threo*-3-hydroxy-L-aspartate ammonia-lyase
Reaction: *threo*-3-hydroxy-L-aspartate = oxaloacetate + NH_3
Other name(s): L-*threo*-3-hydroxyaspartate dehydratase; *threo*-3-hydroxyaspartate ammonia-lyase
Systematic name: *threo*-3-hydroxy-L-aspartate ammonia-lyase (oxaloacetate-forming)
Comments: A pyridoxal-phosphate protein. The enzyme, purified from the bacterium *Pseudomonas* sp. T62, is highly specific, and does not accept any other stereoisomer of 3-hydroxyaspartate. Different from EC 4.3.1.20, *erythro*-3-hydroxy-L-aspartate ammonia-lyase and EC 4.3.1.27, *threo*-3-hydroxy-D-aspartate ammonia-lyase. Requires a divalent cation such as Mn^{2+}, Mg^{2+}, or Ca^{2+}.
References: [1431]

[EC 4.3.1.16 created 2001, modified 2011]

EC 4.3.1.17

Accepted name: L-serine ammonia-lyase
Reaction: L-serine = pyruvate + NH_3 (overall reaction)
(1a) L-serine = 2-aminoprop-2-enoate + H_2O
(1b) 2-aminoprop-2-enoate = 2-iminopropanoate (spontaneous)
(1c) 2-iminopropanoate + H_2O = pyruvate + NH_3 (spontaneous)
Other name(s): serine deaminase; L-hydroxyaminoacid dehydratase; L-serine deaminase; L-serine dehydratase; L-serine hydro-lyase (deaminating)
Systematic name: L-serine ammonia-lyase (pyruvate-forming)
Comments: Most enzymes that catalyse this reaction are pyridoxal-phosphate-dependent, although some enzymes contain an iron-sulfur cluster instead [460]. The reaction catalysed by both types of enzymes involves the initial elimination of water to form an enamine intermediate (hence the enzyme's original classification as EC 4.2.1.13, L-serine dehydratase), followed by tautomerization to an imine form and hydrolysis of the C-N bond. The latter reaction, which can occur spontaneously, is also be catalysed by EC 3.5.99.10, 2-iminobutanoate/2-iminopropanoate deaminase. This reaction is also carried out by EC 4.3.1.19, threonine ammonia-lyase, from a number of sources.
References: [1129, 1278, 1317, 1181, 1164, 460, 1492]

[EC 4.3.1.17 created 1961 as EC 4.2.1.13, transferred 2001 to EC 4.3.1.17, modified 2014]

EC 4.3.1.18

Accepted name: D-serine ammonia-lyase

Reaction: D-serine = pyruvate + NH_3 (overall reaction)
(1a) D-serine = 2-aminoprop-2-enoate + H_2O
(1b) 2-aminoprop-2-enoate = 2-iminopropanoate (spontaneous)
(1c) 2-iminopropanoate + H_2O = pyruvate + NH_3 (spontaneous)

Other name(s): D-hydroxyaminoacid dehydratase; D-serine dehydrase; D-hydroxy amino acid dehydratase; D-serine hydrolase; D-serine dehydratase (deaminating); D-serine deaminase; D-serine hydro-lyase (deaminating)

Systematic name: D-serine ammonia-lyase (pyruvate-forming)

Comments: A pyridoxal-phosphate protein. The enzyme cleaves a carbon-oxygen bond, releasing a water molecule (hence the enzyme's original classification as EC 4.2.1.14, D-serine dehydratase) and an unstable enamine product that tautomerizes to an imine form, which undergoes a hydrolytic deamination to form pyruvate and ammonia. The latter reaction, which can occur spontaneously, can also be catalysed by EC 3.5.99.10, 2-iminobutanoate/2-iminopropanoate deaminase. Also acts, slowly, on D-threonine.

References: [341, 932]

[EC 4.3.1.18 created 1961 as EC 4.2.1.14, transferred 2001 to EC 4.3.1.18]

EC 4.3.1.19

Accepted name: threonine ammonia-lyase

Reaction: L-threonine = 2-oxobutanoate + NH_3 (overall reaction)
(1a) L-threonine = 2-aminobut-2-enoate + H_2O
(1b) 2-aminobut-2-enoate = 2-iminobutanoate (spontaneous)
(1c) 2-iminobutanoate + H_2O = 2-oxobutanoate + NH_3 (spontaneous)

Other name(s): threonine deaminase; L-serine dehydratase; serine deaminase; L-threonine dehydratase; threonine dehydrase; L-threonine deaminase; threonine dehydratase; L-threonine hydro-lyase (deaminating); L-threonine ammonia-lyase

Systematic name: L-threonine ammonia-lyase (2-oxobutanoate-forming)

Comments: Most enzymes that catalyse this reaction are pyridoxal-phosphate-dependent, although some enzymes contain an iron-sulfur cluster instead. The reaction catalysed by both types of enzymes involves the initial elimination of water to form an enamine intermediate (hence the enzyme's original classification as EC 4.2.1.16, threonine dehydratase), followed by tautomerization to an imine form and hydrolysis of the C-N bond [1076, 781]. The latter reaction, which can occur spontaneously, is also be catalysed by EC 3.5.99.10, 2-iminobutanoate/2-iminopropanoate deaminase [781]. The enzymes from a number of sources also act on L-serine, *cf.* EC 4.3.1.17, L-serine ammonia-lyase.

References: [241, 1009, 1076, 1268, 781]

[EC 4.3.1.19 created 1961 as EC 4.2.1.16, transferred 2001 to EC 4.3.1.19, modified 2014]

EC 4.3.1.20

Accepted name: *erythro*-3-hydroxy-L-aspartate ammonia-lyase

Reaction: *erythro*-3-hydroxy-L-aspartate = oxaloacetate + NH_3

Other name(s): *erythro*-β-hydroxyaspartate dehydratase; *erythro*-3-hydroxyaspartate dehydratase; *erythro*-3-hydroxy-L_s-aspartate hydro-lyase (deaminating); *erythro*-3-hydroxy-L_s-aspartate ammonia-lyase

Systematic name: *erythro*-3-hydroxy-L-aspartate ammonia-lyase (oxaloacetate-forming)

Comments: A pyridoxal-phosphate protein. The enzyme, which was characterized from the bacterium *Paracoccus denitrificans* NCIMB 8944, is highly specific for the L-isomer of *erythro*-3-hydroxyaspartate. Different from EC 4.3.1.16, *threo*-3-hydroxy-L-aspartate ammonia-lyase and EC 4.3.1.27, *threo*-3-hydroxy-D-aspartate ammonia-lyase. Requires a divalent cation such as Mn^{2+}, Mg^{2+}, and Ca^{2+}.

References: [438]

[EC 4.3.1.20 created 1972 as EC 4.2.1.38, transferred 2001 to EC 4.3.1.20, modified 2011]

[4.3.1.21 Deleted entry. aminodeoxygluconate ammonia-lyase. Enzyme is identical to EC 4.3.1.9, glucosaminate ammonia-lyase]

[EC 4.3.1.21 created 1965 as EC 4.2.1.26, transferred 2002 to EC 4.3.1.21, deleted 2004]

EC 4.3.1.22

Accepted name: 3,4-dihydroxyphenylalanine reductive deaminase
Reaction: L-dopa + NADH = 3,4-dihydroxyphenylpropanoate + NAD^+ + NH_3
Other name(s): reductive deaminase; DOPA-reductive deaminase; DOPARDA
Systematic name: 3,4-dihydroxy-L-phenylalanine ammonia-lyase (3,4-dihydroxyphenylpropanoate-forming)
Comments: Forms part of the L-phenylalanine-catabolism pathway in the anoxygenic phototrophic bacterium *Rhodobacter sphaeroides* OU5. NADPH is oxidized more slowly than NADH.
References: [1130]

[EC 4.3.1.22 created 2007]

EC 4.3.1.23

Accepted name: tyrosine ammonia-lyase
Reaction: L-tyrosine = *trans*-*p*-hydroxycinnamate + NH_3
Other name(s): TAL; tyrase; L-tyrosine ammonia-lyase
Systematic name: L-tyrosine ammonia-lyase (*trans*-*p*-hydroxycinnamate-forming)
Comments: This enzyme is a member of the aromatic amino acid lyase family, other members of which are EC 4.3.1.3 (histidine ammonia-lyase), EC 4.3.1.24 (phenylalanine ammonia-lyase) and EC 4.3.1.25 (phenylalanine/tyrosine ammonia-lyase). The enzyme contains the cofactor 3,5-dihydro-5-methylidene-4*H*-imidazol-4-one (MIO), which is common to this family [845]. This unique cofactor is formed autocatalytically by cyclization and dehydration of the three amino-acid residues alanine, serine and glycine [1240]. The enzyme is far more active with tyrosine than with phenylalanine as substrate, but the substrate specificity can be switched by mutation of a single amino acid ($H_{89}F$) in the enzyme from the bacterium *Rhodobacter sphaeroides* [845, 1457].
References: [845, 1457, 1240]

[EC 4.3.1.23 created 2008 (EC 4.3.1.5 created 1965, part-incorporated 2008)]

EC 4.3.1.24

Accepted name: phenylalanine ammonia-lyase
Reaction: L-phenylalanine = *trans*-cinnamate + NH_3
Other name(s): phenylalanine deaminase; phenylalanine ammonium-lyase; PAL; L-phenylalanine ammonia-lyase; Phe ammonia-lyase
Systematic name: L-phenylalanine ammonia-lyase (*trans*-cinnamate-forming)
Comments: This enzyme is a member of the aromatic amino acid lyase family, other members of which are EC 4.3.1.3 (histidine ammonia-lyase) and EC 4.3.1.23 (tyrosine ammonia-lyase) and EC 4.3.1.25 (phenylalanine/tyrosine ammonia-lyase). The enzyme contains the cofactor 3,5-dihydro-5-methylidene-4*H*-imidazol-4-one (MIO), which is common to this family [845]. This unique cofactor is formed autocatalytically by cyclization and dehydration of the three amino-acid residues alanine, serine and glycine [1240]. The enzyme from some species is highly specific for phenylalanine [36, 240].
References: [735, 1517, 845, 169, 1159, 1457, 36, 240, 1240]

[EC 4.3.1.24 created 2008 (EC 4.3.1.5 created 1965, part-incorporated 2008)]

EC 4.3.1.25

Accepted name: phenylalanine/tyrosine ammonia-lyase
Reaction: (1) L-phenylalanine = *trans*-cinnamate + NH_3
(2) L-tyrosine = *trans*-*p*-hydroxycinnamate + NH_3

Other name(s): PTAL; bifunctional PAL

Systematic name: L-phenylalanine(or L-tyrosine):*trans*-cinnamate(or *trans*-*p*-hydroxycinnamate) ammonia-lyase

Comments: This enzyme is a member of the aromatic amino acid lyase family, other members of which are EC 4.3.1.3 (histidine ammonia-lyase), EC 4.3.1.23 (tyrosine ammonia-lyase) and EC 4.3.1.24 (phenylalanine ammonia-lyase). The enzyme from some monocots, including maize, and from the yeast *Rhodosporidium toruloides*, deaminate L-phenylalanine and L-tyrosine with similar catalytic efficiency [845]. The enzyme contains the cofactor 3,5-dihydro-5-methylidene-4*H*-imidazol-4-one (MIO), which is common to this family [845]. This unique cofactor is formed autocatalytically by cyclization and dehydration of the three amino-acid residues alanine, serine and glycine [1240].

References: [1170, 1457, 845, 1240]

[EC 4.3.1.25 created 2008 (EC 4.3.1.5 created 1965, part-incorporated 2008)]

[4.3.1.26 Transferred entry. chromopyrrolate synthase. Now EC 1.21.3.9, dichlorochromopyrrolate synthase]

[EC 4.3.1.26 created 2010, deleted 2013]

EC 4.3.1.27

Accepted name: *threo*-3-hydroxy-D-aspartate ammonia-lyase

Reaction: *threo*-3-hydroxy-D-aspartate = oxaloacetate + NH_3

Other name(s): D-*threo*-3-hydroxyaspartate dehydratase

Systematic name: *threo*-3-hydroxy-D-aspartate ammonia-lyase (oxaloacetate-forming)

Comments: A pyridoxal-phosphate protein. The enzyme, purified from the bacterium *Delftia* sp. HT23, also has activity against L-*threo*-3-hydroxyaspartate, L-*erythro*-3-hydroxyaspartate, and D-serine. Different from EC 4.3.1.20, *erythro*-3-hydroxy-L-aspartate ammonia-lyase and EC 4.3.1.16, *threo*-3-hydroxy-L-aspartate ammonia-lyase. Requires a divalent cation such as Mn^{2+}, Co^{2+} or Ni^{2+}.

References: [860]

[EC 4.3.1.27 created 2011]

EC 4.3.1.28

Accepted name: L-lysine cyclodeaminase

Reaction: L-lysine = L-pipecolate + NH_3

Other name(s): *rapL* (gene name); *fkbL* (gene name); *tubZ* (gene name); *visC* (gene name)

Systematic name: L-lysine ammonia-lyase (cyclizing; ammonia-forming)

Comments: Requires bound NAD^+. The enzyme produces the non-proteinogenic amino acid L-pipecolate, which is incorporated into multiple secondary metabolite products, including rapamycin, tobulysin, virginiamycin and pristinamycin.

References: [694, 431, 1396]

[EC 4.3.1.28 created 2012]

EC 4.3.1.29

Accepted name: D-glucosaminate-6-phosphate ammonia-lyase

Reaction: 2-amino-2-deoxy-D-gluconate 6-phosphate = 2-dehydro-3-deoxy-6-phospho-D-gluconate + NH_3

Other name(s): DgaE; 6-phospho-D-glucosaminate ammonia-lyase (2-dehydro-3-deoxy-6-phospho-D-gluconate-forming)

Systematic name: 2-amino-2-deoxy-D-gluconate 6-phosphate ammonia-lyase (2-dehydro-3-deoxy-6-phospho-D-gluconate-forming)

Comments: The enzyme, from the bacterium *Salmonella typhimurium*, is involved in the degradation pathway of 2-amino-2-deoxy-D-gluconate.

References: [941]

[EC 4.3.1.29 created 2013]

EC 4.3.1.30

Accepted name: dTDP-4-amino-4,6-dideoxy-D-glucose ammonia-lyase

Reaction: dTDP-4-amino-4,6-dideoxy-α-D-glucopyranose + *S*-adenosyl-L-methionine + reduced acceptor = dTDP-3-dehydro-4,6-dideoxy-α-D-glucopyranose + NH_3 + L-methionine + 5′-deoxyadenosine + acceptor

Other name(s): *desII* (gene name); *eryCV* (gene name); MegCV

Systematic name: dTDP-4-amino-4,6-dideoxy-α-D-glucopyranose ammonia lyase (dTDP-3-dehydro-4,6-dideoxy-α-D-glucopyranose-forming)

Comments: The enzyme, which is a member of the ‘AdoMet radical’ (radical SAM) family, is involved in biosynthesis of TDP-α-D-desosamine. The reaction starts by the transfer of an electron from the reduced form of the enzyme’s [4Fe-4S] cluster to *S*-adenosyl-L-methionine, spliting it into methionine and the radical 5-deoxyadenosin-5′-yl, which attacks the sugar substrate.

References: [1333, 1176, 1177]

[EC 4.3.1.30 created 2011]

EC 4.3.1.31

Accepted name: L-tryptophan ammonia lyase

Reaction: L-tryptophan = 3-indoleacrylate + NH_3

Other name(s): WAL

Systematic name: L-tryptophan ammonia-lyase (3-indoleacrylate-forming)

Comments: The enzyme, characterized from the bacterium *Rubrivivax benzoatilyticus* JA2, requires no cofactors. It acts on L-phenylalanine and L-glutamate with about 60% of the activity with L-tryptophan, and on L-tyrosine, glycine, and L-alanine with about 30% of the activity.

References: [761]

[EC 4.3.1.31 created 2016]

EC 4.3.1.32

Accepted name: 7,8-didemethyl-8-hydroxy-5-deazariboflavin synthase

Reaction: 5-amino-5-(4-hydroxybenzyl)-6-(D-ribitylimino)-5,6-dihydrouracil + *S*-adenosyl-L-methionine = 7,8-didemethyl-8-hydroxy-5-deazariboflavin + NH_3 + L-methionine + 5′-deoxyadenosine

Other name(s): FO synthase; *fbiC* (gene name) (ambiguous); *cofG* (gene name)

Systematic name: 5-amino-5-(4-hydroxybenzyl)-6-(D-ribitylimino)-5,6-dihydrouracil ammonia-lyase (7,8-didemethyl-8-hydroxy-5-deazariboflavin-forming)

Comments: The enzyme produces the 7,8-didemethyl-8-hydroxy-5-deazariboflavin (FO) precursor of the redox cofactor coenzyme F_{420}, which is found in methanogens and in various actinobacteria. FO is also produced by some cyanobacteria and eukaryotes. The enzyme, which forms a complex with EC 2.5.1.147, 5-amino-6-(D-ribitylamino)uracil—L-tyrosine 4-hydroxyphenyl transferase, is a radical SAM enzyme that uses the 5′-deoxyadenosyl radical to catalyse the condensation reaction.

References: [305, 1080]

[EC 4.3.1.32 created 2010 as EC 2.5.1.77, part transferred 2018 to EC 4.3.1.32]

EC 4.3.2 Amidine-lyases

EC 4.3.2.1

Accepted name: argininosuccinate lyase

Reaction: 2-(N^{ω}-L-arginino)succinate = fumarate + L-arginine

Other name(s): arginosuccinase; argininosuccinic acid lyase; arginine-succinate lyase; *N*-(L-argininosuccinate) arginine-lyase; ω-*N*-(L-arginino)succinate arginine-lyase; 2-(ω-*N*-L-arginino)succinate arginine-lyase (fumarate-forming)

Systematic name: 2-(N^{ω}-L-arginino)succinate arginine-lyase (fumarate-forming)
References: [297]

[EC 4.3.2.1 created 1961]

EC 4.3.2.2

Accepted name: adenylosuccinate lyase
Reaction: (1) N^6-(1,2-dicarboxyethyl)AMP = fumarate + AMP
(2) (*S*)-2-[5-amino-1-(5-phospho-D-ribosyl)imidazole-4-carboxamido]succinate = fumarate + 5-amino-1-(5-phospho-D-ribosyl)imidazole-4-carboxamide
Other name(s): adenylosuccinase; succino AMP-lyase; 6-*N*-(1,2-dicarboxyethyl)AMP AMP-lyase; 6-*N*-(1,2-dicarboxyethyl)AMP AMP-lyase (fumarate-forming)
Systematic name: N^6-(1,2-dicarboxyethyl)AMP AMP-lyase (fumarate-forming)
Comments: Also acts on 1-(5-phosphoribosyl)-4-(*N*-succinocarboxamide)-5-aminoimidazole.
References: [193]

[EC 4.3.2.2 created 1961, modified 2000]

EC 4.3.2.3

Accepted name: ureidoglycolate lyase
Reaction: (*S*)-ureidoglycolate = glyoxylate + urea
Other name(s): ureidoglycolatase (ambiguous); ureidoglycolase (ambiguous); ureidoglycolate hydrolase (misleading); (*S*)-ureidoglycolate urea-lyase
Systematic name: (*S*)-ureidoglycolate urea-lyase (glyoxylate-forming)
Comments: This microbial enzyme is involved in the degradation of ureidoglycolate, an intermediate of purine degradation. Not to be confused with EC 3.5.1.116, ureidoglycolate amidohydrolase, which releases ammonia rather than urea.
References: [1389, 1461]

[EC 4.3.2.3 created 1972, modified 2014]

EC 4.3.2.4

Accepted name: purine imidazole-ring cyclase
Reaction: DNA 4,6-diamino-5-formamidopyrimidine = DNA adenine + H_2O
Other name(s): DNA-4,6-diamino-5-formamidopyrimidine 8-C,9-*N*-lyase (cyclizing); DNA-4,6-diamino-5-formamidopyrimidine 8-C,9-*N*-lyase (cyclizing; DNA-adenine-forming)
Systematic name: DNA-4,6-diamino-5-formamidopyrimidine C^8-N^9-lyase (cyclizing; DNA-adenine-forming)
Comments: Also acts on 2,6-diamino-5-formamido-3,4-dihydro-4-oxopyrimidine residues. Brings about the reclosure of the imidazole rings of purine residues damaged by γ-rays.
References: [222]

[EC 4.3.2.4 created 1989]

EC 4.3.2.5

Accepted name: peptidylamidoglycolate lyase
Reaction: [peptide]-(2*S*)-2-hydroxyglycine = [peptide]-amide + glyoxylate
Other name(s): α-hydroxyglycine amidating dealkylase; peptidyl-α-hydroxyglycine α-amidating lyase; HGAD; PGL; PAL; peptidylamidoglycolate peptidylamide-lyase
Systematic name: [peptide]-(2*S*)-2-hydroxyglycine peptidyl-amide-lyase (glyoxylate-forming)
Comments: Requires zinc. The enzyme acts on the product of the reaction catalysed by EC 1.14.17.3 peptidylglycine monooxygenase, thus removing a terminal glycine residue and leaving a des-glycine peptide amide. In mammals, the two activities are part of a bifunctional protein.
References: [674, 83]

[EC 4.3.2.5 created 1992, modified 2019]

EC 4.3.2.6

Accepted name: γ-L-glutamyl-butirosin B γ-glutamyl cyclotransferase

Reaction: γ-L-glutamyl-butirosin B = butirosin B + 5-oxo-L-proline

Other name(s): *btrG* (gene name); γ-L-glutamyl-butirosin B γ-glutamyl cyclotransferase (5-oxoproline producing)

Systematic name: γ-L-glutamyl-butirosin B γ-glutamyl cyclotransferase (5-oxo-L-proline producing)

Comments: The enzyme catalyses the last step in the biosynthesis of the aminoglycoside antibiotic butirosin B. The enzyme acts as a cyclotransferase, cleaving the amide bond via transamidation using the α-amine of the terminal γ-L-glutamate of the side chain, releasing it as the cyclic 5-oxo-L-proline.

References: [836]

[EC 4.3.2.6 created 2012]

EC 4.3.2.7

Accepted name: glutathione-specific γ-glutamylcyclotransferase

Reaction: glutathione = L-cysteinylglycine + 5-oxo-L-proline

Other name(s): γ-GCG; CHAC (gene name); CHAC1 (gene name); CHAC2 (gene name)

Systematic name: glutathione γ-glutamyl cyclotransferase (5-oxo-L-proline producing)

Comments: The enzyme, found in bacteria, fungi and animals, is specific for glutathione (*cf.* EC 4.3.2.9, γ-glutamylcyclotransferase). The enzyme acts as a cyclotransferase, cleaving the amide bond via transamidation using the α-amine of the L-glutamyl residue, releasing it as the cyclic 5-oxo-L-proline.

References: [758, 681]

[EC 4.3.2.7 created 2017]

EC 4.3.2.8

Accepted name: γ-glutamylamine cyclotransferase

Reaction: ε-(γ-L-glutamyl)-L-lysine = L-lysine + 5-oxo-L-proline

Other name(s): GGACT

Systematic name: ε-(γ-L-glutamyl)-L-lysine γ-glutamyl cyclotransferase (5-oxo-L-proline producing)

Comments: The enzyme, found in vertebrates, has no activity toward α-(γ-L-glutamyl)-L-amino acids (*cf.* EC 4.3.2.9, γ-glutamylcyclotransferase). The enzyme acts as a cyclotransferase, cleaving the amide bond via transamidation using the α-amine of the γ-L-glutamyl residue, releasing it as the cyclic 5-oxo-L-proline.

References: [383, 1017]

[EC 4.3.2.8 created 2017]

EC 4.3.2.9

Accepted name: γ-glutamylcyclotransferase

Reaction: α-(γ-L-glutamyl)-L-amino acid = α-L-amino acid + 5-oxo-L-proline

Other name(s): γ-glutamyl-amino acid cyclotransferase; γ-L-glutamylcyclotransferase; L-glutamic cyclase; (5-L-glutamyl)-L-amino-acid 5-glutamyltransferase (cyclizing); GGCT

Systematic name: α-(γ-L-glutamyl)-L-amino-acid γ-glutamyl cyclotransferase (5-oxo-L-proline producing)

Comments: The enzyme, found in animals and plants, acts on derivatives of L-glutamate, L-2-aminobutanoate, L-alanine and glycine. The enzyme acts as a cyclotransferase, cleaving the amide bond via transamidation using the α-amine of the L-glutamyl residue, releasing it as the cyclic 5-oxo-L-proline.

References: [110, 1038, 1018, 1058]

[EC 4.3.2.9 created 1972 as EC 2.3.2.4, transferred 2017 to EC 4.3.2.9]

EC 4.3.2.10

Accepted name: imidazole glycerol-phosphate synthase

Reaction: 5-[(5-phospho-1-deoxy-D-ribulos-1-ylamino)methylideneamino]-1-(5-phospho-β-D-ribosyl)imidazole-4-carboxamide + L-glutamine = 5-amino-1-(5-phospho-β-D-ribosyl)imidazole-4-carboxamide + D-*erythro*-1-(imidazol-4-yl)glycerol 3-phosphate + L-glutamate (overall reaction)
(1a) L-glutamine + H_2O = L-glutamate + NH_3
(1b) 5-[(5-phospho-1-deoxy-D-ribulos-1-ylamino)methylideneamino]-1-(5-phospho-β-D-ribosyl)imidazole-4-carboxamide + NH_3 = 5-amino-1-(5-phospho-β-D-ribosyl)imidazole-4-carboxamide + D-*erythro*-1-(imidazol-4-yl)glycerol 3-phosphate + H_2O

Other name(s): IGP synthase; *hisFH* (gene names); HIS7 (gene name)

Systematic name: 5-[(5-phospho-1-deoxy-D-ribulos-1-ylamino)methylideneamino]-1-(5-phospho-β-D-ribosyl)imidazole-4-carboxamide D-*erythro*-1-(imidazol-4-yl)glycerol 3-phosphate-lyase (L-glutamine-hydrolysing; 5-amino-1-(5-phospho-β-D-ribosyl)imidazole-4-carboxamide-forming)

Comments: The enzyme is involved in histidine biosynthesis, as well as purine nucleotide biosynthesis. The enzymes from archaea and bacteria are heterodimeric. A glutaminase component (*cf.* EC 3.5.1.2, glutaminase) produces an ammonia molecule that is transferred by a 25 Å tunnel to a cyclase component, which adds it to the imidazole ring, leading to lysis of the molecule and cyclization of one of the products. The glutminase subunit is only active within the dimeric complex. In fungi and plants the two subunits are combined into a single polypeptide.

References: [710, 411, 81, 329, 214]

[EC 4.3.2.10 created 2018]

EC 4.3.2.11

Accepted name: (3*R*)-3-[(carboxylmethyl)amino]fatty acid synthase

Reaction: (3*R*)-3-[(carboxylmethyl)amino]fatty acid + an [acyl-carrier protein] = a (2*E*)-unsaturated fatty acyl-[acyl-carrier protein] + glycine + H_2O

Other name(s): *scoD* (gene name); *mmaD* (gene name)

Systematic name: (3*R*)-3-[(carboxylmethyl)amino]fatty acid glycine-lyase ((2*E*)-unsaturated fatty acyl-[acyl-carrier protein]-forming)

Comments: The enzyme, found in some actinobacterial species, participates in the biosynthesis of isonitrile-containing lipopeptides. It catalyses the formation of (3*R*)-3-[(carboxylmethyl)amino]fatty acid by the addition of glycine and the release of the product from the acyl-carrier protein.

References: [515, 514]

[EC 4.3.2.11 created 2022]

EC 4.3.3 Amine-lyases

EC 4.3.3.1

Accepted name: 3-ketovalidoxylamine C-N-lyase

Reaction: 4-nitrophenyl-3-ketovalidamine = 4-nitroaniline + 5-D-(5/6)-5-*C*-(hydroxymethyl)-2,6-dihydroxycyclohex-2-en-1-one

Other name(s): 3-ketovalidoxylamine A C-N-lyase; *p*-nitrophenyl-3-ketovalidamine *p*-nitroaniline lyase; 4-nitrophenyl-3-ketovalidamine 4-nitroaniline-lyase

Systematic name: 4-nitrophenyl-3-ketovalidamine 4-nitroaniline-lyase [5-D-(5/6)-5-*C*-(hydroxymethyl)-2,6-dihydroxycyclohex-2-en-1-one-forming]

Comments: Requires Ca^{2+}. Eliminates 4-nitroaniline from 4-nitrophenyl-3-ketovalidamine, or 4-nitrophenol from 4-nitrophenyl-α-D-3-dehydroglucoside. Involved in the degradation of the fungicide validamycin A by *Flavobacterium saccharophilum*.

References: [43, 1345]

[EC 4.3.3.1 created 1989]

EC 4.3.3.2

Accepted name: strictosidine synthase
Reaction: 3-α(*S*)-strictosidine + H_2O = tryptamine + secologanin
Other name(s): strictosidine synthetase; STR; 3-α(*S*)-strictosidine tryptamine-lyase
Systematic name: 3-α(*S*)-strictosidine tryptamine-lyase (secologanin-forming)
Comments: Catalyses a Pictet-Spengler reaction between the aldehyde group of secologanin and the amino group of tryptamine [1174, 908]. Involved in the biosynthesis of the monoterpenoid indole alkaloids.
References: [1388, 771, 304, 1174, 908, 857]

[EC 4.3.3.2 created 1990]

EC 4.3.3.3

Accepted name: deacetylisoipecoside synthase
Reaction: deacetylisoipecoside + H_2O = dopamine + secologanin
Other name(s): deacetylisoipecoside dopamine-lyase
Systematic name: deacetylisoipecoside dopamine-lyase (secologanin-forming)
Comments: The enzyme from the leaves of *Alangium lamarckii* differs in enantiomeric specificity from EC 4.3.3.4 deacetylipecoside synthase. The product is rapidly converted to demethylisoalangiside.
References: [306]

[EC 4.3.3.3 created 2000]

EC 4.3.3.4

Accepted name: deacetylipecoside synthase
Reaction: deacetylipecoside + H_2O = dopamine + secologanin
Other name(s): deacetylipecoside dopamine-lyase
Systematic name: deacetylipecoside dopamine-lyase (secologanin-forming)
Comments: The enzyme from the leaves of *Alangium lamarckii* differs in enantiomeric specificity from EC 4.3.3.3 deacetylisoipecoside synthase. The product is rapidly converted to demethylalangiside.
References: [306]

[EC 4.3.3.4 created 2000]

EC 4.3.3.5

Accepted name: 4′-demethylrebeccamycin synthase
Reaction: 4′-*O*-demethylrebeccamycin + H_2O = dichloro-arcyriaflavin A + β-D-glucose
Other name(s): arcyriaflavin A *N*-glycosyltransferase; RebG
Systematic name: 4′-demethylrebeccamycin D-glucose-lyase
Comments: This enzyme catalyses a step in the biosynthesis of rebeccamycin, an indolocarbazole alkaloid produced by the bacterium *Lechevalieria aerocolonigenes*. The enzyme is a glycosylase, and acts in the reverse direction to that shown. It has a wide substrate range, and was shown to glycosylate several substrates, including the staurosporine aglycone, EJG-III-108A, J-104303, 6-*N*-methyl-arcyriaflavin C and indolo-[2,3-*a*]-carbazole [1025, 1549].
References: [1025, 1549]

[EC 4.3.3.5 created 2010]

EC 4.3.3.6

Accepted name: pyridoxal 5′-phosphate synthase (glutamine hydrolysing)
Reaction: D-ribose 5-phosphate + D-glyceraldehyde 3-phosphate + L-glutamine = pyridoxal 5′-phosphate + L-glutamate + **3** H_2O + phosphate (overall reaction)
(1a) L-glutamine + H_2O = L-glutamate + NH_3

(1b) D-ribose 5-phosphate + D-glyceraldehyde 3-phosphate + NH_3 = pyridoxal 5′-phosphate + **4** H_2O + phosphate

Other name(s): PdxST

Systematic name: D-ribose 5-phosphate,D-glyceraldehyde 3-phosphate pyridoxal 5′-phosphate-lyase

Comments: The ammonia is provided by the glutaminase subunit and channeled to the active site of the lyase subunit by a 100 Å tunnel. The enzyme can also use ribulose 5-phosphate and dihydroxyacetone phosphate. The enzyme complex is found in aerobic bacteria, archaea, fungi and plants.

References: [160, 1133, 1313, 1134, 502, 500, 501, 1436]

[EC 4.3.3.6 created 2011]

EC 4.3.3.7

Accepted name: 4-hydroxy-tetrahydrodipicolinate synthase

Reaction: pyruvate + L-aspartate-4-semialdehyde = (2*S*,4*S*)-4-hydroxy-2,3,4,5-tetrahydrodipicolinate + H_2O

Other name(s): dihydrodipicolinate synthase (incorrect); dihydropicolinate synthetase (incorrect); dihydrodipicolinic acid synthase (incorrect); L-aspartate-4-semialdehyde hydro-lyase (adding pyruvate and cyclizing); *dapA* (gene name).

Systematic name: L-aspartate-4-semialdehyde hydro-lyase [adding pyruvate and cyclizing; (4*S*)-4-hydroxy-2,3,4,5-tetrahydro-(2*S*)-dipicolinate-forming]

Comments: The reaction can be divided into three consecutive steps: Schiff base formation with pyruvate, the addition of L-aspartate-semialdehyde, and finally transimination leading to cyclization with simultaneous dissociation of the product. The product of the enzyme was initially thought to be (*S*)-2,3-dihydrodipicolinate [1536, 103], and the enzyme was classified accordingly as EC 4.2.1.52, dihydrodipicolinate synthase. Later studies of the enzyme from the bacterium *Escherichia coli* have suggested that the actual product of the enzyme is (2*S*,4*S*)-4-hydroxy-2,3,4,5-tetrahydrodipicolinate [318], and thus the enzyme has been reclassified as 4-hydroxy-tetrahydrodipicolinate synthase. However, the identity of the product is still controversial, as more recently it has been suggested that it may be (*S*)-2,3-dihydrodipicolinate after all [668].

References: [1536, 103, 318, 278, 668]

[EC 4.3.3.7 created 1972 as EC 4.2.1.52, transferred 2012 to EC 4.3.3.7, modified 2020]

EC 4.3.3.8

Accepted name: mimosinase

Reaction: L-mimosine + H_2O = 3-hydroxy-4*H*-pyrid-4-one + pyruvate + ammonia (overall reaction)
(1a) L-mimosine = 3-hydroxy-4*H*-pyrid-4-one + 2-aminoprop-2-enoate
(1b) 2-aminoprop-2-enoate = 2-iminopropanoate
(1c) 2-iminopropanoate + H_2O = pyruvate + ammonia

Other name(s): mimosine amidohydrolase (incorrect)

Systematic name: (2*S*)-2-amino-3-[3-hydroxy-4-oxopyridin-1(4*H*)-yl]propanoate 3-hydroxy-4*H*-pyrid-4-one-lyase (2-aminoprop-2-enoate-forming)

Comments: A pyridoxal 5′-phosphate protein. The enzyme degrades the toxic amino acid L-mimosine. It cleaves a carbon-nitrogen bond, releasing 3-hydroxy-4*H*-pyrid-4-one and an unstable enamine product that tautomerizes to an imine form, which undergoes a hydrolytic deamination to form pyruvate and ammonia. It is thought to have evolved from EC 4.4.1.13, cysteine-*S*-conjugate β-lyase. It has been described in both mimosine-producing plants and some bacteria.

References: [1353, 998, 1036, 1035]

[EC 4.3.3.8 created 1989 as EC 3.5.1.61, transferred 2022 to EC 4.3.3.8]

EC 4.3.99 Other carbon-nitrogen lyases

[4.3.99.1 Transferred entry. cyanate lyase. Now EC 4.2.1.104, cyanate hydratase]

[EC 4.3.99.1 created 1972 as EC 3.5.5.3, transferred 1990 to EC 4.3.99.1, deleted 2001]

[4.3.99.2 Transferred entry. carboxybiotin decarboxylase. Now EC 7.2.4.1, carboxybiotin decarboxylase]

[EC 4.3.99.2 created 2008, deleted 2018]

EC 4.3.99.3

Accepted name: 7-carboxy-7-deazaguanine synthase

Reaction: 6-carboxy-5,6,7,8-tetrahydropterin = 7-carboxy-7-carbaguanine + NH_3

Other name(s): 7-carboxy-7-carbaguanine synthase; *queE* (gene name)

Systematic name: 6-carboxy-5,6,7,8-tetrahydropterin ammonia-lyase

Comments: Requires Mg^{2+}. The enzyme is a member of the superfamily of *S*-adenosyl-L-methionine-dependent radical (radical AdoMet) enzymes. Binds a [4Fe-4S] cluster that is coordinated by 3 cysteines and an exchangeable *S*-adenosyl-L-methionine molecule. The *S*-adenosyl-L-methionine is catalytic as it is regenerated at the end of the reaction. The reaction is part of the biosynthesis pathway of queuosine.

References: [906, 904]

[EC 4.3.99.3 created 2012]

EC 4.3.99.4

Accepted name: choline trimethylamine-lyase

Reaction: choline = trimethylamine + acetaldehyde

Other name(s): *cutC* (gene name)

Systematic name: choline trimethylamine-lyase (acetaldehyde-forming)

Comments: The enzyme utilizes a glycine radical to break the C-N bond in choline. Found in choline-degrading anaerobic bacteria.

References: [258]

[EC 4.3.99.4 created 2013]

EC 4.3.99.5

Accepted name: nitrosuccinate lyase

Reaction: 2-nitrobutanedioate = fumarate + nitrite

Other name(s): *creD* (gene name)

Systematic name: 2-nitrobutanedioate lyase (fumarate-forming)

Comments: The enzyme, found in some Actinobacteria, is involved in a pathway that forms nitrite, which is subsequently used to generate a diazo group in some secondary metabolites.

References: [1318, 485]

[EC 4.3.99.5 created 2021]

EC 4.4 Carbon-sulfur lyases

This subclass contains the carbon-sulfur lyases in a single sub-subclass for enzymes that eliminate H_2S or substituted H_2S (EC 4.4.1).

EC 4.4.1 Carbon-sulfur lyases (only sub-subclass identified to date)

EC 4.4.1.1

Accepted name: cystathionine γ-lyase

Reaction: L-cystathionine + H_2O = L-cysteine + 2-oxobutanoate + NH_3 (overall reaction)

(1a) L-cystathionine = L-cysteine + 2-aminobut-2-enoate
(1b) 2-aminobut-2-enoate = 2-iminobutanoate (spontaneous)
(1c) 2-iminobutanoate + H_2O = 2-oxobutanoate + NH_3 (spontaneous)

Other name(s): homoserine deaminase; homoserine dehydratase; cystine desulfhydrase; cysteine desulfhydrase; γ-cystathionase; cystathionase; homoserine deaminase-cystathionase; γ-CTL; cystalysin; cysteine lyase; L-cystathionine cysteine-lyase (deaminating); CGL

Systematic name: L-cystathionine cysteine-lyase (deaminating; 2-oxobutanoate-forming)

Comments: A multifunctional pyridoxal-phosphate protein. The enzyme cleaves a carbon-sulfur bond, releasing L-cysteine and an unstable enamine product that tautomerizes to an imine form, which undergoes a hydrolytic deamination to form 2-oxobutanoate and ammonia. The latter reaction, which can occur spontaneously, can also be catalysed by EC 3.5.99.10, 2-iminobutanoate/2-iminopropanoate deaminase. Also catalyses the conversion of L-homoserine to 2-oxobutanoate and ammonia, of L-cystine to thiocysteine, pyruvate and ammonia, and of L-cysteine to pyruvate, hydrogen sulfide and ammonia.

References: [131, 132, 389, 896, 897]

[EC 4.4.1.1 created 1961 (EC 4.2.1.15 created 1961, incorporated 1972)]

EC 4.4.1.2

Accepted name: homocysteine desulfhydrase

Reaction: L-homocysteine + H_2O = hydrogen sulfide + NH_3 + 2-oxobutanoate (overall reaction)
(1a) L-homocysteine = hydrogen sulfide + 2-aminobut-2-enoate
(1b) 2-aminobut-2-enoate = 2-iminobutanoate (spontaneous)
(1c) 2-iminobutanoate + H_2O = 2-oxobutanoate + NH_3 (spontaneous)

Other name(s): homocysteine desulfurase; L-homocysteine hydrogen-sulfide-lyase (deaminating)

Systematic name: L-homocysteine hydrogen-sulfide-lyase (deaminating; 2-oxobutanoate-forming)

Comments: A pyridoxal-phosphate protein. The enzyme cleaves a carbon-sulfur bond, releasing hydrogen sulfide and an unstable enamine product that tautomerizes to an imine form, which undergoes a hydrolytic deamination to form 2-oxobutanoate and ammonia. The latter reaction, which can occur spontaneously, can also be catalysed by EC 3.5.99.10, 2-iminobutanoate/2-iminopropanoate deaminase

References: [654]

[EC 4.4.1.2 created 1961]

EC 4.4.1.3

Accepted name: dimethylpropiothetin dethiomethylase

Reaction: *S*,*S*-dimethyl-β-propiothetin = dimethyl sulfide + acrylate

Other name(s): desulfhydrase; *S*,*S*-dimethyl-β-propiothetin dimethyl-sulfide-lyase

Systematic name: *S*,*S*-dimethyl-β-propiothetin dimethyl-sulfide-lyase (acrylate-forming)

References: [189]

[EC 4.4.1.3 created 1961]

EC 4.4.1.4

Accepted name: alliin lyase

Reaction: an *S*-alkyl-L-cysteine *S*-oxide = an alkyl sulfenate + 2-aminoacrylate

Other name(s): alliinase; cysteine sulfoxide lyase; alkylcysteine sulfoxide lyase; *S*-alkylcysteine sulfoxide lyase; L-cysteine sulfoxide lyase; *S*-alkyl-L-cysteine sulfoxide lyase; alliin alkyl-sulfenate-lyase

Systematic name: *S*-alkyl-L-cysteine *S*-oxide alkyl-sulfenate-lyase (2-aminoacrylate-forming)

Comments: A pyridoxal-phosphate protein.

References: [342, 454, 612]

[EC 4.4.1.4 created 1961]

EC 4.4.1.5

Accepted name: lactoylglutathione lyase
Reaction: (*R*)-*S*-lactoylglutathione = glutathione + 2-oxopropanal
Other name(s): methylglyoxalase; aldoketomutase; ketone-aldehyde mutase; glyoxylase I; (*R*)-*S*-lactoylglutathione methylglyoxal-lyase (isomerizing)
Systematic name: (*R*)-*S*-lactoylglutathione methylglyoxal-lyase (isomerizing; glutathione-forming)
Comments: Also acts on 3-phosphoglycerol-glutathione.
References: [354, 1122]

[EC 4.4.1.5 created 1961]

[4.4.1.6 Transferred entry. S-alkylcysteine lyase. Now included in EC 4.4.1.13, cysteine-S-conjugate β-lyase]

[EC 4.4.1.6 created 1965, deleted 1972, reinstated 1976, deleted 2018]

[4.4.1.7 Deleted entry. S-(hydroxyalkyl)glutathione lyase. Now included with EC 2.5.1.18 glutathione transferase]

[EC 4.4.1.7 created 1972, deleted 1976]

[4.4.1.8 Transferred entry. cystathionine β-lyase. Now included in EC 4.4.1.13, cysteine-S-conjugate β-lyase]

[EC 4.4.1.8 created 1972, deleted 2018]

EC 4.4.1.9

Accepted name: L-3-cyanoalanine synthase
Reaction: L-cysteine + hydrogen cyanide = L-3-cyanoalanine + hydrogen sulfide
Other name(s): β-cyanoalanine synthase; β-cyanoalanine synthetase; β-cyano-L-alanine synthase; L-cysteine hydrogen-sulfide-lyase (adding HCN)
Systematic name: L-cysteine hydrogen-sulfide-lyase (adding hydrogen cyanide; L-3-cyanoalanine-forming)
Comments: Contains pyridoxal phospate.
References: [9, 197, 537, 538]

[EC 4.4.1.9 created 1972, deleted 1976, reinstated 1978]

EC 4.4.1.10

Accepted name: cysteine lyase
Reaction: L-cysteine + sulfite = L-cysteate + hydrogen sulfide
Other name(s): cysteine (sulfite) lyase; L-cysteine hydrogen-sulfide-lyase (adding sulfite)
Systematic name: L-cysteine hydrogen-sulfide-lyase (adding sulfite; L-cysteate-forming)
Comments: A pyridoxal-phosphate protein. Can use a second molecule of cysteine (producing lanthionine), or other alkyl thiols, as a replacing agent.
References: [1377]

[EC 4.4.1.10 created 1972]

EC 4.4.1.11

Accepted name: methionine γ-lyase
Reaction: L-methionine + H_2O = methanethiol + NH_3 + 2-oxobutanoate (overall reaction)
(1a) L-methionine = methanethiol + 2-aminobut-2-enoate
(1b) 2-aminobut-2-enoate = 2-iminobutanoate (spontaneous)
(1c) 2-iminobutanoate + H_2O = 2-oxobutanoate + NH_3 (spontaneous)
Other name(s): L-methioninase; methionine lyase; methioninase; methionine dethiomethylase; L-methionine γ-lyase; L-methionine methanethiol-lyase (deaminating)
Systematic name: L-methionine methanethiol-lyase (deaminating; 2-oxobutanoate-forming)

Comments: A pyridoxal-phosphate protein. The enzyme cleaves a carbon-sulfur bond, releasing methanethiol and an unstable enamine product that tautomerizes to an imine form, which undergoes a hydrolytic deamination to form 2-oxobutanoate and ammonia. The latter reaction, which can occur spontaneously, can also be catalysed by EC 3.5.99.10, 2-iminobutanoate/2-iminopropanoate deaminase. The enzyme is involved in L-methionine catabolism.

References: [738]

[EC 4.4.1.11 created 1976]

[4.4.1.12 Deleted entry. sulfoacetaldehyde lyase. Activity due to EC 2.3.3.15, sulfoacetaldehyde acetyltransferase]

[EC 4.4.1.12 created 1976, deleted 2003]

EC 4.4.1.13

Accepted name: cysteine-*S*-conjugate β-lyase

Reaction: an L-cysteine-*S*-conjugate + H_2O = a thiol + NH_3 + pyruvate (overall reaction)
(1a) an L-cysteine-*S*-conjugate = a thiol + 2-aminoprop-2-enoate
(1b) 2-aminoprop-2-enoate = 2-iminopropanoate (spontaneous)
(1c) 2-iminopropanoate + H_2O = pyruvate + NH_3 (spontaneous)

Other name(s): cysteine conjugate β-lyase; glutamine transaminase K/cysteine conjugate β-lyase; L-cysteine-*S*-conjugate thiol-lyase (deaminating); cystathionine β-lyase; β-cystathionase; cystine lyase; cystathionine L-homocysteine-lyase (deaminating); L-cystathionine L-homocysteine-lyase (deaminating); CBL; *S*-alkylcysteine lyase; *S*-alkylcysteinase; alkylcysteine lyase; *S*-alkyl-L-cysteine lyase; *S*-alkyl-L-cysteinase; alkyl cysteine lyase; *S*-alkyl-L-cysteine alkylthiol-lyase (deaminating)

Systematic name: L-cysteine-*S*-conjugate thiol-lyase (deaminating; 2-aminoprop-2-enoate-forming)

Comments: A pyridoxal-phosphate protein. The enzyme is promiscuous regarding the moiety conjugated to L-cysteine, and can accept both aliphatic and aromatic substitutions. The enzyme cleaves a carbon-sulfur bond, releasing a thiol and an unstable enamine product that tautomerizes to an imine form, which undergoes a hydrolytic deamination to form pyruvate and ammonia. While bacteria and plants have dedicated enzymes, all of the animal enzymes discovered thus far are bifunctional, most of which also act as aminotransferases.

References: [391, 1357, 1304, 1305, 429, 249, 248, 996, 250]

[EC 4.4.1.13 created 1981, modified 2018 (EC 4.4.1.6 created 1965, deleted 1972, reinstated 1976, incorporated 2018) (EC 4.4.1.8 created 1972, incorporated 2018)]

EC 4.4.1.14

Accepted name: 1-aminocyclopropane-1-carboxylate synthase

Reaction: *S*-adenosyl-L-methionine = 1-aminocyclopropane-1-carboxylate + *S*-methyl-5′-thioadenosine

Other name(s): 1-aminocyclopropanecarboxylate synthase; 1-aminocyclopropane-1-carboxylic acid synthase; 1-aminocyclopropane-1-carboxylate synthetase; aminocyclopropanecarboxylic acid synthase; aminocyclopropanecarboxylate synthase; ACC synthase; *S*-adenosyl-L-methionine methylthioadenosine-lyase; *S*-adenosyl-L-methionine methylthioadenosine-lyase (1-aminocyclopropane-1-carboxylate-forming)

Systematic name: *S*-adenosyl-L-methionine *S*-methyl-5′-thioadenosine-lyase (1-aminocyclopropane-1-carboxylate-forming)

Comments: A pyridoxal 5′-phosphate protein. The enzyme catalyses an α,γ-elimination.

References: [115, 1531]

[EC 4.4.1.14 created 1984, modified 2021]

EC 4.4.1.15

Accepted name: D-cysteine desulfhydrase

Reaction: D-cysteine + H_2O = sulfide + NH_3 + pyruvate

Other name(s): D-cysteine lyase; D-cysteine sulfide-lyase (deaminating)
Systematic name: D-cysteine sulfide-lyase (deaminating; pyruvate-forming)
References: [980, 1215, 1216]

[EC 4.4.1.15 created 1986]

EC 4.4.1.16

Accepted name: selenocysteine lyase
Reaction: L-selenocysteine + reduced acceptor = selenide + L-alanine + acceptor
Other name(s): selenocysteine reductase; selenocysteine β-lyase
Systematic name: L-selenocysteine selenide-lyase (L-alanine-forming)
Comments: A pyridoxal-phosphate protein. Dithiothreitol or 2-sulfanylethan-1-ol (2-mercaptoethanol) can act as the reducing agent in the reaction. The enzyme from animals does not act on cysteine, serine or chloroalanine [365, 1031], while the enzyme from bacteria shows activity with cysteine (*cf.* EC 2.8.1.7, cysteine desulfurase) [938].
References: [365, 938, 1031]

[EC 4.4.1.16 created 1986]

EC 4.4.1.17

Accepted name: holocytochrome-*c* synthase
Reaction: holocytochrome *c* = apocytochrome *c* + heme
Other name(s): cytochrome *c* heme-lyase; holocytochrome *c* synthetase; holocytochrome-*c* apocytochrome-*c*-lyase
Systematic name: holocytochrome-*c* apocytochrome-*c*-lyase (heme-forming)
Comments: In the reverse direction, the enzyme catalyses the attachment of heme to two cysteine residues in the protein, forming thioether links.
References: [339]

[EC 4.4.1.17 created 1990]

[4.4.1.18 Transferred entry. prenylcysteine lyase. Now EC 1.8.3.5, prenylcysteine oxidase]

[EC 4.4.1.18 created 2000, deleted 2002]

EC 4.4.1.19

Accepted name: phosphosulfolactate synthase
Reaction: (2*R*)-2-*O*-phospho-3-sulfolactate = phospho*enol*pyruvate + sulfite
Other name(s): (2*R*)-phospho-3-sulfolactate synthase; (2*R*)-*O*-phospho-3-sulfolactate sulfo-lyase
Systematic name: (2*R*)-2-*O*-phospho-3-sulfolactate hydrogen-sulfite-lyase (phospho*enol*pyruvate-forming)
Comments: Requires Mg^{2+}. The enzyme from the archaeon *Methanococcus jannaschii* catalyses the Michael addition of sulfite to phospho*enol*pyruvate. It specifically requires phospho*enol*pyruvate and its broad alkaline pH optimum suggests that it uses sulfite rather than hydrogensulfite.
References: [462]

[EC 4.4.1.19 created 2003]

EC 4.4.1.20

Accepted name: leukotriene-C_4 synthase
Reaction: leukotriene C_4 = leukotriene A_4 + glutathione
Other name(s): leukotriene C_4 synthetase; LTC4 synthase; LTC4 synthetase; leukotriene A_4:glutathione *S*-leukotrienyltransferase; (7*E*,9*E*,11*Z*,14*Z*)-(5*S*,6*R*)-5,6-epoxyicosa-7,9,11,14-tetraenoate:glutathione leukotriene-transferase (epoxide-ring-opening); (7*E*,9*E*,11*Z*,14*Z*)-(5*S*,6*R*)-6-(glutathion-*S*-yl)-5-hydroxyicosa-7,9,11,14-tetraenoate glutathione-lyase (epoxide-forming)

Systematic name: leukotriene-C_4 glutathione-lyase (leukotriene-A_4-forming)
Comments: The reaction proceeds in the direction of addition. Not identical with EC 2.5.1.18, glutathione transferase.
References: [53, 1265, 777, 234]

[EC 4.4.1.20 created 1989 as EC 2.5.1.37, transferred 2004 to EC 4.4.1.20]

EC 4.4.1.21

Accepted name: *S*-ribosylhomocysteine lyase
Reaction: *S*-(5-deoxy-D-ribos-5-yl)-L-homocysteine = L-homocysteine + (4*S*)-4,5-dihydroxypentan-2,3-dione
Other name(s): *S*-ribosylhomocysteinase; LuxS
Systematic name: *S*-(5-deoxy-D-ribos-5-yl)-L-homocysteine L-homocysteine-lyase [(4*S*)-4,5-dihydroxypentan-2,3-dione-forming]
Comments: Contains Fe^{2+}. The 4,5-dihydroxypentan-2,3-dione formed spontaneously cyclizes and combines with borate to form an autoinducer (AI-2) in the bacterial quorum-sensing mechanism, which is used by many bacteria to control gene expression in response to cell density [942].
References: [1570, 942]

[EC 4.4.1.21 created 2004]

EC 4.4.1.22

Accepted name: *S*-(hydroxymethyl)glutathione synthase
Reaction: *S*-(hydroxymethyl)glutathione = glutathione + formaldehyde
Other name(s): glutathione-dependent formaldehyde-activating enzyme; Gfa; *S*-(hydroxymethyl)glutathione formaldehyde-lyase
Systematic name: *S*-(hydroxymethyl)glutathione formaldehyde-lyase (glutathione-forming)
Comments: The enzyme from *Paracoccus denitrificans* accelerates the spontaneous reaction in which the adduct of formaldehyde and glutathione is formed, i.e. the substrate for EC 1.1.1.284, *S*-(hydroxymethyl)glutathione dehydrogenase, in the formaldehyde-detoxification pathway.
References: [448]

[EC 4.4.1.22 created 2005 (EC 1.2.1.1 created 1961, modified 1982, modified 2002, part transferred 2005 to EC 4.4.1.22)]

EC 4.4.1.23

Accepted name: 2-hydroxypropyl-CoM lyase
Reaction: (1) (*R*)-2-hydroxypropyl-CoM = (*R*)-1,2-epoxypropane + HS-CoM
(2) (*S*)-2-hydroxypropyl-CoM = (*S*)-1,2-epoxypropane + HS-CoM
Other name(s): epoxyalkane:coenzyme M transferase; epoxyalkane:CoM transferase; epoxyalkane:2-mercaptoethanesulfonate transferase; coenzyme M-epoxyalkane ligase; epoxyalkyl:CoM transferase; epoxypropane:coenzyme M transferase; epoxypropyl:CoM transferase; EaCoMT; 2-hydroxypropyl-CoM:2-mercaptoethanesulfonate lyase (epoxyalkane-ring-forming); (*R*)-2-hydroxypropyl-CoM 2-mercaptoethanesulfonate lyase (cyclizing; (*R*)-1,2-epoxypropane-forming)
Systematic name: (*R*)[or (*S*)]-2-hydroxypropyl-CoM:2-sulfanylethane-1-sulfonate lyase (epoxyalkane-ring-forming)
Comments: Requires zinc. Acts on both enantiomers of chiral epoxyalkanes to form the corresponding (*R*)- and (*S*)-2-hydroxyalkyl-CoM adducts. The enzyme will function with some other thiols (e.g., 2-sulfanylethanol) as the nucleophile. Uses short-chain epoxyalkanes from C_2 (epoxyethane) to C_6 (1,2-epoxyhexane). This enzyme forms component I of a four-component enzyme system (comprising EC 4.4.1.23 (2-hydroxypropyl-CoM lyase; component I), EC 1.8.1.5 [2-oxopropyl-CoM reductase (carboxylating); component II], EC 1.1.1.268 [2-(*R*)-hydroxypropyl-CoM dehydrogenase; component III] and EC 1.1.1.269 [2-(*S*)-hydroxypropyl-CoM dehydrogenase; component IV]) that is involved in epoxyalkane carboxylation in *Xanthobacter* sp. strain Py2.
References: [20, 743, 244]

[EC 4.4.1.23 created 2001 as EC 4.2.99.19, transferred 2005 to EC 4.4.1.23]

EC 4.4.1.24

Accepted name: (2*R*)-sulfolactate sulfo-lyase

Reaction: (2*R*)-3-sulfolactate = pyruvate + hydrogensulfite

Other name(s): Suy; SuyAB; 3-sulfolactate bisulfite-lyase; sulfolactate sulfo-lyase (ambigious); (2*R*)-3-sulfolactate bisulfite-lyase (pyruvate-forming)

Systematic name: (2*R*)-3-sulfolactate hydrogensulfite-lyase (pyruvate-forming)

Comments: Requires iron(II). This inducible enzyme participates in cysteate degradation by the bacterium *Paracoccus pantotrophus* NKNCYSA and in 3-sulfolactate degradation by the bacterium *Chromohalobacter salexigens*. The enzyme is specific for the (*R*) isomer of its substrate.

References: [461, 1143, 312]

[EC 4.4.1.24 created 2006, modified 2011]

EC 4.4.1.25

Accepted name: L-cysteate sulfo-lyase

Reaction: L-cysteate + H_2O = hydrogensulfite + pyruvate + NH_3 (overall reaction)
(1a) L-cysteate = hydrogensulfite + 2-aminoprop-2-enoate
(1b) 2-aminoprop-2-enoate = 2-iminopropanoate (spontaneous)
(1c) 2-iminopropanoate + H_2O = pyruvate + NH_3 (spontaneous)

Other name(s): L-cysteate sulfo-lyase (deaminating); CuyA; L-cysteate bisulfite-lyase (deaminating; pyruvate-forming)

Systematic name: L-cysteate hydrogensulfite-lyase (deaminating; pyruvate-forming)

Comments: A pyridoxal-phosphate protein. The enzyme cleaves a carbon-sulfur bond, releasing hydrogensulfite and an unstable enamine product that tautomerizes to an imine form, which undergoes a hydrolytic deamination to form pyruvate and ammonia. The latter reaction, which can occur spontaneously, can also be catalysed by EC 3.5.99.10, 2-iminobutanoate/2-iminopropanoate deaminase. D-Cysteine can also act as a substrate, but more slowly. It is converted into hydrogen sulfide, pyruvate, and ammonia. This inducible enzyme from the marine bacterium *Silicibacter pomeroyi* DSS-3 forms part of the cysteate-degradation pathway.

References: [313]

[EC 4.4.1.25 created 2006]

EC 4.4.1.26

Accepted name: olivetolic acid cyclase

Reaction: 3,5,7-trioxododecanoyl-CoA = CoA + 2,4-dihydroxy-6-pentylbenzoate

Other name(s): OAC

Systematic name: 3,5,7-trioxododecanoyl-CoA CoA-lyase (2,4-dihydroxy-6-pentylbenzoate-forming)

Comments: Part of the cannabinoids biosynthetic pathway in the plant *Cannabis sativa*.

References: [421]

[EC 4.4.1.26 created 2012]

[4.4.1.27 Transferred entry. carbon disulfide lyase. Now EC 3.13.1.5, carbon disulfide hydrolase]

[EC 4.4.1.27 created 2013, deleted 2017]

EC 4.4.1.28

Accepted name: L-cysteine desulfidase

Reaction: L-cysteine + H_2O = sulfide + NH_3 + pyruvate (overall reaction)
(1a) L-cysteine = 2-aminoprop-2-enoate + sulfide
(1b) 2-aminoprop-2-enoate = 2-iminopropanoate (spontaneous)
(1c) 2-iminopropanoate + H_2O = pyruvate + NH_3 (spontaneous)

Other name(s): L-cysteine desulfhydrase

Systematic name: L-cysteine sulfide-lyase (deaminating; pyruvate-forming)

Comments: The enzyme from the archaeon *Methanocaldococcus jannaschii* contains a [4Fe-4S] cluster and is specific for L-cysteine (*cf.* EC 4.4.1.1, cystathionine γ-lyase). It cleaves a carbon-sulfur bond releasing sulfide and the unstable enamine product 2-aminoprop-2-enoate that tautomerizes to an imine form, which undergoes a hydrolytic deamination to form pyruvate and ammonia. The same reaction can also be catalysed by some pyridoxal-phosphate proteins (*cf.* EC 4.4.1.1, cystathionine γ-lyase).

References: [1361]

[EC 4.4.1.28 created 2014]

EC 4.4.1.29

Accepted name: phycobiliprotein cysteine-84 phycobilin lyase

Reaction: (1) [C-phycocyanin β-subunit]-Cys^{84}-phycocyanobilin = apo-[C-phycocyanin β-subunit] + (2*R*,3*E*)-phycocyanobilin
(2) [phycoerythrocyanin β-subunit]-Cys^{84}-phycocyanobilin = apo-[phycoerythrocyanin β-subunit] + (2*R*,3*E*)-phycocyanobilin
(3) [allophycocyanin α-subunit]-Cys^{84}-phycocyanobilin = apo-[allophycocyanin α-subunit] + (2*R*,3*E*)-phycocyanobilin
(4) [allophycocyanin β-subunit]-Cys^{84}-phycocyanobilin = apo-[allophycocyanin β-subunit] + (2*R*,3*E*)-phycocyanobilin
(5) [C-phycoerythrin α-subunit]-Cys^{84}-phycoerythrobilin = apo-[C-phycoerythrin α-subunit] + (2*R*,3*E*)-phycoerythrobilin
(6) [C-phycoerythrin β-subunit]-Cys^{84}-phycoerythrobilin = apo-[C-phycoerythrin β-subunit] + (2*R*,3*E*)-phycoerythrobilin

Other name(s): *cpcS* (gene name); *cpeS* (gene name); *cpcS*1 (gene name); *cpcU* (gene name); phycocyanobilin:Cys-β84-phycobiliprotein lyase

Systematic name: [phycobiliprotein]-Cys^{84}-phycobilin:phycobilin lyase

Comments: The enzyme, found in cyanobacteria and red algae, catalyses the attachment of phycobilin chromophores to cysteine 84 of several phycobiliproteins (the numbering used here corresponds to the enzyme from *Anabaena*, in other organisms the number may vary slightly). It can attach phycocyanobilin to the β subunits of C-phycocyanin and phycoerythrocyanin and to both subunits of allophycocyanin. In addition, it can attach phycoerythrobilin to both subunits of C-phycoerythrin.

References: [1560, 1561, 1198, 766]

[EC 4.4.1.29 created 2015]

EC 4.4.1.30

Accepted name: phycobiliprotein β-cysteine-155 phycobilin lyase

Reaction: (1) [C-phycocyanin β-subunit]-Cys^{155}-phycocyanobilin = apo-[C-phycocyanin β-subunit] + (2*R*,3*E*)-phycocyanobilin
(2) [phycoerythrocyanin β-subunit]-Cys^{155}-phycocyanobilin = apo-[phycoerythrocyanin β-subunit] + (2*R*,3*E*)-phycocyanobilin

Other name(s): *cpcT* (gene name); *cpeT*1 (gene name); *cpcT*1 (gene name)

Systematic name: [phycobiliprotein β-subunit]-Cys^{155}-phycocyanobilin:phycocyanobilin lyase

Comments: The enzyme, found in cyanobacteria and red algae, catalyses the attachment of the phycobilin chromophore phycocyanobilin to cysteine 155 of the β subunits of the phycobiliproteins C-phycocyanin and phycoerythrocyanin. The numbering used here corresponds to the enzyme from *Anabaena*, and could vary slightly in other organisms.

References: [1563, 1552, 1569]

[EC 4.4.1.30 created 2015]

EC 4.4.1.31

Accepted name: phycoerythrocyanin α-cysteine-84 phycoviolobilin lyase/isomerase

Reaction: [phycoerythrocyanin α-subunit]-Cys^{84}-phycoviolobilin = apo-[phycoerythrocyanin α-subunit] + (2*R*,3*E*)-phycocyanobilin

Other name(s): *pecE* (gene name); *pecF* (gene name); phycoviolobilin phycoerythrocyanin-α84-cystein-lyase; PecE/PecF; PEC-Cys-R84 PCB lyase/isomerase

Systematic name: [phycoerythrocyanin α-subunit]-Cys^{84}-phycoviolobilin:(2*R*,3*E*)-phycocyanobilin lyase/isomerase

Comments: The enzyme, characterized from the cyanobacteria *Nostoc* sp. PCC 7120 and *Mastigocladus laminosus*, catalyses the covalent attachment of the phycobilin chromophore phycocyanobilin to cysteine 84 of the β subunit of the phycobiliprotein phycoerythrocyanin and its isomerization to phycoviolobilin.

References: [650, 1559, 1308, 1562]

[EC 4.4.1.31 created 2015]

EC 4.4.1.32

Accepted name: C-phycocyanin α-cysteine-84 phycocyanobilin lyase

Reaction: [C-phycocyanin α-subunit]-Cys^{84}-phycocyanobilin = apo-[C-phycocyanin α-subunit] + (2*R*,3*E*)-phycocyanobilin

Other name(s): *cpcE* (gene name); *cpcF* (gene name)

Systematic name: [C-phycocyanin α-subunit]-Cys^{84}-phycocyanobilin:(2*R*,3*E*)-phycocyanobilin lyase

Comments: The enzyme, characterized from the cyanobacterium *Synechococcus elongatus* PCC 7942, catalyses the covalent attachment of the phycobilin chromophore phycocyanobilin to cysteine 84 of the α subunit of the phycobiliprotein C-phycocyanin.

References: [369, 368, 94]

[EC 4.4.1.32 created 2015]

EC 4.4.1.33

Accepted name: R-phycocyanin α-cysteine-84 phycourobilin lyase/isomerase

Reaction: [R-phycocyanin α-subunit]-Cys^{84}-phycourobilin = apo-[R-phycocyanin α-subunit] + (2*R*,3*E*)-phycoerythrobilin

Other name(s): *rpcG* (gene name)

Systematic name: [R-phycocyanin α-subunit]-Cys^{84}-phycourobilin:(2*R*,3*E*)-phycoerythrobilin lyase/isomerase

Comments: The enzyme, characterized from the cyanobacterium *Synechococcus* sp. WH8102, catalyses the covalent attachment of the phycobilin chromophore phycoerythrobilin to cysteine 84 of the α subunit of the phycobiliprotein R-phycocyanin and its isomerization to phycourobilin.

References: [106]

[EC 4.4.1.33 created 2015]

EC 4.4.1.34

Accepted name: isoprene-epoxide—glutathione *S*-transferase

Reaction: 2-(glutathion-*S*-yl)-2-methylbut-3-en-1-ol = (3*R*)-3,4-epoxy-3-methylbut-1-ene + glutathione

Other name(s): *isoI* (gene name)

Systematic name: 2-(glutathion-*S*-yl)-2-methylbut-3-en-1-ol lyase [(3*R*)-3,4-epoxy-3-methylbut-1-ene-forming]

Comments: The enzyme, characterized from the bacterium *Rhodococcus* sp. AD45, is involved in isoprene degradation. The enzyme can catalyse the glutathione-dependent ring opening of various epoxides, but the highest activity is with (3*R*)-3,4-epoxy-3-methylbut-1-ene, which is derived from isoprene by EC 1.14.13.69, alkene monooxygenase.

References: [1414, 1413]

[EC 4.4.1.34 created 2016]

EC 4.4.1.35

Accepted name: L-cystine β-lyase

Reaction: L-cystine + H_2O = L-thiocysteine + pyruvate + NH_3 (overall reaction)
(1a) L-cystine = L-thiocysteine + 2-aminoprop-2-enoate
(1b) 2-aminoprop-2-enoate = 2-iminopropanoate (spontaneous)
(1c) 2-iminopropanoate + H_2O = pyruvate + NH_3 (spontaneous)

Other name(s): CORI3 (gene name)

Systematic name: L-cystine thiocysteine-lyase (deaminating; pyruvate-forming)

Comments: A pyridoxal 5′-phosphate protein. The enzyme cleaves a carbon-sulfur bond, releasing L-thiocysteine and an unstable enamine product that tautomerizes to an imine form, which undergoes a hydrolytic deamination to form pyruvate and ammonia. The latter reaction, which can occur spontaneously, can also be catalysed by EC 3.5.99.10, 2-iminobutanoate/2-iminopropanoate deaminase. The enzyme from *Brassica oleracea* var. *italica* (broccoli) does not act on cysteine or cystathionine.

References: [1409, 647]

[EC 4.4.1.35 created 2017]

EC 4.4.1.36

Accepted name: hercynylcysteine *S*-oxide lyase

Reaction: *S*-(hercyn-2-yl)-L-cysteine *S*-oxide + reduced acceptor = ergothioneine + pyruvate + NH_3 + acceptor (overall reaction)
(1a) *S*-(hercyn-2-yl)-L-cysteine *S*-oxide + H_2O = 2-(hydroxysulfanyl)hercynine + pyruvate + NH_3
(1b) 2-(hydroxysulfanyl)hercynine + reduced acceptor = ergothioneine + acceptor + H_2O (spontaneous)

Other name(s): *egtE* (gene name)

Systematic name: *S*-(hercyn-2-yl)-L-cysteine ergothioneine-hydroxysulfanolate-lyase

Comments: Contains pyridoxal 5′-phosphate. The enzyme, characterized from the bacterium *Mycobacterium smegmatis*, cayalyses the last step in the pathway of ergothioneine biosynthesis. The enzyme forms a 2-(hydroxysulfanyl)hercynine intermediate, which is reduced to ergothioneine non-enzymically by a thiol. *In vitro*, DTT can serve this function.

