The Enzyme List
Class 5 — Isomerases

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 5.1 Racemases and epimerases

This subclass contains enzymes that catalyse either racemization or epimerization of a centre of chirality. Sub-subclasses are based on the substrate: amino acids and derivatives (EC 5.1.1), hydroxy acids and derivatives (EC 5.1.2), carbohydrates and derivatives (EC 5.1.3), or other compounds (EC 5.1.99).

EC 5.1.1 Acting on amino acids and derivatives

EC 5.1.1.1
Accepted name: alanine racemase
Reaction: L-alanine = D-alanine
Other name(s): L-alanine racemase
Systematic name: alanine racemase
Comments: A pyridoxal-phosphate protein.
References: [398, 677, 678]

[EC 5.1.1.1 created 1961]

EC 5.1.1.2
Accepted name: methionine racemase
Reaction: L-methionine = D-methionine
Systematic name: methionine racemase
Comments: A pyridoxal-phosphate protein.
References: [289]

[EC 5.1.1.2 created 1961]

EC 5.1.1.3
Accepted name: glutamate racemase
Reaction: L-glutamate = D-glutamate
Systematic name: glutamate racemase
Comments: A pyridoxal-phosphate protein.
References: [196]

[EC 5.1.1.3 created 1961]

EC 5.1.1.4
Accepted name: proline racemase
Reaction: L-proline = D-proline
Systematic name: proline racemase
References: [582]

[EC 5.1.1.4 created 1961]

EC 5.1.1.5

Accepted name: lysine racemase
Reaction: L-lysine = D-lysine
Systematic name: lysine racemase
Comments: The enzyme is involved in a lysine catabolic pathway.
References: [250, 249, 91, 299]

[EC 5.1.1.5 created 1961]

EC 5.1.1.6

Accepted name: threonine racemase
Reaction: L-threonine = D-threonine
Systematic name: threonine racemase
Comments: Inverts both chiral centres.
References: [19]

[EC 5.1.1.6 created 1961, modified 1981]

EC 5.1.1.7

Accepted name: diaminopimelate epimerase
Reaction: LL-2,6-diaminoheptanedioate = *meso*-diaminoheptanedioate
Systematic name: LL-2,6-diaminoheptanedioate 2-epimerase
References: [27]

[EC 5.1.1.7 created 1961]

EC 5.1.1.8

Accepted name: 4-hydroxyproline epimerase
Reaction: *trans*-4-hydroxy-L-proline = *cis*-4-hydroxy-D-proline
Other name(s): hydroxyproline epimerase; hydroxyproline 2-epimerase; L-hydroxyproline epimerase
Systematic name: 4-hydroxyproline 2-epimerase
Comments: Also interconverts *trans*-4-hydroxy-D-proline and *cis*-4-hydroxy-L-proline.
References: [7]

[EC 5.1.1.8 created 1965, modified 1983]

EC 5.1.1.9

Accepted name: arginine racemase
Reaction: L-arginine = D-arginine
Systematic name: arginine racemase
Comments: A pyridoxal-phosphate protein.
References: [699]

[EC 5.1.1.9 created 1972]

EC 5.1.1.10

Accepted name: amino-acid racemase
Reaction: an L-amino acid = a D-amino acid
Other name(s): L-amino acid racemase
Systematic name: amino-acid racemase
Comments: A pyridoxal-phosphate protein.
References: [575]

[EC 5.1.1.10 created 1972]

EC 5.1.1.11

Accepted name: phenylalanine racemase (ATP-hydrolysing)
Reaction: ATP + L-phenylalanine + H_2O = AMP + diphosphate + D-phenylalanine
Other name(s): phenylalanine racemase; phenylalanine racemase (adenosine triphosphate-hydrolysing); gramicidin S synthetase I
Systematic name: phenylalanine racemase (ATP-hydrolysing)
References: [690]

[EC 5.1.1.11 created 1972]

EC 5.1.1.12

Accepted name: ornithine racemase
Reaction: L-ornithine = D-ornithine
Systematic name: ornithine racemase
References: [90]

[EC 5.1.1.12 created 1972 as EC 5.4.3.1, transferred 1976 to EC 5.1.1.12]

EC 5.1.1.13

Accepted name: aspartate racemase
Reaction: L-aspartate = D-aspartate
Other name(s): D-aspartate racemase; McyF
Systematic name: aspartate racemase
Comments: Also acts, at half the rate, on L-alanine.
References: [350, 694, 374, 566, 693]

[EC 5.1.1.13 created 1976]

EC 5.1.1.14

Accepted name: nocardicin A epimerase
Reaction: (1) isonocardicin C = nocardicin C
(2) isonocardicin A = nocardicin A
Other name(s): isonocardicin A epimerase; *nocJ* (gene name)
Systematic name: nocardicin-C epimerase
Comments: Requires pyridoxal 5′-phosphate. The enzyme, characterized from the bacterium *Nocardia uniformis*, is involved in the biosynthesis of the monolactam antibiotic nocardicin A. It catalyses the epimerization of the amino group at position 9′ from (*S*)- configuration to (*R*)-. The enzyme can act on both isonocardicin A and isonocardicin C, but the *in vivo* substrate appears to be the latter [308].
References: [664, 307, 308]

[EC 5.1.1.14 created 1992, modified 2016]

EC 5.1.1.15

Accepted name: 2-aminohexano-6-lactam racemase
Reaction: (*S*)-2-aminohexano-6-lactam = (*R*)-2-aminohexano-6-lactam
Other name(s): α-amino-ε-caprolactam racemase
Systematic name: 2-aminohexano-6-lactam racemase
Comments: Contains pyridoxal 5′-phosphate. Also racemises 2-aminopentano-5-lactam (α-amino-δ-valerolactam) and 2-amino-4-thiahexano-6-lactam (where S replaces CH_2 of C-4). It does not catalyse the racemisation of α-amino acids but has some transaminase activity with them.

References: [9, 10, 468]

[EC 5.1.1.15 created 1999]

EC 5.1.1.16

Accepted name: protein-serine epimerase
Reaction: [protein]-L-serine = [protein]-D-serine
Other name(s): protein-serine racemase
Systematic name: [protein]-serine epimerase
Comments: The enzyme specifically interconverts the configuration of Ser-46 of the peptide ω-agatoxin-KT, found in the venom of the funnel web spider, *Agelenopsis aperta*, but not that of the other serine residue, Ser-28.
References: [560]

[EC 5.1.1.16 created 1999]

EC 5.1.1.17

Accepted name: isopenicillin-N epimerase
Reaction: isopenicillin N = penicillin N
Systematic name: penicillin-N 5-amino-5-carboxypentanoyl-epimerase
Comments: This enzyme contains pyridoxal phosphate. Epimerization at C-5 of the 5-amino-5-carboxypentanoyl group to form penicillin N is required to make a substrate for EC 1.14.20.1, deactoxycephalosporin-C synthase, to produce cephalosporins. Forms part of the penicillin biosynthesis pathway (for pathway, click here).
References: [635, 349, 77, 696]

[EC 5.1.1.17 created 2002]

EC 5.1.1.18

Accepted name: serine racemase
Reaction: L-serine = D-serine
Other name(s): SRR
Systematic name: serine racemase
Comments: A pyridoxal-phosphate protein that is highly selective for L-serine as substrate. D-Serine is found in type-II astrocytes in mammalian brain, where it appears to be an endogenous ligand of the glycine site of *N*-methyl-D-aspartate (NMDA) receptors [674, 675]. The reaction can also occur in the reverse direction but does so more slowly at physiological serine concentrations [173].
References: [674, 675, 427, 173]

[EC 5.1.1.18 created 2007]

EC 5.1.1.19

Accepted name: *O*-ureido-serine racemase
Reaction: *O*-ureido-L-serine = *O*-ureido-D-serine
Other name(s): *dcsC* (gene name)
Systematic name: (2*S*)-2-amino-3-[(carbamoylamino)oxy]propanoate 2-epimerase
Comments: The enzyme employs a two-base mechanism, with a thiolate-thiol pair in the active site. It participates in the biosynthetic pathway of D-cycloserine, an antibiotic substance produced by several *Streptomyces* species.
References: [340, 142]

[EC 5.1.1.19 created 2013]

EC 5.1.1.20

Accepted name: L-Ala-D/L-Glu epimerase
Reaction: L-alanyl-D-glutamate = L-alanyl-L-glutamate
Other name(s): YkfB; YcjG; AEE; AE epimerase
Systematic name: L-alanyl-D-glutamate epimerase
Comments: The enzyme, characterized from the bacteria *Escherichia coli* and *Bacillus subtilis*, is involved in the recycling of the murein peptide, of which L-Ala-D-Glu is a component. *In vitro* the enzyme from *Escherichia coli* epimerizes several L-Ala-L-X dipeptides with broader specificity than the enzyme from *Bacillus subtilis*.
References: [542, 209]

[EC 5.1.1.20 created 2015]

EC 5.1.1.21

Accepted name: isoleucine 2-epimerase
Reaction: L-isoleucine = D-*allo*-isoleucine
Other name(s): BCAA racemase
Systematic name: isoleucine 2-epimerase
Comments: A pyridoxal phosphate protein. The enzyme, characterized from the bacterium *Lactobacillus buchneri*, specifically catalyses racemization of nonpolar amino acids at the C-2 position.
References: [444]

[EC 5.1.1.21 created 2015]

EC 5.1.1.22

Accepted name: 4-hydroxyproline betaine 2-epimerase
Reaction: (1) *trans*-4-hydroxy-L-proline betaine = *cis*-4-hydroxy-D-proline betaine
(2) L-proline betaine = D-proline betaine
Other name(s): *hpbD* (gene name); Hyp-B 2-epimerase; (4*R*)-4-hydroxyproline betaine 2-epimerase
Systematic name: 4-hydroxyproline betaine 2-epimerase
Comments: The enzyme, characterized from the bacteria *Pelagibaca bermudensis* and *Paracoccus denitrificans*, specifically catalyses racemization of *trans*-4-hydroxy-L-proline betaine and L-proline betaine at the C-2 position.
References: [725, 341]

[EC 5.1.1.22 created 2017]

EC 5.1.1.23

Accepted name: UDP-*N*-acetyl-α-D-muramoyl-L-alanyl-L-glutamate epimerase
Reaction: ATP + UDP-*N*-acetyl-α-D-muramoyl-L-alanyl-L-glutamate + H_2O = AMP + diphosphate + UDP-*N*-acetyl-α-D-muramoyl-L-alanyl-D-glutamate
Other name(s): *murL* (gene name); UDP-MurNAc-L-Ala-L-Glu epimerase
Systematic name: UDP-*N*-acetyl-α-D-muramoyl-L-alanyl-L-glutamate L-glutamate-epimerase
Comments: The enzyme, characterized from the bacterium *Xanthomonas oryzae*, catalyses epimerization of the terminal L-glutamate in UDP-*N*-acetyl-α-D-muramoyl-L-alanyl-L-glutamate. The reaction proceeds only in one direction and involves an adenylated intermediate. The combined activity of this enzyme and EC 6.3.2.53, UDP-*N*-acetylmuramoyl-L-alanine—L-glutamate ligase, provides an alternative route for incorporating D-glutamate into peptidoglycan, replacing the more common combination of EC 5.1.1.3, glutamate racemase, and EC 6.3.2.9, UDP-*N*-acetylmuramoyl-L-alanine—D-glutamate ligase.
References: [164]

[EC 5.1.1.23 created 2018]

EC 5.1.1.24

Accepted name: histidine racemase
Reaction: L-histidine = D-histidine
Other name(s): *cntK* (gene name)
Systematic name: histidine racemase
Comments: The enzyme, characterized from the bacterium *Staphylococcus aureus*, participates in the biosynthesis of the metallophore staphylopine, which is involved in the acquisition of nickel, copper, and cobalt.
References: [193]

[EC 5.1.1.24 created 2019]

EC 5.1.2 Acting on hydroxy acids and derivatives

EC 5.1.2.1

Accepted name: lactate racemase
Reaction: (*S*)-lactate = (*R*)-lactate
Other name(s): lacticoracemase; hydroxyacid racemase; lactic acid racemase; *larA* (gene name)
Systematic name: lactate racemase
Comments: The enzyme has been characterized from the bacterium *Lactobacillus plantarum* and appears to be restricted to lactic acid bacteria. It contains a unique nickel-containing cofactor, pyridinium-3-thioamide-5-thiocarboxylate mononucleotide Ni pincer complex.
References: [252, 318, 199, 134, 135, 705]

[EC 5.1.2.1 created 1961]

EC 5.1.2.2

Accepted name: mandelate racemase
Reaction: (*S*)-mandelate = (*R*)-mandelate
Systematic name: mandelate racemase
References: [210]

[EC 5.1.2.2 created 1961]

EC 5.1.2.3

Accepted name: 3-hydroxybutyryl-CoA epimerase
Reaction: (*S*)-3-hydroxybutanoyl-CoA = (*R*)-3-hydroxybutanoyl-CoA
Other name(s): 3-hydroxybutyryl coenzyme A epimerase; 3-hydroxyacyl-CoA epimerase
Systematic name: 3-hydroxybutanoyl-CoA 3-epimerase
References: [585, 645]

[EC 5.1.2.3 created 1961]

EC 5.1.2.4

Accepted name: acetoin racemase
Reaction: (*S*)-acetoin = (*R*)-acetoin
Other name(s): acetylmethylcarbinol racemase
Systematic name: acetoin racemase
References: [611]

[EC 5.1.2.4 created 1972]

EC 5.1.2.5

Accepted name: tartrate epimerase
Reaction: (*R*,*R*)-tartrate = *meso*-tartrate
Other name(s): tartaric racemase
Systematic name: tartrate epimerase
References: [503]

[EC 5.1.2.5 created 1972]

EC 5.1.2.6

Accepted name: isocitrate epimerase
Reaction: (1*R*,2*S*)-1-hydroxypropane-1,2,3-tricarboxylate = (1*S*,2*S*)-1-hydroxypropane-1,2,3-tricarboxylate
Systematic name: (1*R*,2*S*)-1-hydroxypropane-1,2,3-tricarboxylate 1-epimerase
Comments: (1*R*,2*S*)-1-hydroxypropane-1,2,3-tricarboxylate is the commonly occurring isomer of isocitrate.
References: [245]

[EC 5.1.2.6 created 1984]

EC 5.1.2.7

Accepted name: tagaturonate epimerase
Reaction: D-tagaturonate = D-fructuronate
Other name(s): fructuronate epimerase; tagaturonate/fructuronate epimerase; UxaE
Systematic name: D-tagaturonate 3-epimerase
Comments: The enzyme, present in bacteria, is involved in a degradation pathway of D-galacturonate.
References: [522]

[EC 5.1.2.7 created 2017]

EC 5.1.3 Acting on carbohydrates and derivatives

EC 5.1.3.1

Accepted name: ribulose-phosphate 3-epimerase
Reaction: D-ribulose 5-phosphate = D-xylulose 5-phosphate
Other name(s): phosphoribulose epimerase; erythrose-4-phosphate isomerase; phosphoketopentose 3-epimerase; xylulose phosphate 3-epimerase; phosphoketopentose epimerase; ribulose 5-phosphate 3-epimerase; D-ribulose phosphate-3-epimerase; D-ribulose 5-phosphate epimerase; D-ribulose-5-P 3-epimerase; D-xylulose-5-phosphate 3-epimerase; pentose-5-phosphate 3-epimerase
Systematic name: D-ribulose-5-phosphate 3-epimerase
Comments: The enzyme also converts D-erythrose 4-phosphate into D-erythrulose 4-phosphate and D-threose 4-phosphate.
References: [32, 139, 255, 591, 613]

[EC 5.1.3.1 created 1961, modified 1989]

EC 5.1.3.2

Accepted name: UDP-glucose 4-epimerase
Reaction: UDP-α-D-glucose = UDP-α-D-galactose
Other name(s): UDP-galactose 4-epimerase; uridine diphosphoglucose epimerase; galactowaldenase; UDPG-4-epimerase; uridine diphosphate galactose 4-epimerase; uridine diphospho-galactose-4-epimerase; UDP-glucose epimerase; 4-epimerase; uridine diphosphoglucose 4-epimerase; uridine diphosphate glucose 4-epimerase; UDP-D-galactose 4-epimerase
Systematic name: UDP-α-D-glucose 4-epimerase

Comments: Requires NAD^+. Also acts on UDP-2-deoxyglucose.
References: [357, 410, 665]

[EC 5.1.3.2 created 1961]

EC 5.1.3.3
Accepted name: aldose 1-epimerase
Reaction: α-D-glucose = β-D-glucose
Other name(s): mutarotase; aldose mutarotase; galactose mutarotase; galactose 1-epimerase; D-galactose 1-epimerase
Systematic name: aldose 1-epimerase
Comments: Also acts on L-arabinose, D-xylose, D-galactose, maltose and lactose. This enzyme catalyses the first step in galactose metabolism by converting β-D-galactose into α-D-galactose, which is the substrate for EC 2.7.1.6, galactokinase [45, 618].
References: [53, 54, 306, 361, 45, 618, 617]

[EC 5.1.3.3 created 1961]

EC 5.1.3.4
Accepted name: L-ribulose-5-phosphate 4-epimerase
Reaction: L-ribulose 5-phosphate = D-xylulose 5-phosphate
Other name(s): phosphoribulose isomerase; ribulose phosphate 4-epimerase; L-ribulose-phosphate 4-epimerase; L-ribulose 5-phosphate 4-epimerase; AraD; L-Ru5P
Systematic name: L-ribulose-5-phosphate 4-epimerase
Comments: Requires a divalent cation for activity.
References: [74, 136, 354, 673, 23, 353, 534]

[EC 5.1.3.4 created 1965, modified 2005]

EC 5.1.3.5
Accepted name: UDP-arabinose 4-epimerase
Reaction: UDP-L-arabinose = UDP-D-xylose
Other name(s): uridine diphosphoarabinose epimerase; UDP arabinose epimerase; uridine 5′-diphosphate-D-xylose 4-epimerase; UDP-D-xylose 4-epimerase
Systematic name: UDP-L-arabinose 4-epimerase
References: [162]

[EC 5.1.3.5 created 1965]

EC 5.1.3.6
Accepted name: UDP-glucuronate 4-epimerase
Reaction: UDP-glucuronate = UDP-D-galacturonate
Other name(s): uridine diphospho-D-galacturonic acid; UDP glucuronic epimerase; uridine diphosphoglucuronic epimerase; UDP-galacturonate 4-epimerase; uridine diphosphoglucuronate epimerase; UDP-D-galacturonic acid 4-epimerase
Systematic name: UDP-glucuronate 4-epimerase
References: [162]

[EC 5.1.3.6 created 1965]

EC 5.1.3.7
Accepted name: UDP-*N*-acetylglucosamine 4-epimerase
Reaction: UDP-*N*-acetyl-α-D-glucosamine = UDP-*N*-acetyl-α-D-galactosamine

Other name(s): UDP acetylglucosamine epimerase; uridine diphosphoacetylglucosamine epimerase; uridine diphosphate *N*-acetylglucosamine-4-epimerase; uridine 5′-diphospho-*N*-acetylglucosamine-4-epimerase; UDP-*N*-acetyl-D-glucosamine 4-epimerase
Systematic name: UDP-*N*-acetyl-α-D-glucosamine 4-epimerase
References: [195, 334]

[EC 5.1.3.7 created 1965]

EC 5.1.3.8
Accepted name: *N*-acylglucosamine 2-epimerase
Reaction: *N*-acyl-D-glucosamine = *N*-acyl-D-mannosamine
Other name(s): acylglucosamine 2-epimerase; *N*-acetylglucosamine 2-epimerase
Systematic name: *N*-acyl-D-glucosamine 2-epimerase
Comments: Requires catalytic amounts of ATP.
References: [192]

[EC 5.1.3.8 created 1972]

EC 5.1.3.9
Accepted name: *N*-acylglucosamine-6-phosphate 2-epimerase
Reaction: *N*-acyl-D-glucosamine 6-phosphate = *N*-acyl-D-mannosamine 6-phosphate
Other name(s): acylglucosamine-6-phosphate 2-epimerase; acylglucosamine phosphate 2-epimerase
Systematic name: *N*-acyl-D-glucosamine-6-phosphate 2-epimerase
References: [191]

[EC 5.1.3.9 created 1972]

EC 5.1.3.10
Accepted name: CDP-paratose 2-epimerase
Reaction: CDP-α-D-paratose = CDP-α-D-tyvelose
Other name(s): CDP-paratose epimerase; cytidine diphosphoabequose epimerase; cytidine diphosphodideoxyglucose epimerase; cytidine diphosphoparatose epimerase; cytidine diphosphate paratose-2-epimerase; CDP-abequose epimerase (incorrect); CDP-D-abequose 2-epimerase (incorrect); CDP-tyvelose 2-epimerase,
Systematic name: CDP-3,6-dideoxy-D-glucose 2-epimerase
Comments: Requires NAD^+.
References: [408, 372, 335]

[EC 5.1.3.10 created 1972, modified 2005]

EC 5.1.3.11
Accepted name: cellobiose epimerase
Reaction: cellobiose = 4-*O*-β-D-glucopyranosyl-D-mannose
Systematic name: cellobiose 2-epimerase
Comments: The enzyme catalyses the interconversion between D-glucose and D-mannose residues at the reducing end of β-1,4-linked disaccharides by epimerizing the hydroxyl group at the C-2 position of the glucose moiety.
References: [630, 265, 181]

[EC 5.1.3.11 created 1972]

[5.1.3.12 Deleted entry. UDP-glucuronate 5-epimerase. The enzyme has never been purified and the activity was later shown not to exist.]

[EC 5.1.3.12 created 1972, deleted 2020]

EC 5.1.3.13

Accepted name: dTDP-4-dehydrorhamnose 3,5-epimerase
Reaction: dTDP-4-dehydro-6-deoxy-α-D-glucose = dTDP-4-dehydro-β-L-rhamnose
Other name(s): dTDP-L-rhamnose synthetase; dTDP-L-rhamnose synthase; thymidine diphospho-4-ketorhamnose 3,5-epimerase; TDP-4-ketorhamnose 3,5-epimerase; dTDP-4-dehydro-6-deoxy-D-glucose 3,5-epimerase; TDP-4-keto-L-rhamnose-3,5-epimerase
Systematic name: dTDP-4-dehydro-6-deoxy-α-D-glucose 3,5-epimerase
Comments: The enzyme occurs in a complex with EC 1.1.1.133 dTDP-4-dehydrorhamnose reductase.
References: [185, 418]

[EC 5.1.3.13 created 1972]

EC 5.1.3.14

Accepted name: UDP-*N*-acetylglucosamine 2-epimerase (non-hydrolysing)
Reaction: UDP-*N*-acetyl-α-D-glucosamine = UDP-*N*-acetyl-α-D-mannosamine
Other name(s): UDP-*N*-acetylglucosamine 2′-epimerase (ambiguous); uridine diphosphoacetylglucosamine 2′-epimerase (ambiguous); uridine diphospho-*N*-acetylglucosamine 2′-epimerase (ambiguous); uridine diphosphate-*N*-acetylglucosamine-2′-epimerase (ambiguous); *rffE* (gene name); *mnaA* (gene name); UDP-*N*-acetyl-D-glucosamine 2-epimerase
Systematic name: UDP-*N*-acetyl-α-D-glucosamine 2-epimerase
Comments: This bacterial enzyme catalyses the reversible interconversion of UDP-GlcNAc and UDP-ManNAc. The latter is used in a variety of bacterial polysaccharide biosyntheses. *cf.* EC 3.2.1.183, UDP-*N*-acetylglucosamine 2-epimerase (hydrolysing).
References: [303, 416, 433, 75, 535, 578]

[EC 5.1.3.14 created 1976, modified 2012]

EC 5.1.3.15

Accepted name: glucose-6-phosphate 1-epimerase
Reaction: α-D-glucose 6-phosphate = β-D-glucose 6-phosphate
Systematic name: D-glucose-6-phosphate 1-epimerase
References: [684]

[EC 5.1.3.15 created 1976]

EC 5.1.3.16

Accepted name: UDP-glucosamine 4-epimerase
Reaction: UDP-α-D-glucosamine = UDP-α-D-galactosamine
Systematic name: UDP-α-D-glucosamine 4-epimerase
References: [390, 567]

[EC 5.1.3.16 created 1984]

EC 5.1.3.17

Accepted name: heparosan-*N*-sulfate-glucuronate 5-epimerase
Reaction: Epimerization of D-glucuronate in heparosan-*N*-sulfate to L-iduronate.
Other name(s): heparosan epimerase; heparosan-*N*-sulfate-D-glucuronosyl 5-epimerase; C-5 uronosyl epimerase; polyglucuronate epimerase; D-glucuronyl C-5 epimerase; poly[(1,4)-β-D-glucuronosyl-(1,4)-*N*-sulfo-α-D-glucosaminyl] glucurono-5-epimerase
Systematic name: poly[(1→4)-β-D-glucuronosyl-(1→4)-*N*-sulfo-α-D-glucosaminyl] glucurono-5-epimerase

Comments: The enzyme acts on D-glucosyluronate residues in *N*-sulfated heparosan polymers, converting them to L-iduronate, thus modifying the polymer to heparan-*N*-sulfate. The enzyme requires that at least the *N*-acetylglucosamine residue linked to C-4 of the substrate has been deacetylated and *N*-sulfated, and activity is highest with fully *N*-sulfated substrate. It does not act on glucuronate residues that are *O*-sulfated or are adjacent to *N*-acetylglucosamine residues that are *O*-sulfated at the 6 position. Thus the epimerization from D-glucuronate to L-iduronate occurs after *N*-sulfation of glucosamine residues but before *O*-sulfation. Not identical with EC 5.1.3.19 chondroitin-glucuronate 5-epimerase or with EC 5.1.3.36, heparosan-glucuronate 5-epimerase.
References: [271, 272, 214]

[EC 5.1.3.17 created 1984, modified 2015]

EC 5.1.3.18
Accepted name: GDP-mannose 3,5-epimerase
Reaction: (1) GDP-α-D-mannose = GDP-β-L-galactose
(2) GDP-α-D-mannose = GDP-β-L-gulose
Other name(s): GME (gene name); GDP-D-mannose:GDP-L-galactose epimerase; guanosine 5′-diphosphate D-mannose:guanosine 5′-diphosphate L-galactose epimerase
Systematic name: GDP-α-D-mannose 3,5-epimerase
Comments: The enzyme catalyses the formation of the stable intermediate GDP-β-L-gulose as well as GDP-β-L-galactose. The reaction proceeds by C4′ oxidation of GDP-α-D-mannose followed by epimerization of the C5′ position to give GDP-β-L-4-dehydro-gulose. This intermediate is either reduced to give GDP-β-L-gulose or the C3′ position is epimerized to give GDP-β-L-4-dehydro-galactose, followed by C4′ reduction to yield GDP-β-L-galactose. Both products serve as intermediates in two different variants of plant L-ascorbate biosynthesis pathways.
References: [232, 37, 676, 389, 652]

[EC 5.1.3.18 created 1986, modified 2020]

EC 5.1.3.19
Accepted name: chondroitin-glucuronate 5-epimerase
Reaction: chondroitin D-glucuronate = dermatan L-iduronate
Other name(s): polyglucuronate 5-epimerase; dermatan-sulfate 5-epimerase; urunosyl C-5 epimerase; chondroitin D-glucuronosyl 5-epimerase
Systematic name: chondroitin-D-glucuronate 5-epimerase
Comments: Not identical with EC 5.1.3.17 heparosan-*N*-sulfate-glucuronate 5-epimerase.
References: [391]

[EC 5.1.3.19 created 1986]

EC 5.1.3.20
Accepted name: ADP-*glyceromanno*-heptose 6-epimerase
Reaction: ADP-D-*glycero*-D-*manno*-heptose = ADP-L-*glycero*-D-*manno*-heptose
Systematic name: ADP-L-*glycero*-D-*manno*-heptose 6-epimerase
Comments: Requires NAD^+.
References: [143, 499]

[EC 5.1.3.20 created 1999]

EC 5.1.3.21
Accepted name: maltose epimerase
Reaction: α-maltose = β-maltose
Systematic name: maltose 1-epimerase

Comments: The enzyme catalyses the interconversion of α and β anomers of maltose more effectively than those of disaccharides such as lactose and cellobiose.
References: [564]

[EC 5.1.3.21 created 2002]

EC 5.1.3.22
Accepted name: L-ribulose-5-phosphate 3-epimerase
Reaction: L-ribulose 5-phosphate = L-xylulose 5-phosphate
Other name(s): L-xylulose 5-phosphate 3-epimerase; UlaE; SgaU
Systematic name: L-ribulose-5-phosphate 3-epimerase
Comments: Along with EC 4.1.1.85, 3-dehydro-L-gulonate-6-phosphate decarboxylase, this enzyme is involved in a pathway for the utilization of L-ascorbate by *Escherichia coli*.
References: [697]

[EC 5.1.3.22 created 2005]

EC 5.1.3.23
Accepted name: UDP-2,3-diacetamido-2,3-dideoxyglucuronic acid 2-epimerase
Reaction: UDP-2,3-diacetamido-2,3-dideoxy-α-D-glucuronate = UDP-2,3-diacetamido-2,3-dideoxy-α-D-mannuronate
Other name(s): UDP-GlcNAc3NAcA 2-epimerase; UDP-α-D-GlcNAc3NAcA 2-epimerase; 2,3-diacetamido-2,3-dideoxy-α-D-glucuronic acid 2-epimerase; WbpI; WlbD
Systematic name: 2,3-diacetamido-2,3-dideoxy-α-D-glucuronate 2-epimerase
Comments: This enzyme participates in the biosynthetic pathway for UDP-α-D-ManNAc3NAcA (UDP-2,3-diacetamido-2,3-dideoxy-α-D-mannuronic acid), an important precursor of the B-band lipopolysaccharide of *Pseudomonas aeroginosa* serotype O5 and of the band-A trisaccharide of *Bordetella pertussis*, both important respiratory pathogens [655]. The enzyme is highly specific as UDP-α-D-GlcNAc, UDP-α-D-GlcNAcA (UDP-2-acetamido-2-deoxy-α-D-glucuronic acid) and UDP-α-D-GlcNAc3NAc (UDP-2,3-diacetamido-2,3-dideoxy-α-D-glucose) cannot act as substrates [655].
References: [655, 654, 293]

[EC 5.1.3.23 created 2007]

EC 5.1.3.24
Accepted name: *N*-acetylneuraminate epimerase
Reaction: *N*-acetyl-α-neuraminate = *N*-acetyl-β-neuraminate (oveall reaction)
(1a) *N*-acetyl-α-neuraminate = aceneuramate
(1b) aceneuramate = *N*-acetyl-β-neuraminate
Other name(s): sialic acid epimerase; *N*-acetylneuraminate mutarotase; NanM; NanQ
Systematic name: *N*-acetyl-α-neuraminate 2-epimerase
Comments: Sialoglycoconjugates present in vertebrates are linked exclusively by α-linkages and are released in α form during degradation. This enzyme accelerates maturotation to the β form via the open form (which also occurs as a slow spontaneous reaction). The open form is necessary for further metabolism by the bacteria.
References: [551, 310]

[EC 5.1.3.24 created 2011, modified 2021]

EC 5.1.3.25
Accepted name: dTDP-L-rhamnose 4-epimerase
Reaction: dTDP-6-deoxy-β-L-talose = dTDP-β-L-rhamnose
Other name(s): dTDP-4-L-rhamnose 4-epimerase; *wbiB* (gene name)

Systematic name: dTDP-6-deoxy-β-L-talose 4-epimerase
Comments: The equilibrium is strongly towards dTDP-β-L-rhamnose.
References: [698]

[EC 5.1.3.25 created 2012]

EC 5.1.3.26
Accepted name: *N*-acetyl-α-D-glucosaminyl-diphospho-*ditrans*,*octacis*-undecaprenol 4-epimerase
Reaction: *N*-acetyl-α-D-glucosaminyl-diphospho-*ditrans*,*octacis*-undecaprenol = *N*-acetyl-α-D-galactosaminyl-diphospho-*ditrans*,*octacis*-undecaprenol
Other name(s): GlcNAc-P-P-Und epimerase; GlcNAc-P-P-Und 4-epimerase; *gne* (gene name)
Systematic name: *N*-acetyl-α-D-glucosaminyl-diphospho-*ditrans*,*octacis*-undecaprenol 4-epimerase
Comments: The enzyme is involved in biosynthesis of the repeating tetrasaccharide unit of the O-antigen produced by some Gram-negative bacteria.
References: [528]

[EC 5.1.3.26 created 2013]

EC 5.1.3.27
Accepted name: dTDP-4-dehydro-6-deoxy-D-glucose 3-epimerase
Reaction: dTDP-4-dehydro-6-deoxy-α-D-glucose = dTDP-4-dehydro-6-deoxy-α-D-gulose
Other name(s): dTDP-deoxyglucose 3-epimerase; dTDP-4-keto-6-deoxy-D-glucose 3-epimerase; dTDP-4-keto-6-deoxyglucose 3-epimerase; *gerF* (gene name); *tylJ* (gene name); *chmJ* (gene name); *mydH* (gene name)
Systematic name: dTDP-4-dehydro-6-deoxy-α-D-glucose 3-epimerase
Comments: The enzyme is involved in the biosynthetic pathway of dTDP-6-deoxy-α-D-allose, which is converted to mycinose after attachment to the aglycones of several macrolide antibiotics, including tylosin, chalcomycin, dihydrochalcomycin, and mycinamicin II.
References: [576, 620, 337]

[EC 5.1.3.27 created 2013]

EC 5.1.3.28
Accepted name: UDP-*N*-acetyl-L-fucosamine synthase
Reaction: UDP-2-acetamido-2,6-dideoxy-β-L-talose = UDP-*N*-acetyl-β-L-fucosamine
Other name(s): WbjD; Cap5G
Systematic name: UDP-2-acetamido-2,6-dideoxy-β-L-talose 2-epimerase
Comments: Isolated from the bacteria *Pseudomonas aeruginosa* and *Staphylococcus aureus*. Involved in bacterial polysaccharide biosynthesis.
References: [325, 442]

[EC 5.1.3.28 created 2014]

EC 5.1.3.29
Accepted name: L-fucose mutarotase
Reaction: α-L-fucopyranose = β-L-fucopyranose
Other name(s): FucU; fucose mutarotase; FucM
Systematic name: L-fucose 1-epimerase
Comments: This enzyme shows no 1-epimerase activity with D-glucose, L-rhamnose and D-fucose (*cf.* EC 5.1.3.3, aldose 1-epimerase) [530].
References: [530, 478]

[EC 5.1.3.29 created 2014]

EC 5.1.3.30

Accepted name: D-psicose 3-epimerase
Reaction: D-psicose = D-fructose
Other name(s): D-allulose 3-epimerase; DPEase (ambiguous)
Systematic name: D-psicose 3-epimerase
Comments: The enzyme is highly specific for D-psicose and shows very low activity with D-tagatose (*cf.* EC 5.1.3.31, D-tagatose 3-epimerase). The enzyme from the bacterium *Clostridium scindens* requires Mn^{2+} [438], whereas the enzymes from the bacteria *Clostridium cellulolyticum* [83, 439], *Clostridium* sp. BNL1100 [730], and *Clostridium bolteae* [722] require Co^{2+} as optimum cofactor. The enzyme from *Ruminococcus* sp. [277] is not dependent on the presence of metal ions, but its activity is enhanced by Mn^{2+}.
References: [438, 83, 730, 722, 439, 277]

[EC 5.1.3.30 created 2014]

EC 5.1.3.31

Accepted name: D-tagatose 3-epimerase
Reaction: (1) D-tagatose = D-sorbose
(2) D-psicose = D-fructose
Other name(s): L-ribulose 3-epimerase; ketose 3-epimerase
Systematic name: D-tagatose 3-epimerase
Comments: The enzymes isolated from the bacteria *Pseudomonas cichorii* [700], *Pseudomonas* sp. ST-24 [266], *Rhodobacter sphaeroides* [720] and *Mesorhizobium loti* [631] catalyse the epimerization of various ketoses at the C-3 position, interconverting D-fructose and D-psicose, D-tagatose and D-sorbose, D-ribulose and D-xylulose, and L-ribulose and L-xylulose. The specificity depends on the species. The enzymes from *Pseudomonas cichorii* and *Rhodobacter sphaeroides* require Mn^{2+} [700, 720].
References: [266, 700, 720, 631]

[EC 5.1.3.31 created 2014]

EC 5.1.3.32

Accepted name: L-rhamnose mutarotase
Reaction: α-L-rhamnopyranose = β-L-rhamnopyranose
Other name(s): rhamnose 1-epimerase; type-3 mutarotase; YiiL
Systematic name: L-rhamnopyranose 1-epimerase
Comments: The enzyme is specific for L-rhamnopyranose.
References: [530, 531]

[EC 5.1.3.32 created 2014]

EC 5.1.3.33

Accepted name: 2-*epi*-5-*epi*-valiolone epimerase
Reaction: 2-*epi*-5-*epi*-valiolone = 5-*epi*-valiolone
Other name(s): CetB; EVE
Systematic name: 2-*epi*-5-*epi*-valiolone 2-epimerase
Comments: The enzyme, characterized from the bacterium *Actinomyces* sp. Lu 9419, is involved in the biosynthesis of the antitumor agent cetoniacytone A.
References: [683]

[EC 5.1.3.33 created 2015]

EC 5.1.3.34

Accepted name: monoglucosyldiacylglycerol epimerase

Reaction: a 1,2-diacyl-3-*O*-(β-D-glucopyranosyl)-*sn*-glycerol = a 1,2-diacyl-3-*O*-(β-D-galactopyranosyl)-*sn*-glycerol
Other name(s): glucolipid epimerase; *mgdE* (gene name)
Systematic name: 1,2-diacyl-3-*O*-(β-D-glucopyranosyl)-*sn*-glycerol 4-epimerase
Comments: The enzyme, characterized from cyanobacteria, is involves in the biosynthesis of galactolipids found in their photosynthetic membranes.
References: [536, 34]

[EC 5.1.3.34 created 2015]

EC 5.1.3.35
Accepted name: 2-*epi*-5-*epi*-valiolone 7-phosphate 2-epimerase
Reaction: 2-*epi*-5-*epi*-valiolone 7-phosphate = 5-*epi*-valiolone 7-phosphate
Other name(s): AcbO
Systematic name: 2-*epi*-5-*epi*-valiolone-7-phosphate 2-epimerase
Comments: The enzyme, isolated from the bacterium *Actinoplanes* sp. SE 50/110, is involved in the biosynthesis of the α-glucosidase inhibitor acarbose.
References: [716]

[EC 5.1.3.35 created 2015]

EC 5.1.3.36
Accepted name: heparosan-glucuronate 5-epimerase
Reaction: [heparosan]-D-glucuronate = [acharan]-L-iduronate
Other name(s): HG-5epi
Systematic name: [heparosan]-D-glucuronate 5-epimerase
Comments: The enzyme, characterized from the giant African snail *Achatina fulica*, participates in the biosynthetic pathway of acharan sulfate. Unlike EC 5.1.3.17, heparosan-*N*-sulfate-glucuronate 5-epimerase, it shows no activity with D-glucuronate residues in heparosan-*N*-sulfate.
References: [428]

[EC 5.1.3.36 created 2015]

EC 5.1.3.37
Accepted name: mannuronan 5-epimerase
Reaction: [mannuronan]-β-D-mannuronate = [alginate]-α-L-guluronate
Other name(s): *algG* (gene name); alginate epimerase; C^5-mannuronan epimerase; mannuronan C-5-epimerase
Systematic name: [mannuronan]-β-D-mannuronate 5-epimerase
Comments: The enzyme epimerizes the C-5 bond in some β-D-mannuronate residues in mannuronan, converting them to α-L-guluronate residues, and thus modifying the mannuronan into alginate. It is found in brown algae and alginate-producing bacterial species from the *Pseudomonas* and *Azotobacter* genera.
References: [175, 432, 465, 273, 146, 672]

[EC 5.1.3.37 created 2015]

EC 5.1.3.38
Accepted name: D-erythrulose 1-phosphate 3-epimerase
Reaction: D-erythrulose 1-phosphate = L-erythrulose 1-phosphate
Other name(s): *eryC* (gene name)
Systematic name: D-erythrulose-1-phosphate 3-epimerase
Comments: The enzyme, characterized from the pathogenic bacterium *Brucella abortus*, which causes brucellosis in livestock, participates in erythritol catabolism.
References: [38]

[EC 5.1.3.38 created 2016]

[5.1.3.39 Deleted entry. L-erythrulose 4-phosphate epimerase. The activity has been shown not to take place.]

[EC 5.1.3.39 created 2016, deleted 2018]

EC 5.1.3.40

Accepted name: D-tagatose 6-phosphate 4-epimerase
Reaction: D-tagatose 6-phosphate = D-fructose 6-phosphate
Systematic name: D-tagatose 6-phosphate 4-epimerase
Comments: The enzyme from *Agrobacterium fabrum* C58 is part of D-altritol and galactitol degradation pathways.
References: [661]

[EC 5.1.3.40 created 2017]

EC 5.1.3.41

Accepted name: fructoselysine 3-epimerase
Reaction: N^6-(D-fructosyl)-L-lysine = N^6-(D-psicosyl)-L-lysine
Other name(s): *frlC* (gene name)
Systematic name: D-fructosyl-L-lysine 3-epimerase
Comments: The enzyme, characterized from the bacterium *Escherichia coli*, is involved in the catabolism of fructoseamines, amino acid sugar complexes that are formed non-enzymically.
References: [660]

[EC 5.1.3.41 created 2017]

EC 5.1.3.42

Accepted name: D-glucosamine-6-phosphate 4-epimerase
Reaction: D-glucosamine 6-phosphate = D-galactosamine 6-phosphate
Other name(s): ST2245 (locus name)
Systematic name: D-glucosamine 6-phosphate 4-epimerase
Comments: The enzyme, characterized from the archaeon *Sulfolobus tokodaii*, participates in a pathway for the biosynthesis of UDP-*N*-acetyl-α-D-galactosamine.
References: [122]

[EC 5.1.3.42 created 2018]

EC 5.1.3.43

Accepted name: sulfoquinovose mutarotase
Reaction: 6-sulfo-α-D-quinovose = 6-sulfo-β-D-quinovose
Systematic name: 6-sulfo-D-quinovose 1-epimerase
Comments: The enzyme is found in bacteria that possess sulfoglycolytic pathways. The enzyme can also act on other aldohexoses such as D-galactose, D-glucose, D-glucose-6-phosphate, and D-glucuronate, but with lower efficiency. Does not act on D-mannose.
References: [2]

[EC 5.1.3.43 created 2019]

EC 5.1.3.44

Accepted name: mannose 2-epimerase
Reaction: β-D-mannopyranose = β-D-glucopyranose
Systematic name: β-D-mannopyranose 2-epimerase

Comments: The enzyme, characterized from multiple bacterial species, catalyses the interconversion between β-D-glucopyranose and β-D-mannopyranose through proton abstraction-addition at the C_2 position.
References: [533]

[EC 5.1.3.44 created 2020]

EC 5.1.99 Acting on other compounds

EC 5.1.99.1
Accepted name: methylmalonyl-CoA epimerase
Reaction: (*R*)-methylmalonyl-CoA = (*S*)-methylmalonyl-CoA
Other name(s): methylmalonyl-CoA racemase; methylmalonyl coenzyme A racemase; DL-methylmalonyl-CoA racemase; 2-methyl-3-oxopropanoyl-CoA 2-epimerase [incorrect]
Systematic name: methylmalonyl-CoA 2-epimerase
References: [411, 474]

[EC 5.1.99.1 created 1965, modified 1981]

EC 5.1.99.2
Accepted name: 16-hydroxysteroid epimerase
Reaction: 16α-hydroxysteroid = 16β-hydroxysteroid
Systematic name: 16-hydroxysteroid 16-epimerase
References: [124]

[EC 5.1.99.2 created 1972]

EC 5.1.99.3
Accepted name: allantoin racemase
Reaction: (*S*)(+)-allantoin = (*R*)(-)-allantoin
Systematic name: allantoin racemase
References: [639]

[EC 5.1.99.3 created 1976]

EC 5.1.99.4
Accepted name: α-methylacyl-CoA racemase
Reaction: (2*S*)-2-methylacyl-CoA = (2*R*)-2-methylacyl-CoA
Systematic name: 2-methylacyl-CoA 2-epimerase
Comments: α-methyl-branched acyl-CoA derivatives with chain lengths of more than C_{10} are substrates. Also active towards some aromatic compounds (e.g. ibuprofen) and bile acid intermediates, such as trihydroxycoprostanoyl-CoA. Not active towards free acids
References: [544]

[EC 5.1.99.4 created 1999]

EC 5.1.99.5
Accepted name: hydantoin racemase
Reaction: D-5-monosubstituted hydantoin = L-5-monosubstituted hydantoin
Other name(s): 5′-monosubstituted-hydantoin racemase; HyuA; HyuE
Systematic name: D-5-monosubstituted-hydantoin racemase

Comments: This enzyme, along with *N*-carbamoylase (EC 3.5.1.77 and EC 3.5.1.87) and hydantoinase, forms part of the reaction cascade known as the "hydantoinase process", which allows the total conversion of D,L-5-monosubstituted hydantoins into optically pure D- or L-amino acids [18]. The enzyme from *Pseudomonas* sp. (HyuE) has a preference for hydantoins with aliphatic substituents, e.g. D- and L-5-[2-(methylsulfanyl)ethyl]hydantoin, whereas that from *Arthrobacter aurescens* shows highest activity with arylalkyl substituents, especially 5-benzylhydantoin, at the 5-position [662]. In the enzyme from *Sinorhizobium meliloti*, Cys^{76} is responsible for recognition and proton retrieval of D-isomers, while Cys^{181} is responsible for L-isomer recognition and racemization [402].
References: [651, 662, 404, 403, 602, 402, 18]

[EC 5.1.99.5 created 2008]

EC 5.1.99.6
Accepted name: NAD(P)H-hydrate epimerase
Reaction: (1) (6*R*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine dinucleotide = (6*S*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine dinucleotide
(2) (6*R*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine dinucleotide phosphate = (6*S*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine dinucleotide phosphate
Other name(s): NAD(P)HX epimerase
Systematic name: (6*R*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine dinucleotide 6-epimerase
Comments: The enzyme can use either (*R*)-NADH-hydrate or (*R*)-NADPH-hydrate as a substrate. Its physiological role is to convert the (*R*) forms to the (*S*) forms, which could then be restored to active dinucleotides by EC 4.2.1.93, ATP-dependent NAD(P)H-hydrate dehydratase.
References: [393]

[EC 5.1.99.6 created 2012]

EC 5.1.99.7
Accepted name: dihydroneopterin triphosphate 2′-epimerase
Reaction: 7,8-dihydroneopterin 3′-triphosphate = 7,8-dihydromonapterin 3′-triphosphate
Other name(s): D-*erythro*-7,8-dihydroneopterin triphosphate epimerase; *folX* (gene name)
Systematic name: 7,8-dihydroneopterin 3′-triphosphate 2′-epimerase
Comments: The enzyme, found in gammaproteobacteria, has almost no activity with 7,8-dihydroneopterin [224].
References: [11, 224]

[EC 5.1.99.7 created 2015]

EC 5.1.99.8
Accepted name: 7,8-dihydroneopterin epimerase
Reaction: 7,8-dihydroneopterin = 7,8-dihydromonapterin
Systematic name: 7,8-dihydroneopterin 2′-epimerase
Comments: The enzyme, which has been characterized in bacteria and plants, also has the activity of EC 4.1.2.25, dihydroneopterin aldolase. The enzyme from the bacterium *Mycobacterium tuberculosis* has an additional oxygenase function (EC 1.13.11.81, 7,8-dihydroneopterin oxygenase) [60].
References: [224, 202, 121, 60]

[EC 5.1.99.8 created 2015]

EC 5.2 *cis-trans*-Isomerases

This subclass contains a single sub-subclass for enzymes that rearrange the geometry at double bonds (*cis-trans* isomerases; EC 5.2.1).