References: [1244, 1089, 1289]

[EC 4.4.1.36 created 2017]

EC 4.4.1.37

Accepted name: pyridinium-3,5-bisthiocarboxylic acid mononucleotide synthase

Reaction: (1) [LarE]-L-cysteine + pyridin-1-ium-3,5-dicarboxylate mononucleotide + ATP = [LarE]-dehydroalanine + pyridin-1-ium-3-carboxylate-5-thiocarboxylate mononucleotide + AMP + diphosphate (overall reaction)
(1a) ATP + pyridin-1-ium-3,5-dicarboxylate mononucleotide = diphosphate + 5-carboxy-1-(5-*O*-phospho-β-D-ribofuranosyl)pyridin-1-ium-3-carbonyl adenylate
(1b) 5-carboxy-1-(5-*O*-phospho-β-D-ribofuranosyl)pyridin-1-ium-3-carbonyl adenylate + [LarE]-L-cysteine = AMP + [LarE]-*S*-[5-carboxy-1-(5-*O*-phosphono-β-D-ribofuranosyl)pyridin-1-ium-3-carbonyl]-L-cysteine
(1c) [LarE]-*S*-[5-carboxy-1-(5-*O*-phosphono-β-D-ribofuranosyl)pyridin-1-ium-3-carbonyl]-L-cysteine = [LarE]-dehydroalanine + pyridin-1-ium-3-carboxylate-5-thiocarboxylate mononucleotide
(2) [LarE]-L-cysteine + pyridin-1-ium-3-carboxylate-5-thiocarboxylate mononucleotide + ATP = [LarE]-dehydroalanine + pyridin-1-ium-3,5-bisthiocarboxylate mononucleotide + AMP + diphosphate (overall reaction)
(2a) ATP + pyridin-1-ium-3-carboxylate-5-thiocarboxylate mononucleotide = diphosphate + 1-(5-*O*-phospho-β-D-ribofuranosyl)-5-(sulfanylcarbonyl)pyridin-1-ium-3-carbonyl adenylate
(2b) 1-(5-*O*-phospho-β-D-ribofuranosyl)-5-(sulfanylcarbonyl)pyridin-1-ium-3-carbonyl adenylate + [LarE]-L-cysteine = AMP + [LarE]-*S*-[1-(5-*O*-phosphono-β-D-ribofuranosyl)-5-(sulfanylcarbonyl)pyridin-1-ium-3-carbonyl]-L-cysteine

(2c) [LarE]-*S*-[1-(5-*O*-phosphono-β-D-ribofuranosyl)-5-(sulfanylcarbonyl)pyridin-1-ium-3-carbonyl]-L-cysteine = [LarE]-dehydroalanine + pyridin-1-ium-3,5-bisthiocarboxylate mononucleotide

Other name(s): LarE; P2CMN sulfurtransferase; pyridinium-3,5-biscarboxylic acid mononucleotide sulfurtransferase; P2TMN synthase

Systematic name: [LarE]-*S*-[1-(5-*O*-phosphono-β-D-ribofuranosyl)-5-(sulfanylcarbonyl)pyridin-1-ium-3-carbonyl]-L-cysteine pyridin-1-ium-3,5-dicarbothioate-mononucleotide-lyase (ATP-consuming)

Comments: This enzyme, found in *Lactobacillus plantarum*, is involved in the biosynthesis of a nickel-pincer cofactor. The process starts when one enzyme molecule adenylates pyridinium-3,5-dicarboxylate mononucleotide (P2CMN) and covalently binds the adenylated product to an intrinsic cysteine residue. Next, the enzyme cleaves the carbon-sulfur bond, liberating pyridinium-3-carboxylate-5-thiocarboxylate mononucleotide (PCTMN) and leaving a 2-aminoprop-2-enoate (dehydroalanine) residue attached to the protein. Since the cysteine residue is not regenerated *in vivo*, the enzyme is inactivated during the process. A second enzyme molecule then repeats the process with PCTMN, adenylating it and covalently binding it to the same cysteine residue, followed by liberation of pyridinium-3,5-bisthiocarboxylate mononucleotide (P2TMN) and the inactivation of the second enzyme molecule.

References: [316, 317, 379]

[EC 4.4.1.37 created 2018]

EC 4.4.1.38

Accepted name: isethionate sulfite-lyase

Reaction: isethionate = acetaldehyde + sulfite

Other name(s): *islA* (gene name)

Systematic name: isethionate sulfite-lyase

Comments: The enzyme, characterized from the human gut bacterium *Bilophila wadsworthia*, participates in a taurine degradation pathway that leads to sulfide production. The active form of the enzyme contains a glycyl radical that is generated by a dedicated activating enzyme via chemistry involving *S*-adenosyl-L-methionine (SAM) and a [4Fe-4S] cluster.

References: [1061, 1483]

[EC 4.4.1.38 created 2021]

EC 4.4.1.39

Accepted name: C-phycoerythrin α-cysteine-82 phycoerythrobilin lyase

Reaction: a [C-phycoerythrin α-subunit]-Cys^{82}-phycoerythrobilin = apo-[C-phycoerythrin α-subunit] + (3*E*)-phycoerythrobilin

Other name(s): *cpeY* (gene name)

Systematic name: [*C*-phycoerythrin α-subunit]-Cys^{82}-phycoerythrobilin:phycoerythrobilin lyase

Comments: The enzyme, characterized from the cyanobacterium *Microchaete diplosiphon*, catalyses the attachment of the phycobilin chromophore (3*E*)-phycoerythrobilin (PEB) to cysteine 82 of the α subunit of the phycobiliprotein C-phycoerythrin. The numbering used here corresponds to the enzyme from *Microchaete diplosiphon*, and could vary slightly in other organisms. Activity is greatly enhanced in the presence of the chaperone-like protein CpeZ. The reaction could also be catalysed by EC 4.4.1.29, phycobiliprotein cysteine-84 phycobilin lyase, but much less efficiently.

References: [97, 741]

[EC 4.4.1.39 created 2021]

EC 4.4.1.40

Accepted name: C-phycoerythrin β-cysteine-48/59 phycoerythrobilin lyase

Reaction: a [C-phycoerythrin β-subunit]-Cys$^{48/59}$-phycoerythrobilin = apo-[C-phycoerythrin β-subunit] + (3*E*)-phycoerythrobilin

Other name(s): *cpeF* (gene name)
Systematic name: [*C*-phycoerythrin β-subunit]-Cys$^{48/59}$-phycoerythrobilin:phycoerythrobilin lyase
Comments: The enzyme, characterized from the cyanobacterium *Microchaete diplosiphon*, catalyses the attachment of the phycobilin chromophore (3*E*)-phycoerythrobilin (PEB) to cysteine 48 and 59 of the β subunits of the phycobiliprotein C-phycoerythrin. The enzyme first ligates the A ring of PEB to cysteine-48, followed by the attachment of the D ring to cysteine-59. The numbering used here corresponds to the enzyme from *Microchaete diplosiphon*, and could vary slightly in other organisms. The reaction requires the presence of the chaperone-like protein CpeZ.
References: [742]

[EC 4.4.1.40 created 2021]

EC 4.4.1.41

Accepted name: (2*S*)-3-sulfopropanediol sulfolyase
Reaction: (2*S*)-2,3-dihydroxypropane-1-sulfonate = hydroxyacetone + sulfite
Other name(s): DHPS sulfolyase; *hpsG* (gene name)
Systematic name: (2*S*)-2,3-dihydroxypropane-1-sulfonate sulfite-lyase
Comments: The enzyme, characterized from the human gut bacterium *Bilophila wadsworthia*, contains a glycyl radical that is generated by a dedicated activating enzyme via chemistry involving *S*-adenosyl-L-methionine (AdoMet) and a [4Fe-4S] cluster.
References: [828]

[EC 4.4.1.41 created 2021]

EC 4.4.1.42

Accepted name: *S*-adenosyl-L-methionine lyase
Reaction: *S*-adenosyl-L-methionine = L-homoserine lactone + *S*-methyl-5′-thioadenosine
Other name(s): T3p01 (gene name); SAM lyase; SAMase; adenosylmethionine cyclotransferase; *S*-adenosyl-L-methionine alkyltransferase (cyclizing)
Systematic name: *S*-adenosyl-L-methionine *S*-methyl-5′-thioadenosine-lyase (cyclizing; L-homoserine lactone-forming)
Comments: The enzyme was originally described from the yeast *Saccharomyces cerevisiae* (as EC 2.5.1.4), though it had not been well characterized. It was also incorrectly described from several bacteriophages as a hydrolase (EC 3.13.2.2). Later work has shown the bacteriophage enzyme to be a lyase. The enzyme binds its substrate at the border between two subunits of a trimeric complex in a position that prevents it from interacting with water. Instead, the substrate reacts with itself and splits in two. The product, L-homoserine lactone, spontaneously hydrolyses to L-homoserine.
References: [965, 964, 526, 1314, 479]

[EC 4.4.1.42 created 2022 (EC 2.5.1.4 created 1965, incorporated 2022, EC 3.13.2.2 created 1972 as EC 3.3.1.2, modified 1976, modified 2018, transferred 2022 to EC 3.13.2.2, incorporated 2022)]

EC 4.4.1.43

Accepted name: canavanine-γ-lyase
Reaction: L-canavanine + H_2O = L-homoserine + *N*-hydroxyguanidine (overall reaction)
(1a) L-canavanine = vinylglycine + *N*-hydroxyguanidine
(1b) vinylglycine = (2*E*)-2-aminobut-2-enoate (spontaneous)
(1c) (2*E*)-2-aminobut-2-enoate + H_2O = L-homoserine (spontaneous)
Other name(s): CangL
Systematic name: L-canavanine *N*-hydroxyguanidine-lyase (L-homoserine-forming)
Comments: A pyridoxal 5′-phosphate protein. The enzyme, characterized from the bacterium *Pseudomonas canavaninivorans*, cleaves a carbon-oxygen bond, releasing *N*-hydroxyguanidine and an unstable enamine product that tautomerizes to an imine form, which is attacked by a water molecule to form L-homoserine.

References: [528]

[EC 4.4.1.43 created 2022]

EC 4.5 Carbon-halide lyases

This subclass contains a single sub-subclass for enzymes that eliminate chloride (carbon-halide lyases; EC 4.5.1).

EC 4.5.1 Carbon-halide lyases (only sub-subclass identified to date)

EC 4.5.1.1

Accepted name: DDT-dehydrochlorinase

Reaction: 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane = 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene + chloride

Other name(s): DDT-ase; 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane chloride-lyase; DDTase

Systematic name: 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane chloride-lyase [1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene-forming]

References: [824, 825, 953]

[EC 4.5.1.1 created 1961]

EC 4.5.1.2

Accepted name: 3-chloro-D-alanine dehydrochlorinase

Reaction: 3-chloro-D-alanine + H_2O = pyruvate + chloride + NH_3 (overall reaction)
(1a) 3-chloro-D-alanine = chloride + 2-aminoprop-2-enoate
(1b) 2-aminoprop-2-enoate = 2-iminopropanoate (spontaneous)
(1c) 2-iminopropanoate + H_2O = pyruvate + NH_3 (spontaneous)

Other name(s): β-chloro-D-alanine dehydrochlorinase; 3-chloro-D-alanine chloride-lyase (deaminating)

Systematic name: 3-chloro-D-alanine chloride-lyase (deaminating; pyruvate-forming)

Comments: A pyridoxal-phosphate protein. The enzyme cleaves a carbon-chlorine bond, releasing a chloride and an unstable enamine product that tautomerizes to an imine form, which undergoes a hydrolytic deamination to form pyruvate and ammonia. The latter reaction, which can occur spontaneously, can also be catalysed by EC 3.5.99.10, 2-iminobutanoate/2-iminopropanoate deaminase. The enzyme's activity can also result in β-replacement reactions, e.g. in the presence of hydrogen sulfide it can convert 3-chloro-D-alanine into D-cysteine and chloride.

References: [981, 1491]

[EC 4.5.1.2 created 1984]

EC 4.5.1.3

Accepted name: dichloromethane dehalogenase

Reaction: dichloromethane + H_2O = formaldehyde + **2** chloride

Other name(s): dichloromethane chloride-lyase (chloride-hydrolysing)

Systematic name: dichloromethane chloride-lyase (adding H_2O; chloride-hydrolysing; formaldehyde-forming)

Comments: Requires glutathione.

References: [723]

[EC 4.5.1.3 created 1989]

EC 4.5.1.4

Accepted name: L-2-amino-4-chloropent-4-enoate dehydrochlorinase

Reaction: L-2-amino-4-chloropent-4-enoate + H_2O = 2-oxopent-4-enoate + chloride + NH_3

Other name(s): L-2-amino-4-chloro-4-pentenoate dehalogenase; L-2-amino-4-chloropent-4-enoate chloride-lyase (deaminating); L-2-amino-4-chloropent-4-enoate chloride-lyase (adding H_2O; deaminating; 2-oxopent-4-enoate-forming)

Systematic name: L-2-amino-4-chloropent-4-enoate chloride-lyase (adding water; deaminating; 2-oxopent-4-enoate-forming)

References: [957]

[EC 4.5.1.4 created 1990]

EC 4.5.1.5

Accepted name: *S*-carboxymethylcysteine synthase

Reaction: 3-chloro-L-alanine + thioglycolate = *S*-carboxymethyl-L-cysteine + chloride

Other name(s): *S*-carboxymethyl-L-cysteine synthase

Systematic name: 3-chloro-L-alanine chloride-lyase (adding thioglycolate; *S*-carboxymethyl-L-cysteine-forming)

Comments: A pyridoxal-phosphate protein.

References: [755]

[EC 4.5.1.5 created 1992]

EC 4.6 Phosphorus-oxygen lyases

This subclass contains a single sub-subclass (phosphorus-oxygenase lyases; EC 4.6.1). The so-called ‘nucleotidyl-cyclases’ are included here, on the grounds that diphosphate is eliminated from the nucleoside triphosphate.

EC 4.6.1 Phosphorus-oxygen lyases (only sub-subclass identified to date)

EC 4.6.1.1

Accepted name: adenylate cyclase

Reaction: ATP = $3',5'$-cyclic AMP + diphosphate

Other name(s): adenylylcyclase; adenyl cyclase; $3',5'$-cyclic AMP synthetase; ATP diphosphate-lyase (cyclizing)

Systematic name: ATP diphosphate-lyase (cyclizing; $3',5'$-cyclic-AMP-forming)

Comments: Also acts on dATP to form $3',5'$-cyclic dAMP. Requires pyruvate. Activated by NAD$^+$ in the presence of EC 2.4.2.31 NAD(P)$^+$—arginine ADP-ribosyltransferase.

References: [557]

[EC 4.6.1.1 created 1972]

EC 4.6.1.2

Accepted name: guanylate cyclase

Reaction: GTP = $3',5'$-cyclic GMP + diphosphate

Other name(s): guanylyl cyclase; guanyl cyclase; GTP diphosphate-lyase (cyclizing)

Systematic name: GTP diphosphate-lyase (cyclizing; $3',5'$-cyclic-GMP-forming)

Comments: Also acts on ITP and dGTP.

References: [425, 513]

[EC 4.6.1.2 created 1972]

[4.6.1.3 Transferred entry. 3-dehydroquinate synthase. Now EC 4.2.3.4, 3-dehydroquinate synthase]

[EC 4.6.1.3 created 1978, deleted 2000]

[4.6.1.4 Transferred entry. chorismate synthase. Now EC 4.2.3.5, chorismate synthase]

[EC 4.6.1.4 created 1978, modified 1983, deleted 2000]

[4.6.1.5 Transferred entry. pentalenene synthase. Now EC 4.2.3.7, pentalenene synthase]

[EC 4.6.1.5 created 1989, deleted 2000]

EC 4.6.1.6

Accepted name: cytidylate cyclase
Reaction: CTP = 3′,5′-cyclic CMP + diphosphate
Other name(s): 3′,5′-cyclic-CMP synthase; cytidylyl cyclase; cytidyl cyclase; CTP diphosphate-lyase (cyclizing); *pycC* (gene name) (ambiguous)
Systematic name: CTP diphosphate-lyase (cyclizing; 3′,5′-cyclic-CMP-forming)
Comments: In bacteria and archaea the enzyme's product, cCMP, functions as a second messenger in bacterial immunity against viruses. The enzyme is synthesized following phage infection and activates immune effectors that execute an antiviral response.
References: [200, 1001, 1346]

[EC 4.6.1.6 created 1989]

[4.6.1.7 Transferred entry. casbene synthase. Now EC 4.2.3.8, casbene synthase]

[EC 4.6.1.7 created 1989, deleted 2000]

[4.6.1.8 Transferred entry. (-)-endo-fenchol synthase. Now EC 4.2.3.10, (-)-endo-fenchol synthase]

[EC 4.6.1.8 created 1992, deleted 2000]

[4.6.1.9 Transferred entry. sabinene-hydrate synthase. Now EC 4.2.3.11, sabinene-hydrate synthase]

[EC 4.6.1.9 created 1992, deleted 2000]

[4.6.1.10 Transferred entry. 6-pyruvoyltetrahydropterin synthase. Now EC 4.2.3.12, 6-pyruvoyltetrahydropterin synthase]

[EC 4.6.1.10 created 1999, deleted 2000]

[4.6.1.11 Transferred entry. (+)-δ-cadinene synthase. Now EC 4.2.3.13, (+)-δ-cadinene synthase]

[EC 4.6.1.11 created 1999, deleted 2000]

EC 4.6.1.12

Accepted name: 2-*C*-methyl-D-erythritol 2,4-cyclodiphosphate synthase
Reaction: 2-phospho-4-(cytidine 5′-diphospho)-2-*C*-methyl-D-erythritol = 2-*C*-methyl-D-erythritol 2,4-cyclodiphosphate + CMP
Other name(s): MECDP-synthase; 2-phospho-4-(cytidine 5′-diphospho)-2-*C*-methyl-D-erythritol CMP-lyase (cyclizing)
Systematic name: 2-phospho-4-(cytidine 5′-diphospho)-2-*C*-methyl-D-erythritol CMP-lyase (cyclizing; 2-*C*-methyl-D-erythritol 2,4-cyclodiphosphate-forming)
Comments: The enzyme from *Escherichia coli* requires Mg^{2+} or Mn^{2+}. Forms part of an alternative nonmevalonate pathway for terpenoid biosynthesis (for diagram, click here).
References: [546, 1341]

[EC 4.6.1.12 created 2001]

EC 4.6.1.13

Accepted name: phosphatidylinositol diacylglycerol-lyase

Reaction: 1-phosphatidyl-1D-*myo*-inositol = 1D-*myo*-inositol 1,2-cyclic phosphate + 1,2-diacyl-*sn*-glycerol

Other name(s): monophosphatidylinositol phosphodiesterase; phosphatidylinositol phospholipase C; 1-phosphatidylinositol phosphodiesterase; 1-phosphatidyl-D-*myo*-inositol inositolphosphohydrolase (cyclic-phosphate-forming); 1-phosphatidyl-1D-*myo*-inositol diacylglycerol-lyase (1,2-cyclic-phosphate-forming)

Systematic name: 1-phosphatidyl-1D-*myo*-inositol 1,2-diacyl-*sn*-glycerol-lyase (1D-*myo*-inositol-1,2-cyclic-phosphate-forming)

Comments: This enzyme is bacterial. Activity is also found in animals, but this activity is due to the presence of EC 3.1.4.11, phosphoinositide phospholipase C.

References: [19, 407, 602, 936, 849, 539]

[EC 4.6.1.13 created 1972 as EC 3.1.4.10, modified 1976, transferred 2002 to EC 4.6.1.13]

EC 4.6.1.14

Accepted name: glycosylphosphatidylinositol diacylglycerol-lyase

Reaction: 6-(α-D-glucosaminyl)-1-phosphatidyl-1D-*myo*-inositol = 6-(α-D-glucosaminyl)-1D-*myo*-inositol 1,2-cyclic phosphate + 1,2-diacyl-*sn*-glycerol

Other name(s): (glycosyl)phosphatidylinositol-specific phospholipase C; GPI-PLC; GPI-specific phospholipase C; VSG-lipase; glycosyl inositol phospholipid anchor-hydrolyzing enzyme; glycosylphosphatidylinositol-phospholipase C; glycosylphosphatidylinositol-specific phospholipase C; variant-surface-glycoprotein phospholipase C; 6-(α-D-glucosaminyl)-1-phosphatidyl-1D-*myo*-inositol diacylglycerol-lyase (1,2-cyclic-phosphate-forming)

Systematic name: 6-(α-D-glucosaminyl)-1-phosphatidyl-1D-*myo*-inositol 1,2-diacyl-*sn*-glycerol-lyase [6-(α-D-glucosaminyl)-1D-*myo*-inositol 1,2-cyclic phosphate-forming]

Comments: This enzyme is also active when O-4 of the glucosamine is substituted by carrying the oligosaccharide that can link a protein to the structure. It therefore cleaves proteins from the lipid part of the glycosylphostphatidylinositol (GPI) anchors. In some cases, the long-chain acyl group at the *sn*-1 position of glycerol is replaced by an alkyl or alk-1-enyl group. In other cases, the diacylglycerol is replaced by ceramide (see Lip-1.4 and Lip-1.5 for definition). The only characterized enzyme with this specificity is from *Trypanosoma brucei*, where the acyl groups are myristoyl, but the function of the trypanosome enzyme is unknown. Substitution on O-2 of the inositol blocks action of this enzyme. It is not identical with EC 3.1.4.50, glycosylphosphatidylinositol phospholipase D.

References: [544, 191, 40]

[EC 4.6.1.14 created 1989 as EC 3.1.4.47, transferred 2002 to EC 4.6.1.14]

EC 4.6.1.15

Accepted name: FAD-AMP lyase (cyclizing)

Reaction: FAD = AMP + riboflavin cyclic-4′,5′-phosphate

Other name(s): FMN cyclase; FAD AMP-lyase (cyclic-FMN-forming)

Systematic name: FAD AMP-lyase (riboflavin-cyclic-4′,5′-phosphate-forming)

Comments: Requires Mn^{2+} or Co^{2+}. While FAD was the best substrate tested [166], the enzyme also splits ribonucleoside diphosphate-X compounds in which X is an acyclic or cyclic monosaccharide or derivative bearing an X-OH group that is able to attack internally the proximal phosphorus with the geometry necessary to form a P=X product; either a five-atom monocyclic phosphodiester or a *cis*-bicyclic phosphodiester-pyranose fusion. The reaction is strongly inhibited by ADP or ATP but is unaffected by the presence of the product, cFMN.

References: [400, 166]

[EC 4.6.1.15 created 2002]

EC 4.6.1.16

Accepted name: tRNA-intron lyase

Reaction: pretRNA = a 3′-half-tRNA molecule with a 5′-OH end + a 5′-half-tRNA molecule with a 2′,3′-cyclic phosphate end + an intron with a 2′,3′-cyclic phosphate and a 5′-hydroxyl terminus

Other name(s): transfer ribonucleate intron endoribonuclease; tRNA splicing endonuclease; splicing endonuclease; tRNATRPintron endonuclease; transfer splicing endonuclease

Systematic name: pretRNA lyase (intron-removing; cyclic-2′,3′-phosphate-forming)

Comments: The enzyme catalyses the final stage in the maturation of tRNA molecules.

References: [47, 1063, 1367, 1368]

[EC 4.6.1.16 created 1992 as EC 3.1.27.9, transferred 2014 to EC 4.6.1.16]

EC 4.6.1.17

Accepted name: cyclic pyranopterin monophosphate synthase

Reaction: (8*S*)-3′,8-cyclo-7,8-dihydroguanosine 5′-triphosphate = cyclic pyranopterin phosphate + diphosphate

Other name(s): MOCS1B (gene name); *moaC* (gene name); cnx3 (gene name)

Systematic name: (8*S*)-3′,8-cyclo-7,8-dihydroguanosine 5′-triphosphate lyase (cyclic pyranopterin phosphate-forming)

Comments: The enzyme catalyses an early step in the biosynthesis of the molybdenum cofactor (MoCo). In bacteria and plants the reaction is catalysed by MoaC and Cnx3, respectively. In mammals the reaction is catalysed by the MOCS1B domain of the bifuctional MOCS1 protein, which also catalyses EC 4.1.99.22, GTP 3′,8-cyclase.

References: [1150, 1479, 579]

[EC 4.6.1.17 created 2011 as EC 4.1.99.18, part transferred 2016 to EC 4.6.1.17]

EC 4.6.1.18

Accepted name: pancreatic ribonuclease

Reaction: (1) an [RNA] containing cytidine + H_2O = an [RNA]-3′-cytidine-3′-phosphate + a 5′-hydroxy-ribonucleotide-3′-[RNA] (overall reaction)

(1a) an [RNA] containing cytidine = an [RNA]-3′-cytidine-2′,3′-cyclophosphate + a 5′-hydroxy-ribonucleotide-3′-[RNA]

(1b) an [RNA]-3′-cytidine-2′,3′-cyclophosphate + H_2O = an [RNA]-3′-cytidine-3′-phosphate

(2) an [RNA] containing uridine + H_2O = an [RNA]-3′-uridine-3′-phosphate + a 5′-hydroxy-ribonucleotide-3′-[RNA]

(2a) an [RNA] containing uridine = an [RNA]-3′-uridine-2′,3′-cyclophosphate + a 5′-hydroxy-ribonucleotide-3′-[RNA]

(2b) an [RNA]-3′-uridine-2′,3′-cyclophosphate + H_2O = an [RNA]-3′-uridine-3′-phosphate

Other name(s): RNase; RNase I; RNase A; pancreatic RNase; ribonuclease I; endoribonuclease I; ribonucleic phosphatase; alkaline ribonuclease; ribonuclease; gene S glycoproteins; *Ceratitis capitata* alkaline ribonuclease; SLSG glycoproteins; gene S locus-specific glycoproteins; *S*-genotype-asssocd. glycoproteins; ribonucleate 3′-pyrimidino-oligonucleotidohydrolase

Systematic name: RNA lyase ([RNA]-3′-cytidine/uridine-3′-phosphate and 5′-hydroxy-ribonucleotide-3′-[RNA] producing)

Comments: Specifically cleaves at the 3′-side of pyrimidine (uracil or cytosine) phosphate bonds in RNA. The reaction takes place in two steps, with the 2′,3′-cyclic phosphodiester intermediates released from the enzyme at the completion of the first step. Hydrolysis of these cyclic compounds occurs at a much slower rate through a reversal of the first step, in which the -OH group of water substitutes for the 2′-OH group of the ribose used in the first step, and does not take place until essentially all the susceptible 3′,5′-phosphodiester bonds have been cyclised. The enzyme can act as an endo- or exo ribonuclease.

References: [199, 80, 188, 274, 848]

[EC 4.6.1.18 created 1972 as EC 3.1.4.22, transferred 1978 to EC 3.1.27.5, modified 1981, transferred 2018 to EC 4.6.1.18]

EC 4.6.1.19

Accepted name: ribonuclease T_2

Reaction: RNA + H_2O = an [RNA fragment]-3′-nucleoside-3′-phosphate + a 5′-hydroxy-ribonucleotide-3′-[RNA fragment] (overall reaction)
(1a) RNA = an [RNA fragment]-3′-nucleoside-2′,3′-cyclophosphate + a 5′-hydroxy-ribonucleotide-3′-[RNA fragment]
(1b) an [RNA fragment]-3′-nucleoside-2′,3′-cyclophosphate + H_2O = an [RNA fragment]-3′-nucleoside-3′-phosphate

Other name(s): ribonuclease II; base-non-specific ribonuclease; nonbase-specific RNase; RNase (non-base specific); non-base specific ribonuclease; nonspecific RNase; RNase Ms; RNase M; RNase II; *Escherichia coli* ribonuclease II; ribonucleate nucleotido-2′-transferase (cyclizing); acid ribonuclease; RNAase CL; *Escherichia coli* ribonuclease I′ ribonuclease PP2; ribonuclease N_2; ribonuclease M; acid RNase; ribonnuclease (non-base specific); ribonuclease (non-base specific); RNase T_2; ribonuclease PP3; ribonucleate 3′-oligonucleotide hydrolase; ribonuclease U_4

Systematic name: [RNA] 5′-hydroxy-ribonucleotide-3′-[RNA fragment]-lyase (cyclicizing; [RNA fragment]-3′-nucleoside-2′,3′-cyclophosphate-forming and hydrolysing)

Comments: A widely distributed family of related enzymes found in protozoans, plants, bacteria, animals and viruses that cleave ssRNA 3′-phosphate group with little base specificity. The enzyme catalyses a two-stage endonucleolytic cleavage. The first reaction produces 5′-hydroxy-phosphooligonucletides and 3′-phosphooligonucleotides ending with a 2′,3′-cyclic phosphodiester, which are released from the enzyme. The enzyme then hydrolyses the cyclic products in a second reaction that takes place only when all the susceptible 3′,5′-phosphodiester bonds have been cyclised. The second reaction is a reversal of the first reaction using the hydroxyl group of water instead of the 5′-hydroxyl group of ribose. The overall process is that of a phosphorus-oxygen lyase followed by hydrolysis to form the 3′-nucleotides.

References: [426, 541, 1141, 1400, 600, 855]

[EC 4.6.1.19 created 1972 as EC 3.1.4.23, transferred 1978 to EC 3.1.27.1, modified 1981, transferred 2018 to EC 4.6.1.19]

EC 4.6.1.20

Accepted name: ribonuclease U_2

Reaction: (1) [RNA] containing adenosine + H_2O = an [RNA fragment]-3′-adenosine-3′-phosphate + a 5′-hydroxy-ribonucleotide-3′-[RNA fragment] (overall reaction)
(1a) [RNA] containing adenosine = an [RNA fragment]-3′-adenosine-2′,3′-cyclophosphate + a 5′-hydroxy-ribonucleotide-3′-[RNA fragment]
(1b) an [RNA fragment]-3′-adenosine-2′,3′-cyclophosphate + H_2O = an [RNA fragment]-3′-adenosine-3′-phosphate
(2) [RNA] containing guanosine + H_2O = an [RNA fragment]-3′-guanosine-3′-phosphate + a 5′-hydroxy-ribonucleotide-3′-[RNA fragment] (overall reaction)
(2a) [RNA] containing guanosine = an [RNA fragment]-3′-guanosine-2′,3′-cyclophosphate + a 5′-hydroxy-ribonucleotide-3′-[RNA fragment]
(2b) an [RNA fragment]-3′-guanosine-2′,3′-cyclophosphate + H_2O = an [RNA fragment]-3′-guanosine-3′-phosphate

Other name(s): purine specific endoribonuclease; ribonuclease U_3; RNase U_3; RNase U_2; purine-specific ribonuclease; purine-specific RNase; *Pleospora* RNase; *Trichoderma koningi* RNase III; ribonuclease (purine)

Systematic name: [RNA]-purine 5′-hydroxy-ribonucleotide-3′-[RNA fragment]-lyase (cyclicizing; [RNA fragment]-3′-purine-nucleoside -2′,3′-cyclophosphate-forming and hydrolysing)

Comments: The enzyme secreted by the fungus *Ustilago sphaerogena* cleaves at the 3′-phosphate group of purines, and catalyses a two-stage endonucleolytic cleavage. The first reaction produces 5′-hydroxy-phosphooligonucletides and 3′-phosphooligonucleotides ending in Ap or Gp with 2′,3′-cyclic phosphodiester, which are released from the enzyme. The enzyme then hydrolyses these cyclic compounds in a second reaction that takes place only when all the susceptible 3′,5′-phosphodiester bonds have been cyclised. The second reaction is a reversal of the first reaction using the hydroxyl group of water instead of the 5′-hydroxyl group of ribose. The overall process is that of a phosphorus-oxygen lyase followed by hydrolysis to form the 3′-nucleotides.

References: [445, 446, 1334, 885]

[EC 4.6.1.20 created 1978 as 3.1.27.4, modified 1981, transferred 2018 to EC 4.6.1.20]

EC 4.6.1.21

Accepted name: *Enterobacter* ribonuclease

Reaction: RNA containing adenosine-cytidine + H_2O = an [RNA fragment]-3′-cytidine-3′-phosphate + a 5′-a hydroxy-adenosine -3′-[RNA fragment] (overall reaction)
(1a) RNA containing adenosine-cytidine = an [RNA fragment]-3′-cytidine-2′,3′-cyclophosphate + a 5′-a hydroxy-adenosine -3′-[RNA fragment]
(1b) an [RNA fragment]-3′-cytidine-2′,3′-cyclophosphate + H_2O = an [RNA fragment]-3′-cytidine-3′-phosphate

Systematic name: [RNA]-adenosine-cytidine 5′-hydroxy-adenosoine ribonucleotide-3′-[RNA fragment]-lyase (cyclicizing; [RNA fragment]-3′-cytidine-2′,3′-cyclophosphate-forming and hydrolysing)

Comments: Preference for cleavage at Cp-A bonds. Homopolymers of A, U or G are not hydrolysed. CpG bonds are hydrolysed less well and there is no detectable hydrolysis between two purines or two pyrimidines. The enzyme catalyses a two-stage endonucleolytic cleavage. The first reaction produces 5′-hydroxy-phosphooligonucletides and 3′-phosphooligonucleotides ending a with 2′,3′-cyclic phosphodiester, which are released from the enzyme. The enzyme then hydrolyses these cyclic compounds in a second reaction that takes place only when all the susceptible 3′,5′-phosphodiester bonds have been cyclised. The second reaction is a reversal of the first reaction using the hydroxyl group of water instead of the 5′-hydroxyl group of ribose. The overall process is that of a phosphorus-oxygen lyase followed by hydrolysis to form the 3′-nucleotides.

References: [800, 877]

[EC 4.6.1.21 created 1978 as EC 3.1.27.6, modified 1981, transferred 2018 to 4.6.1.21]

EC 4.6.1.22

Accepted name: *Bacillus subtilis* ribonuclease

Reaction: RNA = a 5′-hydroxy-ribonucleotide + ***n*** nucleoside-2′,3′-cyclophosphates

Other name(s): *Proteus mirabilis* RNase; ribonucleate nucleotido-2′-transferase (cyclizing); bacterial RNA lyase; *Bacillus subtilis* intracellular ribonuclease

Systematic name: [RNA] 5′-hydroxy-ribonucleotide-3′-[RNA fragment]-lyase (cyclicizing; [RNA fragment]-3′- nucleoside -2′,3′-cyclophosphate-forming)

Comments: This enzyme catalyses endonucleolytic cleavage to 2′,3′-cyclic nucleotides. The cyclic products may be hydrolysed to the corresponding 3′-phosphates by 2′,3′-cyclic-nucleotide 2′-phosphodiesterase (EC 3.1.4.16). The enzyme from *B. subtilis* is inhibited by ATP.

References: [1008, 1499, 1500, 202]

[EC 4.6.1.22 created 1978 as EC 3.1.27.2, transferred 2028 to EC 4.6.1.22]

EC 4.6.1.23

Accepted name: ribotoxin

Reaction: a 28S rRNA containing guanosine-adenosine pair + H_2O = an [RNA fragment]-3′-adenosine-3′-phosphate + a 5′-a hydroxy-guanosine-3′-[RNA fragment] (overall reaction)
(1a) a 28S rRNA containing guanosine-adenosine pair = an [RNA fragment]-3′-adenosine-2′,3′-cyclophosphate + a 5′-hydroxy-guanosine-3′-[RNA fragment]
(1b) an [RNA fragment]-3′-adenosine-2′,3′-cyclophosphate + H_2O = an [RNA fragment]-3′-adenosine-3′-phosphate

Other name(s): α-sarcin; rRNA endonuclease (ambiguous)

Systematic name: [28S-rRNA]-guanosine-adenosine 5′-hydroxy-guanosine-ribonucleotide-3′-[RNA fragment]-lyase (cyclicizing; [RNA fragment]-3′-adenosine-2′,3′-cyclophosphate-forming and hydrolysing)

Comments: Ribotoxins are rRNA endonucleases that catalyse the cleavage of the phosphodiester bond between guanosine and adenosine residues at one specific position in 28S rRNA. The enzyme secreted by *Aspergillus giganteus* specifically cleaves rat 28S rRNA between G^{4325} and A^{4326} and displays cytotoxic activity toward animal cells. It can also act on bacterial rRNAs. The enzyme catalyses a two-stage endonucleolytic cleavage. The first reaction produces 5′-hydroxy-phosphooligonucletides and 3′-phosphooligonucleotides ending with 2′,3′-cyclic phosphodiester, which are released from the enzyme. The enzyme then hydrolyses these cyclic compounds in a second reaction that takes place only when all the susceptible 3′,5′-phosphodiester bonds have been cyclised. The second reaction is a reversal of the first reaction using the hydroxyl group of water instead of the 5′-hydroxyl group of ribose. The overall process is that of a phosphorus-oxygen lyase followed by hydrolysis to form the 3′-nucleotides.

References: [205, 774, 237]

[EC 4.6.1.23 created 1992 as EC 3.1.27.10, transferred 2019 to EC 4.6.1.23]

EC 4.6.1.24

Accepted name: ribonuclease T_1

Reaction: [RNA] containing guanosine + H_2O = an [RNA fragment]-3′-guanosine-3′-phosphate + a 5′-hydroxy-ribonucleotide-3′-[RNA fragment] (overall reaction)

(1a) [RNA] containing guanosine = [RNA fragment]-3′-guanosine-2′,3′-cyclophosphate + a 5′-hydroxy-ribonucleotide-3′-[RNA fragment]

(1b) [RNA fragment]-3′-guanosine-2′,3′-cyclophosphate + H_2O = [RNA fragment]-3′-guanosine-3′-phosphate

Other name(s): barnase; bacterial ribonuclease Sa; guanyloribonuclease; *Aspergillus oryzae* ribonuclease; RNase N_1; RNase N_2; ribonuclease N_3; ribonuclease U_1; ribonuclease F_1; ribonuclease Ch; ribonuclease PP1; ribonuclease SA; RNase F_1; ribonuclease C2; binase; RNase Sa; guanyl-specific RNase; RNase G; RNase T_1; ribonuclease guaninenucleotido-2′-transferase (cyclizing); ribonuclease N_1

Systematic name: [RNA]-guanosine 5′-hydroxy-ribonucleotide-3′-[RNA fragment]-lyase (cyclicizing; [RNA fragment]-3′-guanosine-2′,3′-cyclophosphate-forming and hydrolysing)

Comments: A family of related enzymes found in some fungi and bacteria. The enzyme is specific for cleavage at the 3′-phosphate group of guanosine in single stranded RNA, and catalyses a two-stage endonucleolytic cleavage. The first reaction produces 5′-hydroxy-phosphooligonucletides and 3′-phosphooligonucleotides ending in Gp with 2′,3′-cyclic phosphodiester, which are released from the enzyme. The enzyme then hydrolyses these cyclic compounds in a second reaction that takes place only when all the susceptible 3′,5′-phosphodiester bonds have been cyclised. The second reaction is a reversal of the first reaction using the hydroxyl group of water instead of the 5′-hydroxyl group of ribose. The overall process is that of a phosphorus-oxygen lyase followed by hydrolysis to form the 3′-nucleotides.

References: [1342, 671, 848]

[EC 4.6.1.24 created 1961 as EC 3.1.4.8, transferred 1965 to EC 2.7.7.26, reinstated 1972 as EC 3.1.4.8, transferred 1978 to EC 3.1.27.3, transferred 2020 to EC 4.6.1.24]

EC 4.6.1.25

Accepted name: bacteriophage T_4 restriction endoribonuclease RegB

Reaction: a [pre-mRNA]-containing guanosine-adenosine + H_2O = a 5′ hydroxy-guanosine-[pre-mRNA fragment] + a [pre-mRNA fragment]-3′-adenosine-3′-phosphate (overall reaction)

(1a) a [pre-mRNA]-containing guanosine-adenosine + H_2O = a 5′ hydroxy-guanosine-[pre-mRNA fragment] + a [pre-mRNA fragment]-adenosine-2′,3′-cyclophosphate

(1b) a [pre-mRNA fragment]- adenosine-2′,3′-cyclophosphate + H_2O = a [pre-mRNAfragment]-3′-adenosine-3′-phosphate

Other name(s): RegB

Systematic name: [pre-mRNA]-guanosine-adenosine 5′-hydroxy-guanosine-ribonucleotide-3′-[RNA fragment]-lyase (cyclicizing; [RNA fragment]-3′- adenosine -2′,3′-cyclophosphate-forming and hydrolysing)

Comments: The enzyme from bacteriophage T_4 cleaves early mRNAs between Ap and Gp at one specific specific GpGpApGp site, favouring their further transition to middle-phase mRNA. The activity is enhanced by Ribosomal S1 protein. The enzyme catalyses a two-stage endonucleolytic cleavage. The first reaction produces 5′-hydroxy-phosphooligonucletides and 3′-phosphooligonucleotides ending with 2′,3′-cyclic phosphodiester, which are released from the enzyme. The enzyme then hydrolyses these cyclic compounds in a second reaction that takes place only when all the susceptible 3′,5′-phosphodiester bonds have been cyclised. The second reaction is a reversal of the first reaction using the hydroxyl group of water instead of the 5′-hydroxyl group of ribose. The overall process is that of a phosphorus-oxygen lyase followed by hydrolysis to form the 3′-nucleotides.

References: [1192, 1182, 1023]

[EC 4.6.1.25 created 2020]

EC 4.6.1.26

Accepted name: uridylate cyclase

Reaction: UTP = 3′,5′-cyclic UMP + diphosphate

Other name(s): *pycC* (gene name) (ambiguous)

Systematic name: UTP diphosphate-lyase (cyclizing; 3′,5′-cyclic-UMP-forming)

Comments: The enzyme, found in bacteria and archaea, forms cUMP, which functions as a second messenger in bacterial immunity against viruses. The enzyme is synthesized following phage infection and activates immune effectors that execute an antiviral response.

References: [1346]

[EC 4.6.1.26 created 2022]

EC 4.7 carbon-phosphorus lyases

EC 4.7.1 carbon-phosphorus lyases (only sub-subclass identified to date)

EC 4.7.1.1

Accepted name: α-D-ribose 1-methylphosphonate 5-phosphate C-P-lyase

Reaction: α-D-ribose 1-methylphosphonate 5-phosphate + *S*-adenosyl-L-methionine + reduced electron acceptor = α-D-ribose 1,2-cyclic phosphate 5-phosphate + methane + L-methionine + 5′-deoxyadenosine + oxidized electron acceptor

Other name(s): *phnJ* (gene name)

Systematic name: α-D-ribose-1-methylphosphonate-5-phosphate C-P-lyase (methane-forming)

Comments: This radical SAM (AdoMet) enzyme is part of the C-*P* lyase complex, which is responsible for processing phophonates into usable phosphate. Contains an [4Fe-4S] cluster. The enzyme from the bacterium *Escherichia coli* can act on additional α-D-ribose phosphonate substrates with different substituents attached to the phosphonate phosphorus (e.g. α-D-ribose-1-[*N*-(phosphonomethyl)glycine]-5-phosphate and α-D-ribose-1-(2-*N*-acetamidomethylphosphonate)-5-phosphate).

References: [655, 637, 1551]

[EC 4.7.1.1 created 2013, modified 2016]

EC 4.8 Nitrogen-oxygen lyases

This subclass contains enzymes that catalyse the breakage of a nitrogen-oxygen bond. Sub-subclasses are based on the group that is eliminated: Currently the only subclass is EC 4.8.1, hydro-lyases, in which water is eliminated.

EC 4.8.1 Hydro-lyases

EC 4.8.1.1
Accepted name: L-piperazate synthase
Reaction: N^5-hydroxy-L-ornithine = (3*S*)-1,2-diazinane-3-carboxylate + H_2O
Other name(s): *ktzT* (gene name)
Systematic name: (3*S*)-1,2-diazinane-3-carboxylate hydrolase (N^5-hydroxy-L-ornithine-forming)
Comments: Contains a heme *b* cofactor. The enzyme, characterized from the bacterium *Kutzneria* sp. 744, is one of very few enzymes known to result in the formation of an N-N bond. (3*S*)-1,2-diazinane-3-carboxylate (piperazate) is known to be incorporated into assorted secondary products that are produced by nonribosomal peptide synthetase or nonribosomal peptide synthetase/polyketide synthase hybrid pathways, such as the kutznerides, padanamides, himastatins, and sanglifehrins.
References: [335]

[EC 4.8.1.1 created 2021]

EC 4.8.1.2
Accepted name: aliphatic aldoxime dehydratase
Reaction: an aliphatic aldoxime = an aliphatic nitrile + H_2O
Other name(s): OxdA; aliphatic aldoxime hydro-lyase
Systematic name: aliphatic aldoxime hydro-lyase (aliphatic-nitrile-forming)
Comments: The enzyme from *Pseudomonas chlororaphis* contains Ca^{2+} and protoheme IX, the iron of which must be in the form iron(II) for activity. The enzyme exhibits a strong preference for aliphatic aldoximes, such as butyraldoxime and acetaldoxime, over aromatic aldoximes, such as pyridine-2-aldoxime, which is a poor substrate. No activity was found with the aromatic aldoximes benzaldoxime and pyridine-4-aldoxime.
References: [1027, 1481, 680]

[EC 4.8.1.2 created 2004 as EC 4.99.1.5, transferred 2021 to EC 4.8.1.2]

EC 4.8.1.3
Accepted name: indoleacetaldoxime dehydratase
Reaction: (indol-3-yl)acetaldehyde oxime = (indol-3-yl)acetonitrile + H_2O
Other name(s): indoleacetaldoxime hydro-lyase; 3-indoleacetaldoxime hydro-lyase; indole-3-acetaldoxime hydro-lyase; indole-3-acetaldehyde-oxime hydro-lyase; (indol-3-yl)acetaldehyde-oxime hydro-lyase
Systematic name: (indol-3-yl)acetaldehyde-oxime hydro-lyase [(indol-3-yl)acetonitrile-forming]
References: [760, 863]

[EC 4.8.1.3 created 1965 as EC 4.2.1.29, transferred 2004 to EC 4.99.1.6, transferred 2021 to EC 4.8.1.3]

EC 4.8.1.4
Accepted name: phenylacetaldoxime dehydratase
Reaction: (*Z*)-phenylacetaldehyde oxime = phenylacetonitrile + H_2O
Other name(s): PAOx dehydratase; arylacetaldoxime dehydratase; OxdB; (*Z*)-phenylacetaldehyde-oxime hydro-lyase
Systematic name: (*Z*)-phenylacetaldehyde-oxime hydro-lyase (phenylacetonitrile-forming)

Comments: The enzyme from *Bacillus* sp. OxB-1 contains protoheme IX, the iron of which must be in the form iron(II) for activity. (*Z*)-Phenylacetaldoxime binds to ferric heme (the iron(III) form) via the oxygen atom whereas it binds to the active ferrous form via the nitrogen atom. In this way, the oxidation state of the heme controls the coordination stucture of the substrate—heme complex, which regulates enzyme activity [717]. The enzyme is active towards several (*Z*)-arylacetaldoximes and (*E*/*Z*)-alkylaldoximes as well as towards arylalkylaldoximes such as 3-phenylpropionaldoxime and 4-phenylbutyraldoxime. However, it is inactive with phenylacetaldoximes that have a substituent group at an α-site of an oxime group, for example, with (*E*/*Z*)-2-phenylpropionaldoxime and (*E*/*Z*)-mandelaldoxime. The activity of the enzyme is inhibited completely by the heavy-metal cations Cu^{+}, Cu^{2+}, Ag^{+} and Hg^{+} whereas Fe^{2+} and Sn^{2+} have an activatory effect.

References: [678, 717]

[EC 4.8.1.4 created 2005 as EC 4.99.1.7, transferred 2021 to EC 4.8.1.4]

EC 4.8.1.5

Accepted name: thiohydroximate-*O*-sulfate sulfate/sulfur-lyase (nitrile-forming)

Reaction: an *N*-(sulfonatooxy)alkanimidothioate = a nitrile + sulfate + sulfur

Other name(s): NSP (gene name); nitrile-specifier protein

Systematic name: thiohydroximate-*O*-sulfate sulfate/sulfur-lyase (nitrile-forming)

Comments: The enzyme is involved in the breakdown of glucosinolates. It can act on both aliphatic and aromatic glucosinolates, and forms nitrile-containing products. *cf.* EC 4.8.1.6, *N*-(sulfonatooxy)alkenimidothioic acid sulfate-lyase (epithionitrile-forming), and EC 4.8.1.7, phenyl-*N*-(sulfonatooxy)methanimidothioate sulfolyase.

References: [708, 163]

[EC 4.8.1.5 created 2022]

EC 4.8.1.6

Accepted name: *N*-(sulfonatooxy)alkenimidothioic acid sulfate-lyase (epithionitrile-forming)

Reaction: *N*-(sulfonatooxy)alkenimidothioic acid with a terminal double bond = an epithionitrile + sulfate

Other name(s): ESP (gene name); epithionitrile-specifier protein; epithiospecifier protein

Systematic name: *N*-(sulfonatooxy)alkenimidothioic acid sulfate-lyase (epithionitrile-forming)

Comments: The enzyme is involved in the breakdown of glucosinolates. It acts only on aliphatic *N*-(sulfonatooxy)alkenimidothioic acids produced from ω-alkenyl-glucosinolates, and forms epithionitrile-containing products. *cf.* EC 4.8.1.5, thiohydroximate-*O*-sulfate sulfate/sulfur-lyase (nitrile-forming), and EC 4.8.1.7, phenyl-*N*-(sulfonatooxy)methanimidothioate sulfolyase.

References: [782, 299]

[EC 4.8.1.6 created 2022]

EC 4.8.1.7

Accepted name: phenyl-*N*-(sulfonatooxy)methanimidothioate sulfolyase

Reaction: phenyl-*N*-(sulfonatooxy)methanimidothioate = benzylthiocyanate + sulfate

Other name(s): TFP (gene name) (ambiguous); thiocyanate-forming protein (ambiguous)

Systematic name: phenyl-*N*-(sulfonatooxy)methanimidothioate sulfate-lyase (benzylthiocyanate-forming)

Comments: The enzyme, characterized from the plant *Lepidium sativum*, is involved in the breakdown of the glucosinolate glucotropaeolin. Depending on the substrate, it can also form simple nitrile- and epithionitrile-containing products. *cf.* EC 4.8.1.5, thiohydroximate-*O*-sulfate sulfate/sulfur-lyase (nitrile-forming), and EC 4.8.1.6, *N*-(sulfonatooxy)alkenimidothioic acid sulfate-lyase (epithionitrile-forming).

References: [162]

[EC 4.8.1.7 created 2022]

EC 4.8.1.8

Accepted name: *N*-(sulfonatooxy)prop-2-enimidothioate sulfolyase
Reaction: (1) *N*-(sulfonatooxy)prop-2-enimidothioate = prop-2-enylthiocyanate + sulfate
(2) *N*-(sulfonatooxy)prop-2-enimidothioate = 2-(thiiran-2-yl)acetonitrile + sulfate
Other name(s): TFP (gene name) (ambiguous); thiocyanate-forming protein (ambiguous)
Systematic name: *N*-(sulfonatooxy)prop-2-enimidothioate sulfate-lyase (prop2-enylthiocyanate-forming)
Comments: The enzyme, characterized from the plant *Thlaspi arvense*, is involved in the breakdown of the glucosinolate sinigrin. Depending on the substrate, it can also form simple nitrile-containing products. *cf.* EC 4.8.1.5, thiohydroximate-*O*-sulfate sulfate/sulfur-lyase (nitrile-forming) and EC 4.8.1.6, *N*-(sulfonatooxy)alkenimidothioic acid sulfate-lyase (epithionitrile-forming).
References: [744, 475, 352]

[EC 4.8.1.8 created 2022]

EC 4.98 ATP-independent chelatases

ATP-independent chelatases are a special kind of lyases that catalyse the insertion of a metal cation into a an organic molecule, usually a porphyrin ring. The reactions catalysed by the chelatases occur in the opposite direction to the way they are written. Note that chletases that utilize ATP hydrolysis to drive the reaction are classified under subclass EC 6.6.

EC 4.98.1 Forming coordination complexes

EC 4.98.1.1

Accepted name: protoporphyrin ferrochelatase
Reaction: protoheme + **2** H^+ = protoporphyrin + Fe^{2+}
Other name(s): ferro-protoporphyrin chelatase; iron chelatase (ambiguous); heme synthetase (ambiguous); heme synthase (ambiguous); protoheme ferro-lyase; ferrochelatase (ambiguous)
Systematic name: protoheme ferro-lyase (protoporphyrin-forming)
Comments: The enzyme catalyses the terminal step in the heme biosynthesis pathways of eukaryotes and Gram-negative bacteria. The reaction is catalysed only in the reverse direction.
References: [1095, 1096, 105]

[EC 4.98.1.1 created 1965 as EC 4.99.1.1, modified 2016, transferred 2021 to EC 4.98.1.1]

EC 4.99 Other lyases

This subclass contains miscellaneous enzymes in a single sub-subclass (EC 4.99.1).

EC 4.99.1 Sole sub-subclass for lyases that do not belong in the other subclasses

[4.99.1.1 Transferred entry. protoporphyrin ferrochelatase, now classified as EC 4.98.1.1, protoporphyrin ferrochelatase]

[EC 4.99.1.1 created 1965, modified 2016, deleted 2021]

EC 4.99.1.2

Accepted name: alkylmercury lyase
Reaction: an alkylmercury + H^+ = an alkane + Hg^{2+}
Other name(s): organomercury lyase; organomercurial lyase; alkylmercury mercuric-lyase
Systematic name: alkylmercury mercury(II)-lyase (alkane-forming)

Comments: Acts on $CH3Hg^{+}$ and a number of other alkylmercury compounds, in the presence of cysteine or other thiols, liberating mercury as a mercaptide.
References: [1363]

[EC 4.99.1.2 created 1978]

EC 4.99.1.3

Accepted name: sirohydrochlorin cobaltochelatase
Reaction: cobalt-sirohydrochlorin + **2** H^{+} = sirohydrochlorin + Co^{2+}
Other name(s): CbiK; CbiX; CbiXS; anaerobic cobalt chelatase; cobaltochelatase [ambiguous]; sirohydrochlorin cobalt-lyase
Systematic name: cobalt-sirohydrochlorin cobalt-lyase (sirohydrochlorin-forming)
Comments: This enzyme, which forms part of the anaerobic (early cobalt insertion) cobalamin biosynthesis pathway, is an ATP-independent type II chelatase. Two distinct forms are known - a primordial form named CbiX, which is most common in archaea, and a strictly bacterial form named CbiK. See EC 6.6.1.2, cobaltochelatase, for the cobaltochelatase that participates in the aerobic cobalamin biosynthesis pathway.
References: [1136, 1235, 1453, 136, 401, 837, 838]

[EC 4.99.1.3 created 2004, modified 2020]

EC 4.99.1.4

Accepted name: sirohydrochlorin ferrochelatase
Reaction: siroheme + **2** H^{+} = sirohydrochlorin + Fe^{2+}
Other name(s): CysG; Met8P; SirB; sirohydrochlorin ferro-lyase (incorrect)
Systematic name: siroheme ferro-lyase (sirohydrochlorin-forming)
Comments: This enzyme catalyses the third of three steps leading to the formation of siroheme from uroporphyrinogen III. The first step involves the donation of two *S*-adenosyl-L-methionine-derived methyl groups to carbons 2 and 7 of uroporphyrinogen III to form precorrin-2 (EC 2.1.1.107, uroporphyrin-III *C*-methyltransferase) and the second step involves an NAD^{+}-dependent dehydrogenation to form sirohydrochlorin from precorrin-2 (EC 1.3.1.76, precorrin-2 dehydrogenase). In *Saccharomyces cerevisiae*, the last two steps are carried out by a single bifunctional enzyme, Met8p. In some bacteria, steps 1-3 are catalysed by a single multifunctional protein called CysG, whereas in *Bacillus megaterium*, three separate enzymes carry out each of the steps, with SirB being responsible for the above reaction.
References: [1234, 1453]

[EC 4.99.1.4 created 2004]

[4.99.1.5 Transferred entry. aliphatic aldoxime dehydratase, now classified as EC 4.8.1.2, aliphatic aldoxime dehydratase]

[EC 4.99.1.5 created 2004, deleted 2021]

[4.99.1.6 Transferred entry. indoleacetaldoxime dehydratase, now classified as EC 4.8.1.3, indoleacetaldoxime dehydratase]

[EC 4.99.1.6 created 1965 as EC 4.2.1.29, transferred 2004 to EC 4.99.1.6, deleted 2021]

[4.99.1.7 Transferred entry. phenylacetaldoxime dehydratase, now classified as EC 4.8.1.4, phenylacetaldoxime dehydratase]

[EC 4.99.1.7 created 2005, deleted 2021]

EC 4.99.1.8

Accepted name: heme ligase
Reaction: **2** ferriprotoporphyrin IX = β-hematin

Other name(s): heme detoxification protein; HDP; hemozoin synthase
Systematic name: Fe^{3+}:ferriprotoporphyrin IX ligase (β-hematin-forming)
Comments: This heme detoxifying enzyme is found in *Plasmodium* parasites and converts toxic heme to crystalline hemozoin. These organisms lack the mammalian heme oxygenase for elimination of heme.
References: [621]

[EC 4.99.1.8 created 2009]

EC 4.99.1.9

Accepted name: coproporphyrin ferrochelatase
Reaction: Fe-coproporphyrin III + **2** H^{+} = coproporphyrin III + Fe^{2+}
Other name(s): *hemH* (gene name)
Systematic name: protoheme ferro-lyase (protoporphyrin-forming)
Comments: The enzyme, present in Gram-positive bacteria, participates in heme biosynthesis. It can also catalyse the reaction of EC 4.99.1.1, protoporphyrin IX ferrochelatase, at a much lower level.
References: [505, 10, 506, 286]

[EC 4.99.1.9 created 2016]

EC 4.99.1.10

Accepted name: magnesium dechelatase
Reaction: (1) chlorophyll *a* + **2** H^{+} = pheophytin *a* + Mg^{2+}
(2) chlorophyllide *a* + **2** H^{+} = pheophorbide *a* + Mg^{2+}
Other name(s): SGR (gene name); SGRL (gene name); Mg-dechelatase
Systematic name: chlorophyll *a* magnesium lyase
Comments: Inhibited by Ca^{2+}, Mg^{2+} and especially Hg^{2+}. SGR has very low activity with chlorophyllide *a* and none with chlorophyll *b*. It acts on chlorophyll *a* both in its free form and in protein complex. SGRL, on the other hand, is more active with chlorophyllide *a* than with chlorophyll *a*. The magnesium formed is scavenged by MCS (metal-chelating substance).
References: [1352, 254, 1446, 1329, 763, 1266]

[EC 4.99.1.10 created 2017]

EC 4.99.1.11

Accepted name: sirohydrochlorin nickelchelatase
Reaction: Ni-sirohydrochlorin + **2** H^{+} = sirohydrochlorin + Ni^{2+}
Other name(s): *cfbA* (gene name)
Systematic name: Ni-sirohydrochlorin nickel-lyase (sirohydrochlorin-forming)
Comments: The enzyme, studied from the methanogenic archaeon *Methanosarcina acetivorans*, participates in the biosynthesis of the nickel-containing tetrapyrrole cofactor coenzyme F$_{430}$, which is required by EC 2.8.4.1, coenzyme-B sulfoethylthiotransferase. It catalyses the insertion of the nickel ion into sirohydrochlorin.
References: [1565]

[EC 4.99.1.11 created 2017]

EC 4.99.1.12

Accepted name: pyridinium-3,5-bisthiocarboxylic acid mononucleotide nickel chelatase
Reaction: Ni(II)-pyridinium-3,5-bisthiocarboxylate mononucleotide = pyridinium-3,5-bisthiocarboxylate mononucleotide + Ni^{2+}
Other name(s): LarC; P2TMN nickel chelatase
Systematic name: Ni(II)-pyridinium-3,5-bisthiocarboxylate mononucleotide nickel-lyase (pyridinium-3,5-bisthiocarboxylate-mononucleotide-forming)

Comments: This enzyme, found in *Lactobacillus plantarum*, is involved in the biosynthesis of a nickel-pincer cofactor. It catalyses the insertion of Ni^{2+} into the cofactor forming a covalent bond between a carbon atom and the nickel atom.

References: [316, 317]

[EC 4.99.1.12 created 2017]

References

[1] P. Acharya, M. Goenrich, C.H. Hagemeier, U. Demmer, J.A. Vorholt, R.K. Thauer, and U. Ermler. How an enzyme binds the C_1 carrier tetrahydromethanopterin. Structure of the tetrahydromethanopterin-dependent formaldehyde-activating enzyme (Fae) from *Methylobacterium extorquens* AM1. *J. Biol. Chem.*, 280:13712–13719, 2005.

[2] S.A. Acheson, H.N. Kirkman, and R. Wolfenden. Equilibrium of 5,6-hydration of NADH and mechanism of ATP-dependent dehydration. *Biochemistry*, 27:7371–7375, 1988.

[3] N.E. Adams, J.J. Thiaville, J. Proestos, A.L. Juarez-Vazquez, A.J. McCoy, F. Barona-Gomez, D. Iwata-Reuyl, V. de Crecy-Lagard, and A.T. Maurelli. Promiscuous and adaptable enzymes fill ”holes” in the tetrahydrofolate pathway in *Chlamydia* species. *MBio*, 5:e01378–e01314, 2014.

[4] S. Agger, F. Lopez-Gallego, and C. Schmidt-Dannert. Diversity of sesquiterpene synthases in the basidiomycete *Coprinus cinereus*. *Mol. Microbiol.*, 72:1181–1195, 2009.

[5] S.A. Agger, F. Lopez-Gallego, T.R. Hoye, and C. Schmidt-Dannert. Identification of sesquiterpene synthases from *Nostoc punctiforme* PCC 73102 and *Nostoc* sp. strain PCC 7120. *J. Bacteriol.*, 190:6084–6096, 2008.

[6] I. Aguirrezabalaga, C. Olano, N. Allende, L. Rodriguez, A.F. Brana, C. Mendez, and J.A. Salas. Identification and expression of genes involved in biosynthesis of L-oleandrose and its intermediate L-olivose in the oleandomycin producer *Streptomyces antibioticus*. *Antimicrob. Agents Chemother.*, 44:1266–1275, 2000.

[7] A. Aharoni, A.P. Giri, F.W. Verstappen, C.M. Bertea, R. Sevenier, Z. Sun, M.A. Jongsma, W. Schwab, and H.J. Bouwmeester. Gain and loss of fruit flavor compounds produced by wild and cultivated strawberry species. *Plant Cell*, 16:3110–3131, 2004.

[8] H. Ahmed, T.J. Ettema, B. Tjaden, A.C. Geerling, J. van der Oost, and B. Siebers. The semi-phosphorylative Entner-Doudoroff pathway in hyperthermophilic archaea: a re-evaluation. *Biochem. J.*, 390:529–540, 2005.

[9] T.N. Akopyan, A.E. Braunstein, and E.V. Goryachenkova. β-Cyanoalanine synthase: purification and characterization. *Proc. Natl. Acad. Sci. USA*, 72:1617–1621, 1975.

[10] S. Al-Karadaghi, M. Hansson, S. Nikonov, B. Jonsson, and L. Hederstedt. Crystal structure of ferrochelatase: the terminal enzyme in heme biosynthesis. *Structure*, 5:1501–1510, 1997.

[11] J. Alam, N. Beyer, and H.W. Liu. Biosynthesis of colitose: expression, purification, and mechanistic characterization of GDP-4-keto-6-deoxy-D-mannose-3-dehydrase (ColD) and GDP-L-colitose synthase (ColC). *Biochemistry*, 43:16450–16460, 2004.

[12] S. Alam, S.C. Wang, F.J. Ruzicka, P.A. Frey, and J.E. Wedekind. Crystallization and X-ray diffraction analysis of ornithine cyclodeaminase from *Pseudomonas putida*. *Acta Crystallogr. D Biol. Crystallogr.*, 60:941–944, 2004.

[13] P. Albersheim and U. Killias. Studies relating to the purification and properties of pectin transeliminase. *Arch. Biochem. Biophys.*, 97:107–115, 1962.

[14] P. Albersheim, H. Neukom, and H. Deuel. Über die Bildung von ungesättigten Abbauprodukten durch ein pekinabbauendes Enzym. *Helv. Chim. Acta*, 43:1422–1426, 1960.

[15] R.A. Alberty. Fumarase. In P.D. Boyer, H. Lardy, and K. Myrbäck, editors, *The Enzymes*, volume 5, pages 531–544. Academic Press, New York, 2nd edition, 1961.

[16] J. Albrecht, Jansen, and M.R. Improved purification of an (*R*)-oxynitrilase from *Linum usitatissimum* (flax) and investigation of the substrate range. *Biotechnol. Appl. Biochem.*, 17:191–203, 1993.

[17] P.R. Alefounder, S.A. Baldwin, R.N. Perham, , and N.J. Cloning, sequence analysis and over-expression of the gene for the class II fructose 1,6-bisphosphate aldolase of *Escherichia coli*. *Biochem. J.*, 257:529–534, 1989.

[18] A. Alhapel, D.J. Darley, N. Wagener, E. Eckel, N. Elsner, and A.J. Pierik. Molecular and functional analysis of nicotinate catabolism in *Eubacterium barkeri*. *Proc. Natl. Acad. Sci. USA*, 103:12341–12346, 2006.

[19] D. Allan and R.H. Michell. Phosphatidylinositol cleavage catalysed by the soluble fraction from lymphocytes. *Activity at pH5.5 and pH7.0. Biochem. J.*, 142:591–597, 1974.

[20] J.R. Allen, D.D. Clark, J.G. Krum, and S.A. Ensign. A role for coenzyme M (2-mercaptoethanesulfonic acid) in a bacterial pathway of aliphatic epoxide carboxylation. *Proc. Natl. Acad. Sci. USA*, 96:8432–8437, 1999.

[21] W.R. Alonso and R. Croteau. Purification and characterization of the monoterpene cyclase γ-terpinene synthase from *Thymus vulgaris*. *Arch. Biochem. Biophys.*, 286:511–517, 1991.

[22] L. Ambe and K. Sohonie. Purification and properties of glutamate decarboxylase from the field bean (*Dolichos lablab*). *Enzymologia*, 26:98–107, 1963.

[23] B.N. Ames. The biosynthesis of histidine: D-*erythro*-Imidazoleglycerol phosphate dehydrase. *J. Biol. Chem.*, 228:131–143, 1957.

[24] P.M. Anderson. Purification and properties of the inducible enzyme cyanase. *Biochemistry*, 19:2882–2888, 1980.

[25] P.M. Anderson, J.J. Korte, and T.A. Holcomb. Reaction of the N-terminal methionine residues in cyanase with diethylpyrocarbonate. *Biochemistry*, 33:14121–14125, 1994.

[26] R.L. Anderson and J.P. Markwell. D-Tagatose-1,6-bisphosphate aldolase (class II) from *Klebsiella pneumoniae*. *Methods Enzymol.*, 90:232–234, 1982.

[27] W.A. Anderson and B. Magasanik. The pathway of *myo*-inositol degradation in *Aerobacter aerogenes*. Conversion of 2-deoxy-5-keto-D-gluconic acid to glycolytic intermediates. *J. Biol. Chem.*, 246:5662–5675, 1971.

[28] J. Andexer, J. von Langermann, A. Mell, M. Bocola, U. Kragl, T. Eggert, and M. Pohl. An *R*-selective hydroxynitrile lyase from *Arabidopsis thaliana* with an α/β-hydrolase fold. *Angew. Chem. Int. Ed. Engl.*, 46:8679–8681, 2007.

[29] J.N. Andexer, S.G. Kendrew, M. Nur e Alam, O. Lazos, T.A. Foster, A.S. Zimmermann, T.D. Warneck, D. Suthar, N.J. Coates, F.E. Koehn, J.S. Skotnicki, G.T. Carter, M.A. Gregory, C.J. Martin, S.J. Moss, P.F. Leadlay, and B. Wilkinson. Biosynthesis of the immunosuppressants FK506, FK520, and rapamycin involves a previously undescribed family of enzymes acting on chorismate. *Proc. Natl. Acad. Sci. USA*, 108:4776–4781, 2011.

[30] J.R. Andreesen and G. Gottschalk. The occurrence of a modified Entner-Doudoroff pathway in *Clostridium aceticum*. *Arch. Mikrobiol.*, 69:160–170, 1969.

[31] P.I. Andrei, A.J. Pierik, S. Zauner, L.C. Andrei-Selmer, and T. Selmer. Subunit composition of the glycyl radical enzyme *p*-hydroxyphenylacetate decarboxylase. A small subunit, HpdC, is essential for catalytic activity. *Eur. J. Biochem.*, 271:2225–2230, 2004.

[32] H. Ankel and D.S. Feingold. Biosynthesis of uridine diphosphate D-xylose. 1. Uridine diphosphate glucuronate carboxy-lyase of wheat germ. *Biochemistry*, 4:2468–2475, 1965.

[33] D.L. Anton and R. Kutny. *Escherichia coli S*-adenosylmethionine decarboxylase. Subunit structure, reductive amination, and NH_2-terminal sequences. *J. Biol. Chem.*, 262:2817–2822, 1987.

[34] H. Aoki and T. Tabuchi. Purification and properties of 2-methylcitrate dehydratase from *Yarrowia lipolytica*. *Agric. Biol. Chem.*, 45:2831–2837, 1981.

[35] H. Aoki, H. Uchiyama, H. Umetsu, , and T. Isolation of 2-methylisocitrate dehydratase, a new enzyme serving in the methylcitric acid cycle for propionate metabolism, from *Yarrowia lipolytica*. *Biosci. Biotechnol. Biochem.*, 59:1825–1828, 1995.

[36] C. Appert, E. Logemann, K. Hahlbrock, J. Schmid, and N. Amrhein. Structural and catalytic properties of the four phenylalanine ammonia-lyase isoenzymes from parsley (*Petroselinum crispum* Nym.). *Eur. J. Biochem.*, 225:491–499, 1994.

[37] S. Arent, C.E. Christensen, V.E. Pye, A. Norgaard, and A. Henriksen. The multifunctional protein in peroxisomal β-oxidation: structure and substrate specificity of the *Arabidopsis thaliana* protein MFP2. *J. Biol. Chem.*, 285:24066–24077, 2010.

[38] G. Arimura, S. Garms, M. Maffei, S. Bossi, B. Schulze, M. Leitner, A. Mithofer, and W. Boland. Herbivore-induced terpenoid emission in *Medicago truncatula*: concerted action of jasmonate, ethylene and calcium signaling. *Planta*, 227:453–464, 2008.

[39] G. Arimura, R. Ozawa, S. Kugimiya, J. Takabayashi, and J. Bohlmann. Herbivore-induced defense response in a model legume. Two-spotted spider mites induce emission of (*E*)-β-ocimene and transcript accumulation of (*E*)-β-ocimene synthase in *Lotus japonicus*. *Plant Physiol.*, 135:1976–1983, 2004.

[40] D.A. Armah and K. Mensa-Wilmot. Tetramerization of glycosylphosphatidylinositol-specific phospholipase C from *Trypanosoma brucei*. *J. Biol. Chem.*, 275:19334–19342, 2000.

[41] T. Asakawa, H. Wada, and T. Yamano. Enzymatic conversion of phenylpyruvate to phenylacetate. *Biochim. Biophys. Acta*, 170:375–391, 1968.

[42] S. Asamizu, P. Xie, C.J. Brumsted, P.M. Flatt, and T. Mahmud. Evolutionary divergence of sedoheptulose 7-phosphate cyclases leads to several distinct cyclic products. *J. Am. Chem. Soc.*, 134:12219–12229, 2012.

[43] N. Asano, M. Takeuchi, K. Ninomiya, Y. Kameda, and K. Matsui. Microbial degradation of validamycin A by *Flavobacterium saccharophilum*. Enzymatic cleavage of C-N linkage in validoxylamine A. *J. Antibiot.*, 37:859–867, 1984.

[44] Y. Asano, K. Fujishiro, Y. Tani, and H. Yamada. Microbial degradation of nitrile compounds. 5. Aliphatic nitrile hydratase from *Arthrobacter sp* J-1. Purification and characterization. *Agric. Biol. Chem.*, 46:1165–1174, 1982.

[45] G. Ashwell, A.J. Wahba, and J. Hickman. A new pathway of uronic acid metabolism. *Biochim. Biophys. Acta*, 30:186–187, 1958.

[46] E. Attaran, M. Rostas, and J. Zeier. *Pseudomonas syringae* elicits emission of the terpenoid (*E*,*E*)-4,8,12-trimethyl-1,3,7,11-tridecatetraene in *Arabidopsis* leaves via jasmonate signaling and expression of the terpene synthase TPS4. *Mol. Plant Microbe Interact.*, 21:1482–1497, 2008.

[47] D.G. Attardi, I. Margarit, and G.P. Tocchini-Valentini. Structural alterations in mutant precursors of the yeast tRNA^{Leu3} gene which behave as defective substrates for a highly purified splicing endoribonuclease. *EMBO J.*, 4:3289–3297, 1985.

[48] M. Attia, S.U. Kim, and D.K. Ro. Molecular cloning and characterization of (+)-*epi*-α-bisabolol synthase, catalyzing the first step in the biosynthesis of the natural sweetener, hernandulcin, in *Lippia dulcis*. *Arch. Biochem. Biophys.*, 527:37–44, 2012.

[49] M. Avi, R.M. Wiedner, H. Griengl, and H. Schwab. Improvement of a stereoselective biocatalytic synthesis by substrate and enzyme engineering: 2-hydroxy-(4′-oxocyclohexyl)acetonitrile as the model. *Chemistry*, 14:11415–11422, 2008.

[50] R. Ayikpoe, T. Ngendahimana, M. Langton, S. Bonitatibus, L.M. Walker, S.S. Eaton, G.R. Eaton, M.E. Pandelia, S.J. Elliott, and J.A. Latham. Spectroscopic and electrochemical characterization of the mycofactocin biosynthetic protein, MftC, provides insight into its redox flipping mechanism. *Biochemistry*, 58:940–950, 2019.

[51] P. Azadi, M.A. O'Neill, C. Bergmann, A.G. Darvill, and P. Albersheim. The backbone of the pectic polysaccharide rhamnogalacturonan I is cleaved by an endohydrolase and an endolyase. *Glycobiology*, 5:783–789, 1995.

[52] L. Bach, L.V. Michaelson, R. Haslam, Y. Bellec, L. Gissot, J. Marion, M. Da Costa, J.P. Boutin, M. Miquel, F. Tellier, F. Domergue, J.E. Markham, F. Beaudoin, J.A. Napier, and J.D. Faure. The very-long-chain hydroxy fatty acyl-CoA dehydratase PASTICCINO$_2$ is essential and limiting for plant development. *Proc. Natl. Acad. Sci. USA*, 105:14727–14731, 2008.

[53] M.K. Bach, J.R., Morton Brashler, , and Jr. Solubilization and characterization of the leukotriene C$_4$ synthetase of rat basophil leukemia cells: a novel, particulate glutathione *S*-transferase. *Arch. Biochem. Biophys.*, 230:455–465, 1984.

[54] B.K. Bachhawat, W.G. Robinson, and M.J. Coon. The enzymatic cleavage of β-hydroxy-β-methylglutaryl coenzyme A to acetoacetate and acetyl coenzyme A. *J. Biol. Chem.*, 216:727–736, 1955.

[55] K. Back and J. Chappell. Cloning and bacterial expression of a sesquiterpene cyclase from Hyoscyamus muticus and its molecular comparison to related terpene cyclases. *J. Biol. Chem.*, 270:7375–7381, 1995.

[56] K. Back, S. He, K.U. Kim, and D.H. Shin. Cloning and bacterial expression of sesquiterpene cyclase, a key branch point enzyme for the synthesis of sesquiterpenoid phytoalexin capsidiol in UV-challenged leaves of *Capsicum annuum*. *Plant Cell Physiol.*, 39:899–904, 1998.

[57] K. Back, S. Yin, and J. Chappell. Expression of a plant sesquiterpene cyclase gene in *Escherichia coli*. *Arch. Biochem. Biophys.*, 315:527–532, 1994.

[58] P. Baer, P. Rabe, C.A. Citron, C.C. de Oliveira Mann, N. Kaufmann, M. Groll, and J.S. Dickschat. Hedycaryol synthase in complex with nerolidol reveals terpene cyclase mechanism. *ChemBioChem*, 15:213–216, 2014.

[59] P. Baer, P. Rabe, K. Fischer, C.A. Citron, T.A. Klapschinski, M. Groll, and J.S. Dickschat. Induced-fit mechanism in class I terpene cyclases. *Angew. Chem. Int. Ed. Engl.*, 53:7652–7656, 2014.

[60] G.B. Bailey and W.B. Dempsey. Purification and properties of an α-dialkyl amino acid transaminase. *Biochemistry*, 6:1526–1533, 1967.

[61] V. Bailly, B. Sente, and W.G. Verly. Bacteriophage-T4 and *Micrococcus luteus* UV endonucleases are not endonucleases but β-elimination and sometimes β δ-elimination catalysts. *Biochem. J.*, 259:751–759, 1989.

[62] V. Bailly and W.G. Verly. *Escherichia coli* endonuclease III is not an endonuclease but a β-elimination catalyst. *Biochem. J.*, 242:565–572, 1987.

[63] V. Bailly and W.G. Verly. AP endonucleases and AP lyases. *Nucleic Acids Res.*, 17:3617–3618, 1989.

[64] P. Baker, J. Carere, and S.Y.K. Seah. Probing the molecular basis of substrate specificity, stereospecificity, and catalysis in the class II pyruvate aldolase, BphI. *Biochemistry*, 50:3559–3569, 2011.

[65] P. Baker, C. Hillis, J. Carere, and S.Y.K. Seah. Protein-protein interactions and substrate channeling in orthologous and chimeric aldolase-dehydrogenase complexes. *Biochemistry*, 51:1942–1952, 2012.

[66] P. Baker, D. Pan, J. Carere, A. Rossi, W. Wang, and S.Y.K. Seah. Characterization of an aldolase-dehydrogenase complex that exhibits substrate channeling in the polychlorinated biphenyls degradation pathway. *Biochemistry*, 48:6551–6558, 2009.

[67] P. Baker and S.Y.K. Seah. Rational design of stereoselectivity in the class II pyruvate aldolase BphI. *J. Am. Chem. Soc.*, 134:507–513, 2012.

[68] T. Baker and I.P. Crawford. Anthranilate synthetase. Partial purification and some kinetic studies on the enzyme from *Escherichia coli*. *J. Biol. Chem.*, 241:5577–5584, 1966.

[69] R.L. Baldwin, W.A. Wood, and R.S. Emery. Lactate metabolism by *Peptostreptococcus elsdenii*: evidence for lactyl coenzyme a dehydrase. *Biochim. Biophys. Acta*, 97:202–213, 1965.

[70] S. Bali, A.D. Lawrence, S.A. Lobo, L.M. Saraiva, B.T. Golding, D.J. Palmer, M.J. Howard, S.J. Ferguson, and M.J. Warren. Molecular hijacking of siroheme for the synthesis of heme and d1 heme. *Proc. Natl. Acad. Sci. USA*, 108:18260–18265, 2011.

[71] E.P. Balskus and C.T. Walsh. The genetic and molecular basis for sunscreen biosynthesis in cyanobacteria. *Science*, 329:1653–1656, 2010.

[72] D.V. Banthorp, J.T. Brown, and G.S. Morris. Partial purification of farnesyl pyrophosphate:drimenol cyclase and geranylgerany pyrophosphate:sclareol cyclase, using cell culture as a source of material. *Phytochemistry*, 31:3391–3395, 1992.

[73] H.A. Barker. Citramalate lyase of *Clostridium tetanomorphum*. *Arch. Mikrobiol.*, 59:4–12, 1967.

[74] H.A. Barker, J.M. Kahn, , and S. Enzymes involved in 3,5-diaminohexanoate degradation by *Brevibacterium* sp. *J. Bacteriol.*, 143:1165–1170, 1980.

[75] H.A. Barker, R.O. Smyth, E.J. Wawszkiewicz, M.N. Lee, and R.M. Wilson. Enzymic preparation and characterization of an α-L-β-methylaspartic acid. *Arch. Biochem. Biophys.*, 78:468–476, 1958.

[76] E.A. Barnsley. Phthalate pathway of phenanthrene metabolism: formation of 2′-carboxybenzalpyruvate. *J. Bacteriol.*, 154:113–117, 1983.

[77] L.R. Barran and W.A. Wood. The mechanism of 2-keto-3-deoxy-6-phosphogluconate aldolase. 3. Nature of the inactivation by fluorodinitrobenzene. *J. Biol. Chem.*, 246:4028–4035, 1971.

[78] R.G. Bartsch and H.A. Barker. A vinylacetyl isomerase from *Clostridium kluyveri*. *Arch. Biochem. Biophys.*, 92:122–132, 1961.

[79] A.R. Battersby, C.J.R. Fookes, G.W.J. Matcham, and E. McDonald. Biosynthesis of the pigments of life: formation of the macrocycle. *Nature*, 285:17–21, 1980.

[80] J.R. Beard and W.E. Razzell. Purification of alkaline ribonuclease II from mitochondrial and soluble fractions of liver. *J. Biol. Chem.*, 239:4186–4193, 1964.

[81] S. Beismann-Driemeyer and R. Sterner. Imidazole glycerol phosphate synthase from *Thermotoga maritima*. Quaternary structure, steady-state kinetics, and reaction mechanism of the bienzyme complex. *J. Biol. Chem.*, 276:20387–20396, 2001.

[82] L. Belingher, A. Cartayrade, G. Pauly, and M. Gleizes. Partial purification and properties of the sesquiterpene β-selinene cyclase from *Citrofortunella mitis*. *Plant Sci.*, 84:129–136, 1992.

[83] J. Bell, D.E. Ash, L.M. Snyder, R. Kulathila, N.J. Blackburn, and D.J. Merkler. Structural and functional investigations on the role of zinc in bifunctional rat peptidylglycine α-amidating enzyme. *Biochemistry*, 36:16239–16246, 1997.

[84] H.R. Beller, A.V. Rodrigues, K. Zargar, Y.W. Wu, A.K. Saini, R.M. Saville, J.H. Pereira, P.D. Adams, S.G. Tringe, C.J. Petzold, and J.D. Keasling. Discovery of enzymes for toluene synthesis from anoxic microbial communities. *Nat. Chem. Biol.*, 14:451–457, 2018.

[85] H.R. Beller and A.M. Spormann. Analysis of the novel benzylsuccinate synthase reaction for anaerobic toluene activation based on structural studies of the product. *J. Bacteriol.*, 180:5454–5457, 1998.

[86] R. Bender and G. Gottschalk. Purification and properties of D-gluconate dehydratase from *Clostridium pasteurianum*. *Eur. J. Biochem.*, 40:309–321, 1973.

[87] S.L. Bender, S. Mehdi, and J.R. Knowles. Dehydroquinate synthase: the role of divalent metal cations and of nicotinamide adenine dinucleotide in catalysis. *Biochemistry*, 28:7555–7560, 1989.

[88] J.P. Bennett, L. Bertin, B. Moulton, I.J. Fairlamb, A.M. Brzozowski, N.J. Walton, and G. Grogan. A ternary complex of hydroxycinnamoyl-CoA hydratase-lyase (HCHL) with acetyl-CoA and vanillin gives insights into substrate specificity and mechanism. *Biochem. J.*, 414:281–289, 2008.

[89] R. Bentley and C.P. Thiessen. Biosynthesis of itaconic acid in *Aspergillus terreus*. III. The properties and reaction mechanism of *cis*-aconitic acid decarboxylase. *J. Biol. Chem.*, 226:703–720, 1957.

[90] R. Bentley and C.P. Thiessen. Biosynthesis of tropolones in *Penicillium stipitatum*. V. Preparation and properties of stipitatonic acid decarboxylase. *J. Biol. Chem.*, 238:3811–3816, 1963.

[91] S. Berensmeier, S.A. Singh, J. Meens, and K. Buchholz. Cloning of the *pelA* gene from *Bacillus licheniformis* 14A and biochemical characterization of recombinant, thermostable, high-alkaline pectate lyase. *Appl. Microbiol. Biotechnol.*, 64:560–567, 2004.

[92] I.A. Berg, D. Kockelkorn, W. Buckel, and G. Fuchs. A 3-hydroxypropionate/4-hydroxybutyrate autotrophic carbon dioxide assimilation pathway in *Archaea*. *Science*, 318:1782–1786, 2007.

[93] T. Berman and B. Magasanik. The pathway of *myo*-inositol degradation in *Aerobacter aerogenes*. Dehydrogenation and dehydration. *J. Biol. Chem.*, 241:800–806, 1966.

[94] R.P. Bhalerao, L.K. Lind, and P. Gustafsson. Cloning of the *cpcE* and *cpcF* genes from *Synechococcus* sp. PCC 6301 and their inactivation in *Synechococcus* sp. PCC 7942. *Plant Mol. Biol.*, 26:313–326, 1994.

[95] S. Bhowmik, H.P. Chiu, D.H. Jones, H.J. Chiu, M.D. Miller, Q. Xu, C.L. Farr, J.M. Ridlon, J.E. Wells, M.A. Elsliger, I.A. Wilson, P.B. Hylemon, and S.A. Lesley. Structure and functional characterization of a bile acid 7α dehydratase BaiE in secondary bile acid synthesis. *Proteins*, 84:316–331, 2016.

[96] M.W. Bhuiya, S.G. Lee, J.M. Jez, and O. Yu. Structure and mechanism of ferulic acid decarboxylase (FDC1) from *Saccharomyces cerevisiae*. *Appl. Environ. Microbiol.*, 81:4216–4223, 2015.

[97] A. Biswas, M.N. Boutaghou, R.M. Alvey, C.M. Kronfel, R.B. Cole, D.A. Bryant, and W.M. Schluchter. Characterization of the activities of the CpeY, CpeZ, and CpeS bilin lyases in phycoerythrin biosynthesis in Fremyella diplosiphon strain UTEX 481. *J. Biol. Chem.*, 286:35509–35521, 2011.

[98] A.H. Blair and H.A. Barker. Assay and purification of (+)-citramalate hydro-lyase components from *Clostridium tetanomorphum*. *J. Biol. Chem.*, 241:400–408, 1966.

[99] J. Blaszczyk, Z. Lu, Y. Li, H. Yan, and X. Ji. Crystallographic and molecular dynamics simulation analysis of *Escherichia coli* dihydroneopterin aldolase. *Cell Biosci*, 4:52–52, 2014.

[100] P.M. Bleeker, R. Mirabella, P.J. Diergaarde, A. Vandoorn, A. Tissier, M.R. Kant, M. Prins, M. de Vos, M.A. Haring, and R.C. Schuurink. Improved herbivore resistance in cultivated tomato with the sesquiterpene biosynthetic pathway from a wild relative. *Proc. Natl. Acad. Sci. USA*, 109:20124–20129, 2012.

[101] P.M. Bleeker, E.A. Spyropoulou, P.J. Diergaarde, H. Volpin, M.T. De Both, P. Zerbe, J. Bohlmann, V. Falara, Y. Matsuba, E. Pichersky, M.A. Haring, and R.C. Schuurink. RNA-seq discovery, functional characterization, and comparison of sesquiterpene synthases from *Solanum lycopersicum* and *Solanum habrochaites* trichomes. *Plant Mol. Biol.*, 77:323–336, 2011.

[102] S.L. Blethen, E.A. Boeker, and E.E. Snell. Arginine decarboxylase from *Escherichia coli*. I. Purification and specificity for substrates and coenzyme. *J. Biol. Chem.*, 243:1671–1677, 1968.

[103] S. Blickling, C. Renner, B. Laber, H.D. Pohlenz, T.A. Holak, and R. Huber. Reaction mechanism of *Escherichia coli* dihydrodipicolinate synthase investigated by X-ray crystallography and NMR spectroscopy. *Biochemistry*, 36:24–33, 1997.

[104] K. Bloch, S. Chaykin, A.H. Phillips, and A. de Waard. Mevalonic acid pyrophosphate and isopentenyl pyrophosphate. *J. Biol. Chem.*, 234:2595–2604, 1959.

[105] J.R. Bloomer, H.D. Hill, K.O. Morton, L.A. Anderson-Burnham, and J.G. Straka. The enzyme defect in bovine protoporphyria. Studies with purified ferrochelatase. *J. Biol. Chem.*, 262:667–671, 1987.

[106] N. Blot, X.J. Wu, J.C. Thomas, J. Zhang, L. Garczarek, S. Bohm, J.M. Tu, M. Zhou, M. Ploscher, L. Eichacker, F. Partensky, H. Scheer, and K.H. Zhao. Phycourobilin in trichromatic phycocyanin from oceanic cyanobacteria is formed post-translationally by a phycoerythrobilin lyase-isomerase. *J. Biol. Chem.*, 284:9290–9298, 2009.

[107] H.J. Blumenthal. D-Glucarate dehydrase. *Methods Enzymol.*, 9:660–665, 1966.

[108] H.J. Blumenthal and T. Jepson. Galactarate dehydrase. *Methods Enzymol.*, 9:665–669, 1966.

[109] T.A. Bobik, E.J. Morales, A. Shin, D. Cascio, M.R. Sawaya, M. Arbing, T.O. Yeates, and M.E. Rasche. Structure of the methanofuran/methanopterin-biosynthetic enzyme MJ1099 from *Methanocaldococcus jannaschii*. *Acta Crystallogr. F Struct. Biol. Commun.*, 70:1472–1479, 2014.

[110] R.P. Bodnaryk and L. McGirr. Purification, properties and function of a unique γ-glutamyl cyclotransferase from the housefly, *Musca domestica* L. *Biochim. Biophys. Acta*, 315:352–362, 1973.

[111] J. Bohlmann, J. Crock, R. Jetter, and R. Croteau. Terpenoid-based defenses in conifers: cDNA cloning, characterization, and functional expression of wound-inducible (*E*)-α-bisabolene synthase from grand fir (*Abies grandis*). *Proc. Natl. Acad. Sci. USA*, 95:6756–6761, 1998.

[112] J. Bohlmann, M. Phillips, V. Ramachandiran, S. Katoh, and R. Croteau. cDNA cloning, characterization, and functional expression of four new monoterpene synthase members of the *Tpsd* gene family from grand fir (*Abies grandis*). *Arch. Biochem. Biophys.*, 368:232–243, 1999.

[113] J. Bohlmann, E.J. Stauber, B. Krock, N.J. Oldham, J. Gershenzon, and I.T. Baldwin. Gene expression of 5-*epi*-aristolochene synthase and formation of capsidiol in roots of *Nicotiana attenuata* and *N. sylvestris*. *Phytochemistry*, 60:109–116, 2002.

[114] J. Bohlmann, C.L. Steele, and R. Croteau. Monoterpene synthases from grand fir (*Abies grandis*). cDNA isolation, characterization, and functional expression of myrcene synthase, (-)-(4*S*)-limonene synthase, and (-)-(1*S*,5*S*)-pinene synthase. *J. Biol. Chem.*, 272:21784–21792, 1997.

[115] T. Boller, R.C. Herner, and H. Kende. Assay for and enzymatic formation of an ethylene precursor, 1-aminocyclopropane-1-carboxylic acid. *Planta*, 145:293–303, 1979.

[116] F. Borjian, J. Han, J. Hou, H. Xiang, J. Zarzycki, and I.A. Berg. Malate Synthase and β-Methylmalyl Coenzyme A Lyase Reactions in the Methylaspartate Cycle in *Haloarcula hispanica*. *J. Bacteriol.*, 199, 2017.

[117] S. Bornemann, D.J. Lowe, and R.N. Thorneley. The transient kinetics of *Escherichia coli* chorismate synthase: substrate consumption, product formation, phosphate dissociation, and characterization of a flavin intermediate. *Biochemistry*, 35:9907–9916, 1996.

[118] S. Bornemann, M.E. Theoclitou, M. Brune, M.R. Webb, R.N. Thorneley, and C. Abell. A secondary β deuterium kinetic isotope effect in the chorismate synthase reaction. *Bioorg. Chem.*, 28:191–204, 2000.

[119] H.J. Bouwmeester, J. Gershenzon, M.C.J.M. Konings, and R. Croteau. Biosynthesis of the monoterpenes limonene and carvone in the fruit of caraway. I. Demonstration of enzyme activities and their changes with development. *Plant Physiol.*, 117:901–912, 1998.

[120] H.J. Bouwmeester, J. Kodde, F.W. Verstappen, I.G. Altug, J.W. de Kraker, and T.E. Wallaart. Isolation and characterization of two germacrene A synthase cDNA clones from chicory. *Plant Physiol.*, 129:134–144, 2002.

[121] H.J. Bouwmeester, F.W. Verstappen, M.A. Posthumus, and M. Dicke. Spider mite-induced (3*S*)-(*E*)-nerolidol synthase activity in cucumber and lima bean. The first dedicated step in acyclic C11-homoterpene biosynthesis. *Plant Physiol.*, 121:173–180, 1999.

[122] H.J. Bouwmeester, T.E. Wallaart, M.H. Janssen, B. van Loo, B.J. Jansen, M.A. Posthumus, C.O. Schmidt, J.W. De Kraker, W.A. König, and M.C. Franssen. Amorpha-4,11-diene synthase catalyses the first probable step in artemisinin biosynthesis. *Phytochemistry*, 52:843–854, 1999.

[123] C. Bové and E.E. Conn. Metabolism of aromatic compounds in higher plants. II. Purification and properties of the oxynitrilase of *Sorghum vulgare*. *J. Biol. Chem.*, 236:207–210, 1961.

[124] G. Bowles, W.L. Ogren, and R.H. Hageman. Phosphoglycolate production catalyzed by ribulose diphosphate carboxylase. *Biochem. Biophys. Res. Commun.*, 45:716–722, 1971.

[125] J. Boyd and J.R. Turvey. Isolation of poly-α-L-guluronate lyase from *Klebsiella aerogenes*. *Carbohydr. Res.*, 57:163–171, 1977.

[126] Z.L. Boynton, G.N. Bennet, and F.B. Rudolph. Cloning, sequencing, and expression of clustered genes encoding β-hydroxybutyryl-coenzyme A (CoA) dehydrogenase, crotonase, and butyryl-CoA dehydrogenase from *Clostridium acetobutylicum* ATCC 824. *J. Bacteriol.*, 178:3015–3024, 1996.

[127] C. Bradbeer. The clostridial fermentations of choline and ethanolamine. 1. Preparation and properties of cell-free extracts. *J. Biol. Chem.*, 240:4669–4474, 1965.

[128] C. Bradbeer. The clostridial fermentations of choline and ethanolamine. II. Requirement for a cobamide coenzyme by an ethanolamine deaminase. *J. Biol. Chem.*, 240:4675–4681, 1965.

[129] S.F. Brady and J. Clardy. Cloning and heterologous expression of isocyanide biosynthetic genes from environmental DNA. *Angew. Chem. Int. Ed. Engl.*, 44:7063–7065, 2005.

[130] S.F. Brady and J. Clardy. Systematic investigation of the *Escherichia coli* metabolome for the biosynthetic origin of an isocyanide carbon atom. *Angew. Chem. Int. Ed. Engl.*, 44:7045–7048, 2005.

[131] A.E. Braunstein and R.M. Azarkh. [Participation of vitamin B_6 in enzymic formation of hydrogen sulfide from L-cysteine.]. *Dokl. Akad. Nauk S.S.S.R.*, 71:93–96, 1950.

[132] A.E. Braunstein and R.M. Azarkh. [Phosphopyridoxal in aerobic deamination of homoserine and serine.]. *Dokl. Akad. Nauk S.S.S.R.*, 85:385–388, 1952.

[133] A.E. Braunstein, E.V. Goryachinkova, E.A. Tolosa, I.H. Willhardt, and L.L. Yefremova. Specificity and some other properties of liver serine sulphhydrase: evidence for its identity with cystathionine-synthase. *Biochim. Biophys. Acta.*, 242:247–260, 1971.

[134] H. Breithaupt, M. Pohl, W. Bönigk, P. Heim, K.-L. Schimz, and M.-R. Kula. Cloning and expression of (*R*)-hydroxynitrile lyase from *Linum usitatissimum* (flax). *J. Mol. Catal. B*, 6:315–332, 1999.

[135] H.J. Bright and L.L. Ingraham. The preparation of crystalline β-methylaspartase. *Biochim. Biophys. Acta*, 44:586–588, 1960.

[136] A.A. Brindley, E. Raux, H.K. Leech, H.L. Schubert, and M.J. Warren. A story of chelatase evolution: Identification and characterisation of a small 13-15 kDa 'ancestral' cobaltochelatase (CbiXS) in the *Archaea*. *J. Biol. Chem.*, 278:22388–22395, 2003.

[137] J.S. Britten, H. Morell, and J.V. Taggart. Anion activation of maleate hydratase. *Biochim. Biophys. Acta*, 185:220–227, 1969.

[138] A. Broberg, L. Kenne, and M. Pedersén. Presence of microthecin in the red alga *Gracilariopsis lemaneiformis* and its formation from 1,5-anhydro-D-fructose. *Phytochemistry*, 41:151–154, 1996.

[139] M. Brock, C. Maerker, A. Schütz, U. Völker, and W. Buckel. Oxidation of propionate to pyruvate in *Escherichia coli*. Involvement of methylcitrate dehydratase and aconitase. *Eur. J. Biochem.*, 269:6184–6194, 2002.

[140] D. Brodkorb, M. Gottschall, R. Marmulla, F. Lüddeke, and J. Harder. Linalool dehydratase-isomerase, a bifunctional enzyme in the anaerobic degradation of monoterpenes. *J. Biol. Chem.*, 285:30436–30442, 2010.

[141] S.J. Brouns, T.R. Barends, P. Worm, J. Akerboom, A.P. Turnbull, L. Salmon, and J. van der Oost. Structural insight into substrate binding and catalysis of a novel 2-keto-3-deoxy-D-arabinonate dehydratase illustrates common mechanistic features of the FAH superfamily. *J. Mol. Biol.*, 379:357–371, 2008.

[142] S.J. Brouns, J. Walther, A.P. Snijders, H.J. van de Werken, H.L. Willemen, P. Worm, M.G. de Vos, A. Andersson, M. Lundgren, H.F. Mazon, R.H. van den Heuvel, P. Nilsson, L. Salmon, W.M. de Vos, P.C. Wright, R. Bernander, and J. van der Oost. Identification of the missing links in prokaryotic pentose oxidation pathways: evidence for enzyme recruitment. *J. Biol. Chem.*, 281:27378–27388, 2006.

[143] G.M. Brown. Pantothenylcysteine, a precursor of pantotheine in *Lactobacillus helveticus*. *J. Biol. Chem.*, 226:651–661, 1957.

[144] G.M. Brown. Requirement of cytidine triphosphate for the biosynthesis of phosphopantetheine. *J. Am. Chem. Soc.*, 80:3161–3161, 1958.

[145] G.M. Brown. The metabolism of pantothenic acid. *J. Biol. Chem.*, 234:370–378, 1959.

[146] T.B. Bruck and R.G. Kerr. Purification and kinetic properties of elisabethatriene synthase from the coral *Pseudopterogorgia elisabethae*. *Comp. Biochem. Physiol. B Biochem. Mol. Biol.*, 143:269–278, 2006.

[147] K. Bruckner, D. Bozic, D. Manzano, D. Papaefthimiou, I. Pateraki, U. Scheler, A. Ferrer, R.C. de Vos, A.K. Kanellis, and A. Tissier. Characterization of two genes for the biosynthesis of abietane-type diterpenes in rosemary (*Rosmarinus officinalis*) glandular trichomes. *Phytochemistry*, 101:52–64, 2014.

[148] N.A. Bruender and V. Bandarian. The radical *S*-adenosyl-L-methionine enzyme MftC catalyzes an oxidative decarboxylation of the C-terminus of the MftA peptide. *Biochemistry*, 55:2813–2816, 2016.

[149] F.H. Bruns and L. Fiedler. Enzymatic cleavage and synthesis of L-*threo*-β-phenylserine and L-*erythro*-β-phenylserine. *Nature*, 181:1533–1534, 1958.

[150] K.R. Brushaber, G.A. O'Toole, and J.C. Escalante-Semerena. CobD, a novel enzyme with L-threonine-*O*-3-phosphate decarboxylase activity, is responsible for the synthesis of (*R*)-1-amino-2-propanol *O*-2-phosphate, a proposed new intermediate in cobalamin biosynthesis in *Salmonella typhimurium* LT2. *J. Biol. Chem.*, 273:2684–2691, 1998.

[151] C.L. Buchanan, H. Connaris, M.J. Danson, C.D. Reeve, and D.W. Hough. An extremely thermostable aldolase from *Sulfolobus solfataricus* with specificity for non-phosphorylated substrates. *Biochem. J.*, 343:563–570, 1999.

[152] W. Buckel. The reversible dehydration of (*R*)-2-hydroxyglutarate to (*E*)-glutaconate. *Eur. J. Biochem.*, 106:439–447, 1980.

[153] J.S. Buckner, P.E. Kolattudy, and A.J. Poulose. Purification and properties of malonyl-coenzyme A decarboxylase, a regulatory enzyme from the uropygial gland of goose. *Arch. Biochem. Biophys.*, 177:539–551, 1976.

[154] H. Bühler, F. Effenberger, S. Förster, J. Roos, and H. Wajant. Substrate specificity of mutants of the hydroxynitrile lyase from *Manihot esculenta*. *ChemBioChem*, 4:211–216, 2003.

[155] J.M. Buis, J. Cheek, E. Kalliri, and J.B. Broderick. Characterization of an active spore photoproduct lyase, a DNA repair enzyme in the radical *S*-adenosylmethionine superfamily. *J. Biol. Chem.*, 281:25994–26003, 2006.

[156] K.G. Buki, D.Q. Vinh, and I. Horvath. Partial purification and some properties of tryptophan decarboxylase from a *Bacillus* strain. *Acta Microbiol Hung*, 32:65–73, 1985.

[157] D.H. Burke, M. Alberti, and J.E. Hearst. bchFNBH bacteriochlorophyll synthesis genes of *Rhodobacter capsulatus* and identification of the third subunit of light-independent protochlorophyllide reductase in bacteria and plants. *J. Bacteriol.*, 175:2414–2422, 1993.

[158] I. Burkhardt, T. Siemon, M. Henrot, L. Studt, S. Rosler, B. Tudzynski, M. Christmann, and J.S. Dickschat. Mechanistic characterisation of two sesquiterpene cyclases from the plant pathogenic fungus *Fusarium fujikuroi*. *Angew. Chem. Int. Ed. Engl.*, 55:8748–8751, 2016.

[159] E.A. Burks, W.H. Johnson, Whitman Jr., and C.P. Stereochemical and isotopic labeling studies of 2-oxo-hept-4-ene-1,7-dioate hydratase: evidence for an enzyme-catalyzed ketonization step in the hydration reaction. *J. Am. Chem. Soc.*, 120:7665–7675, 1998.

[160] K.E. Burns, Y. Xiang, C.L. Kinsland, F.W. McLafferty, and T.P. Begley. Reconstitution and biochemical characterization of a new pyridoxal-5$'$-phosphate biosynthetic pathway. *J. Am. Chem. Soc.*, 127:3682–3683, 2005.

[161] R.O. Burns and R.D. DeMoss. Properties of tryptophanase from *Escherichia coli*. *Biochim. Biophys. Acta*, 65:233–244, 1962.

[162] M. Burow, A. Bergner, J. Gershenzon, and U. Wittstock. Glucosinolate hydrolysis in *Lepidium sativum* - identification of the thiocyanate-forming protein. *Plant Mol. Biol.*, 63:49–61, 2007.

[163] M. Burow, A. Losansky, R. Muller, A. Plock, D.J. Kliebenstein, and U. Wittstock. The genetic basis of constitutive and herbivore-induced ESP-independent nitrile formation in *Arabidopsis*. *Plant Physiol.*, 149:561–574, 2009.

[164] M.J. Butler, G. Lazarovits, V.J. Higgins, and M.-A. Lachance. Partial-purification and characterization of a dehydratase associated with the pentaketide melanogenesis pathway of *Phaeococcomyces* sp and other fungi. *Exp. Mycol.*, 12:367–376, 1988.

[165] H.S. Byun and Y.S. Kim. Subunit organization of bacterial malonate decarboxylases: the smallest δ subunit as an acyl-carrier protein. *J. Biochem. Mol. Biol.*, 30:132–137, 1997.

[166] A. Cabezas, R.M. Pinto, F. Fraiz, J. Canales, S. Gonzalez-Santiago, and J.C. Cameselle. Purification, characterization, and substrate and inhibitor structure-activity studies of rat liver FAD-AMP lyase (cyclizing): preference for FAD and specificity for splitting ribonucleoside diphosphate-X into ribonucleotide and a five-atom cyclic phosphodiester of X, either a monocyclic compound or a *cis*-bicyclic phosphodiester-pyranose fusion. *Biochemistry*, 40:13710–13722, 2001.

[167] F.L. Cabirol, P.L. Tan, B. Tay, S. Cheng, U. Hanefeld, and R.A. Sheldon. *Linum usitatissimum* hydroxynitrile lyase cross-linked enzyme aggregates: a recyclable enantioselective catalyst. *Adv. Synth. Catal.*, 350:2329–2338, 2008.

[168] Y. Cai, J.W. Jia, J. Crock, Z.X. Lin, X.Y. Chen, and R. Croteau. A cDNA clone for β-caryophyllene synthase from *Artemisia annua*. *Phytochemistry*, 61:523–529, 2002.

[169] J.C. Calabrese, D.B. Jordan, A. Boodhoo, S. Sariaslani, and T. Vannelli. Crystal structure of phenylalanine ammonia lyase: multiple helix dipoles implicated in catalysis. *Biochemistry*, 43:11403–11416, 2004.

[170] M.J. Calvert, P.R. Ashton, and R.K. Allemann. Germacrene A is a product of the aristolochene synthase-mediated conversion of farnesylpyrophosphate to aristolochene. *J. Am. Chem. Soc.*, 124:11636–11641, 2002.

[171] J. Calvo. M., Stevens, C. M., Kalyanpur, M. G., and Umbarger, H. E. The absolute configuration of α-hydroxy-β-carboxyisocaproic acid (3-isopropylmalic acid), an intermediate in leucine biosynthesis. *Biochemistry*, 3:2024–2027, 1964.

[172] D.W. Cameron, W.H. Sawyer, and V.M. Trikojus. Colouring matters of the Aphidoidea. XLII. Purification and properties of the cyclising enzyme [Protoaphin dehydratase (cyclising)] concerned with pigment transformation in the wooly aphid *Eriosoma lanigerum* Hausmann (Hemiptera: Insecta). *Aust. J. Biol. Sci.*, 30:173–181, 1977.

[173] D.E. Cane. Cell-free studies of monoterpene and sesquiterpene biosynthesis. *Biochem. Soc. Trans.*, 11:510–515, 1983.

[174] D.E. Cane, C. Abell, P.H. Harrison, B.R. Hubbard, C.T. Kane, R. Lattman, J.S. Oliver, and S.W. Weiner. Terpenoid biosynthesis and the stereochemistry of enzyme-catalysed allylic addition-elimination reactions. *Philos. Trans. R. Soc. Lond. B Biol. Sci.*, 332:123–129, 1991.

[175] D.E. Cane, X. He, S. Kobayashi, S. Omura, and H. Ikeda. Geosmin biosynthesis in *Streptomyces avermitilis*. Molecular cloning, expression, and mechanistic study of the germacradienol/geosmin synthase. *J. Antibiot. (Tokyo)*, 59:471–479, 2006.

[176] D.E. Cane, P.C. Prabhakaran, J.S. Oliver, and D.B. McIlwaine. Aristolochene biosynthesis. Stereochemistry of the deprotonation steps in the enzymatic cyclization of farnesyl pyrophosphate. *J. Am. Chem. Soc.*, 112:3209–3210, 1990.

[177] D.E. Cane, P.C. Prabhakaran, E.J. Salaski, P.M.H. Harrison, H. Noguchi, and B.J. Rawlings. Aristolochene biosynthesis and enzymatic cyclization of farnesyl pyrophosphate. *J. Am. Chem. Soc.*, 111:8914–8916, 1989.

[178] D.E. Cane, J.K. Sohng, C.R. Lamberson, S.M. Rudnicki, Z. Wu, M.D. Lloyd, J.S. Oliver, and B.R. Hubbard. Pentalenene synthase. Purification, molecular cloning, sequencing, and high-level expression in *Escherichia coli* of a terpenoid cyclase from *Streptomyces* UC5319. *Biochemistry*, 33:5846–5857, 1994.

[179] D.E. Cane, M. Tandon, , and P.C. Epicubenol synthase and the enzymatic cyclization of farnesyl diphosphate. *J. Am. Chem. Soc.*, 115:8103–8106, 1993.

[180] D.E. Cane and M. Tandon. Biosynthesis of (+)-epicubenol. *Tetrahedron Lett.*, 35:5355–5358, 1994.

[181] D.E. Cane and M. Tandon. Epicubenol synthase and the stereochemistry of the enzymatic cyclization of farnesyl and nerolidyl diphosphate. *J. Am. Chem. Soc.*, 117:5602–5603, 1995.

[182] D.E. Cane and A.M. Tillman. Pentalenene biosynthesis and the enzymic cyclization of farnesyl pyrophosphate. *J. Am. Chem. Soc.*, 105:122–124, 1983.

[183] D.E. Cane and R.M. Watt. Expression and mechanistic analysis of a germacradienol synthase from *Streptomyces coelicolor* implicated in geosmin biosynthesis. *Proc. Natl. Acad. Sci. USA*, 100:1547–1551, 2003.

[184] A. Caniard, P. Zerbe, S. Legrand, A. Cohade, N. Valot, J.L. Magnard, J. Bohlmann, and L. Legendre. Discovery and functional characterization of two diterpene synthases for sclareol biosynthesis in *Salvia sclarea* (L.) and their relevance for perfume manufacture. *BMC Plant Biol.*, 12:119–119, 2012.

[185] J.J.B. Cannata. Phosphoenolpyruvate carboxykinase from bakers' yeast. Isolation of the enzyme and study of its physical properties. *J. Biol. Chem.*, 245:792–798, 1970.

[186] J.J.B. Cannata and A.O.M. Stoppani. Phosphopyruvate carboxylase from baker's yeast. I. Isolation, purification, and characterization. *J. Biol. Chem.*, 238:1196–1207, 1963.

[187] J.J.B. Cannata and A.O.M. Stoppani. Phosphopyruvate carboxylase from baker's yeast. II. Properties of enzyme. *J. Biol. Chem.*, 238:1208–1212, 1963.

[188] V.J. Cannistraro and D. Kennell. Purification and characterization of ribonuclease M and mRNA degradation in *Escherichia coli*. *Int. J. Biochem.*, 181:363–370, 1989.

[189] G.L. Cantoni and D.G. Anderson. Enzymatic cleavage of dimethylpropiothetin by *Polysiphonia lanosa*. *J. Biol. Chem.*, 222:171–177, 1956.

[190] J. Carere, P. Baker, and S.Y.K. Seah. Investigating the molecular determinants for substrate channeling in BphI-BphJ, an aldolase-dehydrogenase complex from the polychlorinated biphenyls degradation pathway. *Biochemistry*, 50:8407–8416, 2011.

[191] N. Carnall, H. Webb, and M. Carrington. Mutagenesis study of the glycosylphosphatidylinositol phospholipase C of *Trypanosoma brucei*. *Mol. Biochem. Parasitol.*, 90:423–432, 1997.

[192] E.P. Carpenter, A.R. Hawkins, J.W. Frost, and K.A. Brown. Structure of dehydroquinate synthase reveals an active site capable of multistep catalysis. *Nature*, 394:299–302, 1998.

[193] C.E. Carter and L.H. Cohen. The preparation and properties of adenylosuccinase and adenylosuccinic acid. *J. Biol. Chem.*, 222:17–30, 1956.

[194] M.S. Carter, X. Zhang, H. Huang, J.T. Bouvier, B.S. Francisco, M.W. Vetting, N. Al-Obaidi, J.B. Bonanno, A. Ghosh, R.G. Zallot, H.M. Andersen, S.C. Almo, and J.A. Gerlt. Functional assignment of multiple catabolic pathways for D-apiose. *Nat. Chem. Biol.*, 14:696–705, 2018.

[195] G. Caspritz and F. Radler. Malolactic enzyme of *Lactobacillus plantarum*. Purification, properties, and distribution among bacteria. *J. Biol. Chem.*, 258:4907–4910, 1983.

[196] M. Casteels, M. Sniekers, P. Fraccascia, G.P. Mannaerts, and P.P. Van Veldhoven. The role of 2-hydroxyacyl-CoA lyase, a thiamin pyrophosphate-dependent enzyme, in the peroxisomal metabolism of 3-methyl-branched fatty acids and 2-hydroxy straight-chain fatty acids. *Biochem Soc Trans.*, 35:876–880, 2007.

[197] P.A. Castric and E.E. Conn. Formation of β-cyanoalanine by *O*-acetylserine sulfhydrylase. *J. Bacteriol.*, 108:132–136, 1971.

[198] P.A. Castric, K.J.F. Farnden, and E.E. Conn. Cyanide metabolism in higher plants. V. The formation of asparagine from β-cyanoalanine. *Arch. Biochem. Biophys.*, 152:62–69, 1972.

[199] C.B., White Anfinsen, , and Jr. The ribonucleases: occurrence, structure, and properties. In P.D. Boyer, H. Lardy, and K. Myrbäck, editors, *The Enzymes*, volume 5, pages 95–122. Academic Press, New York, 2nd edition, 1961.

[200] S.Y. Cech and L.J. Ignarro. Cytidine 3′,5′-monophosphate (cyclic CMP) formation by homogenates of mouse liver. *Biochem. Biophys. Res. Commun.*, 80:119–125, 1978.

[201] L. Cendron, R. Berni, C. Folli, I. Ramazzina, R. Percudani, and G. Zanotti. The structure of 2-oxo-4-hydroxy-4-carboxy-5-ureidoimidazoline decarboxylase provides insights into the mechanism of uric acid degradation. *J. Biol. Chem.*, 282:18182–18189, 2007.

[202] M.S. Center and F.J. Behal. Studies on the ribonuclease activity of *Proteus mirabilis*. *Biochim. Biophys. Acta*, 151:698–699, 1968.

[203] P. Cerutti and G. Guroff. Enzymatic formation of phenylpyruvic acid in *Pseudomonas* sp. (ATCC 11299A) and its regulation. *J. Biol. Chem.*, 240:3034–3048, 1965.

[204] M.R. Challand, F.T. Martins, and P.L. Roach. Catalytic activity of the anaerobic tyrosine lyase required for thiamine biosynthesis in *Escherichia coli*. *J. Biol. Chem.*, 285:5240–5248, 2010.

[205] Y.L. Chan, Y. Endo, and I.G. Wool. The sequence of the nucleotides at the α-sarcin cleavage site in rat 28 S ribosomal ribonucleic acid. *J. Biol. Chem.*, 258:12768–12770, 1983.

[206] A. Chandor, O. Berteau, T. Douki, D. Gasparutto, Y. Sanakis, S. Ollagnier de Choudens, M. Atta, and M. Fontecave. Dinucleotide spore photoproduct, a minimal substrate of the DNA repair spore photoproduct lyase enzyme from *Bacillus subtilis*. *J. Biol. Chem.*, 281:26922–26931, 2006.

[207] W.C. Chang, D. Sanyal, J.L. Huang, K. Ittiamornkul, Q. Zhu, and X. Liu. *In vitro* stepwise reconstitution of amino acid derived vinyl isocyanide biosynthesis: detection of an elusive intermediate. *Org. Lett.*, 19:1208–1211, 2017.

[208] Y.J. Chang, J. Jin, H.Y. Nam, and S.U. Kim. Point mutation of (+)-germacrene A synthase from *Ixeris dentata*. *Biotechnol. Lett.*, 27:285–288, 2005.

[209] Y.J. Chang, S.H. Song, S.H. Park, and S.U. Kim. Amorpha-4,11-diene synthase of *Artemisia annua*: cDNA isolation and bacterial expression of a terpene synthase involved in artemisinin biosynthesis. *Arch. Biochem. Biophys.*, 383:178–184, 2000.

[210] H.-C. Change and M.D. Lane. The enzymatic carboxylation of phospho*enol*pyruvate. II. Purification and properties of liver mitochondrial phospho*enol*pyruvate carboxykinase. *J. Biol. Chem.*, 241:2413–2420, 1966.

[211] F.C. Charalampous and G.C. Mueller. Synthesis of erythrulose phosphate by a soluble enzyme from rat tissue. *J. Biol. Chem.*, 201:161–173, 1953.

[212] A. Chatterjee, A.B. Hazra, S. Abdelwahed, D.G. Hilmey, and T.P. Begley. A ”radical dance” in thiamin biosynthesis: mechanistic analysis of the bacterial hydroxymethylpyrimidine phosphate synthase. *Angew. Chem. Int. Ed. Engl.*, 49:8653–8656, 2010.

[213] A. Chatterjee, Y. Li, Y. Zhang, T.L. Grove, M. Lee, C. Krebs, S.J. Booker, T.P. Begley, and S.E. Ealick. Reconstitution of ThiC in thiamine pyrimidine biosynthesis expands the radical SAM superfamily. *Nat. Chem. Biol.*, 4:758–765, 2008.

[214] B.N. Chaudhuri, S.C. Lange, R.S. Myers, V.J. Davisson, and J.L. Smith. Toward understanding the mechanism of the complex cyclization reaction catalyzed by imidazole glycerolphosphate synthase: crystal structures of a ternary complex and the free enzyme. *Biochemistry*, 42:7003–7012, 2003.

[215] F. Chen, D.K. Ro, J. Petri, J. Gershenzon, J. Bohlmann, E. Pichersky, and D. Tholl. Characterization of a root-specific *Arabidopsis* terpene synthase responsible for the formation of the volatile monoterpene 1,8-cineole. *Plant Physiol.*, 135:1956–1966, 2004.

[216] H. Chen, M.G. Thomas, B.K. Hubbard, H.C. Losey, C.T. Walsh, and M.D. Burkart. Deoxysugars in glycopeptide antibiotics: enzymatic synthesis of TDP-L-epivancosamine in chloroeremomycin biosynthesis. *Proc. Natl. Acad. Sci. USA*, 97:11942–11947, 2000.

[217] J.H. Chen and R.F. Jones. Multiple forms of phospho*enol*pyruvate carboxylase from *Chlamydomonas reeinhardtii*. *Biochim. Biophys. Acta*, 214:318–325, 1970.

[218] X. Chen, J.M. Hagel, L. Chang, J.E. Tucker, S.A. Shiigi, Y. Yelpaala, H.Y. Chen, R. Estrada, J. Colbeck, M. Enquist-Newman, A.B. Ibanez, G. Cottarel, G.M. Vidanes, and P.J. Facchini. A pathogenesis-related 10 protein catalyzes the final step in thebaine biosynthesis. *Nat. Chem. Biol.*, 14:738–743, 2018.

[219] X. Chen, T.G. Kollner, Q. Jia, A. Norris, B. Santhanam, P. Rabe, J.S. Dickschat, G. Shaulsky, J. Gershenzon, and F. Chen. Terpene synthase genes in eukaryotes beyond plants and fungi: occurrence in social amoebae. *Proc. Natl. Acad. Sci. USA*, 113:12132–12137, 2016.

[220] X.-Y. Chen, Y. Chen, P. Heinstein, , and V.J. Cloning, expression and characterization of (+)-δ-cadinene synthase: a catalyst for cotton phytoalexin biosynthesis. *Arch. Biochem. Biophys.*, 324:255–266, 1995.

[221] C.G. Cheong, C.B. Bauer, K.R. Brushaber, J.C. Escalante-Semerena, and I. Rayment. Three-dimensional structure of the L-threonine-*O*-3-phosphate decarboxylase (CobD) enzyme from *Salmonella enterica*. *Biochemistry*, 41:4798–4808, 2002.

[222] C.J. Chetsanga and C. Grigorian. In situ enzymatic reclosure of opened imidazole rings of purines in DNA damaged by γ-irradiation. *Proc. Natl. Acad. Sci. USA*, 82:633–637, 1985.

[223] J. Cheung, F.C. Beasley, S. Liu, G.A. Lajoie, and D.E. Heinrichs. Molecular characterization of staphyloferrin B biosynthesis in *Staphylococcus aureus*. *Mol. Microbiol.*, 74:594–608, 2009.

[224] R. Chiba, A. Minami, K. Gomi, and H. Oikawa. Identification of ophiobolin F synthase by a genome mining approach: a sesterterpene synthase from *Aspergillus clavatus*. *Org. Lett.*, 15:594–597, 2013.

[225] T.-H. Chiu and D.S. Feingold. L-Rhamnulose 1-phosphate aldolase from *Escherichia coli*. Crystallization and properties. *Biochemistry*, 8:98–108, 1969.

[226] E.M. Cho, A. Okada, H. Kenmoku, K. Otomo, T. Toyomasu, W. Mitsuhashi, T. Sassa, A. Yajima, G. Yabuta, K. Mori, H. Oikawa, H. Toshima, N. Shibuya, H. Nojiri, T. Omori, M. Nishiyama, and H. Yamane. Molecular cloning and characterization of a cDNA encoding *ent*-cassa-12,15-diene synthase, a putative diterpenoid phytoalexin biosynthetic enzyme, from suspension-cultured rice cells treated with a chitin elicitor. *Plant J.*, 37:1–8, 2004.

[227] S. Chohnan, K. Akagi, and Y. Takamura. Functions of malonate decarboxylase subunits from *Pseudomonas putida*. *Biosci. Biotechnol. Biochem.*, 67:214–217, 2003.

[228] S. Chohnan, T. Fujio, T. Takaki, M. Yonekura, H. Nishihara, and Y. Takamura. Malonate decarboxylase of *Pseudomonas putida* is composed of five subunits. *FEMS Microbiol. Lett.*, 169:37–43, 1998.

[229] W.S. Choi, X. Wu, Y.H. Choeng, T. Mahmud, B.C. Jeong, S.H. Lee, Y.K. Chang, C.J. Kim, and S.K. Hong. Genetic organization of the putative salbostatin biosynthetic gene cluster including the 2-*epi*-5-*epi*-valiolone synthase gene in *Streptomyces albus* ATCC 21838. *Appl. Microbiol. Biotechnol.*, 80:637–645, 2008.

[230] W.K. Chou, I. Fanizza, T. Uchiyama, M. Komatsu, H. Ikeda, and D.E. Cane. Genome mining in *Streptomyces avermitilis*: cloning and characterization of SAV_76, the synthase for a new sesquiterpene, avermitilol. *J. Am. Chem. Soc.*, 132:8850–8851, 2010.

[231] J.G. Christenson, W. Dairman, and S. Udenfriend. On the identity of DOPA decarboxylase and 5-hydroxytryptophan decarboxylase (immunological titration-aromatic L-amino acid decarboxylase-serotonin-dopamine-norepinephrine). *Proc. Natl. Acad. Sci. USA*, 69:343–347, 1972.

[232] J.K. Christenson, M.R. Jensen, B.R. Goblirsch, F. Mohamed, W. Zhang, C.M. Wilmot, and L.P. Wackett. Active multienzyme assemblies for long-chain olefinic hydrocarbon biosynthesis. *J. Bacteriol.*, 199, 2017.

[233] J.K. Christenson, J.E. Richman, M.R. Jensen, J.Y. Neufeld, C.M. Wilmot, and L.P. Wackett. β-Lactone synthetase found in the olefin biosynthesis pathway. *Biochemistry*, 56:348–351, 2017.

[234] P. Christmas, B.M. Weber, M. McKee, D. Brown, and R.J. Soberman. Membrane localization and topology of leukotriene C_4 synthase. *J. Biol. Chem.*, 277:28902–28908, 2002.

[235] L. Chuang, C.H. Wen, Y.R. Lee, Y.L. Lin, L.R. Hsu, S.Y. Wang, and F.H. Chu. Identification, functional characterization, and seasonal expression patterns of five sesquiterpene synthases in *Liquidambar formosana*. *J Nat Prod*, 81:1162–1172, 2018.

[236] N. Cicmil and L. Shi. Crystallization and preliminary X-ray characterization of *queD* from *Bacillus subtilis*, an enzyme involved in queuosine biosynthesis. *Acta Crystallogr. Sect. F Struct. Biol. Cryst. Commun.*, 64:119–122, 2008.

[237] L. Citores, R. Iglesias, S. Ragucci, A. Di Maro, and J.M. Ferreras. Antifungal activity of α-sarcin against *Penicillium digitatum*: proposal of a new role for fungal ribotoxins. *ACS Chem. Biol.*, 13:1978–1982, 2018.

[238] B.A. Citron, M.D. Davis, S. Milstien, J. Gutierrez, D.B. Mendel, G.R. Crabtree, and S. Kaufman. Identity of 4a-carbinolamine dehydratase, a component of the phenylalanine hydroxylation system, and DCoH, a transregulator of homeodomain proteins. *Proc. Natl. Acad. Sci. USA*, 89:11891–11894, 1992.

[239] M.F. Clarke-Pearson and S.F. Brady. Paerucumarin, a new metabolite produced by the pvc gene cluster from *Pseudomonas aeruginosa*. *J. Bacteriol.*, 190:6927–6930, 2008.

[240] F.C. Cochrane, L.B. Davin, and N.G. Lewis. The *Arabidopsis* phenylalanine ammonia lyase gene family: kinetic characterization of the four PAL isoforms. *Phytochemistry*, 65:1557–1564, 2004.

[241] M.S. Cohn and A.T. Phillips. Purification and characterization of a B6-independent threonine dehydratase from *Pseudomonas putida*. *Biochemistry*, 13:1208–1214, 1974.

[242] S.M. Colby, J. Crock, B. Dowdle-Rizzo, P.G. Lemaux, and R. Croteau. Germacrene C synthase from *Lycopersicon esculentum* cv. VFNT cherry tomato: cDNA isolation, characterization, and bacterial expression of the multiple product sesquiterpene cyclase. *Proc. Natl. Acad. Sci. USA*, 95:2216–2221, 1998.

[243] F.E. Cole, , and M. G. and Stevens, C. M. Absolute configuration of α-isopropylmalate and the mechanism of its conversion to β-isopropylmalate in the biosynthesis of leucine. *Biochemistry*, 12:3346–3350, 1973.

[244] N.V. Coleman and J.C. Spain. Epoxyalkane: coenzyme M transferase in the ethene and vinyl chloride biodegradation pathways of *Mycobacterium* strain JS60. *J. Bacteriol.*, 185:5536–5545, 2003.

[245] S.M. Collby, W.R. Alonso, E.J. Katahira, D.J. McGarvey, and R. Croteau. 4S-Limonene synthase from the oil glands of spearmint (*Mentha spicata*). cDNA isolation, characterization, and bacterial expression of the catalytically active monoterpene cyclase. *J. Biol. Chem.*, 268:23016–23024, 1993.

[246] D.G. Comb and S. Roseman. The sialic acids. I. The structure and enzymatic synthesis of *N*-acetylneuraminic acid. *J. Biol. Chem.*, 235:2529–2537, 1960.

[247] P.D. Cook and H.M. Holden. A structural study of GDP-4-keto-6-deoxy-D-mannose-3-dehydratase: caught in the act of geminal diamine formation. *Biochemistry*, 46:14215–14224, 2007.

[248] A.J. Cooper, S.A. Bruschi, M. Conway, and S.M. Hutson. Human mitochondrial and cytosolic branched-chain aminotransferases are cysteine *S*-conjugate β-lyases, but turnover leads to inactivation. *Biochem. Pharmacol.*, 65:181–192, 2003.

[249] A.J. Cooper, S.A. Bruschi, A. Iriarte, and M. Martinez-Carrion. Mitochondrial aspartate aminotransferase catalyses cysteine *S*-conjugate β-lyase reactions. *Biochem. J.*, 368:253–261, 2002.

[250] A.J. Cooper and J.T. Pinto. Cysteine *S*-conjugate β-lyases. *Amino Acids*, 30:1–15, 2006.

[251] A.J.L. Cooper and A. Meister. Enzymatic conversion of *O*-carbamyl-L-serine to pyruvate and ammonia. *Biochem. Biophys. Res. Commun.*, 55:780–787, 1973.

[252] R.A. Cooper and A. Anderson. The formation and catabolism of methylglyoxal during glycolysis in *Escherichia coli*. *FEBS Lett.*, 11:273–276, 1970.

[253] R.A. Cooper and H.L. Kornberg. The utilization of itaconate by *Pseudomonas* sp. *Biochem. J.*, 91:82–91, 1964.

[254] M.A. Costa, P.M. Civello, A.R. Chaves, and G.A. Martínez. Characterization of Mg-dechelatase activity obtained from *Fragaria x ananassa* fruit. *Plant Physiol. Biochem.*, 40:111–118, 2002.

[255] R.N. Costilow and L. Laycock. Ornithine cyclase (deaminating). Purification of a protein that converts ornithine to proline and definition of the optimal assay conditions. *J. Biol. Chem.*, 246:6655–6660, 1971.

[256] R.G.H. Cotton and F. Gibson. The biosynthesis of phenylalanine and tyrosine; enzymes converting chorismic acid into prephenic acid and their relationships to prephenate dehydratase and prephenate dehydrogenase. *Biochim. Biophys. Acta*, 100:76–88, 1965.

[257] J.L. Cowell, K. Maser, and R.D. DeMoss. Tryptophanase from *Aeromonas liquifaciens*. Purification, molecular weight and some chemical, catalytic and immunological properties. *Biochim. Biophys. Acta*, 315:449–463, 1973.

[258] S. Craciun and E.P. Balskus. Microbial conversion of choline to trimethylamine requires a glycyl radical enzyme. *Proc. Natl. Acad. Sci. USA*, 109:21307–21312, 2012.

[259] I.P. Crawford and C. Yanofsky. On the separation of the tryptophan synthetase of *Escherichia coli* into two protein components. *Proc. Natl. Acad. Sci. USA*, 44:1161–1170, 1958.

[260] T.E. Creighton and C. Yanofsky. Indole-3-glycerol phosphate synthetase of *Escherichia coli*, an enzyme of the tryptophan operon. *J. Biol. Chem.*, 241:4616–4624, 1966.

[261] T.E. Creighton and C. Yanofsky. Chorismate to tryptophan (*Escherichia coli*) - anthranilate synthetase, PR transferase, PRA isomerase, InGP synthetase, tryptophan synthetase. *Methods Enzymol.*, 17A:365–380, 1970.

[262] J. Crock, M. Wildung, and R. Croteau. Isolation and bacterial expression of a sesquiterpene synthase cDNA clone from peppermint (*Mentha* × *piperita*, L.) that produces the aphid alarm pheromone (*E*)-β-farnesene. *Proc. Natl. Acad. Sci. USA*, 94:12833–12838, 1997.

[263] C. Crocoll, J. Asbach, J. Novak, J. Gershenzon, and J. Degenhardt. Terpene synthases of oregano (*Origanum vulgare* L.) and their roles in the pathway and regulation of terpene biosynthesis. *Plant Mol. Biol.*, 73:587–603, 2010.

[264] J.D. Cronk, J.A. Endrizzi, and T. Alber. High-resolution structures of the bifunctional enzyme and transcriptional coactivator DCoH and its complex with a product analogue. *Protein Sci.*, 5:1963–1972, 1996.

[265] J.D. Cronk, J.A. Endrizzi, M.R. Cronk, J.W. O'neill, and K.Y. Zhang. Crystal structure of *E. coli* β-carbonic anhydrase, an enzyme with an unusual pH-dependent activity. *Protein Sci.*, 10:911–922, 2001.

[266] R. Croteau, W.R. Alonso, A.E. Koepp, and M.A. Johnson. Biosynthesis of monoterpenes: partial purification, characterization, and mechanism of action of 1,8-cineole synthase. *Arch. Biochem. Biophys.*, 309:184–192, 1994.

[267] R. Croteau, J.H. Miyazaki, and C.J. Wheeler. Monoterpene biosynthesis: mechanistic evaluation of the geranyl pyrophosphate:(-)-*endo*-fenchol cyclase from fennel (*Foeniculum vulgare*). *Arch. Biochem. Biophys.*, 269:507–516, 1989.

[268] R. Croteau, S.L. Munck, C.C. Akoh, H.J. Fisk, and D.M. Satterwhite. Biosynthesis of the sesquiterpene patchoulol from farnesyl pyrophosphate in leaf extracts of *Pogostemon cablin* (patchouli): mechanistic considerations. *Arch. Biochem. Biophys.*, 256:56–68, 1987.

[269] R. Croteau and D.M. Satterwhite. Biosynthesis of monoterpenes. Stereochemical implications of acyclic and monocyclic olefin formation by (+)- and (-)-pinene cyclases from sage. *J. Biol. Chem.*, 264:15309–15315, 1989.

[270] R. Croteau, D.M. Satterwhite, D.E. Cane, and C.C. Chang. Biosynthesis of monoterpenes. Enantioselectivity in the enzymatic cyclization of (+)- and (-)-linalyl pyrophosphate to (+)- and (-)-pinene and (+)- and (-)-camphene. *J. Biol. Chem.*, 263:10063–10071, 1988.

[271] R. Croteau, D.M. Satterwhite, C.J. Wheeler, and N.M. Felton. Biosynthesis of monoterpenes. Stereochemistry of the enzymatic cyclization of geranyl pyrophosphate to (-)-*endo*-fenchol. *J. Biol. Chem.*, 263:15449–15453, 1988.

[272] R.B. Croteau, C.J. Wheeler, D.E. Cane, R. Ebert, and H.J. Ha. Isotopically sensitive branching in the formation of cyclic monoterpenes: proof that (-)-α-pinene and (-)-β-pinene are synthesized by the same monoterpene cyclase via deprotonation of a common intermediate. *Biochemistry*, 26:5383–5389, 1987.

[273] A.L. Crowell, D.C. Williams, E.M. Davis, M.R. Wildung, and R. Croteau. Molecular cloning and characterization of a new linalool synthase. *Arch. Biochem. Biophys.*, 405:112–121, 2002.

[274] C.M. Cuchillo, X. Pares, A. Guasch, T. Barman, F. Travers, and M.V. Nogues. The role of 2′,3′-cyclic phosphodiesters in the bovine pancreatic ribonuclease A catalysed cleavage of RNA: intermediates or products. *FEBS Lett.*, 333:207–210, 1993.

[275] G. Cui, L. Duan, B. Jin, J. Qian, Z. Xue, G. Shen, J.H. Snyder, J. Song, S. Chen, L. Huang, R.J. Peters, and X. Qi. Functional divergence of diterpene syntheses in the medicinal plant *Salvia miltiorrhiza*. *Plant Physiol.*, 169:1607–1618, 2015.

[276] S.M. Cuskey, V. Peccoraro, and R.H. Olsen. Initial catabolism of aromatic biogenic amines by *Pseudomonas aeruginosa* PAO: pathway description, mapping of mutations, and cloning of essential genes. *J. Bacteriol.*, 169:2398–2404, 1987.

[277] C.M. Czekster and J.S. Blanchard. One substrate, five products: reactions catalyzed by the dihydroneopterin aldolase from *Mycobacterium tuberculosis*. *J. Am. Chem. Soc.*, 134:19758–19771, 2012.

[278] T.P. Soares da Costa, A.C. Muscroft-Taylor, R.C. Dobson, S.R. Devenish, G.B. Jameson, and J.A. Gerrard. How essential is the 'essential' active-site lysine in dihydrodipicolinate synthase. *Biochimie*, 92:837–845, 2010.

[279] M. Veiga da Cunha, F. Hadi, T. Balligand, V. Stroobant, and E. Van Schaftingen. Molecular identification of hydroxylysine kinase and of ammoniophospholyases acting on 5-phosphohydroxy-L-lysine and phosphoethanolamine. *J. Biol. Chem.*, 287:7246–7255, 2012.

[280] S. Dagley and E.A. Dawes. Citridesmolase: its properties and mode of action. *Biochim. Biophys. Acta*, 17:177–184, 1955.

[281] A.S. Dahms. 3-Deoxy-D-pentulosonic acid aldolase and its role in a new pathway of D-xylose degradation. *Biochem. Biophys. Res. Commun.*, 60:1433–1439, 1974.

[282] A.S. Dahms and R.L. Anderson. 2-Keto-3-deoxy-L-arabonate aldolase and its role in a new pathway of L-arabinose degradation. *Biochem. Biophys. Res. Commun.*, 36:809–814, 1969.

[283] A.S. Dahms and R.L. Anderson. D-Fucose metabolism in a pseudomonad. 3. Conversion of D-fuconate to 2-keto-3-deoxy-D-fuconate by a dehydratase. *J. Biol. Chem.*, 247:2233–2237, 1972.

[284] A.S. Dahms and A. Donald. 2-Keto-3-deoxy-D-xylonate aldolase (3-deoxy-D-pentulosonic acid aldolase). *Methods Enzymol.*, 90:269–272, 1982.

[285] A.S. Dahms and A. Donald. D-*xylo*-Aldonate dehydratase. *Methods Enzymol.*, 90:302–305, 1982.

[286] H.A. Dailey, S. Gerdes, T.A. Dailey, J.S. Burch, and J.D. Phillips. Noncanonical coproporphyrin-dependent bacterial heme biosynthesis pathway that does not use protoporphyrin. *Proc. Natl. Acad. Sci. USA*, 112:2210–2215, 2015.

[287] R.H. Dainty. Purification and properties of threonine aldolase from *Clostridium pasteurianum*. *Biochem. J.*, 117:585–592, 1970.

[288] T. Dairi, Y. Hamano, T. Kuzuyama, N. Itoh, K. Furihata, and H. Seto. Eubacterial diterpene cyclase genes essential for production of the isoprenoid antibiotic terpentecin. *J. Bacteriol.*, 183:6085–6094, 2001.

[289] L. D'Ari and H.A. Barker. *p*-Cresol formation by cell-free extracts of *Clostridium difficile*. *Arch. Microbiol.*, 143:311–312, 1985.

[290] R. Davidovich-Rikanati, E. Lewinsohn, E. Bar, Y. Iijima, E. Pichersky, and Y. Sitrit. Overexpression of the lemon basil α-zingiberene synthase gene increases both mono- and sesquiterpene contents in tomato fruit. *Plant J.*, 56:228–238, 2008.

[291] I.W. Davidson, C.J. Lawson, and I.W. Sutherland. An alginate lysate from *Azotobacter vinelandii* phage. *J. Gen. Microbiol.*, 98:223–229, 1977.

[292] I.W. Davidson, I.W. Sutherland, and C.J. Lawson. Purification and properties of an alginate lyase from a marine bacterium. *Biochem. J.*, 159:707–713, 1976.

[293] R. Davies. Studies of the acetone-butanol fermentation. 4. Acetoacetic acid decarboxylase of *Cl. acetobutylicum* (BY). *Biochem. J.*, 37:230–238, 1943.

[294] E.M. Davis, J. Tsuji, G.D. Davis, M.L. Pierce, , and M. Purification of (+)-δ-cadinene synthase, a sesquiterpene cyclase from bacteria-inoculated cotton foliar tissue. *Phytochemistry*, 41:1047–1055, 1996.

[295] E.N. Davis, L.L. Wallen, J.C. Goodwin, W.K. Rohwedder, and R.A. Rhodes. Microbial hydration of *cis*-9-alkenoic acids. *Lipids*, 4:356–362, 1969.

[296] G.D. Davis, , and M. (+)-δ-Cadinene is a product of sesquiterpene cyclase activity in cotton. *Phytochemistry*, 39:553–567, 1995.

[297] D.C. Davison and W.H. Elliott. Enzymic reaction between arginine and fumarate in plant and animal tissue. *Nature*, 169:313–314, 1952.

[298] J.A. Dawson, D.H. Mallonee, I. Björkhem, and P.B. Hylemon. Expression and characterization of a C24 bile acid 7α-dehydratase from *Eubacterium* sp. strain VPI 12708 in *Escherichia coli*. *J. Lipid Res.*, 37:1258–1267, 1996.

[299] T. Zabala M. de, M. Grant, A.M. Bones, R. Bennett, Y.S. Lim, R. Kissen, and J.T. Rossiter. Characterisation of recombinant epithiospecifier protein and its over-expression in *Arabidopsis thaliana*. *Phytochemistry*, 66:859–867, 2005.