EC 5.2.1 *cis-trans* Isomerases (only sub-subclass identified to date)

EC 5.2.1.1
Accepted name: maleate isomerase
Reaction: maleate = fumarate
Systematic name: maleate *cis-trans*-isomerase
References: [49]

[EC 5.2.1.1 created 1961]

EC 5.2.1.2
Accepted name: maleylacetoacetate isomerase
Reaction: 4-maleylacetoacetate = 4-fumarylacetoacetate
Other name(s): maleylacetoacetic isomerase; maleylacetone isomerase; maleylacetone *cis-trans*-isomerase
Systematic name: 4-maleylacetoacetate *cis-trans*-isomerase
Comments: Also acts on maleylpyruvate.
References: [150, 347, 550]

[EC 5.2.1.2 created 1961]

[5.2.1.3 Deleted entry. retinal isomerase. Now known to be catalysed by a pathway involving EC 1.1.1.300, NADP-retinol dehydrogenase; EC 2.3.1.135, phosphatidylcholine—retinol O-acyltransferase; EC 3.1.1.64, retinoid isomerohydrolase; and EC 1.1.1.315, 11-cis-retinol dehydrogenase.]

[EC 5.2.1.3 created 1961, modified 1976, deleted 2011]

EC 5.2.1.4
Accepted name: maleylpyruvate isomerase
Reaction: 3-maleylpyruvate = 3-fumarylpyruvate
Systematic name: 3-maleylpyruvate *cis-trans*-isomerase
References: [347]

[EC 5.2.1.4 created 1965]

EC 5.2.1.5
Accepted name: linoleate isomerase
Reaction: 9-*cis*,12-*cis*-octadecadienoate = 9-*cis*,11-*trans*-octadecadienoate
Other name(s): linoleic acid isomerase
Systematic name: linoleate Δ^{12}-*cis*-Δ^{11}-*trans*-isomerase
References: [311]

[EC 5.2.1.5 created 1972]

EC 5.2.1.6
Accepted name: furylfuramide isomerase
Reaction: (*E*)-2-(2-furyl)-3-(5-nitro-2-furyl)acrylamide = (*Z*)-2-(2-furyl)-3-(5-nitro-2-furyl)acrylamide
Systematic name: 2-(2-furyl)-3-(5-nitro-2-furyl)acrylamide *cis-trans*-isomerase
Comments: Requires NADH.
References: [622]

[EC 5.2.1.6 created 1978]

[5.2.1.7 Transferred entry. retinol isomerase. Transferred to EC 3.1.1.64, retinoid isomerohydrolase.]

[EC 5.2.1.7 created 1989, deleted 2011]

EC 5.2.1.8

Accepted name: peptidylprolyl isomerase
Reaction: peptidylproline (ω=180) = peptidylproline (ω=0)
Other name(s): PPIase; cyclophilin [misleading, see comments]; peptide bond isomerase; peptidyl-prolyl *cis-trans* isomerase
Systematic name: peptidylproline *cis-trans*-isomerase
Comments: The first type of this enzyme found [170] proved to be the protein cyclophilin, which binds the immunosuppressant cyclosporin A. Other distinct families of the enzyme exist, one being FK-506 binding proteins (FKBP) and another that includes parvulin from *Escherichia coli*. The three families are structurally unrelated and can be distinguished by being inhibited by cyclosporin A, FK-506 and 5-hydroxy-1,4-naphthoquinone, respectively.
References: [170, 171, 172, 603, 235, 169, 220, 153]

[EC 5.2.1.8 created 1989, modified 2002]

EC 5.2.1.9

Accepted name: farnesol 2-isomerase
Reaction: (2*E*,6*E*)-farnesol = (2*Z*,6*E*)-farnesol
Other name(s): farnesol isomerase
Systematic name: (2*E*,6*E*)-farnesol 2-*cis-trans*-isomerase
References: [20]

[EC 5.2.1.9 created 1989]

EC 5.2.1.10

Accepted name: 2-chloro-4-carboxymethylenebut-2-en-1,4-olide isomerase
Reaction: *cis*-2-chloro-4-carboxymethylenebut-2-en-1,4-olide = *trans*-2-chloro-4-carboxymethylenebut-2-en-1,4-olide
Other name(s): 2-chlorocarboxymethylenebutenolide isomerase; chlorodienelactone isomerase
Systematic name: 2-chloro-4-carboxymethylenebut-2-en-1,4-olide *cis-trans*-isomerase
References: [546]

[EC 5.2.1.10 created 1992]

[5.2.1.11 Deleted entry. 4-hydroxyphenylacetaldehyde-oxime isomerase. The existence of this enzyme has been called into question by one of the authors of the reference cited]

[EC 5.2.1.11 created 1992, deleted 2005]

EC 5.2.1.12

Accepted name: ζ-carotene isomerase
Reaction: 9,15,9′-*tricis*-ζ-carotene = 9,9′-*dicis*-ζ-carotene
Other name(s): Z-ISO; 15-*cis*-ζ-carotene isomerase
Systematic name: 9,15,9′-*tricis*-ζ-carotene *cis-trans*-isomerase
Comments: The enzyme catalyses the *cis-trans* isomerization of the 15-15′ carbon-carbon double bond in 9,15,9′-*tricis*-ζ-carotene, which is required for biosynthesis of all plant carotenoids. Requires heme *b*.
References: [95, 362, 50]

[EC 5.2.1.12 created 2011]

EC 5.2.1.13

Accepted name: prolycopene isomerase
Reaction: 7,9,7′,9′-*tetracis*-lycopene = *all-trans*-lycopene
Other name(s): CRTISO; carotene *cis-trans* isomerase; ZEBRA2 (gene name); carotene isomerase; carotenoid isomerase
Systematic name: 7,9,7′,9′-*tetracis*-lycopene *cis-trans*-isomerase
Comments: Requires $FADH_2$ [706]. The enzyme is involved in carotenoid biosynthesis.
References: [706, 363, 262, 81]

[EC 5.2.1.13 created 2011]

EC 5.2.1.14

Accepted name: β-carotene isomerase
Reaction: *all-trans*-β-carotene = 9-*cis*-β-carotene
Other name(s): DWARF27 (gene name)
Systematic name: β-carotene 9-*cis*-*all-trans* isomerase
Comments: The enzyme participates in a pathway leading to biosynthesis of strigolactones, plant hormones involved in promotion of symbiotic associations known as arbuscular mycorrhiza.
References: [371, 14]

[EC 5.2.1.14 created 2012]

EC 5.3 Intramolecular oxidoreductases

These enzymes bring about the oxidation of one part of a molecule with a corresponding reduction of another part. They include the enzymes interconverting, in the sugar series, aldoses and ketoses, and related compounds (sugar isomerases, EC 5.3.1), enzymes catalysing a keto-enol equilibrium (tautomerases, EC 5.3.2), enzymes shifting a carbon-carbon double bond from one position to another (EC 5.3.3), enzymes transposing S-S bonds (EC 5.3.4), and a group of miscellaneous enzymes (EC 5.3.99).

EC 5.3.1 Interconverting aldoses and ketoses, and related compounds

EC 5.3.1.1

Accepted name: triose-phosphate isomerase
Reaction: D-glyceraldehyde 3-phosphate = glycerone phosphate
Other name(s): phosphotriose isomerase; triose phosphoisomerase; triose phosphate mutase; D-glyceraldehyde-3-phosphate ketol-isomerase
Systematic name: D-glyceraldehyde-3-phosphate aldose-ketose-isomerase
References: [424, 425]

[EC 5.3.1.1 created 1961]

[5.3.1.2 Deleted entry. erythrose isomerase]

[EC 5.3.1.2 created 1961, deleted 1976]

EC 5.3.1.3

Accepted name: D-arabinose isomerase
Reaction: D-arabinose = D-ribulose
Other name(s): D-arabinose(L-fucose) isomerase; L-fucose isomerase; D-arabinose ketol-isomerase; arabinose isomerase (misleading)
Systematic name: D-arabinose aldose-ketose-isomerase

Comments: Requires a divalent metal ion (the enzyme from the bacterium *Escherichia coli* prefers Mn^{2+}). The enzyme binds the closed form of the sugar and catalyses ring opening to generate a form of open-chain conformation that facilitates the isomerization reaction, which proceeds via an ene-diol mechanism [547]. The enzyme catalyses the aldose-ketose isomerization of several sugars. Most enzymes also catalyse the reaction of EC 5.3.1.25, L-fucose isomerase [547]. The enzyme from the bacterium *Falsibacillus pallidus* also converts D-altrose to D-psicose [605]. *cf.* EC 5.3.1.4, L-arabinose isomerase.
References: [98, 204, 547, 605]

[EC 5.3.1.3 created 1961, modified 2013]

EC 5.3.1.4
Accepted name: L-arabinose isomerase
Reaction: β-L-arabinopyranose = L-ribulose
Other name(s): L-arabinose ketol-isomerase; *araA* (gene name)
Systematic name: β-L-arabinopyranose aldose-ketose-isomerase
Comments: Requires a divalent metal ion (the enzyme from the bacterium *Escherichia coli* prefers Mn^{2+}) [484]. The enzyme binds β-L-arabinopyranose [545] and catalyses ring opening to generate a form of open-chain conformation that facilitates the isomerization reaction, which proceeds via an ene-diol mechanism [36]. The enzyme can also convert α-D-galactose to D-tagatose with lower efficiency [89].
References: [231, 484, 452, 545, 89, 36, 392]

[EC 5.3.1.4 created 1961, modified 2022]

EC 5.3.1.5
Accepted name: xylose isomerase
Reaction: α-D-xylopyranose = α-D-xylulofuranose
Other name(s): D-xylose isomerase; D-xylose ketoisomerase; D-xylose ketol-isomerase; D-xylose aldose-ketose-isomerase
Systematic name: α-D-xylopyranose aldose-ketose-isomerase
Comments: Contains two divalent metal ions, preferably magnesium, located at different metal-binding sites within the active site. The enzyme catalyses the interconversion of aldose and ketose sugars with broad substrate specificity. The enzyme binds the closed form of its sugar substrate (in the case of xylose and glucose, only the α anomer [545]) and catalyses ring opening to generate a form of open-chain conformation that is coordinated to one of the metal sites. Isomerization proceeds via a hydride-shift mechanism.
References: [241, 573, 692, 545, 79, 99, 656, 17]

[EC 5.3.1.5 created 1961 (EC 5.3.1.18 created 1972, part incorporated 1978), modified 2022]

EC 5.3.1.6
Accepted name: ribose-5-phosphate isomerase
Reaction: D-ribose 5-phosphate = D-ribulose 5-phosphate
Other name(s): phosphopentosisomerase; phosphoriboisomerase; ribose phosphate isomerase; 5-phosphoribose isomerase; D-ribose 5-phosphate isomerase; D-ribose-5-phosphate ketol-isomerase
Systematic name: D-ribose-5-phosphate aldose-ketose-isomerase
Comments: Also acts on D-ribose 5-diphosphate and D-ribose 5-triphosphate.
References: [139, 243, 256]

[EC 5.3.1.6 created 1961]

EC 5.3.1.7
Accepted name: mannose isomerase

Reaction: D-mannose = D-fructose
Other name(s): D-mannose isomerase; D-mannose ketol-isomerase
Systematic name: D-mannose aldose-ketose-isomerase
Comments: Also acts on D-lyxose and D-rhamnose.
References: [476]

[EC 5.3.1.7 created 1961]

EC 5.3.1.8
Accepted name: mannose-6-phosphate isomerase
Reaction: D-mannose 6-phosphate = D-fructose 6-phosphate
Other name(s): phosphomannose isomerase; phosphohexomutase; phosphohexoisomerase; mannose phosphate isomerase; phosphomannoisomerase; D-mannose-6-phosphate ketol-isomerase
Systematic name: D-mannose-6-phosphate aldose-ketose-isomerase
Comments: A zinc protein.
References: [73, 203, 572]

[EC 5.3.1.8 created 1961, modified 1976]

EC 5.3.1.9
Accepted name: glucose-6-phosphate isomerase
Reaction: α-D-glucose 6-phosphate = β-D-fructofuranose 6-phosphate
Other name(s): phosphohexose isomerase; phosphohexomutase; oxoisomerase; hexosephosphate isomerase; phosphosaccharomutase; phosphoglucoisomerase; phosphohexoisomerase; phosphoglucose isomerase; glucose phosphate isomerase; hexose phosphate isomerase; D-glucose-6-phosphate ketol-isomerase
Systematic name: α-D-glucose-6-phosphate aldose-ketose-isomerase (configuration-inverting)
Comments: The enzyme from yeast catalyses the reversible conversion specifically between the α-D-glucose 6-phosphate and β-D-fructofuranose 6-phosphate. The enzyme also catalyses the anomerization of both D-hexose 6-phosphates [663].
References: [502, 627, 459, 35, 460, 451, 663]

[EC 5.3.1.9 created 1961, modified 1976 (EC 5.3.1.18 created part 1972, incorporated 1978), modified 2021]

[5.3.1.10 Transferred entry. glucosamine-6-phosphate isomerase. Now EC 3.5.99.6, glucosamine-6-phosphate deaminase]

[EC 5.3.1.10 created 1961, deleted 2000]

[5.3.1.11 Deleted entry. acetylglucosaminephosphate isomerase]

[EC 5.3.1.11 created 1961, deleted 1978]

EC 5.3.1.12
Accepted name: glucuronate isomerase
Reaction: D-glucuronate = D-fructuronate
Other name(s): uronic isomerase; uronate isomerase; D-glucuronate isomerase; uronic acid isomerase; D-glucuronate ketol-isomerase
Systematic name: D-glucuronate aldose-ketose-isomerase
Comments: Also converts D-galacturonate to D-tagaturonate.
References: [33, 312]

[EC 5.3.1.12 created 1961]

EC 5.3.1.13
Accepted name: arabinose-5-phosphate isomerase

Reaction: D-arabinose 5-phosphate = D-ribulose 5-phosphate
Other name(s): *kdsD* (gene name); *gutQ* (gene name); arabinose phosphate isomerase; phosphoarabinoisomerase; D-arabinose-5-phosphate ketol-isomerase
Systematic name: D-arabinose-5-phosphate aldose-ketose-isomerase
Comments: The enzyme is involved in the pathway for synthesis of 3-deoxy-D-*manno*-octulosonate (Kdo), a component of bacterial lipopolysaccharides and plant call walls.
References: [643, 370, 421, 201, 96]

[EC 5.3.1.13 created 1965]

EC 5.3.1.14
Accepted name: L-rhamnose isomerase
Reaction: L-rhamnopyranose = L-rhamnulose
Other name(s): rhamnose isomerase; L-rhamnose ketol-isomerase
Systematic name: L-rhamnose aldose-ketose-isomerase
Comments: Contains two divalent metal ions located at different metal-binding sites within the active site. The enzyme binds the closed ring form of the substrate and catalyses ring opening to generate a form of open-chain conformation that is coordinated to one of the metal sites. Isomerization proceeds via a hydride-shift mechanism. While the enzyme from the bacterium *Escherichia coli* is specific for L-rhamnose, the enzyme from the bacterium *Pseudomonas stutzeri* has broad substrate specificity and catalyses the interconversion of L-mannose and L-fructose, L-lyxose and L-xylulose, D-ribose and D-ribulose, and D-allose and D-psicose [351].
References: [144, 351, 333, 701]

[EC 5.3.1.14 created 1965]

EC 5.3.1.15
Accepted name: D-lyxose ketol-isomerase
Reaction: D-lyxose = D-xylulose
Other name(s): D-lyxose isomerase; D-lyxose ketol-isomerase
Systematic name: D-lyxose aldose-ketose-isomerase
References: [22]

[EC 5.3.1.15 created 1972]

EC 5.3.1.16
Accepted name: 1-(5-phosphoribosyl)-5-[(5-phosphoribosylamino)methylideneamino]imidazole-4-carboxamide isomerase
Reaction: 1-(5-phospho-β-D-ribosyl)-5-[(5-phospho-β-D-ribosylamino)methylideneamino]imidazole-4-carboxamide = 5-[(5-phospho-1-deoxy-D-ribulos-1-ylamino)methylideneamino]-1-(5-phospho-β-D-ribosyl)imidazole-4-carboxamide
Other name(s): *N*-(5′-phospho-D-ribosylformimino)-5-amino-1-(5″-phosphoribosyl)-4-imidazolecarboxamide isomerase; phosphoribosylformiminoaminophosphoribosylimidazolecarboxamide isomerase; *N*-(phosphoribosylformimino) aminophosphoribosylimidazolecarboxamide isomerase; 1-(5-phosphoribosyl)-5-[(5-phosphoribosylamino)methylideneamino]imidazole-4-carboxamide ketol-isomerase; 1-(5-phosphoribosyl)-5-[(5-phosphoribosylamino)methylideneamino]imidazole-4-carboxamide aldose-ketose-isomerase
Systematic name: 1-(5-phospho-β-D-ribosyl)-5-[(5-phospho-β-D-ribosylamino)methylideneamino]imidazole-4-carboxamide aldose-ketose-isomerase
Comments: Involved in histidine biosynthesis.
References: [395]

[EC 5.3.1.16 created 1972, modified 2000]

EC 5.3.1.17

Accepted name: 5-dehydro-4-deoxy-D-glucuronate isomerase
Reaction: 5-dehydro-4-deoxy-D-glucuronate = 3-deoxy-D-*glycero*-2,5-hexodiulosonate
Other name(s): 4-deoxy-L-*threo*-5-hexulose uronate isomerase; 4-deoxy-L-*threo*-5-hexosulose-uronate ketol-isomerase; *kduI* (gene name)
Systematic name: 5-dehydro-4-deoxy-D-glucuronate aldose-ketose-isomerase
Comments: The enzyme is involved in the degradation of polygalacturonate, a later stage in the degradation of pectin by many microorganisms.
References: [497, 100, 147, 116]

[EC 5.3.1.17 created 1972, modified 2012]

[5.3.1.18 Deleted entry. glucose isomerase. Reaction is due to EC 5.3.1.9 glucose-6-phosphate isomerase, in the presence of arsenate, or EC 5.3.1.5 xylose isomerase]

[EC 5.3.1.18 created 1972, deleted 1978]

[5.3.1.19 Transferred entry. glucosaminephosphate isomerase. Now EC 2.6.1.16, glutamine—fructose-6-phosphate transaminase (isomerizing)]

[EC 5.3.1.19 created 1972, deleted 1984]

EC 5.3.1.20

Accepted name: ribose isomerase
Reaction: D-ribose = D-ribulose
Other name(s): D-ribose isomerase; D-ribose ketol-isomerase
Systematic name: D-ribose aldose-ketose-isomerase
Comments: Also acts on L-lyxose and L-rhamnose.
References: [270]

[EC 5.3.1.20 created 1978]

EC 5.3.1.21

Accepted name: corticosteroid side-chain-isomerase
Reaction: 11-deoxycorticosterone = 20-hydroxy-3-oxopregn-4-en-21-al
Systematic name: 11-deoxycorticosterone aldose-ketose-isomerase
Comments: An epimerization at C-20 and C-21 is probably catalysed by the same enzyme.
References: [400, 430]

[EC 5.3.1.21 created 1983]

EC 5.3.1.22

Accepted name: hydroxypyruvate isomerase
Reaction: hydroxypyruvate = 2-hydroxy-3-oxopropanoate
Systematic name: hydroxypyruvate aldose-ketose-isomerase
References: [667]

[EC 5.3.1.22 created 1983]

EC 5.3.1.23

Accepted name: *S*-methyl-5-thioribose-1-phosphate isomerase
Reaction: *S*-methyl-5-thio-α-D-ribose 1-phosphate = *S*-methyl-5-thio-D-ribulose 1-phosphate

Other name(s): methylthioribose 1-phosphate isomerase; 1-PMTR isomerase; 5-methylthio-5-deoxy-D-ribose-1-phosphate ketol-isomerase; *S*-methyl-5-thio-5-deoxy-D-ribose-1-phosphate ketol-isomerase; *S*-methyl-5-thio-5-deoxy-D-ribose-1-phosphate aldose-ketose-isomerase; 1-phospho-5′-*S*-methylthioribose isomerase; *S*-methyl-5-thio-D-ribose-1-phosphate aldose-ketose-isomerase
Systematic name: *S*-methyl-5-thio-α-D-ribose-1-phosphate aldose-ketose-isomerase
References: [190, 625, 182]

[EC 5.3.1.23 created 1989]

EC 5.3.1.24
Accepted name: phosphoribosylanthranilate isomerase
Reaction: *N*-(5-phospho-β-D-ribosyl)anthranilate = 1-(2-carboxyphenylamino)-1-deoxy-D-ribulose 5-phosphate
Other name(s): PRA isomerase; PRAI; IGPS:PRAI (indole-3-glycerol-phosphate synthetase/*N*-5′-phosphoribosylanthranilate isomerase complex); *N*-(5-phospho-β-D-ribosyl)anthranilate ketol-isomerase
Systematic name: *N*-(5-phospho-β-D-ribosyl)anthranilate aldose-ketose-isomerase
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 4.1.1.48 (indole-3-glycerol-phosphate synthase), EC 4.1.3.27 (anthranilate synthase) and EC 4.2.1.20 (tryptophan synthase)].
References: [67, 107, 258]

[EC 5.3.1.24 created 1990]

EC 5.3.1.25
Accepted name: L-fucose isomerase
Reaction: L-fucopyranose = L-fuculose
Systematic name: L-fucose aldose-ketose-isomerase
Comments: Requires a divalent metal ion (the enzyme from the bacterium *Escherichia coli* prefers Mn^{2+}). The enzyme binds the closed form of the sugar and catalyses ring opening to generate a form of open-chain conformation that facilitates the isomerization reaction, which proceeds via an ene-diol mechanism [547]. The enzyme from *Escherichia coli* can also convert D-arabinose to D-ribulose [204]. The enzyme from the thermophilic bacterium *Caldicellulosiruptor saccharolyticus* also converts D-altrose to D-psicose and L-galactose to L-tagatose [285].
References: [204, 383, 547, 285]

[EC 5.3.1.25 created 1999]

EC 5.3.1.26
Accepted name: galactose-6-phosphate isomerase
Reaction: D-galactose 6-phosphate = D-tagatose 6-phosphate
Systematic name: D-galactose-6-phosphate aldose-ketose-isomerase
Comments: Involved in the tagatose 6-phosphate pathway of lactose catabolism in bacteria.
References: [644, 524]

[EC 5.3.1.26 created 1999]

EC 5.3.1.27
Accepted name: 6-phospho-3-hexuloisomerase
Reaction: D-*arabino*-hex-3-ulose 6-phosphate = D-fructose 6-phosphate
Other name(s): 3-hexulose-6-phosphate isomerase; phospho-3-hexuloisomerase; PHI; 6-phospho-3-hexulose isomerase; YckF
Systematic name: D-*arabino*-hex-3-ulose-6-phosphate isomerase

Comments: This enzyme, along with EC 4.1.2.43, 3-hexulose-6-phosphate synthase, 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 [165]. The hyperthermophilic and anaerobic archaeon *Pyrococcus horikoshii* OT3 constitutively produces a bifunctional enzyme that sequentially catalyses the reactions of EC 4.1.2.43 (3-hexulose-6-phosphate synthase) and this enzyme [469].
References: [165, 713, 298, 469, 401, 610]

[EC 5.3.1.27 created 2008]

EC 5.3.1.28
Accepted name: D-sedoheptulose-7-phosphate isomerase
Reaction: D-sedoheptulose 7-phosphate = D-*glycero*-D-*manno*-heptose 7-phosphate
Other name(s): sedoheptulose-7-phosphate isomerase; phosphoheptose isomerase; *gmhA* (gene name); *lpcA* (gene name)
Systematic name: D-*glycero*-D-*manno*-heptose 7-phosphate aldose-ketose-isomerase
Comments: In Gram-negative bacteria the enzyme is involved in biosynthesis of ADP-L-*glycero*-β-D-*manno*-heptose, which is utilized for assembly of the lipopolysaccharide inner core. In Gram-positive bacteria the enzyme is involved in biosynthesis of GDP-D-*glycero*-α-D-*manno*-heptose, which is required for assembly of S-layer glycoprotein.
References: [324, 323, 638, 316, 612]

[EC 5.3.1.28 created 2010]

EC 5.3.1.29
Accepted name: ribose-1,5-bisphosphate isomerase
Reaction: α-D-ribose 1,5-bisphosphate = D-ribulose 1,5-bisphosphate
Other name(s): R15P isomerase; ribulose 1,5-bisphosphate synthase; RuBP synthase
Systematic name: α-D-ribose 1,5-bisphosphate aldose-ketose-isomerase
Comments: This archaeal enzyme is involved in AMP metabolism and CO_2 fixation through type III RubisCO enzymes. The enzyme is activated by cAMP [28].
References: [537, 28, 453]

[EC 5.3.1.29 created 2013]

EC 5.3.1.30
Accepted name: 5-deoxy-glucuronate isomerase
Reaction: 5-deoxy-D-glucuronate = 5-dehydro-2-deoxy-D-gluconate
Other name(s): 5DG isomerase; IolB
Systematic name: 5-deoxy-D-glucuronate aldose-ketose-isomerase
Comments: The enzyme, found in the bacterium *Bacillus subtilis*, is part of a *myo*-inositol degradation pathway leading to acetyl-CoA.
References: [703]

[EC 5.3.1.30 created 2014]

EC 5.3.1.31
Accepted name: sulfoquinovose isomerase
Reaction: (1) β-sulfoquinovose = 6-deoxy-6-sulfo-D-fructose
(2) β-sulfoquinovose = 6-sulfo-D-rhamnose
Other name(s): *yihS* (gene name)
Systematic name: 6-deoxy-6-sulfo-β-D-glucopyranose aldose-ketose-isomerase

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: [133, 552]

[EC 5.3.1.31 created 2014, modified 2022]

EC 5.3.1.32
Accepted name: (4*S*)-4-hydroxy-5-phosphooxypentane-2,3-dione isomerase
Reaction: (2*S*)-2-hydroxy-3,4-dioxopentyl phosphate = 3-hydroxy-2,4-dioxopentyl phosphate
Other name(s): *lsrG* (gene name); phospho-AI-2 isomerase; (4*S*)-4-hydroxy-5-phosphonooxypentane-2,3-dione aldose-ketose-isomerase; (4*S*)-4-hydroxy-5-phosphonooxypentane-2,3-dione isomerase; (4*S*)-4-hydroxy-5-phosphooxypentane-2,3-dione aldose-ketose-isomerase
Systematic name: (2*S*)-2-hydroxy-3,4-dioxopentyl phosphate aldose-ketose-isomerase
Comments: The enzyme participates in a degradation pathway of the bacterial quorum-sensing autoinducer molecule AI-2.
References: [685, 397]

[EC 5.3.1.32 created 2015]

EC 5.3.1.33
Accepted name: L-erythrulose-1-phosphate isomerase
Reaction: L-erythrulose 1-phosphate = D-erythrulose 4-phosphate
Other name(s): *eryH* (gene name)
Systematic name: L-erythrulose-1-phosphate isomerase
Comments: The enzyme, characterized from the pathogenic bacterium *Brucella abortus*, which causes brucellosis in livestock, participates in erythritol catabolism.
References: [38]

[EC 5.3.1.33 created 2016]

EC 5.3.1.34
Accepted name: D-erythrulose 4-phosphate isomerase
Reaction: D-erythrulose-4-phosphate = D-erythrose 4-phosphate
Other name(s): *eryI* (gene name)
Systematic name: D-erythrulose-4-phosphate ketose-aldose isomerase
Comments: The enzyme, characterized from the pathogenic bacterium *Brucella abortus*, which causes brucellosis in livestock, participates in erythritol catabolism.
References: [38]

[EC 5.3.1.34 created 2016]

EC 5.3.1.35
Accepted name: 2-dehydrotetronate isomerase
Reaction: (1) 2-dehydro-L-erythronate = 3-dehydro-L-erythronate
(2) 2-dehydro-D-erythronate = 3-dehydro-D-erythronate
Other name(s): *otnI* (gene name)
Systematic name: 2-dehydrotetronate isomerase
Comments: The enzyme, characterized from bacteria, is involved in D-erythronate and L-threonate catabolism.
References: [723]

[EC 5.3.1.35 created 2017]

EC 5.3.1.36

Accepted name: D-apiose isomerase
Reaction: D-apiose = apulose
Other name(s): *apsI* (gene name)
Systematic name: D-apiose isomerase
Comments: The enzyme, characterized from several bacterial species, is involved in a catabolic pathway for D-apiose.
References: [80]

[EC 5.3.1.36 created 2020]

EC 5.3.1.37

Accepted name: 4-deoxy-4-sulfo-D-erythrose isomerase
Reaction: 4-deoxy-4-sulfo-D-erythrose = 4-deoxy-4-sulfo-D-erythrulose
Other name(s): *sqwI* (gene name)
Systematic name: 4-deoxy-4-sulfo-D-erythrose ketose-aldose isomerase
Comments: The enzyme, characterized from the bacterium *Clostridium* sp. MSTE9, is involved in a D-sulfoquinovose degradation pathway.
References: [373]

[EC 5.3.1.37 created 2022]

EC 5.3.2 Interconverting keto- and enol-groups

EC 5.3.2.1

Accepted name: phenylpyruvate tautomerase
Reaction: *keto*-phenylpyruvate = *enol*-phenylpyruvate
Other name(s): phenylpyruvic keto-enol isomerase
Systematic name: phenylpyruvate *keto—enol*-isomerase
Comments: Also acts on other arylpyruvates.
References: [59, 326, 327]

[EC 5.3.2.1 created 1961]

EC 5.3.2.2

Accepted name: oxaloacetate tautomerase
Reaction: *keto*-oxaloacetate = *enol*-oxaloacetate
Other name(s): oxalacetic keto-enol isomerase
Systematic name: oxaloacetate *keto—enol*-isomerase
References: [24]

[EC 5.3.2.2 created 1972]

EC 5.3.2.3

Accepted name: TDP-4-oxo-6-deoxy-α-D-glucose-3,4-oxoisomerase (dTDP-3-dehydro-6-deoxy-α-D-galactopyranose-forming)
Reaction: dTDP-4-dehydro-6-deoxy-α-D-glucopyranose = dTDP-3-dehydro-6-deoxy-α-D-galactopyranose
Other name(s): dTDP-6-deoxy-hex-4-ulose isomerase; TDP-6-deoxy-hex-4-ulose isomerase; FdtA
Systematic name: dTDP-4-dehydro-6-deoxy-α-D-glucopyranose:dTDP-3-dehydro-6-deoxy-α-D-galactopyranose isomerase

Comments: The enzyme is involved in the biosynthesis of dTDP-3-acetamido-3,6-dideoxy-α-D-galactose. Four moieties of α-D-rhamnose and two moities of 3-acetamido-3,6-dideoxy-α-D-galactose form the repeating unit of the glycan chain in the S-layer of the bacterium *Aneurinibacillus thermoaerophilus*.
References: [492, 130]

[EC 5.3.2.3 created 2011]

EC 5.3.2.4

Accepted name: TDP-4-oxo-6-deoxy-α-D-glucose-3,4-oxoisomerase (dTDP-3-dehydro-6-deoxy-α-D-glucopyranose-forming)
Reaction: dTDP-4-dehydro-6-deoxy-α-D-glucopyranose = dTDP-3-dehydro-6-deoxy-α-D-glucopyranose
Other name(s): TDP-4-keto-6-deoxy-D-glucose-3,4-ketoisomerase (ambiguous); Tyl1a; dTDP-4-keto-6-deoxy-D-glucose-3,4-ketoisomerase (ambiguous)
Systematic name: dTDP-4-dehydro-6-deoxy-α-D-glucopyranose:dTDP-3-dehydro-6-deoxy-α-D-glucopyranose isomerase
Comments: The enzyme is involved in biosynthesis of D-mycaminose.
References: [417]

[EC 5.3.2.4 created 2011]

EC 5.3.2.5

Accepted name: 2,3-diketo-5-methylthiopentyl-1-phosphate enolase
Reaction: 5-(methylsulfanyl)-2,3-dioxopentyl phosphate = 2-hydroxy-5-(methylsulfanyl)-3-oxopent-1-enyl phosphate
Other name(s): DK-MTP-1-*P* enolase; MtnW; YkrW; RuBisCO-like protein; RLP; 2,3-diketo-5-methylthiopentyl-1-phosphate *keto—enol*-isomerase
Systematic name: 5-(methylsulfanyl)-2,3-dioxopentyl phosphate *keto—enol*-isomerase
Comments: The enzyme participates in the methionine salvage pathway in *Bacillus subtilis* [31].In some species a single bifunctional enzyme, EC 3.1.3.77, acireductone synthase, catalyses both this reaction and EC 3.1.3.87, 2-hydroxy-3-keto-5-methylthiopentenyl-1-phosphate phosphatase [445].
References: [445, 31]

[EC 5.3.2.5 created 2012]

EC 5.3.2.6

Accepted name: 2-hydroxymuconate tautomerase
Reaction: (2*Z*,4*E*)-2-hydroxyhexa-2,4-dienedioate = (3*E*)-2-oxohex-3-enedioate
Other name(s): 4-oxalocrotonate tautomerase (misleading); 4-oxalocrotonate isomerase (misleading); *cnbG* (gene name); *praC* (gene name); *xylH* (gene name)
Systematic name: (2*Z*,4*E*)-2-hydroxyhexa-2,4-dienedioate *keto—enol* isomerase
Comments: Involved in the *meta*-cleavage pathway for the degradation of phenols, modified phenols and catechols. The enol form (2*Z*,4*E*)-2-hydroxyhexa-2,4-dienedioate is produced as part of this pathway and is converted to the keto form (3*E*)-2-oxohex-3-enedioate by the enzyme [295]. Another keto form, (4*E*)-2-oxohex-4-enedioate (4-oxalocrotonate), was originally thought to be produced by the enzyme [657, 658] but later shown to be produced non-enzymically [647].
References: [657, 658, 594, 587, 647, 295]

[EC 5.3.2.6 created 2012]

EC 5.3.2.7

Accepted name: ascopyrone tautomerase
Reaction: 1,5-anhydro-4-deoxy-D-*glycero*-hex-3-en-2-ulose = 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose

Other name(s): ascopyrone isomerase; ascopyrone intramolecular oxidoreductase; 1,5-anhydro-D-*glycero*-hex-3-en-2-ulose tautomerase; APM tautomerase; ascopyrone P tautomerase; APTM
Systematic name: 1,5-anhydro-4-deoxy-D-*glycero*-hex-3-en-2-ulose Δ^3-Δ^1-isomerase
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 [709, 708]. The other enzymes involved in this pathway are EC 4.2.1.110 (aldos-2-ulose dehydratase), EC 4.2.1.111 (1,5-anhydro-D-fructose dehydratase) and EC 4.2.2.13 [exo-(1→4)-α-D-glucan lyase]. Ascopyrone P is an anti-oxidant [708].
References: [709, 708]

[EC 5.3.2.7 created 2006 as EC 5.3.3.15, transferred 2012 to EC 5.3.2.7]

EC 5.3.2.8
Accepted name: 4-oxalomesaconate tautomerase
Reaction: (1*E*)-4-oxobut-1-ene-1,2,4-tricarboxylate = (1*E*,3*E*)-4-hydroxybuta-1,3-diene-1,2,4-tricarboxylate
Other name(s): GalD
Systematic name: 4-oxalomesaconate *keto—enol*-isomerase
Comments: This enzyme has been characterized from the bacterium *Pseudomonas putida* KT2440 and is involved in the degradation pathway of syringate and 3,4,5-trihydroxybenzoate. It catalyses the interconversion of two of the tautomers of 4-oxalomesaconate, a reaction that can also occur spontaneously.
References: [458]

[EC 5.3.2.8 created 2011 as EC 5.3.3.16, modified 2011, transferred 2012 to EC 5.3.2.8]

EC 5.3.3 Transposing C=C bonds

EC 5.3.3.1
Accepted name: steroid Δ-isomerase
Reaction: a 3-oxo-Δ^5-steroid = a 3-oxo-Δ^4-steroid
Other name(s): hydroxysteroid isomerase; steroid isomerase; Δ^5-ketosteroid isomerase; Δ^5(or Δ^4)-3-keto steroid isomerase; Δ^5-steroid isomerase; 3-oxosteroid isomerase; Δ^5-3-keto steroid isomerase; Δ^5-3-oxosteroid isomerase
Systematic name: 3-oxosteroid Δ^5-Δ^4-isomerase
Comments: This activity is catalysed by several distinct enzymes (*cf.* EC 1.1.3.6, cholesterol oxidase and EC 1.1.1.145, 3-hydroxy-5-steroid dehydrogenase).
References: [159, 301, 606, 387]

[EC 5.3.3.1 created 1961]

EC 5.3.3.2
Accepted name: isopentenyl-diphosphate Δ-isomerase
Reaction: 3-methylbut-3-en-1-yl diphosphate = prenyl diphosphate
Other name(s): isopentenylpyrophosphate Δ-isomerase; methylbutenylpyrophosphate isomerase; isopentenylpyrophosphate isomerase; isopentenyl-diphosphate Δ^3-Δ^2-isomerase
Systematic name: 3-methylbut-3-en-1-yl-diphosphate Δ^3-Δ^2-isomerase
Comments: The enzyme from *Streptomyces* sp. strain CL190 requires FMN and NAD(P)H as cofactors. Activity is reduced if FMN is replaced by FAD, but the enzyme becomes inactive when NAD(P)H is replaced by NAD^+ or $NADP^+$. That enzyme also requires Mg^{2+}, Mn^{2+} or Ca^{2+} for activity.
References: [292, 56, 8]

[EC 5.3.3.2 created 1961, modified 2002]

EC 5.3.3.3

Accepted name: vinylacetyl-CoA Δ-isomerase
Reaction: vinylacetyl-CoA = (*E*)-but-2-enoyl-CoA
Other name(s): vinylacetyl coenzyme A Δ-isomerase; vinylacetyl coenzyme A isomerase; Δ^3-*cis*-Δ^2-*trans*-enoyl-CoA isomerase
Systematic name: vinylacetyl-CoA Δ^3-Δ^2-isomerase
Comments: Also acts on 3-methyl-vinylacetyl-CoA.
References: [386, 520]

[EC 5.3.3.3 created 1961, modified 2011]

EC 5.3.3.4

Accepted name: muconolactone Δ-isomerase
Reaction: (+)-muconolactone = (4,5-dihydro-5-oxofuran-2-yl)-acetate
Other name(s): muconolactone isomerase; 5-oxo-4,5-dihydrofuran-2-acetate Δ^3-Δ^2-isomerase
Systematic name: (+)-muconolactone Δ^3-Δ^2-isomerase
References: [470, 472]

[EC 5.3.3.4 created 1961 as EC 3.1.1.16, part transferred 1972 to EC 5.3.3.4 rest to EC 5.3.3.4]

EC 5.3.3.5

Accepted name: cholestenol Δ-isomerase
Reaction: 5α-cholest-7-en-3β-ol = 5α-cholest-8-en-3β-ol
Systematic name: Δ^7-cholestenol Δ^7-Δ^8-isomerase
References: [666]

[EC 5.3.3.5 created 1972]

EC 5.3.3.6

Accepted name: methylitaconate Δ-isomerase
Reaction: methylitaconate = 2,3-dimethylmaleate
Other name(s): methylitaconate isomerase
Systematic name: methylitaconate Δ^2-Δ^3-isomerase
References: [343]

[EC 5.3.3.6 created 1972]

EC 5.3.3.7

Accepted name: aconitate Δ-isomerase
Reaction: *trans*-aconitate = *cis*-aconitate
Other name(s): aconitate isomerase
Systematic name: aconitate Δ^2-Δ^3-isomerase
Comments: *cis*-Aconitate is used to designate the isomer (*Z*)-prop-1-ene-1,2,3-tricarboxylate. This isomerization could take place either in a direct *cis-trans* interconversion or by an allylic rearrangement; the enzyme has been shown to catalyse the latter change.
References: [321, 320]

[EC 5.3.3.7 created 1972]

EC 5.3.3.8

Accepted name: Δ^3-Δ^2-enoyl-CoA isomerase
Reaction: (1) a (3*Z*)-alk-3-enoyl-CoA = a (2*E*)-alk-2-enoyl-CoA

(2) a (3*E*)-alk-3-enoyl-CoA = a (2*E*)-alk-2-enoyl-CoA

Other name(s): ECI (gene name); dodecenoyl-CoA isomerase; dodecenoyl-CoA Δ-isomerase; Δ^3-*cis*-Δ^2-*trans*-enoyl-CoA isomerase; acetylene-allene isomerase; dodecenoyl-CoA Δ^3-*cis*-Δ^2-*trans*-isomerase; dodecenoyl-CoA (3*Z*)-(2*E*)-isomerase

Systematic name: (3*Z*/3*E*)-alk-3-enoyl-CoA (2*E*)-isomerase

Comments: The enzyme participates in the β-oxidation of fatty acids with double bonds at an odd position. Processing of these substrates via the β-oxidation system results in intermediates with a *cis*- or *trans*-double bond at position C_3, which cannot be processed further by the regular enzymes of the β-oxidation system. This enzyme isomerizes the bond to a *trans* bond at position C_2, which can be processed further. The reaction rate is ten times higher for the (3*Z*) isomers than for (3*E*) isomers. The enzyme can also catalyse the isomerization of 3-acetylenic fatty acyl thioesters to 2,3-dienoyl fatty acyl thioesters.

References: [588, 589, 590, 426, 155, 188, 718, 198]

[EC 5.3.3.8 created 1978, modified 1980, modified 2018]

EC 5.3.3.9

Accepted name: prostaglandin-A_1 Δ-isomerase

Reaction: (13*E*)-(15*S*)-15-hydroxy-9-oxoprosta-10,13-dienoate = (13*E*)-(15*S*)-15-hydroxy-9-oxoprosta-11,13-dienoate

Other name(s): prostaglandin A isomerase

Systematic name: (13*E*)-(15*S*)-15-hydroxy-9-oxoprosta-10,13-dienoate Δ^{10}-Δ^{11}-isomerase

Comments: Interconverts prostaglandin A_1 and prostaglandin C_1.

References: [213]

[EC 5.3.3.9 created 1978]

EC 5.3.3.10

Accepted name: 5-carboxymethyl-2-hydroxymuconate Δ-isomerase

Reaction: 5-carboxymethyl-2-hydroxymuconate = (3*E*,5*R*)-5-carboxy-2-oxohept-3-enedioate

Other name(s): CHM isomerase; 5-carboxymethyl-2-hydroxymuconic acid isomerase

Systematic name: 5-carboxymethyl-2-hydroxymuconate Δ^2,Δ^4-2-oxo,Δ^3-isomerase

Comments: Part of the homoprotocatechuate degradation pathway in *Escherichia coli C*.

References: [183, 279]

[EC 5.3.3.10 created 1984]

EC 5.3.3.11

Accepted name: isopiperitenone Δ-isomerase

Reaction: isopiperitenone = piperitenone

Systematic name: isopiperitenone Δ^8-Δ^4-isomerase

Comments: Involved in the biosynthesis of menthol and related monoterpenes in peppermint (*Mentha piperita*) leaves.

References: [319]

[EC 5.3.3.11 created 1989]

EC 5.3.3.12

Accepted name: L-dopachrome isomerase

Reaction: L-dopachrome = 5,6-dihydroxyindole-2-carboxylate

Other name(s): dopachrome tautomerase; tyrosinase-related protein 2; TRP-1; TRP2; TRP-2; tyrosinase-related protein-2; dopachrome Δ^7,Δ^2-isomerase; dopachrome Δ-isomerase; dopachrome conversion factor; dopachrome isomerase; dopachrome oxidoreductase; dopachrome-rearranging enzyme; DCF; DCT; dopachrome keto-enol isomerase; L-dopachrome-methyl ester tautomerase
Systematic name: L-dopachrome keto-enol isomerase
Comments: A zinc enzyme. Stereospecific for L-dopachrome. Dopachrome methyl ester is a substrate, but dopaminochrome (2,3-dihydroindole-5,6-quinone) is not (see also EC 4.1.1.84, D-dopachrome decarboxylase).
References: [577, 485, 487]

[EC 5.3.3.12 created 1992, modified 1999, modified 2005]

EC 5.3.3.13

Accepted name: polyenoic fatty acid isomerase
Reaction: (5*Z*,8*Z*,11*Z*,14*Z*,17*Z*)-icosapentaenoate = (5*Z*,7*E*,9*E*,14*Z*,17*Z*)-icosapentaenoate
Other name(s): PFI; eicosapentaenoate *cis*-$\Delta^{5,8,11,14,17}$-eicosapentaenoate *cis*-Δ^5-*trans*-$\Delta^{7,9}$-*cis*-$\Delta^{14,17}$ isomerase; (5*Z*,8*Z*,11*Z*,14*Z*,17*Z*)-eicosapentaenoate $\Delta^{8,11}$-$\Delta^{7,8}$-isomerase (incorrect); (5*Z*,8*Z*,11*Z*,14*Z*,17*Z*)-eicosapentaenoate $\Delta^{8,11}$-$\Delta^{7,9}$-isomerase (*trans*-double-bond-forming)
Systematic name: (5*Z*,8*Z*,11*Z*,14*Z*,17*Z*)-icosapentaenoate $\Delta^{8,11}$-$\Delta^{7,9}$-isomerase (*trans*-double-bond-forming)
Comments: The enzyme from the red alga *Ptilota filicina* catalyses the isomerization of skip dienes (methylene-interrupted double bonds) in a broad range of fatty acids and fatty-acid analogues, such as arachidonate and γ-linolenate, to yield a conjugated triene.
References: [668, 671, 669, 727]

[EC 5.3.3.13 created 2004]

EC 5.3.3.14

Accepted name: *trans*-2-decenoyl-[acyl-carrier protein] isomerase
Reaction: a *trans*-dec-2-enoyl-[acyl-carrier protein] = a *cis*-dec-3-enoyl-[acyl-carrier protein]
Other name(s): β-hydroxydecanoyl thioester dehydrase; *trans*-2-*cis*-3-decenoyl-ACP isomerase; *trans*-2,*cis*-3-decenoyl-ACP isomerase; *trans*-2-decenoyl-ACP isomerase; FabM; decenoyl-[acyl-carrier-protein] Δ^2-*trans*-Δ^3-*cis*-isomerase
Systematic name: decenoyl-[acyl-carrier protein] Δ^2-*trans*-Δ^3-*cis*-isomerase
Comments: While the enzyme from *Escherichia coli* is highly specific for the 10-carbon enoyl-ACP, the enzyme from *Streptococcus pneumoniae* can also use the 12-carbon enoyl-ACP as substrate in vitro but not 14- or 16-carbon enoyl-ACPs [399]. ACP can be replaced by either CoA or *N*-acetylcysteamine thioesters. The *cis*-3-enoyl product is required to form unsaturated fatty acids, such as palmitoleic acid and *cis*-vaccenic acid, in dissociated (or type II) fatty-acid biosynthesis.
References: [69, 61, 399, 108]

[EC 5.3.3.14 created 2006]

[5.3.3.15 Transferred entry. ascopyrone tautomerase. Now EC 5.3.2.7, ascopyrone tautomerase]

[EC 5.3.3.15 created 2006, deleted 2013]

[5.3.3.16 Transferred entry. 4-oxalomesaconate tautomerase. Now EC 5.3.2.8, 4-oxalomesaconate tautomerase]

[EC 5.3.3.16 created 2011, modified 2011, deleted 2013]

EC 5.3.3.17

Accepted name: *trans*-2,3-dihydro-3-hydroxyanthranilate isomerase
Reaction: (5*S*,6*S*)-6-amino-5-hydroxycyclohexa-1,3-diene-1-carboxyate = (1*R*,6*S*)-6-amino-5-oxocyclohex-2-ene-1-carboxylate

Other name(s): *phzF* (gene name); (5*S*,6*S*)-6-amino-5-hydroxycyclohexane-1,3-diene-1-carboxyate isomerase (incorrect)
Systematic name: (5*S*,6*S*)-6-amino-5-hydroxycyclohexa-1,3-diene-1-carboxyate isomerase
Comments: The enzyme is involved in phenazine biosynthesis. The product probably spontaneously dimerises to 1,4,5a,6,9,10a-hexahydrophenazine-1,6-dicarboxylate
References: [482, 58, 481, 409, 12]

[EC 5.3.3.17 created 2011]

EC 5.3.3.18
Accepted name: 2-(1,2-epoxy-1,2-dihydrophenyl)acetyl-CoA isomerase
Reaction: 2-(1,2-epoxy-1,2-dihydrophenyl)acetyl-CoA = 2-oxepin-2(3*H*)-ylideneacetyl-CoA
Other name(s): *paaG* (gene name); 1,2-epoxyphenylacetyl-CoA isomerase (misleading)
Systematic name: 2-(1,2-epoxy-1,2-dihydrophenyl)acetyl-CoA isomerase
Comments: The enzyme catalyses the reversible isomerization of 2-(1,2-epoxy-1,2-dihydrophenyl)acetyl-CoA to the unusual unsaturated, oxygen-containing, seven-member heterocyclic enol ether 2-oxepin-2(3*H*)-ylideneacetyl-CoA, as part of an aerobic phenylacetate degradation pathway.
References: [263, 614]

[EC 5.3.3.18 created 2011]

EC 5.3.3.19
Accepted name: 3-[(4*R*)-4-hydroxycyclohexa-1,5-dien-1-yl]-2-oxopropanoate isomerase
Reaction: 3-[(4*R*)-4-hydroxycyclohexa-1,5-dien-1-yl]-2-oxopropanoate = 3-[(1*E*,4*R*)-4-hydroxycyclohex-2-en-1-ylidene]-2-oxopropanoate
Other name(s): BacB
Systematic name: 3-[(4*R*)-4-hydroxycyclohexa-1,5-dien-1-yl]-2-oxopropanoate isomerase
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 can interconvert the (*E*) isomer formed in the reaction into the (*Z*) isomer [479], although this isomerization is not part of the pathway leading to bacilysin [480].
References: [388, 479, 480]

[EC 5.3.3.19 created 2015]

[5.3.3.20 Transferred entry. 2-hydroxyisobutanoyl-CoA mutase. Now EC 5.4.99.64, 2-hydroxyisobutanoyl-CoA mutase]

[EC 5.3.3.20 created 2016, deleted 2017]

EC 5.3.3.21
Accepted name: $\Delta^{3,5}$-$\Delta^{2,4}$-dienoyl-CoA isomerase
Reaction: a (3*E*,5*Z*)-alka-3,5-dienoyl-CoA = a (2*E*,4*E*)-alka-2,4-dienoyl-CoA
Other name(s): 3,5-tetradecadienoyl-CoA isomerase; DCI1 (gene name)
Systematic name: (3*E*,5*Z*)-alka-3,5-dienoyl-CoA $\Delta^{3,5}$-$\Delta^{2,4}$ isomerase
Comments: The enzyme participates in an alternative degradation route of fatty acids with *cis*-double bonds on odd-number carbons such as oleate and linoleate. The main physiological substrate is (3*E*,5*Z*)-tetradeca-3,5-dienoyl-CoA, but other (3*E*,5*Z*)-dienoyl-CoAs with varying carbon chain lengths are also substrates.
References: [166, 429, 187, 212, 717, 197]

[EC 5.3.3.21 created 2018]

EC 5.3.3.22

Accepted name: lutein isomerase
Reaction: lutein = *meso*-zeaxanthin
Other name(s): RPE65 (gene name); *meso*-zeaxanthin isomerase
Systematic name: lutein Δ^4-Δ^5-isomerase
Comments: The enzyme is found in the retinal pigment epithelium (RPE) of vertebrates. It also has the activity of EC 3.1.1.64, retinoid isomerohydrolase.
References: [565]

[EC 5.3.3.22 created 2018]

EC 5.3.3.23

Accepted name: *S*-methyl-5-thioribulose 1-phosphate isomerase
Reaction: (1) *S*-methyl-5-thio-D-ribulose 1-phosphate = *S*-methyl-1-thio-D-xylulose 5-phosphate
(2) *S*-methyl-5-thio-D-ribulose 1-phosphate = *S*-methyl-1-thio-D-ribulose 5-phosphate
Other name(s): *rlp* (gene name); 5-methylthioribulose-1-phosphate isomerase (incorrect)
Systematic name: *S*-methyl-5-thio-D-ribulose 1-phosphate 1,3-isomerase
Comments: The enzyme, characterized from the bacterium *Rhodospirillum rubrum*, participates in methionine salvage from *S*-methyl-5′-thioadenosine. It is a RuBisCO-like protein (RLP) that is not capable of carbon fixation, and catalyses an isomerization reaction that converts *S*-methyl-5-thio-D-ribulose 1-phosphate to a 3:1 mixture of *S*-methyl-1-thioxylulose 5-phosphate and *S*-methyl-1-thioribulose 5-phosphate. The reaction is an overall 1,3-proton transfer, which likely consists of two 1,2-proton transfer events.
References: [261, 156]

[EC 5.3.3.23 created 2021]

EC 5.3.3.24

Accepted name: neopinone isomerase
Reaction: neopinone = codeinone
Other name(s): NISO (gene name)
Systematic name: neopinone Δ^8-Δ^7-isomerase
Comments: The enzyme, characterized from the opium poppy (*Papaver somniferum*), participates in the biosynthesis of morphine. It also catalyses the isomerization of neomorphinone and morphinone.
References: [128]

[EC 5.3.3.24 created 2022]

EC 5.3.4 Transposing S-S bonds

EC 5.3.4.1

Accepted name: protein disulfide-isomerase
Reaction: Catalyses the rearrangement of -S-S- bonds in proteins
Other name(s): S-S rearrangase
Systematic name: protein disulfide-isomerase
Comments: Needs reducing agents or partly reduced enzyme; the reaction depends on sulfhydryl-disulfide interchange.
References: [382, 179]

[EC 5.3.4.1 created 1972]

EC 5.3.99 Other intramolecular oxidoreductases

[5.3.99.1 Deleted entry. hydroperoxide isomerase. Reaction due to combined action of EC 4.2.1.92 (hydroperoxide dehydratase) and EC 5.3.99.6 (allene-oxide cyclase)]

[EC 5.3.99.1 created 1972, deleted 1992]

EC 5.3.99.2

Accepted name: prostaglandin-D synthase
Reaction: (5*Z*,13*E*,15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate = (5*Z*,13*E*,15*S*)-9α,15-dihydroxy-11-oxoprosta-5,13-dienoate
Other name(s): prostaglandin-H_2 Δ-isomerase; prostaglandin-R-prostaglandin D isomerase; PGH-PGD isomerase(5,13)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate Δ-isomerase (incorrect); (5,13)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate D-isomerase; prostaglandin endoperoxide Δ-isomerase; prostaglandin D synthetase
Systematic name: (5*Z*,13*E*,15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate D-isomerase
Comments: Brings about the opening of the epidioxy bridge. Some enzymes require glutathione.
References: [97, 561]

[EC 5.3.99.2 created 1976, modified 1990]

EC 5.3.99.3

Accepted name: prostaglandin-E synthase
Reaction: (5*Z*,13*E*)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate = (5*Z*,13*E*)-(15*S*)-11α,15-dihydroxy-9-oxoprosta-5,13-dienoate
Other name(s): prostaglandin-H_2 E-isomerase; endoperoxide isomerase; endoperoxide isomerase; prostaglandin *R*-prostaglandin E isomerase; prostaglandin endoperoxide E isomerase; PGE isomerase; PGH-PGE isomerase; PGE_2 isomerase; prostaglandin endoperoxide E_2 isomerase; prostaglandin H-E isomerase
Systematic name: (5*Z*,13*E*)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate E-isomerase
Comments: Brings about the opening of the epidioxy bridge. Requires glutathione.
References: [466, 607]

[EC 5.3.99.3 created 1976, modified 1990]

EC 5.3.99.4

Accepted name: prostaglandin-I synthase
Reaction: (5*Z*,13*E*,15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate = (5*Z*,13*E*,15*S*)-6,9α-epoxy-11α,15-dihydroxyprosta-5,13-dienoate
Other name(s): prostacyclin synthase; prostacycline synthetase; prostagladin I2 synthetase; PGI_2 synthase; PGI_2 synthetase; (5*Z*,13*E*)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate 6-isomerase
Systematic name: (5*Z*,13*E*,15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate 6-isomerase
Comments: A cytochrome *P*-450 heme-thiolate enzyme. Converts prostaglandin H_2 into prostaglandin I_2 (prostacyclin).
References: [137, 632]

[EC 5.3.99.4 created 1984, modified 1990]

EC 5.3.99.5

Accepted name: thromboxane-A synthase
Reaction: (5*Z*,13*E*)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate = (5*Z*,13*E*)-(15*S*)-9α,11α-epoxy-15-hydroxythromboxa-5,13-dienoate
Other name(s): thromboxane synthase; (5*Z*,13*E*)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate thromboxane-A_2-isomerase

Systematic name: (5*Z*,13*E*)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate isomerase
Comments: A cytochrome *P*-450 heme-thiolate enzyme. Converts prostaglandin H_2 into thromboxane A_2.
References: [553, 633]

[EC 5.3.99.5 created 1984, modified 1990]

EC 5.3.99.6
Accepted name: allene-oxide cyclase
Reaction: (9*Z*)-(13*S*)-12,13-epoxyoctadeca-9,11,15-trienoate = (15*Z*)-12-oxophyto-10,15-dienoate
Systematic name: (9*Z*)-(13*S*)-12,13-epoxyoctadeca-9,11,15-trienoate isomerase (cyclizing)
Comments: Allene oxides formed by the action of EC 4.2.1.92 hydroperoxide dehydratase, are converted into cyclopentenone derivatives.
References: [216]

[EC 5.3.99.6 created 1992]

EC 5.3.99.7
Accepted name: styrene-oxide isomerase
Reaction: styrene oxide = phenylacetaldehyde
Other name(s): SOI
Systematic name: styrene-oxide isomerase (epoxide-cleaving)
Comments: Highly specific.
References: [222]

[EC 5.3.99.7 created 1992]

EC 5.3.99.8
Accepted name: capsanthin/capsorubin synthase
Reaction: (1) violaxanthin = capsorubin
(2) antheraxanthin = capsanthin
Other name(s): CCS; ketoxanthophyll synthase; capsanthin-capsorubin synthase
Systematic name: violaxanthin—capsorubin isomerase (ketone-forming)
Comments: This multifunctional enzyme is induced during chromoplast differentiation in plants [64]. Isomerization of the epoxide ring of violaxanthin gives the cyclopentyl-ketone of capsorubin or capsanthin.
References: [64, 356, 687]

[EC 5.3.99.8 created 2005]

EC 5.3.99.9
Accepted name: neoxanthin synthase
Reaction: violaxanthin = neoxanthin
Other name(s): NSY
Systematic name: violaxanthin—neoxanthin isomerase (epoxide-opening)
Comments: The opening of the epoxide ring of violaxanthin generates a chiral allene. Neoxanthin is a precursor of the plant hormone abscisic acid and the last product of carotenoid synthesis in green plants [63].
References: [13, 63]

[EC 5.3.99.9 created 2005]

EC 5.3.99.10
Accepted name: thiazole tautomerase

Reaction: 2-[(2*R*,5*Z*)-2-carboxy-4-methylthiazol-5(2*H*)-ylidene]ethyl phosphate = 2-(2-carboxy-4-methylthiazol-5-yl)ethyl phosphate
Other name(s): *tenI* (gene name)
Systematic name: 2-(2-carboxy-4-methylthiazol-5-yl)ethyl phosphate isomerase
Comments: The enzyme catalyses the irreversible aromatization of the thiazole moiety of 2-[(2*R*,5*Z*)-2-carboxy-4-methylthiazol-5(2*H*)-ylidene]ethyl phosphate.
References: [228]

[EC 5.3.99.10 created 2012]

EC 5.3.99.11
Accepted name: 2-keto-*myo*-inositol isomerase
Reaction: 2,4,6/3,5-pentahydroxycyclohexanone = 2D-2,3,5/4,6-pentahydroxycyclohexanone
Other name(s): IolI; inosose isomerase; 2KMI isomerase.
Systematic name: 2,4,6/3,5-pentahydroxycyclohexanone 2-isomerase
Comments: Requires a divalent metal ion for activity. Mn^{2+}, Fe^{2+} and Co^{2+} can be used. The enzyme, found in the bacterium *Bacillus subtilis*, is part of the *myo*-inositol/D-*chiro*-inositol degradation pathway leading to acetyl-CoA.
References: [721, 702]

[EC 5.3.99.11 created 2014]

EC 5.3.99.12
Accepted name: lachrymatory-factor synthase
Reaction: (*E*)-alk-1-en-1-*SO*-peroxol = (*Z*)-alkanethial oxide
Other name(s): LFS
Systematic name: (*E*)-alk-1-en-1-*SO*-peroxol isomerase [(*Z*)-alkanethial *S*-oxide-forming]
Comments: The enzyme is responsible for production of the irritating lachrymatory factor that is released by onions and related species when they are chopped. It acts of the product of EC 4.4.1.4, alliin lyase. The enzyme from *Allium cepa* (onion) acts on (*E*)-prop-1-en-1-*SO*-peroxol and produces (*Z*)-propanethial oxide, while the enzyme from *Allium siculum* (honey garlic) acts on (*E*)-but-1-en-1-*SO*-peroxol and produces (*Z*)-butanethial oxide.
References: [461, 260, 148, 336]

[EC 5.3.99.12 created 2021]

EC 5.4 Intramolecular transferases

This subclass contains enzymes that transfer a group from one position to another within a molecule. Sub-subclasses are based on the group transferred: acyl group (EC 5.4.1), phospho group (EC 5.4.2), amino group (EC 5.4.3), hydroxy group (EC 5.4.4), or some other group (EC 5.4.99).

EC 5.4.1 Transferring acyl groups

EC 5.4.1.1
Accepted name: lysolecithin acylmutase
Reaction: 2-lysolecithin = 3-lysolecithin
Other name(s): lysolecithin migratase
Systematic name: lysolecithin 2,3-acylmutase
References: [636]

[EC 5.4.1.1 created 1961]

[5.4.1.2 Transferred entry. precorrin-8X methylmutase. Now EC 5.4.99.61, precorrin-8X methylmutase]

[EC 5.4.1.2 created 1999, deleted 2014]

EC 5.4.1.3

Accepted name: 2-methylfumaryl-CoA isomerase
Reaction: 2-methylfumaryl-CoA = 3-methylfumaryl-CoA
Other name(s): mesaconyl-CoA C_1-C_4 CoA transferase; Mct
Systematic name: 2-methylfumaryl-CoA 1,4-CoA-mutase
Comments: The enzyme, purified from the bacterium *Chloroflexus aurantiacus*, acts as an intramolecular CoA transferase and does not transfer CoA to free mesaconate. It is part of the 3-hydroxypropanoate cycle for carbon assimilation.
References: [715]

[EC 5.4.1.3 created 2014]

EC 5.4.1.4

Accepted name: D-galactarolactone isomerase
Reaction: D-galactaro-1,5-lactone = D-galactaro-1,4-lactone
Other name(s): GLI
Systematic name: D-galactaro-1,5-lactone isomerase (D-galactaro-1,4-lactone-forming)
Comments: The enzyme, characterized from the bacterium *Agrobacterium fabrum* strain C58, belongs to the amidohydrolase superfamily. It participates in the degradation of D-galacturonate.
References: [65]

[EC 5.4.1.4 created 2015]

EC 5.4.2 Phosphotransferases (phosphomutases)

Most of these enzymes were previously listed as sub-subclass EC 2.7.5, under the heading: 'Phosphotransferases with regeneration of donors, apparently catalysing intramolecular transfers'. The reaction for these enzymes was written in the form:¡p¿

X-(*P*)2 + A*P* = B*P* + X-$(P)_2$.

In fact, since phosphorylation of the acceptor produces a bisphosphate that is identical to the donor, the overall reaction is an isomerization of AP into BP, with the bisphosphate acting catalytically. It has been shown in some cases that the enzyme has a functional phosphate group, which can act as the donor. Phosphate is transferred to the substrate, forming the intermediate bisphosphate; the other phosphate group is subsequently transferred to the enzyme:¡p¿

E-*P* + A*P* = E + X-$(P)_2$¡p¿

X-$(P)_2$ + E = B*P* + E-*P*.

The bisphosphate may be firmly attached to the enzyme during the catalytic cycle, or, in other cases, may be released so that free bisphosphate is required as an activator. Under these circumstances, it was agreed in 1983 that all of these enzymes should be listed together in this sub-subclass based on the overall isomerase reaction.

[5.4.2.1 Transferred entry. phosphoglycerate mutase. Now recognized as two separate enzymes EC 5.4.2.11, phosphoglycerate mutase (2,3-diphosphoglycerate-dependent) and EC 5.4.2.12, phosphoglycerate mutase (2,3-diphosphoglycerate-independent)]

[EC 5.4.2.1 created 1961 (EC 2.7.5.3 created 1961, incorporated 1984), deleted 2013]

EC 5.4.2.2

Accepted name: phosphoglucomutase (α-D-glucose-1,6-bisphosphate-dependent)
Reaction: α-D-glucose 1-phosphate = D-glucose 6-phosphate
Other name(s): glucose phosphomutase (ambiguous); phosphoglucose mutase (ambiguous)
Systematic name: α-D-glucose 1,6-phosphomutase

Comments: Maximum activity is only obtained in the presence of α-D-glucose 1,6-bisphosphate. This bisphosphate is an intermediate in the reaction, being formed by transfer of a phosphate residue from the enzyme to the substrate, but the dissociation of bisphosphate from the enzyme complex is much slower than the overall isomerization. The enzyme also catalyses (more slowly) the interconversion of 1-phosphate and 6-phosphate isomers of many other α-D-hexoses, and the interconversion of α-D-ribose 1-phosphate and 5-phosphate. *cf.* EC 5.4.2.5, phosphoglucomutase (glucose-cofactor).
References: [283, 446, 509, 508, 601]

[EC 5.4.2.2 created 1961 as EC 2.7.5.1, transferred 1984 to EC 5.4.2.2]

EC 5.4.2.3
Accepted name: phosphoacetylglucosamine mutase
Reaction: *N*-acetyl-α-D-glucosamine 1-phosphate = *N*-acetyl-D-glucosamine 6-phosphate
Other name(s): acetylglucosamine phosphomutase; acetylglucosamine phosphomutase; acetylaminodeoxyglucose phosphomutase; phospho-*N*-acetylglucosamine mutase; *N*-acetyl-D-glucosamine 1,6-phosphomutase
Systematic name: *N*-acetyl-α-D-glucosamine 1,6-phosphomutase
Comments: The enzyme is activated by *N*-acetyl-α-D-glucosamine 1,6-bisphosphate.
References: [78, 358, 508, 514]

[EC 5.4.2.3 created 1961 as EC 2.7.5.2, transferred 1984 to EC 5.4.2.3]

EC 5.4.2.4
Accepted name: bisphosphoglycerate mutase
Reaction: 3-phospho-D-glyceroyl phosphate = 2,3-bisphospho-D-glycerate
Other name(s): diphosphoglycerate mutase; glycerate phosphomutase; bisphosphoglycerate synthase; bisphosphoglyceromutase; biphosphoglycerate synthase; diphosphoglyceric mutase; 2,3-diphosphoglycerate mutase; phosphoglyceromutase; 2,3-diphosphoglycerate synthase; DPGM; 2,3-bisphosphoglycerate mutase; BPGM; diphosphoglyceromutase; 2,3-diphosphoglyceromutase
Systematic name: 3-phospho-D-glycerate 1,2-phosphomutase
Comments: In the direction shown, this enzyme is phosphorylated by 3-phosphoglyceroyl phosphate, to give phosphoenzyme and 3-phosphoglycerate. The latter is rephosphorylated by the enzyme to yield 2,3-bisphosphoglycerate, but this reaction is slowed by dissociation of 3-phosphoglycerate from the enzyme, which is therefore more active in the presence of added 3-phosphoglycerate. This enzyme also catalyses, slowly, the reaction of EC 5.4.2.11 [phosphoglycerate mutase (2,3-diphosphoglycerate-dependent)] and EC 5.4.2.12 [phosphoglycerate mutase (2,3-diphosphoglycerate-independent)].
References: [508, 525, 526]

[EC 5.4.2.4 created 1961 as EC 2.7.5.4, transferred 1984 to EC 5.4.2.4]

EC 5.4.2.5
Accepted name: phosphoglucomutase (glucose-cofactor)
Reaction: α-D-glucose 1-phosphate = D-glucose 6-phosphate
Other name(s): glucose phosphomutase (ambiguous); glucose-1-phosphate phosphotransferase
Systematic name: α-D-glucose 1,6-phosphomutase (glucose-cofactor)
Comments: The enzyme is activated by D-glucose, which probably acts as an acceptor for a phosphate residue from the substrate, thus being itself converted into the product. *cf.* EC 5.4.2.2, phosphoglucomutase (α-D-glucose-1,6-bisphosphate-dependent).
References: [180, 508]

[EC 5.4.2.5 created 1972 as EC 2.7.5.5, transferred 1984 to EC 5.4.2.5]

EC 5.4.2.6
Accepted name: β-phosphoglucomutase

Reaction: β-D-glucose 1-phosphate = β-D-glucose 6-phosphate
Other name(s): β-*pgm* (gene name)
Systematic name: β-D-glucose 1,6-phosphomutase
Comments: The enzyme requires Mg^{2+} and phosphorylation of an aspartate residue at the active site. The enzyme is able to autophosphorylate itself with its substrate β-D-glucose 1-phosphate. Although this is a slow reaction, only a single turnover is required for activation. Once the phosphorylated enzyme is formed, it generates the reaction intermediate β-D-glucose 1,6-bisphosphate, which can be used to phosphorylate the enzyme in subsequent cycles [125]. *cf.* EC 5.4.2.2, phosphoglucomutase (α-D-glucose-1,6-bisphosphate-dependent).
References: [51, 508, 348, 125]

[EC 5.4.2.6 created 1984]

EC 5.4.2.7
Accepted name: phosphopentomutase
Reaction: α-D-ribose 1-phosphate = D-ribose 5-phosphate
Other name(s): phosphodeoxyribomutase; deoxyribose phosphomutase; deoxyribomutase; phosphoribomutase; α-D-glucose-1,6-bisphosphate:deoxy-D-ribose-1-phosphate phosphotransferase; D-ribose 1,5-phosphomutase
Systematic name: α-D-ribose 1,5-phosphomutase
Comments: Also converts 2-deoxy-α-D-ribose 1-phosphate into 2-deoxy-D-ribose 5-phosphate. α-D-Ribose 1,5-bisphosphate, 2-deoxy-α-D-ribose 1,5-bisphosphate, or α-D-glucose 1,6-bisphosphate can act as cofactor.
References: [218, 290, 508]

[EC 5.4.2.7 created 1972 as EC 2.7.5.6, transferred 1984 to EC 5.4.2.7]

EC 5.4.2.8
Accepted name: phosphomannomutase
Reaction: α-D-mannose 1-phosphate = D-mannose 6-phosphate
Other name(s): mannose phosphomutase; phosphomannose mutase; D-mannose 1,6-phosphomutase
Systematic name: α-D-mannose 1,6-phosphomutase
Comments: α-D-Mannose 1,6-bisphosphate or α-D-glucose 1,6-bisphosphate can act as cofactor.
References: [574]

[EC 5.4.2.8 created 1981 as EC 2.7.5.7, transferred 1984 to EC 5.4.2.8]

EC 5.4.2.9
Accepted name: phospho*enol*pyruvate mutase
Reaction: phospho*enol*pyruvate = 3-phosphonopyruvate
Other name(s): phospho*enol*pyruvate-phosphonopyruvate phosphomutase; PEP phosphomutase; phospho*enol*pyruvate phosphomutase; PEPPM; PEP phosphomutase
Systematic name: phospho*enol*pyruvate 2,3-phosphonomutase
Comments: Involved in the biosynthesis of the C-P bond, although the equilibrium greatly favours phospho*enol*pyruvate.
References: [66, 238, 549]

[EC 5.4.2.9 created 1990]

EC 5.4.2.10
Accepted name: phosphoglucosamine mutase
Reaction: α-D-glucosamine 1-phosphate = D-glucosamine 6-phosphate
Systematic name: α-D-glucosamine 1,6-phosphomutase

Comments: The enzyme is involved in the pathway for bacterial cell-wall peptidoglycan and lipopolysaccharide biosyntheses, being an essential step in the pathway for UDP-*N*-acetylglucosamine biosynthesis. The enzyme from *Escherichia coli* is activated by phosphorylation and can be autophosphorylated in vitro by α-D-glucosamine 1,6-bisphosphate, which is an intermediate in the reaction, α-D-glucose 1,6-bisphosphate or ATP. It can also catalyse the interconversion of α-D-glucose 1-phosphate and glucose 6-phosphate, although at a much lower rate.

References: [419, 131, 282, 280, 281]

[EC 5.4.2.10 created 2001]

EC 5.4.2.11

Accepted name: phosphoglycerate mutase (2,3-diphosphoglycerate-dependent)

Reaction: 2-phospho-D-glycerate = 3-phospho-D-glycerate (overall reaction)
(1a) [enzyme]-L-histidine + 2,3-bisphospho-D-glycerate = [enzyme]-N^{τ}-phospho-L-histidine + 2/3-phospho-D-glycerate
(1b) [enzyme]-N^{τ}-phospho-L-histidine + 2-phospho-D-glycerate = [enzyme]-L-histidine + 2,3-bisphospho-D-glycerate
(1c) [enzyme]-L-histidine + 2,3-bisphospho-D-glycerate = [enzyme]-N^{τ}-phospho-L-histidine + 3-phospho-D-glycerate
(1d) [enzyme]-N^{τ}-phospho-L-histidine + 2/3-bisphospho-D-glycerate = [enzyme]-L-histidine + 2,3-bisphospho-D-glycerate

Other name(s): glycerate phosphomutase (diphosphoglycerate cofactor); 2,3-diphosphoglycerate dependent phosphoglycerate mutase; cofactor dependent phosphoglycerate mutase; phosphoglycerate phosphomutase (ambiguous); phosphoglyceromutase (ambiguous); monophosphoglycerate mutase (ambiguous); monophosphoglyceromutase (ambiguous); GriP mutase (ambiguous); PGA mutase (ambiguous); MPGM; PGAM; PGAM-d; PGM; dPGM

Systematic name: D-phosphoglycerate 2,3-phosphomutase (2,3-diphosphoglycerate-dependent)

Comments: The enzymes from vertebrates, platyhelminths, mollusks, annelids, crustaceans, insects, algae, some fungi and some bacteria (particularly Gram-negative) require 2,3-bisphospho-D-glycerate as a cofactor. The enzyme is activated by 2,3-bisphospho-D-glycerate by transferring a phosphate to histidine (His^{10} in man and *Escherichia coli*, His^{8} in *Saccharomyces cerevisiae*). This phosphate can be transferred to the free OH of 2-phospho-D-glycerate, followed by transfer of the phosphate already on the phosphoglycerate back to the histidine. *cf.* EC 5.4.2.12 phosphoglycerate mutase. The enzyme has no requirement for metal ions. This enzyme also catalyse, slowly, the reactions of EC 5.4.2.4 bisphosphoglycerate mutase.

References: [206, 508, 526, 519, 62, 518, 517]

[EC 5.4.2.11 created 1961 as EC 5.4.2.1 (EC 2.7.5.3 created 1961, incorporated 1984) transferred 2013 to EC 5.4.2.11, modified 2014]

EC 5.4.2.12

Accepted name: phosphoglycerate mutase (2,3-diphosphoglycerate-independent)

Reaction: 2-phospho-D-glycerate = 3-phospho-D-glycerate

Other name(s): cofactor independent phosphoglycerate mutase; 2,3-diphosphoglycerate-independent phosphoglycerate mutase; phosphoglycerate phosphomutase (ambiguous); phosphoglyceromutase (ambiguous); monophosphoglycerate mutase (ambiguous); monophosphoglyceromutase (ambiguous); GriP mutase (ambiguous); PGA mutase (ambiguous); iPGM; iPGAM; PGAM-i

Systematic name: D-phosphoglycerate 2,3-phosphomutase (2,3-diphosphoglycerate-independent)

Comments: The enzymes from higher plants, algae, some fungi, nematodes, sponges, coelenterates, myriapods, arachnids, echinoderms, archaea and some bacteria (particularly Gram-positive) have maximum activity in the absence of 2,3-bisphospho-D-glycerate. *cf.* EC 5.4.2.11 phosphoglycerate mutase (2,3-diphosphoglycerate-dependent). The enzyme contains two Mn^{2+} (or in some species two Co^{2+} ions). The reaction involves a phosphotransferase reaction to serine followed by transfer back to the glycerate at the other position. Both metal ions are involved in the reaction.

References: [274, 516, 724, 463, 462, 420]

[EC 5.4.2.12 created 2013]

EC 5.4.2.13

Accepted name: phosphogalactosamine mutase
Reaction: D-galactosamine 6-phosphate = α-D-galactosamine-1-phosphate
Other name(s): ST0242 (locus name)
Systematic name: α-D-galactosamine 1,6-phosphomutase
Comments: The enzyme, characterized from the archaeon *Sulfolobus tokodaii*, is also active toward D-glucosamine 6-phosphate (*cf.* EC 5.4.2.10, phosphoglucosamine mutase).
References: [122]

[EC 5.4.2.13 created 2018]

EC 5.4.3 Transferring amino groups

[5.4.3.1 Deleted entry. ornithine 4,5-aminomutase. This reaction was due to a mixture of EC 5.1.1.12 (ornithine racemase) and EC 5.4.3.5 (D-ornithine 4,5-aminomutase)]

[EC 5.4.3.1 created 1972, deleted 1976]

EC 5.4.3.2

Accepted name: lysine 2,3-aminomutase
Reaction: L-lysine = (3*S*)-3,6-diaminohexanoate
Systematic name: L-lysine 2,3-aminomutase
Comments: This enzyme is a member of the 'AdoMet radical' (radical SAM) family. It contains pyridoxal phosphate and a [4Fe-4S] cluster and binds an exchangeable *S*-adenosyl-L-methionine molecule. Activity *in vitro* requires a strong reductant such as dithionite and strictly anaerobic conditions. A 5′-deoxyadenosyl radical is generated during the reaction cycle by reductive cleavage of *S*-adenosyl-L-methionine, mediated by the iron-sulfur cluster. *S*-adenosyl-L-methionine is regenerated at the end of the reaction.
References: [714, 5, 177, 369, 359, 178]

[EC 5.4.3.2 created 1972]

EC 5.4.3.3

Accepted name: lysine 5,6-aminomutase
Reaction: (1) (3*S*)-3,6-diaminohexanoate = (3*S*,5*S*)-3,5-diaminohexanoate
(2) D-lysine = (2*R*,5*S*)-2,5-diaminohexanoate
Other name(s): β-lysine 5,6-aminomutase; β-lysine mutase; L-β-lysine 5,6-aminomutase; D-lysine 5,6-aminomutase; D-α-lysine mutase; adenosylcobalamin-dependent D-lysine 5,6-aminomutase
Systematic name: (3*S*)-3,6-diaminohexanoate 5,6-aminomutase
Comments: This enzyme is a member of the 'AdoMet radical' (radical SAM) family. It requires pyridoxal 5′-phosphate and adenosylcobalamin for activity. A 5′-deoxyadenosyl radical is generated during the reaction cycle by reductive cleavage of adenosylcobalamin, which is regenerated at the end of the reaction.
References: [584, 583, 436, 515, 85, 608, 609, 55]

[EC 5.4.3.3 created 1972 (EC 5.4.3.4 created 1972, incorporated 2017), modified 2017]

[5.4.3.4 Transferred entry. D-lysine 5,6-aminomutase. Now included in EC 5.4.3.3, lysine 5,6-aminomutase]

[EC 5.4.3.4 created 1972, modified 2003, deleted 2017]

EC 5.4.3.5

Accepted name: D-ornithine 4,5-aminomutase
Reaction: D-ornithine = (2*R*,4*S*)-2,4-diaminopentanoate
Other name(s): D-α-ornithine 5,4-aminomutase; D-ornithine aminomutase
Systematic name: D-ornithine 4,5-aminomutase
Comments: A pyridoxal-phosphate protein that requires a cobamide coenzyme for activity.
References: [579]

[EC 5.4.3.5 created 1972 as EC 5.4.3.1, transferred 1976 to EC 5.4.3.5, modified 2003]

EC 5.4.3.6

Accepted name: tyrosine 2,3-aminomutase
Reaction: L-tyrosine = 3-amino-3-(4-hydroxyphenyl)propanoate
Other name(s): tyrosine α,β-mutase
Systematic name: L-tyrosine 2,3-aminomutase
Comments: Requires ATP.
References: [345]

[EC 5.4.3.6 created 1976]

EC 5.4.3.7

Accepted name: leucine 2,3-aminomutase
Reaction: (2*S*)-α-leucine = (3*R*)-β-leucine
Systematic name: (2*S*)-α-leucine 2,3-aminomutase
Comments: Requires a cobamide coenzyme.
References: [176, 496, 495]

[EC 5.4.3.7 created 1982]

EC 5.4.3.8

Accepted name: glutamate-1-semialdehyde 2,1-aminomutase
Reaction: L-glutamate 1-semialdehyde = 5-aminolevulinate
Other name(s): glutamate-1-semialdehyde aminotransferase
Systematic name: (*S*)-4-amino-5-oxopentanoate 4,5-aminomutase
Comments: Requires pyridoxal phosphate.
References: [200]

[EC 5.4.3.8 created 1983]

EC 5.4.3.9

Accepted name: glutamate 2,3-aminomutase
Reaction: L-glutamate = 3-aminopentanedioate
Systematic name: L-glutamate 2,3-aminomutase
Comments: This enzyme is a member of the 'AdoMet radical' (radical SAM) family. It contains pyridoxal phosphate and a [4Fe-4S] cluster, which is coordinated by 3 cysteines and binds an exchangeable *S*-adenosyl-L-methionine molecule. During the reaction cycle, the AdoMet forms a 5′-deoxyadenosyl radical, which is regenerated at the end of the reaction.
References: [529]

[EC 5.4.3.9 created 2012]

EC 5.4.3.10

Accepted name: phenylalanine aminomutase (L-β-phenylalanine forming)
Reaction: L-phenylalanine = L-β-phenylalanine
Systematic name: L-phenylalanine 2,3-aminomutase [(*R*)-3-amino-3-phenylpropanoate-forming]
Comments: The enzyme contains the cofactor 3,5-dihydro-5-methylidene-4*H*-imidazol-4-one (MIO). This unique cofactor is formed autocatalytically by cyclization and dehydration of the three amino-acid residues alanine, serine and glycine. *cf.* EC 5.4.3.11, phenylalanine aminomutase (D-β-phenylalanine forming).
References: [163]

[EC 5.4.3.10 created 2013]

EC 5.4.3.11

Accepted name: phenylalanine aminomutase (D-β-phenylalanine forming)
Reaction: L-phenylalanine = D-β-phenylalanine
Other name(s): *admH* (gene name); L-phenylalanine 2,3-aminomutase [(*S*)-3-amino-3-phenylpropanoate]
Systematic name: L-phenylalanine 2,3-aminomutase [(*S*)-3-amino-3-phenylpropanoate-forming]
Comments: The enzyme from the bacterium *Pantoea agglomerans* produces D-β-phenylalanine, an intermediate in the biosynthesis of the polyketide non-ribosomal antibiotic andrimid. The enzyme contains the cofactor 3,5-dihydro-5-methylidene-4*H*-imidazol-4-one (MIO), which is formed autocatalytically by cyclization and dehydration of the three amino-acid residues alanine, serine and glycine. *cf.* EC 5.4.3.10, phenylalanine aminomutase (L-β-phenylalanine forming).
References: [506]

[EC 5.4.3.11 created 2013]

EC 5.4.4 Transferring hydroxy groups

EC 5.4.4.1

Accepted name: (hydroxyamino)benzene mutase
Reaction: (hydroxyamino)benzene = 2-aminophenol
Other name(s): HAB mutase; hydroxylaminobenzene hydroxymutase; hydroxylaminobenzene mutase
Systematic name: (hydroxyamino)benzene hydroxymutase
References: [230, 129]

[EC 5.4.4.1 created 2003]

EC 5.4.4.2

Accepted name: isochorismate synthase
Reaction: chorismate = isochorismate
Other name(s): MenF
Systematic name: isochorismate hydroxymutase
Comments: Requires Mg^{2+}. The reaction is reversible.
References: [704, 641, 123, 127]

[EC 5.4.4.2 created 1972 as EC 5.4.99.6, transferred 2003 to EC 5.4.4.2]

EC 5.4.4.3

Accepted name: 3-(hydroxyamino)phenol mutase
Reaction: 3-hydroxyaminophenol = aminohydroquinone
Other name(s): 3-hydroxylaminophenol mutase; 3*H*AP mutase
Systematic name: 3-(hydroxyamino)phenol hydroxymutase

References: [541]

[EC 5.4.4.3 created 2003]

EC 5.4.4.4

Accepted name: geraniol isomerase
Reaction: geraniol = (3*S*)-linalool
Systematic name: geraniol hydroxymutase
Comments: In absence of oxygen the bifunctional linalool dehydratase-isomerase can catalyse *in vitro* two reactions, the isomerization of (3*S*)-linalool to geraniol and the hydration of myrcene to (3*S*)-linalool, the latter activity being classified as EC 4.2.1.127, linalool dehydratase.
References: [71, 385]

[EC 5.4.4.4 created 2011, modified 2012]

EC 5.4.4.5

Accepted name: 9,12-octadecadienoate 8-hydroperoxide 8*R*-isomerase
Reaction: (8*R*,9*Z*,12*Z*)-8-hydroperoxyoctadeca-9,12-dienoate = (5*S*,8*R*,9*Z*,12*Z*)-5,8-dihydroxyoctadeca-9,12-dienoate
Other name(s): 5,8-LDS (bifunctional enzyme); 5,8-linoleate diol synthase (bifunctional enzyme); 8-hydroperoxide isomerase; (8*R*,9*Z*,12*Z*)-8-hydroperoxy-9,12-octadecadienoate mutase ((5*S*,8*R*,9*Z*,12*Z*)-5,8-dihydroxy-9,12-octadecadienoate-forming); PpoA
Systematic name: (8*R*,9*Z*,12*Z*)-8-hydroperoxyoctadeca-9,12-dienoate hydroxymutase [(5*S*,8*R*,9*Z*,12*Z*)-5,8-dihydroxyoctadeca-9,12-dienoate-forming]
Comments: The enzyme contains heme [70]. The bifunctional enzyme from *Aspergillus nidulans* uses different heme domains to catalyse two separate reactions. Linoleic acid is oxidized within the N-terminal heme peroxidase domain to (8*R*,9*Z*,12*Z*)-8-hydroperoxyoctadeca-9,12-dienoate (*cf.* EC 1.13.11.60, linoleate 8*R*-lipoxygenase), which is subsequently isomerized to (5*S*,8*R*,9*Z*,12*Z*)-5,8-dihydroxyoctadeca-9,12-dienoate within the C-terminal *P*-450 heme thiolate domain [70].
References: [242, 275, 70]

[EC 5.4.4.5 created 2011]