[300] V. de Crecy-Lagard, G. Phillips, L.L. Grochowski, B. El Yacoubi, F. Jenney, M.W. Adams, A.G. Murzin, and R.H. White. Comparative genomics guided discovery of two missing archaeal enzyme families involved in the biosynthesis of the pterin moiety of tetrahydromethanopterin and tetrahydrofolate. *ACS Chem. Biol.*, 7:1807–1816, 2012.

[301] G. de Gonzalo, R. Brieva, and V. Gotor. (*R*)-Oxynitrilase-catalyzed transformation of ω-hydroxyalkanals. *J. Mol. Catal. B*, 19-20:223–230, 2002.

[302] J.W. de Kraker, M.C. Franssen, A. de Groot, W.A. König, and H.J. Bouwmeester. (+)-Germacrene A biosynthesis . The committed step in the biosynthesis of bitter sesquiterpene lactones in chicory. *Plant Physiol.*, 117:1381–1392, 1998.

[303] M. de la Plaza, P. Fernandez de Palencia, C. Pelaez, and T. Requena. Biochemical and molecular characterization of α-ketoisovalerate decarboxylase, an enzyme involved in the formation of aldehydes from amino acids by *Lactococcus lactis*. *FEMS Microbiol. Lett.*, 238:367–374, 2004.

[304] A. de Waal, A.H. Meijer, and R. Verpoorte. Strictosidine synthase from *Catharanthus roseus*: purification and characterization of multiple forms. *Biochem. J.*, 306:571–580, 1995.

[305] L. Decamps, B. Philmus, A. Benjdia, R. White, T.P. Begley, and O. Berteau. Biosynthesis of F_0, precursor of the F_{420} cofactor, requires a unique two radical-SAM domain enzyme and tyrosine as substrate. *J. Am. Chem. Soc.*, 134:18173–18176, 2012.

[306] W. DeEknamkul, A. Ounaroon, T. Tanahashi, T. Kutchan, and M.H. Zenk. Enzymatic condensation of dopamine and secologanin by cell-free extracts of *Alangium lamarckii*. *Phytochemistry*, 45:477–484, 1997.

[307] J. Degenhardt and J. Gershenzon. Demonstration and characterization of (*E*)-nerolidol synthase from maize: a herbivore-inducible terpene synthase participating in (3*E*)-4,8-dimethyl-1,3,7-nonatriene biosynthesis. *Planta*, 210:815–822, 2000.

[308] F. Deguerry, L. Pastore, S. Wu, A. Clark, J. Chappell, and M. Schalk. The diverse sesquiterpene profile of patchouli, *Pogostemon cablin*, is correlated with a limited number of sesquiterpene synthases. *Arch. Biochem. Biophys.*, 454:123–136, 2006.

[309] N. Dellas, S.T. Thomas, G. Manning, and J.P. Noel. Discovery of a metabolic alternative to the classical mevalonate pathway. *Elife*, 2:e00672–e00672, 2013.

[310] W.J.J. Van den Tweel and J.A.M. De Bont. Metabolism of 3-butyn-1-ol by *Pseudomonas* BB_1. *J. Gen. Microbiol.*, 131:3155–3162, 1985.

[311] X. Deng, J. Lee, A.J. Michael, D.R. Tomchick, E.J. Goldsmith, and M.A. Phillips. Evolution of substrate specificity within a diverse family of β/α-barrel-fold basic amino acid decarboxylases: X-ray structure determination of enzymes with specificity for L-arginine and carboxynorspermidine. *J. Biol. Chem.*, 285:25708–25719, 2010.

[312] K. Denger and A.M. Cook. Racemase activity effected by two dehydrogenases in sulfolactate degradation by *Chromohalobacter salexigens*: purification of (*S*)-sulfolactate dehydrogenase. *Microbiology*, 156:967–974, 2010.

[313] K. Denger, T.H.M. Smits, and A.M. Cook. L-Cysteate sulpho-lyase, a widespread pyridoxal 5′-phosphate-coupled desulphonative enzyme purified from *Silicibacter pomeroyi* DSS-3(T). *Biochem. J.*, 394:657–664, 2006.

[314] K. Denger, M. Weiss, A.K. Felux, A. Schneider, C. Mayer, D. Spiteller, T. Huhn, A.M. Cook, and D. Schleheck. Sulphoglycolysis in *Escherichia coli* K-12 closes a gap in the biogeochemical sulphur cycle. *Nature*, 507:114–117, 2014.

[315] R.F. Denman, D.S. Hoare, and E. Work. Diaminopimelic acid decarboxylase in pyridoxin-deficient *Escherichia coli*. *Biochim. Biophys. Acta*, 16:442–443, 1955.

[316] B. Desguin, P. Goffin, E. Viaene, M. Kleerebezem, V. Martin-Diaconescu, M.J. Maroney, J.P. Declercq, P. Soumillion, and P. Hols. Lactate racemase is a nickel-dependent enzyme activated by a widespread maturation system. *Nat. Commun.*, 5:3615–3615, 2014.

[317] B. Desguin, P. Soumillion, P. Hols, and R.P. Hausinger. Nickel-pincer cofactor biosynthesis involves LarB-catalyzed pyridinium carboxylation and LarE-dependent sacrificial sulfur insertion. *Proc. Natl. Acad. Sci. USA*, 113:5598–5603, 2016.

[318] S.R. Devenish, J.W. Blunt, and J.A. Gerrard. NMR studies uncover alternate substrates for dihydrodipicolinate synthase and suggest that dihydrodipicolinate reductase is also a dehydratase. *J. Med. Chem.*, 53:4808–4812, 2010.

[319] S. Dickert, A.J. Pierik, and W. Buckel. Molecular characterization of phenyllactate dehydratase and its initiator from *Clostridium sporogenes*. *Mol. Microbiol.*, 44:49–60, 2002.

[320] S. Dickert, A.J. Pierik, D. Linder, and W. Buckel. The involvement of coenzyme A esters in the dehydration of (*R*)-phenyllactate to (*E*)-cinnamate by *Clostridium sporogenes*. *Eur. J. Biochem.*, 267:3874–3884, 2000.

[321] S.R. Dickman. Aconitase. In P.D. Boyer, H. Lardy, and K Myrbäck, editors, *The Enzymes*, volume 5, pages 495–510. Academic Press, New York, 2nd edition, 1961.

[322] P. Dimroth, W. Buckel, R. Loyal, and H. Eggerer. Isolation and function of the subunits of citramalate lyase and formation of hybrids with the subunits of citrate lyase. *Eur. J. Biochem.*, 80:469–477, 1977.

[323] P. Dimroth and H. Hilbi. Enzymic and genetic basis for bacterial growth on malonate. *Mol. Microbiol.*, 25:3–10, 1997.

[324] P. Dimroth, R. Loyal, and H. Eggerer. Characterization of the isolated transferase subunit of citrate lyase as a CoA-transferase. Evidence against a covalent enzyme-substrate intermediate. *Eur. J. Biochem.*, 80:479–488, 1977.

[325] S. Dittrich, S.L. Mitchell, A.M. Blagborough, Q. Wang, P. Wang, P.F. Sims, and J.E. Hyde. An atypical orthologue of 6-pyruvoyltetrahydropterin synthase can provide the missing link in the folate biosynthesis pathway of malaria parasites. *Mol. Microbiol.*, 67:609–618, 2008.

[326] D. Dodd, M.H. Spitzer, W. Van Treuren, B.D. Merrill, A.J. Hryckowian, S.K. Higginbottom, A. Le, T.M. Cowan, G.P. Nolan, M.A. Fischbach, and J.L. Sonnenburg. A gut bacterial pathway metabolizes aromatic amino acids into nine circulating metabolites. *Nature*, 551:648–652, 2017.

[327] D. Domik, N. Magnus, and B. Piechulla. Analysis of a new cluster of genes involved in the synthesis of the unique volatile organic compound sodorifen of *Serratia plymuthica* 4Rx13. *FEMS Microbiol. Lett.*, 363(14):fnw139–, 2016.

[328] A. Donald, D. Sibley, D.E. Lyons, and A.S. Dahms. D-Galactonate dehydrase. Purification and properties. *J. Biol. Chem.*, 254:2132–2137, 1979.

[329] A. Douangamath, M. Walker, S. Beismann-Driemeyer, M.C. Vega-Fernandez, R. Sterner, and M. Wilmanns. Structural evidence for ammonia tunneling across the $(\beta\,\alpha)_8$ barrel of the imidazole glycerol phosphate synthase bienzyme complex. *Structure*, 10:185–193, 2002.

[330] P. Dowd, R. Hershline, S.W. Ham, and S. Naganathan. Vitamin K and energy transduction: a base strength amplification mechanism. *Science*, 269:1684–1691, 1995.

[331] E.J. Drake and A.M. Gulick. Three-dimensional structures of *Pseudomonas aeruginosa* PvcA and PvcB, two proteins involved in the synthesis of 2-isocyano-6,7-dihydroxycoumarin. *J. Mol. Biol.*, 384:193–205, 2008.

[332] R.M. Drevland, Y. Jia, D.R. Palmer, and D.E. Graham. Methanogen homoaconitase catalyzes both hydrolyase reactions in coenzyme B biosynthesis. *J. Biol. Chem.*, 283:28888–28896, 2008.

[333] M.K. Dreyer and G.E. Schulz. The spatial structure of the class II L-fuculose-1-phosphate aldolase from *Escherichia coli*. *J. Mol. Biol.*, 231:549–553, 1993.

[334] M.K. Dreyer and G.E. Schulz. Catalytic mechanism of the metal-dependent fuculose aldolase from *Escherichia coli* as derived from the structure. *J. Mol. Biol.*, 259:458–466, 1996.

[335] Y.L. Du, H.Y. He, M.A. Higgins, and K.S. Ryan. A heme-dependent enzyme forms the nitrogen-nitrogen bond in piperazate. *Nat. Chem. Biol.*, 13:836–838, 2017.

[336] J. Dubois, C. Dugave, C. Foures, M. Kaminsky, J.C. Tabet, S. Bory, M. Gaudry, and A. Marquet. Vitamin K dependent carboxylation: determination of the stereochemical course using 4-fluoroglutamyl-containing substrate. *Biochemistry*, 30:10506–10512, 1991.

[337] N. Dudareva, L. Cseke, V.M. Blanc, and E. Pichersky. Evolution of floral scent in *Clarkia*: novel patterns of *S*-linalool synthase gene expression in the *C. breweri* flower. *Plant Cell*, 8:1137–1148, 1996.

[338] N. Dudareva, D. Martin, C.M. Kish, N. Kolosova, N. Gorenstein, J. Faldt, B. Miller, and J. Bohlmann. (*E*)-β-ocimene and myrcene synthase genes of floral scent biosynthesis in snapdragon: function and expression of three terpene synthase genes of a new terpene synthase subfamily. *Plant Cell*, 15:1227–1241, 2003.

[339] M.E. Dumont, J.F. Ernst, D.M. Hampsey, and F. Sherman. Identification and sequence of the gene encoding cytochrome *c* heme lyase in the yeast *Saccharomyces cerevisiae*. *EMBO J.*, 6:235–241, 1987.

[340] P.M. Dunnill and L. Fowden. The biosynthesis of β-pyrazol-1-ylalanine. *J. Exp. Bot.*, 14:237–248, 1963.

[341] D. Dupourque, W.A. Newton, and E.E. Snell. Purification and properties of D-serine dehydrase from *Escherichia coli*. *J. Biol. Chem.*, 241:1233–1238, 1966.

[342] R.D. Durbin and T.F. Uchytil. Purification and properties of alliin lyase from the fungus *Penicillium corymbiferum*. *Biochim. Biophys. Acta*, 235:518–520, 1971.

[343] L. Dwiarti, K. Yamane, H. Yamatani, P. Kahar, and M. Okabe. Purification and characterization of *cis*-aconitic acid decarboxylase from *Aspergillus terreus* TN484-M1. *J. Biosci. Bioeng.*, 94:29–33, 2002.

[344] J.C. Eads, M. Beeby, G. Scapin, T.W. Yu, and H.G. Floss. Crystal structure of 3-amino-5-hydroxybenzoic acid (AHBA) synthase. *Biochemistry*, 38:9840–9849, 1999.

[345] R.W. Eaton. Organization and evolution of naphthalene catabolic pathways: sequence of the DNA encoding 2-hydroxychromene-2-carboxylate isomerase and *trans-o*-hydroxybenzylidenepyruvate hydratase-aldolase from the NAH7 plasmid. *J. Bacteriol.*, 176:7757–7762, 1994.

[346] R.W. Eaton. *trans-o*-Hydroxybenzylidenepyruvate hydratase-aldolase as a biocatalyst. *Appl. Environ. Microbiol.*, 66:2668–2672, 2000.

[347] R.W. Eaton and D.W. Ribbons. Metabolism of dibutylphthalate and phthalate by *Micrococcus* sp. strain 12B. *J. Gen. Microbiol.*, 151:48–57, 1982.

[348] S. Echt, S. Bauer, S. Steinbacher, R. Huber, A. Bacher, and M. Fischer. Potential anti-infective targets in pathogenic yeasts: structure and properties of 3,4-dihydroxy-2-butanone 4-phosphate synthase of *Candida albicans*. *J. Mol. Biol.*, 341:1085–1096, 2004.

[349] R.D. Edstrom and H.J. Phaff. Eliminative cleavage of pectin and of oligogalacturonide methyl esters by pectin *trans*-eliminase. *J. Biol. Chem.*, 239:2409–2415, 1964.

[350] R.D. Edstrom and H.J. Phaff. Purification and certain properties of pectin *trans*-eliminase from *Aspergillus fonsecaeus*. *J. Biol. Chem.*, 239:2403–2408, 1964.

[351] T. Eguchi, Y. Dekishima, Y. Hamano, T. Dairi, H. Seto, and K. Kakinuma. A new approach for the investigation of isoprenoid biosynthesis featuring pathway switching, deuterium hyperlabeling, and ^{1}H NMR spectroscopy. The reaction mechanism of a novel streptomyces diterpene cyclase. *J. Org. Chem.*, 68:5433–5438, 2003.

[352] D. Eisenschmidt-Bonn, N. Schneegans, A. Backenkohler, U. Wittstock, and W. Brandt. Structural diversification during glucosinolate breakdown: mechanisms of thiocyanate, epithionitrile and simple nitrile formation. *Plant J.*, 99:329–343, 2019.

[353] A.P.M. Eker and A.M.J. Fichtinger-Schepman. Studies on a DNA photoreactivating enzyme from *Streptomyces griseus*. II. Purification of the enzyme. *Biochim. Biophys. Acta*, 378:54–63, 1975.

[354] K. Ekwall and B. Mannervik. The stereochemical configuration of the lactoyl group of *S*-lactoylglutathionine formed by the action of glyoxalase I from porcine erythrocytes and yeast. *Biochim. Biophys. Acta*, 297:297–299, 1973.

[355] A.D. Elbein and E.C. Heath. The biosynthesis of cell wall lipopolysaccharide in *Escherichia coli*. II. Guanosine diphosphate 4-keto-6-deoxy-D-mannose, an intermediate in the biosynthesis of guanosine diphosphate colitose. *J. Biol. Chem.*, 240:1926–1931, 1965.

[356] N. Ellfolk. Studies on aspartase. 1. Quantitative separation of aspartase from bacterial cells, and its partial purification. *Acta Chem. Scand.*, 7:824–830, 1953.

[357] T. Elssner, C. Engemann, K. Baumgart, and H.P. Kleber. Involvement of coenzyme A esters and two new enzymes, an enoyl-CoA hydratase and a CoA-transferase, in the hydration of crotonobetaine to L-carnitine by *Escherichia coli*. *Biochemistry*, 40:11140–11148, 2001.

[358] J.A. Endrizzi, J.D. Cronk, W. Wang, G.R. Crabtree, and T. Alber. Crystal structure of DCoH, a bifunctional, protein-binding transcriptional coactivator. *Science*, 268:556–559, 1995.

[359] K. Engeland and H. Kindl. Evidence for a peroxisomal fatty acid β-oxidation involving D-3-hydroxyacyl-CoAs. Characterization of two forms of hydro-lyase that convert D-(-)-3-hydroxyacyl-CoA into 2-*trans*-enoyl-CoA. *Eur. J. Biochem.*, 200:171–178, 1991.

[360] B. Engels, U. Heinig, T. Grothe, M. Stadler, and S. Jennewein. Cloning and characterization of an *Armillaria gallica* cDNA encoding protoilludene synthase, which catalyzes the first committed step in the synthesis of antimicrobial melleolides. *J. Biol. Chem.*, 286:6871–6878, 2011.

[361] C. Engemann, T. Elssner, and H.P. Kleber. Biotransformation of crotonobetaine to L-(–)-carnitine in *Proteus* sp. *Arch. Microbiol.*, 175:353–359, 2001.

[362] C. Engemann, T. Elssner, S. Pfeifer, C. Krumbholz, T. Maier, and H.P. Kleber. Identification and functional characterisation of genes and corresponding enzymes involved in carnitine metabolism of *Proteus* sp. *Arch. Microbiol.*, 183:176–189, 2005.

[363] H.M.R. Epps. Studies on bacterial amino-acid decarboxylases. 4. *l*(–)-Histidine decarboxylase from *Cl. welchii* type A. *Biochem. J.*, 39:42–46, 1945.

[364] T.J. Erb, L. Frerichs-Revermann, G. Fuchs, and B.E. Alber. The apparent malate synthase activity of *Rhodobacter sphaeroides* is due to two paralogous enzymes, (3*S*)-malyl-coenzyme A (CoA)/β-methylmalyl-CoA lyase and (3*S*)-malyl-CoA thioesterase. *J. Bacteriol.*, 192:1249–1258, 2010.

[365] N. Esaki, T. Nakamura, H. Tanaka, and K. Soda. Selenocysteine lyase, a novel enzyme that specifically acts on selenocysteine. Mammalian distribution and purification and properties of pig liver enzyme. *J. Biol. Chem.*, 257:4386–4391, 1982.

[366] C.E. Espineda, A.S. Linford, D. Devine, and J.A. Brusslan. The *AtCAO* gene, encoding chlorophyll *a* oxygenase, is required for chlorophyll *b* synthesis in *Arabidopsis thaliana*. *Proc. Natl. Acad. Sci. USA*, 96:10507–10511, 1999.

[367] W.J. Esselman and C.O. Clagett. Products of linoleic hydroperoxide-decomposing enzyme of alfalfa seed. *J. Lipid Res.*, 15:173–178, 1974.

[368] C.D. Fairchild and A.N. Glazer. Oligomeric structure, enzyme kinetics, and substrate specificity of the phycocyanin α subunit phycocyanobilin lyase. *J. Biol. Chem.*, 269:8686–8694, 1994.

[369] C.D. Fairchild, J. Zhao, J. Zhou, S.E. Colson, D.A. Bryant, and A.N. Glazer. Phycocyanin α-subunit phycocyanobilin lyase. *Proc. Natl. Acad. Sci. USA*, 89:7017–7021, 1992.

[370] V. Falara, T.A. Akhtar, T.T. Nguyen, E.A. Spyropoulou, P.M. Bleeker, I. Schauvinhold, Y. Matsuba, M.E. Bonini, A.L. Schilmiller, R.L. Last, R.C. Schuurink, and E. Pichersky. The tomato terpene synthase gene family. *Plant Physiol.*, 157:770–789, 2011.

[371] V. Falara, E. Pichersky, and A.K. Kanellis. A copal-8-ol diphosphate synthase from the angiosperm *Cistus creticus* subsp. *creticus* is a putative key enzyme for the formation of pharmacologically active, oxygen-containing labdane-type diterpenes. *Plant Physiol.*, 154:301–310, 2010.

[372] J. Faldt, G. Arimura, J. Gershenzon, J. Takabayashi, and J. Bohlmann. Functional identification of AtTPS03 as (*E*)-β-ocimene synthase: a monoterpene synthase catalyzing jasmonate- and wound-induced volatile formation in *Arabidopsis thaliana*. *Planta*, 216:745–751, 2003.

[373] J. Faldt, D. Martin, B. Miller, S. Rawat, and J. Bohlmann. Traumatic resin defense in Norway spruce (*Picea abies*): methyl jasmonate-induced terpene synthase gene expression, and cDNA cloning and functional characterization of (+)-3-carene synthase. *Plant Mol. Biol.*, 51:119–133, 2003.

[374] R.R. Fall, , and C.A. Purification and properties of kaurene synthetase from *Fusarium moniliforme*. *J. Biol. Chem.*, 246:6913–6928, 1971.

[375] A. Fammartino, F. Cardinale, C. Gobel, L. Mene-Saffrane, J. Fournier, I. Feussner, and M.T. Esquerre-Tugaye. Characterization of a divinyl ether biosynthetic pathway specifically associated with pathogenesis in tobacco. *Plant Physiol.*, 143:378–388, 2007.

[376] D.-F. Fan and D.S. Feingold. UDPgalacturonic acid decarboxylase from *Ampullariella digitata*. *Methods Enzymol.*, 28B:438–439, 1972.

[377] X. Fang, C.Y. Li, Y. Yang, M.Y. Cui, X.Y. Chen, and L. Yang. Identification of a novel (–)-5-epieremophilene synthase from *Salvia miltiorrhiza* via transcriptome mining. *Front. Plant Sci.*, 8:627–627, 2017.

[378] J.A. Faraldos, S. Wu, J. Chappell, and R.M. Coates. Doubly deuterium-labeled patchouli alcohol from cyclization of singly labeled [2-$^2H_1$]farnesyl diphosphate catalyzed by recombinant patchoulol synthase. *J. Am. Chem. Soc.*, 132:2998–3008, 2010.

[379] M. Fellner, B. Desguin, R.P. Hausinger, and J. Hu. Structural insights into the catalytic mechanism of a sacrificial sulfur insertase of the *N*-type ATP pyrophosphatase family, LarE. *Proc. Natl. Acad. Sci. USA*, 114:9074–9079, 2017.

[380] A.K. Felux, D. Spiteller, J. Klebensberger, and D. Schleheck. Entner-Doudoroff pathway for sulfoquinovose degradation in *Pseudomonas putida* SQ1. *Proc. Natl. Acad. Sci. USA*, 112:E4298–E4305, 2015.

[381] T. Ferenci, T. Strøm, and J.R. Quayle. Purification and properties of 3-hexulose phosphate synthase and phospho-3-hexuloisomerase from *Methylococcus capsulatus*. *Biochem. J.*, 144:477–486, 1974.

[382] J. Fethiere, B.H. Shilton, Y. Li, M. Allaire, M. Laliberte, B. Eggimann, and M. Cygler. Crystallization and preliminary analysis of chondroitinase AC from *Flavobacterium heparinum*. *Acta Crystallogr. D Biol. Crystallogr.*, 54:279–280, 1998.

[383] M.L. Fink, S.I. Chung, and J.E. Folk. γ-Glutamylamine cyclotransferase: specificity toward ε-(L-γ-glutamyl)-L-lysine and related compounds. *Proc. Natl. Acad. Sci. USA*, 77:4564–4568, 1980.

[384] S.M. Firestine, S. Misialek, D.L. Toffaletti, T.J. Klem, J.R. Perfect, and V.J. Davisson. Biochemical role of the *Cryptococcus neoformans* ADE2 protein in fungal de novo purine biosynthesis. *Arch. Biochem. Biophys.*, 351:123–134, 1998.

[385] S.M. Firestine, S.W. Poon, E.J. Mueller, J. Stubbe, and V.J. Davisson. Reactions catalyzed by 5-aminoimidazole ribonucleotide carboxylases from *Escherichia coli* and *Gallus gallus*: a case for divergent catalytic mechanisms. *Biochemistry*, 33:11927–11934, 1994.

[386] M. Fischer, W. Römisch, S. Schiffmann, M. Kelly, H. Oschkinat, S. Steinbacher, R. Huber, W. Eisenreich, G. Richter, and A. Bacher. Biosynthesis of riboflavin in archaea studies on the mechanism of 3,4-dihydroxy-2-butanone-4-phosphate synthase of *Methanococcus jannaschii*. *J. Biol. Chem.*, 277:41410–41416, 2002.

[387] R. Fischer and R. Jensen. Arogenate dehydratase. *Methods Enzymol.*, 142:495–502, 1987.

[388] D.C. Fish and H.J. Blumenthal. 2-Keto-3-deoxy-D-glucarate aldolase. *Methods Enzymol.*, 9:529–534, 1966.

[389] M. Flavin and A. Segal. Purification and properties of the cystathionine γ-cleavage enzyme of *Neurospora*. *J. Biol. Chem.*, 239:2220–2227, 1964.

[390] M. Flavin and C. Slaughter. Purification and properties of threonine synthetase of *Neurospora*. *J. Biol. Chem.*, 235:1103–1108, 1960.

[391] M. Flavin and C. Slaughter. Cystathionine cleavage enzymes of *Neurospora*. *J. Biol. Chem.*, 239:2212–2219, 1964.

[392] H.L. Fleshood and H.C. Pitot. The metabolism of *O*-phosphorylethanolamine in animal tissues. I. *O*-Phosphorylethanolamine phospho-lyase: partial purification and characterization. *J. Biol. Chem.*, 245:4414–4420, 1970.

[393] H.G. Floss, T.W. Yu, and K. Arakawa. The biosynthesis of 3-amino-5-hydroxybenzoic acid (AHBA), the precursor of mC_7N units in ansamycin and mitomycin antibiotics: a review. *J. Antibiot. (Tokyo)*, 64:35–44, 2011.

[394] J.C. Fong and H. Schulz. Purification and properties of pig heart crotonase and the presence of short chain and long chain enoyl coenzyme A hydratases in pig and guinea pig tissues. *J. Biol. Chem.*, 252:542–547, 1977.

[395] R.G. Forage and M.A. Foster. Glycerol fermentation in *Klebsiella pneumoniae*: functions of the coenzyme B_{12}-dependent glycerol and diol dehydratases. *J. Bacteriol.*, 149:413–419, 1982.

[396] S. Förster, J. Roos, F. Effenberger, H. Wajant, and A. Sprauer. The first recombinant hydroxynitrile lyase and its application in the synthesis of (*S*)-cyanohydrins. *Angew. Chem. Int. Ed.*, 35:437–439, 1996.

[397] V. Foulon, V.D. Antonenkov, K. Croes, E. Waelkens, G.P. Mannaerts, P.P. Van Veldhoven, and M. Casteels. Purification, molecular cloning, and expression of 2-hydroxyphytanoyl-CoA lyase, a peroxisomal thiamine pyrophosphate-dependent enzyme that catalyzes the carbon-carbon bond cleavage during α-oxidation of 3-methyl-branched fatty acids. *Proc. Natl. Acad. Sci. USA*, 96:10039–10044, 1999.

[398] V. Foulon, M. Sniekers, E. Huysmans, S. Asselberghs, V. Mahieu, G.P. Mannaerts, P.P. Van Veldhoven, and M. Casteels. Breakdown of 2-hydroxylated straight chain fatty acids via peroxisomal 2-hydroxyphytanoyl-CoA lyase: a revised pathway for the α-oxidation of straight chain fatty acids. *J. Biol. Chem.*, 280:9802–9812, 2005.

[399] D.T. Fox, K. Hotta, C.Y. Kim, and A.T. Koppisch. The missing link in petrobactin biosynthesis: *asbF* encodes a (-)-3-dehydroshikimate dehydratase. *Biochemistry*, 47:12251–12253, 2008.

[400] F.J. Fraiz, R.M. Pinto, M.J. Costas, M. Avalos, J. Canales, A. Cabezas, and J.C. Cameselle. Enzymic formation of riboflavin 4′,5′-cyclic phosphate from FAD: evidence for a specific low-K_m FMN cyclase in rat liver. *Biochem. J.*, 330:881–888, 1998.

[401] S. Frank, A.A. Brindley, E. Deery, P. Heathcote, A.D. Lawrence, H.K. Leech, R.W. Pickersgill, and M.J. Warren. Anaerobic synthesis of vitamin B_{12}: characterization of the early steps in the pathway. *Biochem Soc Trans.*, 33:811–814, 2005.

[402] W. Franke, A. Platzeck, and G. Eichhorn. [On the knowledge of fatty acid catabolism by mold fungi. III. On a decarboxylase for average β-ketomonocarbonic acids (β-ketolaurate decarboxylase)]. *Arch. Mikrobiol.*, 40:73–93, 1961.

[403] J.B. French and S.E. Ealick. Structural and mechanistic studies on *Klebsiella pneumoniae* 2-oxo-4-hydroxy-4-carboxy-5-ureidoimidazoline decarboxylase. *J. Biol. Chem.*, 285:35446–35454, 2010.

[404] M. Frey, P. Chomet, E. Glawischnig, C. Stettner, S. Grün, A. Winklmair, W. Eisenreich, A. Bacher, R.B. Meeley, S.P. Briggs, K. Simcox, and A. Gierl. Analysis of a chemical plant defense mechanism in grasses. *Science*, 277:696–699, 1997.

[405] M. Frey, C. Stettner, P.W. Paré, E.A. Schmelz, J.H. Tumlinson, and A. Gierl. An herbivore elicitor activates the gene for indole emission in maize. *Proc. Natl. Acad. Sci. USA*, 97:14801–14806, 2000.

[406] J. Fricke, F. Blei, and D. Hoffmeister. Enzymatic synthesis of psilocybin. *Angew. Chem. Int. Ed. Engl.*, 56:12352–12355, 2017.

[407] R.O. Friedel, J.D. Brown, and J. Durell. Monophosphatidyl inositol inositolphosphohydrolase in guinea-pig brain. *Biochim. Biophys. Acta*, 144:684–686, 1967.

[408] S. Friedmann, B.E. Alber, and G. Fuchs. Properties of R-citramalyl-coenzyme A lyase and its role in the autotrophic 3-hydroxypropionate cycle of *Chloroflexus aurantiacus*. *J. Bacteriol.*, 189:2906–2914, 2007.

[409] N.U. Frigaard, A.G. Chew, H. Li, J.A. Maresca, and D.A. Bryant. *Chlorobium tepidum*: insights into the structure, physiology, and metabolism of a green sulfur bacterium derived from the complete genome sequence. *Photosynth. Res.*, 78:93–117, 2003.

[410] W.E. Fry and R.L. Millar. Cyanide degradion by an enzyme from *Stemphylium loti*. *Arch. Biochem. Biophys.*, 151:468–474, 1972.

[411] K. Fujimori and D. Ohta. An *Arabidopsis* cDNA encoding a bifunctional glutamine amidotransferase/cyclase suppresses the histidine auxotrophy of a *Saccharomyces cerevisiae* his7 mutant. *FEBS Lett.*, 428:229–234, 1998.

[412] Y. Fujimoto, T. Kinoshita, I. Oya, K. Kakinuma, S.M. Ismail, Y. Sonoda, Y. Sato, and M. Morisaki. Non-stereoselective conversion of the four diastereoisomers at the C-24 and C-25 positions of 3α,7α,12α,24-tetrahydroxy-5β-cholestan-26-oic acid and cholic acid. *Chem. Pharm. Bull.*, 36:142–145, 1988.

[413] M. Fujisawa, H. Harada, H. Kenmoku, S. Mizutani, and N. Misawa. Cloning and characterization of a novel gene that encodes (*S*)-β-bisabolene synthase from ginger, *Zingiber officinale*. *Planta*, 232:121–130, 2010.

[414] T. Fukui, N. Shiomi, and Y. Doi. Expression and characterization of (*R*)-specific enoyl coenzyme A hydratase involved in polyhydroxyalkanoate biosynthesis by *Aeromonas caviae*. *J. Bacteriol.*, 180:667–673, 1998.

[415] K. Fukumaga. Metabolism of dihydroxyfumarate, hydroxypyruvate, and their related compounds. I. Enzymic formation of xylulose in liver. *J. Biochem. (Tokyo)*, 47:741–754, 1960.

[416] E.S. Furfine and R.H. Abeles. Intermediates in the conversion of 5′-*S*-methylthioadenosine to methionine in *Klebsiella pneumoniae*. *J. Biol. Chem.*, 263:9598–9606, 1988.

[417] B. Furie, B.A. Bouchard, and B.C. Furie. Vitamin K-dependent biosynthesis of γ-carboxyglutamic acid. *Blood*, 93:1798–1808, 1999.

[418] S. Furuyoshi, N. Kawabata, H. Tanaka, and K. Soda. Enzymatic production of D-glycerate from L-tartrate. *Agric. Biol. Chem.*, 53:2101–2105, 1989.

[419] J. Gabriel, J. Volc, P. Sedmera, G. Daniel, and E. Kubátová. Pyranosone dehydratase from the basidiomycete *Phanerochaete chrysosporium*: improved purification, and identification of 6-deoxy-D-glucosone and D-xylosone reaction products. *Arch. Microbiol.*, 160:27–34, 1993.

[420] F.H. Gaertner and K.W. Cole. Properties of chorismate synthase in *Neurospora crassa*. *J. Biol. Chem.*, 248:4602–4609, 1973.

[421] S.J. Gagne, J.M. Stout, E. Liu, Z. Boubakir, S.M. Clark, and J.E. Page. Identification of olivetolic acid cyclase from *Cannabis sativa* reveals a unique catalytic route to plant polyketides. *Proc. Natl. Acad. Sci. USA*, 109:12811–12816, 2012.

[422] E.F. Gale and H.M.R. Epps. Studies on bacterial amino-acid decarboxylases. 1. l(+)-lysine decarboxylase. *Biochem. J.*, 38:232–242, 1944.

[423] H. Gambliel and R. Croteau. Pinene cyclases I and II. Two enzymes from sage (*Salvia officinalis*) which catalyze stereospecific cyclizations of geranyl pyrophosphate to monoterpene olefins of opposite configuration. *J. Biol. Chem.*, 259:740–748, 1984.

[424] W. Gao, M.L. Hillwig, L. Huang, G. Cui, X. Wang, J. Kong, B. Yang, and R.J. Peters. A functional genomics approach to tanshinone biosynthesis provides stereochemical insights. *Org. Lett.*, 11:5170–5173, 2009.

[425] D.L. Garbers, J.L. Suddath, and J.G. Hardman. Enzymatic formation of inosine 3′,5′-monophosphate and of 2′-deoxyguanosine 3′,5′-monophosphate. Inosinate and deoxyguanylate cyclase activity. *Biochim. Biophys. Acta*, 377:174–185, 1975.

[426] J.M. Garcia-Segura, M.M. Orozco, J.M. Fominaya, and J.G. Gavilanes. Purification, molecular and enzymic characterization of an acid RNase from the insect *Ceratitis capitata*. *Eur. J. Biochem.*, 158:367–372, 1986.

[427] A. Garrido-Pertierra and R.A. Cooper. Identification and purification of distinct isomerase and decarboxylase enzymes involved in the 4-hydroxyphenylacetate pathway of *Escherichia coli*. *Eur. J. Biochem.*, 117:581–584, 1981.

[428] G. Gartler, C. Kratky, and K. Gruber. Structural determinants of the enantioselectivity of the hydroxynitrile lyase from *Hevea brasiliensis*. *J. Biotechnol.*, 129:87–97, 2007.

[429] P.J. Gaskin, H.J. Adcock, L.D. Buckberry, P.H. Teesdale-Spittle, and P.N. Shaw. The C-S lysis of L-cysteine conjugates by aspartate and alanine aminotransferase enzymes. *Hum Exp Toxicol*, 14:422–427, 1995.

[430] M.J. Gasson, Y. Kitamura, W.R. McLauchlan, A. Narbad, A.J. Parr, E.L. Parsons, J. Payne, M.J. Rhodes, and N.J. Walton. Metabolism of ferulic acid to vanillin. A bacterial gene of the enoyl-SCoA hydratase/isomerase superfamily encodes an enzyme for the hydration and cleavage of a hydroxycinnamic acid SCoA thioester. *J. Biol. Chem.*, 273:4163–4170, 1998.

[431] G.J. Gatto, Boyne Jr., 2nd M.T., N.L. Kelleher, and C.T. Walsh. Biosynthesis of pipecolic acid by RapL, a lysine cyclodeaminase encoded in the rapamycin gene cluster. *J. Am. Chem. Soc.*, 128:3838–3847, 2006.

[432] E. Geiser, S.K. Przybilla, A. Friedrich, W. Buckel, N. Wierckx, L.M. Blank, and M. Bolker. *Ustilago maydis* produces itaconic acid via the unusual intermediate *trans*-aconitate. *Microb. Biotechnol.*, 9:116–126, 2016.

[433] J. Gescher, W. Eisenreich, J. Worth, A. Bacher, and G. Fuchs. Aerobic benzoyl-CoA catabolic pathway in *Azoarcus evansii*: studies on the non-oxygenolytic ring cleavage enzyme. *Mol. Microbiol.*, 56:1586–1600, 2005.

[434] M.A. Ghalambor and E.C. Heath. The biosynthesis of cell wall lipopolysaccharide in *Escherichia coli*. IV. Purification and properties of cytidine monophosphate 3-deoxy-D-*manno*-octulosonate synthetase. *J. Biol. Chem.*, 241:3216–3221, 1966.

[435] M.A. Ghalambor and E.C. Heath. The biosynthesis of cell wall lipopolysaccharide in *Escherichia coli*. V. Purification and properties of 3-deoxy-D-*manno*-octulosonate aldolase. *J. Biol. Chem.*, 241:3222–3227, 1966.

[436] S. Ghasempur, S. Eswaramoorthy, B.S. Hillerich, R.D. Seidel, S. Swaminathan, S.C. Almo, and J.A. Gerlt. Discovery of a novel L-lyxonate degradation pathway in *Pseudomonas aeruginosa* PAO1. *Biochemistry*, 53:3357–3366, 2014.

[437] R.G. Gibbs and J.G. Morris. Assay and properties of β-hydroxyaspartate aldolase from *Micrococcus denitrificans*. *Biochim. Biophys. Acta*, 85:501–503, 1964.

[438] R.G. Gibbs and J.G. Morris. Purification and properties of *erythro*-β-hydroxyaspartate dehydratase from *Micrococcus denitrificans*. *Biochem. J.*, 97:547–554, 1965.

[439] K.D. Gibson, A. Neuberger, and J.J. Scott. The purification and properties of δ-aminolaevulic acid dehydrase. *Biochem. J.*, 61:618–629, 1955.

[440] S. Giglio, W.K. Chou, H. Ikeda, D.E. Cane, and P.T. Monis. Biosynthesis of 2-methylisoborneol in cyanobacteria. *Environ. Sci. Technol.*, 45:992–998, 2011.

[441] M. Gijzen, E. Lewinsohn, and R. Croteau. Characterization of the constitutive and wound-inducible monoterpene cyclases of grand fir (*Abies grandis*). *Arch. Biochem. Biophys.*, 289:267–273, 1991.

[442] J.M. Gilbert, M. Matsuhashi, and J.L. Strominger. Thymidine diphosphate 4-acetamido-4,6-dideoxyhexoses. II. Purification and properties of thymidine diphosphate D-glucose oxidoreductase. *J. Biol. Chem.*, 240:1305–1308, 1965.

[443] J.L. Giner, S. Rocchetti, S. Neunlist, M. Rohmer, and D. Arigoni. Detection of 1,2-hydride shifts in the formation of euph-7-ene by the squalene-tetrahymanol cyclase of *Tetrahymena pyriformis*. *Chem. Commun. (Camb.)*, pages 3089–3091, 2005.

[444] T.L. Glass and R.S. Lamppa. Purification and properties of 16α-hydroxyprogesterone dehydroxylase from *Eubacterium* sp. strain 144. *Biochim. Biophys. Acta*, 837:103–110, 1985.

[445] D.G. Glitz and C.A. Dekker. Studies on a ribonuclease from *Ustilago sphaerogena*. I. Purification and properties of the enzyme. *Biochemistry*, 3:1391–1399, 1964.

[446] D.G. Glitz and C.A. Dekker. Studies on a ribonuclease from *Ustilago sphaerogena*. II. Specificity of the enzyme. *Biochemistry*, 3:1399–1406, 1964.

[447] M. Goda, Y. Hashimoto, S. Shimizu, and M. Kobayashi. Discovery of a novel enzyme, isonitrile hydratase, involved in nitrogen-carbon triple bond cleavage. *J. Biol. Chem.*, 276:23480–23485, 2001.

[448] M. Goenrich, S. Bartoschek, C.H. Hagemeier, C. Griesinger, and J.A. Vorholt. A glutathione-dependent formaldehyde-activating enzyme (Gfa) from *Paracoccus denitrificans* detected and purified via two-dimensional proton exchange NMR spectroscopy. *J. Biol. Chem.*, 277:3069–3072, 2002.

[449] S. Goepfert, J.K. Hiltunen, and Y. Poirier. Identification and functional characterization of a monofunctional peroxisomal enoyl-CoA hydratase 2 that participates in the degradation of even *cis*-unsaturated fatty acids in *Arabidopsis thaliana*. *J. Biol. Chem.*, 281:35894–35903, 2006.

[450] A. Gonzalez, L.L. Remsing, F. Lombo, M.J. Fernandez, L. Prado, A.F. Brana, E. Kunzel, J. Rohr, C. Mendez, and J.A. Salas. The mtmVUC genes of the mithramycin gene cluster in *Streptomyces argillaceus* are involved in the biosynthesis of the sugar moieties. *Mol. Gen. Genet.*, 264:827–835, 2001.

[451] B. González and R. Vicu nna. Benzaldehyde lyase, a novel thiamine PPi-requiring enzyme, from *Pseudomonas fluorescens* biovar I. *J. Bacteriol.*, 171:2401–2405, 1989.

[452] J.L. Goodman, S. Wang, S. Alam, F.J. Ruzicka, P.A. Frey, and J.E. Wedekind. Ornithine cyclodeaminase: structure, mechanism of action, and implications for the μ-crystallin family. *Biochemistry*, 43:13883–13891, 2004.

[453] J.C. Gopfert, G. Macnevin, D.K. Ro, and O. Spring. Identification, functional characterization and developmental regulation of sesquiterpene synthases from sunflower capitate glandular trichomes. *BMC Plant Biol.*, 9:86–86, 2009.

[454] E.V. Goryachenkova. [Enzyme in garlic which forms allycine (allyinase), a protein with phosphopyridoxal.]. *Dokl. Akad. Nauk S.S.S.R.*, 87:457–460, 1952.

[455] M. Goto, H. Hayashi, I. Miyahara, K. Hirotsu, M. Yoshida, and T. Oikawa. Crystal structures of nonoxidative zinc-dependent 2,6-dihydroxybenzoate (γ-resorcylate) decarboxylase from *Rhizobium* sp. strain MTP-10005. *J. Biol. Chem.*, 281:34365–34373, 2006.

[456] S. Goto-Ito, R. Ishii, T. Ito, R. Shibata, E. Fusatomi, S.I. Sekine, Y. Bessho, and S. Yokoyama. Structure of an archaeal TYW1, the enzyme catalyzing the second step of wye-base biosynthesis. *Acta Crystallogr. D Biol. Crystallogr.*, 63:1059–1068, 2007.

[457] H. Gotouda, T. Takatori, K. Terazawa, M. Nagao, and H. Tarao. The mechanism of experimental adipocere formation: hydration and dehydrogenation in microbial synthesis of hydroxy and oxo fatty acids. *Forensic Sci. Int.*, 37:249–257, 1988.

[458] J.B. Gou, Z.Q. Li, C.F. Li, F.F. Chen, S.Y. Lv, and Y.S. Zhang. Molecular cloning and functional analysis of a 10-*epi*-junenol synthase from *Inula hupehensis*. *Plant Physiol. Biochem.*, 106:288–294, 2016.

[459] A. Goyer, V. Illarionova, S. Roje, M. Fischer, A. Bacher, and A.D. Hanson. Folate biosynthesis in higher plants. cDNA cloning, heterologous expression, and characterization of dihydroneopterin aldolases. *Plant Physiol.*, 135:103–111, 2004.

[460] R. Grabowski, A.E. Hofmeister, and W. Buckel. Bacterial L-serine dehydratases: a new family of enzymes containing iron-sulfur clusters. *Trends Biochem. Sci.*, 18:297–300, 1993.

[461] D.E. Graham and R.H. White. Elucidation of methanogenic coenzyme biosyntheses: from spectroscopy to genomics. *Nat. Prod. Rep.*, 19:133–147, 2002.

[462] D.E. Graham, H. Xu, and R.H. White. Identification of coenzyme M biosynthetic phosphosulfolactate synthase: a new family of sulfonate-biosynthesizing enzymes. *J. Biol. Chem.*, 277:13421–13429, 2002.

[463] D.J.W. Grant and J.C. Patel. Non-oxidative decarboxylation of *p*-hydroxybenzoic acid, gentisic acid, protocatechuic acid, and gallic acid by *Klebsiella aerogenes* (*Aerobacter aerogenes*). *J. Microbiol. Serol.*, 35:325–343, 1969.

[464] M. Graupner, H. Xu, and R.H. White. Identification of the gene encoding sulfopyruvate decarboxylase, an enzyme involved in biosynthesis of coenzyme M. *J. Bacteriol.*, 182:4862–4867, 2000.

[465] J.M. Green, W.K. Merkel, and B.P. Nichols. Characterization and sequence of *Escherichia coli* pabC, the gene encoding aminodeoxychorismate lyase, a pyridoxal phosphate-containing enzyme. *J. Bacteriol.*, 174:5317–5323, 1992.

[466] S. Green, C.J. Squire, N.J. Nieuwenhuizen, E.N. Baker, and W. Laing. Defining the potassium binding region in an apple terpene synthase. *J. Biol. Chem.*, 284:8661–8669, 2009.

[467] T.L. Grimek and J.C. Escalante-Semerena. The *acnD* genes of *Shewenella oneidensis* and *Vibrio cholerae* encode a new Fe/S-dependent 2-methylcitrate dehydratase enzyme that requires *prpF* function in vivo. *J. Bacteriol.*, 186:454–462, 2004.

[468] J.W. Gross, A.D. Hegeman, B. Gerratana, and P.A. Frey. Dehydration is catalyzed by glutamate-136 and aspartic acid-135 active site residues in *Escherichia coli* dTDP-glucose 4,6-dehydratase. *Biochemistry*, 40:12497–12504, 2001.

[469] S.R. Gross, R.O. Burns, and H.E. Umbarger. The biosynthesis of leucine. II. The enzymic isomerization of β-carboxy-β-hydroxyisocaproate and α-hydroxy-β-carboxyisocaproate. *Biochemistry*, 2:1046–1052, 1963.

[470] K. Gu, R.J. Linhardt, M. Laliberte, K. Gu, and J. Zimmermann. Purification, characterization and specificity of chondroitin lyases and glycuronidase from *Flavobacterium heparinum*. *Biochem. J.*, 312:569–577, 1995.

[471] M.C. Guion-Rain, C. Portemer, and F. Chatagner. Rat liver cysteine sulfinate decarboxylase: purification, new appraisal of the molecular weight and determination of catalytic properties. *Biochim. Biophys. Acta*, 384:265–276, 1975.

[472] U. Güldener, G.J. Koehler, C. Haussmann, A. Bacher, J. Kricke, D. Becher, and J.H. Hegemann. Characterization of the *Saccharomyces cerevisiae* Fol1 protein: starvation for C_1 carrier induces pseudohyphal growth. *Mol. Biol. Cell*, 15:3811–3828, 2004.

[473] M. Gulmezian, K.R. Hyman, B.N. Marbois, C.F. Clarke, and G.T. Javor. The role of UbiX in *Escherichia coli* coenzyme Q biosynthesis. *Arch. Biochem. Biophys.*, 467:144–153, 2007.

[474] M.F. Gulyi and N.V. Silonova. [Various metabolic reactions of formate in animal tissues.]. *Ukr. Biokhim. Zh.*, 59:29–35, 1987.

[475] F. Gumz, J. Krausze, D. Eisenschmidt, A. Backenkohler, L. Barleben, W. Brandt, and U. Wittstock. The crystal structure of the thiocyanate-forming protein from *Thlaspi arvense*, a kelch protein involved in glucosinolate breakdown. *Plant Mol. Biol.*, 89:67–81, 2015.

[476] C.F. Gunsalus, R.Y. Stanier, and I.C. Gunsalus. The enzymatic conversion of mandelic acid to benzoic acid. III. Fractionation and properties of the soluble enzymes. *J. Bacteriol.*, 66:548–553, 1953.

[477] L. Guo, R.A. Dixon, and N.L. Paiva. Conversion of vestitone to medicarpin in alfalfa (*Medicago sativa* L.) is catalyzed by two independent enzymes. Identification, purification, and characterization of vestitone reductase and 7,2′-dihydroxy-4′-methoxyisoflavanol dehydratase. *J. Biol. Chem.*, 269:22372–22378, 1994.

[478] L. Guo, R.A. Dixon, and N.L. Paiva. The 'pterocarpan synthase' of alfalfa: association and co-induction of vestitone reductase and 7,2′-dihydroxy-4′-methoxy-isoflavanol (DMI) dehydratase, the two final enzymes in medicarpin biosynthesis. *FEBS Lett.*, 356:221–225, 1994.

[479] X. Guo, A. Soderholm, P. Kanchugal, Isaksen S., Warsi G.V., Eckhard O., Triguis U., Gogoll S., Jerlstrom-Hultqvist A., Aqvist J., Andersson J., Selmer D.I., and M. Structure and mechanism of a phage-encoded SAM lyase revises catalytic function of enzyme family. *Elife*, 10, 2021.

[480] N.K. Gupta and B. Vennesland. Glyoxylate carboligase of *Escherichia coli*: a flavoprotein. *J. Biol. Chem.*, 239:3787–3789, 1964.

[481] B. Gust, G.L. Challis, K. Fowler, T. Kieser, and K.F. Chater. PCR-targeted *Streptomyces* gene replacement identifies a protein domain needed for biosynthesis of the sesquiterpene soil odor geosmin. *Proc. Natl. Acad. Sci. USA*, 100:1541–1546, 2003.

[482] J.K. Guterl, J.N. Andexer, T. Sehl, J. von Langermann, I. Frindi-Wosch, T. Rosenkranz, J. Fitter, K. Gruber, U. Kragl, T. Eggert, and M. Pohl. Uneven twins: comparison of two enantiocomplementary hydroxynitrile lyases with α/β-hydrolase fold. *J. Biotechnol.*, 141:166–173, 2009.

[483] T. Hadi, U. Dahl, C. Mayer, and M.E. Tanner. Mechanistic studies on *N*-acetylmuramic acid 6-phosphate hydrolase (MurQ): an etherase involved in peptidoglycan recycling. *Biochemistry*, 47:11547–11558, 2008.

[484] D.H. Haft. Bioinformatic evidence for a widely distributed, ribosomally produced electron carrier precursor, its maturation proteins, and its nicotinoprotein redox partners. *BMC Genomics*, 12:21–21, 2011.

[485] R. Hagihara, Y. Katsuyama, Y. Sugai, H. Onaka, and Y. Ohnishi. Novel desferrioxamine derivatives synthesized using the secondary metabolism-specific nitrous acid biosynthetic pathway in *Streptomyces davawensis*. *J. Antibiot. (Tokyo)*, 71:911–919, 2018.

[486] H. Hagion and K. Nakayama. Amino acid metabolism in microorganisms. Part IV. L-Methionine decarboxylase produced by *Streptomyces* strain. *Agric. Biol. Chem.*, 32:727–733, 1968.

[487] T. Hakamatsuka, K. Mori, S. Ishida, Y Ebizuka, and U. Sankawa. Purification of 2-hydroxyisoflavanone dehydratase from the cell cultures of *Pueraria lobata*. *Phytochemistry*, 49:497–505, 1998.

[488] D.E. Hall, J.A. Robert, C.I. Keeling, D. Domanski, A.L. Quesada, S. Jancsik, M.A. Kuzyk, B. Hamberger, C.H. Borchers, and J. Bohlmann. An integrated genomic, proteomic and biochemical analysis of (+)-3-carene biosynthesis in Sitka spruce (*Picea sitchensis*) genotypes that are resistant or susceptible to white pine weevil. *Plant J.*, 65:936–948, 2011.

[489] D.E. Hall, P. Zerbe, S. Jancsik, A.L. Quesada, H. Dullat, L.L. Madilao, M. Yuen, and J. Bohlmann. Evolution of conifer diterpene synthases: diterpene resin acid biosynthesis in lodgepole pine and jack pine involves monofunctional and bifunctional diterpene synthases. *Plant Physiol.*, 161:600–616, 2013.

[490] T.W. Hallahan and R. Croteau. Monoterpene biosynthesis: demonstration of a geranyl pyrophosphate:sabinene hydrate cyclase in soluble enzyme preparations from sweet marjoram (*Majorana hortensis*). *Arch. Biochem. Biophys.*, 264:618–631, 1988.

[491] T.W. Hallahan and R. Croteau. Monoterpene biosynthesis: mechanism and stereochemistry of the enzymatic cyclization of geranyl pyrophosphate to (+)-*cis*- and (+)-*trans*-sabinene hydrate. *Arch. Biochem. Biophys.*, 269:313–326, 1989.

[492] A. Hamai, N. Hashimoto, H. Mochizuki, F. Kato, Y. Makiguchi, K. Horie, and S. Suzuki. Two distinct chondroitin sulfate ABC lyases. An endoeliminase yielding tetrasaccharides and an exoeliminase preferentially acting on oligosaccharides. *J. Biol. Chem.*, 272:9123–9130, 1997.

[493] Y. Hamano, T. Kuzuyama, N. Itoh, K. Furihata, H. Seto, and T. Dairi. Functional analysis of eubacterial diterpene cyclases responsible for biosynthesis of a diterpene antibiotic, terpentecin. *J. Biol. Chem.*, 277:37098–37104, 2002.

[494] M. Hamberg. Mechanism of corn hydroperoxide isomerase - detection of 12,13(*S*)-oxido-9(Z),11-octadecadienoic acid. *Biochim. Biophys. Acta*, 920:76–84, 1987.

[495] M. Hamberg. Biosynthesis of 12-oxo-10,15(*Z*)-phytodienoic acid: identification of an allene oxide cyclase. *Biochem. Biophys. Res. Commun.*, 156:543–550, 1988.

[496] M. Hamberg. Hidden stereospecificity in the biosynthesis of divinyl ether fatty acids. *FEBS J.*, 272:736–743, 2005.

[497] B. Hamberger, D. Hall, M. Yuen, C. Oddy, B. Hamberger, C.I. Keeling, C. Ritland, K. Ritland, and J. Bohlmann. Targeted isolation, sequence assembly and characterization of two white spruce (*Picea glauca*) BAC clones for terpenoid synthase and cytochrome P_{450} genes involved in conifer defence reveal insights into a conifer genome. *BMC Plant Biol.*, 9:106–106, 2009.

[498] J.Y. Han, Y.S. Kwon, D.C. Yang, Y.R. Jung, and Y.E. Choi. Expression and RNA interference-induced silencing of the dammarenediol synthase gene in *Panax ginseng*. *Plant Cell Physiol.*, 47:1653–1662, 2006.

[499] S. Handa, J.H. Koo, Y.S. Kim, and H.G. Floss. Stereochemical course of biotin-independent malonate decarboxylase catalysis. *Arch. Biochem. Biophys.*, 370:93–96, 1999.

[500] J.W. Hanes, K.E. Burns, D.G. Hilmey, A. Chatterjee, P.C. Dorrestein, and T.P. Begley. Mechanistic studies on pyridoxal phosphate synthase: the reaction pathway leading to a chromophoric intermediate. *J. Am. Chem. Soc.*, 130:3043–3052, 2008.

[501] J.W. Hanes, I. Keresztes, and T.P. Begley. ^{13}C NMR snapshots of the complex reaction coordinate of pyridoxal phosphate synthase. *Nat. Chem. Biol.*, 4:425–430, 2008.

[502] J.W. Hanes, I. Keresztes, and T.P. Begley. Trapping of a chromophoric intermediate in the Pdx1-catalyzed biosynthesis of pyridoxal 5′-phosphate. *Angew. Chem. Int. Ed. Engl.*, 47:2102–2105, 2008.

[503] C.C. Hanfrey, B.M. Pearson, S. Hazeldine, J. Lee, D.J. Gaskin, P.M. Woster, M.A. Phillips, and A.J. Michael. Alternative spermidine biosynthetic route is critical for growth of *Campylobacter jejuni* and is the dominant polyamine pathway in human gut microbiota. *J. Biol. Chem.*, 286:43301–43312, 2011.

[504] M. Hans, J. Sievers, U. Muller, E. Bill, J.A. Vorholt, D. Linder, and W. Buckel. 2-hydroxyglutaryl-CoA dehydratase from *Clostridium symbiosum*. *Eur. J. Biochem.*, 265:404–414, 1999.

[505] M. Hansson and L. Hederstedt. Purification and characterisation of a water-soluble ferrochelatase from *Bacillus subtilis*. *Eur. J. Biochem.*, 220:201–208, 1994.

[506] M.D. Hansson, T. Karlberg, C.A. Soderberg, S. Rajan, M.J. Warren, S. Al-Karadaghi, S.E. Rigby, and M. Hansson. Bacterial ferrochelatase turns human: Tyr^{13} determines the apparent metal specificity of *Bacillus subtilis* ferrochelatase. *J. Biol. Inorg. Chem.*, 16:235–242, 2011.

[507] P. Hänzelmann, H.L. Hernandez, C. Menzel, R. Garcia-Serres, B.H. Huynh, M.K. Johnson, R.R. Mendel, and H. Schindelin. Characterization of MOCS1A, an oxygen-sensitive iron-sulfur protein involved in human molybdenum cofactor biosynthesis. *J. Biol. Chem.*, 279:34721–34732, 2004.

[508] P. Hänzelmann and H. Schindelin. Crystal structure of the *S*-adenosylmethionine-dependent enzyme MoaA and its implications for molybdenum cofactor deficiency in humans. *Proc. Natl. Acad. Sci. USA*, 101:12870–12875, 2004.

[509] P. Hänzelmann and H. Schindelin. Binding of 5′-GTP to the C-terminal FeS cluster of the radical *S*-adenosylmethionine enzyme MoaA provides insights into its mechanism. *Proc. Natl. Acad. Sci. USA*, 103:6829–6834, 2006.

[510] H. Hara, E. Masai, Y. Katayama, and M. Fukuda. The 4-oxalomesaconate hydratase gene, involved in the protocatechuate 4,5-cleavage pathway, is essential to vanillate and syringate degradation in *Sphingomonas paucimobilis* SYK-6. *J. Bacteriol.*, 182:6950–6957, 2000.

[511] J. Harada, M. Teramura, T. Mizoguchi, Y. Tsukatani, K. Yamamoto, and H. Tamiaki. Stereochemical conversion of C3-vinyl group to 1-hydroxyethyl group in bacteriochlorophyll *c* by the hydratases BchF and BchV: adaptation of green sulfur bacteria to limited-light environments. *Mol. Microbiol.*, 98:1184–1198, 2015.

[512] S. Harayama, M. Rekik, K.L. Ngai, and L.N. Ornston. Physically associated enzymes produce and metabolize 2-hydroxy-2,4-dienoate, a chemically unstable intermediate formed in catechol metabolism via *meta* cleavage in *Pseudomonas putida*. *J. Bacteriol.*, 171:6251–6258, 1989.

[513] J.G. Hardman and E.W. Sutherland. Guanyl cyclase, an enzyme catalyzing the formation of guanosine 3′,5′-monophosphate from guanosine triphosphate. *J. Biol. Chem.*, 244:6363–6370, 1969.

[514] N.C. Harris, D.A. Born, W. Cai, Y. Huang, J. Martin, R. Khalaf, C.L. Drennan, and W. Zhang. Isonitrile formation by a non-heme iron(II)-dependent oxidase/decarboxylase. *Angew. Chem. Int. Ed. Engl.*, 57:9707–9710, 2018.

[515] N.C. Harris, M. Sato, N.A. Herman, F. Twigg, W. Cai, J. Liu, X. Zhu, J. Downey, R. Khalaf, J. Martin, H. Koshino, and W. Zhang. Biosynthesis of isonitrile lipopeptides by conserved nonribosomal peptide synthetase gene clusters in Actinobacteria. *Proc. Natl. Acad. Sci. USA*, 114:7025–7030, 2017.

[516] C.S. Harwood and J. Gibson. Shedding light on anaerobic benzene ring degradation: a process unique to prokaryotes? *J. Bacteriol.*, 179:301–309, 1997.

[517] W. Hashimoto, K. Maesaka, N. Sato, S. Kimura, K. Yamamoto, H. Kumagai, and K. Murata. Microbial system for polysaccharide depolymerization: enzymatic route for gellan depolymerization by *Bacillus* sp. GL1. *Arch. Biochem. Biophys.*, 339:17–23, 1997.

[518] W. Hashimoto, O. Miyake, K. Momma, S. Kawai, and K. Murata. Molecular identification of oligoalginate lyase of *Sphingomonas* sp. strain A1 as one of the enzymes required for complete depolymerization of alginate. *J. Bacteriol.*, 182:4572–4577, 2000.

[519] W. Hashimoto, N. Sato, S. Kimura, and K. Murata. Polysaccharide lyase: molecular cloning of gellan lyase gene and formation of the lyase from a huge precursor protein in *Bacillus* sp. GL1. *Arch. Biochem. Biophys.*, 354:31–39, 1998.

[520] S. Hasim, N.A. Hussin, F. Alomar, K.R. Bidasee, K.W. Nickerson, and M.A. Wilson. A glutathione-independent glyoxalase of the DJ-1 superfamily plays an important role in managing metabolically generated methylglyoxal in *Candida albicans*. *J. Biol. Chem.*, 289:1662–1674, 2014.

[521] H. Hassall and D.M. Greenberg. Urocanase (beef liver). *Methods Enzymol.*, 17B:84–88, 1971.

[522] J. Hattan, K. Shindo, T. Ito, Y. Shibuya, A. Watanabe, C. Tagaki, F. Ohno, T. Sasaki, J. Ishii, A. Kondo, and N. Misawa. Identification of a novel hedycaryol synthase gene isolated from *Camellia brevistyla* flowers and floral scent of *Camellia* cultivars. *Planta*, 243:959–972, 2016.

[523] J.I. Hattan, K. Shindo, T. Sasaki, F. Ohno, H. Tokuda, K. Ishikawa, and N. Misawa. Identification of novel sesquiterpene synthase genes that mediate the biosynthesis of valerianol, which was an unknown ingredient of tea. *Sci. Rep.*, 8:12474–12474, 2018.

[524] C.R. Hauer, I. Rebrin, B. Thöny, F. Neuheiser, H.C. Curtius, P. Hunziker, N. Blau, S. Ghisla, , and C.W. Phenylalanine hydroxylase-stimulating protein: pterin-4α-carbinolamine dehydratase from rat and human liver. *J. Biol. Chem.*, 268:4828–4831, 1993.

[525] K. Haufschildt, S. Schmelz, T.M. Kriegler, A. Neumann, J. Streif, H. Arai, D.W. Heinz, and G. Layer. The crystal structure of siroheme decarboxylase in complex with iron-uroporphyrin III reveals two essential histidine residues. *J. Mol. Biol.*, 426:3272–3286, 2014.

[526] R. Hausmann. Synthesis of an *S*-adenosylmethionine-cleaving enzyme in T_3-infected *Escherichia coli* and its disturbance by co-infection with enzymatically incompetent bacteriophage. *J. Virol.*, 1:57–63, 1967.

[527] C. Haussmann, F. Rohdich, E. Schmidt, A. Bacher, and G. Richter. Biosynthesis of pteridines in *Escherichia coli*. Structural and mechanistic similarity of dihydroneopterin-triphosphate epimerase and dihydroneopterin aldolase. *J. Biol. Chem.*, 273:17418–17424, 1998.

[528] F. Hauth, H. Buck, M. Stanoppi, and J.S. Hartig. Canavanine utilization via homoserine and hydroxyguanidine by a PLP-dependent γ-lyase in Pseudomonadaceae and Rhizobiales. *RSC Chem. Biol.*, 3:1240–1250, 2022.

[529] A.B. Hazra, A.W. Han, A.P. Mehta, K.C. Mok, V. Osadchiy, T.P. Begley, and M.E. Taga. Anaerobic biosynthesis of the lower ligand of vitamin B_{12}. *Proc. Natl. Acad. Sci. USA*, 112:10792–10797, 2015.

[530] X. He and D.E. Cane. Mechanism and stereochemistry of the germacradienol/germacrene D synthase of *Streptomyces coelicolor* A3(2). *J. Am. Chem. Soc.*, 126:2678–2679, 2004.

[531] E.C. Heath, J. Hurwitz, B.L. Horecker, and A. Ginsburg. Pentose fermentation by *Lactobacillus plantarum*. I. The cleavage of xylulose 5-phosphate by phosphoketolase. *J. Biol. Chem.*, 231:1009–1029, 1958.

[532] R.J. Heath and C.O. Rock. Roles of the FabA and FabZ β-hydroxyacyl-acyl carrier protein dehydratases in *Escherichia coli* fatty acid biosynthesis. *J. Biol. Chem.*, 271:27795–27801, 1996.

[533] J.L. Hedrick and H.J. Sallach. The nonoxidative decarboxylation of hydroxypyruvate in mammalian systems. *Arch. Biochem. Biophys.*, 105:261–269, 1964.

[534] A.D. Hegeman, J.W. Gross, and P.A. Frey. Probing catalysis by *Escherichia coli* dTDP-glucose-4,6-dehydratase: identification and preliminary characterization of functional amino acid residues at the active site. *Biochemistry*, 40:6598–6610, 2001.

[535] R.L. Heinrikson and E. Goldwasser. Studies on the biosynthesis of 5-ribosyluracil 5′-monophosphate in *Tetrahymena pyriformis*. *J. Biol. Chem.*, 239:1177–1187, 1964.

[536] E. Heinzelmann, G. Kienzlen, S. Kaspar, J. Recktenwald, W. Wohlleben, and D. Schwartz. The phosphinomethylmalate isomerase gene pmi, encoding an aconitase-like enzyme, is involved in the synthesis of phosphinothricin tripeptide in *Streptomyces viridochromogenes*. *Appl. Environ. Microbiol.*, 67:3603–3609, 2001.

[537] H.R. Hendrickson. The β-cyanoalanine synthase of blue lupine. *Fed. Proc.*, 27:593–593, 1968.

[538] H.R. Hendrickson and E.E. Conn. Cyanide metabolism in higher plants. IV. Purification and properties of the β-cyanoalanine synthase of blue lupine. *J. Biol. Chem.*, 244:2632–2640, 1969.

[539] D.J. Henner, M. Yang, E. Chen, R. Helmikss, and M.G. Low. Sequence of the *Bacillus thuringiensis* phosphatidylinositol-specific phospholipase C. *Nucleic Acids Res.*, 16:10383–10383, 1988.

[540] M.GL. Henquet, N. Prota, J.JJ. van der Hooft, M. Varbanova-Herde, R.JM. Hulzink, M. de Vos, M. Prins, M.TJ. de Both, M.CR. Franssen, H. Bouwmeester, and M. Jongsma. Identification of a drimenol synthase and drimenol oxidase from *Persicaria hydropiper*, involved in the biosynthesis of insect deterrent drimanes. *Plant J.*, 90:1052–1063, 2017.

[541] L.A. Heppel. Pig liver nuclei ribonuclease. In G.L. Cantoni and D.R. Davies, editors, *Procedures in Nucleic Acid Research*, pages 31–36. Procedures in Nucleic Acid Research, New York, 1966.

[542] D. Herbert. Oxalacetic carboxylase of *Micrococcus lysodeikticus*. *Methods Enzymol.*, 1:753–757, 1955.

[543] M. Herde, K. Gartner, T.G. Kollner, B. Fode, W. Boland, J. Gershenzon, C. Gatz, and D. Tholl. Identification and regulation of TPS04/GES, an *Arabidopsis* geranyllinalool synthase catalyzing the first step in the formation of the insect-induced volatile C^{16}-homoterpene TMTT. *Plant Cell*, 20:1152–1168, 2008.

[544] D. Hereld, J.L. Krakow, J.D. Bangs, G.W. Hart, and P.T. Englund. A phospholipase C from *Trypanosoma brucei* which selectively cleaves the glycolipid on the variant surface glycoprotein. *J. Biol. Chem.*, 261:13813–13819, 1986.

[545] S. Herter, A. Busch, and G. Fuchs. L-Malyl-coenzyme A lyase/β-methylmalyl-coenzyme A lyase from *Chloroflexus aurantiacus*, a bifunctional enzyme involved in autotrophic CO_2 fixation. *J. Bacteriol.*, 184:5999–6006, 2002.

[546] S. Herz, J. Wungsintaweekul, C.A. Schuhr, S. Hecht, H. Lüttgen, S. Sagner, M. Fellermeier, W. Eisenreich, M.H. Zenk, A. Bacher, and F. Rohdich. Biosynthesis of terpenoids: YgbB protein converts 4-diphosphocytidyl-2C-methyl-D-erithritol 2-phosphate to 2-*C*-methyl-D-erithritol 2,4-cyclodiphosphate. *Proc. Natl. Acad. Sci. USA*, 97:2486–2490, 2000.

[547] A.M. Heskes, T.CM. Sundram, B.A. Boughton, N.B. Jensen, N.L. Hansen, C. Crocoll, F. Cozzi, S. Rasmussen, B. Hamberger, B. Hamberger, D. Staerk, B.L. Møller, and I. Pateraki. Biosynthesis of bioactive diterpenoids in the medicinal plant *Vitex agnus-castus*. *Plant J.*, 93:943–958, 2018.

[548] S. Hettwer and R. Sterner. A novel tryptophan synthase β-subunit from the hyperthermophile *Thermotoga maritima*. Quaternary structure, steady-state kinetics, and putative physiological role. *J. Biol. Chem.*, 277:8194–8201, 2002.

[549] A.E. Hey and A.D. Elbein. Biosynthesis of tyvelose. The purification and properties of cytidine diphosphate D-glucose oxidoreductase. *J. Biol. Chem.*, 241:5473–5478, 1966.

[550] M. Hezari, R.E. Ketchum, D.M. Gibson, and R. Croteau. Taxol production and taxadiene synthase activity in *Taxus canadensis* cell suspension cultures. *Arch. Biochem. Biophys.*, 337:185–90, 1997.

[551] M. Hezari, N.G. Lewis, and R. Croteau. Purification and characterization of taxa-4(5),11(12)-diene synthase from Pacific yew (*Taxus brevifolia*) that catalyzes the first committed step of taxol biosynthesis. *Arch. Biochem. Biophys.*, 322:437–444, 1995.

[552] S. Hilditch, S. Berghall, N. Kalkkinen, M. Penttila, and P. Richard. The missing link in the fungal D-galacturonate pathway: identification of the L-*threo*-3-deoxy-hexulosonate aldolase. *J. Biol. Chem.*, 282:26195–26201, 2007.

[553] R.K. Hill, S. Sawada, and S.M. Arfin. Stereochemistry of valine and isoleucine biosynthesis. IV. Synthesis, configuration, and enzymatic specificity of α-acetolactate and α-aceto-α-hydroxybutyrate. *Bioorg. Chem.*, 8:175–189, 1979.

[554] M.L. Hillwig, Q. Zhu, and X. Liu. Biosynthesis of ambiguine indole alkaloids in cyanobacterium *Fischerella ambigua*. *ACS Chem. Biol.*, 9:372–377, 2014.

[555] H. Hilz, J. Knappe, E. Ringelmann, and F. Lynen. Methylglutaconase, eine neue Hydratase, die am Stoffwechsel verzweigter Carbonsäuren beteiligt ist. *Biochem. Z.*, 329:476–489, 1958.

[556] H. Hirakawa, A.L. Schaefer, E.P. Greenberg, and C.S. Harwood. Anaerobic *p*-coumarate degradation by *Rhodopseudomonas palustris* and identification of CouR, a MarR repressor protein that binds *p*-coumaroyl coenzyme A. *J. Bacteriol.*, 194:1960–1967, 2012.

[557] M. Hirata and O. Hayaishi. Adenyl cyclase of *Brevibacterium liquefaciens*. *Biochim. Biophys Acta*, 149:1–11, 1967.

[558] T. Hisano, T. Fukui, T. Iwata, and Y. Doi. Crystallization and preliminary X-ray analysis of (*R*)-specific enoyl-CoA hydratase from *Aeromonas caviae* involved in polyhydroxyalkanoate biosynthesis. *Acta Crystallogr. D Biol. Crystallogr.*, 57:145–147, 2001.

[559] A. Hiseni, I.W. Arends, and L.G. Otten. Biochemical characterization of the carotenoid 1,2-hydratases (CrtC) from *Rubrivivax gelatinosus* and *Thiocapsa roseopersicina*. *Appl. Microbiol. Biotechnol.*, 91:1029–1036, 2011.

[560] K. Hitomi, L. DiTacchio, A.S. Arvai, J. Yamamoto, S.T. Kim, T. Todo, J.A. Tainer, S. Iwai, S. Panda, and E.D. Getzoff. Functional motifs in the (6-4) photolyase crystal structure make a comparative framework for DNA repair photolyases and clock cryptochromes. *Proc. Natl. Acad. Sci. USA*, 106:6962–6967, 2009.

[561] M.C. Ho, J.F. Menetret, H. Tsuruta, and K.N. Allen. The origin of the electrostatic perturbation in acetoacetate decarboxylase. *Nature*, 459:393–397, 2009.

[562] S. Hoenke, M. Schmid, and P. Dimroth. Sequence of a gene cluster from *Klebsiella pneumoniae* encoding malonate decarboxylase and expression of the enzyme in *Escherichia coli*. *Eur. J. Biochem.*, 246:530–538, 1997.

[563] S. Hoenke, M. Schmid, and P. Dimroth. Identification of the active site of phosphoribosyl-dephospho-coenzyme A transferase and relationship of the enzyme to an ancient class of nucleotidyltransferases. *Biochemistry*, 39:13233–13240, 2000.

[564] P. Rosen Hoffee, Horecker O.M., and B.L. The mechanism of action of aldolases. VI. Crystallization of deoxyribose 5-phosphate aldolase and the number of active sites. *J. Biol. Chem.*, 240:1512–1516, 1965.

[565] P.A. Hoffee. 2-Deoxyribose-5-phosphate aldolase of *Salmonella typhimurium*: purification and properties. *Arch. Biochem. Biophys.*, 126:795–802, 1968.

[566] A.E. Hofmeister and W. Buckel. (*R*)-Lactyl-CoA dehydratase from *Clostridium propionicum*. Stereochemistry of the dehydration of (*R*)-2-hydroxybutyryl-CoA to crotonyl-CoA. *Eur. J. Biochem.*, 206:547–552, 1992.

[567] T.M. Hohn and P.D. Beremand. Isolation and nucleotide sequence of a sesquiterpene cyclase gene from the trichothecene-producing fungus *Fusarium sporotrichioides*. *Gene*, 79:131–138, 1989.

[568] T.M. Hohn and R.D. Plattner. Purification and characterization of the sesquiterpene cyclase aristolochene synthase from *Penicillium roqueforti*. *Arch. Biochem. Biophys.*, 272:137–143, 1989.

[569] T.M. Hohn and F. Vanmiddlesworth. Purification and characterization of the sesquiterpene cyclase trichodiene synthetase from *Fusarium sporotrichioides*. *Arch. Biochem. Biophys.*, 251:756–761, 1986.

[570] A. Holt and F. Wold. The isolation and characterization of rabbit muscle enolase. *J. Biol. Chem.*, 236:3227–3231, 1961.

[571] L. Hong, Z. Zhao, and H.W. Liu. Characterization of SpnQ from the spinosyn biosynthetic pathway of *Saccharopolyspora spinosa*: mechanistic and evolutionary implications for C-3 deoxygenation in deoxysugar biosynthesis. *J. Am. Chem. Soc.*, 128:14262–14263, 2006.

[572] L. Hong, Z. Zhao, C.E. Melancon, Zhang 3rd, Liu H., and H.W. *In vitro* characterization of the enzymes involved in TDP-D-forosamine biosynthesis in the spinosyn pathway of *Saccharopolyspora spinosa*. *J. Am. Chem. Soc.*, 130:4954–4967, 2008.

[573] D.J. Hopper and R.A. Cooper. The regulation of *Escherichia coli* methylglyoxal synthase; a new control site in glycolysis? *FEBS Lett.*, 13:213–216, 1971.

[574] B.L. Horecker, O. Tsolas, and C.Y. Lai. Aldolases. In P.D. Boyer, editor, *The Enzymes*, volume 7, pages 213–258. Academic Press, New York, 3rd edition, 1972.

[575] M. Horinouchi, T. Hayashi, H. Koshino, T. Kurita, and T. Kudo. Identification of 9,17-dioxo-1,2,3,4,10,19-hexanorandrostan-5-oic acid, 4-hydroxy-2-oxohexanoic acid, and 2-hydroxyhexa-2,4-dienoic acid and related enzymes involved in testosterone degradation in *Comamonas testosteroni* TA441. *Appl. Environ. Microbiol.*, 71:5275–5281, 2005.

[576] A.A. Horton and H.L. Kornberg. Oxaloacetate 4-carboxy-lyase from *Pseudomonas ovalis* chester. *Biochim. Biophys. Acta*, 89:381–383, 1964.

[577] T. Hoshino, S. Nakano, T. Kondo, T. Sato, and A. Miyoshi. Squalene-hopene cyclase: final deprotonation reaction, conformational analysis for the cyclization of (3*R*,*S*)-2,3-oxidosqualene and further evidence for the requirement of an isopropylidene moiety both for initiation of the polycyclization cascade and for the formation of the 5-membered E-ring. *Org Biomol Chem*, 2:1456–1470, 2004.

[578] B.M. Hover, A. Lioksztejn, A.A. Ribeiro, and K. Yokoyama. Identification of a cyclic nucleotide as a cryptic intermediate in molybdenum cofactor biosynthesis. *J. Am. Chem. Soc.*, 135:7019–7032, 2013.

[579] B.M. Hover, N.K. Tonthat, M.A. Schumacher, and K. Yokoyama. Mechanism of pyranopterin ring formation in molybdenum cofactor biosynthesis. *Proc. Natl. Acad. Sci. USA*, 112:6347–6352, 2015.

[580] B.M. Hover and K. Yokoyama. C-Terminal glycine-gated radical initiation by GTP 3′,8-cyclase in the molybdenum cofactor biosynthesis. *J. Am. Chem. Soc.*, 137:3352–3359, 2015.

[581] P. Hovingh and A. Linker. The enzymatic degradation of heparin and heparitin sulfate. 3. Purification of a heparitinase and a heparinase from flavobacteria. *J. Biol. Chem.*, 245:6170–6175, 1970.

[582] Y. Hu, W.K. Chou, R. Hopson, and D.E. Cane. Genome mining in *Streptomyces clavuligerus*: expression and biochemical characterization of two new cryptic sesquiterpene synthases. *Chem. Biol.*, 18:32–37, 2011.

[583] L. Hua and S.P. Matsuda. The molecular cloning of 8-epicedrol synthase from *Artemisia annua*. *Arch. Biochem. Biophys.*, 369:208–212, 1999.

[584] W. Huang, A. Matte, Y. Li, Y.S. Kim, R.J. Linhardt, H. Su, and M. Cygler. Crystal structure of chondroitinase B from *Flavobacterium heparinum* and its complex with a disaccharide product at 1.7 Å resolution. *J. Mol. Biol.*, 294:1257–1269, 1999.

[585] Z. Huang, K. Kakinuma, and T. Eguchi. Stereospecificity of hydride transfer in NAD^+-catalyzed 2-deoxy-*scyllo*-inosose synthase, the key enzyme in the biosynthesis of 2-deoxystreptamine-containing aminocyclitol antibiotics. *Bioorg. Chem.*, 33:82–89, 2005.

[586] B.K. Hubbard, M. Koch, D.R. Palmer, P.C. Babbitt, and J.A. Gerlt. Evolution of enzymatic activities in the enolase superfamily: characterization of the (D)-glucarate/galactarate catabolic pathway in *Escherichia coli*. *Biochemistry*, 37:14369–14375, 1998.

[587] D.P.W. Huber, R.N. Philippe, K.-A. Godard, R.N. Sturrock, and J. Bohlmann. Characterization of four terpene synthase cDNAs from methyl jasmonate-induced Douglas-fir, *Pseudotsuga menziesii*. *Phytochemistry*, 66:1427–1439, 2005.

[588] T.N. Huckerby, I.A. Nieduszynski, M. Giannopoulos, S.D. Weeks, I.H. Sadler, and R.M. Lauder. Characterization of oligosaccharides from the chondroitin/dermatan sulfates. ^{1}H-NMR and ^{13}C-NMR studies of reduced trisaccharides and hexasaccharides. *FEBS J.*, 272:6276–6286, 2005.

[589] R.E. Hurlbert and W.B. Jakoby. Tartaric acid metabolism. I. Subunits of L(+)-tartaric acid dehydrase. *J. Biol. Chem.*, 240:2772–2777, 1965.

[590] R. Hütter, P. Niederberger, and J.A. DeMoss. Tryptophan synthetic genes in eukaryotic microorganisms. *Annu. Rev. Microbiol.*, 40:55–77, 1986.

[591] D.C. Hyatt and R. Croteau. Mutational analysis of a monoterpene synthase reaction: altered catalysis through directed mutagenesis of (-)-pinene synthase from *Abies grandis*. *Arch. Biochem. Biophys.*, 439:222–233, 2005.

[592] C.C. Hyde, S.A. Ahmed, E.A. Padlan, E.W. Miles, and D.R. Davies. Three-dimensional structure of the tryptophan synthase $\alpha 2 \beta 2$ multienzyme complex from *Salmonella typhimurium*. *J. Biol. Chem.*, 263:17857–17871, 1988.

[593] J.E. Hyde, S. Dittrich, P. Wang, P.F. Sims, V. de Crecy-Lagard, and A.D. Hanson. *Plasmodium falciparum*: a paradigm for alternative folate biosynthesis in diverse microorganisms. *Trends Parasitol.*, 24:502–508, 2008.

[594] A. Ichiyama, S. Nakamura, H. Kawai, T. Honjo, Y. Nishizuka, O. Hayaishi, and S. Senoh. Studies on the metabolism of the benzene ring of tryptophan in mammalian tissues. II. Enzymic formation of α-aminomuconic acid from 3-hydroxyanthranilic acid. *J. Biol. Chem.*, 240:740–749, 1965.

[595] Y. Iijima, R. Davidovich-Rikanati, E. Fridman, D.R. Gang, E. Bar, E. Lewinsohn, and E. Pichersky. The biochemical and molecular basis for the divergent patterns in the biosynthesis of terpenes and phenylpropenes in the peltate glands of three cultivars of basil. *Plant Physiol.*, 136:3724–3736, 2004.

[596] H. Ikai and S. Yamamoto. Cloning and expression in *Escherichia coli* of the gene encoding a novel L-2,4-diaminobutyrate decarboxylase of *Acinetobacter baumannii*. *FEMS Microbiol. Lett.*, 124:225–228, 1994.

[597] H. Ikai and S. Yamamoto. Identification and analysis of a gene encoding L-2,4-diaminobutyrate:2-ketoglutarate 4-aminotransferase involved in the 1,3-diaminopropane production pathway in *Acinetobacter baumannii*. *J. Bacteriol.*, 179:5118–5125, 1997.

[598] C. Ikeda, Y. Hayashi, N. Itoh, H. Seto, and T. Dairi. Functional analysis of eubacterial *ent*-copalyl diphosphate synthase and pimara-9(11),15-diene synthase with unique primary sequences. *J. Biochem.*, 141:37–45, 2007.

[599] Y. Imanaga. Metabolism of D-glucosamine. III. Enzymic degradation of D-glucosaminic acid. *J. Biochem. (Tokyo)*, 45:647–650, 1958.

[600] M. Irie and K. Ohgi. Ribonuclease T_2. *Methods Enzymol.*, 341:42–55, 2001.

[601] S. Irmisch, S.T. Krause, G. Kunert, J. Gershenzon, J. Degenhardt, and T.G. Kollner. The organ-specific expression of terpene synthase genes contributes to the terpene hydrocarbon composition of chamomile essential oils. *BMC Plant Biol.*, 12:84–84, 2012.

[602] R.F. Irvine. The enzymology of stimulated inositol lipid turnover. *Cell Calcium*, 3:295–309, 1982.

[603] Y. Ishii, Y. Narimatsu, Y. Iwasaki, N. Arai, K. Kino, and K. Kirimura. Reversible and nonoxidative γ-resorcylic acid decarboxylase: characterization and gene cloning of a novel enzyme catalyzing carboxylation of resorcinol, 1,3-dihydroxybenzene, from *Rhizobium radiobacter*. *Biochem. Biophys. Res. Commun.*, 324:611–620, 2004.

[604] N. Ishiyama, C. Creuzenet, W.L. Miller, M. Demendi, E.M. Anderson, G. Harauz, J.S. Lam, and A.M. Berghuis. Structural studies of FlaA1 from *Helicobacter pylori* reveal the mechanism for inverting 4,6-dehydratase activity. *J. Biol. Chem.*, 281:24489–24495, 2006.

[605] J. Ito and C. Yanofsky. Anthranilate synthetase, an enzyme specified by the tryptophan operon of *Escherichia coli*: Comparative studies on the complex and the subunits. *J. Bacteriol.*, 97:734–742, 1969.

[606] A. Itoh and G.A. Howe. Molecular cloning of a divinyl ether synthase. Identification as a CYP74 cytochrome *P*-450. *J. Biol. Chem.*, 276:3620–3627, 2001.

[607] T.M. Iverson, B.E. Alber, C. Kisker, J.G. Ferry, and D.C. Rees. A closer look at the active site of γ-class carbonic anhydrases: high-resolution crystallographic studies of the carbonic anhydrase from *Methanosarcina thermophila*. *Biochemistry*, 39:9222–9231, 2000.

[608] R. Iwamoto, Y. Imanaga, and K. Soda. D-Glucosaminate dehydratase from *Agrobacterium radiobacter*. Physicochemical and enzymological properties. *J. Biochem. (Tokyo)*, 91:283–289, 1982.

[609] R. Iwamoto, H. Taniki, J. Koishi, and S. Nakura. D-Glucosaminate aldolase activity of D-glucosaminate dehydratase from *Pseudomonas fluorescens* and its requirement for Mn^{2+} ion. *Biosci. Biotechnol. Biochem.*, 59:408–411, 1995.

[610] A. Izumi, D. Rea, T. Adachi, S. Unzai, S.Y. Park, D.I. Roper, and J.R. Tame. Structure and mechanism of HpcG, a hydratase in the homoprotocatechuate degradation pathway of *Escherichia coli*. *J. Mol. Biol.*, 370:899–911, 2007.

[611] J.G. Jacobsen, L.L., Smith Thomas, , and Jr. Properties and distribution of mammalian L-cysteine sulfinate carboxy-lyases. *Biochim. Biophys. Acta*, 85:103–116, 1964.

[612] J.V. Jacobsen, M. Yamaguchi, F.D. Howard, and R.A. Bernhard. Product inhibition of the cysteine sulfoxide lyase of *Tulbaghia violacea*. *Arch. Biochem. Biophys.*, 127:252–258, 1968.

[613] T. Jaeger, M. Arsic, and C. Mayer. Scission of the lactyl ether bond of *N*-acetylmuramic acid by *Escherichia coli* ”etherase”. *J. Biol. Chem.*, 280:30100–30106, 2005.

[614] T. Jaeger and C. Mayer. *N*-acetylmuramic acid 6-phosphate lyases (MurNAc etherases): role in cell wall metabolism, distribution, structure, and mechanism. *Cell. Mol. Life Sci.*, 65:928–939, 2008.

[615] E.K. Jaffe, S. Ali, L.W. Mitchell, K.M. Taylor, M. Volin, and G.D. Markham. Characterization of the role of the stimulatory magnesium of *Escherichia coli* porphobilinogen synthase. *Biochemistry*, 34:244–251, 1995.

[616] E.K. Jaffe and S.H. Lawrence. Allostery and the dynamic oligomerization of porphobilinogen synthase. *Arch. Biochem. Biophys.*, 519:144–153, 2012.

[617] S.S. Jagtap, J.H. Hehemann, M.F. Polz, J.K. Lee, and H. Zhao. Comparative biochemical characterization of three exolytic oligoalginate lyases from *Vibrio splendidus* reveals complementary substrate scope, temperature, and pH adaptations. *Appl. Environ. Microbiol.*, 80:4207–4214, 2014.

[618] W.B. Jakoby, E. Ohmura, and O. Hayaishi. Enzymatic decarboxylation of oxalic acid. *J. Biol. Chem.*, 222:435–446, 1956.

[619] K.H. Jang, E.J. Ryu, B.S. Park, K.B. Song, S.A. Kang, C.H. Kim, T.B. Uhm, Y.I., Rhee Park, , and J. 17-21 catalyzes the formation of the di-D-fructose dianhydride IV from levan. *J. Agric. Food Chem.*, 51:2632–2636, 2003.

[620] S. Jang and J.A. Imlay. Micromolar intracellular hydrogen peroxide disrupts metabolism by damaging iron-sulfur enzymes. *J. Biol. Chem.*, 282:929–937, 2007.

[621] D. Jani, R. Nagarkatti, W. Beatty, R. Angel, C. Slebodnick, J. Andersen, S. Kumar, and D. Rathore. HDP-a novel heme detoxification protein from the malaria parasite. *PLoS Pathog.*, 4:e1000053–e1000053, 2008.

[622] R. Janke, C. Gorner, M. Hirte, T. Bruck, and B. Loll. The first structure of a bacterial diterpene cyclase: CotB2. *Acta Crystallogr. D Biol. Crystallogr.*, 70:1528–1537, 2014.

[623] J.A. Jedziniak and F.J. Lionetti. Purification and properties of deoxyriboaldolase from human erythrocytes. *Biochim. Biophys. Acta*, 212:478–487, 1970.

[624] R. Jeffcoat, H. Hassall, and S. Dagley. Purification and properties of D-4-deoxy-5-oxoglucarate hydro-lyase (decarboxylating). *Biochem. J.*, 115:977–983, 1969.

[625] I.-M. Jeng, , and H.A. Purification and properties of L-3-aminobutyryl coenzyme A deaminase from a lysine-fermenting *Clostridium*. *J. Biol. Chem.*, 249:6578–6584, 1974.

[626] M.H. Jensen, H. Otten, U. Christensen, T.V. Borchert, L.L. Christensen, S. Larsen, and L.L. Leggio. Structural and biochemical studies elucidate the mechanism of rhamnogalacturonan lyase from *Aspergillus aculeatus*. *J. Mol. Biol.*, 404:100–111, 2010.

[627] J.W. Jia, J. Crock, S. Lu, R. Croteau, and X.Y. Chen. (3*R*)-Linalool synthase from *Artemisia annua* L.: cDNA isolation, characterization, and wound induction. *Arch. Biochem. Biophys.*, 372:143–149, 1999.

[628] Y. Jia, T. Tomita, K. Yamauchi, M. Nishiyama, and D.R. Palmer. Kinetics and product analysis of the reaction catalysed by recombinant homoaconitase from *Thermus thermophilus*. *Biochem. J.*, 396:479–485, 2006.

[629] J. Jiang, X. He, and D.E. Cane. Geosmin biosynthesis. *Streptomyces coelicolor* germacradienol/germacrene D synthase converts farnesyl diphosphate to geosmin. *J. Am. Chem. Soc.*, 128:8128–8129, 2006.

[630] J. Jiang, X. He, and D.E. Cane. Biosynthesis of the earthy odorant geosmin by a bifunctional *Streptomyces coelicolor* enzyme. *Nat. Chem. Biol.*, 3:711–715, 2007.

[631] M. Jiang, Y. Cao, Z.F. Guo, M. Chen, X. Chen, and Z. Guo. Menaquinone biosynthesis in *Escherichia coli*: identification of 2-succinyl-5-enolpyruvyl-6-hydroxy-3-cyclohexene-1-carboxylate as a novel intermediate and re-evaluation of MenD activity. *Biochemistry*, 46:10979–10989, 2007.

[632] M. Jiang, X. Chen, Z.F. Guo, Y. Cao, M. Chen, and Z. Guo. Identification and characterization of (1*R*,6*R*)-2-succinyl-6-hydroxy-2,4-cyclohexadiene-1-carboxylate synthase in the menaquinone biosynthesis of *Escherichia coli*. *Biochemistry*, 47:3426–3434, 2008.

[633] Y. Jiang, H. Wang, C. Lu, Y. Ding, Y. Li, and Y. Shen. Identification and characterization of the cuevaene A biosynthetic gene cluster in *Streptomyces* sp. LZ35. *ChemBioChem*, 14:1468–1475, 2013.

[634] N. Jimenez, J.A. Curiel, I. Reveron, B. de Las Rivas, and R. Munoz. Uncovering the *Lactobacillus plantarum* WCFS1 gallate decarboxylase involved in tannin degradation. *Appl. Environ. Microbiol.*, 79:4253–4263, 2013.

[635] B. Jin, G. Cui, J. Guo, J. Tang, L. Duan, H. Lin, Y. Shen, T. Chen, H. Zhang, and L. Huang. Functional diversification of kaurene synthase-like genes in *Isodon rubescens*. *Plant Physiol.*, 174:943–955, 2017.

[636] J. Jin, M.J. Kim, S. Dhandapani, J.G. Tjhang, J.L. Yin, L. Wong, R. Sarojam, N.H. Chua, and I.C. Jang. The floral transcriptome of ylang ylang (*Cananga odorata* var. *fruticosa*) uncovers biosynthetic pathways for volatile organic compounds and a multifunctional and novel sesquiterpene synthase. *J. Exp. Bot.*, 66:3959–3975, 2015.

[637] B. Jochimsen, S. Lolle, F.R. McSorley, M. Nabi, J. Stougaard, D.L. Zechel, and B. Hove-Jensen. Five phosphonate operon gene products as components of a multi-subunit complex of the carbon-phosphorus lyase pathway. *Proc. Natl. Acad. Sci. USA*, 108:11393–11398, 2011.

[638] U. Johnsen, M. Dambeck, H. Zaiss, T. Fuhrer, J. Soppa, U. Sauer, and P. Schonheit. D-Xylose degradation pathway in the halophilic archaeon *Haloferax volcanii*. *J. Biol. Chem.*, 284:27290–27303, 2009.

[639] T.W. Johnson, G. Shen, B. Zybailov, D. Kolling, R. Reategui, S. Beauparlant, I.R. Vassiliev, D.A. Bryant, A.D. Jones, J.H. Golbeck, and P.R. Chitnis. Recruitment of a foreign quinone into the A(1) site of photosystem I. I. Genetic and physiological characterization of phylloquinone biosynthetic pathway mutants in *Synechocystis* sp. PCC 6803. *J. Biol. Chem.*, 275:8523–8530, 2000.

[640] W.H. Johnson, Hajipour Jr., Whitman G., and C.P. Characterization of a dienol intermediate in the 5-(carboxymethyl)-2-oxo-3-hexene-1,6-dioate decarboxylase reaction. *J. Am. Chem. Soc.*, 114:11001–11003, 1992.

[641] W.H. Johnson, Hajipour Jr., Whitman G., and C.P. Stereochemical studies of 5-(carboxymethyl)-2-hydroxymuconate isomerase and 5-(carboxymethyl)-2-oxo-3-hexene-1,6-dioate decarboxylase from *Escherichia coli C*: mechanistic and evolutionary implications. *J. Am. Chem. Soc.*, 117:8719–8726, 1995.

[642] W.V. Johnson and P.M. Anderson. Bicarbonate is a recycling substrate for cyanase. *J. Biol. Chem.*, 262:9021–9025, 1987.

[643] A. Jones, A. Faulkner, and J.M. Turner. Microbial metabolism of amino alcohols. Metabolism of ethanolamine and 1-aminopropan-2-ol in species of *Erwinia* and the roles of amino alcohol kinase and amino alcohol *o*-phosphate phospholyase in aldehyde formation. *Biochem. J.*, 134:959–968, 1973.

[644] C.G. Jones, C.I. Keeling, E.L. Ghisalberti, E.L. Barbour, J.A. Plummer, and J. Bohlmann. Isolation of cDNAs and functional characterisation of two multi-product terpene synthase enzymes from sandalwood, *Santalum album* L. *Arch. Biochem. Biophys.*, 477:121–130, 2008.

[645] C.G. Jones, J. Moniodis, K.G. Zulak, A. Scaffidi, J.A. Plummer, E.L. Ghisalberti, E.L. Barbour, and J. Bohlmann. Sandalwood fragrance biosynthesis involves sesquiterpene synthases of both the terpene synthase (TPS)-a and TPS-b subfamilies, including santalene synthases. *J. Biol. Chem.*, 286:17445–17454, 2011.

[646] M.E. Jones, P.R. Kavipurapu, and T.W. Traut. Orotate phosphoribosyltransferase: orotidylate decarboxylase (Ehrlich ascites cell). *Methods Enzymol.*, 51:155–167, 1978.

[647] P.R. Jones, T. Manabe, M. Awazuhara, and K. Saito. A new member of plant CS-lyases. A cystine lyase from *Arabidopsis thaliana*. *J. Biol. Chem.*, 278:10291–10296, 2003.

[648] J. Ju, S.G. Ozanick, B. Shen, and M.G. Thomas. Conversion of (2*S*)-arginine to (2*S*,3*R*)-capreomycidine by VioC and VioD from the viomycin biosynthetic pathway of *Streptomyces* sp. strain ATCC11861. *ChemBioChem*, 5:1281–1285, 2004.

[649] F. Jullien, S. Moja, A. Bony, S. Legrand, C. Petit, T. Benabdelkader, K. Poirot, S. Fiorucci, Y. Guitton, F. Nicole, S. Baudino, and J.L. Magnard. Isolation and functional characterization of a τ-cadinol synthase, a new sesquiterpene synthase from *Lavandula angustifolia*. *Plant Mol. Biol.*, 84:227–241, 2014.

[650] L.J. Jung, C.F. Chan, and A.N. Glazer. Candidate genes for the phycoerythrocyanin α subunit lyase. Biochemical analysis of *pecE* and *pecF* interposon mutants. *J. Biol. Chem.*, 270:12877–12884, 1995.

[651] M. Junghare, D. Spiteller, and B. Schink. Anaerobic degradation of xenobiotic isophthalate by the fermenting bacterium Syntrophorhabdus aromaticivorans. *ISME J.*, 13:1252–1268, 2019.

[652] R. Kadirvelraj, P. Harris, J.C. Poulsen, S. Kauppinen, and S. Larsen. A stepwise optimization of crystals of rhamnogalacturonan lyase from *Aspergillus aculeatus*. *Acta Crystallogr. D Biol. Crystallogr.*, 58:1346–1349, 2002.

[653] T. Kakimoto, J. Kato, T. Shibitani, N. Nishimura, and I. Chibata. Crystalline L-aspartate β-decarboxylase of *Pseudomonas dacunhae*. I. Crystallization and some physiocochemical properties. *J. Biol. Chem.*, 244:353–358, 1969.

[654] R.E. Kallio. Function of pyridoxal phosphate in desulfhydrase systems of *Proteus morganii*. *J. Biol. Chem.*, 192:371–377, 1951.

[655] S.S. Kamat, H.J. Williams, and F.M. Raushel. Intermediates in the transformation of phosphonates to phosphate by bacteria. *Nature*, 480:570–573, 2011.

[656] Y. Kaminaga, J. Schnepp, G. Peel, C.M. Kish, G. Ben-Nissan, D. Weiss, I. Orlova, O. Lavie, D. Rhodes, K. Wood, D.M. Porterfield, A.J. Cooper, J.V. Schloss, E. Pichersky, A. Vainstein, and N. Dudareva. Plant phenylacetaldehyde synthase is a bifunctional homotetrameric enzyme that catalyzes phenylalanine decarboxylation and oxidation. *J. Biol. Chem.*, 281:23357–23366, 2006.

[657] E. Kaminskas, Y. Kimhi, and B. Magasanik. Urocanase and *N*-formimino-L-glutamate formiminohydrolase of *Bacillus subtilis*, two enzymes of the histidine degradation pathway. *J. Biol. Chem.*, 245:3536–3544, 1970.

[658] J. Kamsteeg, J. van Brederode, and G. van Nigtevecht. The formation of UDP-L-rhamnose from UDP-D-glucose by an enzyme preparation of red campion (*Silene dioica* (L) Clairv) leaves. *FEBS Lett.*, 91:281–284, 1978.

[659] S. Kanamasa, L. Dwiarti, M. Okabe, and E.Y. Park. Cloning and functional characterization of the *cis*-aconitic acid decarboxylase (CAD) gene from *Aspergillus terreus*. *Appl. Microbiol. Biotechnol.*, 80:223–229, 2008.

[660] M. Kanamori and R.L. Wixom. Studies in valine biosynthesis. V. Characteristics of the purified dihydroxyacid dehydratase from spinach leaves. *J. Biol. Chem.*, 238:998–1005, 1963.

[661] L. Kanarek and R.L. Hill. The preparation and characterization of fumarase from swine heart muscle. *J. Biol. Chem.*, 239:4202–4206, 1964.

[662] J. Kanfer and E.P. Kennedy. Metabolism and function of bacterial lipids. II. Biosynthesis of phospholipids in *Escherichia coli*. *J. Biol. Chem.*, 239:1720–1726, 1964.

[663] K.K. Kannan, M. Ramanadham, and T.A. Jones. Structure, refinement, and function of carbonic anhydrase isozymes: refinement of human carbonic anhydrase I. *Ann. N.Y. Acad. Sci.*, 429:49–60, 1984.

[664] T. Kanno, K. Kasai, Y. Ikejiri-Kanno, K. Wakasa, and Y. Tozawa. *In vitro* reconstitution of rice anthranilate synthase: distinct functional properties of the α subunits OASA1 and OASA2. *Plant Mol. Biol.*, 54:11–22, 2004.

[665] Y. Kanno, K. Otomo, H. Kenmoku, W. Mitsuhashi, H. Yamane, H. Oikawa, H. Toshima, M. Matsuoka, T. Sassa, and T. Toyomasu. Characterization of a rice gene family encoding type-A diterpene cyclases. *Biosci. Biotechnol. Biochem.*, 70:1702–1710, 2006.

[666] B.H. Kaplan and E.R. Stadtman. Ethanolamine deaminase, a cobamide coenzyme-dependent enzyme. I. Purification, assay, and properties of the enzyme. *J. Biol. Chem.*, 243:1787–1793, 1968.

[667] M.A. Karasek and D.M. Greenberg. Studies on the properties of threonine aldolases. *J. Biol. Chem.*, 227:191–205, 1957.

[668] W.E. Karsten, S.A. Nimmo, J. Liu, and L. Chooback. Identification of 2,3-dihydrodipicolinate as the product of the dihydrodipicolinate synthase reaction from *Escherichia coli*. *Arch. Biochem. Biophys.*, 653:50–62, 2018.

[669] D. Kasai, N. Araki, K. Motoi, S. Yoshikawa, T. Iino, S. Imai, E. Masai, and M. Fukuda. γ-Resorcylate catabolic-pathway genes in the soil actinomycete *Rhodococcus jostii* RHA1. *Appl. Environ. Microbiol.*, 81:7656–7665, 2015.

[670] D. Kasai, T. Fujinami, T. Abe, K. Mase, Y. Katayama, M. Fukuda, and E. Masai. Uncovering the protocatechuate 2,3-cleavage pathway genes. *J. Bacteriol.*, 191:6758–6768, 2009.

[671] K. Kasai, T. Uchida, F. Egami, K. Yoshida, and M. Nomoto. Purification and crystallization of ribonuclease N_1 from *Neurospora crassa*. *J. Biochem. (Tokyo)*, 66:389–396, 1969.

[672] M. Kataoka, M. Ikemi, T. Morikawa, T. Miyoshi, K. Nishi, M. Wada, H. Yamada, and S. Shimizu. Isolation and characterization of D-threonine aldolase, a pyridoxal-5′-phosphate-dependent enzyme from *Arthrobacter sp*. DK-38. *Eur. J. Biochem.*, 248:385–393, 1997.

[673] M. Kataoka, M. Wada, K. Nishi, H. Yamada, and S. Shimizu. Purification and characterization of L-*allo*-threonine aldolase from *Aeromonas jandaei* DK-39. *FEMS Microbiol. Lett.*, 151:245–248, 1997.

[674] A.G. Katapodis, D. Ping, and S.W. May. A novel enzyme from bovine neurointermediate pituitary catalyzes dealkylation of α-hydroxyglycine derivatives, thereby functioning sequentially with peptidylglycine α-amidating monooxygenase in peptide amidation. *Biochemistry*, 29:6115–6120, 1990.

[675] N. Kato, N. Miyamoto, M. Shimao, and C. Sakazawa. 3-Hexulose phosphate pynthase from a new facultative methylotroph, *Mycobacterium gastri* MB19. *Agric. Biol. Chem.*, 52:2659–2661, 1988.

[676] N. Kato, H. Ohashi, Y. Tani, and K. Ogata. 3-Hexulosephosphate synthase from *Methylomonas aminofaciens* 77a. Purification, properties and kinetics. *Biochim. Biophys. Acta*, 523:236–244, 1978.

[677] N. Kato, H. Yurimoto, and R.K. Thauer. The physiological role of the ribulose monophosphate pathway in bacteria and archaea. *Biosci. Biotechnol. Biochem.*, 70:10–21, 2006.

[678] Y. Kato, K. Nakamura, H. Sakiyama, S.G. Mayhew, and Y. Asano. Novel heme-containing lyase, phenylacetaldoxime dehydratase from *Bacillus* sp. strain OxB-1: purification, characterization, and molecular cloning of the gene. *Biochemistry*, 39:800–809, 2000.

[679] Y. Kato, K. Shoji, M. Ubukata, K. Shigetomi, Y. Sato, N. Nakajima, and S. Ogita. Purification and characterization of a tuliposide-converting enzyme from bulbs of *Tulipa gesneriana*. *Biosci. Biotechnol. Biochem.*, 73:1895–1897, 2009.

[680] Y. Kato, S. Yoshida, S.-X. Xie, and Y. Asano. Aldoxime dehydratase co-existing with nitrile hydratase and amidase in the iron-type nitrile hydratase-producer *Rhodococcus* sp. *N*-771. *J. Biosci. Bioeng.*, 97:250–259, 2004.

[681] A. Kaur, R. Gautam, R. Srivastava, A. Chandel, A. Kumar, S. Karthikeyan, and A.K. Bachhawat. $ChaC_2$, an enzyme for slow turnover of cytosolic glutathione. *J. Biol. Chem.*, 292:638–651, 2017.

[682] H. Kawaide, R. Imai, T. Sassa, and Y. Kamiya. *Ent*-kaurene synthase from the fungus *Phaeosphaeria* sp. L487. cDNA isolation, characterization, and bacterial expression of a bifunctional diterpene cyclase in fungal gibberellin biosynthesis. *J. Biol. Chem.*, 272:21706–21712, 1997.

[683] K.M. Kean, S.J. Codding, S. Asamizu, T. Mahmud, and P.A. Karplus. Structure of a sedoheptulose 7-phosphate cyclase: ValA from *Streptomyces hygroscopicus*. *Biochemistry*, 53:4250–4260, 2014.

[684] A. Keck, D. Conradt, A. Mahler, A. Stolz, R. Mattes, and J. Klein. Identification and functional analysis of the genes for naphthalenesulfonate catabolism by *Sphingomonas xenophaga* BN6. *Microbiology*, 152:1929–1940, 2006.

[685] D. Keilin and T. Mann. Carbonic anhydrase. *Nature*, 144:442–443, 1939.

[686] H. Keller, P. Czernic, M. Ponchet, P.H. Ducrot, K. Back, J. Chappell, P. Ricci, and Y. Marco. Sesquiterpene cyclase is not a determining factor for elicitor- and pathogen-induced capsidiol accumulation in tobacco. *Planta*, 205:467–476, 1998.

[687] M.J. Kelly, L.J. Ball, C. Krieger, Y. Yu, M. Fischer, S. Schiffmann, P. Schmieder, R. Kühne, W. Bermel, A. Bacher, G. Richter, and H. Oschkinat. The NMR structure of the 47-kDa dimeric enzyme 3,4-dihydroxy-2-butanone-4-phosphate synthase and ligand binding studies reveal the location of the active site. *Proc. Natl. Acad. Sci. USA*, 98:13025–13030, 2001.

[688] T. Kentache, L. Thabault, G. Deumer, V. Haufroid, R. Frederick, C.L. Linster, A. Peracchi, M. Veiga da Cunha, G.T. Bommer, and E. Van Schaftingen. The metalloprotein YhcH is an anomerase providing *N*-acetylneuraminate aldolase with the open form of its substrate. *J. Biol. Chem.*, pages 100699–100699, 2021.

[689] O. Kerbarh, A. Ciulli, N.I. Howard, and C. Abell. Salicylate biosynthesis: overexpression, purification, and characterization of Irp9, a bifunctional salicylate synthase from *Yersinia enterocolitica*. *J. Bacteriol.*, 187:5061–5066, 2005.

[690] H.C.M Kester and J. Visser. Purification and characterization of pectin lyase B, a novel pectinolytic enzyme from *Aspergillus niger*. *FEMS Microbiol. Lett.*, 120:63–68, 1994.

[691] A. Keszei, C.L. Brubaker, R. Carter, T. Kollner, J. Degenhardt, and W.J. Foley. Functional and evolutionary relationships between terpene synthases from Australian Myrtaceae. *Phytochemistry*, 71:844–852, 2010.

[692] E.A. Khairallah and G. Wolf. Carnitine decarboxylase. The conversion of carnitine to β-methylcholine. *J. Biol. Chem.*, 242:32–39, 1967.

[693] B. Khaliullin, R. Ayikpoe, M. Tuttle, and J.A. Latham. Mechanistic elucidation of the mycofactocin-biosynthetic radical *S*-adenosylmethionine protein, MftC. *J. Biol. Chem.*, 292:13022–13033, 2017.

[694] L.E. Khaw, G.A. Bohm, S. Metcalfe, J. Staunton, and P.F. Leadlay. Mutational biosynthesis of novel rapamycins by a strain of *Streptomyces hygroscopicus* NRRL 5491 disrupted in *rapL*, encoding a putative lysine cyclodeaminase. *J. Bacteriol.*, 180:809–814, 1998.

[695] A. Kihara, H. Sakuraba, M. Ikeda, A. Denpoh, and Y. Igarashi. Membrane topology and essential amino acid residues of Phs1, a 3-hydroxyacyl-CoA dehydratase involved in very long-chain fatty acid elongation. *J. Biol. Chem.*, 283:11199–11209, 2008.

[696] C.G. Kim, T.W. Yu, C.B. Fryhle, S. Handa, and H.G. Floss. 3-Amino-5-hydroxybenzoic acid synthase, the terminal enzyme in the formation of the precursor of mC_7N units in rifamycin and related antibiotics. *J. Biol. Chem.*, 273:6030–6040, 1998.

[697] H.T. Kim, J.H. Chung, D. Wang, J. Lee, H.C. Woo, I.G. Choi, and K.H. Kim. Depolymerization of alginate into a monomeric sugar acid using Alg17C, an exo-oligoalginate lyase cloned from *Saccharophagus degradans* 2-40. *Appl. Microbiol. Biotechnol.*, 93:2233–2239, 2012.

[698] J. Kim, D. Darley, and W. Buckel. 2-Hydroxyisocaproyl-CoA dehydratase and its activator from *Clostridium difficile*. *FEBS J.*, 272:550–561, 2005.

[699] J. Kim, D.J. Darley, W. Buckel, and A.J. Pierik. An allylic ketyl radical intermediate in clostridial amino-acid fermentation. *Nature*, 452:239–242, 2008.

[700] J. Kim, M. Hetzel, C.D. Boiangiu, and W. Buckel. Dehydration of (*R*)-2-hydroxyacyl-CoA to enoyl-CoA in the fermentation of α-amino acids by anaerobic bacteria. *FEMS Microbiol. Rev.*, 28:455–468, 2004.

[701] J. Kim, J.P. Kershner, Y. Novikov, R.K. Shoemaker, and S.D. Copley. Three serendipitous pathways in *E. coli* can bypass a block in pyridoxal-5′-phosphate synthesis. *Mol. Syst. Biol.*, 6:436–436, 2010.

[702] K. Kim, J. Park, and S. Rhee. Structural and functional basis for (*S*)-allantoin formation in the ureide pathway. *J. Biol. Chem.*, 282:23457–23464, 2007.

[703] S.Y. Kim, P. Zhao, M. Igarashi, R. Sawa, T. Tomita, M. Nishiyama, and T. Kuzuyama. Cloning and heterologous expression of the cyclooctatin biosynthetic gene cluster afford a diterpene cyclase and two P450 hydroxylases. *Chem. Biol.*, 16:736–743, 2009.

[704] Y.S. Kim. Malonate metabolism: biochemistry, molecular biology, physiology, and industrial application. *J. Biochem. Mol. Biol.*, 35:443–451, 2002.

[705] T. Kinoshita, M. Miyata, S.M. Ismail, Y. Fujimoto, K. Kakinuma, N.I. Kokawa, and M. Morisaki. Synthesis and determination of stereochemistry of four diastereoisomers at the C-24 and C-25 positions of 3α,7α,12α,24-tetrahydroxy-5β-cholestan-26-oic acid and cholic acid. *Chem. Pharm. Bull.*, 36:134–141, 1988.

[706] K. Kirimura, H. Gunji, R. Wakayama, T. Hattori, and Y. Ishii. Enzymatic Kolbe-Schmitt reaction to form salicylic acid from phenol: enzymatic characterization and gene identification of a novel enzyme, *Trichosporon moniliiforme* salicylic acid decarboxylase. *Biochem. Biophys. Res. Commun.*, 394:279–284, 2010.

[707] S. Kishimoto, K. Hara, H. Hashimoto, Y. Hirayama, P.A. Champagne, K.N. Houk, Y. Tang, and K. Watanabe. Enzymatic one-step ring contraction for quinolone biosynthesis. *Nat. Commun.*, 9:2826–2826, 2018.

[708] R. Kissen and A.M. Bones. Nitrile-specifier proteins involved in glucosinolate hydrolysis in *Arabidopsis thaliana*. *J. Biol. Chem.*, 284:12057–12070, 2009.

[709] T.A. Klapschinski, P. Rabe, and J.S. Dickschat. Pristinol, a sesquiterpene alcohol with an unusual skeleton from *Streptomyces pristinaespiralis*. *Angew. Chem. Int. Ed. Engl.*, 55:10141–10144, 2016.

[710] T.J. Klem and V.J. Davisson. Imidazole glycerol phosphate synthase: the glutamine amidotransferase in histidine biosynthesis. *Biochemistry*, 32:5177–5186, 1993.

[711] N. Klempier and H. Griengl. Aliphatic (*S*)-cyanohydrins by enzyme catalyzed synthesis. *Tetrahedron Lett.*, 34:4769–4772, 1993.

[712] V.A. Klenchin, E.A. Taylor Ringia, J.A. Gerlt, and I. Rayment. Evolution of enzymatic activity in the enolase superfamily: structural and mutagenic studies of the mechanism of the reaction catalyzed by *o*-succinylbenzoate synthase from *Escherichia coli*. *Biochemistry*, 42:14427–14433, 2003.

[713] L.D. Kluskens, G.J. van Alebeek, A.G. Voragen, W.M. de Vos, and J. van der Oost. Molecular and biochemical characterization of the thermoactive family 1 pectate lyase from the hyperthermophilic bacterium *Thermotoga maritima*. *Biochem. J.*, 370:651–659, 2003.

[714] S.H. Knauer, W. Buckel, and H. Dobbek. Structural basis for reductive radical formation and electron recycling in (*R*)-2-hydroxyisocaproyl-CoA dehydratase. *J. Am. Chem. Soc.*, 133:4342–4347, 2011.

[715] B. Kneidinger, M. Graninger, G. Adam, M. Puchberger, P. Kosma, S. Zayni, and P. Messner. Identification of two GDP-6-deoxy-D-*lyxo*-4-hexulose reductases synthesizing GDP-D-rhamnose in *Aneurinibacillus thermoaerophilus* L420-91^T. *J. Biol. Chem.*, 276:5577–5583, 2001.

[716] T. Knill, M. Reichelt, C. Paetz, J. Gershenzon, and S. Binder. *Arabidopsis thaliana* encodes a bacterial-type heterodimeric isopropylmalate isomerase involved in both Leu biosynthesis and the Met chain elongation pathway of glucosinolate formation. *Plant Mol. Biol.*, 71:227–239, 2009.

[717] K. Kobayashi, S. Yoshioka, Y. Kato, Y. Asano, and S. Aono. Regulation of aldoxime dehydratase activity by redox-dependent change in the coordination structure of the aldoxime-heme complex. *J. Biol. Chem.*, 280:5486–5490, 2005.

[718] R.D. Kobes and E.E. Dekker. 2-Keto-4-hydroxyglutarate aldolase of bovine liver. Purification, criteria of purity, and general properties. *J. Biol. Chem.*, 244:1919–1925, 1969.

[719] J. Koch, W. Eisenreich, A. Bacher, and G. Fuchs. Products of enzymatic reduction of benzoyl-CoA, a key reaction in anaerobic aromatic metabolism. *Eur. J. Biochem.*, 211:649–661, 1993.

[720] A.E. Koepp, M. Hezari, J. Zajicek, B.S. Vogel, R.E. LaFever, N.G. Lewis, and R. Croteau. Cyclization of geranylgeranyl diphosphate to taxa-4(5),11(12)-diene is the committed step of taxol biosynthesis in Pacific yew. *J. Biol. Chem.*, 270:8686–8690, 1995.

[721] J. Koga. Structure and function of indolepyruvate decarboxylase, a key enzyme in indole-3-pyruvic acid biosynthesis. *Biochim. Biophys. Acta*, 1249:1–13, 1995.

[722] A.C. Kohl and R.G. Kerr. Identification and characterization of the pseudopterosin diterpene cyclase, elisabethatriene synthase, from the marine gorgonian, *Pseudopterogorgia elisabethae*. *Arch. Biochem. Biophys.*, 424:97–104, 2004.

[723] D. Kohler-Staub and T. Leisinger. Dichloromethane dehalogenase of *Hyphomicrobium* sp. strain DM2. *J. Bacteriol.*, 162:676–681, 1985.

[724] R. Kolkmann and E. Leistner. 4-(2′-Carboxyphenyl)-4-oxobutyryl coenzyme A ester, an intermediate in vitamin K_2 (menaquinone) biosynthesis. *Z. Naturforsch. C: Sci.*, 42:1207–1214, 1987.

[725] A. Kollmann-Koch and H. Eggerer. Nicotinic acid metabolism. Dimethylmaleate hydratase. *Hoppe-Seyler's Z. Physiol. Chem.*, 365:847–857, 1984.

[726] T.G. Kollner, J. Gershenzon, and J. Degenhardt. Molecular and biochemical evolution of maize terpene synthase 10, an enzyme of indirect defense. *Phytochemistry*, 70:1139–1145, 2009.

[727] T.G. Köllner, C. Schnee, J. Gershenzon, and J. Degenhardt. The variability of sesquiterpenes emitted from two *Zea mays* cultivars is controlled by allelic variation of two terpene synthase genes encoding stereoselective multiple product enzymes. *Plant Cell*, 16:1115–1131, 2004.

[728] H. Komai and J.B. Neilands. The metalloprotein nature of *Ustilago* δ-aminolevulinate dehydratase. *Biochim. Biophys. Acta*, 171:311–320, 1969.

[729] M. Komatsu, M. Tsuda, S. Omura, H. Oikawa, and H. Ikeda. Identification and functional analysis of genes controlling biosynthesis of 2-methylisoborneol. *Proc. Natl. Acad. Sci. USA*, 105:7422–7427, 2008.

[730] T. Kondo, M. Kichijo, A. Maruta, M. Nakaya, S. Takenaka, T. Arakawa, S. Fushinobu, and T. Sakamoto. Structural and functional analysis of gum arabic L-rhamnose-α-1,4-D-glucuronate lyase establishes a novel polysaccharide lyase family. *J. Biol. Chem.*, 297:101001–101001, 2021.

[731] J.H. Koo and Y.S. Kim. Functional evaluation of the genes involved in malonate decarboxylation by *Acinetobacter calcoaceticus*. *Eur. J. Biochem.*, 266:683–690, 1999.

[732] D. Köpke, R. Schröder, H.M. Fischer, J. Gershenzon, M. Hilker, and A. Schmidt. Does egg deposition by herbivorous pine sawflies affect transcription of sesquiterpene synthases in pine? *Planta*, 228:427–438, 2008.

[733] K.M. Koski, A.M. Haapalainen, J.K. Hiltunen, and T. Glumoff. Crystal structure of 2-enoyl-CoA hydratase 2 from human peroxisomal multifunctional enzyme type 2. *J. Mol. Biol.*, 345:1157–1169, 2005.

[734] M.K. Koski, A.M. Haapalainen, J.K. Hiltunen, and T. Glumoff. Crystallization and preliminary crystallographic data of 2-enoyl-CoA hydratase 2 domain of *Candida tropicalis* peroxisomal multifunctional enzyme type 2. *Acta Crystallogr. D Biol. Crystallogr.*, 59:1302–1305, 2003.

[735] J. Koukol and E.E. Conn. The metabolism of aromatic compounds in higher plants. IV. Purification and properties of the phenylalanine deaminase of *Hordeum vulgare*. *J. Biol. Chem.*, 236:2692–2698, 1961.

[736] E.I. Kozliak, J.A. Fuchs, M.B. Guilloton, and P.M. Anderson. Role of bicarbonate/CO_2 in the inhibition of *Escherichia coli* growth by cyanate. *J. Bacteriol.*, 177:3213–3219, 1995.

[737] G. Krakow and S.S. Barkulis. Conversion of glyoxylate to hydroxypyruvate by extracts of *Escherichia coli*. *Biochim. Biophys. Acta*, 21:593–594, 1956.

[738] W. Kreis and C. Hession. Isolation and purification of L-methionine-α-deamino-γ-mercaptomethane-lyase (L-methioninase) from *Clostridium sporogenes*. *Cancer Res.*, 33:1862–1865, 1973.

[739] M. Kriek, F. Martins, M.R. Challand, A. Croft, and P.L. Roach. Thiamine biosynthesis in *Escherichia coli*: identification of the intermediate and by-product derived from tyrosine. *Angew. Chem. Int. Ed. Engl.*, 46:9223–9226, 2007.

[740] M. Kriek, F. Martins, R. Leonardi, S.A. Fairhurst, D.J. Lowe, and P.L. Roach. Thiazole synthase from *Escherichia coli*: an investigation of the substrates and purified proteins required for activity *in vitro*. *J. Biol. Chem.*, 282:17413–17423, 2007.

[741] C.M. Kronfel, A. Biswas, J.P. Frick, A. Gutu, T. Blensdorf, J.A. Karty, D.M. Kehoe, and W.M. Schluchter. The roles of the chaperone-like protein CpeZ and the phycoerythrobilin lyase CpeY in phycoerythrin biogenesis. *Biochim Biophys Acta Bioenerg*, 1860:S0005–2728(–S0005–2728(, 2019.

[742] C.M. Kronfel, C.V. Hernandez, J.P. Frick, L.S. Hernandez, A. Gutu, J.A. Karty, M.N. Boutaghou, D.M. Kehoe, R.B. Cole, and W.M. Schluchter. CpeF is the bilin lyase that ligates the doubly linked phycoerythrobilin on β-phycoerythrin in the cyanobacterium *Fremyella diplosiphon*. *J. Biol. Chem.*, 294:3987–3999, 2019.

[743] J.G. Krum, H. Ellsworth, R.R. Sargeant, G. Rich, and S.A. Ensign. Kinetic and microcalorimetric analysis of substrate and cofactor interactions in epoxyalkane:CoM transferase, a zinc-dependent epoxidase. *Biochemistry*, 41:5005–5014, 2002.

[744] J.C. Kuchernig, A. Backenkohler, M. Lubbecke, M. Burow, and U. Wittstock. A thiocyanate-forming protein generates multiple products upon allylglucosinolate breakdown in *Thlaspi arvense*. *Phytochemistry*, 72:1699–1709, 2011.

[745] R.D. Kuchta and R.H. Abeles. Lactate reduction in *Clostridium propionicum*. Purification and properties of lactyl-CoA dehydratase. *J. Biol. Chem.*, 260:13181–13189, 1985.

[746] R.D. Kuchta, G.R. Hanson, B. Holmquist, and R.H. Abeles. Fe-S centers in lactyl-CoA dehydratase. *Biochemistry*, 25:7301–7307, 1986.

[747] F. Kudo, Y. Hosomi, H. Tamegai, and K. Kakinuma. Purification and characterization of 2-deoxy-*scyllo*-inosose synthase derived from *Bacillus circulans*. A crucial carbocyclization enzyme in the biosynthesis of 2-deoxystreptamine-containing aminoglycoside antibiotics. *J. Antibiot. (Tokyo)*, 52:81–88, 1999.

[748] F. Kudo, Y. Matsuura, T. Hayashi, M. Fukushima, and T. Eguchi. Genome mining of the sordarin biosynthetic gene cluster from *Sordaria araneosa* Cain ATCC 36386: characterization of cycloaraneosene synthase and GDP-6-deoxyaltrose transferase. *J. Antibiot. (Tokyo)*, 69:541–548, 2016.

[749] F. Kudo, H. Tamegai, T. Fujiwara, U. Tagami, K. Hirayama, and K. Kakinuma. Molecular cloning of the gene for the key carbocycle-forming enzyme in the biosynthesis of 2-deoxystreptamine-containing aminocyclitol antibiotics and its comparison with dehydroquinate synthase. *J. Antibiot. (Tokyo)*, 52:559–571, 1999.

[750] F. Kudo, N. Yamauchi, R. Suzuki, and K. Kakinuma. Kinetic isotope effect and reaction mechanism of 2-deoxy-*scyllo*-inosose synthase derived from butirosin-producing *Bacillus circulans*. *J. Antibiot. (Tokyo)*, 50:424–428, 1997.

[751] A.U. Kuhlmann and E. Bremer. Osmotically regulated synthesis of the compatible solute ectoine in *Bacillus pasteurii* and related *Bacillus* spp. *Appl. Environ. Microbiol.*, 68:772–783, 2002.

[752] A.E. Kuhm, H.J. Knackmuss, and A. Stolz. Purification and properties of 2′-hydroxybenzalpyruvate aldolase from a bacterium that degrades naphthalenesulfonates. *J. Biol. Chem.*, 268:9484–9489, 1993.

[753] M. Kuhner, K. Haufschildt, A. Neumann, S. Storbeck, J. Streif, and G. Layer. The alternative route to heme in the methanogenic archaeon *Methanosarcina barkeri*. *Archaea*, 2014:327637–327637, 2014.

[754] H. Kumagai, T. Nagate, H. Yoshida, and H. Yamada. Threonine aldolase from *Candida humicola*. II. Purification, crystallization and properties. *Biochim. Biophys. Acta*, 258:779–790, 1972.

[755] H. Kumagai, H. Suzuki, H. Shigematsu, and T. Tuchikura. S-Carboxymethylcysteine synthase from *Escherichia coli*. *Agric. Biol. Chem.*, 53:2481–2487, 1989.

[756] H. Kumagai, H. Yamada, H. Matsui, H. Ohkishi, and K. Ogata. Tyrosine phenol lyase. I. Purification, crystallization, and properties. *J. Biol. Chem.*, 245:1767–1772, 1970.

[757] H. Kumagai, H. Yamada, H. Matsui, H. Ohkishi, and K. Ogata. Tyrosine phenol lyase. II. Cofactor requirements. *J. Biol. Chem.*, 245:1773–1777, 1970.

[758] A. Kumar, S. Tikoo, S. Maity, S. Sengupta, S. Sengupta, A. Kaur, and A.K. Bachhawat. Mammalian proapoptotic factor ChaC1 and its homologues function as γ-glutamyl cyclotransferases acting specifically on glutathione. *EMBO Rep.*, 13:1095–1101, 2012.

[759] S. Kumar, C. Kempinski, X. Zhuang, A. Norris, S. Mafu, J. Zi, S.A. Bell, S.E. Nybo, S.E. Kinison, Z. Jiang, S. Goklany, K.B. Linscott, X. Chen, Q. Jia, S.D. Brown, J.L. Bowman, P.C. Babbitt, R.J. Peters, F. Chen, and J. Chappell. Molecular diversity of terpene synthases in the liverwort *Marchantia polymorpha*. *Plant Cell*, 28:2632–2650, 2016.

[760] S.A. Kumar and S. Mahadevan. 3-Indoleacetaldoxime hydro-lyase: a pyridoxal-5′-phosphate activated enzyme. *Arch. Biochem. Biophys.*, 103:516–518, 1963.

[761] R.N. Kumavath, Sasikala Ch Ramana ChV., D. Barh, A.P. Kumar, and V. Azevedo. Isolation and characterization of L-tryptophan ammonia lyase from *Rubrivivax benzoatilyticus* strain JA2. *Curr. Protein Pept. Sci.*, 16:775–781, 2015.

[762] Y. Kumeta and M. Ito. Characterization of δ-guaiene synthases from cultured cells of *Aquilaria*, responsible for the formation of the sesquiterpenes in agarwood. *Plant Physiol.*, 154:1998–2007, 2010.

[763] T. Kunieda, T. Amano, and Y. Shioi. Search for chlorophyll degradation enzyme, Mg-dechelatase, from extracts of *Chenopodium album* with native and artificial substrates. *Plant Sci.*, 169:177–183, 2005.

[764] D.A. Kunz, D.W. Ribbons, and P.J. Chapman. Metabolism of allylglycine and *cis*-crotylglycine by *Pseudomonas putida* (arvilla) mt-2 harboring a TOL plasmid. *J. Bacteriol.*, 148:72–82, 1981.

[765] S. Kuorelahti, P. Jouhten, H. Maaheimo, M. Penttila, and P. Richard. L-Galactonate dehydratase is part of the fungal path for D-galacturonic acid catabolism. *Mol. Microbiol.*, 61:1060–1068, 2006.

[766] M. Kupka, J. Zhang, W.L. Fu, J.M. Tu, S. Bohm, P. Su, Y. Chen, M. Zhou, H. Scheer, and K.H. Zhao. Catalytic mechanism of *S*-type phycobiliprotein lyase: chaperone-like action and functional amino acid residues. *J. Biol. Chem.*, 284:36405–36414, 2009.

[767] K. Kurahashi, R.J. Pennington, and M.J. Utter. Nucleotide specificity of oxalacetic carboxylase. *J. Biol. Chem.*, 226:1059–1075, 1957.

[768] K. Kuratomi and K. Fukunaga. The metabolism of γ-hydroxyglutamate in rat liver. I. Enzymic synthesis of γ-hydroxy-α-ketoglutarate from pyruvate and glyoxalate. *Biochim. Biophys. Acta*, 78:617–628, 1963.

[769] T. Kurosawa, M. Sato, H. Nakano, M. Fujiwara, T. Murai, T. Yoshimura, and T. Hashimoto. Conjugation reactions catalyzed by bifunctional proteins related to β-oxidation in bile acid biosynthesis. *Steroids*, 66:107–114, 2001.

[770] T. Kushiro, M. Hoshino, T. Tsutsumi, K. Kawai, M. Shiro, M. Shibuya, and Y. Ebizuka. Stereochemical course in water addition during LUP1-catalyzed triterpene cyclization. *Org. Lett.*, 8:5589–5592, 2006.

[771] T.M. Kutchan. Strictosidine: from alkaloid to enzyme to gene. *Phytochemistry*, 32:493–506, 1993.

[772] M. Kwon, S.A. Cochrane, J.C. Vederas, and D.K. Ro. Molecular cloning and characterization of drimenol synthase from valerian plant (*Valeriana officinalis*). *FEBS Lett.*, 588:4597–4603, 2014.

[773] M. Laatu and G. Condemine. Rhamnogalacturonate lyase RhiE is secreted by the out system in *Erwinia chrysanthemi*. *J. Bacteriol.*, 185:1642–1649, 2003.

[774] J. Lacadena, A. Martinez del Pozo, V. Lacadena, A. Martinez-Ruiz, J.M. Mancheno, M. Onaderra, and J.G. Gavilanes. The cytotoxin α-sarcin behaves as a cyclizing ribonuclease. *FEBS Lett.*, 424:46–48, 1998.

[775] D. Laempe, W. Eisenreich, A. Bacher, and G. Fuchs. Cyclohexa-1,5-diene-1-carboxyl-CoA hydratase, an enzyme involved in anaerobic metabolism of benzoyl-CoA in the denitrifying bacterium *Thauera aromatica*. *Eur. J. Biochem.*, 255:618–627, 1998.

[776] R.E. LaFever and R. Croteau. Hydride shifts in the biosynthesis of the *p*-menthane monoterpenes α-terpinene, γ-terpinene, and β-phellandrene. *Arch. Biochem. Biophys.*, 301:361–366, 1993.

[777] B.K. Lam and K.F. Austen. Leukotriene C_4 synthase: a pivotal enzyme in cellular biosynthesis of the cysteinyl leukotrienes. *Prostaglandins Other Lipid Mediat.*, 68-69:511–520, 2002.

[778] J.W. LaMattina, N.D. Keul, P. Reitzer, S. Kapoor, F. Galzerani, D.J. Koch, I.E. Gouvea, and W.N. Lanzilotta. 1,2-Propanediol dehydration in *Roseburia inulinivorans*: structural basis for substrate and enantiomer selectivity. *J. Biol. Chem.*, 291:15515–15526, 2016.

[779] H.J. Lamble, C.C. Milburn, G.L. Taylor, D.W. Hough, and M.J. Danson. Gluconate dehydratase from the promiscuous Entner-Doudoroff pathway in *Sulfolobus solfataricus*. *FEBS Lett.*, 576:133–136, 2004.

[780] H.J. Lamble, A. Theodossis, C.C. Milburn, G.L. Taylor, S.D. Bull, D.W. Hough, and M.J. Danson. Promiscuity in the part-phosphorylative Entner-Doudoroff pathway of the archaeon *Sulfolobus solfataricus*. *FEBS Lett.*, 579:6865–6869, 2005.

[781] J.A. Lambrecht, J.M. Flynn, and D.M. Downs. Conserved YjgF protein family deaminates reactive enamine/imine intermediates of pyridoxal 5′-phosphate (PLP)-dependent enzyme reactions. *J. Biol. Chem.*, 287:3454–3461, 2012.

[782] V. Lambrix, M. Reichelt, T. Mitchell-Olds, D.J. Kliebenstein, and J. Gershenzon. The *Arabidopsis* epithiospecifier protein promotes the hydrolysis of glucosinolates to nitriles and influences *Trichoplusia ni* herbivory. *Plant Cell*, 13:2793–2807, 2001.

[783] C. Landmann, B. Fink, M. Festner, M. Dregus, K.H. Engel, and W. Schwab. Cloning and functional characterization of three terpene synthases from lavender (*Lavandula angustifolia*). *Arch. Biochem. Biophys.*, 465:417–429, 2007.

[784] R.S. Lane, A. Shapley, and E.E. Dekker. 2-keto-4-hydroxybutyrate aldolase. Identification as 2-keto-4-hydroxyglutarate aldolase, catalytic properties, and role in the mammalian metabolism of L-homoserine. *Biochemistry*, 10:1353–1364, 1971.

[785] C. Lange, S. Kiesel, S. Peters, S. Virus, H. Scheer, D. Jahn, and J. Moser. Broadened substrate specificity of 3-hydroxyethyl bacteriochlorophyllide *a* dehydrogenase (BchC) indicates a new route for the biosynthesis of bacteriochlorophyll *a*. *J. Biol. Chem.*, 290:19697–19709, 2015.

[786] P.J. Large. Non-oxidative demethylation of trimethyl *N*-oxide by *Pseudomonas aminovorans*. *FEBS Lett.*, 18:297–300, 1971.

[787] H. Lauble, M.C. Kennedy, H. Beinert, and C.D. Stout. Crystal structures of aconitase with *trans*-aconitate and nitrocitrate bound. *J. Mol. Biol.*, 237:437–451, 1994.

[788] D. Laudert, U. Pfannschmidt, F. Lottspeich, H. Holländer-Czytko, and E.W. Weiler. Cloning, molecular and functional characterization of *Arabidopsis thaliana* allene oxide synthase (CYP 74), the first enzyme of the octadecanoid pathway to jasmonates. *Plant Mol. Biol.*, 31:323–335, 1996.

[789] H.A. Lee and R.H. Abeles. Purification and properties of dioldehydrase, and enzyme requiring a cobamide coenzyme. *J. Biol. Chem.*, 238:2367–2373, 1963.

[790] J. Lee, V. Sperandio, D.E. Frantz, J. Longgood, A. Camilli, M.A. Phillips, and A.J. Michael. An alternative polyamine biosynthetic pathway is widespread in bacteria and essential for biofilm formation in *Vibrio cholerae*. *J. Biol. Chem.*, 284:9899–9907, 2009.

[791] S. Lee and J. Chappell. Biochemical and genomic characterization of terpene synthases in *Magnolia grandiflora*. *Plant Physiol.*, 147:1017–1033, 2008.

[792] S.S. Lee, S. Yu, and S.G. Withers. α-1,4-Glucan lyase performs a *trans*-elimination via a nucleophilic displacement followed by a syn-elimination. *J. Am. Chem. Soc.*, 124:4948–4949, 2002.

[793] S.S. Lee, S. Yu, and S.G. Withers. Detailed dissection of a new mechanism for glycoside cleavage: α-1,4-glucan lyase. *Biochemistry*, 42:13081–13090, 2003.

[794] N.S. Lees, P. Hänzelmann, H.L. Hernandez, S. Subramanian, H. Schindelin, M.K. Johnson, and B.M. Hoffman. ENDOR spectroscopy shows that guanine N1 binds to [4Fe-4S] cluster II of the *S*-adenosylmethionine-dependent enzyme MoaA: mechanistic implications. *J. Am. Chem. Soc.*, 131:9184–9185, 2009.

[795] R. Leonardi, S.A. Fairhurst, M. Kriek, D.J. Lowe, and P.L. Roach. Thiamine biosynthesis in *Escherichia coli*: isolation and initial characterisation of the ThiGH complex. *FEBS Lett.*, 539:95–99, 2003.

[796] R.A. Leppik, I.G. Young, and F. Gibson. Membrane-associated reactions in ubiquinone biosynthesis in *Escherichia coli*. 3-Octaprenyl-4-hydroxybenzoate carboxy-lyase. *Biochim. Biophys. Acta*, 436:800–810, 1976.

[797] C.A. Lesburg, G. Zhai, D.E. Cane, and D.W. Christianson. Crystal structure of pentalenene synthase: mechanistic insights on terpenoid cyclization reactions in biology. *Science*, 277:1820–1824, 1997.

[798] B. Leuthner, C. Leutwein, H. Schultz, P. Hörth, W. Haehnel, E. Schiltz, H. Schägger, and J. Heider. Biochemical and genetic characterisation of benzylsuccinate synthase from *Thauera aromatica*: a new glycyl radical enzyme catalysing the first step in anaerobic toluene metabolism. *Mol. Microbiol.*, 28:615–628, 1998.

[799] B.J. Levin, Y.Y. Huang, S.C. Peck, Y. Wei, A. Martinez-Del Campo, J.A. Marks, E.A. Franzosa, C. Huttenhower, and E.P. Balskus. A prominent glycyl radical enzyme in human gut microbiomes metabolizes *trans*-4-hydroxy-L-proline. *Science*, 355, 2017.

[800] C.C. Levy and P. Goldman. Residue specificity of a ribonuclease which hydrolyzes polycytidylic acid. *J. Biol. Chem.*, 245:3257–3262, 1970.

[801] E. Lewinsohn, M. Gijzen, and R. Croteau. Wound-inducible pinene cyclase from grand fir: purification, characterization, and renaturation after SDS-PAGE. *Arch. Biochem. Biophys.*, 293:167–173, 1992.

[802] J. De Ley and M. Doudoroff. The metabolism of D-galactose in *Pseudomonas saccharophila*. *J. Biol. Chem.*, 227:745–757, 1957.

[803] G. Li, T.G. Kollner, Y. Yin, Y. Jiang, H. Chen, Y. Xu, J. Gershenzon, E. Pichersky, and F. Chen. Nonseed plant *Selaginella moellendorfii* has both seed plant and microbial types of terpene synthases. *Proc. Natl. Acad. Sci. USA*, 109:14711–14715, 2012.

[804] N. Li, W.C. Chang, D.M. Warui, S.J. Booker, C., Bollinger Krebs, , and Jr. Evidence for only oxygenative cleavage of aldehydes to alk(a/e)nes and formate by cyanobacterial aldehyde decarbonylases. *Biochemistry*, 51:7908–7916, 2012.