EC 5.4.4.6

Accepted name: 9,12-octadecadienoate 8-hydroperoxide 8*S*-isomerase
Reaction: (8*R*,9*Z*,12*Z*)-8-hydroperoxyoctadeca-9,12-dienoate = (7*S*,8*S*,9*Z*,12*Z*)-7,8-dihydroxyoctadeca-9,12-dienoate
Other name(s): 8-hydroperoxide isomerase (ambiguous); (8*R*,9*Z*,12*Z*)-8-hydroperoxy-9,12-octadecadienoate mutase ((7*S*,8*S*,9*Z*,12*Z*)-7,8-dihydroxy-9,12-octadecadienoate-forming)
Systematic name: (8*R*,9*Z*,12*Z*)-8-hydroperoxyoctadeca-9,12-dienoate hydroxymutase [(7*S*,8*S*,9*Z*,12*Z*)-7,8-dihydroxyoctadeca-9,12-dienoate-forming]
Comments: The enzyme contains heme. The bifunctional enzyme from *Gaeumannomyces graminis* catalyses the oxidation of linoleic acid to (8*R*,9*Z*,12*Z*)-8-hydroperoxyoctadeca-9,12-dienoate (*cf.* EC 1.13.11.60, linoleate 8*R*-lipoxygenase), which is then isomerized to (7*S*,8*S*,9*Z*,12*Z*)-5,8-dihydroxyoctadeca-9,12-dienoate [592].
References: [217, 593, 592]

[EC 5.4.4.6 created 2011]

EC 5.4.4.7

Accepted name: hydroperoxy icosatetraenoate isomerase
Reaction: a hydroperoxyicosatetraenoate = a hydroxyepoxyicosatrienoate
Other name(s): epidermal lipoxygenase-3 (ambiguous); eLOX3 (ambiguous)

Systematic name: hydroperoxyicosatetraenoate hydroxymutase
Comments: Binds Fe^{2+}. The enzyme from mammals accepts a range of hydroperoxyicosatetraenoates producing one or several different hydroxyepoxyicosatrienoates. The human enzyme has highest activity with (12*R*)-HPETE producing (5*Z*,8*R*,9*E*,11*R*,12*R*,14*Z*)-8-hydroxy-11,12-epoxyicosa-5,9,14-trienoate, followed by (12*S*)-HPETE producing (5*Z*,8*Z*,10*R*,11*S*,12*S*,14*Z*)-10-hydroxy-11,12-epoxyicosa-5,8,14-trienoate and (5*Z*,8*R*,9*E*,11*S*,12*S*,14*Z*)-8-hydroxy-11,12-epoxyicosa-5,9,14-trienoate [711]. The mouse enzyme has highest activity with (8*S*)-HPETE, producing (5*Z*,8*S*,9*S*,10*R*,11*Z*,14*Z*)-10-hydroxy-8,9-epoxyicosa-5,11,14-trienoate [710]. The enzymes also have the activity of EC 4.2.1.152, hydroperoxy icosatetraenoate dehydratase.
References: [711, 710, 728]

[EC 5.4.4.7 created 2014]

EC 5.4.4.8
Accepted name: linalool isomerase
Reaction: (*RS*)-linalool = geraniol
Other name(s): 3,1-hydroxyl-Δ^1-Δ^2-mutase (linalool isomerase)
Systematic name: (*RS*)-linalool hydroxymutase
Comments: Isolated from the bacterium *Thauera linaloolentis* grown on (*RS*)-linalool as the sole source of carbon. Unlike EC 5.4.4.4, geraniol isomerase, which only acts on (*S*)-linalool, this enzyme acts equally well on both enantiomers.
References: [396]

[EC 5.4.4.8 created 2017]

EC 5.4.99 Transferring other groups

EC 5.4.99.1
Accepted name: methylaspartate mutase
Reaction: L-*threo*-3-methylaspartate = L-glutamate
Other name(s): glutamate mutase; glutamic mutase; glutamic isomerase; glutamic acid mutase; glutamic acid isomerase; methylaspartic acid mutase; β-methylaspartate-glutamate mutase; glutamate isomerase
Systematic name: L-*threo*-3-methylaspartate carboxy-aminomethylmutase
Comments: Requires a cobamide coenzyme.
References: [40, 653]

[EC 5.4.99.1 created 1961]

EC 5.4.99.2
Accepted name: methylmalonyl-CoA mutase
Reaction: (*R*)-methylmalonyl-CoA = succinyl-CoA
Other name(s): methylmalonyl-CoA CoA-carbonyl mutase; methylmalonyl coenzyme A mutase; methylmalonyl coenzyme A carbonylmutase; (*S*)-methylmalonyl-CoA mutase; (*R*)-2-methyl-3-oxopropanoyl-CoA CoA-carbonylmutase [incorrect]
Systematic name: (*R*)-methylmalonyl-CoA CoA-carbonylmutase
Comments: Requires a cobamide coenzyme.
References: [39]

[EC 5.4.99.2 created 1961, modified 1983]

EC 5.4.99.3
Accepted name: 2-acetolactate mutase

Reaction: 2-acetolactate = 3-hydroxy-3-methyl-2-oxobutanoate
Other name(s): acetolactate mutase; acetohydroxy acid isomerase
Systematic name: 2-acetolactate methylmutase
Comments: Requires ascorbic acid; also converts 2-aceto-2-hydroxybutanoate to 3-hydroxy-3-methyl-2-oxopentanoate.
References: [16]

[EC 5.4.99.3 created 1972]

EC 5.4.99.4
Accepted name: 2-methyleneglutarate mutase
Reaction: 2-methyleneglutarate = 2-methylene-3-methylsuccinate
Other name(s): α-methyleneglutarate mutase
Systematic name: 2-methyleneglutarate carboxy-methylenemethylmutase
Comments: Requires a cobamide coenzyme.
References: [342, 343]

[EC 5.4.99.4 created 1972]

EC 5.4.99.5
Accepted name: chorismate mutase
Reaction: chorismate = prephenate
Other name(s): hydroxyphenylpyruvate synthase
Systematic name: chorismate pyruvatemutase
References: [104, 381, 581, 679]

[EC 5.4.99.5 created 1972]

[5.4.99.6 Transferred entry. isochorismate synthase. Now EC 5.4.4.2, isochorismate synthase]

[EC 5.4.99.6 created 1972, deleted 2003]

EC 5.4.99.7
Accepted name: lanosterol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = lanosterol
Other name(s): 2,3-epoxysqualene lanosterol cyclase; squalene-2,3-oxide-lanosterol cyclase; lanosterol 2,3-oxidosqualene cyclase; squalene 2,3-epoxide:lanosterol cyclase; 2,3-oxidosqualene sterol cyclase; oxidosqualene cyclase; 2,3-oxidosqualene cyclase; 2,3-oxidosqualene-lanosterol cyclase; oxidosqualene-lanosterol cyclase; squalene epoxidase-cyclase; (*S*)-2,3-epoxysqualene mutase (cyclizing, lanosterol-forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, lanosterol-forming)
References: [132]

[EC 5.4.99.7 created 1961 as EC 1.99.1.13, transferred 1965 to EC 1.14.1.3, part transferred 1972 to EC 5.4.99.7 rest to EC 1.14.99.7]

EC 5.4.99.8
Accepted name: cycloartenol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = cycloartenol
Other name(s): 2,3-epoxysqualene cycloartenol-cyclase; squalene-2,3-epoxide-cycloartenol cyclase; 2,3-epoxysqualene-cycloartenol cyclase; 2,3-oxidosqualene-cycloartenol cyclase; (*S*)-2,3-epoxysqualene mutase (cyclizing, cycloartenol-forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, cycloartenol-forming)
References: [512]

[EC 5.4.99.8 created 1972]

EC 5.4.99.9

Accepted name: UDP-galactopyranose mutase
Reaction: UDP-α-D-galactopyranose = UDP-α-D-galactofuranose
Other name(s): UGM; UDP-D-galactopyranose furanomutase
Systematic name: UDP-α-D-galactopyranose furanomutase
Comments: A flavoenzyme which generates UDP-α-D-glactofuranose required for cell wall formation in bacteria, fungi, and protozoa.
References: [626, 483, 138, 640]

[EC 5.4.99.9 created 1984, modified 2012]

[5.4.99.10 Deleted entry. isomaltulose synthetase. Now included with EC 5.4.99.11, isomaltulose synthase]

[EC 5.4.99.10 created 1984, deleted 1992]

EC 5.4.99.11

Accepted name: isomaltulose synthase
Reaction: sucrose = 6-*O*-α-D-glucopyranosyl-D-fructofuranose
Other name(s): isomaltulose synthetase; sucrose α-glucosyltransferase; trehalulose synthase
Systematic name: sucrose glucosylmutase
Comments: The enzyme simultaneously produces isomaltulose (6-*O*-α-D-glucopyranosyl-D-fructose) and smaller amounts of trehalulose (1-*O*-α-D-glucopyranosyl-β-D-fructose) from sucrose.
References: [87, 88]

[EC 5.4.99.11 created 1989 (EC 5.4.99.10 created 1984, incorporated 1992)]

EC 5.4.99.12

Accepted name: tRNA pseudouridine$^{38-40}$ synthase
Reaction: tRNA uridine$^{38-40}$ = tRNA pseudouridine$^{38-40}$
Other name(s): TruA; tRNA pseudouridine synthase I; PSUI; *hisT* (gene name)
Systematic name: tRNA-uridine$^{38-40}$ uracil mutase
Comments: The uridylate residues at positions 38, 39 and 40 of nearly all tRNAs are isomerized to pseudouridine. TruA specifically modifies uridines at positions 38, 39, and/or 40 in the anticodon stem loop of tRNAs with highly divergent sequences and structures [254].
References: [254, 251, 291, 628, 726, 174, 145, 30]

[EC 5.4.99.12 created 1990, modified 2011]

EC 5.4.99.13

Accepted name: isobutyryl-CoA mutase
Reaction: 2-methylpropanoyl-CoA = butanoyl-CoA
Other name(s): isobutyryl coenzyme A mutase; butyryl-CoA:isobutyryl-CoA mutase; *icmA* (gene name); *icmB* (gene name); *icmF* (gene name)
Systematic name: 2-methylpropanoyl-CoA CoA-carbonylmutase

Comments: This bacterial enzyme utilizes 5′-deoxyadenosylcobalamin as a cofactor. Following substrate binding, the enzyme catalyses the homolytic cleavage of the cobalt-carbon bond of AdoCbl, yielding cob(II)alamin and a 5′-deoxyadenosyl radical, which initiates the the carbon skeleton rearrangement reaction by hydrogen atom abstraction from the substrate. At the end of each catalytic cycle the 5′-deoxyadenosyl radical and cob(II)alamin recombine, regenerating the resting form of the cofactor. The enzyme is prone to inactivation resulting from occassional loss of the 5′-deoxyadenosyl molecule. Inactivated enzymes are repaired by the action of EC 2.5.1.17, cob(I)yrinic acid *a*,*c*-diamide adenosyltransferase, and a G-protein chaperone, which restore cob(II)alamin (which is first reduced to cob(I)alamin by an unidentified reductase) to 5′-deoxyadenosylcobalamin and load it back on the mutase. Some mutases are fused with their G-protein chaperone. These enzyme can also catalyse the interconversion of isovaleryl-CoA with pivalyl-CoA.
References: [68, 505, 106, 105, 284, 366]

[EC 5.4.99.13 created 1992, revised 2017]

EC 5.4.99.14
Accepted name: 4-carboxymethyl-4-methylbutenolide mutase
Reaction: 4-carboxymethyl-4-methylbut-2-en-1,4-olide = 4-carboxymethyl-3-methylbut-2-en-1,4-olide
Other name(s): 4-methyl-2-enelactone isomerase; 4-methylmuconolactone methylisomerase; 4-methyl-3-enelactone methyl isomerase
Systematic name: 4-carboxymethyl-4-methylbut-2-en-1,4-olide methylmutase
References: [72]

[EC 5.4.99.14 created 1992]

EC 5.4.99.15
Accepted name: (1→4)-α-D-glucan 1-α-D-glucosylmutase
Reaction: 4-[(1→4)-α-D-glucosyl]$_{n-1}$-D-glucose = 1-α-D-[(1→4)-α-D-glucosyl]$_{n-1}$-α-D-glucopyranoside
Other name(s): malto-oligosyltrehalose synthase; maltodextrin α-D-glucosyltransferase
Systematic name: (1→4)-α-D-glucan 1-α-D-glucosylmutase
Comments: The enzyme from *Arthrobacter sp.*, *Sulfolobus acidocaldarius* acts on (1→4)-α-D-glucans containing three or more (1→4)-α-linked D-glucose units. Not active towards maltose.
References: [405, 448, 447]

[EC 5.4.99.15 created 1999]

EC 5.4.99.16
Accepted name: maltose α-D-glucosyltransferase
Reaction: maltose = α,α-trehalose
Other name(s): trehalose synthase; maltose glucosylmutase
Systematic name: maltose α-D-glucosylmutase
References: [456, 457]

[EC 5.4.99.16 created 1999]

EC 5.4.99.17
Accepted name: squalene—hopene cyclase
Reaction: squalene = hop-22(29)-ene
Systematic name: squalene mutase (cyclizing, hop-22(29)-ene-forming)
Comments: The enzyme also produces the cyclization product hopan-22-ol by addition of water (*cf.* EC 4.2.1.129, squalene—hopanol cyclase). Hopene and hopanol are formed at a constant ratio of 5:1.
References: [247, 246, 538, 513]

[EC 5.4.99.17 created 2002, modified 2011]

EC 5.4.99.18

Accepted name: 5-(carboxyamino)imidazole ribonucleotide mutase
Reaction: 5-carboxyamino-1-(5-phospho-D-ribosyl)imidazole = 5-amino-1-(5-phospho-D-ribosyl)imidazole-4-carboxylate
Other name(s): N^5-CAIR mutase; PurE; N^5-carboxyaminoimidazole ribonucleotide mutase; class I PurE
Systematic name: 5-carboxyamino-1-(5-phospho-D-ribosyl)imidazole carboxymutase
Comments: In eubacteria, fungi and plants, this enzyme, along with EC 6.3.4.18, 5-(carboxyamino)imidazole ribonucleotide synthase, is required to carry out the single reaction catalysed by EC 4.1.1.21, phosphoribosylaminoimidazole carboxylase, in vertebrates [167]. In the absence of EC 6.3.2.6, phosphoribosylaminoimidazolesuccinocarboxamide synthase, the reaction is reversible [422]. The substrate is readily converted into 5-amino-1-(5-phospho-D-ribosyl)imidazole by non-enzymic decarboxylation [422].
References: [423, 440, 422, 407, 168, 167]

[EC 5.4.99.18 created 2006]

EC 5.4.99.19

Accepted name: 16S rRNA pseudouridine^{516} synthase
Reaction: 16S rRNA uridine^{516} = 16S rRNA pseudouridine^{516}
Other name(s): 16S RNA pseudouridine^{516} synthase; 16S PsiI516 synthase; 16S RNA Ψ^{516} synthase; RNA pseudouridine synthase RsuA; RsuA; 16S RNA pseudouridine 516 synthase
Systematic name: 16S rRNA-uridine^{516} uracil mutase
Comments: The enzyme is specific for uridine^{516} in 16S rRNA. *In vitro*, the enzyme does not modify free 16S rRNA. The preferred substrate is a 5′-terminal fragment of 16S rRNA complexed with 30S ribosomal proteins [680].
References: [680, 101, 571]

[EC 5.4.99.19 created 2011]

EC 5.4.99.20

Accepted name: 23S rRNA pseudouridine^{2457} synthase
Reaction: 23S rRNA uridine^{2457} = 23S rRNA pseudouridine^{2457}
Other name(s): RluE; YmfC
Systematic name: 23S rRNA-uridine^{2457} uracil mutase
Comments: The enzyme modifies uridine^{2457} in a stem of 23S RNA in *Escherichia coli*.
References: [76, 477]

[EC 5.4.99.20 created 2011]

EC 5.4.99.21

Accepted name: 23S rRNA pseudouridine^{2604} synthase
Reaction: 23S rRNA uridine^{2604} = 23S rRNA pseudouridine^{2604}
Other name(s): RluF; YjbC
Systematic name: 23S rRNA-uridine^{2604} uracil mutase
Comments: The enzyme is not completely specific for uridine^{2604} and can, to a small extent, also react with uridine^{2605} [76].
References: [76, 15, 600]

[EC 5.4.99.21 created 2011]

EC 5.4.99.22

Accepted name: 23S rRNA pseudouridine^{2605} synthase

Reaction: 23S rRNA uridine^{2605} = 23S rRNA pseudouridine^{2605}
Other name(s): RluB; YciL
Systematic name: 23S rRNA-uridine^{2605} uracil mutase
Comments: Pseudouridine synthase RluB converts uridine^{2605} of 23S rRNA to pseudouridine.
References: [76, 278]

[EC 5.4.99.22 created 2011]

EC 5.4.99.23
Accepted name: 23S rRNA pseudouridine$^{1911/1915/1917}$ synthase
Reaction: 23S rRNA uridine^{1911}/uridine^{1915}/uridine^{1917} = 23S rRNA pseudouridine^{1911}/pseudouridine^{1915}/pseudouridine^{1917}
Other name(s): RluD; pseudouridine synthase RluD
Systematic name: 23S rRNA-uridine$^{1911/1915/1917}$ uracil mutase
Comments: Pseudouridine synthase RluD converts uridines at positions 1911, 1915, and 1917 of 23S rRNA to pseudouridines. These nucleotides are located in the functionally important helix-loop 69 of 23S rRNA [360].
References: [360, 154, 570, 681]

[EC 5.4.99.23 created 2011]

EC 5.4.99.24
Accepted name: 23S rRNA pseudouridine$^{955/2504/2580}$ synthase
Reaction: 23S rRNA uridine^{955}/uridine^{2504}/uridine^{2580} = 23S rRNA pseudouridine^{955}/pseudouridine^{2504}/pseudouridine^{2580}
Other name(s): RluC; pseudouridine synthase RluC
Systematic name: 23S rRNA-uridine$^{955/2504/2580}$ uracil mutase
Comments: The enzyme converts uridines at position 955, 2504 and 2580 of 23S rRNA to pseudouridines.
References: [278, 102, 103, 621]

[EC 5.4.99.24 created 2011]

EC 5.4.99.25
Accepted name: tRNA pseudouridine^{55} synthase
Reaction: tRNA uridine^{55} = tRNA pseudouridine^{55}
Other name(s): TruB; aCbf5; Pus4; YNL292w (gene name); Ψ^{55} tRNA pseudouridine synthase; tRNA:Ψ^{55}-synthase; tRNA pseudouridine 55 synthase; tRNA:pseudouridine-55 synthase; Ψ^{55} synthase; tRNA Ψ^{55} synthase; tRNA:Ψ^{55} synthase; tRNA-uridine^{55} uracil mutase; Pus10; tRNA-uridine$^{54/55}$ uracil mutase
Systematic name: tRNA-uridine^{55} uracil mutase
Comments: Pseudouridine synthase TruB from *Escherichia coli* specifically modifies uridine^{55} in tRNA molecules [464]. The bifunctional archaeal enzyme also catalyses the pseudouridylation of uridine^{54} [211]. It is not known whether the enzyme from *Escherichia coli* can also act on position 54 *in vitro*, since this position is occupied in *Escherichia coli* tRNAs by thymine.
References: [464, 44, 493, 86, 240, 211]

[EC 5.4.99.25 created 2011, modified 2011]

EC 5.4.99.26
Accepted name: tRNA pseudouridine^{65} synthase
Reaction: tRNA uridine^{65} = tRNA pseudouridine^{65}
Other name(s): TruC; YqcB
Systematic name: tRNA-uridine^{65} uracil mutase

Comments: TruC specifically modifies uridines at positions 65 in tRNA.
References: [76]

[EC 5.4.99.26 created 2011]

EC 5.4.99.27
Accepted name: tRNA pseudouridine^{13} synthase
Reaction: tRNA uridine^{13} = tRNA pseudouridine^{13}
Other name(s): TruD; YgbO; tRNA PSI13 synthase; RNA:PSI-synthase Pus7p; Pus7p; RNA:pseudouridine-synthase Pus7p; Pus7 protein
Systematic name: tRNA-uridine^{13} uracil mutase
Comments: Pseudouridine synthase TruD from *Escherichia coli* specifically acts on uridine^{13} in tRNA [82, 304]. The Pus7 protein from *Saccharomyces cerevisiae* is a multisite-multisubstrate pseudouridine synthase that is able to modify uridine^{13} in several yeast tRNAs, uridine^{35} in the pre-tRNA^{Tyr}, uridine^{35} in U2 small nuclear RNA, and uridine^{50} in 5S rRNA [634].
References: [158, 82, 304, 48, 634]

[EC 5.4.99.27 created 2011]

EC 5.4.99.28
Accepted name: tRNA pseudouridine^{32} synthase
Reaction: tRNA uridine^{32} = tRNA pseudouridine^{32}
Other name(s): RluA (ambiguous); pseudouridine synthase RluA (ambiguous); Pus9p; Rib$_2$/Pus8p
Systematic name: tRNA-uridine^{32} uracil mutase
Comments: The dual-specificity enzyme from *Escherichia coli* also catalyses the formation of pseudouridine^{746} in 23S rRNA [682]. *cf.* EC 5.4.99.29 (23S rRNA pseudouridine^{746} synthase).
References: [239, 580, 510, 501, 682, 47]

[EC 5.4.99.28 created 2011, modified 2011]

EC 5.4.99.29
Accepted name: 23S rRNA pseudouridine^{746} synthase
Reaction: 23S rRNA uridine^{746} = 23S rRNA pseudouridine^{746}
Other name(s): RluA (ambiguous); 23S RNA PSI746 synthase; 23S rRNA pseudouridine synthase; pseudouridine synthase RluA (ambiguous)
Systematic name: 23S rRNA-uridine^{746} uracil mutase
Comments: RluA is the sole protein responsible for the *in vivo* formation of 23S RNA pseudouridine^{746} [510]. The dual-specificity enzyme also catalyses the formation of uridine^{32} in tRNA [682]. *cf.* EC 5.4.99.28 (tRNA pseudouridine^{32} synthase).
References: [239, 510, 682]

[EC 5.4.99.29 created 2011]

EC 5.4.99.30
Accepted name: UDP-arabinopyranose mutase
Reaction: UDP-β-L-arabinofuranose = UDP-β-L-arabinopyranose
Other name(s): Os03g40270 protein; UAM1; UAM3; RGP1; RGP3; OsUAM1; OsUAM2; Os03g0599800 protein; Os07g41360 protein
Systematic name: UDP-arabinopyranose pyranomutase
Comments: The reaction is reversible and at thermodynamic equilibrium the pyranose form is favored over the furanose form (90:10) [332].
References: [332, 331, 330]

[EC 5.4.99.30 created 2011]

EC 5.4.99.31

Accepted name: thalianol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = thalianol
Other name(s): (*S*)-2,3-epoxysqualene mutase (cyclizing, thalianol-forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, thalianol-forming)
References: [161]

[EC 5.4.99.31 created 2011]

EC 5.4.99.32

Accepted name: protostadienol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = (17*Z*)-protosta-17(20),24-dien-3β-ol
Other name(s): PdsA; (*S*)-2,3-epoxysqualene mutase [cyclizing, (17*Z*)-protosta-17(20),24-dien-3β-ol-forming]
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase [cyclizing, (17*Z*)-protosta-17(20),24-dien-3β-ol-forming]
Comments: (17*Z*)-Protosta-17(20),24-dien-3β-ol is a precursor of the steroidal antibiotic helvolic acid.
References: [378]

[EC 5.4.99.32 created 2011]

EC 5.4.99.33

Accepted name: cucurbitadienol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = cucurbitadienol
Other name(s): CPQ (gene name); (*S*)-2,3-epoxysqualene mutase (cyclizing, cucurbitadienol-forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, cucurbitadienol-forming)
References: [556]

[EC 5.4.99.33 created 2011]

EC 5.4.99.34

Accepted name: germanicol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = germanicol
Other name(s): RsM1; (*S*)-2,3-epoxysqualene mutase (cyclizing, germanicol-forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualenee mutase (cyclizing, germanicol-forming)
Comments: The enzyme produces germanicol, β-amyrin and lupeol in the ratio 63:33:4.
References: [43]

[EC 5.4.99.34 created 2011]

EC 5.4.99.35

Accepted name: taraxerol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = taraxerol
Other name(s): RsM2; (*S*)-2,3-epoxysqualene mutase (cyclizing, taraxerol-forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, taraxerol-forming)
Comments: The enzyme gives taraxerol, β-amyrin and lupeol in the ratio 70:17:13.
References: [43]

[EC 5.4.99.35 created 2011]

EC 5.4.99.36

Accepted name: isomultiflorenol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = isomultiflorenol
Other name(s): LcIMS1; (*S*)-2,3-epoxysqualene mutase (cyclizing, isomultiflorenol-forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualenee mutase (cyclizing, isomultiflorenol-forming)
References: [225]

[EC 5.4.99.36 created 2011]

EC 5.4.99.37

Accepted name: dammaradiene synthase
Reaction: squalene = dammara-20,24-diene
Systematic name: squalene mutase (cyclizing, dammara-20,24-diene-forming)
References: [562]

[EC 5.4.99.37 created 2011]

EC 5.4.99.38

Accepted name: camelliol C synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = camelliol C
Other name(s): CAMS1; LUP3 (gene name)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, camelliol-C-forming)
Comments: The product is 97% camelliol, 2% achilleol A and 0.2% β-amyrin. Achilleol is an isomer of camelliol C with a 4-methylenecyclohexanol ring system. This enzyme probably evolved from EC 5.4.99.39, β-amyrin synthase.
References: [328]

[EC 5.4.99.38 created 2011]

EC 5.4.99.39

Accepted name: β-amyrin synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = β-amyrin
Other name(s): 2,3-oxidosqualene β-amyrin cyclase; AsbAS1; BPY; EtAS; GgbAS1; LjAMY1; MtAMY1; PNY; BgbAS
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, β-amyrin-forming)
Comments: Some organism possess a monofunctional β-amyrin synthase [3,4,6-11], other have a multifunctional enzyme that also catalyses the synthesis of α-amyrin (EC 5.4.99.40) [257] or lupeol (EC 5.4.99.41) [267].
References: [3, 4, 346, 226, 257, 267, 719, 227, 287, 43, 375]

[EC 5.4.99.39 created 2011]

EC 5.4.99.40

Accepted name: α-amyrin synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = α-amyrin
Other name(s): 2,3-oxidosqualene α-amyrin cyclase; mixed amyrin synthase
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, α-amyrin-forming)
Comments: A multifunctional enzyme which produces both α- and β-amyrin (see EC 5.4.99.39, β-amyrin synthase).
References: [434]

[EC 5.4.99.40 created 2011]

EC 5.4.99.41

Accepted name: lupeol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = lupeol
Other name(s): LUPI; BPW; *RcLUS*
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, lupeol-forming)
Comments: Also forms some β-amyrin. The recombinant enzyme from *Arabidopsis thaliana* [548] 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 4.2.1.128 (lupan-3β,20-diol synthase).
References: [237, 559, 548, 719, 227, 208, 43]

[EC 5.4.99.41 created 2011]

EC 5.4.99.42

Accepted name: tRNA pseudouridine^{31} synthase
Reaction: tRNA uridine^{31} = tRNA pseudouridine^{31}
Other name(s): Pus6p
Systematic name: tRNA-uridine^{31} uracil mutase
Comments: The enzyme specifically acts on uridine^{31} in tRNA.
References: [26]

[EC 5.4.99.42 created 2011]

EC 5.4.99.43

Accepted name: 21S rRNA pseudouridine^{2819} synthase
Reaction: 21S rRNA uridine^{2819} = 21S rRNA pseudouridine^{2819}
Other name(s): Pus5p
Systematic name: 21S rRNA-uridine^{2819} uracil mutase
Comments: The enzyme specifically acts on uridine^{2819} in 21S rRNA.
References: [25]

[EC 5.4.99.43 created 2011]

EC 5.4.99.44

Accepted name: mitochondrial tRNA pseudouridine$^{27/28}$ synthase
Reaction: mitochondrial tRNA uridine$^{27/28}$ = mitochondrial tRNA pseudouridine$^{27/28}$
Other name(s): Pus2; Pus2p; RNA:pseudouridine synthases 2
Systematic name: mitochondrial tRNA-uridine$^{27/28}$ uracil mutase
Comments: The mitochondrial enzyme Pus2p is specific for position 27 or 28 in mitochondrial tRNA [46].
References: [46]

[EC 5.4.99.44 created 2011]

EC 5.4.99.45

Accepted name: tRNA pseudouridine$^{38/39}$ synthase
Reaction: tRNA uridine$^{38/39}$ = tRNA pseudouridine$^{38/39}$
Other name(s): Deg1; Pus3p; pseudouridine synthase 3
Systematic name: tRNA-uridine$^{38/39}$ uracil mutase
Comments: The enzyme from *Saccharomyces cerevisiae* is active only towards uridine^{38} and uridine^{39}, and shows no activity with uridine^{40} (*cf.* EC 5.4.99.12, tRNA pseudouridine$^{38-40}$ synthase) [352]. *In vitro* the enzyme from mouse is active on uridine^{39} and very slightly on uridine^{38} (human tRNA^{Leu}) [92].
References: [352, 92]

[EC 5.4.99.45 created 2011]

EC 5.4.99.46

Accepted name: shionone synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = shionone
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, shionone-forming)
Comments: The enzyme gives traces of four other triterpenoids
References: [540]

[EC 5.4.99.46 created 2011]

EC 5.4.99.47

Accepted name: parkeol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = parkeol
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, parkeol-forming)
Comments: The enzyme from rice (*Oryza sativa*) produces parkeol as a single product [264].
References: [264]

[EC 5.4.99.47 created 2011]

EC 5.4.99.48

Accepted name: achilleol B synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = achilleol B
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, achilleol-B-forming)
Comments: Achilleol B is probably formed by cleavage of the 8-14 and 9-10 bonds of (3*S*)-2,3-epoxy-2,3-dihydrosqualene as part of the cyclization reaction, after formation of the oleanane skeleton.
References: [264]

[EC 5.4.99.48 created 2011]

EC 5.4.99.49

Accepted name: glutinol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = glutinol
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, glutinol-forming)
Comments: The enzyme from *Kalanchoe daigremontiana* also gives traces of other triterpenoids.
References: [650]

[EC 5.4.99.49 created 2011]

EC 5.4.99.50

Accepted name: friedelin synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = friedelin
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, friedelin-forming)
Comments: The enzyme from *Kalanchoe daigremontiana* also gives traces of other triterpenoids.
References: [650]

[EC 5.4.99.50 created 2011]

EC 5.4.99.51

Accepted name: baccharis oxide synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = baccharis oxide

Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, baccharis-oxide-forming)
Comments: The enzyme from *Stevia rebaudiana* also gives traces of other triterpenoids.
References: [557]

[EC 5.4.99.51 created 2011]

EC 5.4.99.52
Accepted name: α-seco-amyrin synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = α-seco-amyrin
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, α-seco-amyrin-forming)
Comments: The enzyme from *Arabidopsis thaliana* is multifunctional and produces about equal amounts of α- and β-seco-amyrin. See EC 5.4.99.54, β-seco-amyrin synthase.
References: [558]

[EC 5.4.99.52 created 2011]

EC 5.4.99.53
Accepted name: marneral synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = marneral
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, marneral-forming)
Comments: Marneral is a triterpenoid formed by Grob fragmentation of the A ring of 2,3-epoxy-2,3-dihydrosqualene during cyclization.
References: [686]

[EC 5.4.99.53 created 2011]

EC 5.4.99.54
Accepted name: β-seco-amyrin synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = β-seco-amyrin
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, β-seco-amyrin-forming)
Comments: The enzyme from *Arabidopsis thaliana* is multifunctional and produces about equal amounts of α- and β-seco-amyrin. See EC 5.4.99.52, α-seco-amyrin synthase.
References: [558]

[EC 5.4.99.54 created 2011]

EC 5.4.99.55
Accepted name: δ-amyrin synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = δ-amyrin
Other name(s): SlTTS2 (gene name)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, δ-amyrin-forming)
Comments: The enzyme from tomato (*Solanum lycopersicum*) gives 48% δ-amyrin, 18% α-amyrin, 13% β-amyrin and traces of three or four other triterpenoid alcohols [649]. See also EC 5.4.99.40, α-amyrin synthase and EC 5.4.99.39, β-amyrin synthase.
References: [649]

[EC 5.4.99.55 created 2011]

EC 5.4.99.56
Accepted name: tirucalladienol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = tirucalla-7,24-dien-3β-ol
Other name(s): PEN3

Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, tirucalla-7,24-dien-3β-ol-forming)
Comments: The product from *Arabidopsis thaliana* is 85% tirucalla-7,24-dien-3β-ol with trace amounts of other triterpenoids.
References: [435]

[EC 5.4.99.56 created 2011]

EC 5.4.99.57
Accepted name: baruol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = baruol
Other name(s): BARS1
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, baruol-forming)
Comments: The enzyme from *Arabidopsis thaliana* also produces traces of 22 other triterpenoids.
References: [379]

[EC 5.4.99.57 created 2012]

EC 5.4.99.58
Accepted name: methylornithine synthase
Reaction: L-lysine = (3*R*)-3-methyl-D-ornithine
Other name(s): PylB
Systematic name: L-lysine carboxy-aminomethylmutase
Comments: 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 reaction is part of the biosynthesis pathway of pyrrolysine, a naturally occurring amino acid found in some archaeal methyltransferases.
References: [184, 498]

[EC 5.4.99.58 created 2012]

EC 5.4.99.59
Accepted name: dTDP-fucopyranose mutase
Reaction: dTDP-α-D-fucopyranose = dTDP-α-D-fucofuranose
Other name(s): Fcf2
Systematic name: dTDP-α-D-fucopyranose furanomutase
Comments: The enzyme is involved in the biosynthesis of the *Escherichia coli* O52 O antigen.
References: [646]

[EC 5.4.99.59 created 2013]

EC 5.4.99.60
Accepted name: cobalt-precorrin-8 methylmutase
Reaction: cobalt-precorrin-8 = cobyrinate
Other name(s): *cbiC* (gene name)
Systematic name: precorrin-8 11,12-methylmutase
Comments: The enzyme, which participates in the anaerobic (early cobalt insertion) adenosylcobalamin biosynthesis pathway, catalyses the conversion of cobalt-precorrin-8 to cobyrinate by methyl rearrangement. The equivalent enzyme in the aerobic pathway is EC 5.4.99.61, precorrin-8X methylmutase.
References: [523, 527, 689, 431]

[EC 5.4.99.60 created 2014]

EC 5.4.99.61

Accepted name: precorrin-8X methylmutase
Reaction: precorrin-8X = hydrogenobyrinate
Other name(s): precorrin isomerase; hydrogenobyrinic acid-binding protein; *cobH* (gene name)
Systematic name: precorrin-8X 11,12-methylmutase
Comments: The enzyme, which participates in the aerobic (late cobalt insertion) adenosylcobalamin biosynthesis pathway, catalyses the conversion of precorrin-8X to hydrogenobyrinate by methyl rearrangement. The equivalent enzyme in the anaerobic pathway is EC 5.4.99.60, cobalt-precorrin-8 methylmutase.
References: [616, 115, 563]

[EC 5.4.99.61 created 1999 as EC 5.4.1.2, transferred 2014 to EC 5.4.99.61]

EC 5.4.99.62

Accepted name: D-ribose pyranase
Reaction: β-D-ribopyranose = β-D-ribofuranose
Other name(s): RbsD
Systematic name: D-ribopyranose furanomutase
Comments: The enzyme also catalyses the conversion between β-allopyranose and β-allofuranose.
References: [317, 530]

[EC 5.4.99.62 created 2014]

EC 5.4.99.63

Accepted name: ethylmalonyl-CoA mutase
Reaction: (2*R*)-ethylmalonyl-CoA = (2*S*)-methylsuccinyl-CoA
Other name(s): Ecm
Systematic name: (2*R*)-ethylmalonyl-CoA CoA-carbonylmutase
Comments: The enzyme, characterized from the bacterium *Rhodobacter sphaeroides*, is involved in the ethylmalonyl-CoA pathway for acetyl-CoA assimilation. Requires coenzyme B_{12} for activity.
References: [157]

[EC 5.4.99.63 created 2015]

EC 5.4.99.64

Accepted name: 2-hydroxyisobutanoyl-CoA mutase
Reaction: 2-hydroxy-2-methylpropanoyl-CoA = (*S*)-3-hydroxybutanoyl-CoA
Other name(s): *hcmAB* (gene names)
Systematic name: 2-hydroxy-2-methylpropanoyl-CoA mutase
Comments: The enzyme, characterized from the bacterium *Aquincola tertiaricarbonis*, uses radical chemistry to rearrange the positions of both a methyl group and a hydroxyl group. It consists of two subunits, the smaller one containing a cobalamin cofactor. It plays a central role in the degradation of assorted substrates containing a *tert*-butyl moiety.
References: [695, 344]

[EC 5.4.99.64 created 2016 as EC 5.3.3.20, transferred 2017 to EC 5.4.99.64]

EC 5.4.99.65

Accepted name: pre-α-onocerin synthase
Reaction: (3*S*,22*S*)-2,3:22,23-diepoxy-2,3,22,23-tetrahydrosqualene = pre-α-onocerin
Other name(s): LCC
Systematic name: (3*S*,22*S*)-2,3:22,23-diepoxy-2,3,22,23-tetrahydrosqualene mutase (cyclizing, pre-α-onocerin-forming)
Comments: Isolated from the plant *Lycopodium clavatum*. The enzyme does not act on (3*S*)-2,3-epoxy-2,3-dihydrosqualene and does not form any α-onocerin.

References: [29]

[EC 5.4.99.65 created 2017]

EC 5.4.99.66

Accepted name: α-onocerin synthase
Reaction: pre-α-onocerin = α-onocerin
Other name(s): LCD
Systematic name: pre-α-onocerin mutase (cyclizing, α-onocerin-forming)
Comments: Isolated from the plant *Lycopodium clavatum*.
References: [29]

[EC 5.4.99.66 created 2017]

EC 5.4.99.67

Accepted name: 4-amino-4-deoxychorismate mutase
Reaction: 4-amino-4-deoxychorismate = 4-amino-4-deoxyprephenate
Other name(s): *cmlD* (gene name); *papB* (gene name)
Systematic name: 4-amino-4-deoxychorismate pyruvatemutase
Comments: The enzyme, characterized from the bacteria *Streptomyces venezuelae* and *Streptomyces pristinaespiralis*, participates in the biosynthesis of the antibiotics chloramphenicol and pristinamycin IA, respectively. *cf.* EC 5.4.99.5, chorismate mutase.
References: [57, 229]

[EC 5.4.99.67 created 2019]

EC 5.5 Intramolecular lyases

This subclass contains a single sub-subclass for enzymes that catalyse reactions in which a group can be regarded as being eliminated from one part of a molecule, leaving a double bond, while remaining covalently attached to the molecule (intramolecular lyases; EC 5.5.1).

EC 5.5.1 Intramolecular lyases (only sub-subclass identified to date)

EC 5.5.1.1

Accepted name: muconate cycloisomerase
Reaction: (+)-muconolactone = *cis*,*cis*-muconate
Other name(s): muconate cycloisomerase I; *cis*,*cis*-muconate-lactonizing enzyme; *cis*,*cis*-muconate cycloisomerase; muconate lactonizing enzyme; 4-carboxymethyl-4-hydroxyisocrotonolactone lyase (decyclizing); CatB; MCI; 2,5-dihydro-5-oxofuran-2-acetate lyase (decyclizing); 2,5-dihydro-5-oxofuran-2-acetate lyase (ring-opening)
Systematic name: (+)-muconolactone lyase (ring-opening)
Comments: Requires Mn^{2+}. Also acts (in the reverse reaction) on 3-methyl-*cis*,*cis*-muconate and, very slowly, on *cis*,*trans*-muconate. Not identical with EC 5.5.1.7 (chloromuconate cycloisomerase) or EC 5.5.1.11 (dichloromuconate cycloisomerase).
References: [470, 472, 569]

[EC 5.5.1.1 created 1961]

EC 5.5.1.2

Accepted name: 3-carboxy-*cis*,*cis*-muconate cycloisomerase
Reaction: 2-carboxy-2,5-dihydro-5-oxofuran-2-acetate = *cis*,*cis*-butadiene-1,2,4-tricarboxylate
Other name(s): β-carboxymuconate lactonizing enzyme; 3-carboxymuconolactone hydrolase; 2-carboxy-2,5-dihydro-5-oxofuran-2-acetate lyase (decyclizing)
Systematic name: 2-carboxy-2,5-dihydro-5-oxofuran-2-acetate lyase (ring-opening)
References: [471, 472]

[EC 5.5.1.2 created 1972]

EC 5.5.1.3

Accepted name: tetrahydroxypteridine cycloisomerase
Reaction: tetrahydroxypteridine = xanthine-8-carboxylate
Systematic name: tetrahydroxypteridine lyase (isomerizing)
References: [415]

[EC 5.5.1.3 created 1972]

EC 5.5.1.4

Accepted name: inositol-3-phosphate synthase
Reaction: D-glucose 6-phosphate = 1D-*myo*-inositol 3-phosphate
Other name(s): *myo*-inositol-1-phosphate synthase; D-glucose 6-phosphate cycloaldolase; inositol 1-phosphate synthatase; glucose 6-phosphate cyclase; inositol 1-phosphate synthetase; glucose-6-phosphate inositol monophosphate cycloaldolase; glucocycloaldolase; 1L-*myo*-inositol-1-phosphate lyase (isomerizing)
Systematic name: 1D-*myo*-inositol-3-phosphate lyase (isomerizing)
Comments: Requires NAD^+, which dehydrogenates the -CHOH- group to -CO- at C-5 of the glucose 6-phosphate, making C-6 into an active methylene, able to condense with the -CHO at C-1. Finally, the enzyme-bound NADH reconverts C-5 into the -CHOH- form.
References: [152, 555, 41, 42]

[EC 5.5.1.4 created 1972, modified 2001]

EC 5.5.1.5

Accepted name: carboxy-*cis*,*cis*-muconate cyclase
Reaction: 3-carboxy-2,5-dihydro-5-oxofuran-2-acetate = 3-carboxy-*cis*,*cis*-muconate
Other name(s): 3-carboxymuconate cyclase; 3-carboxy-2,5-dihydro-5-oxofuran-2-acetate lyase (decyclizing)
Systematic name: 3-carboxy-2,5-dihydro-5-oxofuran-2-acetate lyase (ring-opening)
References: [207]

[EC 5.5.1.5 created 1972]

EC 5.5.1.6

Accepted name: chalcone isomerase
Reaction: a chalcone = a flavanone
Other name(s): chalcone-flavanone isomerase; flavanone lyase (decyclizing)
Systematic name: flavanone lyase (ring-opening)
References: [437]

[EC 5.5.1.6 created 1972]

EC 5.5.1.7

Accepted name: chloromuconate cycloisomerase

Reaction: (2*R*)-2-chloro-2,5-dihydro-5-oxofuran-2-acetate = 3-chloro-*cis*,*cis*-muconate
Other name(s): muconate cycloisomerase II; 2-chloro-2,5-dihydro-5-oxofuran-2-acetate lyase (decyclizing); 2-chloro-2,5-dihydro-5-oxofuran-2-acetate lyase (ring-opening)
Systematic name: (2*R*)-2-chloro-2,5-dihydro-5-oxofuran-2-acetate lyase (ring-opening)
Comments: Requires Mn^{2+}. The product of cycloisomerization of 3-chloro-*cis*,*cis*-muconate spontaneously eliminates chloride to produce *cis*-4-carboxymethylenebut-2-en-4-olide. Also acts on 2-chloro-*cis*,*cis*-muconate. Not identical with EC 5.5.1.1 (muconate cycloisomerase) or EC 5.5.1.11 (dichloromuconate cycloisomerase).
References: [543, 300, 286]

[EC 5.5.1.7 created 1983]

EC 5.5.1.8

Accepted name: (+)-bornyl diphosphate synthase
Reaction: geranyl diphosphate = (+)-bornyl diphosphate
Other name(s): bornyl pyrophosphate synthase (ambiguous); bornyl pyrophosphate synthetase (ambiguous); (+)-bornylpyrophosphate cyclase; geranyl-diphosphate cyclase (ambiguous); (+)-bornyl-diphosphate lyase (decyclizing)
Systematic name: (+)-bornyl-diphosphate lyase (ring-opening)
Comments: Requires Mg^{2+}. The enzyme from *Salvia officinalis* (sage) can also use (3*R*)-linalyl diphosphate or more slowly neryl diphosphate *in vitro* [112]. The reaction proceeds via isomeration of geranyl diphosphate to (3*R*)-linalyl diphosphate. The oxygen and phosphorus originally linked to C-1 of geranyl diphosphate end up linked to C-2 of (+)-bornyl diphosphate [112]. *cf.* EC 5.5.1.22 [(–)-bornyl diphosphate synthase].
References: [111, 110, 112, 109, 114, 413, 670, 659, 490]

[EC 5.5.1.8 created 1984, modified 2012]

EC 5.5.1.9

Accepted name: cycloeucalenol cycloisomerase
Reaction: cycloeucalenol = obtusifoliol
Other name(s): cycloeucalenol—obtusifoliol isomerase; cycloeucalenol lyase (cyclopropane-decyclizing)
Systematic name: cycloeucalenol lyase (cyclopropane-ring opening)
Comments: Opens the cyclopropane ring of a number of related 4α-methyl-9β-19-cyclosterols, but not those with a 4β-methyl group, with formation of an 8(9) double bond. Involved in the synthesis of plant sterols.
References: [233, 500]

[EC 5.5.1.9 created 1986]

EC 5.5.1.10

Accepted name: α-pinene-oxide decyclase
Reaction: α-pinene oxide = (*Z*)-2-methyl-5-isopropylhexa-2,5-dienal
Other name(s): α-pinene oxide lyase; α-pinene-oxide lyase (decyclizing)
Systematic name: α-pinene-oxide lyase (ring-opening)
Comments: Both rings of pinene are cleaved in the reaction.
References: [205]

[EC 5.5.1.10 created 1990]

EC 5.5.1.11

Accepted name: dichloromuconate cycloisomerase
Reaction: 2,4-dichloro-2,5-dihydro-5-oxofuran-2-acetate = 2,4-dichloro-*cis*,*cis*-muconate

Other name(s): 2,4-dichloro-2,5-dihydro-5-oxofuran-2-acetate lyase (decyclizing)
Systematic name: 2,4-dichloro-2,5-dihydro-5-oxofuran-2-acetate lyase (ring-opening)
Comments: Requires Mn^{2+}. The product of cycloisomerization of dichloro-*cis*,*cis*-muconate spontaneously eliminates chloride to produce *cis*-4-carboxymethylene-3-chlorobut-2-en-4-olide. Also acts, in the reverse direction, on *cis*,*cis*-muconate and its monochloro-derivatives, but with lower affinity. Not identical with EC 5.5.1.1 (muconate cycloisomerase) or EC 5.5.1.7 (chloromuconate cycloisomerase).
References: [338]

[EC 5.5.1.11 created 1992]

EC 5.5.1.12
Accepted name: copalyl diphosphate synthase
Reaction: geranylgeranyl diphosphate = (+)-copalyl diphosphate
Other name(s): (+)-copalyl-diphosphate lyase (decyclizing)
Systematic name: (+)-copalyl-diphosphate lyase (ring-opening)
Comments: In some plants, such as *Salvia miltiorrhiza*, this enzyme is monofunctional. In other plants this activity is often a part of a bifunctional enzyme. For example, in *Selaginella moellendorffii* this activity is catalysed by a bifunctional enzyme that also catalyses EC 4.2.3.131, miltiradiene synthase, while in the tree *Abies grandis* (grand fir) it is catalysed by a bifunctional enzyme that also catalyses EC 4.2.3.18, abietadiene synthase.
References: [491, 595, 489, 507, 488]

[EC 5.5.1.12 created 2002, modified 2012]

EC 5.5.1.13
Accepted name: *ent*-copalyl diphosphate synthase
Reaction: geranylgeranyl diphosphate = *ent*-copalyl diphosphate
Other name(s): *ent*-kaurene synthase A; *ent*-kaurene synthetase A; *ent*-CDP synthase; *ent*-copalyl-diphosphate lyase (decyclizing)
Systematic name: *ent*-copalyl-diphosphate lyase (ring-opening)
Comments: Part of a bifunctional enzyme involved in the biosynthesis of kaurene. See also EC 4.2.3.19 (*ent*-kaurene synthase)
References: [160, 599, 302, 624]

[EC 5.5.1.13 created 2002]

EC 5.5.1.14
Accepted name: *syn*-copalyl-diphosphate synthase
Reaction: geranylgeranyl diphosphate = 9α-copalyl diphosphate
Other name(s): OsCyc1; OsCPSsyn; *syn*-CPP synthase; *syn*-copalyl diphosphate synthase; 9α-copalyl-diphosphate lyase (decyclizing)
Systematic name: 9α-copalyl-diphosphate lyase (ring-opening)
Comments: Requires a divalent metal ion, preferably Mg^{2+}, for activity. This class II terpene synthase produces *syn*-copalyl diphosphate, a precursor of several rice phytoalexins, including oryzalexin S and momilactones A and B. 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. The enzyme is constitutively expressed in the roots of plants where one of its products, momilactone B, acts as an allelochemical (a molecule released into the environment to suppress the growth of neighbouring plants). In other tissues the enzyme is upregulated by conditions that stimulate the biosynthesis of phytoalexins.
References: [473, 688]

[EC 5.5.1.14 created 2008]

EC 5.5.1.15

Accepted name: terpentedienyl-diphosphate synthase
Reaction: geranylgeranyl diphosphate = terpentedienyl diphosphate
Other name(s): terpentedienol diphosphate synthase; Cyc1; clerodadienyl diphosphate synthase; terpentedienyl-diphosphate lyase (decyclizing)
Systematic name: terpentedienyl-diphosphate lyase (ring-opening)
Comments: Requires Mg^{2+}. Contains a DXDD motif, which is a characteristic of diterpene cylases whose reactions are initiated by protonation at the 14,15-double bond of geranylgeranyl diphosphate (GGDP) [215]. The triggering proton is lost at the end of the cyclization reaction [151]. The product of the reaction, terpentedienyl diphosphate, is the substrate for EC 4.2.3.36, terpentetriene synthase and is a precursor of the diterpenoid antibiotic terpentecin.
References: [126, 215, 151]

[EC 5.5.1.15 created 2008]

EC 5.5.1.16

Accepted name: halimadienyl-diphosphate synthase
Reaction: geranylgeranyl diphosphate = tuberculosinyl diphosphate
Other name(s): Rv3377c; halimadienyl diphosphate synthase; tuberculosinol diphosphate synthase; halima-5(6),13-dien-15-yl-diphosphate lyase (cyclizing); halima-5,13-dien-15-yl-diphosphate lyase (decyclizing)
Systematic name: halima-5,13-dien-15-yl-diphosphate lyase (ring-opening)
Comments: Requires Mg^{2+} for activity. This enzyme is found in pathogenic prokaryotes such as *Mycobacterium tuberculosis* but not in non-pathogens such as *Mycobacterium smegmatis* so may play a role in pathogenicity. The product of the reaction is subsequently dephosphorylated yielding tuberculosinol (halima-5,13-dien-15-ol).
References: [454]

[EC 5.5.1.16 created 2008, modified 2012]

EC 5.5.1.17

Accepted name: (*S*)-β-macrocarpene synthase
Reaction: (*S*)-β-bisabolene = (*S*)-β-macrocarpene
Other name(s): TPS6; TPS11; (*S*)-β-macrocarpene lyase (decyclizing)
Systematic name: (*S*)-β-macrocarpene lyase (ring-opening)
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 (*cf.* EC 4.2.3.55, (*S*)-β-bisabolene synthase). The second step is the isomerization to (*S*)-β-macrocarpene.
References: [329]

[EC 5.5.1.17 created 2011]

EC 5.5.1.18

Accepted name: lycopene ε-cyclase
Reaction: carotenoid ψ-end group = carotenoid ε-end group
Other name(s): CrtL-e; LCYe; carotenoid ψ-end group lyase (decyclizing)
Systematic name: carotenoid ψ-end group lyase (ring-opening)
Comments: The carotenoid lycopene has the ψ-end group at both ends. When acting on one end, this enzyme forms δ-carotene. When acting on both ends, it forms ε-carotene.
References: [118, 586]

[EC 5.5.1.18 created 2011]

EC 5.5.1.19

Accepted name: lycopene β-cyclase
Reaction: carotenoid ψ-end group = carotenoid β-end group
Other name(s): CrtL; CrtL-b; CrtY; LCYb; carotenoid β-end group lyase (decyclizing)
Systematic name: carotenoid β-end group lyase (ring-opening)
Comments: The enzyme is a non-redox flavoprotein, containing $FADH_2$ that is used for stabilization of a transition state. Lycopene has a ψ-end group at both ends. When acting on one end, the enzyme forms γ-carotene. When acting on both ends it forms β-carotene. It also acts on neurosporene to give β-zeacarotene.
References: [117, 119, 253, 486, 244, 394, 707]

[EC 5.5.1.19 created 2011]

EC 5.5.1.20

Accepted name: prosolanapyrone-III cycloisomerase
Reaction: prosolanapyrone III = (–)-solanapyrone A
Other name(s): Sol5 (ambiguous); SPS (ambiguous); solanapyrone synthase (bifunctional enzyme: prosolanapyrone II oxidase/prosolanapyrone III cyclosiomerase)
Systematic name: prosolanapyrone-III:(–)-solanapyrone A isomerase
Comments: The enzyme is involved in the biosynthesis of the phytotoxin solanapyrone in some fungi. The bifunctional enzyme catalyses the oxidation of prosolanapyrone II and the subsequent Diels Alder cycloisomerization of the product prosolanapyrone III to (–)-solanapyrone A (*cf.* EC 1.1.3.42, prosolanapyrone II oxidase).
References: [294, 297, 296]

[EC 5.5.1.20 created 2011]

[5.5.1.21 Transferred entry. copal-8-ol diphosphate synthase. The enzyme was discovered at the public-review stage to have been misclassified and so was withdrawn. See EC 4.2.1.133, copal-8-ol diphosphate hydratase]

[EC 5.5.1.21 created 2012, deleted 2012]

EC 5.5.1.22

Accepted name: (–)-bornyl diphosphate synthase
Reaction: geranyl diphosphate = (–)-bornyl diphosphate
Other name(s): bornyl pyrophosphate synthase (ambiguous); bornyl pyrophosphate synthetase (ambiguous); (–)-bornyl pyrophosphate cyclase; bornyl diphosphate synthase; geranyl-diphosphate cyclase (ambiguous); (–)-bornyl-diphosphate lyase (decyclizing)
Systematic name: (–)-bornyl-diphosphate lyase (ring-opening)
Comments: Requires Mg^{2+}. The enzyme from *Tanacetum vulgare* (tansy) can also use (3*S*)-linalyl diphosphate or more slowly neryl diphosphate *in vitro*. The reaction proceeds via isomeration of geranyl diphosphate to (3*S*)-linalyl diphosphate [109]. The oxygen and phosphorus originally linked to C-1 of geranyl diphosphate end up linked to C-2 of (–)-bornyl diphosphate [114]. *cf.* EC 5.5.1.8 (+)-bornyl diphosphate synthase.
References: [110, 113, 109, 114, 6]

[EC 5.5.1.22 created 2012]

EC 5.5.1.23

Accepted name: aklanonic acid methyl ester cyclase
Reaction: aklaviketone = methyl aklanonate
Other name(s): *dauD* (gene name); *aknH* (gene name); *dnrD* (gene name); methyl aklanonate cyclase; methyl aklanonate-aklaviketone isomerase (cyclizing); aklaviketone lyase (decyclizing)
Systematic name: aklaviketone lyase (ring-opening)

Comments: The enzyme is involved in the biosynthesis of aklaviketone, an intermediate in the biosynthetic pathways leading to formation of several anthracycline antibiotics, including aclacinomycin, daunorubicin and doxorubicin.
References: [140, 309, 288]

[EC 5.5.1.23 created 2013, modified 2014]

EC 5.5.1.24
Accepted name: tocopherol cyclase
Reaction: (1) δ-tocopherol = 2-methyl-6-phytylbenzene-1,4-diol
(2) γ-tocopherol = 2,3-dimethyl-6-phytylbenzene-1,4-diol
(3) δ-tocotrienol = 6-geranylgeranyl-2-methylbenzene-1,4-diol
(4) γ-tocotrienol = 6-geranylgeranyl-2,3-dimethylbenzene-1,4-diol
Other name(s): VTE1 (gene name); SXD1 (gene name); δ/γ-tocopherol lyase (decyclizing)
Systematic name: δ/γ-tocopherol lyase (ring-opening)
Comments: The enzyme has been described from plants and cyanobacteria. It has similar activity with all four listed benzoquinol substrates. Involved in the biosynthesis of vitamin E (tocopherols and tocotrienols).
References: [494, 539]

[EC 5.5.1.24 created 2013]

EC 5.5.1.25
Accepted name: 3,6-anhydro-L-galactonate cycloisomerase
Reaction: 3,6-anhydro-L-galactonate = 2-dehydro-3-deoxy-L-galactonate
Other name(s): 3,6-anhydro-α-L-galactonate lyase (ring-opening); 3,6-anhydro-α-L-galactonate cycloisomerase
Systematic name: 3,6-anhydro-L-galactonate lyase (ring-opening)
Comments: The enzyme, characterized from the marine bacteria *Vibrio* sp. EJY3 and *Postechiella marina* M091, is involved in a degradation pathway for 3,6-anhydro-α-L-galactopyranose, a major component of the polysaccharides of red macroalgae.
References: [712, 355]

[EC 5.5.1.25 created 2014, modified 2015]

EC 5.5.1.26
Accepted name: nogalonic acid methyl ester cyclase
Reaction: nogalaviketone = methyl nogalonate
Other name(s): methyl nogalonate cyclase; SnoaL (gene name); methyl nogalonate lyase (cyclizing)
Systematic name: nogalaviketone lyase (ring-opening)
Comments: The enzyme, characterized from the bacterium *Streptomyces nogalater*, is involved in the biosynthesis of the aromatic polyketide nogalamycin.
References: [597, 596]

[EC 5.5.1.26 created 2015]

EC 5.5.1.27
Accepted name: D-galactarolactone cycloisomerase
Reaction: (1) D-galactaro-1,4-lactone = 5-dehydro-4-deoxy-D-glucarate
(2) D-glucaro-1,4-lactone = 5-dehydro-4-deoxy-D-glucarate
Other name(s): GCI
Systematic name: D-galactaro-1,4-lactone lyase (ring-opening)

Comments: The enzyme, characterized from the bacterium *Agrobacterium fabrum* strain C58, is involved in degradation of D-galacturonate and D-glucuronate. Activity with D-galactaro-1,4-lactone is 4-fold higher than with D-glucaro-1,4-lactone.
References: [21, 65]

[EC 5.5.1.27 created 2015]

EC 5.5.1.28
Accepted name: (–)-kolavenyl diphosphate synthase
Reaction: geranylgeranyl diphosphate = (–)-kolavenyl diphosphate
Other name(s): SdKPS; TwTPS14; TwTPS10/KPS; SdCPS2; clerodienyl diphosphate synthase; CLPP
Systematic name: (–)-kolavenyl diphosphate lyase (ring-opening)
Comments: Isolated from the hallucinogenic plant *Salvia divinorum* (seer's sage) and the medicinal plant *Tripterygium wilfordii* (thunder god vine).
References: [219, 94]

[EC 5.5.1.28 created 2017]

EC 5.5.1.29
Accepted name: (+)-kolavenyl diphosphate synthase
Reaction: geranylgeranyl diphosphate = (+)-kolavenyl diphosphate
Systematic name: (+)-kolavenyl-diphosphate lyase (ring-opening)
Comments: Isolated from the bacterium *Herpetosiphon aurantiacus*.
References: [455]

[EC 5.5.1.29 created 2017]

EC 5.5.1.30
Accepted name: labda-7,13-dienyl diphosphate synthase
Reaction: geranylgeranyl diphosphate = (13*E*)-labda-7,13-dien-15-yl diphosphate
Other name(s): SCLAV_p0490
Systematic name: (13*E*)-labda-7,13-dien-15-yl-diphosphate lyase (ring-opening)
Comments: Isolated from the bacterium *Streptomyces clavuligerus*.
References: [691]

[EC 5.5.1.30 created 2017]

EC 5.5.1.31
Accepted name: hapalindole H synthase
Reaction: 3-geranyl-3-[(*Z*)-2-isocyanoethenyl]-1*H*-indole = hapalindole H
Other name(s): *famC*2 (gene name); *famC*3 (gene name)
Systematic name: 3-geranyl-3-[(*Z*)-2-isocyanoethenyl]-1*H*-indole cyclase (hapalindole H-forming)
Comments: The enzyme, characterized from the cyanobacterium *Fischerella ambigua* UTEX 1903, forms the core structure of the hapalindole family of alkaloids. The enzyme is a heterodimeric complex.
References: [364]

[EC 5.5.1.31 created 2018]

EC 5.5.1.32
Accepted name: 12-*epi*-hapalindole U synthase
Reaction: 3-geranyl-3-[(*Z*)-2-isocyanoethenyl]-1*H*-indole = 12-*epi*-hapalindole U
Other name(s): *famC*1 (gene name); HpiC1 (gene name)

Systematic name: 3-geranyl-3-[(*Z*)-2-isocyanoethenyl]-1*H*-indole cyclase (12-*epi*-hapalindole U-forming)
Comments: The enzyme, characterized from the cyanobacterium *Fischerella ambigua* UTEX 1903, forms the core structure of the 12-*epi*-hapalindole family of alkaloids.
References: [365]

[EC 5.5.1.32 created 2018]

EC 5.5.1.33
Accepted name: 12-*epi*-fischerindole U synthase
Reaction: 3-geranyl-3-[(*Z*)-2-isocyanoethenyl]-1*H*-indole = 12-*epi*-fischerindole U
Other name(s): *fisC* (gene name); *fimC*5 (gene name)
Systematic name: 3-geranyl-3-[(*Z*)-2-isocyanoethenyl]-1*H*-indole cyclase (12-*epi*-fischerindole U-forming)
Comments: The enzyme, characterized from multiple species of the cyanobacterial genus *Fischerella*, participates in the biosynthesis of the terpenoid indole alkaloids 12-*epi*-fischerindoles.
References: [364]

[EC 5.5.1.33 created 2018]

EC 5.5.1.34
Accepted name: (+)-*cis*,*trans*-nepetalactol synthase
Reaction: (*S*)-8-oxocitronellyl enol = (+)-*cis*,*trans*-nepetalactol
Other name(s): NEPS1 (gene name); NEPS2 (gene name)
Systematic name: (*S*)-8-oxocitronellyl enol cyclase [(+)-*cis*,*trans*-nepetalactol-forming]
Comments: The enzyme, characterized from the plant *Nepeta mussinii*, binds an NAD^+ cofactor. The product is a precursor of (+)-*cis*,*trans*-nepetalactone, the primary ingredient responsible for the psychoactive effects catnip has on cats.
References: [367, 368]

[EC 5.5.1.34 created 2019]

EC 5.5.1.35
Accepted name: (+)-*cis*,*cis*-nepetalactol synthase
Reaction: (*S*)-8-oxocitronellyl enol = (+)-*cis*,*cis*-nepetalactol
Other name(s): NEPS3 (gene name)
Systematic name: (*S*)-8-oxocitronellyl enol cyclase [(+)-*cis*,*cis*-nepetalactol-forming]
Comments: The enzyme, characterized from the plant *Nepeta mussinii*, binds an NAD^+ cofactor. The product is a precursor of (+)-*cis*,*cis*-nepetalactone, one of the stereoisomers responsible for the psychoactive effects catnip has on cats.
References: [367, 368]

[EC 5.5.1.35 created 2019]

EC 5.6 Isomerases altering macromolecular conformation

These enzyme catalyse changes to the conformations of macromolecules.

EC 5.6.1 Enzymes altering polypeptide conformation or assembly

EC 5.6.1.1
Accepted name: microtubule-severing ATPase

Reaction: ***n*** ATP + ***n*** H_2O + a microtubule = ***n*** ADP + ***n*** phosphate + (***n*+1**) α/β tubulin heterodimers
Other name(s): katanin
Systematic name: ATP phosphohydrolase (tubulin-dimerizing)
Comments: A member of the AAA-ATPase family, active in splitting microtubules into tubulin dimers in the centrosome.
References: [414, 221]

[EC 5.6.1.1 created 2000 as 3.6.4.3, transferred 2018 to EC 5.6.1.1]

EC 5.6.1.2
Accepted name: dynein ATPase
Reaction: ATP + H_2O + a dynein associated with a microtubule at position *n* = ADP + phosphate + a dynein associated with a microtubule at position *n*-1 (toward the minus end)
Other name(s): dynein adenosine 5′-triphosphatase
Systematic name: ATP phosphohydrolase (tubulin-translocating)
Comments: A multisubunit protein complex associated with microtubules. Hydrolysis of ATP provides energy for the movement of organelles (endosomes, lysosomes, mitochondria) along microtubules to the centrosome towards the microtubule's minus end. It also functions in the movement of eukaryotic flagella and cilia. It consists of two heavy chains (about 500 kDa), three-four intermediate chains (about 70 kDa) and four light chains (about 50 kDa).
References: [598, 194, 186]

[EC 5.6.1.2 created 1984 as EC 3.6.1.33, transferred 2000 to EC 3.6.4.2, transferred 2018 to EC 5.6.1.2]

EC 5.6.1.3
Accepted name: plus-end-directed kinesin ATPase
Reaction: ATP + H_2O + a kinesin associated with a microtubule at position *n* = ADP + phosphate a kinesin associated with a microtubule at position *n*+1 (toward the plus end)
Other name(s): kinesin
Systematic name: kinesin ATP phosphohydrolase (plus-end-directed)
Comments: Kinesins are a family of motor proteins that move unidirectionally along microtubules as they hydrolyse ATP. The enzymes described here move towards the plus end of the microtubule, in contrast to EC 5.6.1.2, dynein ATPase and EC 5.6.1.4, minus-end-directed kinesin ATPase. They are involved in organelle movement in mitosis and meiosis, and also power vesicular trafficking toward the synapse in neurons. The motor domain, which contains the ATP- and microtubule-binding activities, is located at the N-terminus while the C-terminus links to the cargo being transported.
References: [637, 339, 248, 450, 568, 648]

[EC 5.6.1.3 created 2000 as 3.6.4.4, transferred 2018 to EC 5.6.1.3]

EC 5.6.1.4
Accepted name: minus-end-directed kinesin ATPase
Reaction: ATP + H_2O + a kinesin associated with a microtubule at position *n* = ADP + phosphate + a kinesin associated with a microtubule at position *n*-1 (toward the minus end)
Other name(s): non-claret disjunctional; *ncd* (gene name)
Systematic name: kinesin ATP phosphohydrolase (minus-end-directed)
Comments: Kinesins are a family of motor proteins that move unidirectionally along microtubules as they hydrolyse ATP and are involved in organelle movement. This enzyme is similar to EC 5.6.1.3, plus-end-directed kinesin ATPase, but the organization of the different domains differs, resulting in movement in the opposite direction along the microtubules.
References: [412, 84, 377, 236, 532]

[EC 5.6.1.4 created 2000 as 3.6.4.5, transferred 2018 to EC 5.6.1.4]

EC 5.6.1.5

Accepted name: proteasome ATPase
Reaction: ATP + H_2O + polypeptide = ADP + phosphate + unfolded polypeptide
Systematic name: ATP phosphohydrolase (polypeptide-degrading)
Comments: Belongs to the AAA-type superfamily and, like EC 5.6.1.4 (minus-end-directed kinesin ATPase), is involved in channel gating and polypeptide unfolding before proteolysis in the proteasome. Six ATPase subunits are present in the regulatory particle (RP) of 26*S* proteasome.
References: [521, 406]

[EC 5.6.1.5 created 2000 as 3.6.4.8, transferred 2018 to EC 5.6.1.5]

EC 5.6.1.6

Accepted name: channel-conductance-controlling ATPase
Reaction: ATP + H_2O + closed Cl^- channel = ADP + phosphate + open Cl^- channel
Other name(s): cystic fibrosis transmembrane conductance regulator; CFTR (gene name)
Systematic name: ATP phosphohydrolase (channel-conductance-controlling)
Comments: ABC-type (ATP-binding cassette-type) ATPase, characterized by the presence of two similar ATP-binding domains. The enzyme is found in animals, and in humans its absence brings about cystic fibrosis. Unlike most of the ABC transporters, chloride pumping is not directly coupled to ATP hydrolysis. Instead, the passive flow of anions through the channel is gated by cycles of ATP binding and hydrolysis by the ATP-binding domains. The enzyme is also involved in the functioning of other transmembrane channels.
References: [93, 629, 554, 259]

[EC 5.6.1.6 created 2000 as EC 3.6.3.49, transferred 2018 to EC 5.6.1.6]

EC 5.6.1.7

Accepted name: chaperonin ATPase
Reaction: ATP + H_2O + an unfolded polypeptide = ADP + phosphate + a folded polypeptide
Other name(s): chaperonin
Systematic name: ATP phosphohydrolase (polypeptide-unfolding)
Comments: Multisubunit proteins with 2x7 (Type I, in most cells) or 2x8 (Type II, in Archaea) ATP-binding sites involved in maintaining an unfolded polypeptide structure before folding or entry into mitochondria and chloroplasts. Molecular masses of subunits ranges from 10-90 kDa. They are a subclass of molecular chaperones that are related to EC 5.6.1.5 (proteasome ATPase).
References: [234, 384, 1, 504]

[EC 5.6.1.7 created 2000 as EC 3.6.4.9, transferred 2018 to EC 5.6.1.7]

EC 5.6.1.8

Accepted name: myosin ATPase
Reaction: ATP + H_2O + myosin bound to actin filament at position n = ADP + phosphate + myosin bound to actin filament at position n+1
Systematic name: ATP phosphohydrolase (actin-translocating)
Comments: Proteins of the contractile apparatus of muscle and nonmuscle cells; myosin molecule consists of two heavy chains (about 200 kDa) and two pairs of light chains (15–27 kDa). The head region of the heavy chain contains actin- and ATP-binding sites. ATP hydrolysis provides energy for actomyosin contraction.
References: [511, 223, 443]

[EC 5.6.1.8 created 1984 as EC 3.6.1.32, transferred 2000 to EC 3.6.4.1, transferred 2018 to EC 5.6.1.8]

EC 5.6.1.9

Accepted name: (*R*)-2-hydroxyacyl-CoA dehydratase activating ATPase

Reaction: **2** ATP + a reduced flavodoxin + an inactive (*R*)-2-hydroxyacyl-CoA dehydratase + **2** H_2O = **2** ADP + **2** phosphate + a flavodoxin semiquinone + an active (*R*)-2-hydroxyacyl-CoA dehydratase

Other name(s): archerase; (*R*)-2-hydroxyacyl-CoA dehydratase activator; (*R*)-2-hydroxyacyl-CoA dehydratase activase; *fldI* (gene name); *hgdC* (gene name); *hadI* (gene name); *lcdC* (gene name)

Systematic name: reduced flavodoxin:(*R*)-2-hydroxyacyl-CoA dehydratase electron transferase (ATP-hydrolyzing)

Comments: Members of the (*R*)-2-hydroxyacyl-CoA dehydratase family (including EC 4.2.1.54, lactoyl-CoA dehydratase, EC 4.2.1.157, (*R*)-2-hydroxyisocaproyl-CoA dehydratase, EC 4.2.1.167, (*R*)-2-hydroxyglutaryl-CoA dehydratase and EC 4.2.1.175, (*R*)-3-(aryl)lactoyl-CoA dehydratase) are two-component systems composed of an activator component and a dehydratase component. The activator is an extremely oxygen-sensitive homodimer with one [4Fe-4S] cluster bound at the dimer interface. Before it can catalyse the dehydration reaction, the dehydratase requires one high-energy electron that is used to transiently reduce the electrophilic thiol ester carbonyl to a nucleophilic ketyl radical anion, facilitating the elimination of the hydroxyl group. The activator, which has been named archerase because its open position resembles an archer shooting arrows, binds two ADP molecules. Upon the reduction of its [4Fe-4S] cluster by a single electron, delivered by a dedicated flavodoxin or a clostridial ferredoxin, the two ADP molecules exchange for two ATP molecules, resulting in a large conformational change. The change allows the activator to bind to the dehydratase component and transfer the electron to it, activating it. During this event the two ATP molecules are hydrolysed and the activator returns to its resting state. Since the electron is regenerated at the end of each reaction cycle of the dehydratase, the activation is required only once, before the first reaction takes place.

References: [52, 441, 376, 141, 615, 315, 313, 314, 322]

[EC 5.6.1.9 created 2019]

EC 5.6.2 Enzymes altering nucleic acid conformation

EC 5.6.2.1

Accepted name: DNA topoisomerase

Reaction: ATP-independent breakage of single-stranded DNA, followed by passage and rejoining

Other name(s): type I DNA topoisomerase; untwisting enzyme; relaxing enzyme; nicking-closing enzyme; swivelase; ω-protein; deoxyribonucleate topoisomerase; topoisomerase

Systematic name: DNA topoisomerase

Comments: These enzymes bring about the conversion of one topological isomer of DNA into another, e.g., the relaxation of superhelical turns in DNA, the interconversion of simple and knotted rings of single-stranded DNA, and the intertwisting of single-stranded rings of complementary sequences, *cf.* EC 5.6.2.2 DNA topoisomerase (ATP-hydrolysing).

References: [189]

[EC 5.6.2.1 created 1984 as 5.99.1.2 transferred 2019 to EC 5.6.2.1]

EC 5.6.2.2

Accepted name: DNA topoisomerase (ATP-hydrolysing)

Reaction: ATP-dependent breakage, passage and rejoining of double-stranded DNA

Other name(s): type II DNA topoisomerase; DNA-gyrase; deoxyribonucleate topoisomerase; deoxyribonucleic topoisomerase; topoisomerase; DNA topoisomerase II

Systematic name: DNA topoisomerase (ATP-hydrolysing)

Comments: The enzyme can introduce negative superhelical turns into double-stranded circular DNA. One unit has nicking-closing activity, and another catalyses super-twisting and hydrolysis of ATP (*cf.* EC 5.6.2.1 DNA topoisomerase).

References: [189]

[EC 5.6.2.2 created 1984 as 5.99.1.3, transferred 2019 to EC 5.6.2.2]

EC 5.6.2.3

Accepted name: DNA 5′-3′ helicase

Reaction: Couples ATP hydrolysis with the unwinding of duplex DNA at the replication fork by translocating in the 5′-3′ direction. This creates two antiparallel DNA single strands (ssDNA). The leading ssDNA polymer is the template for DNA polymerase III holoenzyme which synthesizes a continuous strand.

Other name(s): DnaB helicase; replication fork helicase; 5′ to 3′ DNA helicase; BACH1 helicase; BcMCM; BLM protein; BRCA1-associated C-terminal helicase; CeWRN-1; Dbp9p; DNA helicase A; DNA helicase E; DNA helicase II; DNA helicase III; DNA helicase VI; *dnaB* (gene name); DnaB helicase E1; helicase HDH IV; Hel E; helicase DnaB; helicase domain of bacteriophage T_7 gene 4 protein helicase; PcrA helicase; hHcsA; Hmi1p; hPif1; MCM helicase; MCM protein; MPH1; PcrA; PfDH A; Pfh1p; PIF1; replicative DNA helicase

Systematic name: DNA 5′-3′ helicase (ATP-hydrolysing)

Comments: The activity is stimulated by DNA polymerase III. As the lagging ssDNA is created, it becomes coated with S Single-Stranded DNA Binding protein (SSB). Once every 500-2000 nucleotides, primase is stimulated by DnaB helicase to synthesize a primer at the replication fork. This primer is elongated by the lagging strand half of DNA polymerase III holoenzyme.

References: [380, 276, 269, 729, 268, 623]

[EC 5.6.2.3 created 2009 as EC 3.6.4.12, part transferred 2021 to EC 5.6.2.3]

EC 5.6.2.4

Accepted name: DNA 3′-5′ helicase

Reaction: Couples ATP hydrolysis with the unwinding of duplex DNA by translocating in the 3′-5′ direction.

Other name(s): *uvrD* (gene name); *rep* (gene name); RECQ (gene name); MER3 (gene name); Holliday junction DNA helicase

Systematic name: DNA 3′-5′ helicase (ATP-hydrolysing)

Comments: Helicases are motor proteins that can transiently catalyse the unwinding of energetically stable duplex DNA or RNA molecules by using ATP hydrolysis as the source of energy (although other nucleoside triphosphates can replace ATP in some cases). DNA helicases unwind duplex DNA and are involved in replication, repair, recombination, transcription, pre-rRNA processing, and translation initiation. Mechanistically, DNA helicases are divided into those that can translocate in the 3′-5′ direction and those that translocate in the 5′-3′ direction with respect to the strand on which they initially bind. This entry describes a number of DNA helicases that translocate in the 3′-5′ direction. Many of the enzymes require a 3′ single-stranded DNA tail. The Rep protein is a component of the bacterial replisome, providing a replication fork-specific motor. The UvrD enzyme, found in Gram-negative bacteria, is involved in maintenance of chromosomal integrity. The RecQ proteins are a family of eukaryotic helicases that are involved in DNA replication, transcription and repair. The Mer3 helicase, found in fungi and plants, is required for crossover formation during meiosis. *cf.* EC 5.6.2.3, DNA 5′-3′ helicase.

References: [604, 449, 475, 120]

[EC 5.6.2.4 created 2009 as EC 3.6.4.12, part transferred 2021 to EC 5.6.2.4]

EC 5.99 Other isomerases

This subclass contains miscellaneous enzymes in a single sub-subclass (EC 5.99.1).

EC 5.99.1 Sole sub-subclass for isomerases that do not belong in the other subclasses

EC 5.99.1.1

Accepted name: thiocyanate isomerase

Reaction: benzyl isothiocyanate = benzyl thiocyanate

Other name(s): isothiocyanate isomerase
Systematic name: benzyl-thiocyanate isomerase
References: [642]

[EC 5.99.1.1 created 1965]

[5.99.1.2 Transferred entry. DNA topoisomerase. Now EC 5.6.2.1, DNA topoisomerase]

[EC 5.99.1.2 created 1984, deleted 2018]

[5.99.1.3 Transferred entry. DNA topoisomerase (ATP-hydrolysing). Now EC 5.6.2.2, DNA topoisomerase (ATP-hydrolysing)]

[EC 5.99.1.3 created 1984, deleted 2018]

EC 5.99.1.4
Accepted name: 2-hydroxychromene-2-carboxylate isomerase
Reaction: 2-hydroxy-2*H*-chromene-2-carboxylate = (3*E*)-4-(2-hydroxyphenyl)-2-oxobut-3-enoate
Other name(s): HCCA isomerase; 2HC2CA isomerase; 2-hydroxychromene-2-carboxylic acid isomerase
Systematic name: 2-hydroxy-2*H*-chromene-2-carboxylate—(3*E*)-4-(2-hydroxyphenyl)-2-oxobut-3-enoate isomerase
Comments: This enzyme is involved in naphthalene degradation.
References: [467, 305, 149, 619]

[EC 5.99.1.4 created 2010]

References

[1] In R.J. Ellis, editor, *The Chaperonins*. Academic Press, San Diego, 1996.

[2] P. Abayakoon, J.P. Lingford, Y. Jin, C. Bengt, G.J. Davies, S. Yao, E.D. Goddard-Borger, and S.J. Williams. Discovery and characterization of a sulfoquinovose mutarotase using kinetic analysis at equilibrium by exchange spectroscopy. *Biochem. J.*, 475:1371–1383, 2018.

[3] I Abe, Y. Ebizuka, S. Seo, and U. Sankawa. Purification of squalene-2,3-epoxide cyclases from cell suspension cultures of *Rabdosia japonica* Hara. *FEBS Lett.*, 249:100–104, 1989.

[4] I. Abe, U. Sankawa, and Y. Ebizuka. Purification of 2,3-oxdosqualene:β-amyrin cyclase from pea seedlings. *Chem. Pharm. Bull.*, 37:536–, 1989.

[5] D.J. Aberhart, H.-J. Lim, and B.H. Weiller. Stereochemistry of lysine 2,3-aminomutase. *J. Am. Chem. Soc.*, 103:6750–6752, 1981.

[6] K.P. Adam and R. Croteau. Monoterpene biosynthesis in the liverwort *Conocephalum conicum*: demonstration of sabinene synthase and bornyl diphosphate synthase. *Phytochemistry*, 49:475–480, 1998.

[7] E. Adams and I.L. Norton. Purification and properties of inducible hydroxyproline 2-epimerase from *Pseudomonas*. *J. Biol. Chem.*, 239:1525–1535, 1964.

[8] B.W. Agranoff, H. Eggerer, U. Henning, and F. Lynen. Biosynthesis of terpenes. VII. Isopentenyl pyrophosphate isomerase. *J. Biol. Chem.*, 235:326–332, 1960.

[9] S.A. Ahmed, N. Esaki, H. Tanaka, , and K. L-α-Amino-β-thio-ε-caprolactam, a new sulfur-containing substrate for α-amino-ε-caprolactam racemase. *FEBS Lett.*, 174:76–79, 1984.

[10] S.A. Ahmed, N. Esaki, H. Tanaka, , and K. Mechanism of α-amino-ε-caprolactam racemase reaction. *Biochemistry*, 25:385–388, 1986.

[11] C. Ahn, J. Byun, and J. Yim. Purification, cloning, and functional expression of dihydroneopterin triphosphate 2′-epimerase from *Escherichia coli*. *J. Biol. Chem.*, 272:15323–15328, 1997.

[12] E.G. Ahuja, P. Janning, M. Mentel, A. Graebsch, R. Breinbauer, W. Hiller, B. Costisella, L.S. Thomashow, D.V. Mavrodi, and W. Blankenfeldt. PhzA/B catalyzes the formation of the tricycle in phenazine biosynthesis. *J. Am. Chem. Soc.*, 130:17053–17061, 2008.

[13] S. Al-Babili, P. Hugueney, M. Schledz, R. Welsch, H. Frohnmeyer, O. Laule, and P. Beyer. Identification of a novel gene coding for neoxanthin synthase from Solanum tuberosum. *FEBS Lett.*, 485:168–172, 2000.

[14] A. Alder, M. Jamil, M. Marzorati, M. Bruno, M. Vermathen, P. Bigler, S. Ghisla, H. Bouwmeester, P. Beyer, and S. Al-Babili. The path from β-carotene to carlactone, a strigolactone-like plant hormone. *Science*, 335:1348–1351, 2012.

[15] A. Alian, A. DeGiovanni, S.L. Griner, J.S. Finer-Moore, and R.M. Stroud. Crystal structure of an RluF-RNA complex: a base-pair rearrangement is the key to selectivity of RluF for U^{2604} of the ribosome. *J. Mol. Biol.*, 388:785–800, 2009.

[16] H.S. Allaudeen and T. Ramakrishnan. Biosynthesis of isoleucine and valine in *Mycobacterium tuberculosis* H37 Rv. *Arch. Biochem. Biophys.*, 125:199–209, 1968.

[17] K.N. Allen, A. Lavie, A. Glasfeld, T.N. Tanada, D.P. Gerrity, S.C. Carlson, G.K. Farber, G.A. Petsko, and D. Ringe. Role of the divalent metal ion in sugar binding, ring opening, and isomerization by D-xylose isomerase: replacement of a catalytic metal by an amino acid. *Biochemistry*, 33:1488–1494, 1994.

[18] J. Altenbuchner, M. Siemann-Herzberg, and C. Syldatk. Hydantoinases and related enzymes as biocatalysts for the synthesis of unnatural chiral amino acids. *Curr. Opin. Biotechnol.*, 12:559–563, 2001.

[19] H. Amos. A racemase for threonine in *Escherichia coli*. *J. Am. Chem. Soc.*, 76:3858–3858, 1954.

[20] P. Anastasis, I. Freer, C. Gilmore, H. Mackie, K. Overton, D. Picken, and S. Swanson. Biosynthesis of γ-bisabolene in tissue-cultures of *Andrographis paniculata*. *Can. J. Chem.*, 62:2079–2088, 1984.

[21] M. Andberg, H. Maaheimo, H. Boer, M. Penttila, A. Koivula, and P. Richard. Characterization of a novel *Agrobacterium tumefaciens* galactarolactone cycloisomerase enzyme for direct conversion of D-galactarolactone to 3-deoxy-2-keto-L-*threo*-hexarate. *J. Biol. Chem.*, 287:17662–17671, 2012.

[22] R.L. Anderson and D.P. Allison. Purification and characterization of D-lyxose isomerase. *J. Biol. Chem.*, 240:2367–2372, 1965.

[23] A. Andersson, G. Schneider, and Y. Lindqvist. Purification and preliminary X-ray crystallographic studies of recombinant L-ribulose-5-phosphate 4-epimerase from *Escherichia coli*. *Protein Sci.*, 4:1648–1650, 1995.

[24] R.G. Annett and G.W. Kosicki. Oxalacetate keto-enol tautomerase. Purification and characterization. *J. Biol. Chem.*, 244:2059–2067, 1969.

[25] I. Ansmant, S. Massenet, H. Grosjean, Y. Motorin, and C. Branlant. Identification of the *Saccharomyces cerevisiae* RNA:pseudouridine synthase responsible for formation of Ψ^{2819} in 21S mitochondrial ribosomal RNA. *Nucleic Acids Res.*, 28:1941–1946, 2000.

[26] I. Ansmant, Y. Motorin, S. Massenet, H. Grosjean, and C. Branlant. Identification and characterization of the tRNA:Ψ^{31}-synthase (Pus6p) of *Saccharomyces cerevisiae*. *J. Biol. Chem.*, 276:34934–34940, 2001.

[27] M. Antia, D.S. Hoare, and W. Work. The stereoisomers of αε-diaminopimelic acid. 3. Properties and distribution of diaminopimelic acid racemase, an enzyme causing interconversion of the LL and *meso* isomers. *Biochem. J.*, 65:448–459, 1957.

[28] R. Aono, T. Sato, A. Yano, S. Yoshida, Y. Nishitani, K. Miki, T. Imanaka, and H. Atomi. Enzymatic characterization of AMP phosphorylase and ribose-1,5-bisphosphate isomerase functioning in an archaeal AMP metabolic pathway. *J. Bacteriol.*, 194:6847–6855, 2012.

[29] T. Araki, Y. Saga, M. Marugami, J. Otaka, H. Araya, K. Saito, M. Yamazaki, H. Suzuki, and T. Kushiro. Onocerin biosynthesis requires two highly dedicated triterpene cyclases in a fern *Lycopodium clavatum*. *ChemBioChem*, 17:288–290, 2016.

[30] F. Arena, G. Ciliberto, S. Ciampi, and R. Cortese. Purification of pseudouridylate synthetase I from *Salmonella typhimurium*. *Nucleic Acids Res.*, 5:4523–4536, 1978.

[31] H. Ashida, Y. Saito, C. Kojima, K. Kobayashi, N. Ogasawara, and A. Yokota. A functional link between RuBisCO-like protein of *Bacillus* and photosynthetic RuBisCO. *Science*, 302:286–290, 2003.

[32] G. Ashwell and J. Hickman. Enzymatic formation of xylulose 5-phosphate from ribose 5-phosphate in spleen. *J. Biol. Chem.*, 226:65–76, 1957.

[33] G. Ashwell, A.J. Wahba, and J. Hickman. Uronic acid metabolism in bacteria. I. Purification and properties of uronic acid isomerase in *Escherichia coli*. *J. Biol. Chem.*, 235:1559–1565, 1960.

[34] K. Awai, H. Ohta, and N. Sato. Oxygenic photosynthesis without galactolipids. *Proc. Natl. Acad. Sci. USA*, 111:13571–13575, 2014.

[35] A. Baich, R.G. Wolfe, and F.J. Reithel. The enzymes of mammary gland. I. Isolation of phosphoglucose isomerase. *J. Biol. Chem.*, 235:3130–3133, 1960.

[36] S. Banerjee, F. Anderson, and G.K. Farber. The evolution of sugar isomerases. *Protein Eng.*, 8:1189–1195, 1995.

[37] G.A. Barber and P.A. Hebda. GDP-D-mannose: GDP-L-galactose epimerase from *Chlorella pyrenoidosa*. *Methods Enzymol.*, 83:522–525, 1982.

[38] T. Barbier, F. Collard, A. Zuniga-Ripa, I. Moriyon, T. Godard, J. Becker, C. Wittmann, E. Van Schaftingen, and J.J. Letesson. Erythritol feeds the pentose phosphate pathway via three new isomerases leading to D-erythrose-4-phosphate in *Brucella*. *Proc. Natl. Acad. Sci. USA*, 111:17815–17820, 2014.

[39] H.A. Barker. Coenzyme B_{12}-dependent mutases causing carbon chain rearrangements. In P.D. Boyer, editor, *The Enzymes*, volume 6, pages 509–537. Academic Press, New York, 3rd edition, 1972.

[40] H.A. Barker, V. Rooze, F. Suzuki, and A.A. Iodice. The glutamate mutase system. Assays and properties. *J. Biol. Chem.*, 239:3260–3266, 1964.

[41] J.E.G. Barnett and D.L. Corina. The mechanism of glucose 6-phosphate-D-*myo*-inositol 1-phosphate cyclase of rat testis. The involvement of hydrogen atoms. *Biochem. J.*, 108:125–129, 1968.

[42] J.E.G. Barnett, A. Rasheed, and D.L. Corina. Partial reactions of glucose 6-phosphate-1L-*myo*-inositol 1-phosphate cyclase. *Biochem. J.*, 131:21–30, 1973.

[43] M. Basyuni, H. Oku, E. Tsujimoto, K. Kinjo, S. Baba, and K. Takara. Triterpene synthases from the Okinawan mangrove tribe, Rhizophoraceae. *FEBS J.*, 274:5028–5042, 2007.

[44] H.F. Becker, Y. Motorin, R.J. Planta, and H. Grosjean. The yeast gene YNL292w encodes a pseudouridine synthase (Pus4) catalyzing the formation of Ψ^{55} in both mitochondrial and cytoplasmic tRNAs. *Nucleic Acids Res.*, 25:4493–4499, 1997.

[45] J.A. Beebe and P.A. Frey. Galactose mutarotase: purification, characterization, and investigations of two important histidine residues. *Biochemistry*, 37:14989–14997, 1998.