[805] Y. Li, F. Chen, Z. Li, C. Li, and Y. Zhang. Identification and functional characterization of sesquiterpene synthases from *Xanthium strumarium*. *Plant Cell Physiol.*, 57:630–641, 2016.

[806] Y. Li, N.M. Llewellyn, R. Giri, F. Huang, and J.B. Spencer. Biosynthesis of the unique amino acid side chain of butirosin: possible protective-group chemistry in an acyl carrier protein-mediated pathway. *Chem. Biol.*, 12:665–675, 2005.

[807] Y. Li, A. Matte, H. Su, and M. Cygler. Crystallization and preliminary X-ray analysis of chondroitinase B from *Flavobacterium heparinum*. *Acta Crystallogr. D Biol. Crystallogr.*, 55:1055–1057, 1999.

[808] Y.-T. Li, H. Nakagawa, S.A. Ross, G.C. Hansson, and S.C. Li. A novel sialidase which releases 2,7-anhydro-α-*N*-acetylneuraminic acid from sialoglycoconjugates. *J. Biol. Chem.*, 265:21629–21633, 1990.

[809] J. Liang, J. Liu, R. Brown, M. Jia, K. Zhou, R.J. Peters, and Q. Wang. Direct production of dihydroxylated sesquiterpenoids by a maize terpene synthase. *Plant J.*, 94:847–856, 2018.

[810] D.I. Liao, J.C. Calabrese, Z. Wawrzak, P.V. Viitanen, and D.B. Jordan. Crystal structure of 3,4-dihydroxy-2-butanone 4-phosphate synthase of riboflavin biosynthesis. *Structure*, 9:11–18, 2001.

[811] D.I. Liao, Y.J. Zheng, P.V. Viitanen, and D.B. Jordan. Structural definition of the active site and catalytic mechanism of 3,4-dihydroxy-2-butanone-4-phosphate synthase. *Biochemistry*, 41:1795–1806, 2002.

[812] T.-H. Liao and G.A. Barber. Purification of guanosine 5′-diphosphate D-mannose oxidoreductase from *Phaseolus vulgaris*. *Biochim. Biophys. Acta*, 276:85–93, 1972.

[813] I. Lieberman, A. Kornberg, and E.S. Simms. Enzymatic synthesis of pyrimidine nucleotides. Orotidine-5′-phosphate and uridine-5′-phosphate. *J. Biol. Chem.*, 215:403–415, 1955.

[814] R.J. Light. 6-Methylsalicylic acid decarboxylase from *Penicillium patulum*. *Biochim. Biophys. Acta*, 191:430–438, 1969.

[815] U. Lill, A. Schreil, and H. Eggerer. Isolation of enzymically active fragments formed by limited proteolysis of ATP citrate lyase. *Eur. J. Biochem.*, 125:645–650, 1982.

[816] B.K. Lin and J.A. Anderson. Purification and properties of versiconal cyclase from *Aspergillus parasiticus*. *Arch. Biochem. Biophys.*, 293:67–70, 1992.

[817] F. Lin, K.L. Ferguson, D.R. Boyer, X.N. Lin, and E.N. Marsh. Isofunctional enzymes PAD1 and UbiX catalyze formation of a novel cofactor required by ferulic acid decarboxylase and 4-hydroxy-3-polyprenylbenzoic acid decarboxylase. *ACS Chem. Biol.*, 10:1137–1144, 2015.

[818] G. Lin, S. Han, and Z. Li. Enzymic synthesis of (*R*)-cyanohydrins by three (*R*)-oxynitrilase sources in micro-aqueous organic medium. *Tetrahedron*, 55:3531–3540, 1999.

[819] H.C. Lin, Y.H. Chooi, S. Dhingra, W. Xu, A.M. Calvo, and Y. Tang. The fumagillin biosynthetic gene cluster in *Aspergillus fumigatus* encodes a cryptic terpene cyclase involved in the formation of β-*trans*-bergamotene. *J. Am. Chem. Soc.*, 135:4616–4619, 2013.

[820] X. Lin, M. Hezari, A.E. Koepp, H.G. Floss, and R. Croteau. Mechanism of taxadiene synthase, a diterpene cyclase that catalyzes the first step of taxol biosynthesis in Pacific yew. *Biochemistry*, 35:2968–2977, 1996.

[821] X. Lin, R. Hopson, and D.E. Cane. Genome mining in *Streptomyces coelicolor*: molecular cloning and characterization of a new sesquiterpene synthase. *J. Am. Chem. Soc.*, 128:6022–6023, 2006.

[822] A. Linker, P. Hoffman, K. Meyer, P. Sampson, and E.D. Korn. The formation of unsaturated disacharides from mucopolysaccharides and their cleavage to α-keto acid by bacterial enzymes. *J. Biol. Chem.*, 235:3061–3061, 1960.

[823] C.L. Linster, G. Noel, V. Stroobant, D. Vertommen, M.F. Vincent, G.T. Bommer, M. Veiga da Cunha, and E. Van Schaftingen. Ethylmalonyl-CoA decarboxylase, a new enzyme involved in metabolite proofreading. *J. Biol. Chem.*, 286:42992–43003, 2011.

[824] H. Lipke and C.W. Kearns. DDT dechlorinase. I. Isolation, chemical properties, and spectrophotometric assay. *J. Biol. Chem.*, 234:2123–2128, 1959.

[825] H. Lipke and C.W. Kearns. DDT dechlorinase. II. Substrate and cofactor specificity. *J. Biol. Chem.*, 234:2129–2132, 1959.

[826] D.B. Little and R.B. Croteau. Alteration of product formation by directed mutagenesis and truncation of the multiple-product sesquiterpene synthases δ-selinene synthase and γ-humulene synthase. *Arch. Biochem. Biophys.*, 402:120–135, 2002.

[827] D. Liu, Y. Wei, X. Liu, Y. Zhou, L. Jiang, J. Yin, F. Wang, Y. Hu, A.N. Nanjaraj Urs, Y. Liu, E.L. Ang, S. Zhao, H. Zhao, and Y. Zhang. Indoleacetate decarboxylase is a glycyl radical enzyme catalysing the formation of malodorant skatole. *Nat. Commun.*, 9:4224–4224, 2018.

[828] J. Liu, Y. Wei, L. Lin, L. Teng, J. Yin, Q. Lu, J. Chen, Y. Zheng, Y. Li, R. Xu, W. Zhai, Y. Liu, Y. Liu, P. Cao, E.L. Ang, H. Zhao, Z. Yuchi, and Y. Zhang. Two radical-dependent mechanisms for anaerobic degradation of the globally abundant organosulfur compound dihydroxypropanesulfonate. *Proc. Natl. Acad. Sci. USA*, 117:15599–15608, 2020.

[829] J.Q. Liu, T. Dairi, N. Itoh, M. Kataoka, and S. Shimizu. A novel enzyme, D-3-hydroxyaspartate aldolase from *Paracoccus denitrificans* IFO 13301: purification, characterization, and gene cloning. *Appl. Microbiol. Biotechnol.*, 62:53–60, 2003.

[830] J.Q. Liu, T. Dairi, N. Itoh, M. Kataoka, S. Shimizu, and H. Yamada. A novel metal-activated pyridoxal enzyme with a unique primary structure, low specificity D-threonine aldolase from *Arthrobacter sp.* Strain DK-38. Molecular cloning and cofactor characterization. *J. Biol. Chem.*, 273:16678–16685, 1998.

[831] J.Q. Liu, T. Dairi, N. Itoh, M. Kataoka, S. Shimizu, and H. Yamada. Gene cloning, biochemical characterization and physiological role of a thermostable low-specificity L-threonine aldolase from *Escherichia coli*. *Eur. J. Biochem.*, 255:220–226, 1998.

[832] J.Q. Liu, T. Dairi, N. Itoh, M. Kataoka, S. Shimizu, and H. Yamada. Diversity of microbial threonine aldolases and their application. *J. Mol. Catal. B*, 10:107–115, 2000.

[833] J.Q. Liu, S. Nagata, T. Dairi, H. Misono, S. Shimizu, and H. Yamada. The GLY1 gene of *Saccharomyces cerevisiae* encodes a low-specific L-threonine aldolase that catalyzes cleavage of L-*allo*-threonine and L-threonine to glycine—expression of the gene in *Escherichia coli* and purification and characterization of the enzyme. *Eur. J. Biochem.*, 245:289–293, 1997.

[834] J.Q. Liu, M. Odani, T. Dairi, N. Itoh, S. Shimizu, and H. Yamada. A new route to L-*threo*-3-[4-(methylthio)phenylserine], a key intermediate for the synthesis of antibiotics: recombinant low-specificity D-threonine aldolase-catalyzed stereospecific resolution. *Appl. Microbiol. Biotechnol.*, 51:586–591, 1999.

[835] J.Q. Liu, M. Odani, T. Yasuoka, T. Dairi, N. Itoh, M. Kataoka, S. Shimizu, and H. Yamada. Gene cloning and overproduction of low-specificity D-threonine aldolase from *Alcaligenes xylosoxidans* and its application for production of a key intermediate for parkinsonism drug. *Appl. Microbiol. Biotechnol.*, 54:44–51, 2000.

[836] N.M. Llewellyn, Y. Li, and J.B. Spencer. Biosynthesis of butirosin: transfer and deprotection of the unique amino acid side chain. *Chem. Biol.*, 14:379–386, 2007.

[837] S.A. Lobo, A.A. Brindley, C.V. Romao, H.K. Leech, M.J. Warren, and L.M. Saraiva. Two distinct roles for two functional cobaltochelatases (CbiK) in *Desulfovibrio vulgaris* hildenborough. *Biochemistry*, 47:5851–5857, 2008.

[838] S.A. Lobo, M.A. Videira, I. Pacheco, M.N. Wass, M.J. Warren, M. Teixeira, P.M. Matias, C.V. Romao, and L.M. Saraiva. *Desulfovibrio vulgaris* CbiK(P) cobaltochelatase: evolution of a haem binding protein orchestrated by the incorporation of two histidine residues. *Environ. Microbiol.*, 19:106–118, 2017.

[839] K.P. Locher, M. Hans, A.P. Yeh, B. Schmid, W. Buckel, and D.C. Rees. Crystal structure of the *Acidaminococcus fermentans* 2-hydroxyglutaryl-CoA dehydratase component A. *J. Mol. Biol.*, 307:297–308, 2001.

[840] H. Lochmuller, H.G. Wood, and J.J. Davis. Phosphoenolpyruvate carboxytransphosphorylase. II. Crystallization and properties. *J. Biol. Chem.*, 241:5678–5691, 1966.

[841] A. Lonvaud-Funel and A.M. de Saad. Purification and properties of a malolactic Enzyme from a strain of *Leuconostoc mesenteroides* isolated from grapes. *Appl. Environ. Microbiol.*, 43:357–361, 1982.

[842] F. Lopez-Gallego, S.A. Agger, D. Abate-Pella, M.D. Distefano, and C. Schmidt-Dannert. Sesquiterpene synthases Cop4 and Cop6 from *Coprinus cinereus*: catalytic promiscuity and cyclization of farnesyl pyrophosphate geometric isomers. *ChemBioChem*, 11:1093–1106, 2010.

[843] F. Lopez-Gallego, G.T. Wawrzyn, and C. Schmidt-Dannert. Selectivity of fungal sesquiterpene synthases: role of the active site's H-1α loop in catalysis. *Appl. Environ. Microbiol.*, 76:7723–7733, 2010.

[844] M. Lopez-Meyer and C.L. Nessler. Tryptophan decarboxylase is encoded by two autonomously regulated genes in *Camptotheca acuminata* which are differentially expressed during development and stress. *Plant J.*, 11:1167–1175, 1997.

[845] G.V. Louie, M.E. Bowman, M.C. Moffitt, T.J. Baiga, B.S. Moore, and J.P. Noel. Structural determinants and modulation of substrate specificity in phenylalanine-tyrosine ammonia-lyases. *Chem. Biol.*, 13:1327–1338, 2006.

[846] P. Louis and E.A. Galinski. Characterization of genes for the biosynthesis of the compatible solute ectoine from *Marinococcus halophilus* and osmoregulated expression in *Escherichia coli*. *Microbiology*, 143:1141–1149, 1997.

[847] W. Lovenberg, H. Weissbach, and S. Udenfriend. Aromatic L-amino acid decarboxylase. *J. Biol. Chem.*, 237:89–93, 1962.

[848] S. Loverix, G. Laus, J.C. Martins, L. Wyns, and J. Steyaert. Reconsidering the energetics of ribonuclease catalysed RNA hydrolysis. *Eur. J. Biochem.*, 257:286–290, 1998.

[849] M.G. Low and J.B. Finean. Release of alkaline phosphatase from membranes by a phosphatidylinositol-specific phospholipase C. *Biochem. J.*, 167:281–284, 1977.

[850] S. Lu, R. Xu, J.W. Jia, J. Pang, S.P. Matsuda, and X.Y. Chen. Cloning and functional characterization of a β-pinene synthase from *Artemisia annua* that shows a circadian pattern of expression. *Plant Physiol.*, 130:477–486, 2002.

[851] J. Lücker, H.J. Bouwmeester, W. Schwab, J. Blaas, L.H. van der Plas, and H.A. Verhoeven. Expression of *Clarkia S*-linalool synthase in transgenic petunia plants results in the accumulation of *S*-linalyl-β-D-glucopyranoside. *Plant J.*, 27:315–324, 2001.

[852] J. Lucker, P. Bowen, and J. Bohlmann. *Vitis vinifera* terpenoid cyclases: functional identification of two sesquiterpene synthase cDNAs encoding (+)-valencene synthase and (-)-germacrene D synthase and expression of mono- and sesquiterpene synthases in grapevine flowers and berries. *Phytochemistry*, 65:2649–2659, 2004.

[853] J. Lücker, M.K. El Tamer, W. Schwab, F.W. Verstappen, L.H. van der Plas, H.J. Bouwmeester, and H.A. Verhoeven. Monoterpene biosynthesis in lemon (*Citrus limon*). cDNA isolation and functional analysis of four monoterpene synthases. *Eur. J. Biochem.*, 269:3160–3171, 2000.

[854] F. Lüddeke and J. Harder. Enantiospecific (*S*)-(+)-linalool formation from β-myrcene by linalool dehydratase-isomerase. *Z. Naturforsch. C*, 66:409–412, 2011.

[855] N. Luhtala and R. Parker. T2 Family ribonucleases: ancient enzymes with diverse roles. *Trends Biochem. Sci.*, 35:253–259, 2010.

[856] L.N. Lukens and J.M. Buchanan. Biosynthesis of purines. XXIV. The enzymatic synthesis of 5-amino-1-ribosyl-4-imidazolecarboxylic acid 5′-phosphate from 5-amino-1-ribosylimidazole 5′-phosphate and carbon dioxide. *J. Biol. Chem.*, 234:1799–1805, 1959.

[857] X. Ma, S. Panjikar, J. Koepke, E. Loris, and J. Stöckigt. The structure of *Rauvolfia serpentina* strictosidine synthase is a novel six-bladed β-propeller fold in plant proteins. *Plant Cell*, 18:907–920, 2006.

[858] J.M. Machinist, W.H. Orme-Johnson, and D.M. Ziegler. Microsomal oxidases. II. Properties of a pork liver microsomal *N*-oxide dealkylase. *Biochemistry*, 5:2939–2943, 1966.

[859] J.D. Macmillan and R.H. Vaughn. Purification and properties of a polygalacturonic acid-*trans*-eliminase produced by *Clostridium* multifermentans. *Biochemistry*, 3:564–572, 1964.

[860] T. Maeda, Y. Takeda, T. Murakami, A. Yokota, and M. Wada. Purification, characterization and amino acid sequence of a novel enzyme, D-*threo*-3-hydroxyaspartate dehydratase, from *Delftia* sp. HT23. *J. Biochem.*, 148:705–712, 2010.

[861] S. Mafu, Y. Ding, K.M. Murphy, O. Yaacoobi, J.B. Addison, Q. Wang, Z. Shen, S.P. Briggs, J. Bohlmann, G. Castro-Falcon, C.C. Hughes, M. Betsiashvili, A. Huffaker, E.A. Schmelz, and P. Zerbe. Discovery, biosynthesis and stress-related accumulation of dolabradiene-derived defenses in maize. *Plant Physiol.*, 176:2677–2690, 2018.

[862] S. Mafu, P.S. Karunanithi, T.A. Palazzo, B.L. Harrod, S.M. Rodriguez, I.N. Mollhoff, T.E. O'Brien, S. Tong, O. Fiehn, D.J. Tantillo, J. Bohlmann, and P. Zerbe. Biosynthesis of the microtubule-destabilizing diterpene pseudolaric acid B from golden larch involves an unusual diterpene synthase. *Proc. Natl. Acad. Sci. USA*, 114:974–979, 2017.

[863] S. Mahadevan. Conversion of 3-indoleacetoxime to 3-indoleacetonitrile by plants. *Arch. Biochem. Biophys.*, 100:557–558, 1963.

[864] N. Mahanta, D. Fedoseyenko, T. Dairi, and T.P. Begley. Menaquinone biosynthesis: formation of aminofutalosine requires a unique radical SAM enzyme. *J. Am. Chem. Soc.*, 135:15318–15321, 2013.

[865] S. Mahlstedt, E.N. Fielding, B.S. Moore, and C.T. Walsh. Prephenate decarboxylases: a new prephenate-utilizing enzyme family that performs nonaromatizing decarboxylation en route to diverse secondary metabolites. *Biochemistry*, 49:9021–9023, 2010.

[866] S.A. Mahlstedt and C.T. Walsh. Investigation of anticapsin biosynthesis reveals a four-enzyme pathway to tetrahydrotyrosine in *Bacillus subtilis*. *Biochemistry*, 49:912–923, 2010.

[867] M. Malatesta, G. Mori, D. Acquotti, B. Campanini, A. Peracchi, P.B. Antin, and R. Percudani. Birth of a pathway for sulfur metabolism in early amniote evolution. *Nat Ecol Evol*, 4:1239–1246, 2020.

[868] D.H. Mallonee, W.B. White, and P.B. Hylemon. Cloning and sequencing of a bile acid-inducible operon from *Eubacterium* sp. strain VPI 12708. *J. Bacteriol.*, 172:7011–7019, 1990.

[869] B.G. Malmström. Enolase. In P.D. Boyer, H. Lardy, and K. Myrbäck, editors, *The Enzymes*, volume 5, pages 471–494. Academic Press, New York, 2nd edition, 1961.

[870] B.A. Manjasetty, N. Croteau, J. Powlowski, and A. Vrielink. Crystallization and preliminary X-ray analysis of *dmpFG*-encoded 4-hydroxy-2-ketovalerate aldolase—aldehyde dehydrogenase (acylating) from *Pseudomonas* sp. strain CF600. *Acta Crystallogr. D Biol. Crystallogr.*, 57:582–585, 2001.

[871] B.A. Manjasetty, J. Powlowski, and A. Vrielink. Crystal structure of a bifunctional aldolase-dehydrogenase: sequestering a reactive and volatile intermediate. *Proc. Natl. Acad. Sci. USA*, 100:6992–6997, 2003.

[872] V. Manne, K.R. Kutty, and S.R. Pillarisetti. Purification and properties of synephrinase from *Arthrobacter synephrinum*. *Arch. Biochem. Biophys.*, 248:324–334, 1986.

[873] M. Manoharan, A. Mazumder, S.C. Ransom, J.A. Gerlt, and P.H. Bolton. Mechanism of UV endonuclease-V cleavage of abasic sites in DNA determined by C-13 labeling. *J. Am. Chem. Soc.*, 110:2690–2691, 1988.

[874] C. Mantel, A. Chandor, D. Gasparutto, T. Douki, M. Atta, M. Fontecave, P.-A. Bayle, J.-M. Mouesca, and M. Bardet. Combined NMR and DFT studies for the absolute configuration elucidation of the spore photoproduct, a UV-induced DNA lesion. *J. Am. Chem. Soc.*, 130:16978–16984, 2008.

[875] A.Y. Marbaix, G. Noel, A.M. Detroux, D. Vertommen, E. Van Schaftingen, and C.L. Linster. Extremely conserved ATP- or ADP-dependent enzymatic system for nicotinamide nucleotide repair. *J. Biol. Chem.*, 286:41246–41252, 2011.

[876] P. Decottignies-Le Maréchal, C. Ducrocq, A. Marquet, and R. Azerad. The stereochemistry of hydrogen abstraction in vitamin K-dependent carboxylation. *J. Biol. Chem.*, 259:15010–15012, 1984.

[877] C.A. Marotta, C.C. Levy, S.M. Weissman, and F. Varricchio. Preferred sites of digestion of a ribonuclease from *Enterobacter* sp. in the sequence analysis of *Bacillus stearothermophilus* 5S ribonucleic acid. *Biochemistry*, 12:2901–2904, 1973.

[878] E.S. Martens-Uzunova and P.J. Schaap. An evolutionary conserved D-galacturonic acid metabolic pathway operates across filamentous fungi capable of pectin degradation. *Fungal Genet. Biol.*, 45:1449–1457, 2008.

[879] D.M. Martin and J. Bohlmann. Identification of *Vitis vinifera* (-)-α-terpineol synthase by in silico screening of full-length cDNA ESTs and functional characterization of recombinant terpene synthase. *Phytochemistry*, 65:1223–1229, 2004.

[880] D.M. Martin, J. Faldt, and J. Bohlmann. Functional characterization of nine Norway Spruce TPS genes and evolution of gymnosperm terpene synthases of the TPS-d subfamily. *Plant Physiol.*, 135:1908–1927, 2004.

[881] D.M. Martin, O. Toub, A. Chiang, B.C. Lo, S. Ohse, S.T. Lund, and J. Bohlmann. The bouquet of grapevine (*Vitis vinifera* L. cv. Cabernet Sauvignon) flowers arises from the biosynthesis of sesquiterpene volatiles in pollen grains. *Proc. Natl. Acad. Sci. USA*, 106:7245–7250, 2009.

[882] V.J. Martin, D.J. Pitera, S.T. Withers, J.D. Newman, and J.D. Keasling. Engineering a mevalonate pathway in *Escherichia coli* for production of terpenoids. *Nat. Biotechnol.*, 21:796–802, 2003.

[883] V.J. Martin, Y. Yoshikuni, and J.D. Keasling. The in vivo synthesis of plant sesquiterpenes by *Escherichia coli*. *Biotechnol. Bioeng.*, 75:497–503, 2001.

[884] N.C. Martinez-Gomez, R.R. Poyner, S.O. Mansoorabadi, G.H. Reed, and D.M. Downs. Reaction of AdoMet with ThiC generates a backbone free radical. *Biochemistry*, 48:217–219, 2009.

[885] A. Martinez-Ruiz, L. Garcia-Ortega, R. Kao, M. Onaderra, J.M. Mancheno, J. Davies, A. Martinez del Pozo, and J.G. Gavilanes. Ribonuclease U_2: cloning, production in *Pichia pastoris* and affinity chromatography purification of the active recombinant protein. *FEMS Microbiol. Lett.*, 189:165–169, 2000.

[886] K. Maruyama. Enzymes responsible for degradation of 4-oxalmesaconic acid in *Pseudomonas ochraceae*. *J. Biochem.*, 93:567–574, 1983.

[887] K. Maruyama. Purification and properties of γ-oxalomesaconate hydratase from *Pseudomonas ochraceae* grown with phthalate. *Biochem. Biophys. Res. Commun.*, 128:271–277, 1985.

[888] K. Maruyama. Purification and properties of 4-hydroxy-4-methyl-2-oxoglutarate aldolase from *Pseudomonas ochraceae* grown on phthalate. *J. Biochem.*, 108:327–333, 1990.

[889] T. Maruyama, M. Ito, and G. Honda. Molecular cloning, functional expression and characterization of (*E*)-β farnesene synthase from *Citrus junos*. *Biol. Pharm. Bull.*, 24:1171–1175, 2001.

[890] T. Maruyama, M. Ito, F. Kiuchi, and G. Honda. Molecular cloning, functional expression and characterization of *d*-limonene synthase from *Schizonepeta tenuifolia*. *Biol. Pharm. Bull.*, 24:373–377, 2001.

[891] J.B. Mathis and G.M. Brown. The biosynthesis of folic acid. XI. Purification and properties of dihydroneopterin aldolase. *J. Biol. Chem.*, 245:3015–3025, 1970.

[892] J.R. Mathis, K. Back, C. Starks, J. Noel, C.D. Poulter, and J. Chappell. Pre-steady-state study of recombinant sesquiterpene cyclases. *Biochemistry*, 36:8340–8348, 1997.

[893] Y. Matsuda, T. Mitsuhashi, Z. Quan, and I. Abe. Molecular basis for stellatic acid biosynthesis: a genome mining approach for discovery of sesterterpene synthases. *Org. Lett.*, 17:4644–4647, 2015.

[894] S. Matsuhashi, M. Matsuhashi, J.G. Brown, and J.L. Strominger. Enzymatic synthesis of cytidine diphosphate 3,6-dideoxyhexoses. 3. Cytidine diphosphate D-glucose oxidoreductase. *J. Biol. Chem.*, 241:4283–4287, 1966.

[895] T. Matsui, T. Yoshida, T. Yoshimura, and T. Nagasawa. Regioselective carboxylation of 1,3-dihydroxybenzene by 2,6-dihydroxybenzoate decarboxylase of *Pandoraea* sp. 12B-2. *Appl. Microbiol. Biotechnol.*, 73:95–102, 2006.

[896] Y. Matsuo and D.M. Greenberg. A crystalline enzyme that cleaves homoserine and cystathionine. III. Coenzyme resolution, activation, and inhibitors. *J. Biol. Chem.*, 234:507–515, 1959.

[897] Y. Matsuo and D.M. Greenberg. A crystalline enzyme that cleaves homoserine and cystathionine. IV. Mechanism of action, reversibility, and substrate specificity. *J. Biol. Chem.*, 234:516–519, 1959.

[898] T. Matsushita and F.F. Davis. Studies on pseudouridylic acid synthetase from various sources. *Biochim. Biophys. Acta*, 238:165–173, 1971.

[899] T. Matsuyama and K. Tanaka. On the enzyme of *Aspergillus fumigatus* producing difructose anhydride I from inulobiose. *Agric. Biol. Chem.*, 53:831–832, 1989.

[900] T. Matsuyama, K. Tanaka, M. Mashiko, and M. Kanamoto. Enzymic formation of di-D-fructose 1,2′; 2,1′ dianhydride from inulobiose by *Aspergillus fumigatus*. *J. Biochem. (Tokyo)*, 92:1325–1328, 1982.

[901] D. Mauzerall and S. Granick. Porphyrin biosynthesis in erythrocytes. III. Uroporphyrinogen and its decarboxylase. *J. Biol. Chem.*, 232:1141–1162, 1958.

[902] O. Mayans, M. Scott, I. Connerton, T. Gravesen, J. Benen, J. Visser, R. Pickersgill, and J. Jenkins. Two crystal structures of pectin lyase A from *Aspergillus* reveal a pH driven conformational change and striking divergence in the substrate-binding clefts of pectin and pectate lyases. *Structure*, 5:677–689, 1997.

[903] M. Mazelis and B. Vennesland. Carbon dioxide fixation into oxalacetate in higher plants. *Plant Physiol.*, 32:591–600, 1957.

[904] R.M. McCarty, C. Krebs, and V. Bandarian. Spectroscopic, steady-state kinetic, and mechanistic characterization of the radical SAM enzyme QueE, which catalyzes a complex cyclization reaction in the biosynthesis of 7-deazapurines. *Biochemistry*, 52:188–198, 2013.

[905] R.M. McCarty, A. Somogyi, and V. Bandarian. *Escherichia coli* QueD is a 6-carboxy-5,6,7,8-tetrahydropterin synthase. *Biochemistry*, 48:2301–2303, 2009.

[906] R.M. McCarty, A. Somogyi, G. Lin, N.E. Jacobsen, and V. Bandarian. The deazapurine biosynthetic pathway revealed: *in vitro* enzymatic synthesis of preQ$_0$ from guanosine 5′-triphosphate in four steps. *Biochemistry*, 48:3847–3852, 2009.

[907] R.W. McClard, M.J. Black, L.R. Livingstone, and M.E. Jones. Isolation and initial characterization of the single polypeptide that synthesizes uridine 5′-monophosphate from orotate in Ehrlich ascites carcinoma. Purification by tandem affinity chromatography of uridine-5′-monophosphate synthase. *Biochemistry*, 19:4699–4706, 1980.

[908] E. McCoy, M.C. Galan, and S.E. O'Connor. Substrate specificity of strictosidine synthase. *Bioorg. Med. Chem. Lett.*, 16:2475–2478, 2006.

[909] W.G. McCullough, J.T. Piligian, and I.J. Daniel. Enzymatic decarboxylation of three aminobenzoates. *J. Am. Chem. Soc.*, 79:628–630, 1957.

[910] B.A. McFadden and W.V. Howes. Crystallisation and some properties of isocitrate lyase from *Pseudomonas indigofera*. *J. Biol. Chem.*, 238:1737–1742, 1963.

[911] R.W. McGilvery and P.P. Cohen. The decarboxylation of L-phenylalanine by *Streptococcus faecalis* R. *J. Biol. Chem.*, 174:813–816, 1948.

[912] S.M. McGuire, J.C. Silva, E.G. Casillas, and C.A. Townsend. Purification and characterization of versicolorin B synthase from *Aspergillus parasiticus*. Catalysis of the stereodifferentiating cyclization in aflatoxin biosynthesis essential to DNA interaction. *Biochemistry*, 35:11470–11486, 1996.

[913] E.N. McIntosh, M. Purko, and W.A. Wood. Ketopantoate formation by a hydroxymethylation enzyme from *Escherichia coli*. *J. Biol. Chem.*, 228:499–510, 1957.

[914] S.A. McKay, W.L. Hunter, K.A. Godard, S.X. Wang, D.M. Martin, J. Bohlmann, and A.L. Plant. Insect attack and wounding induce traumatic resin duct development and gene expression of (-)-pinene synthase in Sitka spruce. *Plant Physiol.*, 133:368–378, 2003.

[915] R. Meganathan. Ubiquinone biosynthesis in microorganisms. *FEMS Microbiol. Lett.*, 203:131–139, 2001.

[916] R. Meganathan and R. Bentley. Menaquinone (vitamin K_2) biosynthesis: conversion of *o*-succinylbenzoic acid to 1,4-dihydroxy-2-naphthoic acid by *Mycobacterium phlei* enzymes. *J. Bacteriol.*, 140:92–98, 1979.

[917] A. Meguro, Y. Motoyoshi, K. Teramoto, S. Ueda, Y. Totsuka, Y. Ando, T. Tomita, S.Y. Kim, T. Kimura, M. Igarashi, R. Sawa, T. Shinada, M. Nishiyama, and T. Kuzuyama. An unusual terpene cyclization mechanism involving a carbon-carbon bond rearrangement. *Angew. Chem. Int. Ed. Engl.*, 54:4353–4356, 2015.

[918] A. Meguro, T. Tomita, M. Nishiyama, and T. Kuzuyama. Identification and characterization of bacterial diterpene cyclases that synthesize the cembrane skeleton. *ChemBioChem*, 14:316–321, 2013.

[919] A.H. Mehler and H. Tabor. Deamination of histidine to form urocanic acid in liver. *J. Biol. Chem.*, 201:775–784, 1953.

[920] A.P. Mehta, S.H. Abdelwahed, M.K. Fenwick, A.B. Hazra, M.E. Taga, Y. Zhang, S.E. Ealick, and T.P. Begley. Anaerobic 5-hydroxybenzimidazole formation from aminoimidazole ribotide: an unanticipated intersection of thiamin and vitamin B_{12} biosynthesis. *J. Am. Chem. Soc.*, 137:10444–10447, 2015.

[921] J.O. Meinhart, S. Chaykin, and E.G. Krebs. Enzymatic conversion of a reduced diphosphopyridine nucleotide derivative to reduced diphosphopyridine nucleotide. *J. Biol. Chem.*, 220:821–829, 1956.

[922] A. Meister, M.W. Bukenberger, and M. Strassburger. The optically-specific enzymatic cyclization of D-glutamate. *Biochem. Z.*, 338:217–229, 1963.

[923] M. Meister, S. Saum, B.E. Alber, and G. Fuchs. L-Malyl-coenzyme A/β-methylmalyl-coenzyme A lyase is involved in acetate assimilation of the isocitrate lyase-negative bacterium *Rhodobacter capsulatus*. *J. Bacteriol.*, 187:1415–1425, 2005.

[924] D. Melanson, M.D. Chilton, D. Masters-Moore, and W.S. Chilton. A deletion in an indole synthase gene is responsible for the DIMBOA-deficient phenotype of *bxbx* maize. *Proc. Natl. Acad. Sci. USA*, 94:13345–13350, 1997.

[925] A. Melo, H. Elliott, and L. Glaser. The mechanism of 6-deoxyhexose synthesis. I. Intramolecular hydrogen transfer catalyzed by deoxythymidine diphosphate D-glucose oxidoreductase. *J. Biol. Chem.*, 243:1467–1474, 1968.

[926] H.P. Meloche and W.A. Wood. Crystallization and characteristics of 2-keto-3-deoxy-6-phosphogluconic aldolase. *J. Biol. Chem.*, 239:3515–3518, 1964.

[927] H.P. Meloche and W.A. Wood. The mechanism of 6-phosphogluconic dehydrase. *J. Biol. Chem.*, 239:3505–3510, 1964.

[928] P. Mercke, M. Bengtsson, H.J. Bouwmeester, M.A. Posthumus, and P.E. Brodelius. Molecular cloning, expression, and characterization of amorpha-4,11-diene synthase, a key enzyme of artemisinin biosynthesis in *Artemisia annua* L. *Arch. Biochem. Biophys.*, 381:173–180, 2000.

[929] P. Mercke, J. Crock, R. Croteau, and P.E. Brodelius. Cloning, expression, and characterization of *epi*-cedrol synthase, a sesquiterpene cyclase from *Artemisia annua* L. *Arch. Biochem. Biophys.*, 369:213–222, 1999.

[930] C. Merlin, M. Masters, S. McAteer, and A. Coulson. Why is carbonic anhydrase essential to *Escherichia coli*. *J. Bacteriol.*, 185:6415–6424, 2003.

[931] J.M. Merrick and S. Roseman. D-Glucosaminic acid dehydrase. *Methods Enzymol.*, 9:657–660, 1966.

[932] D.E. Metzler and E.E. Snell. Deamination of serine. II. D-Serine dehydrase, a vitamin B_6 enzyme from *Escherichia coli*. *J. Biol. Chem.*, 198:363–373, 1952.

[933] K. Meyer and M.M. Rapport. Hyaluronidases. *Adv. Enzymol. Relat. Subj. Biochem.*, 13:199–236, 1952.

[934] P. Michaud, P. Pheulpin, E. Petit, J.P. Seguin, J.N. Barbotin, A. Heyraud, B. Courtois, and J. Courtois. Identification of glucuronan lyase from a mutant strain of *Rhizobium meliloti*. *Int. J. Biol. Macromol.*, 21:3–9, 1997.

[935] G. Michel, K. Pojasek, Y. Li, T. Sulea, R.J. Linhardt, R. Raman, V. Prabhakar, R. Sasisekharan, and M. Cygler. The structure of chondroitin B lyase complexed with glycosaminoglycan oligosaccharides unravels a calcium-dependent catalytic machinery. *J. Biol. Chem.*, 279:32882–32896, 2004.

[936] R.H. Michell and D. Allan. Inositol cyclic phosphate as a product of phosphatidylinositol breakdown by phospholipase C (*Bacillus cereus*). *FEBS Lett.*, 53:302–304, 1975.

[937] A. Michelucci, T. Cordes, J. Ghelfi, A. Pailot, N. Reiling, O. Goldmann, T. Binz, A. Wegner, A. Tallam, A. Rausell, M. Buttini, C.L. Linster, E. Medina, R. Balling, and K. Hiller. Immune-responsive gene 1 protein links metabolism to immunity by catalyzing itaconic acid production. *Proc. Natl. Acad. Sci. USA*, 110:7820–7825, 2013.

[938] H. Mihara, T. Kurihara, T. Yoshimura, K. Soda, and N. Esaki. Cysteine sulfinate desulfinase, a NIFS-like protein of *Escherichia coli* with selenocysteine lyase and cysteine desulfurase activities. Gene cloning, purification, and characterization of a novel pyridoxal enzyme. *J. Biol. Chem.*, 272:22417–22424, 1997.

[939] B. Miller, C. Oschinski, and W. Zimmer. First isolation of an isoprene synthase gene from poplar and successful expression of the gene in *Escherichia coli*. *Planta*, 213:483–487, 2001.

[940] D. Miller, Y. Wang, H. Xu, K. Harich, and R.H. White. Biosynthesis of the 5-(aminomethyl)-3-furanmethanol moiety of methanofuran. *Biochemistry*, 53:4635–4647, 2014.

[941] K.A. Miller, R.S. Phillips, J. Mrazek, and T.R. Hoover. *Salmonella* utilizes D-glucosaminate via a mannose family phosphotransferase system permease and associated enzymes. *J. Bacteriol.*, 195:4057–4066, 2013.

[942] M.B. Miller and B.L. Bassler. Quorum sensing in bacteria. *Annu. Rev. Microbiol.*, 55:165–199, 2001.

[943] S. Milstien, , and S. The biosynthesis of tetrahydrobiopterin in rat brain. Purification and characterization of 6-pyruvoyl-tetrahydrobiopterin(2′-oxo) reductase. *J. Biol. Chem.*, 264:8066–8073, 1989.

[944] L.W. Mitchell and E.K. Jaffe. Porphobilinogen synthase from *Escherichia coli* is a Zn(II) metalloenzyme stimulated by Mg(II). *Arch. Biochem. Biophys.*, 300:169–177, 1993.

[945] S. Mitsuhashi and B.D. Davis. Aromatic biosynthesis. XII. Conversion of 5-dehydroquinic acid to 5-dehydroshikimic acid by 5-dehydroquinase. *Biochim. Biophys. Acta*, 15:54–61, 1954.

[946] S. Mitsuhashi and B.D. Davis. Aromatic biosynthesis. XIII. Conversion of quinic acid to 5-dehydroquinic acid by quinic dehydrogenase. *Biochim. Biophys. Acta*, 15:268–280, 1954.

[947] O. Miyake, E. Kobayashi, H. Nankai, W. Hashimoto, B. Mikami, and K. Murata. Posttranslational processing of polysaccharide lyase: maturation route for gellan lyase in *Bacillus* sp. GL1. *Arch. Biochem. Biophys.*, 422:211–220, 2004.

[948] K. Miyamoto, , and H. Cloning and heterologous expression of a novel arylmalonate decarboxylase gene from *Alcaligenes bronchisepticus* KU 1201. *Appl. Microbiol. Biotechnol.*, 38:234–238, 1992.

[949] M. Mizugaki, A.C. Swindell, and S.J. Wkil. Intermediate- and long-chain β-hydroxyacyl-ACP dehydrases from *E. coli* fatty acid synthetase. *Biochem. Biophys. Res. Commun.*, 33:520–527, 1968.

[950] P. Moesta and C.A. West. Casbene synthetase: regulation of phytoalexin biosynthesis in *Ricinus communis* L. seedlings. Purification of casbene synthetase and regulation of its biosynthesis during elicitation. *Arch. Biochem. Biophys.*, 238:325–333, 1985.

[951] R.S. Mohan, N.K. Yee, R.M. Coates, Y.Y. Ren, P. Stamenkovic, I. Mendez, and C.A. West. Biosynthesis of cyclic diterpene hydrocarbons in rice cell suspensions: conversion of 9,10-syn-labda-8(17),13-dienyl diphosphate to 9β-pimara-7,15-diene and stemar-13-ene. *Arch. Biochem. Biophys.*, 330:33–47, 1996.

[952] S. Mohan, T.M. Kelly, S.S. Eveland, C.R. Raetz, and M.S. Anderson. An *Escherichia coli* gene (FabZ) encoding (3*R*)-hydroxymyristoyl acyl carrier protein dehydrase. Relation to *fabA* and suppression of mutations in lipid A biosynthesis. *J. Biol. Chem.*, 269:32896–32903, 1994.

[953] H.H. Moorefield. Purification of DDT-dehydrochlorinase from resistant houseflies. *Contr. Boyce Thompson Inst.*, 18:303–310, 1956.

[954] F. Moran, S. Nasuno, and M.P. Starr. Extracellular and intracellular polygalacturonic acid *trans*-eliminases of *Erwinia carotovora*. *Arch. Biochem. Biophys.*, 123:298–306, 1968.

[955] F. Moran, S. Nasuno, and M.P. Starr. Oligogalacturonide *trans*-eliminase of *Erwinia carotovora*. *Arch. Biochem. Biophys.*, 125:734–741, 1968.

[956] H. Morell, M.J. Clark, P.F. Knowles, and D.B. Sprinson. The enzymic synthesis of chorismic and prephenic acids from 3-*enol*pyruvylshikimic acid 5-phosphate. *J. Biol. Chem.*, 242:82–90, 1967.

[957] M. Moriguchi, S. Hoshino, and S.-I. Hatanaka. Dehalogenation and deamination of *l*-2-amino-4-chloro-4-pentenoic acid by *Proteus mirabilis*. *Agric. Biol. Chem.*, 51:3295–3295, 1987.

[958] S. Morimoto, K. Azuma, T. Oshima, and M. Sakamoto. Purification and properties of a new enzyme, propioin synthase in bakers' yeast which forms propioin from propionaldehyde. *J. Ferment. Technol.*, 66:7–12, 1988.

[959] A.A. Morollo and R. Bauerle. Characterization of composite aminodeoxyisochorismate synthase and aminodeoxyisochorismate lyase activities of anthranilate synthase. *Proc. Natl. Acad. Sci. USA*, 90:9983–9987, 1993.

[960] J.F. Morrison. The purification of aconitase. *Biochem. J.*, 56:99–105, 1954.

[961] D. Morrone, M.L. Hillwig, M.E. Mead, L. Lowry, D.B. Fulton, and R.J. Peters. Evident and latent plasticity across the rice diterpene synthase family with potential implications for the evolution of diterpenoid metabolism in the cereals. *Biochem. J.*, 435:589–595, 2011.

[962] D. Morrone, Y. Jin, M. Xu, S.Y. Choi, R.M. Coates, and R.J. Peters. An unexpected diterpene cyclase from rice: functional identification of a stemodene synthase. *Arch. Biochem. Biophys.*, 448:133–140, 2006.

[963] G.J. Moskowitz and J.M. Merrick. Metabolism of poly-β-hydroxybutyrate. II. Enzymatic synthesis of D-(-)-β-hydroxybutyryl coenzyme A by an enoyl hydrase from *Rhodospirillum rubrum*. *Biochemistry*, 8:2748–2755, 1969.

[964] S.H. Mudd. Enzymatic cleavage of *S*-adenosylmethionine. *J. Biol. Chem.*, 234:87–92, 1959.

[965] S.H. Mudd. The mechanism of the enzymatic cleavage of *S*-adenosylmethionine to α-amino-γ-butyrolactone. *J. Biol. Chem.*, 234:1784–1786, 1959.

[966] U. Muh, I. Cinkaya, S.P. Albracht, and W. Buckel. 4-Hydroxybutyryl-CoA dehydratase from *Clostridium aminobutyricum*: characterization of FAD and iron-sulfur clusters involved in an overall non-redox reaction. *Biochemistry*, 35:11710–11718, 1996.

[967] N. Mukai, K. Masaki, T. Fujii, M. Kawamukai, and H. Iefuji. PAD1 and FDC1 are essential for the decarboxylation of phenylacrylic acids in *Saccharomyces cerevisiae*. *J. Biosci. Bioeng.*, 109:564–569, 2010.

[968] A.M. Mulichak, C.P. Bonin, W.D. Reiter, and R.M. Garavito. Structure of the MUR1 GDP-mannose 4,6-dehydratase from *Arabidopsis thaliana*: implications for ligand binding and specificity. *Biochemistry*, 41:15578–15589, 2000.

[969] U. Müller and W. Buckel. Activation of (*R*)-2-hydroxyglutaryl-CoA dehydratase from *Acidaminococcus fermentans*. *Eur. J. Biochem.*, 230:698–704, 1995.

[970] S.L. Munck and R. Croteau. Purification and characterization of the sesquiterpene cyclase patchoulol synthase from *Pogostemon cablin*. *Arch. Biochem. Biophys.*, 282:58–64, 1990.

[971] H. Murakami and W.S. Sly. Purification and characterization of human salivary carbonic anhydrase. *J. Biol. Chem.*, 262:1382–1388, 1987.

[972] K.E. Mutenda, R. Körner, T.M.I.E. Christensen, J. Mikkelsen, and P. Roepstorff. Application of mass spectrometry to determine the activity and specificity of pectin lyase A. *Carbohydr. Res.*, 337:1213–1223, 2002.

[973] W.L. Muth and R.N. Costilow. Ornithine cyclase (deaminating). II. Properties of the homogeneous enzyme. *J. Biol. Chem.*, 249:7457–7462, 1974.

[974] M. Mutter, I.J. Colquhoun, G. Beldman, H.A. Schols, E.J. Bakx, and A.G. Voragen. Characterization of recombinant rhamnogalacturonan α-L-rhamnopyranosyl-(1,4)-α-D-galactopyranosyluronide lyase from *Aspergillus aculeatus*. An enzyme that fragments rhamnogalacturonan I regions of pectin. *Plant Physiol.*, 117:141–152, 1998.

[975] M. Mutter, I.J. Colquhoun, H.A. Schols, G. Beldman, and A.G. Voragen. Rhamnogalacturonase B from *Aspergillus aculeatus* is a rhamnogalacturonan α-L-rhamnopyranosyl-(1→4)-α-D-galactopyranosyluronide lyase. *Plant Physiol.*, 110:73–77, 1996.

[976] J.W. Myers. Dihydroxy acid dehydrase: an enzyme involved in the biosynthesis of isoleucine and valine. *J. Biol. Chem.*, 236:1414–1418, 1961.

[977] P.A. Myers and L.J. Zatman. The metabolism of trimethylamine *N*-oxide by *Bacillus* PM6. *Biochem. J.*, 121:10–10, 1971.

[978] K. Nabeta, M. Fujita, K. Komuro, K. Katayama, , and T. *In vitro* biosynthesis of cadinanes by cell-free extracts of cultured cells of *Heteroscyphus planus*. *J. Chem. Soc., Perkin Trans. 1*, pages 2065–2070, 1997.

[979] K. Nabeta, K. Kigure, M. Fujita, T. Nagoya, T. Ishikawa, H. Okuyama, and T. Takasawa. Bioynthesis of (+)-cubenene and (+)-epicubenol by cell-free extracts of cultured cells of *Heteroscyphus planus* and cyclization of [^{2}H]farnesyl diphosphates. *J. Chem. Soc., Perkin Trans. 1*, pages 1935–1939, 1995.

[980] T. Nagasawa, T. Ishii, H. Kumagai, and H. Yamada. D-Cysteine desulfhydrase of *Escherichia coli*. Purification and characterization. *Eur. J. Biochem.*, 153:541–551, 1985.

[981] T. Nagasawa, T. Ishii, and H. Yamada. Physiological comparison of D-cysteine desulfhydrase of *Escherichia coli* with 3-chloro-D-alanine dehydrochlorinase of *Pseudomonas putida* CR 1-1. *Arch. Microbiol.*, 149:413–416, 1988.

[982] T. Nagasawa, K. Tanizawa, T. Satoda, , and H. Diaminopropionate ammonia-lyase from *Salmonella typhimurium*. Purification and characterization of the crystalline enzyme, and sequence determination of the pyridoxal 5′-phosphate binding peptide. *J. Biol. Chem.*, 263:958–964, 1988.

[983] C.W. Nagel and R.H. Vaughn. The degradation of oligogalacturonides by the polygalacturonase of *Bacillus polymyxa*. *Arch. Biochem. Biophys.*, 94:328–328, 1961.

[984] H.I. Nakada and P.C. Sweeny. Alginic acid degradation by eliminases from abalone hepatopancreas. *J. Biol. Chem.*, 242:845–851, 1967.

[985] H.I. Nakada and J.B. Wolfe. Studies on the enzyme chondroitinase: product structure and ion effects. *Arch. Biochem. Biophys.*, 94:244–251, 1961.

[986] H. Nakagawa and H. Kimura. Purification and properties of cystathionine synthetase synthetase from rat liver: separation of cystathionine synthetase from serine dehydratase. *Biochem. Biophys. Res. Commun.*, 32:209–214, 1968.

[987] T. Nakai, H. Mizutani, I. Miyahara, K. Hirotsu, S. Takeda, K.H. Jhee, T. Yoshimura, and N. Esaki. Three-dimensional structure of 4-amino-4-deoxychorismate lyase from *Escherichia coli*. *J. Biochem.*, 128:29–38, 2000.

[988] C. Nakano, S. Horinouchi, and Y. Ohnishi. Characterization of a novel sesquiterpene cyclase involved in (+)-caryolan-1-ol biosynthesis in *Streptomyces griseus*. *J. Biol. Chem.*, 286:27980–27987, 2011.

[989] Y. Nakano and S. Kitaoka. L-Aspartate α-decarboxylase in a cell-free system from *Escherichia coli*. *J. Biochem. (Tokyo)*, 70:327–327, 1971.

[990] H. Nakashita, K. Watanabe, O. Hara, T. Hidaka, and H. Seto. Studies on the biosynthesis of bialaphos. Biochemical mechanism of C-P bond formation: discovery of phosphonopyruvate decarboxylase which catalyzes the formation of phosphonoacetaldehyde from phosphonopyruvate. *J. Antibiot. (Tokyo)*, 50:212–219, 1997.

[991] H. Nakazawa, H. Kumagai, and H. Yamada. Constitutive aromatic L-amino acid decarboxylase from *Micrococcus percitreus*. *Biochem. Biophys. Res. Commun.*, 61:75–82, 1974.

[992] P. Naouri, P. Chagnaud, A. Arnaud, and P. Galzy. Purification and properties of a malolactic enzyme from *Leuconostoc oenos* ATCC 23278. *J. Basic Microbiol.*, 30:577–585, 1990.

[993] B.C. Narayanan, W. Niu, Y. Han, J. Zou, P.S. Mariano, D. Dunaway-Mariano, and O. Herzberg. Structure and function of PA4872 from *Pseudomonas aeruginosa*, a novel class of oxaloacetate decarboxylase from the PEP mutase/isocitrate lyase superfamily. *Biochemistry*, 47:167–182, 2008.

[994] A. Narbad and M.J. Gasson. Metabolism of ferulic acid via vanillin using a novel CoA-dependent pathway in a newly-isolated strain of *Pseudomonas fluorescens*. *Microbiology*, 144:1397–1405, 1998.

[995] S. Nasuno and M.P. Starr. Polygalacturonic acid *trans*-eliminase of *Xanthomonas campestris*. *Biochem. J.*, 104:178–185, 1967.

[996] A. Natsch, J. Schmid, and F. Flachsmann. Identification of odoriferous sulfanylalkanols in human axilla secretions and their formation through cleavage of cysteine precursors by a C-S lyase isolated from axilla bacteria. *Chem. Biodivers.*, 1:1058–1072, 2004.

[997] W.G. Navia-Gine, J.S. Yuan, A. Mauromoustakos, J.B. Murphy, F. Chen, and K.L. Korth. *Medicago truncatula* (*E*)-β-ocimene synthase is induced by insect herbivory with corresponding increases in emission of volatile ocimene. *Plant Physiol. Biochem.*, 47:416–425, 2009.

[998] V.S. Negi, J.P. Bingham, Q.X. Li, and D. Borthakur. A carbon-nitrogen lyase from *Leucaena leucocephala* catalyzes the first step of mimosine degradation. *Plant Physiol.*, 164:922–934, 2014.

[999] T. Nemoto, E.M. Cho, A. Okada, K. Okada, K. Otomo, Y. Kanno, T. Toyomasu, W. Mitsuhashi, T. Sassa, E. Minami, N. Shibuya, M. Nishiyama, H. Nojiri, and H. Yamane. Stemar-13-ene synthase, a diterpene cyclase involved in the biosynthesis of the phytoalexin oryzalexin S in rice. *FEBS Lett.*, 571:182–186, 2004.

[1000] A. Neubauer, M. Walter, , and K. Formation of inulobiose from difructoseanhydride III catalysed by a lysate from *Arthrobacter ureafaciens* ATCC 21124. *Biocatalysis and Biotransformation*, 18:443–455, 2000.

[1001] R.P. Newton, S.G. Salih, N.A. Hakeem, E.E. Kingston, and J.H. Beynon. 3′,5′-Cyclic UMP, -cyclic IMP, -cyclic TMP and related enzymes in mammalian tissues. *Biochem. Soc. Trans.*, 13:1134–1135, 1985.

[1002] W.A. Newton, Y. Morino, and E.E. Snell. Properties of crystalline tryptophanase. *J. Biol. Chem.*, 240:1211–1218, 1965.

[1003] B.P. Nichols and J.M. Green. Cloning and sequencing of *Escherichia coli ubiC* and purification of chorismate lyase. *J. Bacteriol.*, 174:5309–5316, 1992.

[1004] W.G. Niehaus, Kisic Jr., Torkelson A., Bednarczyk A., D.J., Schroepfer, and Jr. , Stereospecific hydration of the Δ^9 double bond of oleic acid. *J. Biol. Chem.*, 245:3790–3797, 1970.

[1005] N.J. Nieuwenhuizen, M.Y. Wang, A.J. Matich, S.A. Green, X. Chen, Y.K. Yauk, L.L. Beuning, D.A. Nagegowda, N. Dudareva, and R.G. Atkinson. Two terpene synthases are responsible for the major sesquiterpenes emitted from the flowers of kiwifruit (*Actinidia deliciosa*). *J. Exp. Bot.*, 60:3203–3219, 2009.

[1006] H. Nishihara and E.E. Dekker. Purification, substrate specificity and binding, β-decarboxylase activity, and other properties of *Escherichia coli* 2-keto-4-hydroxyglutarate aldolase. *J. Biol. Chem.*, 247:5079–5087, 1972.

[1007] J. Nishihira, M. Fujinaga, T. Kuriyama, M. Suzuki, H. Sugimoto, A. Nakagawa, I. Tanaka, and M. Sakai. Molecular cloning of human D-dopachrome tautomerase cDNA: N-terminal proline is essential for enzyme activation. *Biochem. Biophys. Res. Commun.*, 243:538–544, 1998.

[1008] H. Nishimura and B. Maruo. Intracellular ribonuclease from *Bacillus subtilis*. *Biochim. Biophys. Acta*, 40:355–357, 1960.

[1009] J.S. Nishimura and D.M. Greenberg. Purification and properties of L-threonine dehydrase of sheep liver. *J. Biol. Chem.*, 236:2684–2691, 1961.

[1010] W. Noe, C. Mollenschott, and J. Berlin. Tryptophan decarboxylase from *Catharanthus roseus* cell suspension cultures: purification, molecular and kinetic data of the homogenous protein. *Plant Mol. Biol.*, 3:281–288, 1984.

[1011] J. Nogales, A. Canales, J. Jiménez-Barbero, Pingarrón Serra B., García J. M., Díaz J. L., and E. Unravelling the gallic acid degradation pathway in bacteria: the *gal* cluster from *Pseudomonas putida*. *Mol. Microbiol.*, 79:359–374, 2011.

[1012] T. Nomura, T. Murase, S. Ogita, and Y. Kato. Molecular identification of tuliposide B-converting enzyme: a lactone-forming carboxylesterase from the pollen of tulip. *Plant J.*, 83:252–262, 2015.

[1013] T. Nomura, S. Ogita, and Y. Kato. A novel lactone-forming carboxylesterase: molecular identification of a tuliposide A-converting enzyme in tulip. *Plant Physiol.*, 159:565–578, 2012.

[1014] J.A. North, A.R. Miller, J.A. Wildenthal, S.J. Young, and F.R. Tabita. Microbial pathway for anaerobic 5′-methylthioadenosine metabolism coupled to ethylene formation. *Proc. Natl. Acad. Sci. USA*, 114:E10455–E10464, 2017.

[1015] J.A. North, J.A. Wildenthal, T.J. Erb, B.S. Evans, K.M. Byerly, J.A. Gerlt, and F.R. Tabita. A bifunctional salvage pathway for two distinct *S*-adenosylmethionine by-products that is widespread in bacteria, including pathogenic *Escherichia coli*. *Mol. Microbiol.*, 2020.

[1016] A. Novogrodsky and A. Meister. Control of aspartate β-decarboxylase activity by transamination. *J. Biol. Chem.*, 239:879–888, 1964.

[1017] A.J. Oakley, M. Coggan, and P.G. Board. Identification and characterization of γ-glutamylamine cyclotransferase, an enzyme responsible for γ-glutamyl-ε-lysine catabolism. *J. Biol. Chem.*, 285:9642–9648, 2010.

[1018] A.J. Oakley, T. Yamada, D. Liu, M. Coggan, A.G. Clark, and P.G. Board. The identification and structural characterization of C7orf24 as γ-glutamyl cyclotransferase. An essential enzyme in the γ-glutamyl cycle. *J. Biol. Chem.*, 283:22031–22042, 2008.

[1019] J.R. O'Brien, C. Raynaud, C. Croux, L. Girbal, P. Soucaille, and W.N. Lanzilotta. Insight into the mechanism of the B_{12}-independent glycerol dehydratase from *Clostridium* butyricum: preliminary biochemical and structural characterization. *Biochemistry*, 43:4635–4645, 2004.

[1020] A. Ochiai, T. Itoh, A. Kawamata, W. Hashimoto, and K. Murata. Plant cell wall degradation by saprophytic *Bacillus subtilis* strains: gene clusters responsible for rhamnogalacturonan depolymerization. *Appl. Environ. Microbiol.*, 73:3803–3813, 2007.

[1021] A. Ochiai, T. Itoh, B. Mikami, W. Hashimoto, and K. Murata. Structural determinants responsible for substrate recognition and mode of action in family 11 polysaccharide lyases. *J. Biol. Chem.*, 284:10181–10189, 2009.

[1022] A. Ochiai, M. Yamasaki, T. Itoh, B. Mikami, W. Hashimoto, and K. Murata. Crystallization and preliminary X-ray analysis of the rhamnogalacturonan lyase YesW from *Bacillus subtilis* strain 168, a member of polysaccharide lyase family 11. *Acta Crystallogr. Sect. F Struct. Biol. Cryst. Commun.*, 62:438–440, 2006.

[1023] B. Odaert, F. Saida, P. Aliprandi, S. Durand, J.B. Crechet, R. Guerois, S. Laalami, M. Uzan, and F. Bontems. Structural and functional studies of RegB, a new member of a family of sequence-specific ribonucleases involved in mRNA inactivation on the ribosome. *J. Biol. Chem.*, 282:2019–2028, 2007.

[1024] G. Odh, A. Hindemith, A.M. Rosengren, E. Rosengren, and H. Rorsman. Isolation of a new tautomerase monitored by the conversion of D-dopachrome to 5,6-dihydroxyindole. *Biochem. Biophys. Res. Commun.*, 197:619–624, 1993.

[1025] T. Ohuchi, A. Ikeda-Araki, A. Watanabe-Sakamoto, K. Kojiri, M. Nagashima, M. Okanishi, and H. Suda. Cloning and expression of a gene encoding *N*-glycosyltransferase (ngt) from *Saccharothrix aerocolonigenes* ATCC39243. *J. Antibiot. (Tokyo)*, 53:393–403, 2000.

[1026] H. Oikawa, T. Toyomasu, H. Toshima, S. Ohashi, H. Kawaide, Y. Kamiya, M. Ohtsuka, S. Shinoda, W. Mitsuhashi, and T. Sassa. Cloning and functional expression of cDNA encoding aphidicolan-16 β-ol synthase: a key enzyme responsible for formation of an unusual diterpene skeleton in biosynthesis of aphidicolin. *J. Am. Chem. Soc.*, 123:5154–5155, 2001.

[1027] K.-I. Oinuma, Y. Hashimoto, K. Konishi, M. Goda, T. Noguchi, H. Higashibata, and M. Kobayashi. Novel aldoxime dehydratase involved in carbon-nitrogen triple bond synthesis of *Pseudomonas chlororaphis* B23: Sequencing, gene expression, purification and characterization. *J. Biol. Chem.*, 278:29600–29608, 2003.

[1028] H. Oku and T. Kaneda. Biosynthesis of branched-chain fatty acids in *Bacillus subtilis*. A decarboxylase is essential for branched-chain fatty acid synthetase. *J. Biol. Chem.*, 263:18386–18396, 1988.

[1029] N.B. Olivier, M.M. Chen, J.R. Behr, and B. Imperiali. *In vitro* biosynthesis of UDP-*N*,*N*′-diacetylbacillosamine by enzymes of the *Campylobacter jejuni* general protein glycosylation system. *Biochemistry*, 45:13659–13669, 2006.

[1030] P.E. O'Maille, J. Chappell, and J.P. Noel. Biosynthetic potential of sesquiterpene synthases: alternative products of tobacco 5-*epi*-aristolochene synthase. *Arch. Biochem. Biophys.*, 448:73–82, 2006.

[1031] R. Omi, S. Kurokawa, H. Mihara, H. Hayashi, M. Goto, I. Miyahara, T. Kurihara, K. Hirotsu, and N. Esaki. Reaction mechanism and molecular basis for selenium/sulfur discrimination of selenocysteine lyase. *J. Biol. Chem.*, 285:12133–12139, 2010.

[1032] H. Omura, M. Wieser, and T. Nagasawa. Pyrrole-2-carboxylate decarboxylase from *Bacillus megaterium* PYR2910, an organic-acid-requiring enzyme. *Eur. J. Biochem.*, 253:480–484, 1998.

[1033] H. Ono, K. Sawada, N. Khunajakr, T. Tao, M. Yamamoto, M. Hiramoto, A. Shinmyo, M. Takano, and Y. Murooka. Characterization of biosynthetic enzymes for ectoine as a compatible solute in a moderately halophilic eubacterium, *Halomonas elongata*. *J. Bacteriol.*, 181:91–99, 1999.

[1034] M. Ono, H. Inoue, F. Suzuki, and Y. Takeda. Studies on ornithine decarboxylase from the liver of thioacetamide-treated rats. Purification and some properties. *Biochim. Biophys. Acta*, 284:285–297, 1972.

[1035] S. Oogai, M. Fukuta, M. Inafuku, and H. Oku. Isolation and characterization of mimosine degrading enzyme from *Arthrobacter* sp. Ryudai-S1. *World J. Microbiol. Biotechnol.*, 38:172–172, 2022.

[1036] S. Oogai, M. Fukuta, K. Watanabe, M. Inafuku, and H. Oku. Molecular characterization of mimosinase and cystathionine β-lyase in the Mimosoideae subfamily member *Mimosa pudica*. *J. Plant Res.*, 132:667–680, 2019.

[1037] I. Orita, H. Yurimoto, R. Hirai, Y. Kawarabayasi, Y. Sakai, and N. Kato. The archaeon *Pyrococcus horikoshii* possesses a bifunctional enzyme for formaldehyde fixation via the ribulose monophosphate pathway. *J. Bacteriol.*, 187:3636–3642, 2005.

[1038] M. Orlowski, P.G. Richman, and A. Meister. Isolation and properties of γ-L-glutamylcyclotransferase from human brain. *Biochemistry*, 8:1048–1055, 1969.

[1039] L.N. Ornston. The conversion of catechol and protocatechuate to β-ketoadipate by *Pseudomonas putida*. 3. Enzymes of the catechol pathway. *J. Biol. Chem.*, 241:3795–3799, 1966.

[1040] L.N. Ornston. Conversion of catechol and protocatechuate to β-ketoadipate (*Pseudomonas putida*). *Methods Enzymol.*, 17A:529–549, 1970.

[1041] A. Osborne, R.N. Thorneley, C. Abell, and S. Bornemann. Studies with substrate and cofactor analogues provide evidence for a radical mechanism in the chorismate synthase reaction. *J. Biol. Chem.*, 275:35825–35830, 2000.

[1042] K. Otomo, Y. Kanno, A. Motegi, H. Kenmoku, H. Yamane, W. Mitsuhashi, H. Oikawa, H. Toshima, H. Itoh, M. Matsuoka, T. Sassa, and T. Toyomasu. Diterpene cyclases responsible for the biosynthesis of phytoalexins, momilactones A, B, and oryzalexins A-F in rice. *Biosci. Biotechnol. Biochem.*, 68:2001–2006, 2004.

[1043] N. Ototani and Z. Yosizawa. Purification of chondroitinase B and chondroitinase C using glycosaminoglycan-bound AH-Sepharose 4B. *Carbohydr. Res.*, 70:295–306, 1979.

[1044] H.J. Ougham and P.W. Trudgill. Metabolism of cyclohexaneacetic acid and cyclohexanebutyric acid by *Arthrobacter sp.* strain CA1. *J. Bacteriol.*, 150:1172–1182, 1982.

[1045] J. Overhage, H. Priefert, and A. Steinbuchel. Biochemical and genetic analyses of ferulic acid catabolism in *Pseudomonas* sp. Strain HR199. *Appl. Environ. Microbiol.*, 65:4837–4847, 1999.

[1046] S. Pages, O. Valette, L. Abdou, A. Belaich, and J.P. Belaich. A rhamnogalacturonan lyase in the *Clostridium cellulolyticum* cellulosome. *J. Bacteriol.*, 185:4727–4733, 2003.

[1047] A. Paiardini, R. Contestabile, S. D'Aguanno, S. Pascarella, and F. Bossa. Threonine aldolase and alanine racemase: novel examples of convergent evolution in the superfamily of vitamin B_6-dependent enzymes. *Biochim. Biophys. Acta*, 1647:214–219, 2003.

[1048] A.G. Palekar, S.S. Tate, and A. Meister. Inhibition of aspartate β-decarboxylase by aminomalonate. Stereospecific decarboxylation of aminomalonate to glycine. *Biochemistry*, 9:2310–2315, 1970.

[1049] N.J. Palleroni and M. Doudoroff. Characterization and properties of 2-keto-3-deoxy-D-arabonic acid. *J. Biol. Chem.*, 223:499–508, 1956.

[1050] R.D. Palmatier, R.P. McCroskey, and M.T. Abbott. The enzymatic conversion of uracil 5-carboxylic acid to uracil and carbon dioxide. *J. Biol. Chem.*, 245:6706–6710, 1970.

[1051] D.J. Palmer, S. Schroeder, A.D. Lawrence, E. Deery, S.A. Lobo, L.M. Saraiva, K.J. McLean, A.W. Munro, S.J. Ferguson, R.W. Pickersgill, D.G. Brown, and M.J. Warren. The structure, function and properties of sirohaem decarboxylase^{-}-an enzyme with structural homology to a transcription factor family that is part of the alternative haem biosynthesis pathway. *Mol. Microbiol.*, 93:247–261, 2014.

[1052] D.R. Palmer, J.B. Garrett, V. Sharma, R. Meganathan, P.C. Babbitt, and J.A. Gerlt. Unexpected divergence of enzyme function and sequence: "*N*-acylamino acid racemase" is *o*-succinylbenzoate synthase. *Biochemistry*, 38:4252–4258, 1999.

[1053] J.J. Pan, J.O. Solbiati, G. Ramamoorthy, B.S. Hillerich, R.D. Seidel, J.E. Cronan, S.C. Almo, and C.D. Poulter. Biosynthesis of squalene from farnesyl diphosphate in bacteria: three steps catalyzed by three enzymes. *ACS Cent. Sci.*, 1:77–82, 2015.

[1054] J.B. Parker and C.T. Walsh. Olefin isomerization regiochemistries during tandem action of BacA and BacB on prephenate in bacilysin biosynthesis. *Biochemistry*, 51:3241–3251, 2012.

[1055] A. Parthasarathy, A.J. Pierik, J. Kahnt, O. Zelder, and W. Buckel. Substrate specificity of 2-hydroxyglutaryl-CoA dehydratase from *Clostridium symbiosum*: toward a bio-based production of adipic acid. *Biochemistry*, 50:3540–3550, 2011.

[1056] I. Pateraki, J. Andersen-Ranberg, B. Hamberger, A.M. Heskes, H.J. Martens, P. Zerbe, S.S. Bach, B.L. Moller, J. Bohlmann, and B. Hamberger. Manoyl oxide (13*R*), the biosynthetic precursor of forskolin, is synthesized in specialized root cork cells in *Coleus forskohlii*. *Plant Physiol.*, 164:1222–1236, 2014.

[1057] R.V. Patil and E.E. Dekker. Cloning, nucleotide sequence, overexpression, and inactivation of the *Escherichia coli* 2-keto-4-hydroxyglutarate aldolase gene. *J. Bacteriol.*, 174:102–107, 1992.

[1058] B. Paulose, S. Chhikara, J. Coomey, H.I. Jung, O. Vatamaniuk, and O.P. Dhankher. A γ-glutamyl cyclotransferase protects *Arabidopsis* plants from heavy metal toxicity by recycling glutamate to maintain glutathione homeostasis. *Plant Cell*, 25:4580–4595, 2013.

[1059] K.A. Payne, M.D. White, K. Fisher, B. Khara, S.S. Bailey, D. Parker, N.J. Rattray, D.K. Trivedi, R. Goodacre, R. Beveridge, P. Barran, S.E. Rigby, N.S. Scrutton, S. Hay, and D. Leys. New cofactor supports α,β-unsaturated acid decarboxylation via 1,3-dipolar cycloaddition. *Nature*, 522:497–501, 2015.

[1060] S.W. Pechous and B.D. Whitaker. Cloning and functional expression of an (*E*,*E*)-α-farnesene synthase cDNA from peel tissue of apple fruit. *Planta*, 219:84–94, 2004.

[1061] S.C. Peck, K. Denger, A. Burrichter, S.M. Irwin, E.P. Balskus, and D. Schleheck. A glycyl radical enzyme enables hydrogen sulfide production by the human intestinal bacterium *Bilophila wadsworthia*. *Proc. Natl. Acad. Sci. USA*, 116:3171–3176, 2019.

[1062] D.B. Pedrolli and E.C. Carmona. Purification and characterization of a unique pectin lyase from *Aspergillus giganteus* able to release unsaturated monogalacturonate during pectin degradation. *Enzyme Res.*, 2014:353915–353915, 2014.