[46] I. Behm-Ansmant, C. Branlant, and Y. Motorin. The *Saccharomyces cerevisiae* Pus2 protein encoded by YGL063w ORF is a mitochondrial tRNA:$\Psi^{27/28}$-synthase. *RNA*, 13:1641–1647, 2007.

[47] I. Behm-Ansmant, H. Grosjean, S. Massenet, Y. Motorin, and C. Branlant. Pseudouridylation at position 32 of mitochondrial and cytoplasmic tRNAs requires two distinct enzymes in *Saccharomyces cerevisiae*. *J. Biol. Chem.*, 279:52998–53006, 2004.

[48] I. Behm-Ansmant, A. Urban, X. Ma, Y.T. Yu, Y. Motorin, and C. Branlant. The *Saccharomyces cerevisiae* U2 snRNA:pseudouridine-synthase Pus7p is a novel multisite-multisubstrate RNA:Ψ-synthase also acting on tRNAs. *RNA*, 9:1371–1382, 2003.

[49] E.J. Behrman and R.Y. Stanier. The bacterial oxidation of nicotinic acid. *J. Biol. Chem.*, 228:923–945, 1957.

[50] J. Beltran, B. Kloss, J.P. Hosler, J. Geng, A. Liu, A. Modi, J.H. Dawson, M. Sono, M. Shumskaya, C. Ampomah-Dwamena, J.D. Love, and E.T. Wurtzel. Control of carotenoid biosynthesis through a heme-based *cis-trans* isomerase. *Nat. Chem. Biol.*, 11:598–605, 2015.

[51] R. Ben-Zvi and M. Schramm. A phosphoglucomutase specific for β-glucose 1-phosphate. *J. Biol. Chem.*, 236:2186–2189, 1961.

[52] K. Bendrat, U. Müller, A.G. Klees, and W. Buckel. Identification of the gene encoding the activator of (*R*)-2-hydroxyglutaryl-CoA dehydratase from *Acidaminococcus fermentans* by gene expression in *Escherichia coli*. *FEBS Lett.*, 329:329–331, 1993.

[53] R. Bentley and D.S. Bhate. Mutarotase from *Penicillium notatum*. I. Purification, assay, and general properties of the enzyme. *J. Biol. Chem.*, 235:1219–1224, 1960.

[54] R. Bentley and D.S. Bhate. Mutarotase from *Penicillium notatum*. II. The mechanism of the mutarotation reaction. *J. Biol. Chem.*, 235:1225–1233, 1960.

[55] F. Berkovitch, E. Behshad, K.H. Tang, E.A. Enns, P.A. Frey, and C.L. Drennan. A locking mechanism preventing radical damage in the absence of substrate, as revealed by the x-ray structure of lysine 5,6-aminomutase. *Proc. Natl. Acad. Sci. USA*, 101:15870–15875, 2004.

[56] J.M. Bishop. Cellular oncogenes and retroviruses. *Annu. Rev. Biochem.*, 52:301–354, 1983.

[57] V. Blanc, P. Gil, N. Bamas-Jacques, S. Lorenzon, M. Zagorec, J. Schleuniger, D. Bisch, F. Blanche, L. Debussche, J. Crouzet, and D. Thibaut. Identification and analysis of genes from *Streptomyces pristinaespiralis* encoding enzymes involved in the biosynthesis of the 4-dimethylamino-L-phenylalanine precursor of pristinamycin I. *Mol. Microbiol.*, 23:191–202, 1997.

[58] W. Blankenfeldt, A.P. Kuzin, T. Skarina, Y. Korniyenko, L. Tong, P. Bayer, P. Janning, L.S. Thomashow, and D.V. Mavrodi. Structure and function of the phenazine biosynthetic protein PhzF from *Pseudomonas fluorescens*. *Proc. Natl. Acad. Sci. USA*, 101:16431–16436, 2004.

[59] F. Blasi, F. Fragonmele, and I. Covelli. Thyroidal phenylpyruvate tautomerase. Isolation and characterization. *J. Biol. Chem.*, 244:4864–4870, 1969.

[60] 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.

[61] K. Bloch. Enzymatic synthesis of monounsaturated fatty acids. *Acc. Chem. Res.*, 2:193–202, 1969.

[62] C.S. Bond, M.F. White, and W.N. Hunter. High resolution structure of the phosphohistidine-activated form of *Escherichia coli* cofactor-dependent phosphoglycerate mutase. *J. Biol. Chem.*, 276:3247–3253, 2001.

[63] F. Bouvier, A. d'Harlingue, R.A. Backhaus, M.H. Kumagai, and B. Camara. Identification of neoxanthin synthase as a carotenoid cyclase paralog. *Eur. J. Biochem.*, 267:6346–6352, 2000.

[64] F. Bouvier, P. Hugueney, A. d'Harlingue, M. Kuntz, and B. Camara. Xanthophyll biosynthesis in chromoplasts: isolation and molecular cloning of an enzyme catalyzing the conversion of 5,6-epoxycarotenoid into ketocarotenoid. *Plant J.*, 6:45–54, 1994.

[65] J.T. Bouvier, F.P. Groninger-Poe, M. Vetting, S.C. Almo, and J.A. Gerlt. Galactaro δ-lactone isomerase: lactone isomerization by a member of the amidohydrolase superfamily. *Biochemistry*, 53:614–616, 2014.

[66] E. Bowman, M. McQueney, R.J. Barry, and D. Dunaway-Mariano. Catalysis and thermodynamics of the phospho*enol*pyruvate phosphonopyruvate rearrangement - entry into the phosphonate class of naturally-occurring organophosphorus compounds. *J. Am. Chem. Soc.*, 110:5575–5576, 1988.

[67] G.H. Braus, K. Luger, G. Paravicini, T. Schmidheini, K. Kirschner, and R. Hütter. The role of the TRP1 gene in yeast tryptophan biosynthesis. *J. Biol. Chem.*, 263:7868–7875, 1988.

[68] G. Brendelberger, J. Rétey, D.M. Ashworth, K. Reynolds, F. Willenbrock, and J.A. Robinson. The enzymic interconversion of isobutyryl and *N*-butyrylcarba(dethia)-coenzyme-A - a coenzyme-B_{12}-dependent carbon skeleton rearrangement. *Angew. Chem. Int. Ed. Engl.*, 27:1089–1091, 1988.

[69] D.J.H. Brock, L.R. Kass, and K. Bloch. β-Hydroxydecanoyl thioester dehydrase. II. Mode of action. *J. Biol. Chem.*, 242:4432–4440, 1967.

[70] F. Brodhun, C. Gobel, E. Hornung, and I. Feussner. Identification of PpoA from *Aspergillus nidulans* as a fusion protein of a fatty acid heme dioxygenase/peroxidase and a cytochrome P_{450}. *J. Biol. Chem.*, 284:11792–11805, 2009.

[71] 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.

[72] N.C. Bruce and R.B. Cain. β-Methylmuconolactone, a key intermediate in the dissimilation of methylaromatic compounds by a modified 3-oxoadipate pathway evolved in nocardioform actinomycetes. *FEMS Microbiol. Lett.*, 50:233–239, 1988.

[73] F.H. Bruns, E. Noltmann, and A. Willemsen. Phosphomannose-isomerase. I. Über die Aktivitätsmessung und die Sulfhydryl-sowie die metallabhängigkeit der Enzymirkung in einigen Tierischen Geweben. *Biochem. Z.*, 330:411–420, 1958.

[74] D.P. Burma and B.L. Horecker. IV. ¡stereo¿L¡/stereo¿-Ribulose-5-phosphate 4-epimerase. Pentose formation by *Lactobacillus plantarum*. *J. Biol. Chem.*, 231:1053–1064, 1958.

[75] R.E. Campbell, S.C. Mosimann, M.E. Tanner, and N.C. Strynadka. The structure of UDP-*N*-acetylglucosamine 2-epimerase reveals homology to phosphoglycosyl transferases. *Biochemistry*, 39:14993–15001, 2000.

[76] M. Del Campo, Y. Kaya, and J. Ofengand. Identification and site of action of the remaining four putative pseudouridine synthases in *Escherichia coli*. *RNA*, 7:1603–1615, 2001.

[77] C. Cantwell, R. Beckmann, P. Whiteman, S.W. Queener, and E.P. Abraham. Isolation of deacetoxycephalosporin-c from fermentation broths of *Penicillium chrysogenum* transformants - construction of a new fungal biosynthetic-pathway. *Proc. R. Soc. Lond. B Biol. Sci.*, 248:283–289, 1992.

[78] D.M. Carlson. Phosphoacetylglucosamine mutase from pig submaxillary gland. *Methods Enzymol.*, 8:179–182, 1966.

[79] H.L. Carrell, J.P. Glusker, V. Burger, F. Manfre, D. Tritsch, and J.F. Biellmann. X-ray analysis of D-xylose isomerase at 1.9 Å: native enzyme in complex with substrate and with a mechanism-designed inactivator. *Proc. Natl. Acad. Sci. USA*, 86:4440–4444, 1989.

[80] 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.

[81] C. Chai, J. Fang, Y. Liu, H. Tong, Y. Gong, Y. Wang, M. Liu, Y. Wang, Q. Qian, Z. Cheng, and C. Chu. ZEBRA2, encoding a carotenoid isomerase, is involved in photoprotection in rice. *Plant Mol. Biol.*, 75:211–221, 2011.

[82] C.M. Chan and R.H. Huang. Enzymatic characterization and mutational studies of TruD—the fifth family of pseudouridine synthases. *Arch. Biochem. Biophys.*, 489:15–19, 2009.

[83] H.C. Chan, Y. Zhu, Y. Hu, T.P. Ko, C.H. Huang, F. Ren, C.C. Chen, Y. Ma, R.T. Guo, and Y. Sun. Crystal structures of D-psicose 3-epimerase from *Clostridium cellulolyticum* H10 and its complex with ketohexose sugars. *Protein Cell*, 3:123–131, 2012.

[84] R. Chandra, E.D. Salmon, H.P. Erickson, A. Lockhart, and S.A. Endow. Structural and functional domains of the *Drosophila* ncd microtubule motor protein. *J. Biol. Chem.*, 268:9005–9013, 1993.

[85] C.H. Chang and P.A. Frey. Cloning, sequencing, heterologous expression, purification, and characterization of adenosylcobalamin-dependent D-lysine 5, 6-aminomutase from *Clostridium sticklandii*. *J. Biol. Chem.*, 275:106–114, 2000.

[86] B.N. Chaudhuri, S. Chan, L.J. Perry, and T.O. Yeates. Crystal structure of the apo forms of Ψ55 tRNA pseudouridine synthase from *Mycobacterium tuberculosis*: a hinge at the base of the catalytic cleft. *J. Biol. Chem.*, 279:24585–24591, 2004.

[87] P.S.J. Cheetham. The extraction and mechanism of a novel isomaltulose-synthesizing enzyme from *Erwinia rhapontici*. *Biochem. J.*, 220:213–220, 1984.

[88] P.S.J. Cheetham, C.E. Imber, and J. Isherwood. The formation of isomaltulose by immobilized *Erwinia rhapontici*. *Nature*, 299:628–631, 1982.

[89] P.S.J. Cheetham and A.N. Wootton. Bioconversion of D-galactose into D-tagatose. *Enzyme and Microbial Technology*, 15:105–108, 1993.

[90] H.P. Chen, C.F. Lin, Y.J. Lee, S.S. Tsay, and S.H. Wu. Purification and properties of ornithine racemase from *Clostridium sticklandii*. *J. Bacteriol.*, 182:2052–2054, 2000.

[91] I.C. Chen, W.D. Lin, S.K. Hsu, V. Thiruvengadam, and W.H. Hsu. Isolation and characterization of a novel lysine racemase from a soil metagenomic library. *Appl. Environ. Microbiol.*, 75:5161–5166, 2009.

[92] J. Chen and J.R. Patton. Pseudouridine synthase 3 from mouse modifies the anticodon loop of tRNA. *Biochemistry*, 39:12723–12730, 2000.

[93] M. Chen and J.T. Zhang. Membrane insertion, processing, and topology of cystic fibrosis transmembrane conductance regulator (CFTR) in microsomal membranes. *Mol. Membr. Biol.*, 13:33–40, 1996.

[94] X. Chen, A. Berim, F.E. Dayan, and D.R. Gang. A (–)-kolavenyl diphosphate synthase catalyzes the first step of salvinorin A biosynthesis in *Salvia divinorum*. *J. Exp. Bot.*, 68:1109–1122, 2017.

[95] Y. Chen, F. Li, and E.T. Wurtzel. Isolation and characterization of the *Z*-ISO gene encoding a missing component of carotenoid biosynthesis in plants. *Plant Physiol.*, 153:66–79, 2010.

[96] H.J. Chiu, J.C. Grant, C.L. Farr, L. Jaroszewski, M.W. Knuth, M.D. Miller, M.A. Elsliger, A.M. Deacon, A. Godzik, S.A. Lesley, and I.A. Wilson. Structural analysis of arabinose-5-phosphate isomerase from *Bacteroides fragilis* and functional implications. *Acta Crystallogr. D Biol. Crystallogr.*, 70:2640–2651, 2014.

[97] E. Christ-Hazelhof and D.H. Nugteren. Purification and characterisation of prostaglandin endoperoxide Δ-isomerase, a cytoplasmic, glutathione-requiring enzyme. *Biochim. Biophys. Acta*, 572:43–51, 1979.

[98] S.S. Cohen. Studies on D-ribulose and its enzymatic conversion to D-arabinose. *J. Biol. Chem.*, 201:71–84, 1953.

[99] C.A. Collyer and D.M. Blow. Observations of reaction intermediates and the mechanism of aldose-ketose interconversion by D-xylose isomerase. *Proc. Natl. Acad. Sci. USA*, 87:1362–1366, 1990.

[100] G. Condemine and J. Robert-Baudouy. Analysis of an *Erwinia chrysanthemi* gene cluster involved in pectin degradation. *Mol. Microbiol.*, 5:2191–2202, 1991.

[101] J. Conrad, L. Niu, K. Rudd, B.G. Lane, and J. Ofengand. 16S ribosomal RNA pseudouridine synthase RsuA of *Escherichia coli*: deletion, mutation of the conserved Asp^{102} residue, and sequence comparison among all other pseudouridine synthases. *RNA*, 5:751–763, 1999.

[102] J. Conrad, D. Sun, N. Englund, and J. Ofengand. The *rluC* gene of *Escherichia coli* codes for a pseudouridine synthase that is solely responsible for synthesis of pseudouridine at positions 955, 2504, and 2580 in 23 S ribosomal RNA. *J. Biol. Chem.*, 273:18562–18566, 1998.

[103] D. Corollo, M. Blair-Johnson, J. Conrad, T. Fiedler, D. Sun, L. Wang, J. Ofengand, and R. Fenna. Crystallization and characterization of a fragment of pseudouridine synthase RluC from *Escherichia coli*. *Acta Crystallogr. D Biol. Crystallogr.*, 55:302–304, 1999.

[104] 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.

[105] V. Cracan and R. Banerjee. Novel coenzyme B_{12}-dependent interconversion of isovaleryl-CoA and pivalyl-CoA. *J. Biol. Chem.*, 287:3723–3732, 2012.

[106] V. Cracan, D. Padovani, and R. Banerjee. IcmF is a fusion between the radical B_{12} enzyme isobutyryl-CoA mutase and its G-protein chaperone. *J. Biol. Chem.*, 285:655–666, 2010.

[107] 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.

[108] J.E. Cronan, Rock Jr., and C.O. Biosynthesis of membrane lipids. In F.C. Neidhardt, editor, *Escherichia coli and Salmonella: Cellular and Molecular Biology*, volume 1, pages 612–636. ASM Press, Washington, DC, 2nd edition, 1996.

[109] R. Croteau, N.M. Felton, and C.J. Wheeler. Stereochemistry at C-1 of geranyl pyrophosphate and neryl pyrophosphate in the cyclization to (+)- and (-)-bornyl pyrophosphate. *J. Biol. Chem.*, 260:5956–5962, 1985.

[110] R. Croteau, J. Gershenzon, C.J. Wheeler, and D.M. Satterwhite. Biosynthesis of monoterpenes: stereochemistry of the coupled isomerization and cyclization of geranyl pyrophosphate to camphane and isocamphane monoterpenes. *Arch. Biochem. Biophys.*, 277:374–381, 1990.

[111] R. Croteau and F. Karp. Biosynthesis of monoterpenes: preliminary characterization of bornyl pyrophosphate synthetase from sage (*Salvia officinalis*) and demonstration that geranyl pyrophosphate is the preferred substrate for cyclization. *Arch. Biochem. Biophys.*, 198:512–522, 1979.

[112] 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 (-)-bornyl pyrophosphate. *J. Biol. Chem.*, 261:13438–13445, 1986.

[113] R. Croteau and J. Shaskus. Biosynthesis of monoterpenes: demonstration of a geranyl pyrophosphate:(-)-bornyl pyrophosphate cyclase in soluble enzyme preparations from tansy (*Tanacetum vulgare*). *Arch. Biochem. Biophys.*, 236:535–543, 1985.

[114] R.B. Croteau, J.J. Shaskus, B. Renstrom, N.M. Felton, D.E. Cane, A. Saito, and C. Chang. Mechanism of the pyrophosphate migration in the enzymatic cyclization of geranyl and linalyl pyrophosphates to (+)- and (-)-bornyl pyrophosphates. *Biochemistry*, 24:7077–7085, 1985.

[115] J. Crouzet, B. Cameron, L. Cauchois, S. Rigault, M.C. Rouyez, , and F. , Thibaut D., Debussche, L. Genetic and sequence analysis of an 8.7-kilobase *Pseudomonas denitrificans* fragment carrying eight genes involved in transformation of precorrin-2 to cobyrinic acid. *J. Bacteriol.*, 172:5980–5990, 1990.

[116] R.L. Crowther and M.M. Georgiadis. The crystal structure of 5-keto-4-deoxyuronate isomerase from *Escherichia coli*. *Proteins*, 61:680–684, 2005.

[117] F.X. Cunningham, Chamovitz Jr., Misawa D., Gantt N., Hirschberg E., and J. Cloning and functional expression in *Escherichia coli* of a cyanobacterial gene for lycopene cyclase, the enzyme that catalyzes the biosynthesis of β-carotene. *FEBS Lett.*, 328:130–138, 1993.

[118] F.X. Cunningham, Gantt Jr., and E. One ring or two? Determination of ring number in carotenoids by lycopene ε-cyclases. *Proc. Natl. Acad. Sci. USA*, 98:2905–2910, 2001.

[119] F.X. Cunningham, Sun Jr., Chamovitz Z., Hirschberg D., Gantt J., and E. Molecular structure and enzymatic function of lycopene cyclase from the cyanobacterium *Synechococcus* sp strain PCC7942. *Plant Cell*, 6:1107–1121, 1994.

[120] E. Curti, S.J. Smerdon, and E.O. Davis. Characterization of the helicase activity and substrate specificity of *Mycobacterium tuberculosis* UvrD. *J. Bacteriol.*, 189:1542–1555, 2007.

[121] 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.

[122] M. Dadashipour, M. Iwamoto, M.M. Hossain, J.I. Akutsu, Z. Zhang, and Y. Kawarabayasi. Identification of a direct biosynthetic pathway for UDP-*N*-acetylgalactosamine from glucosamine-6-phosphate in thermophilic crenarchaeon *Sulfolobus tokodaii*. *J. Bacteriol.*, 200, 2018.

[123] C. Dahm, R. Müller, G. Schulte, K. Schmidt, and E. Leistner. The role of isochorismate hydroxymutase genes entC and menF in enterobactin and menaquinone biosynthesis in *Escherichia coli*. *Biochim. Biophys. Acta*, 1425:377–386, 1998.

[124] K. Dahm, M. Lindlau, and H. Breuer. Steroid epimerase-a new enzyme of estrogen metabolism. *Biochim. Biophys. Acta*, 159:377–389, 1968.

[125] J. Dai, L. Wang, K.N. Allen, P. Radstrom, and D. Dunaway-Mariano. Conformational cycling in β-phosphoglucomutase catalysis: reorientation of the β-D-glucose 1,6-(Bis)phosphate intermediate. *Biochemistry*, 45:7818–7824, 2006.

[126] 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.

[127] R. Daruwala, O. Kwon, R. Meganathan, and M.E. Hudspeth. A new isochorismate synthase specifically involved in menaquinone (vitamin K_2) biosynthesis encoded by the *menF* gene. *FEMS Microbiol. Lett.*, 140:159–163, 1996.

[128] M. Dastmalchi, X. Chen, J.M. Hagel, L. Chang, R. Chen, S. Ramasamy, S. Yeaman, and P.J. Facchini. Neopinone isomerase is involved in codeine and morphine biosynthesis in opium poppy. *Nat. Chem. Biol.*, 15:384–390, 2019.

[129] J.K. Davis, G.C. Paoli, Z. He, L.J. Nadeau, C.C. Somerville, and J.C. Spain. Sequence analysis and initial characterization of two isozymes of hydroxylaminobenzene mutase from *Pseudomonas pseudoalcaligenes* JS45. *Appl. Environ. Microbiol.*, 66:2965–2971, 2000.

[130] M.L. Davis, J.B. Thoden, and H.M. Holden. The x-ray structure of dTDP-4-keto-6-deoxy-D-glucose-3,4-ketoisomerase. *J. Biol. Chem.*, 282:19227–19236, 2007.

[131] H. de Reuse, A. Labigne, and D. Mengin-Lecreulx. The *Helicobacter pylori* ureC gene codes for a phosphoglucosamine mutase. *J. Bacteriol.*, 179:3488–3493, 1997.

[132] P.D.G. Dean, P.R. Oritz de Montellano, K. Bloch, and E.J. Corey. A soluble 2,3-oxidosqualene sterol cyclase. *J. Biol. Chem.*, 242:3014–3015, 1967.

[133] 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.

[134] 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.

[135] B. Desguin, T. Zhang, P. Soumillion, P. Hols, J. Hu, and R.P. Hausinger. A tethered niacin-derived pincer complex with a nickel-carbon bond in lactate racemase. *Science*, 349:66–69, 2015.

[136] J.D. Deupree and W.A. Wood. L-Ribulose 5-phosphate 4-epimerase of *Aerobacter aerogenes*. Evidence for nicotinamide adenine dinucleotide-independent 4-epimerization by the crystalline enzyme. *J. Biol. Chem.*, 245:3988–3995, 1970.

[137] D.L. DeWitt and W.L. Smith. Purification of prostacyclin synthase from bovine aorta by immunoaffinity chromatography. Evidence that the enzyme is a hemoprotein. *J. Biol. Chem.*, 258:3285–3293, 1983.

[138] R. Dhatwalia, H. Singh, M. Oppenheimer, D.B. Karr, J.C. Nix, P. Sobrado, and J.J. Tanner. Crystal structures and small-angle x-ray scattering analysis of UDP-galactopyranose mutase from the pathogenic fungus *Aspergillus fumigatus*. *J. Biol. Chem.*, 287:9041–9051, 2012.

[139] F. Dickens and D.H. Williamson. Pentose phosphate isomerase and epimerase from animal tissues. *Biochem. J.*, 64:567–578, 1956.

[140] M.L. Dickens, J. Ye, and W.R. Strohl. Analysis of clustered genes encoding both early and late steps in daunomycin biosynthesis by *Streptomyces* sp. strain C5. *J. Bacteriol.*, 177:536–543, 1995.

[141] 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.

[142] D. Dietrich, M.J. van Belkum, and J.C. Vederas. Characterization of DcsC, a PLP-independent racemase involved in the biosynthesis of D-cycloserine. *Org. Biomol. Chem.*, 10:2248–2254, 2012.

[143] L. Ding, B.L. Seto, S.A. Ahmed, Coleman, and Jr. Purification and properties of the *Escherichia coli* K-12 NAD-dependent nucleotide diphosphosugar epimerase, ADP-L-*glycero*-D-*manno*-heptose 6-epimerase. *J. Biol. Chem.*, 269:24384–24390, 1994.

[144] G.F. Domagk and R. Zech. Über den Abbau der Desoxyzucker durch Bakterienenzyme. I. L-Rhamnose-Isomerase aus *Lactobacillus plantarum*. *Biochem. Z.*, 339:145–153, 1963.

[145] X. Dong, Y. Bessho, R. Shibata, M. Nishimoto, M. Shirouzu, S. Kuramitsu, and S. Yokoyama. Crystal structure of tRNA pseudouridine synthase TruA from *Thermus thermophilus* HB8. *RNA Biol.*, 3:115–122, 2006.

[146] S.A. Douthit, M. Dlakic, D.E. Ohman, and M.J. Franklin. Epimerase active domain of *Pseudomonas aeruginosa* AlgG, a protein that contains a right-handed β-helix. *J. Bacteriol.*, 187:4573–4583, 2005.

[147] P. Dunten, H. Jaffe, and R.R. Aksamit. Crystallization of 5-keto-4-deoxyuronate isomerase from *Escherichia coli*. *Acta Crystallogr. D Biol. Crystallogr.*, 54:678–680, 1998.

[148] C.C. Eady, T. Kamoi, M. Kato, N.G. Porter, S. Davis, M. Shaw, A. Kamoi, and S. Imai. Silencing onion lachrymatory factor synthase causes a significant change in the sulfur secondary metabolite profile. *Plant Physiol.*, 147:2096–2106, 2008.

[149] 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.

[150] S.W. Edwards and W.E. Knox. Homogentisate metabolism: the isomerization of maleylacetoacetate by an enzyme which requires glutathione. *J. Biol. Chem.*, 220:79–91, 1956.

[151] 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.

[152] Eisenberg and Jr. D-Myoinositol 1-phosphate as product of cyclization of glucose 6-phosphate and substrate for a specific phosphatase in rat testis. *J. Biol. Chem.*, 242:1375–1382, 1967.

[153] E.Z. Eisenmesser, D.A. Bosco, M. Akke, and D. Kern. Enzyme dynamics during catalysis. *Science*, 295:1520–1523, 2002.

[154] M. Ejby, M.A. Sorensen, and S. Pedersen. Pseudouridylation of helix 69 of 23S rRNA is necessary for an effective translation termination. *Proc. Natl. Acad. Sci. USA*, 104:19410–19415, 2007.

[155] K. Engeland and H. Kindl. Purification and characterization of a plant peroxisomal Δ^2,Δ^3-enoyl-CoA isomerase acting on 3-*cis*-enoyl-CoA and 3-*trans*-enoyl-CoA. *Eur. J. Biochem.*, 196:699–705, 1991.

[156] T.J. Erb, B.S. Evans, K. Cho, B.P. Warlick, J. Sriram, B.M. Wood, H.J. Imker, J.V. Sweedler, F.R. Tabita, and J.A. Gerlt. A RubisCO-like protein links SAM metabolism with isoprenoid biosynthesis. *Nat. Chem. Biol.*, 8:926–932, 2012.

[157] T.J. Erb, J. Retey, G. Fuchs, and B.E. Alber. Ethylmalonyl-CoA mutase from *Rhodobacter sphaeroides* defines a new subclade of coenzyme B_{12}-dependent acyl-CoA mutases. *J. Biol. Chem.*, 283:32283–32293, 2008.

[158] U.B. Ericsson, P. Nordlund, and B.M. Hallberg. X-ray structure of tRNA pseudouridine synthase TruD reveals an inserted domain with a novel fold. *FEBS Lett.*, 565:59–64, 2004.

[159] W. Ewald, H. Werbein, and I.L. Chaikoff. Evidence for the presence of 17-hydroxypregnenedione isomerase in beef adrenal cortex. *Biochim. Biophys. Acta*, 111:306–312, 1965.

[160] R.R. Fall, , and C.A. Purification and properties of kaurene synthetase from *Fusarium moniliforme*. *J. Biol. Chem.*, 246:6913–6928, 1971.

[161] G.C. Fazio, R. Xu, and S.P.T. Matsuda. Genome mining to identify new plant triterpenoids. *J. Am. Chem. Soc.*, 126:5678–5679, 2004.

[162] D.S. Feingold, E.F. Neufeld, and W.Z. Hassid. The 4-epimerization and decarboxylation of uridine diphosphate D-glucuronic acid by extracts from *Phaseolus aureus* seedlings. *J. Biol. Chem.*, 235:910–913, 1960.

[163] L. Feng, U. Wanninayake, S. Strom, J. Geiger, and K.D. Walker. Mechanistic, mutational, and structural evaluation of a *Taxus* phenylalanine aminomutase. *Biochemistry*, 50:2919–2930, 2011.

[164] R. Feng, Y. Satoh, Y. Ogasawara, T. Yoshimura, and T. Dairi. A glycopeptidyl-glutamate epimerase for bacterial peptidoglycan biosynthesis. *J. Am. Chem. Soc.*, 139:4243–4245, 2017.

[165] 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.

[166] S.A. Filppula, A.I. Yagi, S.H. Kilpelainen, D. Novikov, D.R. FitzPatrick, M. Vihinen, D. Valle, and J.K. Hiltunen. $\Delta^{3,5}$-$\Delta^{2,4}$-dienoyl-CoA isomerase from rat liver. Molecular characterization. *J. Biol. Chem.*, 273:349–355, 1998.

[167] 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.

[168] 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.

[169] G. Fischer. Peptidyl-prolyl *cis*/*trans* isomerases and their effectors. *Angew. Chem. Int. Ed. Engl.*, 33:1415–1436, 1994.

[170] G. Fischer and H. Bang. The refolding of urea-denatured ribonuclease A is catalyzed by peptidyl-prolyl *cis-trans* isomerase. *Biochim. Biophys. Acta*, 828:39–42, 1985.

[171] G. Fischer, H. Bang, and C. Mech. [Determination of enzymatic catalysis for the *cis-trans*-isomerization of peptide binding in proline-containing peptides]. *Biomed. Biochim. Acta*, 43:1101–1111, 1984.

[172] G. Fischer, B. Wittmann-Liebold, K. Lang, T. Kiefhaber, and F.X. Schmid. Cyclophilin and peptidyl-prolyl *cis-trans* isomerase are probably identical proteins. *Nature*, 337:476–478, 1989.

[173] V.N. Foltyn, I. Bendikov, J. De Miranda, R. Panizzutti, E. Dumin, M. Shleper, P. Li, M.D. Toney, E. Kartvelishvily, and H. Wolosker. Serine racemase modulates intracellular D-serine levels through an α,β-elimination activity. *J. Biol. Chem.*, 280:1754–1763, 2005.

[174] P.G. Foster, L. Huang, D.V. Santi, and R.M. Stroud. The structural basis for tRNA recognition and pseudouridine formation by pseudouridine synthase I. *Nat. Struct. Biol.*, 7:23–27, 2000.

[175] M.J. Franklin, C.E. Chitnis, P. Gacesa, A. Sonesson, D.C. White, and D.E. Ohman. *Pseudomonas aeruginosa* AlgG is a polymer level alginate C^5-mannuronan epimerase. *J. Bacteriol.*, 176:1821–1830, 1994.

[176] I. Freer, G. Pedrocchi-Fantoni, D.J. Picken, and K.H. Overton. Stereochemistry of the leucine 2,3-aminomutase from tissue-cultures of *Andrographis paniculata*. *J. Chem. Soc. Chem. Commun.*, pages 80–82, 1981.

[177] P.A. Frey. Lysine 2,3-aminomutase: is adenosylmethionine a poor man's adenosylcobalamin. *FASEB J.*, 7:662–670, 1993.

[178] P.A. Frey and G.H. Reed. Pyridoxal-5′-phosphate as the catalyst for radical isomerization in reactions of PLP-dependent aminomutases. *Biochim. Biophys. Acta*, 1814:1548–1557, 2011.

[179] S. Fuchs, F. De Lorenzo, and C.B. Anfinsen. Studies on the mechanism of the enzymic catalysis of disulfide interchange in proteins. *J. Biol. Chem.*, 242:398–402, 1967.

[180] A. Fujimoto, P. Ingram, and R.A. Smith. D-Glucose-1-phosphate:D-glucose-6-phosphotransferase. *Biochim. Biophys. Acta*, 96:91–101, 1965.

[181] T. Fujiwara, W. Saburi, S. Inoue, H. Mori, H. Matsui, I. Tanaka, and M. Yao. Crystal structure of *Ruminococcus albus* cellobiose 2-epimerase: structural insights into epimerization of unmodified sugar. *FEBS Lett.*, 587:840–846, 2013.

[182] 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.

[183] 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.

[184] M.A. Gaston, L. Zhang, K.B. Green-Church, and J.A. Krzycki. The complete biosynthesis of the genetically encoded amino acid pyrrolysine from lysine. *Nature*, 471:647–650, 2011.

[185] R.W. Gaugler and O. Gabriel. Biological mechanisms involved in the formation of deoxy sugars. VII. Biosynthesis of 6-deoxy-L-talose. *J. Biol. Chem.*, 248:6041–6049, 1973.

[186] M. Gee and R. Vallee. The role of the dynein stalk in cytoplasmic and flagellar motility. *Eur. Biophys. J.*, 27:466–473, 1998.

[187] B.V. Geisbrecht, K. Schulz, K. Nau, M.T. Geraghty, H. Schulz, R. Erdmann, and S.J. Gould. Preliminary characterization of Yor180Cp: identification of a novel peroxisomal protein of saccharomyces cerevisiae involved in fatty acid metabolism. *Biochem. Biophys. Res. Commun.*, 260:28–34, 1999.

[188] B.V. Geisbrecht, D. Zhang, H. Schulz, and S.J. Gould. Characterization of PECI, a novel monofunctional Δ^3, Δ^2-enoyl-CoA isomerase of mammalian peroxisomes. *J. Biol. Chem.*, 274:21797–21803, 1999.

[189] M. Gellert. DNA topoisomerases. *Annu. Rev. Biochem.*, 50:879–910, 1981.

[190] L.Y. Ghoda, T.M. Savarese, D.L. Dexter, R.E. Parks, Trackman Jr., Abeles P.C., and R.H. Characterization of a defect in the pathway for converting 5′-deoxy-5′-methylthioadenosine to methionine in a subline of a cultured heterogeneous human colon carcinoma. *J. Biol. Chem.*, 259:6715–6719, 1984.

[191] S. Ghosh and S. Roseman. The sialic acids. IV. *N*-Acyl-D-glucosamine 6-phosphate 2-epimerase. *J. Biol. Chem.*, 240:1525–1530, 1965.

[192] S. Ghosh and S. Roseman. The sialic acids. V. *N*-Acyl-D-glucosamine 2-epimerase. *J. Biol. Chem.*, 240:1531–1536, 1965.

[193] G. Ghssein, C. Brutesco, L. Ouerdane, C. Fojcik, A. Izaute, S. Wang, C. Hajjar, R. Lobinski, D. Lemaire, P. Richaud, R. Voulhoux, A. Espaillat, F. Cava, D. Pignol, E. Borezee-Durant, and P. Arnoux. Biosynthesis of a broad-spectrum nicotianamine-like metallophore in *Staphylococcus aureus*. *Science*, 352:1105–1109, 2016.

[194] I.R. Gibbons. Dynein ATPases as microtubule motors. *J. Biol. Chem.*, 263:15837–15840, 1988.

[195] L. Glaser. The biosynthesis of *N*-acetylgalactosamine. *J. Biol. Chem.*, 234:2801–2805, 1959.

[196] L. Glaser. Glutamic acid racemase from *Lactobacillus arabinosus*. *J. Biol. Chem.*, 235:2095–2098, 1960.

[197] S. Goepfert, C. Vidoudez, E. Rezzonico, J.K. Hiltunen, and Y. Poirier. Molecular identification and characterization of the *Arabidopsis* $\Delta^{3,5}$,$\Delta^{2,4}$-dienoyl-coenzyme A isomerase, a peroxisomal enzyme participating in the β-oxidation cycle of unsaturated fatty acids. *Plant Physiol.*, 138:1947–1956, 2005.

[198] S. Goepfert, C. Vidoudez, C. Tellgren-Roth, S. Delessert, J.K. Hiltunen, and Y. Poirier. Peroxisomal Δ^3,Δ^2-enoyl CoA isomerases and evolution of cytosolic paralogues in embryophytes. *Plant J.*, 56:728–742, 2008.

[199] P. Goffin, M. Deghorain, J.L. Mainardi, I. Tytgat, M.C. Champomier-Verges, M. Kleerebezem, and P. Hols. Lactate racemization as a rescue pathway for supplying D-lactate to the cell wall biosynthesis machinery in *Lactobacillus plantarum*. *J. Bacteriol.*, 187:6750–6761, 2005.

[200] S.P. Gough and C.G. Kannangara. Biosynthesis of δ-aminolevulinate in greening barley leaves: glutamate 1-semialdehyde aminotransferase. *Carlsberg Res. Commun.*, 43:185–194, 1978.

[201] L.J. Gourlay, S. Sommaruga, M. Nardini, P. Sperandeo, G. Deho, A. Polissi, and M. Bolognesi. Probing the active site of the sugar isomerase domain from *E. coli* arabinose-5-phosphate isomerase via X-ray crystallography. *Protein Sci.*, 19:2430–2439, 2010.

[202] 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.

[203] R.W. Gracy and E.A. Noltmann. Studies on phosphomannose isomerase. II. Characterization as a zinc metalloenzyme. *J. Biol. Chem.*, 243:4109–4116, 1968.

[204] M. Green and S.S. Cohen. Enzymatic conversion of L-fucose to L-fuculose. *J. Biol. Chem.*, 219:557–568, 1956.

[205] E.T. Griffiths, P.C. Harries, R. Jeffcoat, and P.W. Trudgill. Purification and properties of α-pinene oxide lyase from *Nocardia* sp. strain P18.3. *J. Bacteriol.*, 169:4980–4983, 1987.

[206] S. Grisolia. Phosphoglyceric acid mutase. *Methods Enzymol.*, 5:236–242, 1962.

[207] S.R. Gross, R.D. Gafford, and E.L. Tatum. The metabolism of protocatechuic acid by *Neurospora*. *J. Biol. Chem.*, 219:781–796, 1956.

[208] O. Guhling, B. Hobl, T. Yeats, and R. Jetter. Cloning and characterization of a lupeol synthase involved in the synthesis of epicuticular wax crystals on stem and hypocotyl surfaces of *Ricinus communis*. *Arch. Biochem. Biophys.*, 448:60–72, 2006.

[209] A.M. Gulick, D.M. Schmidt, J.A. Gerlt, and I. Rayment. Evolution of enzymatic activities in the enolase superfamily: crystal structures of the L-Ala-D/L-Glu epimerases from *Escherichia coli* and *Bacillus subtilis*. *Biochemistry*, 40:15716–15724, 2001.

[210] 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.

[211] P. Gurha and R. Gupta. Archaeal Pus10 proteins can produce both pseudouridine 54 and 55 in tRNA. *RNA*, 14:2521–2527, 2008.

[212] A. Gurvitz, A.M. Mursula, A.I. Yagi, A. Hartig, H. Ruis, H. Rottensteiner, and J.K. Hiltunen. Alternatives to the isomerase-dependent pathway for the β-oxidation of oleic acid are dispensable in *Saccharomyces cerevisiae*. Identification of YOR180c/DCI1 encoding peroxisomal Δ(3,5)-Δ(2,4)-dienoyl-CoA isomerase. *J. Biol. Chem.*, 274:24514–24521, 1999.

[213] H., Levine Polet, , and A and. C in serum. *J. Biol. Chem.*, 250:351–357, 1975.

[214] A. Hagner-McWhirter, H.H. Hannesson, P. Campbell, J. Westley, L. Roden, U. Lindahl, and J.P. Li. Biosynthesis of heparin/heparan sulfate: kinetic studies of the glucuronyl C^5-epimerase with *N*-sulfated derivatives of the *Escherichia coli* K5 capsular polysaccharide as substrates. *Glycobiology*, 10:159–171, 2000.

[215] 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.

[216] 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.

[217] M. Hamberg, L.-Y. Zhang, I.D. Brodowsky, and E.H. Oliw. Sequential oxygenation of linoleic acid in the fungus *Gaeumannomyces graminis*: stereochemistry of dioxygenase and hydroperoxide isomerase reactions. *Arch. Biochem. Biophys.*, 309:77–80, 1994.

[218] K. Hammen-Jepersen and A. Munch-Petersen. Phosphodeoxyribomutase from *Escherichia coli*. Purification and some properties. *Eur. J. Biochem.*, 17:397–407, 1970.

[219] N.L. Hansen, A.M. Heskes, B. Hamberger, C.E. Olsen, B.M. Hallstrom, J. Andersen-Ranberg, and B. Hamberger. The terpene synthase gene family in *Tripterygium wilfordii* harbors a labdane-type diterpene synthase among the monoterpene synthase TPS-b subfamily. *Plant J.*, 89:429–441, 2017.

[220] R.K. Harrison and R.L. Stein. Substrate specificities of the peptidyl prolyl *cis-trans* isomerase activities of cyclophilin and FK-506 binding protein: evidence for the existence of a family of distinct enzymes. *Biochemistry*, 29:3813–3816, 1990.

[221] J.J. Hartman, J. Mahr, K. McNally, K. Okawa, A. Iwamatsu, S. Thomas, S. Cheesman, J. Heuser, R.D. Vale, and F.J. McNally. Katanin, a microtubule-severing protein, is a novel AAA ATPase that targets to the centrosome using a WD40-containing subunit. *Cell*, 93:277–287, 1998.

[222] S. Hartmans, J.P. Smits, M.J. van der Werf, F. Volkering, and J.A.M. de Bont. Metabolism of styrene oxide and 2-phenylethanol in the styrene-degrading *Xanthobacter* strain 124X. *Appl. Environ. Microbiol.*, 55:2850–2855, 1989.

[223] T. Hasson and M.S. Mooseker. Vertebrate unconventional myosins. *J. Biol. Chem.*, 271:16431–16434, 1996.

[224] 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.

[225] H. Hayashi, P. Huang, K. Inoue, N. Hiraoka, Y. Ikeshiro, K. Yazaki, S. Tanaka, T. Kushiro, M. Shibuya, and Y. Ebizuka. Molecular cloning and characterization of isomultiflorenol synthase, a new triterpene synthase from *Luffa cylindrica*, involved in biosynthesis of bryonolic acid. *Eur. J. Biochem.*, 268:6311–6317, 2001.

[226] H. Hayashi, P. Huang, A. Kirakosyan, K. Inoue, N. Hiraoka, Y. Ikeshiro, T. Kushiro, M. Shibuya, and Y. Ebizuka. Cloning and characterization of a cDNA encoding β-amyrin synthase involved in glycyrrhizin and soyasaponin biosyntheses in licorice. *Biol. Pharm. Bull.*, 24:912–916, 2001.

[227] H. Hayashi, P. Huang, S. Takada, M. Obinata, K. Inoue, M. Shibuya, and Y. Ebizuka. Differential expression of three oxidosqualene cyclase mRNAs in *Glycyrrhiza glabra*. *Biol. Pharm. Bull.*, 27:1086–1092, 2004.

[228] A.B. Hazra, Y. Han, A. Chatterjee, Y. Zhang, R.Y. Lai, S.E. Ealick, and T.P. Begley. A missing enzyme in thiamin thiazole biosynthesis: identification of TenI as a thiazole tautomerase. *J. Am. Chem. Soc.*, 133:9311–9319, 2011.

[229] J. He, N. Magarvey, M. Piraee, and L.C. Vining. The gene cluster for chloramphenicol biosynthesis in *Streptomyces venezuelae* ISP5230 includes novel shikimate pathway homologues and a monomodular non-ribosomal peptide synthetase gene. *Microbiology*, 147:2817–2829, 2001.

[230] Z. He, L.J. Nadeau, and J.C. Spain. Characterization of hydroxylaminobenzene mutase from pNBZ139 cloned from *Pseudomonas pseudoalcaligenes* JS45: a highly-associated sodium-dodecyl-sulfate-stable enzyme catalyzing an intramolecular transfer of hydroxyl group. *Eur. J. Biochem.*, 267:1110–1116, 2000.

[231] E.C. Heath, B.L. Horecker, P.Z. Smyrniotis, and Y. Takagi. Pentose formation by *Lactobacillus plantarum*. II. L-Arabinose isomerase. *J. Biol. Chem.*, 231:1031–1037, 1958.

[232] P.A. Hebda, E.J. Behrman, and G.A. Barber. The guanosine 5′-diphosphate D-mannose: guanosine 5′-diphosphate L-galactose epimerase of *Chlorella pyrenoidosa*. Chemical synthesis of guanosine 5′-diphosphate L-galactose and further studies of the enzyme and the reaction it catalyzes. *Arch. Biochem. Biophys.*, 194:496–502, 1979.

[233] R. Heintz and P. Benveniste. Plant sterol metabolism. Enzymatic cleavage of the 9β,19β-cyclopropane ring of cyclopropyl sterols in bramble tissue cultures. *J. Biol. Chem.*, 249:4267–4274, 1974.

[234] S.M. Hemmingsen, C. Woolford, S.M. van der Vies, K. Tilly, D.T. Dennis, G.C. Georgopoulos, R.W. Hendrix, and R.J. Ellis. Homologous plant and bacterial proteins: chaperone oligomeric protein assembly. *Nature*, 333:330–334, 1988.

[235] L. Hennig, C. Christner, M. Kipping, B. Schelbert, K.P. Rucknagel, S. Grabley, G. Kullertz, and G. Fischer. Selective inactivation of parvulin-like peptidyl-prolyl *cis/trans* isomerases by juglone. *Biochemistry*, 37:5953–5960, 1998.

[236] U. Henningsen and M. Schliwa. Reversal in the direction of movement of a molecular motor. *Nature*, 389:93–96, 1997.

[237] J.B. Herrera, B. Bartel, W.K. Wilson, and S.P. Matsuda. Cloning and characterization of the *Arabidopsis thaliana* lupeol synthase gene. *Phytochemistry*, 49:1905–1911, 1998.

[238] T. Hikada, S. Imai, O. Hara, H. Anzai, T. Murakami, K. Nagaoka, and H. Seto. Carboxyphosphonoenolpyruvate phosphonomutase, a novel enzyme catalyzing C-P bond formation. *J. Bacteriol.*, 172:3066–3072, 1990.

[239] C. Hoang, J. Chen, C.A. Vizthum, J.M. Kandel, C.S. Hamilton, E.G. Mueller, and A.R. Ferre-D'Amare. Crystal structure of pseudouridine synthase RluA: indirect sequence readout through protein-induced RNA structure. *Mol. Cell*, 24:535–545, 2006.

[240] C. Hoang, C.S. Hamilton, E.G. Mueller, and A.R. Ferre-D'Amare. Precursor complex structure of pseudouridine synthase TruB suggests coupling of active site perturbations to an RNA-sequestering peripheral protein domain. *Protein Sci.*, 14:2201–2206, 2005.

[241] R.M. Hochster and R.W. Watson. Enzymatic isomerization of D-xylose to D-xylulose. *Arch. Biochem. Biophys.*, 48:120–129, 1954.

[242] I. Hoffmann, F. Jerneren, U. Garscha, and E.H. Oliw. Expression of 5,8-LDS of *Aspergillus fumigatus* and its dioxygenase domain. A comparison with 7,8-LDS, 10-dioxygenase, and cyclooxygenase. *Arch. Biochem. Biophys.*, 506:216–222, 2011.

[243] B.L. Horecker, P.Z. Smyrniotis, and J.E. Seegmiller. The enzymatic conversion of 6-phosphogluconate to ribulose-5-phosphate and ribose-5-phosphate. *J. Biol. Chem.*, 193:383–396, 1951.

[244] D. Hornero-Mendez and G. Britton. Involvement of NADPH in the cyclization reaction of carotenoid biosynthesis. *FEBS Lett.*, 515:133–136, 2002.

[245] S. Hoshiko, Y. Kunimoto, K. Arima, and T. Beppu. Mechanism of L-alloisocitric acid fermentation: isocitrate epimerase activity in the cell-free-extract of *Penicillium purpurogenum*. *Agric. Biol. Chem.*, 46:143–151, 1982.

[246] 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.

[247] T. Hoshino and T. Sato. Squalene-hopene cyclase: catalytic mechanism and substrate recognition. *Chem. Commun.*, pages 291–301, 2002.

[248] J. Howard. Molecular motors: structural adaptations to cellular functions. *Nature*, 389:561–567, 1997.

[249] H.T. Huang. *dl*-Lysine production by lysine racemase, 1960.

[250] H.T. Huang and J.W. Davisson. Distribution of lysine racemase in bacteria. *J. Bacteriol.*, 76:495–498, 1958.

[251] L. Huang, M. Pookanjanatavip, X. Gu, and D.V. Santi. A conserved aspartate of tRNA pseudouridine synthase is essential for activity and a probable nucleophilic catalyst. *Biochemistry*, 37:344–351, 1998.

[252] F.M. Huennekens, H.R. Mahler, and J. Nordmann. Studies on the cyclophorase system. XVII. The occurrence and properties of an α-hydroxy acid racemase. *Arch. Biochem.*, 30:77–89, 1951.

[253] P. Hugueney, A. Badillo, H.C. Chen, A. Klein, J. Hirschberg, B. Camara, and M. Kuntz. Metabolism of cyclic carotenoids: a model for the alteration of this biosynthetic pathway in *Capsicum annuum* chromoplasts. *Plant J.*, 8:417–424, 1995.

[254] S. Hur and R.M. Stroud. How U38, 39, and 40 of many tRNAs become the targets for pseudouridylation by TruA. *Mol. Cell*, 26:189–203, 2007.

[255] J. Hurwitz and B.L. Horecker. The purification of phosphoketopentoepimerase from *Lactobacillus pentosus* and the preparation of xylulose 5-phosphate. *J. Biol. Chem.*, 223:993–1008, 1956.

[256] J. Hurwitz, A. Weissbach, B.L. Horecker, and P.Z. Smyrniotis. Spinach phosphoribulokinase. *J. Biol. Chem.*, 218:769–783, 1956.

[257] T. Husselstein-Muller, H. Schaller, and P. Benveniste. Molecular cloning and expression in yeast of 2,3-oxidosqualene-triterpenoid cyclases from *Arabidopsis thaliana*. *Plant Mol. Biol.*, 45:75–92, 2001.

[258] R. Hütter, P. Niederberger, and J.A. DeMoss. Tryptophan synthetic genes in eukaryotic microorganisms. *Annu. Rev. Microbiol.*, 40:55–77, 1986.

[259] T.C. Hwang and D.N. Sheppard. Gating of the CFTR Cl^- channel by ATP-driven nucleotide-binding domain dimerisation. *J. Physiol.*, 587:2151–2161, 2009.

[260] S. Imai, N. Tsuge, M. Tomotake, Y. Nagatome, H. Sawada, T. Nagata, and H. Kumagai. Plant biochemistry: an onion enzyme that makes the eyes water. *Nature*, 419:685–685, 2002.

[261] H.J. Imker, J. Singh, B.P. Warlick, F.R. Tabita, and J.A. Gerlt. Mechanistic diversity in the RuBisCO superfamily: a novel isomerization reaction catalyzed by the RuBisCO-like protein from *Rhodospirillum rubrum*. *Biochemistry*, 47:11171–11173, 2008.

[262] T. Isaacson, G. Ronen, D. Zamir, and J. Hirschberg. Cloning of tangerine from tomato reveals a carotenoid isomerase essential for the production of β-carotene and xanthophylls in plants. *Plant Cell*, 14:333–342, 2002.

[263] W. Ismail, M. El-Said Mohamed, B.L. Wanner, K.A. Datsenko, W. Eisenreich, F. Rohdich, A. Bacher, and G. Fuchs. Functional genomics by NMR spectroscopy. Phenylacetate catabolism in *Escherichia coli*. *Eur. J. Biochem.*, 270:3047–3054, 2003.

[264] R. Ito, K. Mori, I. Hashimoto, C. Nakano, T. Sato, and T. Hoshino. Triterpene cyclases from *Oryza sativa* L.: cycloartenol, parkeol and achilleol B synthases. *Org. Lett.*, 13:2678–2681, 2011.

[265] S. Ito, H. Taguchi, S. Hamada, S. Kawauchi, H. Ito, T. Senoura, J. Watanabe, M. Nishimukai, S. Ito, and H. Matsui. Enzymatic properties of cellobiose 2-epimerase from *Ruminococcus albus* and the synthesis of rare oligosaccharides by the enzyme. *Appl. Microbiol. Biotechnol.*, 79:433–441, 2008.

[266] H. Itoh, H. Okaya, A. R. Khan, S. Tajima, S. Hayakawa, , and K. Purification and characterization of D-tagatose 3-epimerase from *Pseudomonas* sp. ST-24. *Biosci. Biotechnol. Biochem.*, 58:2168–2171, 1994.

[267] I. Iturbe-Ormaetxe, K. Haralampidis, K. Papadopoulou, and A.E. Osbourn. Molecular cloning and characterization of triterpene synthases from *Medicago truncatula* and *Lotus japonicus*. *Plant Mol. Biol.*, 51:731–743, 2003.

[268] K.A. Ivanov and J. Ziebuhr. Human coronavirus 229E nonstructural protein 13: characterization of duplex-unwinding, nucleoside triphosphatase, and RNA 5′-triphosphatase activities. *J. Virol.*, 78:7833–7838, 2004.

[269] A.S. Ivessa, J.Q. Zhou, V.P. Schulz, E.K. Monson, and V.A. Zakian. *Saccharomyces* Rrm3p, a 5′ to 3′ DNA helicase that promotes replication fork progression through telomeric and subtelomeric DNA. *Genes Dev.*, 16:1383–1396, 2002.

[270] K. Izumori, A.W. Rees, and A.D. Elbein. Purification, crystallization, and properties of D-ribose isomerase from *Mycobacterium smegmatis*. *J. Biol. Chem.*, 250:8085–8087, 1975.

[271] I. Jacobsson, G. Bäckström, M. Höök, U. Lindahl, D.S. Feingold, A. Malmström, and L. Rodén. Biosynthesis of heparin. Assay and properties of the microsomal uronosyl C-5 epimerase. *J. Biol. Chem.*, 254:2975–2982, 1979.

[272] I. Jacobsson, U. Lindahl, J.W. Jensen, L. Roden, H. Prihar, and D.S. Feingold. Biosynthesis of heparin. Substrate specificity of heparosan *N*-sulfate D-glucuronosyl 5-epimerase. *J. Biol. Chem.*, 259:1056–1063, 1984.

[273] S. Jain, M.J. Franklin, H. Ertesvag, S. Valla, and D.E. Ohman. The dual roles of AlgG in C-5-epimerization and secretion of alginate polymers in *Pseudomonas aeruginosa*. *Mol. Microbiol.*, 47:1123–1133, 2003.

[274] M.J. Jedrzejas, M. Chander, P. Setlow, and G. Krishnasamy. Mechanism of catalysis of the cofactor-independent phosphoglycerate mutase from *Bacillus stearothermophilus*. Crystal structure of the complex with 2-phosphoglycerate. *J. Biol. Chem.*, 275:23146–23153, 2000.

[275] F. Jerneren, U. Garscha, I. Hoffmann, M. Hamberg, and E.H. Oliw. Reaction mechanism of 5,8-linoleate diol synthase, 10*R*-dioxygenase, and 8,11-hydroperoxide isomerase of *Aspergillus clavatus*. *Biochim. Biophys. Acta*, 1801:503–507, 2010.

[276] M.J. Jezewska and W. Bujalowski. Global conformational transitions in *Escherichia coli* primary replicative helicase DnaB protein induced by ATP, ADP, and single-stranded DNA binding. Multiple conformational states of the helicase hexamer. *J. Biol. Chem.*, 271:4261–4265, 1996.

[277] M. Jia, W. Mu, F. Chu, X. Zhang, B. Jiang, L.L. Zhou, and T. Zhang. A D-psicose 3-epimerase with neutral pH optimum from *Clostridium bolteae* for D-psicose production: cloning, expression, purification, and characterization. *Appl. Microbiol. Biotechnol.*, 98:717–725, 2014.

[278] M. Jiang, S.M. Sullivan, A.K. Walker, J.R. Strahler, P.C. Andrews, and J.R. Maddock. Identification of novel *Escherichia coli* ribosome-associated proteins using isobaric tags and multidimensional protein identification techniques. *J. Bacteriol.*, 189:3434–3444, 2007.

[279] 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.

[280] L. Jolly, P. Ferrari, D. Blanot, J. van Heijenoort, F. Fassy, and D. Mengin-Lecreulx. Reaction mechanism of phosphoglucosamine mutase from *Escherichia coli*. *Eur. J. Biochem.*, 262:202–210, 1999.

[281] L. Jolly, F. Pompeo, J. van Heijenoort, F. Fassy, and D. Mengin-Lecreulx. Autophosphorylation of phosphoglucosamine mutase from *Escherichia coli*. *J. Bacteriol.*, 182:1280–1285, 2000.

[282] L. Jolly, S. Wu, J. van Heijenoort, H. de Lencastre, D. Mengin-Lecreulx, and A. Tomas. The femR315 gene from *Staphylococcus aureus*, the interruption of which results in reduced methicillin resistance, encodes a phosphoglucosamine mutase. *J. Bacteriol.*, 179:5321–5325, 1997.

[283] J.G. Joshi and P. Handler. Phosphoglucomutase. I. Purification and properties of phosphoglucomutase from *Escherichia coli*. *J. Biol. Chem.*, 239:2741–2751, 1964.

[284] M. Jost, D.A. Born, V. Cracan, R. Banerjee, and C.L. Drennan. Structural basis for substrate specificity in adenosylcobalamin-dependent isobutyryl-CoA mutase and related acyl-CoA mutases. *J. Biol. Chem.*, 290:26882–26898, 2015.

[285] Y.H. Ju and D.K. Oh. Characterization of a recombinant L-fucose isomerase from *Caldicellulosiruptor saccharolyticus* that isomerizes L-fucose, D-arabinose, D-altrose, and L-galactose. *Biotechnol. Lett.*, 32:299–304, 2010.

[286] T. Kajander, L. Lehtio, M. Schlomann, and A. Goldman. The structure of *Pseudomonas* P51 Cl-muconate lactonizing enzyme: co-evolution of structure and dynamics with the dehalogenation function. *Protein Sci.*, 12:1855–1864, 2003.

[287] M. Kajikawa, K.T. Yamato, H. Fukuzawa, Y. Sakai, H. Uchida, and K. Ohyama. Cloning and characterization of a cDNA encoding β-amyrin synthase from petroleum plant *Euphorbia tirucalli* L. *Phytochemistry*, 66:1759–1766, 2005.

[288] P. Kallio, A. Sultana, J. Niemi, P. Mantsala, and G. Schneider. Crystal structure of the polyketide cyclase AknH with bound substrate and product analogue: implications for catalytic mechanism and product stereoselectivity. *J. Mol. Biol.*, 357:210–220, 2006.

[289] R.E. Kallio and A.D. Larson. Methionine degradation by a species of *Pseudomonas*. In W.D. McElroy and H.B. Glass, editors, *A Symposium on Amino Acid Metabolism*, pages 616–634. Johns Hopkins Press, Baltimore, 1955.

[290] H.O. Kammen and R. Koo. Phosphopentomutases. I. Identification of two activities in rabbit tissues. *J. Biol. Chem.*, 244:4888–4893, 1969.

[291] H.O. Kammen, C.C. Marvel, L. Hardy, and E.E. Penhoet. Purification, structure, and properties of *Escherichia coli* tRNA pseudouridine synthase I. *J. Biol. Chem.*, 263:2255–2263, 1988.

[292] K. Kaneda, T. Kuzuyama, M. Takagi, Y. Hayakawa, and H. Seto. An unusual isopentenyl diphosphate isomerase found in the mevalonate pathway gene cluster from *Streptomyces* sp. strain CL190. *Proc. Natl. Acad. Sci. USA*, 98:932–937, 2001.

[293] V. Sri Kannathasan, A.G. Staines, C.J. Dong, R.A. Field, A.G. Preston, D.J. Maskell, and J.H. Naismith. Overexpression, purification, crystallization and data collection on the *Bordetella pertussis wlbD* gene product, a putative UDP-GlcNAc 2′-epimerase. *Acta Crystallogr. D Biol. Crystallogr.*, 57:1310–1312, 2001.

[294] K. Kasahara, T. Miyamoto, T. Fujimoto, H. Oguri, T. Tokiwano, H. Oikawa, Y. Ebizuka, and I. Fujii. Solanapyrone synthase, a possible Diels-Alderase and iterative type I polyketide synthase encoded in a biosynthetic gene cluster from *Alternaria solani*. *ChemBioChem*, 11:1245–1252, 2010.

[295] 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.

[296] K. Katayama, T. Kobayashi, M. Chijimatsu, A. Ichihara, and H. Oikawa. Purification and N-terminal amino acid sequence of solanapyrone synthase, a natural Diels-Alderase from *Alternaria solani*. *Biosci. Biotechnol. Biochem.*, 72:604–607, 2008.

[297] K. Katayama, T. Kobayashi, H. Oikawa, M. Honma, and A. Ichihara. Enzymatic activity and partial purification of solanapyrone synthase: first enzyme catalyzing Diels-Alder reaction. *Biochim. Biophys. Acta*, 1384:387–395, 1998.

[298] 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.

[299] S. Kato, H. Hemmi, and T. Yoshimura. Lysine racemase from a lactic acid bacterium, *Oenococcus oeni*: structural basis of substrate specificity. *J. Biochem.*, 152:505–508, 2012.

[300] U. Kaulmann, S.R. Kaschabek, and M. Schlomann. Mechanism of chloride elimination from 3-chloro- and 2,4-dichloro-*cis*,*cis*-muconate: new insight obtained from analysis of muconate cycloisomerase variant CatB-K169A. *J. Bacteriol.*, 183:4551–4561, 2001.

[301] F.S. Kawahara and P. Talalay. Crystalline Δ^5-3-ketosteroid isomerase. *J. Biol. Chem.*, 235:PC1–PC2, 1960.

[302] 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.

[303] T. Kawamura, M. Kimura, S. Yamamori, and E. Ito. Enzymatic formation of uridine diphosphate *N*-acetyl-D-mannosamine. *J. Biol. Chem.*, 253:3595–3601, 1978.

[304] Y. Kaya and J. Ofengand. A novel unanticipated type of pseudouridine synthase with homologs in bacteria, archaea, and eukarya. *RNA*, 9:711–721, 2003.

[305] 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.

[306] D. Keilin and E.F. Hartree. Biological catalysis of mutarotation of glucose. *Biochem. J.*, 50:341–348, 1952.

[307] W.L. Kelly and C.A. Townsend. Mutational analysis and characterization of nocardicin C-9′ epimerase. *J. Biol. Chem.*, 279:38220–38227, 2004.

[308] W.L. Kelly and C.A. Townsend. Mutational analysis of *nocK* and *nocL* in the nocardicin a producer *Nocardia uniformis*. *J. Bacteriol.*, 187:739–746, 2005.

[309] S.G. Kendrew, K. Katayama, E. Deutsch, K. Madduri, and C.R. Hutchinson. DnrD cyclase involved in the biosynthesis of doxorubicin: purification and characterization of the recombinant enzyme. *Biochemistry*, 38:4794–4799, 1999.

[310] 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.

[311] C.R. Kepler and S.B. Tove. Biohydrogenation of unsaturated fatty acids. III. Purification and properties of linoleate Δ^{12}-*cis*, Δ^{11}-*trans*-isomerase from *Butyrivibrio fibrosolvens*. *J. Biol. Chem.*, 242:5686–5692, 1967.

[312] W.W. Kilgore and M.P. Starr. Catabolism of galacturonic and glucuronic acids by *Erwinia carotovora*. *J. Biol. Chem.*, 234:2227–2235, 1959.

[313] J. Kim, D. Darley, and W. Buckel. 2-Hydroxyisocaproyl-CoA dehydratase and its activator from *Clostridium difficile*. *FEBS J.*, 272:550–561, 2005.

[314] 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.

[315] 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.

[316] M.S. Kim and D.H. Shin. A preliminary X-ray study of sedoheptulose-7-phosphate isomerase from *Burkholderia pseudomallei*. *Acta Crystallogr. Sect. F Struct. Biol. Cryst. Commun.*, 65:1110–1112, 2009.

[317] M.S. Kim, J. Shin, W. Lee, H.S. Lee, and B.H. Oh. Crystal structures of RbsD leading to the identification of cytoplasmic sugar-binding proteins with a novel folding architecture. *J. Biol. Chem.*, 278:28173–28180, 2003.

[318] K. Kitahara, A. Obayashi, and S. Fukui. Racemase I cell-free racemase. *Enzymologia*, 15:259–266, 1953.

[319] R.B. Kjonaas, K.V. Venkatachalam, and R. Croteau. Metabolism of monoterpenes: oxidation of isopiperitenol to isopiperitenone, and subsequent isomerization to piperitenone by soluble enzyme preparations from peppermint (*Mentha piperita*) leaves. *Arch. Biochem. Biophys.*, 238:49–60, 1985.

[320] J.P. Klinman and I.A. Rose. Mechanism of the aconitate isomerase reaction. *Biochemistry*, 10:2259–2266, 1971.

[321] J.P. Klinman and I.A. Rose. Purification and kinetic properties of aconitate isomerase from *Pseudomonas putida*. *Biochemistry*, 10:2253–2259, 1971.

[322] S.H. Knauer, W. Buckel, and H. Dobbek. On the ATP-dependent activation of the radical enzyme (*R*)-2-hydroxyisocaproyl-CoA dehydratase. *Biochemistry*, 51:6609–6622, 2012.

[323] B. Kneidinger, M. Graninger, M. Puchberger, P. Kosma, and P. Messner. Biosynthesis of nucleotide-activated D-*glycero*-D-*manno*-heptose. *J. Biol. Chem.*, 276:20935–20944, 2001.

[324] B. Kneidinger, C. Marolda, M. Graninger, A. Zamyatina, F. McArthur, P. Kosma, M.A. Valvano, and P. Messner. Biosynthesis pathway of ADP-L-*glycero*-β-D-*manno*-heptose in *Escherichia coli*. *J. Bacteriol.*, 184:363–369, 2002.

[325] B. Kneidinger, K. O'Riordan, J. Li, J.R. Brisson, J.C. Lee, and J.S. Lam. Three highly conserved proteins catalyze the conversion of UDP-*N*-acetyl-D-glucosamine to precursors for the biosynthesis of O antigen in *Pseudomonas aeruginosa* O11 and capsule in *Staphylococcus aureus* type 5. Implications for the UDP-*N*-acetyl-L-fucosamine biosynthetic pathway. *J. Biol. Chem.*, 278:3615–3627, 2003.

[326] W.E. Knox. *p*-Hydroxyphenylpyruvate enol-keto tautomerase. *Methods Enzymol.*, 2:289–295, 1955.

[327] W.E. Knox and B.M. Pitt. Enzymic catalysis of the keto-enol tautomerization of phenylpyruvic acids. *J. Biol. Chem.*, 225:675–688, 1957.

[328] M.D. Kolesnikova, W.K. Wilson, D.A. Lynch, A.C. Obermeyer, and S.P. Matsuda. *Arabidopsis* camelliol C synthase evolved from enzymes that make pentacycles. *Org. Lett.*, 9:5223–5226, 2007.

[329] T.G. Kollner, C. Schnee, S. Li, A. Svatos, B. Schneider, J. Gershenzon, and J. Degenhardt. Protonation of a neutral (*S*)-β-bisabolene intermediate is involved in (*S*)-β-macrocarpene formation by the maize sesquiterpene synthases TPS6 and TPS11. *J. Biol. Chem.*, 283:20779–20788, 2008.

[330] T. Konishi, Y. Miyazaki, S. Yamakawa, H. Iwai, S. Satoh, and T. Ishii. Purification and biochemical characterization of recombinant rice UDP-arabinopyranose mutase generated in insect cells. *Biosci. Biotechnol. Biochem.*, 74:191–194, 2010.

[331] T. Konishi, M. Ohnishi-Kameyama, K. Funane, Y. Miyazaki, T. Konishi, and T. Ishii. An arginyl residue in rice UDP-arabinopyranose mutase is required for catalytic activity and autoglycosylation. *Carbohydr. Res.*, 345:787–791, 2010.

[332] T. Konishi, T. Takeda, Y. Miyazaki, M. Ohnishi-Kameyama, T. Hayashi, M.A. O'Neill, and T. Ishii. A plant mutase that interconverts UDP-arabinofuranose and UDP-arabinopyranose. *Glycobiology*, 17:345–354, 2007.

[333] I.P. Korndorfer, W.D. Fessner, and B.W. Matthews. The structure of rhamnose isomerase from *Escherichia coli* and its relation with xylose isomerase illustrates a change between inter and intra-subunit complementation during evolution. *J. Mol. Biol.*, 300:917–933, 2000.

[334] S. Kornfeld and L. Glaser. The synthesis of thymidine-linked sugars. V. Thymidine diphosphate-amino sugars. *J. Biol. Chem.*, 237:3052–3059, 1962.

[335] N.M. Koropatkin, H.W. Liu, and H.M. Holden. High resolution x-ray structure of tyvelose epimerase from *Salmonella typhi*. *J. Biol. Chem.*, 278:20874–20881, 2003.

[336] R. Kubec, R.B. Cody, A.J. Dane, R.A. Musah, J. Schraml, A. Vattekkatte, and E. Block. Applications of direct analysis in real time-mass spectrometry (DART-MS) in *Allium* chemistry. (*Z*)-butanethial *S*-oxide and 1-butenyl thiosulfinates and their *S*-(*E*)-1-butenylcysteine *S*-oxide precursor from *Allium* siculum. *J. Agric. Food Chem.*, 58:1121–1128, 2010.

[337] R.L. Kubiak, R.K. Phillips, M.W. Zmudka, M.R. Ahn, E.M. Maka, G.L. Pyeatt, S.J. Roggensack, and H.M. Holden. Structural and functional studies on a 3′-epimerase involved in the biosynthesis of dTDP-6-deoxy-D-allose. *Biochemistry*, 51:9375–9383, 2012.

[338] A.E. Kuhm, M. Schlömann, H.-J. Knackmuss, and D.H. Pieper. Purification and characterization of dichloromuconate cycloisomerase from *Alcaligenes eutrophus* JMP 134. *Biochem. J.*, 266:877–883, 1990.

[339] F.J. Kull, E.P. Sablin, R. Lau, R.J. Fletterick, and R.D. Vale. Crystal structure of the kinesin motor domain reveals a structural similarity to myosin. *Nature*, 380:550–555, 1996.

[340] T. Kumagai, Y. Koyama, K. Oda, M. Noda, Y. Matoba, and M. Sugiyama. Molecular cloning and heterologous expression of a biosynthetic gene cluster for the antitubercular agent D-cycloserine produced by *Streptomyces lavendulae*. *Antimicrob. Agents Chemother.*, 54:1132–1139, 2010.

[341] R. Kumar, S. Zhao, M.W. Vetting, B.M. Wood, A. Sakai, K. Cho, J. Solbiati, S.C. Almo, J.V. Sweedler, M.P. Jacobson, J.A. Gerlt, and J.E. Cronan. Prediction and biochemical demonstration of a catabolic pathway for the osmoprotectant proline betaine. *MBio*, 5:e00933–e00913, 2014.

[342] H.-F. Kung, S. Cederbaum, L. Tsai, and T.C. Stadtman. Nicotinic acid metabolism. V. A cobamide coenzyme-dependent conversion of α-methyleneglutaric acid to dimethylmaleic acid. *Proc. Natl. Acad. Sci. USA*, 65:978–984, 1970.

[343] H.-F. Kung and T.C. Stadtman. Nicotinic acid metabolism. VI. Purification and properties of α-methyleneglutarate mutase (B_{12}-dependent) and methylitaconate isomerase. *J. Biol. Chem.*, 246:3378–3388, 1971.

[344] N. Kurteva-Yaneva, M. Zahn, M.T. Weichler, R. Starke, H. Harms, R.H. Muller, N. Strater, and T. Rohwerder. Structural basis of the stereospecificity of bacterial B_{12}-dependent 2-hydroxyisobutyryl-CoA mutase. *J. Biol. Chem.*, 290:9727–9737, 2015.

[345] Z. Kurylo-Borowska and T. Abramsky. Biosynthesis of β-tyrosine. *Biochim. Biophys. Acta*, 264:1–10, 1972.

[346] T. Kushiro, M. Shibuya, and Y. Ebizuka. β-Amyrin synthase-cloning of oxidosqualene cyclase that catalyzes the formation of the most popular triterpene among higher plants. *Eur. J. Biochem.*, 256:238–244, 1998.

[347] L. Lack. Enzymic *cis-trans* isomerization of maleylpyruvic acid. *J. Biol. Chem.*, 236:2835–2840, 1961.

[348] S.D. Lahiri, G. Zhang, D. Dunaway-Mariano, and K.N. Allen. The pentacovalent phosphorus intermediate of a phosphoryl transfer reaction. *Science*, 299:2067–2071, 2003.

[349] L. Laiz, P. Liras, J.M. Castro, and J.F. Martín. Purification and characterization of the isopenicillin-N epimerase from *Nocardia lactamdurans*. *J. Gen. Microbiol.*, 136:663–671, 1990.

[350] H.C. Lamont, W.L. Staudenbauer, and J.L. Strominger. Partial purification and characterization of an aspartate racemase from *Streptococcus faecalis*. *J. Biol. Chem.*, 247:5103–5106, 1972.

[351] K. Leang, G. Takada, A. Ishimura, M. Okita, and K. Izumori. Cloning, nucleotide sequence, and overexpression of the L-rhamnose isomerase gene from *Pseudomonas stutzeri* in *Escherichia coli*. *Appl. Environ. Microbiol.*, 70:3298–3304, 2004.

[352] F. Lecointe, G. Simos, A. Sauer, E.C. Hurt, Y. Motorin, and H. Grosjean. Characterization of yeast protein Deg1 as pseudouridine synthase (Pus3) catalyzing the formation of Ψ^{38} and Ψ^{39} in tRNA anticodon loop. *J. Biol. Chem.*, 273:1316–1323, 1998.

[353] L.V. Lee, R.R. Poyner, M.V. Vu, and W.W. Cleland. Role of metal ions in the reaction catalyzed by L-ribulose-5-phosphate 4-epimerase. *Biochemistry*, 39:4821–4830, 2000.

[354] N. Lee, J.W. Patrick, and M. Masson. Crystalline L-ribulose 5-phosphate 4-epimerase from *Escherichia coli*. *J. Biol. Chem.*, 243:4700–4705, 1968.

[355] S.B. Lee, S.J. Cho, J.A. Kim, S.Y. Lee, S.M. Kim, and H.S. Lim. Metabolic pathway of 3,6-anhydro-L-galactose in agar-degrading microorganisms. *Biotechnol. Bioprocess Eng.*, 19:866–878, 2014.

[356] V. Lefebvre, M. Kuntz, B. Camara, and A. Palloix. The capsanthin-capsorubin synthase gene: a candidate gene for the y locus controlling the red fruit colour in pepper. *Plant Mol. Biol.*, 36:785–789, 1998.

[357] L.F. Leloir. Enzymic isomerization and related processes. *Adv. Enzymol. Relat. Subj. Biochem.*, 14:193–218, 1953.

[358] L.F. Leloir and C.E. Cardini. Enzymes acting on glucosamine phosphates. *Biochim. Biophys. Acta*, 20:33–42, 1956.

[359] B.W. Lepore, F.J. Ruzicka, P.A. Frey, and D. Ringe. The x-ray crystal structure of lysine-2,3-aminomutase from *Clostridium* subterminale. *Proc. Natl. Acad. Sci. USA*, 102:13819–13824, 2005.

[360] M. Leppik, L. Peil, K. Kipper, A. Liiv, and J. Remme. Substrate specificity of the pseudouridine synthase RluD in *Escherichia coli*. *FEBS J.*, 274:5759–5766, 2007.

[361] G.B. Levy and E.S. Cook. A rotographic study of mutarotase. *Biochem. J.*, 57:50–55, 1954.

[362] F. Li, C. Murillo, and E.T. Wurtzel. Maize Y9 encodes a product essential for 15-*cis*-ζ-carotene isomerization. *Plant Physiol.*, 144:1181–1189, 2007.

[363] Q. Li, G. Farre, S. Naqvi, J. Breitenbach, G. Sanahuja, C. Bai, G. Sandmann, T. Capell, P. Christou, and C. Zhu. Cloning and functional characterization of the maize carotenoid isomerase and β-carotene hydroxylase genes and their regulation during endosperm maturation. *Transgenic Res.*, 19:1053–1068, 2010.

[364] S. Li, A.N. Lowell, S.A. Newmister, F. Yu, R.M. Williams, and D.H. Sherman. Decoding cyclase-dependent assembly of hapalindole and fischerindole alkaloids. *Nat. Chem. Biol.*, 13:467–469, 2017.

[365] S. Li, A.N. Lowell, F. Yu, A. Raveh, S.A. Newmister, N. Bair, J.M. Schaub, R.M. Williams, and D.H. Sherman. Hapalindole/ambiguine biogenesis Is mediated by a Cope rearrangement, C-C bond-forming cascade. *J. Am. Chem. Soc.*, 137:15366–15369, 2015.

[366] Z. Li, K. Kitanishi, U.T. Twahir, V. Cracan, D. Chapman, K. Warncke, and R. Banerjee. Cofactor editing by the G-protein metallochaperone domain regulates the radical B_{12} enzyme IcmF. *J. Biol. Chem.*, 292:3977–3987, 2017.

[367] B.R. Lichman, M.O. Kamileen, G.R. Titchiner, G. Saalbach, C.EM. Stevenson, D.M. Lawson, and S.E. O'Connor. Uncoupled activation and cyclization in catmint reductive terpenoid biosynthesis. *Nat. Chem. Biol.*, 15:71–79, 2019.

[368] B.R. Lichman, S.E. O'Connor, and H. Kries. Biocatalytic strategies towards [4+2] cycloadditions. *Chemistry*, 25:6864–6877, 2019.

[369] K.W. Lieder, S. Booker, F.J. Ruzicka, H. Beinert, G.H. Reed, and P.A. Frey. *S*-Adenosylmethionine-dependent reduction of lysine 2,3-aminomutase and observation of the catalytically functional iron-sulfur centers by electron paramagnetic resonance. *Biochemistry*, 37:2578–2585, 1998.

[370] R. Lim and S.S. Cohen. D-Phosphoarabinoisomerase and D-ribulokinase in *Escherichia coli*. *J. Biol. Chem.*, 241:4304–4315, 1966.

[371] H. Lin, R. Wang, Q. Qian, M. Yan, X. Meng, Z. Fu, C. Yan, B. Jiang, Z. Su, J. Li, and Y. Wang. DWARF27, an iron-containing protein required for the biosynthesis of strigolactones, regulates rice tiller bud outgrowth. *Plant Cell*, 21:1512–1525, 2009.

[372] H.-W. Liu and J.S. Thorson. Pathways and mechanisms in the biogenesis of novel deoxysugars by bacteria. *Annu. Rev. Microbiol.*, 48:223–256, 1994.

[373] J. Liu, Y. Wei, K. Ma, J. An, X. Liu, Y. Liu, E.L. Ang, H. Zhao, and Y. Zhang. Mechanistically diverse pathways for sulfoquinovose degradation in bacteria. *ACS Catal.*, 11:14740–14750, 2021.

[374] L. Liu, K. Iwata, A. Kita, Y. Kawarabayasi, M. Yohda, and K. Miki. Crystal structure of aspartate racemase from *Pyrococcus horikoshii* OT3 and its implications for molecular mechanism of PLP-independent racemization. *J. Mol. Biol.*, 319:479–489, 2002.

[375] Y. Liu, Y. Cai, Z. Zhao, J. Wang, J. Li, W. Xin, G. Xia, and F. Xiang. Cloning and functional analysis of a β-amyrin synthase gene associated with oleanolic acid biosynthesis in *Gentiana straminea* MAXIM. *Biol. Pharm. Bull.*, 32:818–824, 2009.

[376] 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.

[377] A. Lockhart and R.A. Cross. Origins of reversed directionality in the ncd molecular motor. *EMBO J.*, 13:751–757, 1994.

[378] S. Lodeiro, Q. Xiong, W.K. Wilson, Y. Ivanova, M.L. Smith, G.S. May, and S.P. Matsuda. Protostadienol biosynthesis and metabolism in the pathogenic fungus *Aspergillus fumigatus*. *Org. Lett.*, 11:1241–1244, 2009.

[379] S. Lodeiro, Q. Xiong, W.K. Wilson, M.D. Kolesnikova, C.S. Onak, and S.P. Matsuda. An oxidosqualene cyclase makes numerous products by diverse mechanisms: a challenge to prevailing concepts of triterpene biosynthesis. *J. Am. Chem. Soc.*, 129:11213–11222, 2007.

[380] T.M. Lohman. Helicase-catalyzed DNA unwinding. *J. Biol. Chem.*, 268:2269–2272, 1993.

[381] J.H. Lorence and E.W. Nester. Multiple molecular forms of chorismate mutase in *Bacillus subtillis*. *Biochemistry*, 6:1541–1543, 1967.

[382] F. De Lorenzo, R.F. Goldberger, E. Steers, D. Givol, and C.B. Anfinsen. Purification and properties of an enzyme from beef liver which catalyzes sulfhydryl-disulfide interchange in proteins. *J. Biol. Chem.*, 241:1562–1567, 1966.

[383] Z. Lu, , and E.C.C. The nucleotide sequence of *Escherichia coli* genes for L-fucose dissimilation. *Nucleic Acids Res.*, 17:4883–4884, 1989.

[384] T.H. Lubber, G.K. Donaldson, P.V. Viitanen, and A.A. Gatenby. Several proteins imported into chloroplasts form stable complexes with the GroEL-related chloroplast molecular chaperone. *Plant Cell*, 1:1223–1230, 1989.

[385] F. Lüddeke and J. Harder. Enantiospecific (*S*)-(+)-linalool formation from β-myrcene by linalool dehydratase-isomerase. *Z. Naturforsch. C*, 66:409–412, 2011.

[386] F. Lynen, J. Knappe, E. Lorch, G. Jütting, and E. Ringelmann. Die biochemische Funktion des Biotins. *Angew. Chem.*, 71:481–486, 1959.

[387] J. MacLachlan, A.T. Wotherspoon, R.O. Ansell, and C.J. Brooks. Cholesterol oxidase: sources, physical properties and analytical applications. *J. Steroid Biochem. Mol. Biol.*, 72:169–195, 2000.

[388] 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.

[389] L.L. Major, B.A. Wolucka, and J.H. Naismith. Structure and function of GDP-mannose-3′,5′-epimerase: an enzyme which performs three chemical reactions at the same active site. *J. Am. Chem. Soc.*, 127:18309–18320, 2005.

[390] F. Maley and G.F. Maley. The enzymic conversion of glucosamine to galactosamine. *Biochim. Biophys. Acta*, 31:577–578, 1959.

[391] A. Malmström and L. Åberg. Biosynthesis of dermatan sulphate. Assay and properties of the uronosyl C-5 epimerase. *Biochem. J.*, 201:489–493, 1982.

[392] B.A. Manjasetty and M.R. Chance. Crystal structure of *Escherichia coli* L-arabinose isomerase (ECAI), the putative target of biological tagatose production. *J. Mol. Biol.*, 360:297–309, 2006.

[393] 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.

[394] J.A. Maresca, J.E. Graham, M. Wu, J.A. Eisen, and D.A. Bryant. Identification of a fourth family of lycopene cyclases in photosynthetic bacteria. *Proc. Natl. Acad. Sci. USA*, 104:11784–11789, 2007.

[395] M.N. Margolies and R.F. Goldberger. Isolation of the fourth (isomerase) of histidine biosynthesis from *Salmonella typhimurium*. *J. Biol. Chem.*, 241:3262–3269, 1966.

[396] R. Marmulla, B. Šafarić, S. Markert, T. Schweder, and J. Harder. Linalool isomerase, a membrane-anchored enzyme in the anaerobic monoterpene degradation in *Thauera linaloolentis* 47Lol. *BMC Biochem.*, 17:6–6, 2016.

[397] J.C. Marques, P. Lamosa, C. Russell, R. Ventura, C. Maycock, M.F. Semmelhack, S.T. Miller, and K.B. Xavier. Processing the interspecies quorum-sensing signal autoinducer-2 (AI-2): characterization of phospho-(*S*)-4,5-dihydroxy-2,3-pentanedione isomerization by LsrG protein. *J. Biol. Chem.*, 286:18331–18343, 2011.

[398] A.G. Marr and P.W. Wilson. The alanine racemase of *Brucella abortus*. *Arch. Biochem. Biophys.*, 49:424–433, 1954.

[399] H. Marrakchi, K.H. Choi, and C.O. Rock. A new mechanism for anaerobic unsaturated fatty acid formation in *Streptococcus pneumoniae*. *J. Biol. Chem.*, 277:44809–44816, 2002.

[400] K.O. Martin, S.-W. Oh, H.J. Lee, and C. Monder. Studies on 21-3*H*-labeled corticosteroids: evidence for isomerization of the ketol side chain of 11-deoxycorticosterone by a hamster liver enzyme. *Biochemistry*, 16:3803–3809, 1977.

[401] L.A. Martinez-Cruz, M.K. Dreyer, D.C. Boisvert, H. Yokota, M.L. Martinez-Chantar, R. Kim, and S.H. Kim. Crystal structure of MJ1247 protein from *M. jannaschii* at 2.0 Å resolution infers a molecular function of 3-hexulose-6-phosphate isomerase. *Structure*, 10:195–204, 2002.

[402] S. Martínez-Rodríguez, M. Andújar-Sánchez, J.L. Neira, J.M. Clemente-Jiménez, V. Jara-Pérez, F. Rodríguez-Vico, and F.J. Las Heras-Vázquez. Site-directed mutagenesis indicates an important role of cysteines 76 and 181 in the catalysis of hydantoin racemase from *Sinorhizobium meliloti*. *Protein Sci.*, 15:2729–2738, 2006.

[403] S. Martínez-Rodríguez, F.J. Las Heras-Vázquez, J.M. Clemente-Jiménez, and F. Rodríguez-Vico. Biochemical characterization of a novel hydantoin racemase from *Agrobacterium tumefaciens* C58. *Biochimie*, 86:77–81, 2004.

[404] S. Martínez-Rodríguez, F.J. Las Heras-Vázquez, L. Mingorance-Cazorla, J.M. Clemente-Jiménez, and F. Rodríguez-Vico. Molecular cloning, purification, and biochemical characterization of hydantoin racemase from the legume symbiont *Sinorhizobium meliloti* CECT 4114. *Appl. Environ. Microbiol.*, 70:625–630, 2004.

[405] K. Maruta, T. Nakada, M. Kubota, H. Chaen, T. Sugimoto, M. Kurimoto, , and Y. Formation of trehalose from maltooligosaccharides by a novel enzymatic system. *Biosci. Biotechnol. Biochem.*, 59:1829–1834, 1995.

[406] G.G. Mason, R.Z. Murray, D. Pappin, and A.J. Rivett. Phosphorylation of ATPase subunits of the 26S proteasome. *FEBS Lett.*, 430:269–274, 1998.

[407] I.I. Mathews, T.J. Kappock, J. Stubbe, and S.E. Ealick. Crystal structure of *Escherichia coli* PurE, an unusual mutase in the purine biosynthetic pathway. *Structure*, 7:1395–1406, 1999.

[408] S. Matsuhashi. Enzymatic synthesis of cytidine diphosphate 3,6-dideoxyhexoses. II. Reversible 2-epimerization of cytidine diphosphate paratose. *J. Biol. Chem.*, 241:4275–4282, 1966.

[409] D.V. Mavrodi, N. Bleimling, L.S. Thomashow, and W. Blankenfeldt. The purification, crystallization and preliminary structural characterization of PhzF, a key enzyme in the phenazine-biosynthesis pathway from *Pseudomonas fluorescens* 2-79. *Acta Crystallogr. D Biol. Crystallogr.*, 60:184–186, 2004.

[410] E.S. Maxwell and H. de Robichon-Szulmajster. Purification of uridine diphosphate galactose-4-epimerase from yeast and the identification of protein-bound diphosphopyridine nucleotide. *J. Biol. Chem.*, 235:308–312, 1960.

[411] R. Mazumder, T. Sasakawa, Y. Kaziro, and S. Ochoa. Metabolism of propionic acid in animal tissues. IX. Methylmalonyl coenzyme A racemase. *J. Biol. Chem.*, 237:3065–3068, 1962.

[412] H.B. McDonald, R.J. Stewart, and L.S. Goldstein. The kinesin-like ncd protein of *Drosophila* is a minus end-directed microtubule motor. *Cell*, 63:1159–1165, 1990.

[413] P. McGeady and R. Croteau. Isolation and characterization of an active-site peptide from a monoterpene cyclase labeled with a mechanism-based inhibitor. *Arch. Biochem. Biophys.*, 317:149–155, 1995.

[414] F.J. McNally and R.D. Vale. Identification of katanin, an ATPase that severs and disassembles stable microtubules. *Cell*, 75:419–429, 1993.

[415] W.S. McNutt and S.P. Damle. Tetraoxypteridine isomerase. *J. Biol. Chem.*, 239:4272–4279, 1964.

[416] U. Meier-Dieter, R. Starman, K. Barr, H. Mayer, and P.D. Rick. Biosynthesis of enterobacterial common antigen in *Escherichia coli*. Biochemical characterization of Tn10 insertion mutants defective in enterobacterial common antigen synthesis. *J. Biol. Chem.*, 265:13490–13497, 1990.

[417] C.E. Melancon, Hong 3rd, White L., Liu J.A., Liu Y.N., and H.W. Characterization of TDP-4-keto-6-deoxy-D-glucose-3,4-ketoisomerase from the D-mycaminose biosynthetic pathway of *Streptomyces fradiae*: *in vitro* activity and substrate specificity studies. *Biochemistry*, 46:577–590, 2007.

[418] A. Melo and L. Glaser. The mechanism of 6-deoxyhexose synthesis. II. Conversion of deoxythymidine diphosphate 4-keto-6-deoxy-D-glucose to deoxythymidine diphosphate L-rhamnose. *J. Biol. Chem.*, 243:1475–1478, 1968.

[419] D. Mengin-Lecreulx and J. van Heijenoort. Characterization of the essential gene glmM encoding phosphoglucosamine mutase in *Escherichia coli*. *J. Biol. Chem.*, 271:32–39, 1996.