[1063] C.L. Peebles, P. Gegenheimer, and J. Abelson. Precise excision of intervening sequences from precursor tRNAs by a membrane-associated yeast endonuclease. *Cell*, 32:525–536, 1983.

[1064] K.A. Pelot, D.M. Hagelthorn, J.B. Addison, and P. Zerbe. Biosynthesis of the oxygenated diterpene nezukol in the medicinal plant *Isodon rubescens* is catalyzed by a pair of diterpene synthases. *PLoS One*, 12:e0176507–e0176507, 2017.

[1065] P. Perche-Letuvée, V. Kathirvelu, G. Berggren, M. Clemancey, J.M. Latour, V. Maurel, T. Douki, J. Armengaud, E. Mulliez, M. Fontecave, R. Garcia-Serres, S. Gambarelli, and M. Atta. 4-Demethylwyosine synthase from *Pyrococcus abyssi* is a radical-*S*-adenosyl-L-methionine enzyme with an additional $[4Fe\text{-}4S]^{2+}$ cluster that interacts with the pyruvate co-substrate. *J. Biol. Chem.*, 287:41174–41185, 2012.

[1066] P. Peters, E.A. Galinski, and H.G. Truper. The biosynthesis of ectoine. *FEMS Microbiol. Lett.*, 71:157–162, 1990.

[1067] R.J. Peters and R.B. Croteau. Abietadiene synthase catalysis: conserved residues involved in protonation-initiated cyclization of geranylgeranyl diphosphate to (+)-copalyl diphosphate. *Biochemistry*, 41:1836–1842, 2002.

[1068] R.J. Peters and R.B. Croteau. Abietadiene synthase catalysis: mutational analysis of a prenyl diphosphate ionization-initiated cyclization and rearrangement. *Proc. Natl. Acad. Sci. USA*, 99:580–584, 2002.

[1069] R.J. Peters and R.B. Croteau. Alternative termination chemistries utilized by monoterpene cyclases: chimeric analysis of bornyl diphosphate, 1,8-cineole, and sabinene synthases. *Arch. Biochem. Biophys.*, 417:203–211, 2003.

[1070] R.J. Peters, J.E. Flory, R. Jetter, M.M. Ravn, H.J. Lee, R.M. Coates, and R.B. Croteau. Abietadiene synthase from grand fir (*Abies grandis*): characterization and mechanism of action of the "pseudomature" recombinant enzyme. *Biochemistry*, 39:15592–15602, 2000.

[1071] R.J. Peters, M.M. Ravn, R.M. Coates, and R.B. Croteau. Bifunctional abietadiene synthase: free diffusive transfer of the (+)-copalyl diphosphate intermediate between two distinct active sites. *J. Am. Chem. Soc.*, 123:8974–8978, 2001.

[1072] D. Peterson and J. Llaneza. Identification of a carbon-oxygen lyase activity cleaving the ether linkage in carboxymethyloxysuccinic acid. *Arch. Biochem. Biophys.*, 162:135–146, 1974.

[1073] G. Pettersson. An orsellinic acid decarboxylase isolated from *Gliocladium roseum*. *Acta Chem. Scand.*, 19:2013–2021, 1965.

[1074] C. Pfaff, N. Glindemann, J. Gruber, M. Frentzen, and R. Sadre. Chorismate pyruvate-lyase and 4-hydroxy-3-solanesylbenzoate decarboxylase are required for plastoquinone biosynthesis in the cyanobacterium *Synechocystis* sp. PCC6803. *J. Biol. Chem.*, 289:2675–2686, 2014.

[1075] B.F. Pfleger, Y. Kim, T.D. Nusca, N. Maltseva, J.Y. Lee, C.M. Rath, J.B. Scaglione, B.K. Janes, E.C. Anderson, N.H. Bergman, P.C. Hanna, A. Joachimiak, and D.H. Sherman. Structural and functional analysis of AsbF: origin of the stealth 3,4-dihydroxybenzoic acid subunit for petrobactin biosynthesis. *Proc. Natl. Acad. Sci. USA*, 105:17133–17138, 2008.

[1076] A.T. Phillips and W.A. Wood. The mechanism of action of 5′-adenylic acid-activated threonine dehydrase. *J. Biol. Chem.*, 240:4703–4709, 1965.

[1077] M.A. Phillips, T.J. Savage, and R. Croteau. Monoterpene synthases of loblolly pine (*Pinus taeda*) produce pinene isomers and enantiomers. *Arch. Biochem. Biophys.*, 372:197–204, 1999.

[1078] M.A. Phillips, M.R. Wildung, D.C. Williams, D.C. Hyatt, and R. Croteau. cDNA isolation, functional expression, and characterization of (+)-α-pinene synthase and (-)-α-pinene synthase from loblolly pine (*Pinus taeda*): stereocontrol in pinene biosynthesis. *Arch. Biochem. Biophys.*, 411:267–276, 2003.

[1079] R.S. Phillips, P. Poteh, K.A. Miller, and T.R. Hoover. STM2360 encodes a D-ornithine/D-lysine decarboxylase in *Salmonella enterica* serovar typhimurium. *Arch. Biochem. Biophys.*, 634:83–87, 2017.

[1080] B. Philmus, L. Decamps, O. Berteau, and T.P. Begley. Biosynthetic versatility and coordinated action of 5′-deoxyadenosyl radicals in deazaflavin biosynthesis. *J. Am. Chem. Soc.*, 137:5406–5413, 2015.

[1081] S. Picaud, M. Brodelius, and P.E. Brodelius. Expression, purification and characterization of recombinant (*E*)-β-farnesene synthase from *Artemisia annua*. *Phytochemistry*, 66:961–967, 2005.

[1082] S. Picaud, P. Mercke, X. He, O. Sterner, M. Brodelius, D.E. Cane, and P.E. Brodelius. Amorpha-4,11-diene synthase: Mechanism and stereochemistry of the enzymatic cyclization of farnesyl diphosphate. *Arch. Biochem. Biophys.*, 448:150–155, 2006.

[1083] S. Picaud, M.E. Olsson, M. Brodelius, and P.E. Brodelius. Cloning, expression, purification and characterization of recombinant (+)-germacrene D synthase from *Zingiber officinale*. *Arch. Biochem. Biophys.*, 452:17–28, 2006.

[1084] E. Pichersky, E. Lewinsohn, and R. Croteau. Purification and characterization of *S*-linalool synthase, an enzyme involved in the production of floral scent in *Clarkia breweri*. *Arch. Biochem. Biophys.*, 316:803–807, 1995.

[1085] B. Pickel, D.P. Drew, T. Manczak, C. Weitzel, H.T. Simonsen, and D.K. Ro. Identification and characterization of a kunzeaol synthase from *Thapsia garganica*: implications for the biosynthesis of the pharmaceutical thapsigargin. *Biochem. J.*, 448:261–271, 2012.

[1086] J.C. Pieck, U. Hennecke, A.J. Pierik, M.G. Friedel, and T. Carell. Characterization of a new thermophilic spore photoproduct lyase from *Geobacillus stearothermophilus* (SplG) with defined lesion containing DNA substrates. *J. Biol. Chem.*, 281:36317–36326, 2006.

[1087] C. Pinedo, C.M. Wang, J.M. Pradier, B. Dalmais, M. Choquer, P. Le Pecheur, G. Morgant, I.G. Collado, D.E. Cane, and M. Viaud. Sesquiterpene synthase from the botrydial biosynthetic gene cluster of the phytopathogen *Botrytis cinerea*. *ACS Chem. Biol.*, 3:791–801, 2008.

[1088] P. Pirzer, U. Lill, and H. Eggerer. Nicotinic acid metabolism. 2,3-Dimethylmalate lyase. *Hoppe-Seyler's Z. Physiol. Chem.*, 360:1693–1702, 1979.

[1089] T. Pluskal, M. Ueno, and M. Yanagida. Genetic and metabolomic dissection of the ergothioneine and selenoneine biosynthetic pathway in the fission yeast, *S. pombe*, and construction of an overproduction system. *PLoS One*, 9:e97774–e97774, 2014.

[1090] K. Pojasek, R. Raman, P. Kiley, G. Venkataraman, and R. Sasisekharan. Biochemical characterization of the chondroitinase B active site. *J. Biol. Chem.*, 277:31179–31186, 2000.

[1091] K. Pojasek, Z. Shriver, P. Kiley, G. Venkataraman, and R. Sasisekharan. Recombinant expression, purification, and kinetic characterization of chondroitinase AC and chondroitinase B from *Flavobacterium heparinum*. *Biochem. Biophys. Res. Commun.*, 286:343–351, 2001.

[1092] J.R. Pollard and T.D. Bugg. Purification, characterisation and reaction mechanism of monofunctional 2-hydroxypentadienoic acid hydratase from *Escherichia coli*. *Eur. J. Biochem.*, 251:98–106, 1998.

[1093] A.L. Pometto and D.L. Crawford. Whole-cell bioconversion of vanillin to vanillic acid by *Streptomyces viridosporus*. *Appl. Environ. Microbiol.*, 45:1582–1585, 1983.

[1094] L. Poppe and J. Rétey. Friedel-Crafts-type mechanism for the enzymatic elimination of ammonia from histidine and phenylalanine. *Angew. Chem. Int. Ed. Engl.*, 44:3668–3688, 2005.

[1095] R.J. Porra and O.T. Jones. Studies on ferrochelatase. 1. Assay and properties of ferrochelatase from a pig-liver mitochondrial extract. *Biochem. J.*, 87:181–185, 1963.

[1096] R.J. Porra and O.T. Jones. Studies on ferrochelatase. 2. An investigation of the role of ferrochelatase in the biosynthesis of various haem prosthetic groups. *Biochem. J.*, 87:186–192, 1963.

[1097] V. Portnoy, Y. Benyamini, E. Bar, R. Harel-Beja, S. Gepstein, J.J. Giovannoni, A.A. Schaffer, J. Burger, Y. Tadmor, E. Lewinsohn, and N. Katzir. The molecular and biochemical basis for varietal variation in sesquiterpene content in melon (*Cucumis melo* L.) rinds. *Plant Mol. Biol.*, 66:647–661, 2008.

[1098] A.J. Poulose and R. Croteau. γ-Terpinene synthetase: a key enzyme in the biosynthesis of aromatic monoterpenes. *Arch. Biochem. Biophys.*, 191:400–411, 1978.

[1099] J. Powlowski, L. Sahlman, and V. Shingler. Purification and properties of the physically associated meta-cleavage pathway enzymes 4-hydroxy-2-ketovalerate aldolase and aldehyde dehydrogenase (acylating) from *Pseudomonas* sp. strain CF600. *J. Bacteriol.*, 175:377–385, 1993.

[1100] J. Preiss and G. Ashwell. Alginic acid metabolism in bacteria. I. Enzymatic formation of unsaturated oligosaccharides and 4-deoxy-L-*erythro*-5-hexoseulose uronic acid. *J. Biol. Chem.*, 237:309–316, 1962.

[1101] G.D. Prestwich, M. Angelastro, A. De Palma, and M.A. Perino. Fucosterol epoxide lyase of insects: synthesis of labeled substrates and development of a partition assay. *Anal. Biochem.*, 151:315–326, 1985.

[1102] A. Preumont, K. Snoussi, V. Stroobant, J.F. Collet, and E. Van Schaftingen. Molecular identification of pseudouridine-metabolizing enzymes. *J. Biol. Chem.*, 283:25238–25246, 2008.

[1103] A. Pribat, L. Jeanguenin, A. Lara-Nunez, M.J. Ziemak, J.E. Hyde, V. de Crecy-Lagard, and A.D. Hanson. 6-pyruvoyltetrahydropterin synthase paralogs replace the folate synthesis enzyme dihydroneopterin aldolase in diverse bacteria. *J. Bacteriol.*, 191:4158–4165, 2009.

[1104] R.H. Proctor and T.M. Hohn. Aristolochene synthase. Isolation, characterization, and bacterial expression of a sesquiterpenoid biosynthetic gene (*Ari1*) from *Penicillium roqueforti*. *J. Biol. Chem.*, 268:4543–4548, 1993.

[1105] I. Prosser, I.G. Altug, A.L. Phillips, W.A. Konig, H.J. Bouwmeester, and M.H. Beale. Enantiospecific (+)- and (-)-germacrene D synthases, cloned from goldenrod, reveal a functionally active variant of the universal isoprenoid-biosynthesis aspartate-rich motif. *Arch. Biochem. Biophys.*, 432:136–144, 2004.

[1106] I. Prosser, A.L. Phillips, S. Gittings, M.J. Lewis, A.M. Hooper, J.A. Pickett, and M.H. Beale. (+)-(10*R*)-Germacrene A synthase from goldenrod, *Solidago canadensis*; cDNA isolation, bacterial expression and functional analysis. *Phytochemistry*, 60:691–702, 2002.

[1107] I.M. Prosser, R.J. Adams, M.H. Beale, N.D. Hawkins, A.L. Phillips, J.A. Pickett, and L.M. Field. Cloning and functional characterisation of a *cis*-muuroladiene synthase from black peppermint (*Mentha* $\times$ *piperita*) and direct evidence for a chemotype unable to synthesise farnesene. *Phytochemistry*, 67:1564–1571, 2006.

[1108] M.R. Pudek and W.R. Richards. A possible alternate pathway of bacteriochlorophyll biosynthesis in a mutant of *Rhodopseudomonas sphaeroides*. *Biochemistry*, 14:3132–3137, 1975.

[1109] B.W. Pyle, H.T. Tran, B. Pickel, T.M. Haslam, Z. Gao, G. Macnevin, J.C. Vederas, S.U. Kim, and D.K. Ro. Enzymatic synthesis of valerena-4,7(11)-diene by a unique sesquiterpene synthase from the valerian plant (*Valeriana officinalis*). *FEBS J.*, 279:3136–3146, 2012.

[1110] H.J. Pyun, K.C. Wagschal, D.I. Jung, R.M. Coates, and R. Croteau. Stereochemistry of the proton elimination in the formation of (+)- and (-)-α-pinene by monoterpene cyclases from sage (*Salvia officinalis*). *Arch. Biochem. Biophys.*, 308:488–496, 1994.

[1111] Y.M. Qin, A.M. Haapalainen, D. Conry, D.A. Cuebas, J.K. Hiltunen, and D.K. Novikov. Recombinant 2-enoyl-CoA hydratase derived from rat peroxisomal multifunctional enzyme 2: role of the hydratase reaction in bile acid synthesis. *Biochem. J.*, 328:377–382, 1997.

[1112] J.R. Quayle. Carbon assimilation by *Pseudomonas oxalaticus* (OX1). 7. Decarboxylation of oxalyl-coenzyme A to formyl-coenzyme A. *Biochem. J.*, 89:492–503, 1963.

[1113] P. Rabe, L. Barra, J. Rinkel, R. Riclea, C.A. Citron, T.A. Klapschinski, A. Janusko, and J.S. Dickschat. Conformational analysis, thermal rearrangement, and EI-MS fragmentation mechanism of ((1(10)*E*,4*E*,6*S*,7*R*)-germacradien-6-ol by ^{13}C-labeling experiments. *Angew. Chem. Int. Ed. Engl.*, 54:13448–13451, 2015.

[1114] P. Rabe and J.S. Dickschat. Rapid chemical characterization of bacterial terpene synthases. *Angew. Chem. Int. Ed. Engl.*, 52:1810–1812, 2013.

[1115] P. Rabe, A. Janusko, B. Goldfuss, and J.S. Dickschat. Experimental and theoretical studies on corvol ether biosynthesis. *ChemBioChem*, 17:146–149, 2016.

[1116] P. Rabe, K.A. Pahirulzaman, and J.S. Dickschat. Structures and biosynthesis of corvol ethers—sesquiterpenes from the actinomycete *Kitasatospora setae*. *Angew. Chem. Int. Ed. Engl.*, 54:6041–6045, 2015.

[1117] P. Rabe, J. Rinkel, E. Dolja, T. Schmitz, B. Nubbemeyer, T.H. Luu, and J.S. Dickschat. Mechanistic investigations of two bacterial diterpene cyclases: spiroviolene synthase and tsukubadiene synthase. *Angew. Chem. Int. Ed. Engl.*, 56:2776–2779, 2017.

[1118] P. Rabe, J. Rinkel, B. Nubbemeyer, T.G. Kollner, F. Chen, and J.S. Dickschat. Terpene cyclases from social Amoebae. *Angew. Chem. Int. Ed. Engl.*, 55:15420–15423, 2016.

[1119] P. Rabe, M. Samborskyy, P.F. Leadlay, and J.S. Dickschat. Isoafricanol synthase from *Streptomyces malaysiensis*. *Org. Biomol. Chem.*, 15:2353–2358, 2017.

[1120] P. Rabe, T. Schmitz, and J.S. Dickschat. Mechanistic investigations on six bacterial terpene cyclases. *Beilstein J. Org. Chem.*, 12:1839–1850, 2016.

[1121] J.C. Rabinowitz and W.E. Pricer. Formiminotetrahydrofolic acid and methenyltetrahydrofolic acid as intermediates in the formation of N^{10}-formyltetrahydrofolic acid. *J. Am. Chem. Soc.*, 78:5702–5704, 1956.

[1122] E. Racker. The mechanism of action of glyoxalase. *J. Biol. Chem.*, 190:685–696, 1951.

[1123] E. Racker. Enzymatic synthesis and breakdown of desoxyribose phosphate. *J. Biol. Chem.*, 196:347–365, 1952.

[1124] J.F. Rakus, A.A. Fedorov, E.V. Fedorov, M.E. Glasner, B.K. Hubbard, J.D. Delli, P.C. Babbitt, S.C. Almo, and J.A. Gerlt. Evolution of enzymatic activities in the enolase superfamily: L-rhamnonate dehydratase. *Biochemistry*, 47:9944–9954, 2008.

[1125] J.F. Rakus, C. Kalyanaraman, A.A. Fedorov, E.V. Fedorov, F.P. Mills-Groninger, R. Toro, J. Bonanno, K. Bain, J.M. Sauder, S.K. Burley, S.C. Almo, M.P. Jacobson, and J.A. Gerlt. Computation-facilitated assignment of the function in the enolase superfamily: a regiochemically distinct galactarate dehydratase from *Oceanobacillus iheyensis*. *Biochemistry*, 48:11546–11558, 2009.

[1126] S. Ramakrishna and P.R. Adiga. Arginine decarboxylase from *Lathyrus sativus* seedlings. Purification and properties. *Eur. J. Biochem.*, 59:377–386, 1975.

[1127] S.G. Ramaswamy. Conversion of 3-hydroxyproline to proline in the rat requires reduced pyridine-nucleotides. *Fed. Proc.*, 42:2232–2232, 1983.

[1128] I. Ramazzina, C. Folli, A. Secchi, R. Berni, and R. Percudani. Completing the uric acid degradation pathway through phylogenetic comparison of whole genomes. *Nat. Chem. Biol.*, 2:144–148, 2006.

[1129] F. Ramos and J.-M. Wiame. Occurrence of a catabolic L-serine (L-threonine) deaminase in *Saccharomyces cerevisiae*. *Eur. J. Biochem.*, 123:571–576, 1982.

[1130] N.K. Ranjith, Ch. Sasikala, and Ch.V. Ramana. Catabolism of L-phenylalanine and L-tyrosine by *Rhodobacter sphaeroides* OU5 occurs through 3,4-dihydroxyphenylalanine. *Res. Microbiol.*, 158:506–511, 2007.

[1131] M.R. Raghavendra Rao, S.S. Subramanian, H.I. Rahatekar, and S.V. Paranjape. Enzymatic hydration of citraconate to (-)citramalate. *Biochem. Biophys. Res. Commun.*, 12:78–82, 1963.

[1132] P.V. Subba Rao, K. Moore, , and G.H.N. O-Pyrocatechiuc acid carboxy-lyase from *Aspergillus niger*. *Arch. Biochem. Biophys.*, 122:466–473, 1967.

[1133] T. Raschle, N. Amrhein, and T.B. Fitzpatrick. On the two components of pyridoxal 5′-phosphate synthase from *Bacillus subtilis*. *J. Biol. Chem.*, 280:32291–32300, 2005.

[1134] T. Raschle, D. Arigoni, R. Brunisholz, H. Rechsteiner, N. Amrhein, and T.B. Fitzpatrick. Reaction mechanism of pyridoxal 5′-phosphate synthase. Detection of an enzyme-bound chromophoric intermediate. *J. Biol. Chem.*, 282:6098–6105, 2007.

[1135] L.J. Rather, B. Knapp, W. Haehnel, and G. Fuchs. Coenzyme A-dependent aerobic metabolism of benzoate via epoxide formation. *J. Biol. Chem.*, 285:20615–20624, 2010.

[1136] E. Raux, C. Thermes, P. Heathcote, A. Rambach, and M.J. Warren. A role for *Salmonella typhimurium cbiK* in cobalamin (vitamin B_{12}) and siroheme biosynthesis. *J. Bacteriol.*, 179:3202–3212, 1997.

[1137] M.M. Ravn, R.J. Peters, R.M. Coates, and R. Croteau. Mechanism of abietadiene synthase catalysis: stereochemistry and stabilization of the cryptic pimarenyl carbocation intermediates. *J. Am. Chem. Soc.*, 124:6998–7006, 2002.

[1138] S. Ray and M. Ray. Isolation of methylglyoxal synthase from goat liver. *J. Biol. Chem.*, 256:6230–6233, 1981.

[1139] D. Rea, V. Fulop, T.D. Bugg, and D.I. Roper. Structure and mechanism of HpcH: a metal ion dependent class II aldolase from the homoprotocatechuate degradation pathway of *Escherichia coli*. *J. Mol. Biol.*, 373:866–876, 2007.

[1140] D. Rea, R. Hovington, J.F. Rakus, J.A. Gerlt, V. Fulop, T.D. Bugg, and D.I. Roper. Crystal structure and functional assignment of YfaU, a metal ion dependent class II aldolase from *Escherichia coli* K12. *Biochemistry*, 47:9955–9965, 2008.

[1141] K.K. Reddi and L.J. Mauser. Studies on the formation of tobacco mosaic virus ribonucleic acid. VI. Mode of degradation of host ribonucleic acid to ribonucleosides and their conversion to ribonucleoside 5′-phosphates. *Proc. Natl. Acad. Sci. USA*, 53:607–613, 1965.

[1142] M. Reher, T. Fuhrer, M. Bott, and P. Schonheit. The nonphosphorylative Entner-Doudoroff pathway in the thermoacidophilic euryarchaeon *Picrophilus torridus* involves a novel 2-keto-3-deoxygluconate- specific aldolase. *J. Bacteriol.*, 192:964–974, 2010.

[1143] U. Rein, R. Gueta, K. Denger, J. Ruff, K. Hollemeyer, and A.M. Cook. Dissimilation of cysteate via 3-sulfolactate sulfo-lyase and a sulfate exporter in *Paracoccus pantotrophus* NKNCYSA. *Microbiology*, 151:737–747, 2005.

[1144] F. Ren, H. Mao, J. Liang, J. Liu, K. Shu, and Q. Wang. Functional characterization of ZmTPS7 reveals a maize τ-cadinol synthase involved in stress response. *Planta*, 244:1065–1074, 2016.

[1145] J.F. Rensen, T. Matsushita, J.G. Chirikjian, and F.F. Davis. Enzymatic synthesis of deoxypseudouridylic acid and a study of certain of its properties. *Biochim. Biophys. Acta*, 281:481–487, 1972.

[1146] J. Rétey. The urocanase story: a novel role of NAD^+ as electrophile. *Arch. Biochem. Biophys.*, 314:1–16, 1994.

[1147] R.H., Lee Abeles, , and Jr. An intramolecular oxidation-reduction requiring a cobamide coenzyme. *J. Biol. Chem.*, 236:2347–2350, 1961.

[1148] D.W. Ribbons and W.C. Evans. Oxidative metabolism of phthalic acid by soil pseudomonads. *Biochem. J.*, 76:310–318, 1966.

[1149] R. Riclea, C.A. Citron, J. Rinkel, and J.S. Dickschat. Identification of isoafricanol and its terpene cyclase in *Streptomyces violaceusniger* using CLSA-NMR. *Chem. Commun. (Camb.)*, 50:4228–4230, 2014.

[1150] C. Rieder, W. Eisenreich, J. O'Brien, G. Richter, E. Götze, P. Boyle, S. Blanchard, A. Bacher, and H. Simon. Rearrangement reactions in the biosynthesis of molybdopterin - an NMR study with multiply $^{13}C/^{15}N$ labelled precursors. *Eur. J. Biochem.*, 255:24–36, 1998.

[1151] L.U. Rigo, L.R. Maréchal, M.M. Vieira, and L.A. Veiga. Oxidative pathway for L-rhamnose degradation in *Pallularia pullulans*. *Can. J. Microbiol.*, 31:817–822, 1985.

[1152] W.O. Riley and E.E. Snell. Histidine decarboxylase of *Lactobacillus* 30a. IV. The presence of covalently bound pyruvate as the prosthetic group. *Biochemistry*, 7:3520–3528, 1968.

[1153] E.A. Taylor Ringia, J.B. Garrett, J.B. Thoden, H.M. Holden, I. Rayment, and J.A. Gerlt. Evolution of enzymatic activity in the enolase superfamily: functional studies of the promiscuous *o*-succinylbenzoate synthase from *Amycolatopsis*. *Biochemistry*, 43:224–229, 2004.

[1154] J. Rinkel, P. Rabe, X. Chen, T.G. Kollner, F. Chen, and J.S. Dickschat. Mechanisms of the diterpene cyclases β-pinacene synthase from *Dictyostelium discoideum* and hydropyrene synthase from *Streptomyces clavuligerus*. *Chem. Eur. J.*, 23:10501–10505, 2017.

[1155] J. Rinkel, P. Rabe, P. Garbeva, and J.S. Dickschat. Lessons from 1,3-hydride shifts in sesquiterpene cyclizations. *Angew. Chem. Int. Ed. Engl.*, 55:13593–13596, 2016.

[1156] M.A. Rishavy and K.L. Berkner. Vitamin K oxygenation, glutamate carboxylation, and processivity: defining the three critical facets of catalysis by the vitamin K-dependent carboxylase. *Adv Nutr*, 3:135–148, 2012.

[1157] M.A. Rishavy, K.W. Hallgren, A.V. Yakubenko, R.L. Shtofman, K.W. Runge, and K.L. Berkner. Bronsted analysis reveals Lys^{218} as the carboxylase active site base that deprotonates vitamin K hydroquinone to initiate vitamin K-dependent protein carboxylation. *Biochemistry*, 45:13239–13248, 2006.

[1158] K.A. Rising, C.M. Starks, J.P. Noel, and J. Chappell. Demonstration of germacrene A as an intermediate in 5-*epi*-aristolochene synthase catalysis. *J. Am. Chem. Soc.*, 122:1861–1866, 2000.

[1159] H. Ritter and G.E. Schulz. Structural basis for the entrance into the phenylpropanoid metabolism catalyzed by phenylalanine ammonia-lyase. *Plant Cell*, 16:3426–3436, 2004.

[1160] D.K. Ro and J. Bohlmann. Diterpene resin acid biosynthesis in loblolly pine (*Pinus taeda*): functional characterization of abietadiene/levopimaradiene synthase (PtTPS-LAS) cDNA and subcellular targeting of PtTPS-LAS and abietadienol/abietadienal oxidase (PtAO, CYP720B1). *Phytochemistry*, 67:1572–1578, 2006.

[1161] D.K. Ro, J. Ehlting, C.I. Keeling, R. Lin, N. Mattheus, and J. Bohlmann. Microarray expression profiling and functional characterization of AtTPS genes: duplicated *Arabidopsis thaliana* sesquiterpene synthase genes At4g13280 and At4g13300 encode root-specific and wound-inducible (*Z*)-γ-bisabolene synthases. *Arch. Biochem. Biophys.*, 448:104–116, 2006.

[1162] J.M. Robert-Baudouy and F.R. Stoeber. [Purification and properties of D-mannonate hydrolyase from *Escherichia coli* K12]. *Biochim. Biophys. Acta*, 309:473–485, 1973.

[1163] E. Roberts and S. Frankel. Further studies of glutamic acid decarboxylase in brain. *J. Biol. Chem.*, 190:505–512, 1951.

[1164] W.G. Robinson and R. Labow. L-Serine dehydratase (*Escherichia coli*). *Methods Enzymol.*, 17B:356–360, 1971.

[1165] H. Rode and F. Giffhorn. D-(-)-Tartrate dehydratase of *Rhodopseudomonas sphaeroides*: purification, characterization, and application to enzymatic determination of D-(-)-tartrate. *J. Bacteriol.*, 150:1061–1068, 1982.

[1166] H. Rode and F. Giffhorn. Ferrous- or cobalt ion-dependent D-(-)-tartrate dehydratase of pseudomonads: purification and properties. *J. Bacteriol.*, 151:1602–1604, 1982.

[1167] A.V. Rodrigues, D.J. Tantillo, A. Mukhopadhyay, J.D. Keasling, and H. Beller. Insights into the mechanism of phenylacetate decarboxylase (PhdB), a toluene-producing glycyl radical enzyme. *ChemBioChem*, 2019.

[1168] R.J. Van Rooijen, S. Van Schalkwijk, , and W.M. Molecular cloning, characterization, and nucleotide sequence of the tagatose 6-phosphate pathway gene cluster of the lactose operon of *Lactococcus lactis*. *J. Biol. Chem.*, 266:7176–7181, 1991.

[1169] J. Rosenthaler, B.M. Guirard, G.W. Chang, and E.E. Snell. Purification and properties of histidine decarboxylase from *Lactobacillus* 30a. *Proc. Natl. Acad. Sci. USA*, 54:152–158, 1965.

[1170] J. Rösler, F. Krekel, N. Amrhein, and J. Schmid. Maize phenylalanine ammonia-lyase has tyrosine ammonia-lyase activity. *Plant Physiol.*, 113:175–179, 1997.

[1171] B.M. Rosner and B. Schink. Purification and characterization of acetylene hydratase of *Pelobacter acetylenicus*, a tungsten iron-sulfur protein. *J. Bacteriol.*, 177:5767–5772, 1995.

[1172] S.L. Rotenberg and D.B. Sprinson. Mechanism and stereochemistry of 5-dehydroquinate synthetase. *Proc. Natl. Acad. Sci. USA*, 67:1669–1672, 1970.

[1173] M. Rueffer and M.H. Zenk. Distant precursors of benzylisoquinoline alkaloids and their enzymatic formation. *Z. Naturforsch. C: Biosci.*, 42:319–332, 1987.

[1174] M. Ruppert, J. Woll, A. Giritch, E. Genady, X. Ma, and J. Stöckigt. Functional expression of an ajmaline pathway-specific esterase from *Rauvolfia* in a novel plant-virus expression system. *Planta*, 222:888–898, 2005.

[1175] D.W. Russell. The enzymes, regulation, and genetics of bile acid synthesis. *Annu. Rev. Biochem.*, 72:137–174, 2003.

[1176] M.W. Ruszczycky, S.H. Choi, and H.W. Liu. Stoichiometry of the redox neutral deamination and oxidative dehydrogenation reactions catalyzed by the radical SAM enzyme DesII. *J. Am. Chem. Soc.*, 132:2359–2369, 2010.

[1177] M.W. Ruszczycky, S.H. Choi, S.O. Mansoorabadi, and H.W. Liu. Mechanistic studies of the radical *S*-adenosyl-L-methionine enzyme DesII: EPR characterization of a radical intermediate generated during its catalyzed dehydrogenation of TDP-D-quinovose. *J. Am. Chem. Soc.*, 133:7292–7295, 2011.

[1178] M.J. Rynkiewicz, D.E. Cane, and D.W. Christianson. Structure of trichodiene synthase from *Fusarium sporotrichioides* provides mechanistic inferences on the terpene cyclization cascade. *Proc. Natl. Acad. Sci. USA*, 98:13543–13548, 2001.

[1179] J. Saar, J.C. Kader, K. Poralla, and G. Ourisson. Purification and some properties of the squalene-tetrahymanol cyclase from *Tetrahymena thermophila*. *Biochim. Biophys. Acta*, 1075:93–101, 1991.

[1180] W. Sacks and C.O. Jensen. Malease, a hydrase from corn kernals. *J. Biol. Chem.*, 192:231–236, 1951.

[1181] R.D. Sagers and J. Carter. E. L-Serine dehydratase (*Clostridium acidiurica*). *Methods Enzymol.*, 17B:351–356, 1971.

[1182] F. Saida, M. Uzan, and F. Bontems. The phage T_4 restriction endoribonuclease RegB: a cyclizing enzyme that requires two histidines to be fully active. *Nucleic Acids Res.*, 31:2751–2758, 2003.

[1183] H. Saito, T. Yamagata, and S. Suzuki. Enzymatic methods for the determination of small quantities of isomeric chondroitin sulfates. *J. Biol. Chem.*, 243:1536–1542, 1968.

[1184] K. Saito, Y. Sumita, Y. Nagasaka, F. Tomita, and A. Yokota. Molecular cloning of the gene encoding the di-D-fructofuranose 1,2′:2,3′ dianhydride hydrolysis enzyme (DFA IIIase) from *Arthrobacter* sp. H65-7. *J. Biosci. Bioeng.*, 95:538–540, 2003.

[1185] K. Saito and F. Tomita. Difructose anhydrides: Their mass-production and physiological functions. *Biosci. Biotechnol. Biochem.*, 64:1321–1327, 2000.

[1186] E. Sakuno, Y. Wen, H. Hatabayashi, H. Arai, C. Aoki, K. Yabe, and H. Nakajima. *Aspergillus parasiticus* cyclase catalyzes two dehydration steps in aflatoxin biosynthesis. *Appl. Environ. Microbiol.*, 71:2999–3006, 2005.

[1187] E. Sakuno, K. Yabe, and H. Nakajima. Involvement of two cytosolic enzymes and a novel intermediate, 5′-oxoaverantin, in the pathway from 5′-hydroxyaverantin to averufin in aflatoxin biosynthesis. *Appl. Environ. Microbiol.*, 69:6418–6426, 2003.

[1188] C. Sallaud, C. Giacalone, R. Topfer, S. Goepfert, N. Bakaher, S. Rosti, and A. Tissier. Characterization of two genes for the biosynthesis of the labdane diterpene *Z*-abienol in tobacco (*Nicotiana tabacum*) glandular trichomes. *Plant J.*, 72:1–17, 2012.

[1189] C. Sallaud, D. Rontein, S. Onillon, F. Jabes, P. Duffe, C. Giacalone, S. Thoraval, C. Escoffier, G. Herbette, N. Leonhardt, M. Causse, and A. Tissier. A novel pathway for sesquiterpene biosynthesis from *Z*,*Z*-farnesyl pyrophosphate in the wild tomato *Solanum habrochaites*. *Plant Cell*, 21:301–317, 2009.

[1190] N. Samanani and P.J. Facchini. Purification and characterization of norcoclaurine synthase. The first committed enzyme in benzylisoquinoline alkaloid biosynthesis in plants. *J. Biol. Chem.*, 277:33878–33883, 2002.

[1191] G.B. Sancar, F.W. Smith, R. Reid, G. Payne, M. Levy, and A. Sancar. Action mechanism of *Escherichia coli* DNA photolyase. I. Formation of the enzyme-substrate complex. *J. Biol. Chem.*, 262:478–485, 1987.

[1192] B. Sanson, R.M. Hu, E. Troitskayadagger, N. Mathy, and M. Uzan. Endoribonuclease RegB from bacteriophage T_4 is necessary for the degradation of early but not middle or late mRNAs. *J. Mol. Biol.*, 297:1063–1074, 2000.

[1193] K. Sasaki, K. Ohara, and K. Yazaki. Gene expression and characterization of isoprene synthase from *Populus alba*. *FEBS Lett.*, 579:2514–2518, 2005.

[1194] T. Sato, M. Kouda, and T. Hoshino. Site-directed mutagenesis experiments on the putative deprotonation site of squalene-hopene cyclase from *Alicyclobacillus acidocaldarius*. *Biosci. Biotechnol. Biochem.*, 68:728–738, 2004.

[1195] T. Sato, H. Yamaga, S. Kashima, Y. Murata, T. Shinada, C. Nakano, and T. Hoshino. Identification of novel sesterterpene/triterpene synthase from *Bacillus clausii*. *ChemBioChem*, 14:822–825, 2013.

[1196] T. Sato, S. Yoshida, H. Hoshino, M. Tanno, M. Nakajima, and T. Hoshino. Sesquarterpenes (C_{35} terpenes) biosynthesized via the cyclization of a linear C_{35} isoprenoid by a tetraprenyl-β-curcumene synthase and a tetraprenyl-β-curcumene cyclase: identification of a new terpene cyclase. *J. Am. Chem. Soc.*, 133:9734–9737, 2011.

[1197] M. Satre and E.P. Kennedy. Identification of bound pyruvate essential for the activity of phosphatidylserine decarboxylase of *Escherichia coli*. *J. Biol. Chem.*, 253:479–483, 1978.

[1198] N.A. Saunee, S.R. Williams, D.A. Bryant, and W.M. Schluchter. Biogenesis of phycobiliproteins: II. CpcS-I and CpcU comprise the heterodimeric bilin lyase that attaches phycocyanobilin to Cys-82 of β-phycocyanin and Cys-81 of allophycocyanin subunits in *Synechococcus* sp. PCC 7002. *J. Biol. Chem.*, 283:7513–7522, 2008.

[1199] T.J. Savage and R. Croteau. Biosynthesis of monoterpenes: regio- and stereochemistry of (+)-3-carene biosynthesis. *Arch. Biochem. Biophys.*, 305:581–587, 1993.

[1200] T.J. Savage, M.W. Hatch, and R. Croteau. Monoterpene synthases of *Pinus contorta* and related conifers. A new class of terpenoid cyclase. *J. Biol. Chem.*, 269:4012–4020, 1994.

[1201] T.J. Savage, H. Ichii, S.D. Hume, D.B. Little, and R. Croteau. Monoterpene synthases from gymnosperms and angiosperms: stereospecificity and inactivation by cysteinyl- and arginyl-directed modifying reagents. *Arch. Biochem. Biophys.*, 320:257–265, 1995.

[1202] H. Sawada and Y. Takagi. The metabolism of L-rhamnose in *Escherichia coli*. 3. L-Rhamulose-phosphate aldolase. *Biochim. Biophys. Acta*, 92:26–32, 1964.

[1203] R. Schauer. Sialic acids. *Adv. Carbohydr. Chem. Biochem.*, 40:131–234, 1982.

[1204] H.G. Schepmann, J. Pang, and S.P. Matsuda. Cloning and characterization of *Ginkgo biloba* levopimaradiene synthase which catalyzes the first committed step in ginkgolide biosynthesis. *Arch. Biochem. Biophys.*, 392:263–269, 2001.

[1205] U. Scherf and W. Buckel. Purification and properties of an iron-sulfur and FAD-containing 4-hydroxybutyryl-CoA dehydratase/vinylacetyl-CoA Δ^3-Δ^2-isomerase from *Clostridium aminobutyricum*. *Eur. J. Biochem.*, 215:421–429, 1993.

[1206] U. Scherf, B. Sohling, G. Gottschalk, D. Linder, and W. Buckel. Succinate-ethanol fermentation in *Clostridium kluyveri*: purification and characterisation of 4-hydroxybutyryl-CoA dehydratase/vinylacetyl-CoA Δ^3-Δ^2-isomerase. *Arch. Microbiol.*, 161:239–245, 1994.

[1207] A. Schifrin, Y. Khatri, P. Kirsch, V. Thiel, S. Schulz, and R. Bernhardt. A single terpene synthase is responsible for a wide variety of sesquiterpenes in *Sorangium cellulosum* Soce56. *Org. Biomol. Chem.*, 14:3385–3393, 2016.

[1208] A. Schifrin, T.T. Ly, N. Gunnewich, J. Zapp, V. Thiel, S. Schulz, F. Hannemann, Y. Khatri, and R. Bernhardt. Characterization of the gene cluster CYP264B1-*geoA* from *Sorangium cellulosum* So ce56: biosynthesis of (+)-eremophilene and its hydroxylation. *ChemBioChem*, 16:337–344, 2015.

[1209] A.L. Schilmiller, I. Schauvinhold, M. Larson, R. Xu, A.L. Charbonneau, A. Schmidt, C. Wilkerson, R.L. Last, and E. Pichersky. Monoterpenes in the glandular trichomes of tomato are synthesized from a neryl diphosphate precursor rather than geranyl diphosphate. *Proc. Natl. Acad. Sci. USA*, 106:10865–10870, 2009.

[1210] M. Schirm, E.C. Soo, A.J. Aubry, J. Austin, P. Thibault, and S.M. Logan. Structural, genetic and functional characterization of the flagellin glycosylation process in *Helicobacter pylori*. *Mol. Microbiol.*, 48:1579–1592, 2003.

[1211] A. Schirmer, M.A. Rude, X. Li, E. Popova, and S.B. del Cardayre. Microbial biosynthesis of alkanes. *Science*, 329:559–562, 2010.

[1212] E. Schleicher, K. Hitomi, C.W. Kay, E.D. Getzoff, T. Todo, and S. Weber. Electron nuclear double resonance differentiates complementary roles for active site histidines in (6-4) photolyase. *J. Biol. Chem.*, 282:4738–4747, 2007.

[1213] K. Schlossmann, J. Brüggemann, and F. Lynen. Biosynthese des Cysteins. I. Nachweis und Isolierung der Serinsulfhydrase aus Bäckerhefe. *Biochem. Z.*, 336:258–273, 1962.

[1214] M. Schmid, M. Berg, H. Hilbi, and P. Dimroth. Malonate decarboxylase of *Klebsiella pneumoniae* catalyses the turnover of acetyl and malonyl thioester residues on a coenzyme-A-like prosthetic group. *Eur. J. Biochem.*, 237:221–228, 1996.

[1215] A. Schmidt. A cysteine desulfhydrase from spinach leaves specific for D-cysteine. *Z. Pflanzenphysiol.*, 107:301–312, 1982.

[1216] A. Schmidt and I. Erdle. A cysteine desulfhydrase specific for D-cysteine from the green-alga *Chlorella fusca*. *Z. Naturforsch. C: Biosci.*, 38:428–435, 1983.

[1217] A. Schmidt, K. Gruber, C. Kratky, and V.S. Lamzin. Atomic resolution crystal structures and quantum chemistry meet to reveal subtleties of hydroxynitrile lyase catalysis. *J. Biol. Chem.*, 283:21827–21836, 2008.

[1218] C.O. Schmidt, H.J. Bouwmeester, N. Bulow, and W.A. Konig. Isolation, characterization, and mechanistic studies of (-)-α-gurjunene synthase from *Solidago canadensis*. *Arch. Biochem. Biophys.*, 364:167–177, 1999.

[1219] C.O. Schmidt, H.J. Bouwmeester, S. Franke, and W.A. König. Mechanisms of the biosynthesis of sesquiterpene enantiomers (+)- and (-)-germacrene D in *Solidago canadensis*. *Chirality*, 11:353–362, 1999.

[1220] J.C. Schmidt and H. Zalkin. Chorismate mutase-prephenate dehydratase. Partial purification and properties of the enzyme from *Salmonella typhimurium*. *Biochemistry*, 8:174–181, 1969.

[1221] M. Schmidt, S. Herve, N. Klempier, and H. Griengl. Preparation of optically active cyanohydrins using the (*S*)-hydroxynitrile lyase from *Hevea brasiliensis*. *Tetrahedron*, 52:7833–7840, 1996.

[1222] R. Schmidt, V. Jager, D. Zuhlke, C. Wolff, J. Bernhardt, K. Cankar, J. Beekwilder, W.V. Ijcken, F. Sleutels, W. Boer, K. Riedel, and P. Garbeva. Fungal volatile compounds induce production of the secondary metabolite sodorifen in *Serratia plymuthica* PRI-2C. *Sci. Rep.*, 7:862–862, 2017.

[1223] A. Schmitt, I. Bottke, and G. Siebert. Eigenschaften einer Oxaloacetat-Decarboxylase aus Dorschmuskulatur. *Hoppe-Seyler's Z. Physiol. Chem.*, 347:18–34, 1966.

[1224] C. Schnee, T.G. Kollner, J. Gershenzon, and J. Degenhardt. The maize gene terpene synthase 1 encodes a sesquiterpene synthase catalyzing the formation of (*E*)-β-farnesene, (*E*)-nerolidol, and (*E*,*E*)-farnesol after herbivore damage. *Plant Physiol.*, 130:2049–2060, 2002.

[1225] C. Schnee, T.G. Kollner, M. Held, T.C. Turlings, J. Gershenzon, and J. Degenhardt. The products of a single maize sesquiterpene synthase form a volatile defense signal that attracts natural enemies of maize herbivores. *Proc. Natl. Acad. Sci. USA*, 103:1129–1134, 2006.

[1226] Z. Schneider, E.G. Larsen, G. Jacobsen, B.C. Johnson, and J. Pawelkiewicz. Purification and properties of glycerol dehydrase. *J. Biol. Chem.*, 245:3388–3396, 1970.

[1227] Z. Schneider and J. Pawelkiewicz. The properties of glycerol dehydratase isolated from *Aerobacter aerogenes*, and the properties of the apoenzyme subunits. *Acta Biochim. Pol.*, 13:311–328, 1966.

[1228] J.-P. Schnitzler, I. Zimmer, A. Bachl, M. Arend, J. Fromm, and R.J. Fischbach. Biochemical properties of isoprene synthase in poplar (*Populus x canescens*). *Planta*, 222:777–786, 2005.

[1229] J.P. Schnitzler, R. Arenz, R. Steinbrecher, and A. Lehming. Characterization of an isoprene synthase from leaves of *Quercus petraea*. *Bot. Acta*, 109:216–221, 1996.

[1230] I.C. Schoenhofen, D.J. McNally, J.R. Brisson, and S.M. Logan. Elucidation of the CMP-pseudaminic acid pathway in *Helicobacter pylori*: synthesis from UDP-*N*-acetylglucosamine by a single enzymatic reaction. *Glycobiology*, 16:8C–14C, 2006.

[1231] I.C. Schoenhofen, D.J. McNally, E. Vinogradov, D. Whitfield, N.M. Young, S. Dick, W.W. Wakarchuk, J.R. Brisson, and S.M. Logan. Functional characterization of dehydratase/aminotransferase pairs from *Helicobacter* and *Campylobacter*: enzymes distinguishing the pseudaminic acid and bacillosamine biosynthetic pathways. *J. Biol. Chem.*, 281:723–732, 2006.

[1232] J.M. Scholtz and S.M. Schuster. Regulation of rat liver 4-hydroxy-2-ketoglutarate aldolase. *Biochim. Biophys. Acta*, 869:192–196, 1986.

[1233] M. Schramm, V. Klybas, and E. Racker. Phospholytic cleavage of fructose-6-phosphate by fructose-6-phosphate phosphoketolase from *Acetobacter xylinum*. *J. Biol. Chem.*, 233:1283–1288, 1958.

[1234] H.L. Schubert, E. Raux, A.A. Brindley, H.K. Leech, K.S. Wilson, C.P. Hill, and M.J. Warren. The structure of *Saccharomyces cerevisiae* Met8p, a bifunctional dehydrogenase and ferrochelatase. *EMBO J.*, 21:2068–2075, 2002.

[1235] H.L. Schubert, E. Raux, K.S. Wilson, and M.J. Warren. Common chelatase design in the branched tetrapyrrole pathways of heme and anaerobic cobalamin synthesis. *Biochemistry*, 38:10660–10669, 1999.

[1236] K. Schuhle and G. Fuchs. Phenylphosphate carboxylase: a new C-C lyase involved in anaerobic phenol metabolism in *Thauera aromatica*. *J. Bacteriol.*, 186:4556–4567, 2004.

[1237] A.R. Schulz and L. Oliner. The possible role of thyroid aromatic amino acid decarboxylase in thyroxine biosynthesis. *Life Sci.*, 6:873–880, 1967.

[1238] H. Schulz. Long chain enoyl coenzyme A hydratase from pig heart. *J. Biol. Chem.*, 249:2704–2709, 1974.

[1239] C. Schumann, H. Michlmayr, A.M. Del Hierro, K.D. Kulbe, V. Jiranek, R. Eder, and T.H. Nguyen. Malolactic enzyme from *Oenococcus oeni*: heterologous expression in *Escherichia coli* and biochemical characterization. *Bioengineered*, 4:147–152, 2013.

[1240] T.F. Schwede, J. Rétey, and G.E. Schulz. Crystal structure of histidine ammonia-lyase revealing a novel polypeptide modification as the catalytic electrophile. *Biochemistry*, 38:5355–5361, 1999.

[1241] G. Schweiger and W. Buckel. On the dehydration of (*R*)-lactate in the fermentation of alanine to propionate by *Clostridium propionicum*. *FEBS Lett.*, 171:79–84, 1984.

[1242] G. Schweiger, R. Dutscho, and W. Buckel. Purification of 2-hydroxyglutaryl-CoA dehydratase from *Acidaminococcus fermentans*. An iron-sulfur protein. *Eur. J. Biochem.*, 169:441–448, 1987.

[1243] K. Schwibbert, A. Marin-Sanguino, I. Bagyan, G. Heidrich, G. Lentzen, H. Seitz, M. Rampp, S.C. Schuster, H.P. Klenk, F. Pfeiffer, D. Oesterhelt, and H.J. Kunte. A blueprint of ectoine metabolism from the genome of the industrial producer *Halomonas elongata* DSM 2581 T. *Environ. Microbiol.*, 13:1973–1994, 2011.

[1244] F.P. Seebeck. *In vitro* reconstitution of mycobacterial ergothioneine biosynthesis. *J. Am. Chem. Soc.*, 132:6632–6633, 2010.

[1245] M.K. Seely, R.S. Criddle, and E.E. Conn. The metabolism of aromatic compounds in higher plants. 8. On the requirement of hydroxynitrile lyase for flavin. *J. Biol. Chem.*, 241:4457–4462, 1966.

[1246] M.J. Segura, M.M. Meyer, and S.P. Matsuda. *Arabidopsis thaliana* LUP1 converts oxidosqualene to multiple triterpene alcohols and a triterpene diol. *Org. Lett.*, 2:2257–2259, 2000.

[1247] H.M. Seidel and J.R. Knowles. Interaction of inhibitors with phospho*enol*pyruvate mutase: implications for the reaction mechanism and the nature of the active site. *Biochemistry*, 33:5641–5646, 1994.

[1248] G.B. Seiffert, G.M. Ullmann, A. Messerschmidt, B. Schink, P.M. Kroneck, and O. Einsle. Structure of the non-redox-active tungsten/[4Fe:4*S*] enzyme acetylene hydratase. *Proc. Natl. Acad. Sci. USA*, 104:3073–3077, 2007.

[1249] C.E. Sekeris. Zur Tyrosinstoffwechsel der Insekten. XII. Reinigung, Eigenschaften und Substratspezifität der DOPA-Decarboxylase. *Hoppe-Seyler's Z. Physiol. Chem.*, 332:70–78, 1963.

[1250] K. Seki, K. Haraguchi, M. Kishimoto, S. Kobayashi, and K. Kainuma. Purification and properties of a novel inulin fructotransferase (DFA I-producing) from *Arthrobacter globiformis* S14-3. *Agric. Biol. Chem.*, 53:2089–2094, 1989.

[1251] Y. Sekizawa, M.E. Maragoudakis, T.E. King, and V.H. Cheldelin. Glutamate biosynthesis in an organism lacking a Krebs tricarboxylic acid cycle. V. Isolation of α-hydroxy-γ-ketoglutarate (HKG) in *Acetobacter suboxydans*. *Biochemistry*, 5:2392–2398, 1966.

[1252] T. Selmer and P.I. Andrei. *p*-Hydroxyphenylacetate decarboxylase from *Clostridium difficile*. A novel glycyl radical enzyme catalysing the formation of *p*-cresol. *Eur. J. Biochem.*, 268:1363–1372, 2001.

[1253] H. Semba, Y. Dobashi, and T. Matsui. Expression of hydroxynitrile lyase from *Manihot esculenta* in yeast and its application in (*S*)-mandelonitrile production using an immobilized enzyme reactor. *Biosci. Biotechnol. Biochem.*, 72:1457–1463, 2008.

[1254] P.D. Sender, M.G. Martin, S. Peiru, and C. Magni. Characterization of an oxaloacetate decarboxylase that belongs to the malic enzyme family. *FEBS Lett.*, 570:217–222, 2004.

[1255] L. Serino, C. Reimmann, H. Baur, M. Beyeler, P. Visca, and D. Haas. Structural genes for salicylate biosynthesis from chorismate in *Pseudomonas aeruginosa*. *Mol. Gen. Genet.*, 249:217–228, 1995.

[1256] J.K. Setlow and F.J. Bollum. The minimum size of the substrate for yeast photoreactivating enzyme. *Biochim. Biophys. Acta*, 157:233–237, 1968.

[1257] W. Seubert and E. Fass. Untersuchungen über den bakterielle Abbau von Isoprenoiden. IV. Reinigung und Eigenschaftender β-Isohexenylglutaconyl-CoA-hydratase und β-Hydroxy-β-isohexenylglutaryl-CoA-lyase. *Biochem. Z.*, 341:23–34, 1964.

[1258] A. Sharma, B.S. Henderson, J.M. Schwab, and J.L. Smith. Crystallization and preliminary X-ray analysis of β-hydroxydecanoyl thiol ester dehydrase from *Escherichia coli*. *J. Biol. Chem.*, 265:5110–5112, 1990.

[1259] V. Sharma, R. Meganathan, and M.E. Hudspeth. Menaquinone (vitamin K_2) biosynthesis: cloning, nucleotide sequence, and expression of the *menC* gene from *Escherichia coli*. *J. Bacteriol.*, 175:4917–4921, 1993.

[1260] B. Shen and C.R. Hutchinson. Tetracenomycin F2 cyclase: intramolecular aldol condensation in the biosynthesis of tetracenomycin C in *Streptomyces glaucescens*. *Biochemistry*, 32:11149–11154, 1993.

[1261] V.E. Shevchik, G. Condemine, J. Robert-Baudouy, and N. Hugouvieux-Cotte-Pattat. The exopolygalacturonate lyase PelW and the oligogalacturonate lyase Ogl, two cytoplasmic enzymes of pectin catabolism in *Erwinia chrysanthemi* 3937. *J. Bacteriol.*, 181:3912–3919, 1999.

[1262] V.E. Shevchik, H.C. Kester, J.A. Benen, J. Visser, J. Robert-Baudouy, and N. Hugouvieux-Cotte-Pattat. Characterization of the exopolygalacturonate lyase PelX of *Erwinia chrysanthemi* 3937. *J. Bacteriol.*, 181:1652–1663, 1999.

[1263] S. Shigeoka, T. Onishi, K. Maeda, Y. Nakano, and S. Kitaoka. Occurrence of thiamin pyrophosphate-dependent 2-oxoglutarate decarboxylase in mitochondria of *Euglena gracilis*. *FEBS Lett.*, 195:43–47, 1986.

[1264] I. Shiio, T. Shiio, and B.A. McFadden. Isocitrate lyase from *Pseudomonas indigofera*. I. Preparation, amino acid composition and molecular weight. *Biochim. Biophys. Acta*, 96:114–122, 1965.

[1265] T. Shimizu. Enzymes functional in the syntheses of leukotrienes and related compounds. *Int. J. Biochem.*, 20:661–666, 1988.

[1266] Y. Shimoda, H. Ito, and A. Tanaka. *Arabidopsis* STAY-GREEN*N*, Mendel's green cotyledon gene, encodes magnesium-dechelatase. *Plant Cell*, 28:2147–2160, 2016.

[1267] V. Shingler, U. Marklund, , and J. Nucleotide sequence and functional analysis of the complete phenol/3,4-dimethylphenol catabolic pathway of *Pseudomonas* sp. strain CF600. *J. Bacteriol.*, 174:711–724, 1992.

[1268] Y. Shizuta, A. Nakazawa, M. Tokushige, and O. Hayaishi. Studies on the interaction between regulatory enzymes and effectors. 3. Crystallization and characterization of adenosine 5′-monophosphate-dependent threonine deaminase from *Escherichia coli*. *J. Biol. Chem.*, 244:1883–1889, 1969.

[1269] C.W. Shuster. 2-Keto-3-deoxy-6-phosphogalactonic acid aldolase. *Methods Enzymol.*, 9:524–528, 1966.

[1270] M. Siebert, K. Severin, and L. Heide. Formation of 4-hydroxybenzoate in *Escherichia coli*: characterization of the *ubiC* gene and its encoded enzyme chorismate pyruvate-lyase. *Microbiology*, 140:897–904, 1994.

[1271] D.L. Siehl and E.E. Conn. Kinetic and regulatory properties of arogenate dehydratase in seedlings of *Sorghum bicolor* (L.) Moench. *Arch. Biochem. Biophys.*, 260:822–829, 1988.

[1272] J.C. Silva, R.E. Minto, C.E. Barry, Holland 3rd, Townsend K.A., and C.A. Isolation and characterization of the versicolorin B synthase gene from *Aspergillus parasiticus*. Expansion of the aflatoxin b1 biosynthetic gene cluster. *J. Biol. Chem.*, 271:13600–13608, 1996.

[1273] J.C. Silva and C.A. Townsend. Heterologous expression, isolation, and characterization of versicolorin B synthase from *Aspergillus parasiticus*. A key enzyme in the aflatoxin B1 biosynthetic pathway. *J. Biol. Chem.*, 272:804–813, 1997.

[1274] P.J. Silva and M.J. Ramos. Reaction mechanism of the vitamin K-dependent glutamate carboxylase: a computational study. *J. Phys. Chem. B*, 111:12883–12887, 2007.

[1275] G.M. Silver and R. Fall. Enzymatic synthesis of isoprene from dimethylallyl diphosphate in aspen leaf extracts. *Plant Physiol.*, 97:1588–1591, 1991.

[1276] G.M. Silver and R. Fall. Characterization of aspen isoprene synthase, an enzyme responsible for leaf isoprene emission to the atmosphere. *J. Biol. Chem.*, 270:13010–13016, 1995.

[1277] S.C. Silver, T. Chandra, E. Zilinskas, S. Ghose, W.E. Broderick, and J.B. Broderick. Complete stereospecific repair of a synthetic dinucleotide spore photoproduct by spore photoproduct lyase. *J. Biol. Inorg. Chem.*, 15:943–955, 2010.

[1278] D. Simon, J. Hoshino, and H. Kröger. L-Serine dehydratase from rat liver. Purification and some properties. *Biochim. Biophys. Acta*, 321:361–368, 1973.

[1279] T.P. Singer and J. Pensky. Isolation and properties of the α-carboxylase of wheat germ. *J. Biol. Chem.*, 196:375–388, 1952.

[1280] T.L. Sivy, M.C. Shirk, and R. Fall. Isoprene synthase activity parallels fluctuations of isoprene release during growth of *Bacillus subtilis*. *Biochem. Biophys. Res. Commun.*, 294:71–75, 2002.

[1281] J.D. Smiley and G. Ashwell. Uronic acid metabolism in bacteria. III. Purification and properties of D-altronic acid and D-mannonic acid dehydrases in *Escherichia coli*. *J. Biol. Chem.*, 235:1571–1575, 1960.

[1282] J.D. Smiley and G. Ashwell. Purification and properties of β-L-hydroxy acid dehydrogenase. II. Isolation of β-keto-L-gluconic acid, an intermediate in L-xylulose biosynthesis. *J. Biol. Chem.*, 236:357–364, 1961.

[1283] K.L. Smiley and M. Sobolov. A cobamide-requiring glycerol dehydrase from an acrolein-forming *Lactobacillus*. *Arch. Biochem. Biophys.*, 97:538–543, 1962.

[1284] B.A. Smit, J.E. van Hylckama Vlieg, W.J. Engels, L. Meijer, J.T. Wouters, and G. Smit. Identification, cloning, and characterization of a *Lactococcus lactis* branched-chain α-keto acid decarboxylase involved in flavor formation. *Appl. Environ. Microbiol.*, 71:303–311, 2005.

[1285] K.S. Smith and J.G. Ferry. Prokaryotic carbonic anhydrases. *FEMS Microbiol. Rev.*, 24:335–366, 2000.

[1286] E.E. Snell. Tryptophanase: structure, catalytic activities, and mechanism of action. *Adv. Enzymol. Relat. Areas Mol. Biol.*, 42:287–333, 1975.

[1287] E.E. Snell, A.A. Smucker, E. Ringelmann, and F. Lynen. Die bakterielle Oxydation des Vitamin B_6. IV. Die enzymatische Decarboxylierung von 2-Methyl-3-hydroxypyridine-4,5-dicarbonsäure. *Biochem. Z.*, 341:109–119, 1964.

[1288] K. Soda and M. Moriguchi. Crystalline lysine decarboxylase. *Biochem. Biophys. Res. Commun.*, 34:34–39, 1969.

[1289] H. Song, W. Hu, N. Naowarojna, A.S. Her, S. Wang, R. Desai, L. Qin, X. Chen, and P. Liu. Mechanistic studies of a novel C-S lyase in ergothioneine biosynthesis: the involvement of a sulfenic acid intermediate. *Sci. Rep.*, 5:11870–11870, 2015.

[1290] K.B. Song, K.S. Bae, Y.B. Lee, K.Y. Lee, and S.K. Rhee. Characteristics of levan fructotransferase from *Arthrobacter ureafaciens* K2032 and difructose anhydride IV formation from levan. *Enzyme Microb. Technol.*, 27:212–218, 2000.

[1291] D. Sorigue, B. Legeret, S. Cuine, S. Blangy, S. Moulin, E. Billon, P. Richaud, S. Brugiere, Y. Coute, D. Nurizzo, P. Muller, K. Brettel, D. Pignol, P. Arnoux, Y. Li-Beisson, G. Peltier, and F. Beisson. An algal photoenzyme converts fatty acids to hydrocarbons. *Science*, 357:903–907, 2017.

[1292] S. Spaepen, W. Versees, D. Gocke, M. Pohl, J. Steyaert, and J. Vanderleyden. Characterization of phenylpyruvate decarboxylase, involved in auxin production of *Azospirillum brasilense*. *J. Bacteriol.*, 189:7626–7633, 2007.

[1293] P.R. Srinivasan, J. Rothschild, and D.B. Sprinson. The enzymic conversion of 3-deoxy-D-*arabino*-heptulosonic acid 7-phosphate to 5-dehydroquinate. *J. Biol. Chem.*, 238:3176–3182, 1963.

[1294] R. Stadler, , and M.H. A revision of the generally accepted pathway for the biosynthesis of the benzyltetrahydroisoquinoline reticuline. *Liebigs Ann. Chem.*, pages 555–562, 1990.

[1295] R. Stadler, T.M. Kutchan, , and M.H. (*S*)-Norcoclaurine is the central intermediate in benzylisoquinoline alkaloid biosynthesis. *Phytochemistry*, 28:1083–1086, 1989.

[1296] E.R. Stadtman. The enzymic synthesis of β-alanyl coenzyme A. *J. Am. Chem. Soc.*, 77:5765–5766, 1955.

[1297] T.M. Stanley, W.H. Johnson, Burks Jr., Whitman E.A., Hwang C.P., Cook C.C., and P.F. Expression and stereochemical and isotope effect studies of active 4-oxalocrotonate decarboxylase. *Biochemistry*, 39:718–726, 2000.

[1298] C.M. Starks, K. Back, J. Chappell, and J.P. Noel. Structural basis for cyclic terpene biosynthesis by tobacco 5-*epi*-aristolochene synthase. *Science*, 277:1815–1820, 1997.

[1299] C.L. Steele, J. Crock, J. Bohlmann, and R. Croteau. Sesquiterpene synthases from grand fir (*Abies grandis*). Comparison of constitutive and wound-induced activities, and cDNA isolation, characterization, and bacterial expression of δ-selinene synthase and γ-humulene synthase. *J. Biol. Chem.*, 273:2078–2089, 1998.

[1300] S. Steiger, A. Mazet, and G. Sandmann. Heterologous expression, purification, and enzymatic characterization of the acyclic carotenoid 1,2-hydratase from *Rubrivivax gelatinosus*. *Arch. Biochem. Biophys.*, 414:51–58, 2003.

[1301] S. Steinbacher, S. Schiffmann, A. Bacher, and M. Fischer. Metal sites in 3,4-dihydroxy-2-butanone 4-phosphate synthase from *Methanococcus jannaschii* in complex with the substrate ribulose 5-phosphate. *Acta Crystallogr. D Biol. Crystallogr.*, 60:1338–1340, 2004.

[1302] S. Steinbacher, S. Schiffmann, G. Richter, R. Huber, A. Bacher, and M. Fischer. Structure of 3,4-dihydroxy-2-butanone 4-phosphate synthase from *Methanococcus jannaschii* in complex with divalent metal ions and the substrate ribulose 5-phosphate: implications for the catalytic mechanism. *J. Biol. Chem.*, 278:42256–42265, 2003.

[1303] J.R. Stern. Thioltranscrotylase and β-hydroxybutyryl CoA racemase activities of crystalline crotonase. *Biochim. Biophys. Acta*, 26:641–643, 1957.

[1304] J.L. Stevens. Isolation and characterization of a rat liver enzyme with both cysteine conjugate β-lyase and kynureninase activity. *J. Biol. Chem.*, 260:7945–7950, 1985.

[1305] J.L. Stevens, J.D. Robbins, and R.A. Byrd. A purified cysteine conjugate β-lyase from rat kidney cytosol. Requirement for *an* α-keto acid or an amino acid oxidase for activity and identity with soluble glutamine transaminase K. *J. Biol. Chem.*, 261:15529–15537, 1986.

[1306] W. Stoffel, D. Le Kim, and G. Sticht. Distribution and properties of dihydrosphingosine-1-phosphate aldolase (sphinganine-1-phosphate alkanal-lyase). *Hoppe-Seyler's Z. Physiol. Chem.*, 350:1233–1241, 1969.

[1307] A.C. Stoolmiller and R.H. Abeles. Formation of α-ketoglutaric semialdehyde from L-2-keto-3-deoxyarabonic acid and isolation of L-2-keto-3-deoxyarabonate dehydratase from *Pseudomonas saccharophila*. *J. Biol. Chem.*, 241:5764–5771, 1966.

[1308] M. Storf, A. Parbel, M. Meyer, B. Strohmann, H. Scheer, M.G. Deng, M. Zheng, M. Zhou, and K.H. Zhao. Chromophore attachment to biliproteins: specificity of PecE/PecF, a lyase-isomerase for the photoactive 3^1-cys-α 84-phycoviolobilin chromophore of phycoerythrocyanin. *Biochemistry*, 40:12444–12456, 2001.

[1309] F.C. Størmer. Isolation of crystalline pH 6 acetolactate-forming enzyme from *Aerobacter aerogenes*. *J. Biol. Chem.*, 242:1756–1759, 1967.

[1310] H. Stransky and A. Amberger. Isolation and properties of a cyanamide hydratase (EC 4.2.1) from *Myrothecium verrucaria*. *Z. Pflanzenphysiol.*, 70:74–87, 1973.

[1311] M. Strassman and L.N. Ceci. Enzymatic formation of *cis*-homoaconitic acid, an intermediate in lysine biosynthesis in yeast. *J. Biol. Chem.*, 241:5401–5407, 1966.

[1312] A. Stratmann, T. Mahmud, S. Lee, J. Distler, H.G. Floss, and W. Piepersberg. The AcbC protein from *Actinoplanes* species is a C_7-cyclitol synthase related to 3-dehydroquinate synthases and is involved in the biosynthesis of the α-glucosidase inhibitor acarbose. *J. Biol. Chem.*, 274:10889–10896, 1999.

[1313] M. Strohmeier, T. Raschle, J. Mazurkiewicz, K. Rippe, I. Sinning, T.B. Fitzpatrick, and I. Tews. Structure of a bacterial pyridoxal 5′-phosphate synthase complex. *Proc. Natl. Acad. Sci. USA*, 103:19284–19289, 2006.

[1314] F.W. Studier and N.R. Movva. SAMase gene of bacteriophage T_3 is responsible for overcoming host restriction. *J. Virol.*, 19:136–145, 1976.

[1315] M. Stumpe, R. Kandzia, C. Gobel, S. Rosahl, and I. Feussner. A pathogen-inducible divinyl ether synthase (CYP74D) from elicitor-treated potato suspension cells. *FEBS Lett.*, 507:371–376, 2001.

[1316] S.S. Subramanian and M.R. Raghavendra Rao. Purification and properties of citraconase. *J. Biol. Chem.*, 243:2367–2372, 1968.

[1317] M. Suda and H. Nakagawa. L-Serine dehydratase (rat liver). *Methods Enzymol.*, 17B:346–351, 1971.

[1318] Y. Sugai, Y. Katsuyama, and Y. Ohnishi. A nitrous acid biosynthetic pathway for diazo group formation in bacteria. *Nat. Chem. Biol.*, 12:73–75, 2016.

[1319] Y. Sugai, Y. Ueno, K. Hayashi, S. Oogami, T. Toyomasu, S. Matsumoto, M. Natsume, H. Nozaki, and H. Kawaide. Enzymatic ^{13}C labeling and multidimensional NMR analysis of miltiradiene synthesized by bifunctional diterpene cyclase in *Selaginella moellendorffii*. *J. Biol. Chem.*, 286:42840–42847, 2011.

[1320] H. Sugimoto, M. Taniguchi, A. Nakagawa, I. Tanaka, M. Suzuki, and J. Nishihira. Crystal structure of human D-dopachrome tautomerase, a homologue of macrophage migration inhibitory factor, at 1.54 Å resolution. *Biochemistry*, 38:3268–3279, 1999.

[1321] F.X. Sullivan, R. Kumar, R. Kriz, M. Stahl, G.Y. Xu, J. Rouse, X.J. Chang, A. Boodhoo, B. Potvin, and D.A. Cumming. Molecular cloning of human GDP-mannose 4,6-dehydratase and reconstitution of GDP-fucose biosynthesis in vitro. *J. Biol. Chem.*, 273:8193–8202, 1988.

[1322] S. Supangat, Y.K. Choi, Y.S. Park, D. Son, C.D. Han, and K.H. Lee. Expression, purification, crystallization and preliminary X-ray analysis of sepiapterin reductase from *Chlorobium tepidum*. *Acta Crystallogr. Sect. F Struct. Biol. Cryst. Commun.*, 61:202–204, 2005.

[1323] I.W. Sutherland. Xanthan lyases-novel enzymes found in various bacterial species. *J. Gen. Microbiol.*, 133:3129–3134, 1987.

[1324] C.R. Sutton and H.K. King. Inhibition of leucine decarboxylase by thiol-binding reagents. *Arch. Biochem. Biophys.*, 96:360–370, 1962.

[1325] H. Suzuki, Y. Ohnishi, Y. Furusho, S. Sakuda, and S. Horinouchi. Novel benzene ring biosynthesis from C_3 and C_4 primary metabolites by two enzymes. *J. Biol. Chem.*, 281:36944–36951, 2006.

[1326] K. Suzuki, Y. Terasaki, and M. Uyeda. Inhibition of hyaluronidases and chondroitinases by fatty acids. J. *Enzyme*, 17:183–186, 2002.

[1327] S. Suzuki, H. Saito, T. Yamagata, K. Anno, N. Seno, Y. Kawai, and T. Furuhashi. Formation of three types of disulfated disaccharides from chondroitin sulfates by chondroitinase digestion. *J. Biol. Chem.*, 243:1543–1550, 1968.

[1328] T. Suzuki and R.M. Hochater. On the biosynthesis of pseudouridine and of pseudouridylic acid in *Agrobacterium tumefaciens*. *Can. J. Biochem.*, 44:259–272, 1966.

[1329] T. Suzuki, T. Kunieda, F. Murai, S. Morioka, and Y. Shioi. Mg-dechelation activity in radish cotyledons with artificial and native substrates, Mg-chlorophyllin *a* and chlorophyllide *a*. *Plant Physiol. Biochem.*, 43:459–464, 2005.

[1330] Y. Suzuki, A. Noma, T. Suzuki, M. Senda, T. Senda, R. Ishitani, and O. Nureki. Crystal structure of the radical SAM enzyme catalyzing tricyclic modified base formation in tRNA. *J. Mol. Biol.*, 372:1204–1214, 2007.

[1331] Y. Suzuki, H. Sakai, T. Shimada, M. Omura, S. Kumazawa, and T. Nakayama. Characterization of γ-terpinene synthase from *Citrus unshiu* (Satsuma mandarin). *Biofactors*, 21:79–82, 2004.

[1332] D. Swaine. The effect of substrate analogues on the activity of cat liver urocanase. *Biochim. Biophys. Acta*, 178:609–618, 1969.

[1333] P.H. Szu, M.W. Ruszczycky, S.H. Choi, F. Yan, and H.W. Liu. Characterization and mechanistic studies of DesII: a radical *S*-adenosyl-L-methionine enzyme involved in the biosynthesis of TDP-D-desosamine. *J. Am. Chem. Soc.*, 131:14030–14042, 2009.

[1334] T., Egami Uchida, F. Microbial ribonucleases with special reference to RNases T1, and N. 1, and U2. In P.D. Boyer, editor, *The Enzymes*, volume 4, pages 205–250. Academic Press, New York, 3rd edition, 1971.

[1335] C.W. Tabor. Adenosylmethionine decarboxylase. *Methods Enzymol.*, 5:756–760, 1962.

[1336] T. Tabuchi and T. Satoh. Distinction between isocitrate lyase and methylisocitrate lyase in *Candida lipolytica*. *Agric. Biol. Chem.*, 40:1863–1869, 1976.

[1337] T. Tabuchi and T. Satoh. Purification and properties of methylisocitrate lyase, a key enzyme in propionate metabolism, from *Candida lipolytica*. *Agric. Biol. Chem.*, 41:169–174, 1977.

[1338] T. Tabuchi, H. Umetsu, H. Aoki, , and H. Characteristics of 2-methylisocitrate dehydratase, isolated from *Yarrowia lipolytica*, in comparison to aconitase. *Biosci. Biotechnol. Biochem.*, 59:2013–2017, 1995.

[1339] B.F. Tack, P.J. Chapman, and S. Dagley. Purification and properties of 4-hydroxy-4-methyl-2-oxoglutarate aldolase. *J. Biol. Chem.*, 247:6444–6449, 1972.

[1340] S. Tajima, Y. Kubo, I. Furusawa, and J. Shishiyama. Purification of a melanin biosynthetic enzyme converting scytalone to 1,3,8-trihydroxynaphthalene from *Cochliobolus miyabeanus*. *Exp. Mycol.*, 13:69–69, 1989.

[1341] M. Takagi, T. Kuzuyama, K. Kaneda, H. Watanabe, T. Dairi, and H. Seto. Studies on the nonmevalonate pathway: Formation of 2-*C*-methyl-D-erythritol 2,4-cyclodiphosphate from 2-phospho-4-(cytidine 5′-diphospho)-2-*C*-methyl-D-erythritol. *Tetrahedron Lett.*, 41:3395–3398, 2000.

[1342] K. Takahashi. The structure and function of ribonuclease T_1. I. Chromatographic purification and properties of ribonuclease T_1. *J. Biochem. (Tokyo)*, 49:1–8, 1961.

[1343] Y. Takamura and Y. Kitayama. Purification and some properties of malonate decarboxylase from *Pseudomonas ovalis*: an oligomeric enzyme with bifunctional properties. *Biochem. Int.*, 3:483–491, 1981.

[1344] S. Takenaka, S. Murakami, R. Shinke, and K. Aoki. Metabolism of 2-aminophenol by *Pseudomonas* sp. AP-3: modified meta-cleavage pathway. *Arch. Microbiol.*, 170:132–137, 1998.

[1345] M. Takeuchi, N. Asano, Y. Kameda, and K. Matsui. Purification and properties of 3-ketovalidoxylamine A C-N lyase from *Flavobacterium saccharophilum*. *J. Biochem. (Tokyo)*, 98:1631–1638, 1985.

[1346] N. Tal, B.R. Morehouse, A. Millman, A. Stokar-Avihail, C. Avraham, T. Fedorenko, E. Yirmiya, E. Herbst, A. Brandis, T. Mehlman, Y. Oppenheimer-Shaanan, A.FA. Keszei, S. Shao, G. Amitai, P.J. Kranzusch, and R. Sorek. Cyclic CMP and cyclic UMP mediate bacterial immunity against phages. *Cell*, 184:5728–5739.e16, 2021.

[1347] Y. Tamaru and R.H. Doi. Pectate lyase A, an enzymatic subunit of the *Clostridium cellulovorans* cellulosome. *Proc. Natl. Acad. Sci. USA*, 98:4125–4129, 2001.

[1348] H. Tamegai, E. Nango, A. Koike-Takeshita, F. Kudo, and K. Kakinuma. Significance of the 20-kDa subunit of heterodimeric 2-deoxy-*scyllo*-inosose synthase for the biosynthesis of butirosin antibiotics in *Bacillus circulans*. *Biosci. Biotechnol. Biochem.*, 66:1538–1545, 2002.

[1349] H. Tamegai, H. Sawada, E. Nango, R. Aoki, H. Hirakawa, T. Iino, and T. Eguchi. Roles of a 20 kDa protein associated with a carbocycle-forming enzyme involved in aminoglycoside biosynthesis in primary and secondary metabolism. *Biosci. Biotechnol. Biochem.*, 74:1215–1219, 2010.

[1350] D. Tan, W.M. Crabb, W.B. Whitman, and L. Tong. Crystal structure of DmdD, a crotonase superfamily enzyme that catalyzes the hydration and hydrolysis of methylthioacryloyl-CoA. *PLoS One*, 8:e63870–e63870, 2013.

[1351] T. Tanaka, T. Uchiyama, H. Kobori, and K. Tanaka. Enzymic hydrolysis of di-D-fructofuranose 1, 2′; 2, 3′ dianhydride with *Arthrobacter ureafaciens*. *J. Biochem.*, 78:1201–1206, 1975.

[1352] L. Tang, A. Okazawa, E. Fukusaki, and A. Kobayashi. Removal of magnesium by Mg-dechelatase is a major step in the chlorophyll-degrading pathway in *Ginkgo biloba* in the process of autumnal tints. *Z. Naturforsch. C*, 55:923–926, 2000.

[1353] B. Tangendjaja, J.B. Lowry, and R.H. Wills. Isolation of a mimosine degrading enzyme from *Leucaena* leaf. *J. Sci. Food Agric.*, 37:523–526, 1986.

[1354] A. Tanner and S. Bornemann. *Bacillus subtilis* YvrK is an acid-induced oxalate decarboxylase. *J. Bacteriol.*, 182:5271–5273, 2000.

[1355] A. Tanner, L. Bowater, S.A. Fairhurst, and S. Bornemann. Oxalate decarboxylase requires manganese and dioxygen for activity: Overexpression and characterization of *Bacillus subtilis* YvrK and YoaN. *J. Biol. Chem.*, 276:43627–43634, 2001.

[1356] P. Tansakul, M. Shibuya, T. Kushiro, and Y. Ebizuka. Dammarenediol-II synthase, the first dedicated enzyme for ginsenoside biosynthesis, in *Panax ginseng*. *FEBS Lett.*, 580:5143–5149, 2006.

[1357] M. Tateishi, S. Suzuki, and H. Shimizu. Cysteine conjugate β-lyase in rat liver. A novel enzyme catalyzing formation of thiol-containing metabolites of drugs. *J. Biol. Chem.*, 253:8854–8859, 1978.

[1358] A. Taussig. The synthesis of the induced enzyme, "cyanase", in *E. coli*. *Biochim. Biophys. Acta*, 44:510–519, 1960.

[1359] A. Taussig. Some properties of the induced enzyme cyanase. *Can. J. Biochem.*, 43:1063–1069, 1965.

[1360] E.S. Taylor and E.F. Gale. Studies on bacterial amino-acid decarboxylases. 6. Codecarboxylase content and action of inhibitors. *Biochem. J.*, 39:52–58, 1945.

[1361] S.I. Tchong, H. Xu, and R.H. White. L-Cysteine desulfidase: an [4Fe-4S] enzyme isolated from *Methanocaldococcus jannaschii* that catalyzes the breakdown of L-cysteine into pyruvate, ammonia, and sulfide. *Biochemistry*, 44:1659–1670, 2005.

[1362] R. Teufel, J.W. Kung, D. Kockelkorn, B.E. Alber, and G. Fuchs. 3-hydroxypropionyl-coenzyme A dehydratase and acryloyl-coenzyme A reductase, enzymes of the autotrophic 3-hydroxypropionate/4-hydroxybutyrate cycle in the *Sulfolobales*. *J. Bacteriol.*, 191:4572–4581, 2009.

[1363] T. Tezuka and K. Tonomura. Purification and properties of an enzyme catalyzing the splitting of carbon-mercury linkages from mercury-resistant *Pseudomonas* K-62 strain. I. Splitting enzyme 1. *J. Biochem. (Tokyo)*, 80:79–87, 1976.

[1364] D. Tholl, F. Chen, J. Petri, J. Gershenzon, and E. Pichersky. Two sesquiterpene synthases are responsible for the complex mixture of sesquiterpenes emitted from *Arabidopsis* flowers. *Plant J.*, 42:757–771, 2005.

[1365] J.H. Thomas and N. Tudball. Studies on the enzymic degradation of L-serine *O*-sulphate by a rat liver preparation. *Biochem. J.*, 105:467–472, 1967.

[1366] S.T. Thomas, G.V. Louie, J.W. Lubin, V. Lundblad, and J.P. Noel. Substrate Specificity and Engineering of Mevalonate 5-Phosphate Decarboxylase. *ACS Chem. Biol.*, 14:1767–1779, 2019.

[1367] L.D. Thompson, L.D. Brandon, D.T. Nieuwlandt, and C.J. Daniels. Transfer RNA intron processing in the halophilic archaebacteria. *Can. J. Microbiol.*, 35:36–42, 1989.

[1368] L.D. Thompson and C.J. Daniels. A tRNA(Trp) intron endonuclease from *Halobacterium volcanii*. Unique substrate recognition properties. *J. Biol. Chem.*, 263:17951–17959, 1988.

[1369] T.B. Thompson, J.B. Garrett, E.A. Taylor, R. Meganathan, J.A. Gerlt, and I. Rayment. Evolution of enzymatic activity in the enolase superfamily: structure of *o*-succinylbenzoate synthase from *Escherichia coli* in complex with Mg^{2+} and *o*-succinylbenzoate. *Biochemistry*, 39:10662–10676, 2000.

[1370] T.B. Thompson, K. Katayama, K. Watanabe, C.R. Hutchinson, and I. Rayment. Structural and functional analysis of tetracenomycin F2 cyclase from *Streptomyces glaucescens*. A type II polyketide cyclase. *J. Biol. Chem.*, 279:37956–37963, 2004.

[1371] B. Thöny, W. Leimbacher, D. Bürgisser, , and C.W. Human 6-pyruvoyl-tetrahydrobiopterin synthase: cDNA cloning and heterologous expression of the recombinant enzyme. *Biochem. Biophys. Res. Commun.*, 189:1437–1443, 1992.

[1372] B. Thony, F. Neuheiser, N. Blau, and C.W. Heizmann. Characterization of the human PCBD gene encoding the bifunctional protein pterin-4 α-carbinolamine dehydratase/dimerization cofactor for the transcription factor HNF-1 α. *Biochem. Biophys. Res. Commun.*, 210:966–973, 1995.

[1373] M.L. Thuy, M.K. Kharel, R. Lamichhane, H.C. Lee, J.W. Suh, K. Liou, and J.K. Sohng. Expression of 2-deoxy-*scyllo*-inosose synthase (*kanA*) from kanamycin gene cluster in *Streptomyces lividans*. *Biotechnol. Lett.*, 27:465–470, 2005.

[1374] B.X. Tian, E. Erdtman, and L.A. Eriksson. Catalytic mechanism of porphobilinogen synthase: the chemical step revisited by QM/MM calculations. *J. Phys. Chem. B*, 116:12105–12112, 2012.

[1375] A.L. Tkalec, D. Fink, F. Blain, G. Zhang-Sun, M. Laliberte, D.C. Bennett, K. Gu, J.J. Zimmermann, and H. Su. Isolation and expression in *Escherichia coli* of cslA and cslB, genes coding for the chondroitin sulfate-degrading enzymes chondroitinase AC and chondroitinase B, respectively, from *Flavobacterium heparinum*. *Appl. Environ. Microbiol.*, 66:29–35, 2000.

[1376] T.M., Cheesbrough, , and P.E. Alkane biosynthesis by decarbonylation of aldehydes catalyzed by a particulate preparation from *Pisum sativum*. *Proc. Natl. Acad. Sci. USA*, 81:6613–6617, 1984.

[1377] E.A. Tolosa, N.K. Chepurnova, R.M. Khomutov, and E.S. Severin. Reactions catalysed by cysteine lyase from the yolk sac of chicken embryo. *Biochim. Biophys. Acta*, 171:369–371, 1969.

[1378] J.M. Tomio, R.C. Garcia, L.C. San Martin de Viale, and M. Grinstein. Porphyrin biosynthesis. VII. Porphyrinogen carboxy-lyase from avian erythrocytes. Purification and properties. *Biochim. Biophys. Acta*, 198:353–363, 1970.

[1379] T. Tomita, S.Y. Kim, K. Teramoto, A. Meguro, T. Ozaki, A. Yoshida, Y. Motoyoshi, N. Mori, K. Ishigami, H. Watanabe, M. Nishiyama, and T. Kuzuyama. Structural Insights into the CotB2-catalyzed cyclization of geranylgeranyl diphosphate to the diterpene cyclooctat-9-en-7-ol. *ACS Chem. Biol.*, 12:1621–1628, 2017.

[1380] R.W. Topham and J.L. Gaylor. Isolation and purification of a 5α-hydroxysterol dehydrase of yeast. *J. Biol. Chem.*, 245:2319–2327, 1970.

[1381] M.P. Torrens-Spence, G. Gillaspy, B. Zhao, K. Harich, R.H. White, and J. Li. Biochemical evaluation of a parsley tyrosine decarboxylase results in a novel 4-hydroxyphenylacetaldehyde synthase enzyme. *Biochem. Biophys. Res. Commun.*, 418:211–216, 2012.

[1382] M.P. Torrens-Spence, P. Liu, H. Ding, K. Harich, G. Gillaspy, and J. Li. Biochemical evaluation of the decarboxylation and decarboxylation-deamination activities of plant aromatic amino acid decarboxylases. *J. Biol. Chem.*, 288:2376–2387, 2013.

[1383] A. Tovar-Mendez, C. Mujica-Jimenez, and R.A. Munoz-Clares. Physiological implications of the kinetics of maize leaf phospho*enol*pyruvate carboxylase. *Plant Physiol.*, 123:149–160, 2000.

[1384] T. Toyomasu, H. Kawaide, A. Ishizaki, S. Shinoda, M. Otsuka, W. Mitsuhashi, and T. Sassa. Cloning of a full-length cDNA encoding *ent*-kaurene synthase from *Gibberella fujikuroi*: functional analysis of a bifunctional diterpene cyclase. *Biosci. Biotechnol. Biochem.*, 64:660–664, 2000.

[1385] T. Toyomasu, K. Nakaminami, H. Toshima, T. Mie, K. Watanabe, H. Ito, H. Matsui, W. Mitsuhashi, T. Sassa, and H. Oikawa. Cloning of a gene cluster responsible for the biosynthesis of diterpene aphidicolin, a specific inhibitor of DNA polymerase α. *Biosci. Biotechnol. Biochem.*, 68:146–152, 2004.

[1386] T. Toyomasu, R. Niida, H. Kenmoku, Y. Kanno, S. Miura, C. Nakano, Y. Shiono, W. Mitsuhashi, H. Toshima, H. Oikawa, T. Hoshino, T. Dairi, N. Kato, and T. Sassa. Identification of diterpene biosynthetic gene clusters and functional analysis of labdane-related diterpene cyclases in *Phomopsis amygdali*. *Biosci. Biotechnol. Biochem.*, 72:1038–1047, 2008.

[1387] T. Toyomasu, M. Tsukahara, A. Kaneko, R. Niida, W. Mitsuhashi, T. Dairi, N. Kato, and T. Sassa. Fusicoccins are biosynthesized by an unusual chimera diterpene synthase in fungi. *Proc. Natl. Acad. Sci. USA*, 104:3084–3088, 2007.

[1388] J.K. Treimer and M.H. Zenk. Purification and properties of strictosidine synthase, the key enzyme in indole alkaloid formation. *Eur. J. Biochem.*, 101:225–233, 1979.

[1389] F. Trijbels and G.D. Vogels. Allantoate and ureidoglycolate degradation by *Pseudomonas aeruginosa*. *Biochim. Biophys. Acta*, 132:115–126, 1967.

[1390] J.J. Truglio, K. Theis, Y. Feng, R. Gajda, C. Machutta, P.J. Tonge, and C. Kisker. Crystal structure of *Mycobacterium tuberculosis* MenB, a key enzyme in vitamin K_2 biosynthesis. *J. Biol. Chem.*, 278:42352–42360, 2003.

[1391] K. Trummler, J. Roos, U. Schwaneberg, F. Effenberger, S. Förster, K. Pfizenmaier, and H. Wajant. Expression of the Zn^{2+}-containing hydroxynitrile lyase from flax (*Linum usitatissimum*) in *Pichia pastoris*— utilization of the recombinant enzyme for enzymatic analysis and site-directed mutagenesis. *Plant Sci.*, 139:19–27, 1998.

[1392] K. Trummler and H. Wajant. Molecular cloning of acetone cyanohydrin lyase from flax (*Linum usitatissimum*). Definition of a novel class of hydroxynitrile lyases. *J. Biol. Chem.*, 272:4770–4774, 1997.

[1393] C.H. Tsai and L.M. Henderson. Degradation of *O*-phosphohydroxylysine by rat liver. Purification of the phospho-lyase. *J. Biol. Chem.*, 249:5784–5789, 1974.

[1394] S.-F. Tsai, D.F. Bishop, and R.J. Desnick. Purification and properties of uroporphyrinogen III synthase from human erythrocytes. *J. Biol. Chem.*, 262:1268–1273, 1987.

[1395] A. Tschech and G. Fuchs. Anaerobic degradation of phenol via carboxylation to 4-hydroxybenzoate - in vitro study of isotope exchange between (CO_2)-*C*-14 and 4-hydroxybenzoate. *Arch. Microbiol.*, 152:594–599, 1989.

[1396] G.E. Tsotsou and F. Barbirato. Biochemical characterisation of recombinant *Streptomyces* pristinaespiralis L-lysine cyclodeaminase. *Biochimie*, 89:591–604, 2007.

[1397] S. Tuboi and G. Kikuchi. Enzymic cleavage of malyl-Coenzyme A into acetyl-Coenzyme A and glyoxylic acid. *Biochim. Biophys. Acta*, 96:148–153, 1965.

[1398] C.S. Turbek, D. Li, G.H. Choi, C.L. Schardl, and D.A. Smith. Induction and purification of kievitone hydratase from *Fusarium solani* f. sp. phaseoli. *Phytochemistry*, 29:2841–2846, 1990.

[1399] C.S. Turbek, D.A. Smith, , and C.L. An extracellular enzyme from *Fusarium solani* f.sp. phaseoli, which catalyses hydration of the isoflavonoid phytoalexin, phaseollidin. *FEMS Microbiol. Lett.*, 94:187–190, 1992.

[1400] I. Uchida and F. Egami. The specificity of ribonuclease T_2. *J. Biochem. (Tokyo)*, 61:44–53, 1967.

[1401] K. Uchida, T. Akashi, and T. Aoki. The missing link in leguminous pterocarpan biosynthesis is a dirigent domain-containing protein with isoflavanol dehydratase activity. *Plant Cell Physiol.*, 58:398–408, 2017.

[1402] T. Uchiyama. Action of *Arthrobacter ureafaciens* inulinase II on several oligofructans and bacterial levans. *Biochim. Biophys. Acta*, 397:153–163, 1975.

[1403] T. Uchiyama, S. Niwa, and K. Tanaka. Purification and properties of *Arthrobacter ureafaciens* inulase II. *Biochim. Biophys. Acta*, 315:412–420, 1973.

[1404] T. Ueatrongchit, A. Kayo, H. Komeda, Y. Asano, and A. H-Kittikun. Purification and characterization of a novel (*R*)-hydroxynitrile lyase from *Eriobotrya japonica* (Loquat). *Biosci. Biotechnol. Biochem.*, 72:1513–1522, 2008.

[1405] T. Ueatrongchit, K. Tamura, T. Ohmiya, A. H-Kittikun, and Y. Asano. Hydroxynitrile lyase from *Passiflora edulis*. Purification, characteristics and application in asymmetric synthesis of (*R*)-mandelonitrile. *Enzyme Microb. Technol.*, 46:456–465, 2010.

[1406] D. Ueda, H. Yamaga, M. Murakami, Y. Totsuka, T. Shinada, and T. Sato. Biosynthesis of sesterterpenes, head-to-tail triterpenes, and sesquarterpenes in *Bacillus clausii*: identification of multifunctional enzymes and analysis of isoprenoid metabolites. *ChemBioChem*, 16:1371–1377, 2015.

[1407] T. Uehara, K. Suefuji, T. Jaeger, C. Mayer, and J.T. Park. MurQ etherase is required by *Escherichia coli* in order to metabolize anhydro-*N*-acetylmuramic acid obtained either from the environment or from its own cell wall. *J. Bacteriol.*, 188:1660–1662, 2006.

[1408] T. Uehara, K. Suefuji, N. Valbuena, B. Meehan, M. Donegan, and J.T. Park. Recycling of the anhydro-*N*-acetylmuramic acid derived from cell wall murein involves a two-step conversion to *N*-acetylglucosamine-phosphate. *J. Bacteriol.*, 187:3643–3649, 2005.

[1409] K. Ukai and J. Sekiya. Purification and characterization of cystine lyase a from broccoli Inflorescence. *Biosci. Biotechnol. Biochem.*, 61:1890–1895, 1997.

[1410] W.W. Umbreit and P. Heneage. β-Hydroxyglutamic acid decarboxylase. *J. Biol. Chem.*, 201:15–20, 1953.

[1411] M. Useglio, S. Peiru, E. Rodriguez, G.R. Labadie, J.R. Carney, and H. Gramajo. TDP-L-megosamine biosynthesis pathway elucidation and megalomicin a production in *Escherichia coli*. *Appl. Environ. Microbiol.*, 76:3869–3877, 2010.

[1412] R.S. van Der Hoeven, A.J. Monforte, D. Breeden, S.D. Tanksley, and J.C. Steffens. Genetic control and evolution of sesquiterpene biosynthesis in *Lycopersicon esculentum* and *L. hirsutum*. *Plant Cell*, 12:2283–2294, 2000.

[1413] J.E. van Hylckama Vlieg, J. Kingma, W. Kruizinga, and D.B. Janssen. Purification of a glutathione *S*-transferase and a glutathione conjugate-specific dehydrogenase involved in isoprene metabolism in *Rhodococcus* sp. strain AD45. *J. Bacteriol.*, 181:2094–2101, 1999.

[1414] J.E. van Hylckama Vlieg, J. Kingma, A.J. van den Wijngaard, and D.B. Janssen. A glutathione *S*-transferase with activity towards *cis*-1, 2-dichloroepoxyethane is involved in isoprene utilization by *Rhodococcus* sp. strain AD45. *Appl. Environ. Microbiol.*, 64:2800–2805, 1998.

[1415] S. Wolterink van Loo, A. van Eerde, M.A. Siemerink, J. Akerboom, B.W. Dijkstra, and J. van der Oost. Biochemical and structural exploration of the catalytic capacity of *Sulfolobus* KDG aldolases. *Biochem. J.*, 403:421–430, 2007.

[1416] A.S. Vanderbilt, N.S. Gaby, , and V.W. Intermediates and enzymes between α-ketoarginine and γ-guanidinobutyrate in the L-arginine catabolic pathway of *Pseudomonas putida*. *J. Biol. Chem.*, 250:5322–5329, 1975.

[1417] J.C. Vannice, D.A. Skaff, A. Keightley, J.K. Addo, G.J. Wyckoff, and H.M. Miziorko. Identification in *Haloferax volcanii* of phosphomevalonate decarboxylase and isopentenyl phosphate kinase as catalysts of the terminal enzyme reactions in an archaeal alternate mevalonate pathway. *J. Bacteriol.*, 196:1055–1063, 2014.

[1418] B. Regueiro Varela, R. Amelunxen, and S. Grisolia. Synthesis and degradation of monohydroxytetrahydronicotinamide adenine dinucleotide phosphate. *Physiol. Chem. Phys.*, 2:445–454, 1970.

[1419] M.M. Vaughan, Q. Wang, F.X. Webster, D. Kiemle, Y.J. Hong, D.J. Tantillo, R.M. Coates, A.T. Wray, W. Askew, C. O'Donnell, J.G. Tokuhisa, and D. Tholl. Formation of the unusual semivolatile diterpene rhizathalene by the *Arabidopsis* class I terpene synthase TPS08 in the root stele is involved in defense against belowground herbivory. *Plant Cell*, 25:1108–1125, 2013.

[1420] C. Vavricka, Q. Han, Y. Huang, S.M. Erickson, K. Harich, B.M. Christensen, and J. Li. From L-dopa to dihydroxyphenylacetaldehyde: a toxic biochemical pathway plays a vital physiological function in insects. *PLoS One*, 6:e16124–e16124, 2011.

[1421] M. Veeraswamy, N.A. Devi, R. Krishnan Kutty, and P.V. Subba Rao. Conversion of (±) synephrine into *p*-hydroxyphenylacetaldehyde by *Arthrobacter synephrinum*. A novel enzymic reaction. *Biochem. J.*, 159:807–809, 1976.

[1422] H.B. Vickery. A suggested new nomenclature for the isomers of isocitric acid. *J. Biol. Chem.*, 237:1739–1741, 1962.

[1423] J.M. Vinokur, M.C. Cummins, T.P. Korman, and J.U. Bowie. An adaptation to life in acid through a novel mevalonate pathway. *Sci. Rep.*, 6:39737–39737, 2016.

[1424] W.F. Visser, N.M. Verhoeven-Duif, and T.J. de Koning. Identification of a human *trans*-3-hydroxy-L-proline dehydratase, the first characterized member of a novel family of proline racemase-like enzymes. *J. Biol. Chem.*, 287:21654–21662, 2012.

[1425] G. Vogel and F. Lynen. 6-Methylsalicylsäure-Decarboxylase. *Naturwissenschaften*, 57:664–664, 1970.

[1426] R. Volk and A. Bacher. Studies on the 4-carbon precursor in the biosynthesis of riboflavin. Purification and properties of L-3,4-dihydroxy-2-butanone-4-phosphate synthase. *J. Biol. Chem.*, 265:19479–19485, 1990.

[1427] S. von Horsten, M.L. Lippert, Y. Geisselbrecht, K. Schuhle, I. Schall, L.O. Essen, and J. Heider. Inactive pseudoenzyme subunits in heterotetrameric BbsCD, a novel short-chain alcohol dehydrogenase involved in anaerobic toluene degradation. *FEBS J.*, 2021.

[1428] J. von Langermann, J.K. Guterl, M. Pohl, H. Wajant, and U. Kragl. Hydroxynitrile lyase catalyzed cyanohydrin synthesis at high pH-values. *Bioprocess Biosyst. Eng.*, 31:155–161, 2008.

[1429] S. von Reuss, D. Domik, M.C. Lemfack, N. Magnus, M. Kai, T. Weise, and B. Piechulla. Sodorifen biosynthesis in the rhizobacterium *Serratia plymuthica* involves methylation and cyclization of MEP-derived farnesyl pyrophosphate by a SAM-dependent *C*-methyltransferase. *J. Am. Chem. Soc.*, 140:11855–11862, 2018.

[1430] J.A. Vorholt, C.J. Marx, M.E. Lidstrom, and R.K. Thauer. Novel formaldehyde-activating enzyme in *Methylobacterium extorquens* AM1 required for growth on methanol. *J. Bacteriol.*, 182:6645–6650, 2000.

[1431] M. Wada, T. Matsumoto, S. Nakamori, M. Sakamoto, M. Kataoka, J.-Q. Liu, N. Itoh, H. Yamada, and S. Shimizu. Purification and characterization of a novel enzyme, L-*threo*-3-hydroxyaspartate dehydratase, from *Pseudomonas* sp. T62. *FEMS Microbiol. Lett.*, 179:147–151, 1999.

[1432] U.G. Wagner, M. Schall, M. Hasslacher, M. Hayn, H. Griengl, H. Schwab, and C. Kratky. Crystallization and preliminary X-ray diffraction studies of a hydroxynitrile lyase from *Hevea brasiliensis*. *Acta Crystallogr. D Biol. Crystallogr.*, 52:591–593, 1996.

[1433] K. Wagschal, T.J. Savage, and R. Croteau. Isotopically sensitive branching as a tool for evaluating multiple product formation by monoterpene cyclases. *Tetrahedron*, 31:5933–5944, 1991.

[1434] K.C. Wagschal, H.J. Pyun, R.M. Coates, and R. Croteau. Monoterpene biosynthesis: isotope effects associated with bicyclic olefin formation catalyzed by pinene synthases from sage (*Salvia officinalis*). *Arch. Biochem. Biophys.*, 308:477–487, 1994.

[1435] T.E. Wallaart, H.J. Bouwmeester, J. Hille, L. Poppinga, and N.C. Maijers. Amorpha-4,11-diene synthase: cloning and functional expression of a key enzyme in the biosynthetic pathway of the novel antimalarial drug artemisinin. *Planta*, 212:460–465, 2001.

[1436] S. Wallner, M. Neuwirth, K. Flicker, I. Tews, and P. Macheroux. Dissection of contributions from invariant amino acids to complex formation and catalysis in the heteromeric pyridoxal 5-phosphate synthase complex from *Bacillus subtilis*. *Biochemistry*, 48:1928–1935, 2009.

[1437] M.A. Walsh, Z. Otwinowski, A. Perrakis, P.M. Anderson, and A. Joachimiak. Structure of cyanase reveals that a novel dimeric and decameric arrangement of subunits is required for formation of the enzyme active site. *Structure*, 8:505–514, 2000.

[1438] C.C. Wang and H.A. Barker. Purification and properties of L-citramalate hydrolyase. *J. Biol. Chem.*, 244:2516–2526, 1969.

[1439] C.M. Wang and D.E. Cane. Biochemistry and molecular genetics of the biosynthesis of the earthy odorant methylisoborneol in *Streptomyces coelicolor*. *J. Am. Chem. Soc.*, 130:8908–8909, 2008.

[1440] C.M. Wang, R. Hopson, X. Lin, and D.E. Cane. Biosynthesis of the sesquiterpene botrydial in *Botrytis cinerea*. Mechanism and stereochemistry of the enzymatic formation of presilphiperfolan-8β-ol. *J. Am. Chem. Soc.*, 131:8360–8361, 2009.

[1441] L. Wang, S. Li, W. Yu, and Q. Gong. Cloning, overexpression and characterization of a new oligoalginate lyase from a marine bacterium, *Shewanella* sp. *Biotechnol. Lett.*, 37:665–671, 2015.

[1442] L. Wang, R.L. White, and L.C. Vining. Biosynthesis of the dideoxysugar component of jadomycin B: genes in the jad cluster of *Streptomyces venezuelae* ISP5230 for L-digitoxose assembly and transfer to the angucycline aglycone. *Microbiology*, 148:1091–1103, 2002.

[1443] Q. Wang, M. Jia, J.H. Huh, A. Muchlinski, R.J. Peters, and D. Tholl. Identification of a dolabellane type diterpene synthase and other root-expressed diterpene synthases in *Arabidopsis*. *Front. Plant Sci.*, 7:1761–1761, 2016.

[1444] S.-F. Wang and O. Gabriel. Biological mechanisms involved in the formation of deoxy sugars. V. Isolation and crystallization of thymidine diphosphate-D-glucose oxidoreductase from *Escherichia coli* B. *J. Biol. Chem.*, 244:3430–3437, 1969.

[1445] S.C. Wang, W.H. Johnson, Czerwinski Jr., Stamps R.M., Whitman S.L., and C.P. Kinetic and stereochemical analysis of YwhB, a 4-oxalocrotonate tautomerase homologue in *Bacillus subtilis*: mechanistic implications for the YwhB- and 4-oxalocrotonate tautomerase-catalyzed reactions. *Biochemistry*, 46:11919–11929, 2007.

[1446] T. Wang, S.S. Quisenberry, X. Ni, and V. Tolmay. Enzymatic chlorophyll degradation in wheat near-isogenic lines elicited by cereal aphid (Homoptera: Aphididae) feeding. *J. Econ. Entomol.*, 97:661–667, 2004.

[1447] W. Wang, P. Baker, and S.Y.K. Seah. Comparison of two metal-dependent pyruvate aldolases related by convergent evolution: substrate specificity, kinetic mechanism, and substrate channeling. *Biochemistry*, 49:3774–3782, 2010.

[1448] W. Wang and S.Y. Seah. Purification and biochemical characterization of a pyruvate-specific class II aldolase, *Hpa*I. *Biochemistry*, 44:9447–9455, 2005.

[1449] W. Wang and S.Y. Seah. The role of a conserved histidine residue in a pyruvate-specific class II aldolase. *FEBS Lett.*, 582:3385–3388, 2008.

[1450] Y. Wang, M.K. Jones, H. Xu, W.K. Ray, and R.H. White. Mechanism of the enzymatic synthesis of 4-(hydroxymethyl)-2-furancarboxaldehyde-phosphate (4-HFC-*P*) from glyceraldehyde-3-phosphate catalyzed by 4-HFC-*P* synthase. *Biochemistry*, 54:2997–3008, 2015.

[1451] Y. Wang, H. Xu, L.L. Grochowski, and R.H. White. Biochemical characterization of a dihydroneopterin aldolase used for methanopterin biosynthesis in methanogens. *J. Bacteriol.*, 196:3191–3198, 2014.

[1452] M.J. Warren, J.B. Cooper, S.P. Wood, and P.M. Shoolingin-Jordan. Lead poisoning, haem synthesis and 5-aminolaevulinic acid dehydratase. *Trends Biochem. Sci.*, 23:217–221, 1998.

[1453] M.J. Warren, E. Raux, H.L. Schubert, and J.C. Escalante-Semerena. The biosynthesis of adenosylcobalamin (vitamin B_{12}). *Nat. Prod. Rep.*, 19:390–412, 2002.

[1454] D.M. Warui, N. Li, H. Nørgaard, C. Krebs, J.M. Bollinger, and S.J. Booker. Detection of formate, rather than carbon monoxide, as the stoichiometric coproduct in conversion of fatty aldehydes to alkanes by a cyanobacterial aldehyde decarbonylase. *J. Am. Chem. Soc.*, 133:3316–3319, 2011.

[1455] R.M. Waterson, F.J. Castellino, G.M. Hass, and R.L. Hill. Purification and characterization of crotonase from *Clostridium acetobutylicum*. *J. Biol. Chem.*, 247:5266–5271, 1972.

[1456] R.M. Waterson and R.S. Conway. Enoyl-CoA hydratases from *Clostridium acetobutylicum* and *Escherichia coli*. *Methods Enzymol.*, 71 Pt C:421–430, 1981.

[1457] K.T. Watts, B.N. Mijts, P.C. Lee, A.J. Manning, and C. Schmidt-Dannert. Discovery of a substrate selectivity switch in tyrosine ammonia-lyase, a member of the aromatic amino acid lyase family. *Chem. Biol.*, 13:1317–1326, 2006.

[1458] R. Weimberg. L-2-Keto-4,5-dihydroxyvaleric acid: an intermediate in the oxidation of L-arabinose by *Pseudomonas*e saccharophila. *J. Biol. Chem.*, 234:727–732, 1959.

[1459] H. Weissbach, D.F. Bogdanski, B.G. Redfield, and S. Udenfriend. Studies on the effect of vitamin B_6 on 5-hydroxytryptamine (serotonin) formation. *J. Biol. Chem.*, 227:617–624, 1957.

[1460] G.R. Welch, K.W. Cole, and F.H. Gaertner. Chorismate synthase of *Neurospora crassa*: a flavoprotein. *Arch. Biochem. Biophys.*, 165:505–518, 1974.

[1461] A.K. Werner, T. Romeis, and C.P. Witte. Ureide catabolism in *Arabidopsis thaliana* and *Escherichia coli*. *Nat. Chem. Biol.*, 6:19–21, 2010.

[1462] E.W. Westhead and G. McLain. Purification of brewers' and bakers' yeast enolase yielding a single active component. *J. Biol. Chem.*, 239:2464–2468, 1964.

[1463] M.H. Wheeler and G.A. Greenblatt. The inhibition of melanin biosynthetic reactions in *Pyricularia oryzae* by compounds that prevent rice blast disease. *Exp. Mycol.*, 12:151–160, 1988.

[1464] M. Wieser, N. Fujii, T. Yoshida, and T. Nagasawa. Carbon dioxide fixation by reversible pyrrole-2-carboxylate decarboxylase from *Bacillus megaterium* PYR2910. *Eur. J. Biochem.*, 257:495–499, 1998.

[1465] M. Wieser, T. Yoshida, and T. Nagasawa. Microbial synthesis of pyrrole-2-carboxylate by *Bacillus megaterium* PYR2910. *Tetrahedron Lett.*, 39:4309–4310, 1998.

[1466] P.R. Wilderman, M. Xu, Y. Jin, R.M. Coates, and R.J. Peters. Identification of syn-pimara-7,15-diene synthase reveals functional clustering of terpene synthases involved in rice phytoalexin/allelochemical biosynthesis. *Plant Physiol.*, 135:2098–2105, 2004.

[1467] M.C. Wildermuth and R. Fall. Light-dependent isoprene emission (characterization of a thylakoid-bound isoprene synthase in *Salix discolor* chloroplasts). *Plant Physiol.*, 112:171–182, 1996.

[1468] D.C. Williams, B.J. Carroll, Q. Jin, C.D. Rithner, S.R. Lenger, H.G. Floss, R.M. Coates, R.M. Williams, and R. Croteau. Intramolecular proton transfer in the cyclization of geranylgeranyl diphosphate to the taxadiene precursor of taxol catalyzed by recombinant taxadiene synthase. *Chem. Biol.*, 7:969–977, 2000.

[1469] J.M. Williamson and G.M. Brown. Purification and properties of L-aspartate-α-decarboxylase, an enzyme that catalyzes the formation of β-alanine in *Escherichia coli*. *J. Biol. Chem.*, 254:8074–8082, 1979.

[1470] E.M. Wilson and H.L. Kornberg. Properties of crystalline L-aspartate 4-carboxy-lyase from *Achromobacter* sp. *Biochem. J.*, 88:578–587, 1963.

[1471] E. Wise, W.S. Yew, P.C. Babbitt, J.A. Gerlt, and I. Rayment. Homologous 8-barrel enzymes that catalyze unrelated reactions: orotidine 5′-monophosphate decarboxylase and 3-keto-L-gulonate 6-phosphate decarboxylase. *Biochemistry*, 41:3861–3869, 2002.

[1472] M.L. Wise, T.J. Savage, E. Katahira, and R. Croteau. Monoterpene synthases from common sage (*Salvia officinalis*). cDNA isolation, characterization, and functional expression of (+)-sabinene synthase, 1,8-cineole synthase, and (+)-bornyl diphosphate synthase. *J. Biol. Chem.*, 273:14891–14899, 1998.

[1473] M. Wishnick, M.D. Lane, M.C. Scrutton, and A.S. Mildvan. The presence of tightly bound copper in ribulose diphosphate carboxylase from spinach. *J. Biol. Chem.*, 244:5761–5763, 1969.

[1474] E. Woehl and M.F. Dunn. Mechanisms of monovalent cation action in enzyme catalysis: the tryptophan synthase α-, β-, and αβ-reactions. *Biochemistry*, 38:7131–7141, 1999.

[1475] W.A. Wood. 2-Keto-3-deoxy-6-phosphogluconic and related aldolases. In P.D. Boyer, editor, *The Enzymes*, volume 7, pages 281–302. Academic Press, New York, 3rd edition, 1972.

[1476] J.W. Wray and R.H. Abeles. The methionine salvage pathway in *Klebsiella pneumoniae* and rat liver. Identification and characterization of two novel dioxygenases. *J. Biol. Chem.*, 270:3147–3153, 1995.

[1477] S. Wu, M.A. Schoenbeck, B.T. Greenhagen, S. Takahashi, S. Lee, R.M. Coates, and J. Chappell. Surrogate splicing for functional analysis of sesquiterpene synthase genes. *Plant Physiol.*, 138:1322–1333, 2005.

[1478] X. Wu, P.M. Flatt, O. Schlorke, A. Zeeck, T. Dairi, and T. Mahmud. A comparative analysis of the sugar phosphate cyclase superfamily involved in primary and secondary metabolism. *ChemBioChem*, 8:239–248, 2007.

[1479] M.M. Wuebbens and K.V. Rajagopalan. Investigation of the early steps of molybdopterin biosynthesis in *Escherichia coli* through the use of *in vivo* labeling studies. *J. Biol. Chem.*, 270:1082–1087, 1995.

[1480] T. Xiang, M. Shibuya, Y. Katsube, T. Tsutsumi, M. Otsuka, H. Zhang, K. Masuda, and Y. Ebizuka. A new triterpene synthase from *Arabidopsis thaliana* produces a tricyclic triterpene with two hydroxyl groups. *Org. Lett.*, 8:2835–2838, 2006.

[1481] S.X. Xie, Y. Kato, H. Komeda, S. Yoshida, and Y. Asano. A gene cluster responsible for alkylaldoxime metabolism coexisting with nitrile hydratase and amidase in *Rhodococcus globerulus* A-4. *Biochemistry*, 42:12056–12066, 2003.

[1482] X. Xie, J. Kirby, and J.D. Keasling. Functional characterization of four sesquiterpene synthases from *Ricinus communis* (castor bean). *Phytochemistry*, 78:20–28, 2012.

[1483] M. Xing, Y. Wei, Y. Zhou, J. Zhang, L. Lin, Y. Hu, Hua G., A. N. Nanjaraj Urs, D. Liu, F. Wang, C. Guo, Y. Tong, M. Li, Y. Liu, E.L. Ang, H. Zhao, Z. Yuchi, and Y. Zhang. Radical-mediated C-S bond cleavage in C_2 sulfonate degradation by anaerobic bacteria. *Nat. Commun.*, 10:1609–1609, 2019.

[1484] L.-L. Xu, B.K. Singh, and E.E. Conn. Purification and characterization of acetone cyanohydrin lyase from *Linum usitatissimum*. *Arch. Biochem. Biophys.*, 263:256–263, 1988.

[1485] M. Xu, P.R. Wilderman, D. Morrone, J. Xu, A. Roy, M. Margis-Pinheiro, N.M. Upadhyaya, R.M. Coates, and R.J. Peters. Functional characterization of the rice kaurene synthase-like gene family. *Phytochemistry*, 68:312–326, 2007.

[1486] M. Xu, P.R. Wilderman, and R.J. Peters. Following evolution's lead to a single residue switch for diterpene synthase product outcome. *Proc. Natl. Acad. Sci. USA*, 104:7397–7401, 2007.

[1487] R. Xu and D.A. Cuebas. The reactions catalyzed by the inducible bifunctional enzyme of rat liver peroxisomes cannot lead to the formation of bile acids. *Biochem. Biophys. Res. Commun.*, 221:271–278, 1996.

[1488] E.W. Yamada and W.B. Jakoby. Enzymatic utilization of acetylenic compounds. I. An enzyme converting acetylenedicarboxylic acid to pyruvate. *J. Biol. Chem.*, 233:706–711, 1958.

[1489] E.W. Yamada and W.B. Jakoby. Enzymatic utilization of acetylenic compounds. II. Acetylenemonocarboxylic acid hydrase. *J. Biol. Chem.*, 234:941–945, 1959.

[1490] H. Yamada, H. Kumagai, T. Nagate, and H. Yoshida. Crystalline threonine aldolase from *Candida humicola*. *Biochem. Biophys. Res. Commun.*, 39:53–58, 1970.

[1491] H. Yamada, T. Nagasawa, H. Ohkishi, B. Kawakami, and Y. Tani. Synthesis of D-cysteine from 3-chloro-D-alanine and hydrogen sulfide by 3-chloro-D-alanine hydrogen chloride-lyase (deaminating) of *Pseudomonas putida*. *Biochem. Biophys. Res. Commun.*, 100:1104–1110, 1981.

[1492] T. Yamada, J. Komoto, Y. Takata, H. Ogawa, H.C. Pitot, and F. Takusagawa. Crystal structure of serine dehydratase from rat liver. *Biochemistry*, 42:12854–12865, 2003.

[1493] Y. Yamada, S. Arima, T. Nagamitsu, K. Johmoto, H. Uekusa, T. Eguchi, K. Shin-ya, D.E. Cane, and H. Ikeda. Novel terpenes generated by heterologous expression of bacterial terpene synthase genes in an engineered *Streptomyces* host. *J. Antibiot. (Tokyo)*, 68:385–394, 2015.

[1494] Y. Yamada, M. Komatsu, and H. Ikeda. Chemical diversity of labdane-type bicyclic diterpene biosynthesis in Actinomycetales microorganisms. *J. Antibiot. (Tokyo)*, 69:515–523, 2016.

[1495] T. Yamagata, H. Saito, O. Habuchi, and S. Suzuki. Purification and properties of bacterial chondroitinases and chondrosulfatases. *J. Biol. Chem.*, 243:1523–1535, 1968.

[1496] S. Yamaguchi, T. Saito, H. Abe, H. Yamane, N. Murofushi, and Y. Kamiya. Molecular cloning and characterization of a cDNA encoding the gibberellin biosynthetic enzyme *ent*-kaurene synthase B from pumpkin (*Cucurbita maxima* L.). *Plant J.*, 10:203–213, 1996.

[1497] S. Yamamoto, Y. Tsuzaki, K. Tougou, and S. Shinoda. Purification and characterization of L-2,4-diaminobutyrate decarboxylase from *Acinetobacter calcoaceticus*. *J. Gen. Microbiol.*, 138:1461–1465, 1992.

[1498] H. Yamasaki and T. Moriyama. δ-Aminolevulinic acid dehydratase of *Mycobacterium phlei*. *Biochim. Biophys. Acta*, 227:698–705, 1971.

[1499] M. Yamasaki and K. Arima. Regulation of intracellular ribonuclease of *Bacillus subtilis* by ATP and ADP. *Biochim. Biophys. Acta*, 139:202–204, 1967.

[1500] M. Yamasaki and K. Arima. Intracellular ribonuclease of *Bacillus subtilis*; specific inhibition by ATP and dATP. *Biochem. Biophys. Res. Commun.*, 37:430–436, 1969.

[1501] H. Yanase, K. Ikeyama, R. Mitsui, S. Ra, K. Kita, Y. Sakai, and N. Kato. Cloning and sequence analysis of the gene encoding 3-hexulose-6-phosphate synthase from the methylotrophic bacterium, *Methylomonas aminofaciens* 77a, and its expression in *Escherichia coli*. *FEMS Microbiol. Lett.*, 135:201–205, 1996.

[1502] W. Yang, H. Tang, J. Ni, Q. Wu, D. Hua, F. Tao, and P. Xu. Characterization of two *Streptomyces* enzymes that convert ferulic acid to vanillin. *PLoS One*, 8:e67339–e67339, 2013.

[1503] Y. Yang, R. Yatsunami, A. Ando, N. Miyoko, T. Fukui, S. Takaichi, and S. Nakamura. Complete biosynthetic pathway of the C_{50} carotenoid bacterioruberin from lycopene in the extremely halophilic archaeon *Haloarcula japonica*. *J. Bacteriol.*, 197:1614–1623, 2015.

[1504] Y.L. Yang, S. Zhang, K. Ma, Y. Xu, Q. Tao, Y. Chen, J. Chen, S. Guo, J. Ren, W. Wang, Y. Tao, W.B. Yin, and H. Liu. Discovery and characterization of a new family of diterpene cyclases in bacteria and fungi. *Angew. Chem. Int. Ed. Engl.*, 56:4749–4752, 2017.

[1505] C. Yanofsky. The enzymatic conversion of anthranilic acid to indole. *J. Biol. Chem.*, 223:171–184, 1956.

[1506] Q.Z. Ye, J. Liu, and C.T. Walsh. *p*-Aminobenzoate synthesis in *Escherichia coli*: purification and characterization of PabB as aminodeoxychorismate synthase and enzyme X as aminodeoxychorismate lyase. *Proc. Natl. Acad. Sci. USA*, 87:9391–9395, 1990.

[1507] Y. Ye, A. Minami, A. Mandi, C. Liu, T. Taniguchi, T. Kuzuyama, K. Monde, K. Gomi, and H. Oikawa. Genome mining for sesterterpenes using bifunctional terpene synthases reveals a unified intermediate of di/sesterterpenes. *J. Am. Chem. Soc.*, 137:11846–11853, 2015.

[1508] Y.S. Yeo, S.E. Nybo, A.G. Chittiboyina, A.D. Weerasooriya, Y.H. Wang, E. Gongora-Castillo, B. Vaillancourt, C.R. Buell, D. DellaPenna, M.D. Celiz, A.D. Jones, E.S. Wurtele, N. Ransom, N. Dudareva, K.A. Shaaban, N. Tibrewal, S. Chandra, T. Smillie, I.A. Khan, R.M. Coates, D.S. Watt, and J. Chappell. Functional identification of valerena-1,10-diene synthase, a terpene synthase catalyzing a unique chemical cascade in the biosynthesis of biologically active sesquiterpenes in *Valeriana officinalis*. *J. Biol. Chem.*, 288:3163–3173, 2013.

[1509] W.S. Yew, A.A. Fedorov, E.V. Fedorov, S.C. Almo, and J.A. Gerlt. Evolution of enzymatic activities in the enolase superfamily: L-talarate/galactarate dehydratase from *Salmonella typhimurium* LT2. *Biochemistry*, 46:9564–9577, 2007.

[1510] W.S. Yew and J.A. Gerlt. Utilization of L-ascorbate by *Escherichia coli* K-12: assignments of functions to products of the yjf-sga and yia-sgb operons. *J. Bacteriol.*, 184:302–306, 2002.

[1511] X. Yin, K.L. McPhail, K.J. Kim, and T.M. Zabriskie. Formation of the nonproteinogenic amino acid (2*S*,3*R*)-capreomycidine by VioD from the viomycin biosynthesis pathway. *ChemBioChem*, 5:1278–1281, 2004.

[1512] H. Yoshida, J. Nishihira, M. Suzuki, and K. Hikichi. NMR characterization of physicochemical properties of rat D-dopachrome tautomerase. *Biochem. Mol. Biol. Int.*, 42:891–899, 1997.

[1513] M. Yoshida, N. Fukuhara, and T. Oikawa. Thermophilic, reversible γ-resorcylate decarboxylase from *Rhizobium* sp. strain MTP-10005: purification, molecular characterization, and expression. *J. Bacteriol.*, 186:6855–6863, 2004.

[1514] T. Yoshida, K. Fujita, and T. Nagasawa. Novel reversible indole-3-carboxylate decarboxylase catalyzing nonoxidative decarboxylation. *Biosci. Biotechnol. Biochem.*, 66:2388–2394, 2002.

[1515] H. Yoshioka, N. Yamada, and N. Doke. cDNA cloning of sesquiterpene cyclase and squalene synthase, and expression of the genes in potato tuber infected with Phytophthora infestans. *Plant Cell Physiol.*, 40:993–998, 1999.

[1516] A.P. Young and V. Bandarian. Pyruvate is the source of the two carbons that are required for formation of the imidazoline ring of 4-demethylwyosine. *Biochemistry*, 50:10573–10575, 2011.

[1517] M.R. Young and A.C. Neish. Properties of the ammonia-lyases deaminating phenylalanine and related compounds in *Triticum sestivum* and *Pteridium aquilinum*. *Phytochemistry*, 5:1121–1132, 1966.

[1518] F. Yu, H. Harada, K. Yamasaki, S. Okamoto, S. Hirase, Y. Tanaka, N. Misawa, and R. Utsumi. Isolation and functional characterization of a β-eudesmol synthase, a new sesquiterpene synthase from *Zingiber zerumbet* Smith. *FEBS Lett.*, 582:565–572, 2008.

[1519] F. Yu, S. Okamto, K. Nakasone, K. Adachi, S. Matsuda, H. Harada, N. Misawa, and R. Utsumi. Molecular cloning and functional characterization of α-humulene synthase, a possible key enzyme of zerumbone biosynthesis in shampoo ginger (*Zingiber zerumbet* Smith). *Planta*, 227:1291–1299, 2008.

[1520] S. Yu, , and M. α-1,4-Glucan lyase, a new class of starch/glycogen degrading enzyme. II. Subcellular localization and partial amino-acid sequence. *Planta*, 191:137–142, 1993.

[1521] S. Yu. Enzymatic description of the anhydrofructose pathway of glycogen degradation. II. Gene identification and characterization of the reactions catalyzed by aldos-2-ulose dehydratase that converts 1,5-anhydro-D-fructose to microthecin with ascopyrone M as the intermediate. *Biochim. Biophys. Acta*, 1723:63–73, 2005.

[1522] S. Yu, T. Ahmad, L. Kenne, and M. Pedersén. α-1,4-Glucan lyase, a new class of starch/glycogen degrading enzyme. III. Substrate specificity, mode of action, and cleavage mechanism. *Biochim. Biophys. Acta*, 1244:1–9, 1995.

[1523] S. Yu, K. Bojsen, B. Svensson, and J. Marcussen. α-1,4-glucan lyases producing 1,5-anhydro-D-fructose from starch and glycogen have sequence similarity to α-glucosidases. *Biochim. Biophys. Acta*, 1433:1–15, 1999.

[1524] S. Yu, T.M. Christensen, K.M. Kragh, K. Bojsen, and J. Marcussen. Efficient purification, characterization and partial amino acid sequencing of two α-1,4-glucan lyases from fungi. *Biochim. Biophys. Acta*, 1339:311–320, 1997.

[1525] S. Yu and R. Fiskesund. The anhydrofructose pathway and its possible role in stress response and signaling. *Biochim. Biophys. Acta*, 1760:1314–1322, 2006.

[1526] S. Yu, L. Kenne, , and M. α-1,4-Glucan lyase, a new class of starch/glycogen degrading enzyme. I. Efficient purification and characterization from red seaweeds. *Biochim. Biophys. Acta*, 1156:313–320, 1993.

[1527] S. Yu, C. Refdahl, and I. Lundt. Enzymatic description of the anhydrofructose pathway of glycogen degradation; I. Identification and purification of anhydrofructose dehydratase, ascopyrone tautomerase and α-1,4-glucan lyase in the fungus *Anthracobia melaloma*. *Biochim. Biophys. Acta*, 1672:120–129, 2004.

[1528] S. Yu, H. Shen, Y. Cheng, Y. Zhu, X. Li, , and W. Structural and functional basis of difructose anhydride III hydrolase, which sequentially converts inulin using the same catalytic residue. *ACS Catalysis*, 8:10683–10697, 2018.

[1529] S. Yu, X. Wang, T. Zhang, T. Stressler, L. Fischer, B. Jiang, and W. Mu. Identification of a novel di-D-fructofuranose 1,2′:2,3′ dianhydride (DFA III) hydrolysis enzyme from *Arthrobacter aurescens* SK8.001. *PLoS One*, 10:e0142640–e0142640, 2015.

[1530] Y. Yu, L. Bai, K. Minagawa, X. Jian, L. Li, J. Li, S. Chen, E. Cao, T. Mahmud, H.G. Floss, X. Zhou, and Z. Deng. Gene cluster responsible for validamycin biosynthesis in *Streptomyces hygroscopicus* subsp. *jinggangensis* 5008. *Appl. Environ. Microbiol.*, 71:5066–5076, 2005.

[1531] Y.-B. Yu, D.O. Adams, and S.F. Yang. 1-Aminocyclopropanecarboxylate synthase, a key enzyme in ethylene biosynthesis. *Arch. Biochem. Biophys.*, 198:280–296, 1979.

[1532] Z. Yu, C. Schneider, W.E. Boeglin, and A.R. Brash. Human and mouse eLOX3 have distinct substrate specificities: implications for their linkage with lipoxygenases in skin. *Arch. Biochem. Biophys.*, 455:188–196, 2006.

[1533] Z. Yu, C. Schneider, W.E. Boeglin, L.J. Marnett, and A.R. Brash. The lipoxygenase gene ALOXE3 implicated in skin differentiation encodes a hydroperoxide isomerase. *Proc. Natl. Acad. Sci. USA*, 100:9162–9167, 2003.

[1534] A. Yuba, K. Yazaki, M. Tabata, G. Honda, and R. Croteau. cDNA cloning, characterization, and functional expression of 4*S*-(-)-limonene synthase from *Perilla frutescens*. *Arch. Biochem. Biophys.*, 332:280–287, 1996.

[1535] R. Yuen and H. Schachter. L-Fucose metabolism in mammals. I. Pork liver L-fuconate hydro-lyase. *Can. J. Biochem.*, 50:798–806, 1972.

[1536] Y. Yugari and C. Gilvarg. The condensation step in diaminopimelate synthesis. *J. Biol. Chem.*, 240:4710–4716, 1965.

[1537] H. Yurimoto, N. Kato, and Y. Sakai. Assimilation, dissimilation, and detoxification of formaldehyde, a central metabolic intermediate of methylotrophic metabolism. *Chem. Rec.*, 5:367–375, 2005.

[1538] T.M. Zabriskie and M.D. Jackson. Lysine biosynthesis and metabolism in fungi. *Nat. Prod. Rep.*, 17:85–97, 2000.

[1539] H. Zalkin and D. Kling. Anthranilate synthetase. Purification and properties of component I from *Salmonella typhimurium*. *Biochemistry*, 7:3566–3573, 1968.

[1540] L.O. Zamir, R. Tiberio, K.A. Devor, F. Sauriol, S. Ahmad, and R.A. Jensen. Structure of D-prephenyllactate. A carboxycyclohexadienyl metabolite from *Neurospora crassa*. *J. Biol. Chem.*, 263:17284–17290, 1988.

[1541] K. Zargar, R. Saville, R.M. Phelan, S.G. Tringe, C.J. Petzold, J.D. Keasling, and H.R. Beller. *In vitro* characterization of phenylacetate decarboxylase, a novel enzyme catalyzing toluene biosynthesis in an anaerobic microbial community. *Sci. Rep.*, 6:31362–31362, 2016.

[1542] J. Zarzycki, V. Brecht, M. Muller, and G. Fuchs. Identifying the missing steps of the autotrophic 3-hydroxypropionate CO_2 fixation cycle in *Chloroflexus aurantiacus*. *Proc. Natl. Acad. Sci. USA*, 106:21317–21322, 2009.

[1543] J. Zarzycki, A. Schlichting, N. Strychalsky, M. Muller, B.E. Alber, and G. Fuchs. Mesaconyl-coenzyme A hydratase, a new enzyme of two central carbon metabolic pathways in bacteria. *J. Bacteriol.*, 190:1366–1374, 2008.

[1544] M. Zeida, M. Wieser, T. Yoshida, T. Sugio, and T. Nagasawa. Purification and characterization of gallic acid decarboxylase from *Pantoea agglomerans* T7. *Appl. Environ. Microbiol.*, 64:4743–4747, 1998.

[1545] P. Zerbe, A. Chiang, H. Dullat, M. O'Neil-Johnson, C. Starks, B. Hamberger, and J. Bohlmann. Diterpene synthases of the biosynthetic system of medicinally active diterpenoids in *Marrubium vulgare*. *Plant J.*, 79:914–927, 2014.

[1546] P. Zerbe, A. Chiang, M. Yuen, B. Hamberger, B. Hamberger, J.A. Draper, R. Britton, and J. Bohlmann. Bifunctional *cis*-abienol synthase from *Abies balsamea* discovered by transcriptome sequencing and its implications for diterpenoid fragrance production. *J. Biol. Chem.*, 287:12121–12131, 2012.

[1547] P. Zerbe, B. Hamberger, M.M. Yuen, A. Chiang, H.K. Sandhu, L.L. Madilao, A. Nguyen, B. Hamberger, S.S. Bach, and J. Bohlmann. Gene discovery of modular diterpene metabolism in nonmodel systems. *Plant Physiol.*, 162:1073–1091, 2013.

[1548] B. Zerner, S.M. Coutts, F. Lederer, H.H. Waters, and F.H. Westheimer. Acetoacetate decarboxylase. Preparation of the enzyme. *Biochemistry*, 5:813–816, 1966.

[1549] C. Zhang, C. Albermann, X. Fu, N.R. Peters, J.D. Chisholm, G. Zhang, E.J. Gilbert, P.G. Wang, D.L. Van Vranken, and J.S. Thorson. RebG- and RebM-catalyzed indolocarbazole diversification. *ChemBioChem*, 7:795–804, 2006.

[1550] G. Zhang, J. Dai, Z. Lu, and D. Dunaway-Mariano. The phosphonopyruvate decarboxylase from *Bacteroides fragilis*. *J. Biol. Chem.*, 278:41302–41308, 2003.

[1551] Q. Zhang and W.A. van der Donk. Answers to the carbon-phosphorus lyase conundrum. *ChemBioChem*, 13:627–629, 2012.

[1552] R. Zhang, X.T. Feng, F. Wu, Y. Ding, X.N. Zang, X.C. Zhang, D.Y. Yuan, and B.R. Zhao. Molecular cloning and expression analysis of a new bilin lyase: the *cpcT* gene encoding a bilin lyase responsible for attachment of phycocyanobilin to Cys-153 on the β-subunit of phycocyanin in *Arthrospira platensis* FACHB314. *Gene*, 544:191–197, 2014.

[1553] X. Zhang, M.S. Carter, M.W. Vetting, B. San Francisco, S. Zhao, N.F. Al-Obaidi, J.O. Solbiati, J.J. Thiaville, V. de Crecy-Lagard, M.P. Jacobson, S.C. Almo, and J.A. Gerlt. Assignment of function to a domain of unknown function: DUF1537 is a new kinase family in catabolic pathways for acid sugars. *Proc. Natl. Acad. Sci. USA*, 113:E4161–E4169, 2016.

[1554] X. Zhang, R. Kumar, M.W. Vetting, S. Zhao, M.P. Jacobson, S.C. Almo, and J.A. Gerlt. A unique *cis*-3-hydroxy-L-proline dehydratase in the enolase superfamily. *J. Am. Chem. Soc.*, 137:1388–1391, 2015.

[1555] X. Zhang, G. Shang, L. Gu, and Y. Shen. Crystallization and preliminary X-ray diffraction analysis of the diterpene cyclooctatin synthase (CYC) from *Streptomyces* sp. LZ35. *Acta Crystallogr. F Struct. Biol. Commun.*, 70:366–369, 2014.

[1556] Z. Zhang, Y. Park, M.M. Kemp, W. Zhao, A.R. Im, D. Shaya, M. Cygler, Y.S. Kim, and R.J. Linhardt. Liquid chromatography-mass spectrometry to study chondroitin lyase action pattern. *Anal. Biochem.*, 385:57–64, 2009.

[1557] B. Zhao, L. Lei, D.G. Vassylyev, X. Lin, D.E. Cane, S.L. Kelly, H. Yuan, D.C. Lamb, and M.R. Waterman. Crystal structure of albaflavenone monooxygenase containing a moonlighting terpene synthase active site. *J. Biol. Chem.*, 284:36711–36719, 2009.

[1558] B. Zhao, X. Lin, L. Lei, D.C. Lamb, S.L. Kelly, M.R. Waterman, and D.E. Cane. Biosynthesis of the sesquiterpene antibiotic albaflavenone in *Streptomyces coelicolor* A3(2). *J. Biol. Chem.*, 283:8183–8189, 2008.

[1559] K.H. Zhao, M.G. Deng, M. Zheng, M. Zhou, A. Parbel, M. Storf, M. Meyer, B. Strohmann, and H. Scheer. Novel activity of a phycobiliprotein lyase: both the attachment of phycocyanobilin and the isomerization to phycoviolobilin are catalyzed by the proteins PecE and PecF encoded by the phycoerythrocyanin operon. *FEBS Lett.*, 469:9–13, 2000.

[1560] K.H. Zhao, P. Su, J. Li, J.M. Tu, M. Zhou, C. Bubenzer, and H. Scheer. Chromophore attachment to phycobiliprotein β-subunits: phycocyanobilin:cysteine-β84 phycobiliprotein lyase activity of CpeS-like protein from *Anabaena* Sp. PCC7120. *J. Biol. Chem.*, 281:8573–8581, 2006.

[1561] K.H. Zhao, P. Su, J.M. Tu, X. Wang, H. Liu, M. Ploscher, L. Eichacker, B. Yang, M. Zhou, and H. Scheer. Phycobilin:cystein-84 biliprotein lyase, a near-universal lyase for cysteine-84-binding sites in cyanobacterial phycobiliproteins. *Proc. Natl. Acad. Sci. USA*, 104:14300–14305, 2007.

[1562] K.H. Zhao, D. Wu, L. Wang, M. Zhou, M. Storf, C. Bubenzer, B. Strohmann, and H. Scheer. Characterization of phycoviolobilin phycoerythrocyanin-α 84-cystein-lyase-(isomerizing) from *Mastigocladus laminosus*. *Eur. J. Biochem.*, 269:4542–4550, 2002.

[1563] K.H. Zhao, J. Zhang, J.M. Tu, S. Bohm, M. Ploscher, L. Eichacker, C. Bubenzer, H. Scheer, X. Wang, and M. Zhou. Lyase activities of CpcS- and CpcT-like proteins from *Nostoc* PCC7120 and sequential reconstitution of binding sites of phycoerythrocyanin and phycocyanin β-subunits. *J. Biol. Chem.*, 282:34093–34103, 2007.

[1564] Q. Zhao, Y. Su, Z. Wang, C. Chen, T. Wu, and Y. Huang. Identification of glutathione (GSH)-independent glyoxalase III from *Schizosaccharomyces pombe*. *BMC Evol Biol*, 14:86–86, 2014.

[1565] K. Zheng, P.D. Ngo, V.L. Owens, X.P. Yang, and S.O. Mansoorabadi. The biosynthetic pathway of coenzyme F_{430} in methanogenic and methanotrophic archaea. *Science*, 354:339–342, 2016.

[1566] Y. Zheng and A.R. Brash. Dioxygenase activity of epidermal lipoxygenase-3 unveiled: typical and atypical features of its catalytic activity with natural and synthetic polyunsaturated fatty acids. *J. Biol. Chem.*, 285:39866–39875, 2010.

[1567] K. Zhou, Y. Gao, J.A. Hoy, F.M. Mann, R.B. Honzatko, and R.J. Peters. Insights into diterpene cyclization from structure of bifunctional abietadiene synthase from *Abies grandis*. *J. Biol. Chem.*, 287:6840–6850, 2012.

[1568] L. Zhou, J.Y. Wang, J. Wang, A. Poplawsky, S. Lin, B. Zhu, C. Chang, T. Zhou, L.H. Zhang, and Y.W. He. The diffusible factor synthase XanB2 is a bifunctional chorismatase that links the shikimate pathway to ubiquinone and xanthomonadins biosynthetic pathways. *Mol. Microbiol.*, 87:80–93, 2013.

[1569] W. Zhou, W.L. Ding, X.L. Zeng, L.L. Dong, B. Zhao, M. Zhou, H. Scheer, K.H. Zhao, and X. Yang. Structure and mechanism of the phycobiliprotein lyase CpcT. *J. Biol. Chem.*, 289:26677–26689, 2014.

[1570] J. Zhu, E. Dizin, X. Hu, A.S. Wavbreille, J. Park, and D. Pei. S-Ribosylhomocysteinase (LuxS) is a mononuclear iron protein. *Biochemistry*, 42:4717–4726, 2003.

[1571] X. Zhuang, T.G. Kollner, N. Zhao, G. Li, Y. Jiang, L. Zhu, J. Ma, J. Degenhardt, and F. Chen. Dynamic evolution of herbivore-induced sesquiterpene biosynthesis in sorghum and related grass crops. *Plant J.*, 69:70–80, 2012.

[1572] L. Zu, M. Xu, M.W. Lodewyk, D.E. Cane, R.J. Peters, and D.J. Tantillo. Effect of isotopically sensitive branching on product distribution for pentalenene synthase: support for a mechanism predicted by quantum chemistry. *J. Am. Chem. Soc.*, 134:11369–11371, 2012.

Index