[420] G.F. Mercaldi, H.M. Pereira, A.T. Cordeiro, P.A. Michels, and O.H. Thiemann. Structural role of the active-site metal in the conformation of *Trypanosoma brucei* phosphoglycerate mutase. *FEBS J.*, 279:2012–2021, 2012.

[421] T.C. Meredith and R.W. Woodard. Identification of GutQ from *Escherichia coli* as a D-arabinose 5-phosphate isomerase. *J. Bacteriol.*, 187:6936–6942, 2005.

[422] E. Meyer, T.J. Kappock, C. Osuji, and J. Stubbe. Evidence for the direct transfer of the carboxylate of N^5-carboxyaminoimidazole ribonucleotide (N^5-CAIR) to generate 4-carboxy-5-aminoimidazole ribonucleotide catalyzed by *Escherichia coli* PurE, an N^5-CAIR mutase. *Biochemistry*, 38:3012–3018, 1999.

[423] E. Meyer, N.J. Leonard, B. Bhat, J. Stubbe, and J.M. Smith. Purification and characterization of the *purE*, *purK*, and *purC* gene products: identification of a previously unrecognized energy requirement in the purine biosynthetic pathway. *Biochemistry*, 31:5022–5032, 1992.

[424] E. Meyer-Arendt, G. Beisenherz, and T. Bücher. Triosephosphate isomerase. *Naturwissenschaften*, 40:59–59, 1953.

[425] O. Meyerhof and L.V. Beck. Triosephosphate isomerase. *J. Biol. Chem.*, 156:109–120, 1944.

[426] F.M. Miesowicz and K. Bloch. Purification of hog liver isomerase. Mechanism of isomerization of 3-alkenyl and 3-alkynyl thioesters. *J. Biol. Chem.*, 254:5868–5877, 1979.

[427] J. De Miranda, A. Santoro, S. Engelender, and H. Wolosker. Human serine racemase: moleular cloning, genomic organization and functional analysis. *Gene*, 256:183–188, 2000.

[428] H. Mochizuki, K. Yamagishi, K. Suzuki, Y.S. Kim, and K. Kimata. Heparosan-glucuronate 5-epimerase: Molecular cloning and characterization of a novel enzyme. *Glycobiology*, 25:735–744, 2015.

[429] Y. Modis, S.A. Filppula, D.K. Novikov, B. Norledge, J.K. Hiltunen, and R.K. Wierenga. The crystal structure of dienoyl-CoA isomerase at 1.5 Å resolution reveals the importance of aspartate and glutamate sidechains for catalysis. *Structure*, 6:957–970, 1998.

[430] C. Monder, K.O. Martin, and J. Bogumil. Presence of epimerase activity in hamster liver corticosteroid side chain isomerase. *J. Biol. Chem.*, 255:7192–7198, 1980.

[431] S.J. Moore, A.D. Lawrence, R. Biedendieck, E. Deery, S. Frank, M.J. Howard, S.E. Rigby, and M.J. Warren. Elucidation of the anaerobic pathway for the corrin component of cobalamin (vitamin B_{12}). *Proc. Natl. Acad. Sci. USA*, 110:14906–14911, 2013.

[432] A. Morea, K. Mathee, M.J. Franklin, A. Giacomini, M. O'Regan, and D.E. Ohman. Characterization of *algG* encoding C^5-epimerase in the alginate biosynthetic gene cluster of *Pseudomonas fluorescens*. *Gene*, 278:107–114, 2001.

[433] P. M. Morgan, R. F. Sala, , and M. E. Eliminations in the reactions catalyzed by UDP-*N*-acetylglucosamine 2-epimerase. *J. Am. Chem. Soc.*, 119:10269–10277, 1997.

[434] M. Morita, M. Shibuya, T. Kushiro, K. Masuda, and Y. Ebizuka. Molecular cloning and functional expression of triterpene synthases from pea (*Pisum sativum*) new α-amyrin-producing enzyme is a multifunctional triterpene synthase. *Eur. J. Biochem.*, 267:3453–3460, 2000.

[435] P. Morlacchi, W.K. Wilson, Q. Xiong, A. Bhaduri, D. Sttivend, M.D. Kolesnikova, and S.P. Matsuda. Product profile of PEN3: the last unexamined oxidosqualene cyclase in *Arabidopsis thaliana*. *Org. Lett.*, 11:2627–2630, 2009.

[436] C.G.D. Morley and T.C. Stadtman. Studies on the fermentation of D-α-lysine. Purification and properties of an adenosine triphosphate regulated B_{12}-coenzyme-dependent D-α-lysine mutase complex from *Clostridium sticklandii*. *Biochemistry*, 9:4890–4900, 1970.

[437] E. Moustafa and E. Wong. Purification and properties of chalcone-flavanone isomerase from soya bean seed. *Phytochemistry*, 6:625–632, 1967.

[438] W. Mu, F. Chu, Q. Xing, S. Yu, L. Zhou, and B. Jiang. Cloning, expression, and characterization of a D-psicose 3-epimerase from *Clostridium cellulolyticum* H10. *J. Agric. Food Chem.*, 59:7785–7792, 2011.

[439] W. Mu, W. Zhang, D. Fang, L. Zhou, B. Jiang, and T. Zhang. Characterization of a D-psicose-producing enzyme, D-psicose 3-epimerase, from *Clostridium* sp. *Biotechnol. Lett.*, 35:1481–1486, 2013.

[440] E.J. Mueller, E. Meyer, J. Rudolph, V.J. Davisson, and J. Stubbe. N^5-Carboxyaminoimidazole ribonucleotide: evidence for a new intermediate and two new enzymatic activities in the de novo purine biosynthetic pathway of *Escherichia coli*. *Biochemistry*, 33:2269–2278, 1994.

[441] U. Müller and W. Buckel. Activation of (*R*)-2-hydroxyglutaryl-CoA dehydratase from *Acidaminococcus fermentans*. *Eur. J. Biochem.*, 230:698–704, 1995.

[442] E.F. Mulrooney, K.K. Poon, D.J. McNally, J.R. Brisson, and J.S. Lam. Biosynthesis of UDP-*N*-acetyl-L-fucosamine, a precursor to the biosynthesis of lipopolysaccharide in *Pseudomonas aeruginosa* serotype O11. *J. Biol. Chem.*, 280:19535–19542, 2005.

[443] C.T. Murphy and J.A. Spudich. The sequence of the myosin 50-20K loop affects myosin's affinity for actin throughout the actin-myosin ATPase cycle and its maximum ATPase activity. *Biochemistry*, 38:3785–3792, 1999.

[444] Y. Mutaguchi, T. Ohmori, T. Wakamatsu, K. Doi, and T. Ohshima. Identification, purification, and characterization of a novel amino acid racemase, isoleucine 2-epimerase, from *Lactobacillus* species. *J. Bacteriol.*, 195:5207–5215, 2013.

[445] R.W. Myers, J.W. Wray, S. Fish, and R.H. Abeles. Purification and characterization of an enzyme involved in oxidative carbon-carbon bond cleavage reactions in the methionine salvage pathway of *Klebsiella pneumoniae*. *J. Biol. Chem.*, 268:24785–24791, 1993.

[446] V.A. Najjar. Phosphoglucomutase. In P.D. Boyer, H. Lardy, and K. Myrbäck, editors, *The Enzymes*, volume 6, pages 161–178. Academic Press, New York, 2nd edition, 1962.

[447] T. Nakada, S. Ikegami, H. Chaen, M. Kubota, S. Fukuda, T. Sugimoto, M. Kurimoto, , and Y. Purification and characterization of thermostable maltooligosyl trehalose synthase from the thermoacidophilic archaebacterium *Sulfolobus acidocaldarius*. *Biosci. Biotechnol. Biochem.*, 60:263–266, 1996.

[448] T. Nakada, K. Maruta, K. Tsusaki, M. Kubota, H. Chaen, T. Sugimoto, M. Kurimoto, , and Y. Purification and properties of a novel enzyme, maltooligosyl trehalose synthase, from *Arthrobacter sp*. Q36. *Biosci. Biotechnol. Biochem.*, 59:2210–2214, 1995.

[449] T. Nakagawa, H. Flores-Rozas, and R.D. Kolodner. The MER3 helicase involved in meiotic crossing over is stimulated by single-stranded DNA-binding proteins and unwinds DNA in the 3′ to 5′ direction. *J. Biol. Chem.*, 276:31487–31493, 2001.

[450] T. Nakagawa, Y. Tanaka, E. Matsuoka, S. Kondo, Y. Okada, F. Noda, Y. Kanai, and N. Hirokawa. Identification and classification of 16 new kinesin superfamily (KIF) proteins in mouse genome. *Proc. Natl. Acad. Sci. USA*, 94:9654–9659, 1997.

[451] Y. Nakagawa and E.A. Noltmann. Isolation of crystalline phosphoglucose isomerase from brewers' yeast. *J. Biol. Chem.*, 240:1877–1881, 1965.

[452] T. Nakamatu and K. Yamanaka. Crystallization and properties of L-arabinose isomerase from *Lactobacillus gayonii*. *Biochim. Biophys. Acta*, 178:156–165, 1969.

[453] A. Nakamura, M. Fujihashi, R. Aono, T. Sato, Y. Nishiba, S. Yoshida, A. Yano, H. Atomi, T. Imanaka, and K. Miki. Dynamic, ligand-dependent conformational change triggers reaction of ribose-1,5-bisphosphate isomerase from *Thermococcus kodakarensis* KOD1. *J. Biol. Chem.*, 287:20784–20796, 2012.

[454] C. Nakano, T. Okamura, T. Sato, T. Dairi, and T. Hoshino. *Mycobacterium tuberculosis* H37Rv3377c encodes the diterpene cyclase for producing the halimane skeleton. *Chem. Commun. (Camb.)*, pages 1016–1018, 2005.

[455] C. Nakano, M. Oshima, N. Kurashima, and T. Hoshino. Identification of a new diterpene biosynthetic gene cluster that produces *O*-methylkolavelool in *Herpetosiphon aurantiacus*. *ChemBioChem*, 16:772–781, 2015.

[456] T. Nishimoto, M. Nakano, S. Ikegami, H. Chaen, S. Fukuda, T. Sugimoto, M. Kurimoto, , and Y. Existence of a novel enzyme converting maltose to trehalose. *Biosci. Biotechnol. Biochem.*, 59:2189–2190, 1995.

[457] T. Nishimoto, M. Nakano, T. Nakada, H. Chaen, S. Fukuda, T. Sugimoto, M. Kurimoto, , and Y. Purification and properties of a novel enzyme, trehalose synthase, from *Pimelobacter* sp. R48. *Biosci. Biotechnol. Biochem.*, 60:640–644, 1996.

[458] 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.

[459] E. Noltmann and F.H. Bruns. Reindarstellung und Eigenschaften von Phosphoglucose-isomerase aus Hefe. *Biochem. Z.*, 331:436–445, 1959.

[460] E.A. Noltmann. Isolation of crystalline phosphoglucose isomerase from rabbit muscle. *J. Biol. Chem.*, 239:1545–1550, 1964.

[461] P.G. Norris, A.V. Nunn, J.L. Hawk, and T.M. Cox. Genetic heterogeneity in erythropoietic protoporphyria: a study of the enzymatic defect in nine affected families. *J. Invest. Dermatol.*, 95:260–263, 1990.

[462] M.W. Nowicki, B. Kuaprasert, I.W. McNae, H.P. Morgan, M.M. Harding, P.A. Michels, L.A. Fothergill-Gilmore, and M.D. Walkinshaw. Crystal structures of *Leishmania mexicana* phosphoglycerate mutase suggest a one-metal mechanism and a new enzyme subclass. *J. Mol. Biol.*, 394:535–543, 2009.

[463] M. Nukui, L.V. Mello, J.E. Littlejohn, B. Setlow, P. Setlow, K. Kim, T. Leighton, and M.J. Jedrzejas. Structure and molecular mechanism of *Bacillus anthracis* cofactor-independent phosphoglycerate mutase: a crucial enzyme for spores and growing cells of *Bacillus* species. *Biophys J*, 92:977–988, 2007.

[464] K. Nurse, J. Wrzesinski, A. Bakin, B.G. Lane, and J. Ofengand. Purification, cloning, and properties of the tRNA Ψ^{55} synthase from *Escherichia coli*. *RNA*, 1:102–112, 1995.

[465] P. Nyvall, E. Corre, C. Boisset, T. Barbeyron, S. Rousvoal, D. Scornet, B. Kloareg, and C. Boyen. Characterization of mannuronan C-5-epimerase genes from the brown alga Laminaria digitata. *Plant Physiol.*, 133:726–735, 2003.

[466] N. Ogino, T. Miyamoto, S. Yamamoto, and O. Hayaishi. Prostaglandin endoperoxide E isomerase from bovine vesicular gland microsomes, a glutathione-requiring enzyme. *J. Biol. Chem.*, 252:890–895, 1977.

[467] T. Ohmoto, T. Kinoshita, K. Moriyoshi, K. Sakai, N. Hamada, and T. Ohe. Purification and some properties of 2-hydroxychromene-2-carboxylate isomerase from naphthalenesulfonate-assimilating *Pseudomonas* sp. TA-2. *J. Biochem.*, 124:591–597, 1998.

[468] S. Okazaki, A. Suzuki, T. Mizushima, T. Kawano, H. Komeda, Y. Asano, and T. Yamane. The novel structure of a pyridoxal 5′-phosphate-dependent fold-type I racemase, α-amino-ε-caprolactam racemase from *Achromobacter obae*. *Biochemistry*, 48:941–950, 2009.

[469] 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.

[470] 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.

[471] L.N. Ornston. The conversion of catechol and protocatechuate to β-ketoadipate by *Pseudomonas putida*. II. Enzymes of the protocatechuate pathway. *J. Biol. Chem.*, 241:3787–3794, 1966.

[472] L.N. Ornston. Conversion of catechol and protocatechuate to β-ketoadipate (*Pseudomonas putida*). *Methods Enzymol.*, 17A:529–549, 1970.

[473] K. Otomo, H. Kenmoku, H. Oikawa, W.A. Konig, H. Toshima, W. Mitsuhashi, H. Yamane, T. Sassa, and T. Toyomasu. Biological functions of *ent*- and *syn*-copalyl diphosphate synthases in rice: key enzymes for the branch point of gibberellin and phytoalexin biosynthesis. *Plant J.*, 39:886–893, 2004.

[474] P. Overath, G.M. Kellerman, F. Lynen, H.P. Fritz, and H.J. Keller. Zum Mechanismus der Umlagerung von Methylmalonyl-CoA in Succinyl-CoA. II. Versuche zur Wirkungsweise von Methylmalonyl-CoA-Isomerase and Methylmalonyl-CoA-Racemase. *Biochem. Z.*, 335:500–518, 1962.

[475] A.Z. Ozsoy, J.J. Sekelsky, and S.W. Matson. Biochemical characterization of the small isoform of *Drosophila melanogaster* RECQ5 helicase. *Nucleic Acids Res.*, 29:2986–2993, 2001.

[476] N.J. Palleroni and M. Doudoroff. Mannose isomerase of *Pseudomonas saccharophila*. *J. Biol. Chem.*, 218:535–548, 1956.

[477] H. Pan, J.D. Ho, R.M. Stroud, and J. Finer-Moore. The crystal structure of *E. coli* rRNA pseudouridine synthase RluE. *J. Mol. Biol.*, 367:1459–1470, 2007.

[478] D. Park, K.S. Ryu, D. Choi, J. Kwak, and C. Park. Characterization and role of fucose mutarotase in mammalian cells. *Glycobiology*, 17:955–962, 2007.

[479] 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.

[480] J.B. Parker and C.T. Walsh. Action and timing of BacC and BacD in the late stages of biosynthesis of the dipeptide antibiotic bacilysin. *Biochemistry*, 52:889–901, 2013.

[481] J.F. Parsons, K. Calabrese, E. Eisenstein, and J.E. Ladner. Structure of the phenazine biosynthesis enzyme PhzG. *Acta Crystallogr. D Biol. Crystallogr.*, 60:2110–2113, 2004.

[482] J.F. Parsons, F. Song, L. Parsons, K. Calabrese, E. Eisenstein, and J.E. Ladner. Structure and function of the phenazine biosynthesis protein PhzF from *Pseudomonas fluorescens* 2-79. *Biochemistry*, 43:12427–12435, 2004.

[483] S. Karunan Partha, S.A. Bonderoff, K.E. van Straaten, and D.A. Sanders. Expression, purification and preliminary X-ray crystallographic analysis of UDP-galactopyranose mutase from *Deinococcus radiodurans*. *Acta Crystallogr. Sect. F Struct. Biol. Cryst. Commun.*, 65:843–845, 2009.

[484] J.W. Patrick and N. Lee. Purification and properties of an L-arabinose isomerase from *Escherichia coli*. *J. Biol. Chem.*, 243:4312–4318, 1968.

[485] J.M. Pawelek. Dopachrome conversion factor functions as an isomerase. *Biochem. Biophys. Res. Commun.*, 166:1328–1333, 1990.

[486] I. Pecker, R. Gabbay, F.X. Cunningham, Hirschberg Jr., and J. Cloning and characterization of the cDNA for lycopene β-cyclase from tomato reveals decrease in its expression during fruit ripening. *Plant Mol. Biol.*, 30:807–819, 1996.

[487] J.L. Pennock, J.M. Behnke, Q.D. Bickle, E. Devaney, R.K. Grencis, , and R.E. , Joshua. G.W., Selkirk. M.E., Zhang. Y. and Meyer, D.J. Rapid purification and characterization of L-dopachrome-methyl ester tautomerase (macrophage-migration-inhibitory factor) from *Trichinella spiralis*, *Trichuris muris* and *Brugia pahangi*. *Biochem. J.*, 335:495–498, 1998.

[488] 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.

[489] 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.

[490] 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.

[491] 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.

[492] A. Pfoestl, A. Hofinger, P. Kosma, and P. Messner. Biosynthesis of dTDP-3-acetamido-3,6-dideoxy-α-D-galactose in *Aneurinibacillus thermoaerophilus* L420-91^T. *J. Biol. Chem.*, 278:26410–26417, 2003.

[493] J. Pienkowska, J. Wrzesinski, and Z. Szweykowska-Kulinska. A cell-free yellow lupin extract containing activities of pseudouridine 35 and 55 synthases. *Acta Biochim. Pol.*, 45:745–754, 1998.

[494] S. Porfirova, E. Bergmuller, S. Tropf, R. Lemke, and P. Dormann. Isolation of an *Arabidopsis* mutant lacking vitamin E and identification of a cyclase essential for all tocopherol biosynthesis. *Proc. Natl. Acad. Sci. USA*, 99:12495–12500, 2002.

[495] J.M. Poston. Coenzyme B_{12}-dependent enzymes in potatoes: leucine 2,3-aminomutase and methylmalonyl-CoA mutase. *Phytochemistry*, 17:401–402, 1976.

[496] J.M. Poston. Leucine 2,3-aminomutase, an enzyme of leucine catabolism. *J. Biol. Chem.*, 251:1859–1863, 1976.

[497] J. Preiss. 4-Deoxy-L-*threo*-5-hexosulose uronic acid isomerase. *Methods Enzymol.*, 9:602–604, 1966.

[498] F. Quitterer, A. List, W. Eisenreich, A. Bacher, and M. Groll. Crystal structure of methylornithine synthase (PylB): insights into the pyrrolysine biosynthesis. *Angew. Chem. Int. Ed. Engl.*, 51:1339–1342, 2012.

[499] C.R.H. Raetz. Biochemistry of endotoxins. *Annu. Rev. Biochem.*, 58:129–170, 1990.

[500] A. Rahier, P. Schmitt, and P. Benveniste. 7-oxo-24ξ(28)-dihydrocycloeucalenol, a potent inhibitor of plant sterol biosynthesis. *Phytochemistry*, 21:1969–1974, 1982.

[501] V. Ramamurthy, S.L. Swann, C.J. Spedaliere, and E.G. Mueller. Role of cysteine residues in pseudouridine synthases of different families. *Biochemistry*, 38:13106–13111, 1999.

[502] T. Ramasarma and K.V. Giri. Phosphoglucose isomerase of green gram (*Phaseolus radiatus*). *Arch. Biochem. Biophys.*, 62:91–96, 1956.

[503] S. Ranjan, K.K. Patnaik, and M.M. Laloraya. Enzymic conversion of *meso*-tartrate to *dextro*-tartrate in tamarind. *Naturwissenschaften*, 48:406–406, 1961.

[504] N.A. Ranson, H.E. White, and H.R. Saibil. Chaperonins. *Biochem. J.*, 333:233–242, 1998.

[505] A. Ratnatilleke, J.W. Vrijbloed, and J.A. Robinson. Cloning and sequencing of the coenzyme B_{12}-binding domain of isobutyryl-CoA mutase from *Streptomyces cinnamonensis*, reconstitution of mutase activity, and characterization of the recombinant enzyme produced in *Escherichia coli*. *J. Biol. Chem.*, 274:31679–31685, 1999.

[506] N.D. Ratnayake, U. Wanninayake, J.H. Geiger, and K.D. Walker. Stereochemistry and mechanism of a microbial phenylalanine aminomutase. *J. Am. Chem. Soc.*, 133:8531–8533, 2011.

[507] 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.

[508] W.J. Ray, Jr., Peck, and Jr. Phosphomutases. In P.D. Boyer, editor, *The Enzymes*, volume 6, pages 407–477. 3rd edition, 1972.

[509] W.J. Ray and G.A. Roscelli. A kinetic study of the phosphoglucomutase pathway. *J. Biol. Chem.*, 239:1228–1236, 1964.

[510] S. Raychaudhuri, L. Niu, J. Conrad, B.G. Lane, and J. Ofengand. Functional effect of deletion and mutation of the *Escherichia coli* ribosomal RNA and tRNA pseudouridine synthase RluA. *J. Biol. Chem.*, 274:18880–18886, 1999.

[511] I. Rayment. The structural basis of myosin ATPase activity. *J. Biol. Chem.*, 271:15850–15853, 1996.

[512] H.H. Rees, L.J. Goad, and T.W. Goodwin. 2,3-Oxidosqualene cycloartenol cyclase from *Ochromonas malhamensis*. *Biochim. Biophys. Acta*, 176:892–894, 1969.

[513] D.J. Reinert, G. Balliano, and G.E. Schulz. Conversion of squalene to the pentacarbocyclic hopene. *Chem. Biol.*, 11:121–126, 2004.

[514] J.L. Reissig and L.F. Leloir. Phosphoacetylglucosamine mutase from *Neurospora*. *Methods Enzymol.*, 8:175–178, 1966.

[515] J. Retey, F. Kunz, D. Arigoni, and T.C. Stadtman. Zur Kenntnis der β-Lysin-Mutase-Reaktion: mechanismus und sterischer Verlauf. *Helv. Chim. Acta*, 61:2989–2998, 1978.

[516] D.J. Rigden, E. Lamani, L.V. Mello, J.E. Littlejohn, and M.J. Jedrzejas. Insights into the catalytic mechanism of cofactor-independent phosphoglycerate mutase from X-ray crystallography, simulated dynamics and molecular modeling. *J. Mol. Biol.*, 328:909–920, 2003.

[517] D.J. Rigden, J.E. Littlejohn, K. Henderson, and M.J. Jedrzejas. Structures of phosphate and trivanadate complexes of *Bacillus stearothermophilus* phosphatase PhoE: structural and functional analysis in the cofactor-dependent phosphoglycerate mutase superfamily. *J. Mol. Biol.*, 325:411–420, 2003.

[518] D.J. Rigden, L.V. Mello, P. Setlow, and M.J. Jedrzejas. Structure and mechanism of action of a cofactor-dependent phosphoglycerate mutase homolog from *Bacillus stearothermophilus* with broad specificity phosphatase activity. *J. Mol. Biol.*, 315:1129–1143, 2002.

[519] D.J. Rigden, R.A. Walter, S.E. Phillips, and L.A. Fothergill-Gilmore. Sulphate ions observed in the 2.12 Å structure of a new crystal form of *S. cerevisiae* phosphoglycerate mutase provide insights into understanding the catalytic mechanism. *J. Mol. Biol.*, 286:1507–1517, 1999.

[520] H.C. Rilling and M.J. Coon. The enzymatic isomerization of α-methylvinylacetyl coenzyme A and the specificity of a bacterial α-methylcrotonyl coenzyme A carboxylase. *J. Biol. Chem.*, 235:3087–3092, 1960.

[521] A.J. Rivett, G.G. Mason, R.Z. Murray, and J. Reidlinger. Regulation of proteasome structure and function. *Mol. Biol. Rep.*, 24:99–102, 1997.

[522] I.A. Rodionova, D.A. Scott, N.V. Grishin, A.L. Osterman, and D.A. Rodionov. Tagaturonate-fructuronate epimerase UxaE, a novel enzyme in the hexuronate catabolic network in *Thermotoga maritima*. *Environ. Microbiol.*, 14:2920–2934, 2012.

[523] C.A. Roessner, M.J. Warren, P.J. Santander, B.P. Atshaves, S. Ozaki, N.J. Stolowich, K. Iida, , and A.I. Expression of *Salmonella typhimurium* enzymes for cobinamide synthesis. Identification of the 11-methyl and 20-methyl transferases of corrin biosynthesis. *FEBS Lett.*, 301:73–78, 1992.

[524] 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.

[525] Z.B. Rose. The purification and properties of diphosphoglycerate mutase from human erythrocytes. *J. Biol. Chem.*, 243:4810–4820, 1968.

[526] Z.B. Rose. The enzymology of 2,3-bisphosphoglycerate. *Adv. Enzymol. Relat. Areas Mol. Biol.*, 51:211–253, 1980.

[527] J.R. Roth, J.G. Lawrence, M. Rubenfield, S. Kieffer-Higgins, , and G.M. Characterization of the cobalamin (vitamin B_{12}) biosynthetic genes of *Salmonella typhimurium*. *J. Bacteriol.*, 175:3303–3316, 1993.

[528] J.S. Rush, C. Alaimo, R. Robbiani, M. Wacker, and C.J. Waechter. A novel epimerase that converts GlcNAc-P-P-undecaprenol to GalNAc-P-P-undecaprenol in *Escherichia coli* O157. *J. Biol. Chem.*, 285:1671–1680, 2010.

[529] F.J. Ruzicka and P.A. Frey. Glutamate 2,3-aminomutase: a new member of the radical SAM superfamily of enzymes. *Biochim. Biophys. Acta*, 1774:286–296, 2007.

[530] K.S. Ryu, C. Kim, I. Kim, S. Yoo, B.S. Choi, and C. Park. NMR application probes a novel and ubiquitous family of enzymes that alter monosaccharide configuration. *J. Biol. Chem.*, 279:25544–25548, 2004.

[531] K.S. Ryu, J.I. Kim, S.J. Cho, D. Park, C. Park, H.K. Cheong, J.O. Lee, and B.S. Choi. Structural insights into the monosaccharide specificity of *Escherichia coli* rhamnose mutarotase. *J. Mol. Biol.*, 349:153–162, 2005.

[532] E.P. Sablin, R.B. CASe, S.C. Dai, C.L. Hart, A. Ruby, R.D. Vale, and R.J. Fletterick. Direction determination in the minus-end-directed kinesin motor ncd. *Nature*, 395:813–816, 1998.

[533] W. Saburi, S. Sato, S. Hashiguchi, H. Muto, T. Iizuka, and H. Mori. Enzymatic characteristics of D-mannose 2-epimerase, a new member of the acylglucosamine 2-epimerase superfamily. *Appl. Microbiol. Biotechnol.*, 103:6559–6570, 2019.

[534] J. Samuel, Y. Luo, P.M. Morgan, N.C. Strynadka, and M.E. Tanner. Catalysis and binding in L-ribulose-5-phosphate 4-epimerase: a comparison with L-fuculose-1-phosphate aldolase. *Biochemistry*, 40:14772–14780, 2001.

[535] J. Samuel and M.E. Tanner. Active site mutants of the "non-hydrolyzing" UDP-*N*-acetylglucosamine 2-epimerase from *Escherichia coli*. *Biochim. Biophys. Acta*, 1700:85–91, 2004.

[536] N. Sato and N. Murata. Lipid biosynthesis in the blue-green alga, *Anabaena variabilis* II. Fatty acids and lipid molecular species. *Biochim. Biophys. Acta*, 710:279–289, 1982.

[537] T. Sato, H. Atomi, and T. Imanaka. Archaeal type III RuBisCOs function in a pathway for AMP metabolism. *Science*, 315:1003–1006, 2007.

[538] 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.

[539] S.E. Sattler, E.B. Cahoon, S.J. Coughlan, and D. DellaPenna. Characterization of tocopherol cyclases from higher plants and cyanobacteria. Evolutionary implications for tocopherol synthesis and function. *Plant Physiol.*, 132:2184–2195, 2003.

[540] S. Sawai, H. Uchiyama, S. Mizuno, T. Aoki, T. Akashi, S. Ayabe, and T. Takahashi. Molecular characterization of an oxidosqualene cyclase that yields shionone, a unique tetracyclic triterpene ketone of *Aster tataricus*. *FEBS Lett.*, 585:1031–1036, 2011.

[541] A. Schenzle, H. Lenke, J.C. Spain, and H.J. Knackmuss. 3-Hydroxylaminophenol mutase from *Ralstonia eutropha* JMP134 catalyzes a Bamberger rearrangement. *J. Bacteriol.*, 181:1444–1450, 1999.

[542] D.M. Schmidt, B.K. Hubbard, and J.A. Gerlt. Evolution of enzymatic activities in the enolase superfamily: functional assignment of unknown proteins in *Bacillus subtilis* and *Escherichia coli* as L-Ala-D/L-Glu epimerases. *Biochemistry*, 40:15707–15715, 2001.

[543] E. Schmidt and H.-J. Knackmuss. Chemical structure and biodegradability of halogenated aromatic compounds. Conversion of chlorinated muconic acids into maleoylacetic acid. *Biochem. J.*, 192:339–347, 1980.

[544] W. Schmitz, R. Fingerhut, , and E. Purification and properties of an α-methylacyl-CoA racemase from rat liver. *Eur. J. Biochem.*, 222:313–323, 1994.

[545] K.J. Schray and I.A. Rose. Anomeric specificity and mechanism of two pentose isomerases. *Biochemistry*, 10:1058–1062, 1971.

[546] U. Schwien, E. Schmidt, H.-J. Knackmuss, and W. Reinecke. Degradation of chlorosubstituted aromatic-compounds by *Pseudomonas* sp. strain-B13 - fate of 3,5-dichlorocatechol. *Arch. Microbiol.*, 150:78–84, 1988.

[547] J.E. Seemann and G.E. Schulz. Structure and mechanism of L-fucose isomerase from *Escherichia coli*. *J. Mol. Biol.*, 273:256–268, 1997.

[548] 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.

[549] H.M. Seidel, S. Freeman, and J.R. Knowles. Phosphonate biosynthesis: isolation of the enzyme responsible for the formation of a carbon-phosphorus bond. *Nature*, 335:457–458, 1988.

[550] S. Seltzer. Purification and properties of maleylacetone *cis-trans* isomerase from *Vibrio* 01. *J. Biol. Chem.*, 248:215–222, 1973.

[551] E. Severi, A. Müller, J.R. Potts, A. Leech, D. Williamson, K.S. Wilson, and G.H. Thomas. Sialic acid mutarotation is catalyzed by the *Escherichia coli* β-propeller protein YjhT. *J. Biol. Chem.*, 283:4841–4849, 2008.

[552] M. Sharma, P. Abayakoon, R. Epa, Y. Jin, J.P. Lingford, T. Shimada, M. Nakano, J.W. Mui, A. Ishihama, E.D. Goddard-Borger, G.J. Davies, and S.J. Williams. Molecular basis of sulfosugar selectivity in sulfoglycolysis. *ACS Cent. Sci.*, 7:476–487, 2021.

[553] R.-F. Shen and H.-H. Tai. Immunoaffinity purification and characterization of thromboxane synthase from porcine lung. *J. Biol. Chem.*, 261:11592–11599, 1986.

[554] D.N. Sheppard and M.J. Welsh. Structure and function of the CFTR chloride channel. *Physiol. Rev.*, 79:S23–S45, 1999.

[555] W.R. Sherman, M.A. Stewart, and M. Zinbo. Mass spectrometric study on the mechanism of D-glucose 6-phosphate-L-*myo*-inositol 1-phosphate cyclase. *J. Biol. Chem.*, 244:5703–5708, 1969.

[556] M. Shibuya, S. Adachi, , and Y. Cucurbitadienol synthase, the first committed enzyme for cucurbitacin biosynthesis, is a distinct enzyme from cycloartenol synthase for phytosterol biosynthesis. *Tetrahedron*, 60:6995–7003, 2004.

[557] M. Shibuya, A. Sagara, A. Saitoh, T. Kushiro, and Y. Ebizuka. Biosynthesis of baccharis oxide, a triterpene with a 3,10-oxide bridge in the A-ring. *Org. Lett.*, 10:5071–5074, 2008.

[558] M. Shibuya, T. Xiang, Y. Katsube, M. Otsuka, H. Zhang, and Y. Ebizuka. Origin of structural diversity in natural triterpenes: direct synthesis of seco-triterpene skeletons by oxidosqualene cyclase. *J. Am. Chem. Soc.*, 129:1450–1455, 2007.

[559] M. Shibuya, H. Zhang, A. Endo, K. Shishikura, T. Kushiro, and Y. Ebizuka. Two branches of the lupeol synthase gene in the molecular evolution of plant oxidosqualene cyclases. *Eur. J. Biochem.*, 266:302–307, 1999.

[560] Y. Shikata, T. Watanabe, T. Teramoto, A. Inoue, Y. Kawakami, Y. Nishizawa, K. Katayama, , and M. Isolation and characterization of a peptide isomerase from funnel web spider venom. *J. Biol. Chem.*, 270:16719–16723, 1995.

[561] T. Shimizu, S. Yamamoto, and O. Hayaishi. Purification and properties of prostaglandin D synthetase from rat brain. *J. Biol. Chem.*, 254:5222–5228, 1979.

[562] J. Shinozaki, M. Shibuya, K. Masuda, and Y. Ebizuka. Dammaradiene synthase, a squalene cyclase, from *Dryopteris crassirhizoma* Nakai. *Phytochemistry*, 69:2559–2564, 2008.

[563] L.W. Shipman, D. Li, C.A. Roessner, A.I. Scott, and J.C. Sacchettini. Crystal structure of precorrin-8x methyl mutase. *Structure*, 9:587–596, 2001.

[564] Y. Shirokane and M. Suzuki. A novel enzyme, maltose 1-epimerase from *Lactobacillus brevis* IFO 3345. *FEBS Lett.*, 367:177–179, 1995.

[565] R. Shyam, A. Gorusupudi, K. Nelson, M.P. Horvath, and P.S. Bernstein. RPE65 has an additional function as the lutein to *meso*-zeaxanthin isomerase in the vertebrate eye. *Proc. Natl. Acad. Sci. USA*, 114:10882–10887, 2017.

[566] H. Sielaff, E. Dittmann, N. Tandeau De Marsac, C. Bouchier, H. von Döhren, T. Börner, and T. Schwecke. The *mcyF* gene of the microcystin biosynthetic gene cluster from *Microcystis aeruginosa* encodes an aspartate racemase. *Biochem. J.*, 373:909–916, 2003.

[567] J.E. Silbert and D.H. Brown. Enzymic synthesis of uridine diphosphate glucosamine and heparin from [14C]glucosamine by a mouse mast-cell tumor. *Biochim. Biophys. Acta*, 54:590–592, 1961.

[568] C.V. Sindelar and K.H. Downing. The beginning of kinesin's force-generating cycle visualized at 9-Å resolution. *J. Cell Biol.*, 177:377–385, 2007.

[569] W.R. Sistrom and R.Y. Stanier. The mechanism of formation of β-ketoadipic acid by bacteria. *J. Biol. Chem.*, 210:821–836, 1954.

[570] J. Sivaraman, P. Iannuzzi, M. Cygler, and A. Matte. Crystal structure of the RluD pseudouridine synthase catalytic module, an enzyme that modifies 23S rRNA and is essential for normal cell growth of *Escherichia coli*. *J. Mol. Biol.*, 335:87–101, 2004.

[571] J. Sivaraman, V. Sauve, R. Larocque, E.A. Stura, J.D. Schrag, M. Cygler, and A. Matte. Structure of the 16S rRNA pseudouridine synthase RsuA bound to uracil and UMP. *Nat. Struct. Biol.*, 9:353–358, 2002.

[572] M.W. Slein. Phosphomannose isomerase. *J. Biol. Chem.*, 186:753–761, 1950.

[573] M.W. Slein. Xylose isomerase from *Pasteurella pestis*, strain A-1122. *J. Am. Chem. Soc.*, 77:1663–1667, 1955.

[574] D.M. Small and N.K. Matheson. Phosphomannomutase and phosphoglucomutase in developing *Cassia corymbosa* seeds. *Phytochemistry*, 18:1147–1150, 1979.

[575] K. Soda and T. Osumi. Crystalline amino acid racemase with low substrate specificity. *Biochem. Biophys. Res. Commun.*, 35:363–368, 1969.

[576] J.K. Sohng, H.J. Kim, D.H. Nam, D.O. Lim, J.M. Han, H.J. Lee, and J.C. Yoo. Cloning, expression, and biological function of a dTDP-deoxyglucose epimerase (*gerF*) gene from *Streptomyces* sp. GERI-155. *Biotechnol. Lett.*, 26:185–191, 2004.

[577] F. Solano, C. Jiménez-Cervantes, J.H. Martinez-Liarte, J.C. Garcia-Borrón, and J.A. Lozano. Molecular mechanism for catalysis by a new zinc enzyme, dopachrome tautomerase. *Biochem. J.*, 313:447–453, 1996.

[578] B. Soldo, V. Lazarevic, H.M. Pooley, and D. Karamata. Characterization of a *Bacillus subtilis* thermosensitive teichoic acid-deficient mutant: gene *mnaA* (*yvyH*) encodes the UDP-*N*-acetylglucosamine 2-epimerase. *J. Bacteriol.*, 184:4316–4320, 2002.

[579] R. Somack and R.N. Costilow. Purification and properties of a pyridoxal phosphate and coenzyme B_{12} dependent D-α-ornithine 5,4-aminomutase. *Biochemistry*, 12:2597–2604, 1973.

[580] C.J. Spedaliere, C.S. Hamilton, and E.G. Mueller. Functional importance of motif I of pseudouridine synthases: mutagenesis of aligned lysine and proline residues. *Biochemistry*, 39:9459–9465, 2000.

[581] B. Sprössler and F. Lingens. Chorismat-Mutase aus *Claviceps*. I. Eigenschaften der Chorismat-Mutase aus verschiedenen *Claviceps*-Stämmen. *Hoppe-Seyler's Z. Physiol. Chem.*, 351:448–458, 1970.

[582] T.C. Stadtman and P. Elliott. Studies on the enzymic reduction of amino acids. II. Purification and properties of a D-proline reductase and a proline racemase from *Clostridium sticklandii*. *J. Biol. Chem.*, 228:983–997, 1957.

[583] T.C. Stadtman and P. Renz. Anaerobic degradation of lysine. V. Some properties of the cobamide coenzyme-dependent β-lysine mutase of *Clostridium sticklandii*. *Arch. Biochem. Biophys.*, 125:226–239, 1968.

[584] T.C. Stadtman and L. Tasi. A cobamide coenzyme dependent migration of the ε-amino group of D-lysine. *Biochem. Biophys. Res. Commun.*, 28:920–926, 1967.

[585] J.R. Stern, A. del Campillo, and A.L. Lehninger. Enzymatic racemization of β-hydroxybutyryl-*S*-CoA and the stereospecificity of enzymes of the fatty acid cycle. *J. Am. Chem. Soc.*, 77:1073–1074, 1955.

[586] P. Stickforth, S. Steiger, W.R. Hess, and G. Sandmann. A novel type of lycopene ε-cyclase in the marine cyanobacterium *Prochlorococcus marinus* MED4. *Arch. Microbiol.*, 179:409–415, 2003.

[587] J.T. Stivers, C. Abeygunawardana, A.S. Mildvan, G. Hajipour, C.P. Whitman, and L.H. Chen. Catalytic role of the amino-terminal proline in 4-oxalocrotonate tautomerase: affinity labeling and heteronuclear NMR studies. *Biochemistry*, 35:803–813, 1996.

[588] W. Stoffel, R. Ditzer, and H. Caesar. Der Stoffwechsel der ungesättigten Fettsäuren. III. Zur β-Oxydation der Mono- und Polyenfettsäuren. Der Mechanismus der enzymatischen Reaktionen an Δ^3*cis*-Enoyl-CoA-Verbindungen. *Hoppe-Seyler's Z. Physiol. Chem.*, 339:167–181, 1964.

[589] W. Stoffel and W. Ecker. Δ^3-*cis*,-Δ^2-*trans*-Enoyl-CoA isomerase from rat liver mitochondria. *Methods Enzymol.*, 14:99–105, 1969.

[590] W. Stoffel and M. Grol. Purification and properties of 3-*cis*-2-*trans*-enoyl-CoA isomerase (dodecenoyl-CoA Δ-isomerase) from rat liver mitochondria. *Hoppe-Seyler's Z. Physiol. Chem.*, 359:1777–1782, 1978.

[591] P.K. Stumpf and B.L. Horecker. The røole of xylulose 5-phosphate in xylose metabolism of *Lactobacillus pentosus*. *J. Biol. Chem.*, 218:753–768, 1956.

[592] C. Su and E.H. Oliw. Purification and characterization of linoleate 8-dioxygenase from the fungus *Gaeumannomyces graminis* as a novel hemoprotein. *J. Biol. Chem.*, 271:14112–14118, 1996.

[593] C. Su, M. Sahlin, and E.H. Oliw. A protein radical and ferryl intermediates are generated by linoleate diol synthase, a ferric hemeprotein with dioxygenase and hydroperoxide isomerase activities. *J. Biol. Chem.*, 273:20744–20751, 1998.

[594] H.S. Subramanya, D.I. Roper, Z. Dauter, E.J. Dodson, G.J. Davies, K.S. Wilson, and D.B. Wigley. Enzymatic ketonization of 2-hydroxymuconate: specificity and mechanism investigated by the crystal structures of two isomerases. *Biochemistry*, 35:792–802, 1996.

[595] 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.

[596] A. Sultana, P. Kallio, A. Jansson, J. Niemi, P. Mantsala, and G. Schneider. Crystallization and preliminary crystallographic data of SnoaL, a polyketide cyclase in nogalamycin biosynthesis. *Acta Crystallogr. D Biol. Crystallogr.*, 60:1118–1120, 2004.

[597] A. Sultana, P. Kallio, A. Jansson, J.S. Wang, J. Niemi, P. Mantsala, and G. Schneider. Structure of the polyketide cyclase SnoaL reveals a novel mechanism for enzymatic aldol condensation. *EMBO J.*, 23:1911–1921, 2004.

[598] K.E. Summers and I.R. Gibbons. Adenosine triphosphate-induced sliding of tubules in trypsin-treated flagella of sea-urchin sperm. *Proc. Natl. Acad. Sci. USA*, 68:3092–3096, 1971.

[599] T.P. Sun and Y. Kamiya. The *Arabidopsis* GA1 locus encodes the cyclase *ent*-kaurene synthetase A of gibberellin biosynthesis. *Plant Cell*, 6:1509–1518, 1994.

[600] S. Sunita, H. Zhenxing, J. Swaathi, M. Cygler, A. Matte, and J. Sivaraman. Domain organization and crystal structure of the catalytic domain of *E. coli* RluF, a pseudouridine synthase that acts on 23S rRNA. *J. Mol. Biol.*, 359:998–1009, 2006.

[601] E.W. Sutherland, M. Cohn, T. Posternak, and C.F. Cori. The mechanism of the phosphoglucomutase reaction. *J. Biol. Chem.*, 180:1285–1295, 1949.

[602] S. Suzuki, N. Onishi, and K. Yokozeki. Purification and characterization of hydantoin racemase from *Microbacterium liquefaciens* AJ 3912. *Biosci. Biotechnol. Biochem.*, 69:530–536, 2005.

[603] N. Takahashi, T. Hayano, and M. Suzuki. Peptidyl-prolyl *cis-trans* isomerase is the cyclosporin A-binding protein cyclophilin. *Nature*, 337:473–475, 1989.

[604] S. Takahashi, C. Hours, A. Chu, and D.T. Denhardt. The rep mutation. VI. Purification and properties of the *Escherichia coli* rep protein, DNA helicase III. *Can. J. Biochem.*, 57:855–866, 1979.

[605] K. Takeda, H. Yoshida, K. Izumori, and S. Kamitori. X-ray structures of *Bacillus pallidus* D-arabinose isomerase and its complex with L-fucitol. *Biochim. Biophys. Acta*, 1804:1359–1368, 2010.

[606] P. Talalay and V.S. Wang. Enzymic isomerization of Δ^5-3-ketosteroids. *Biochim. Biophys. Acta*, 18:300–301, 1955.

[607] Y. Tanaka, S.L. Ward, and W.L. Smith. Immunochemical and kinetic evidence for two different prostaglandin *H*-prostaglandin E isomerases in sheep vesicular gland microsomes. *J. Biol. Chem.*, 262:1374–1381, 1987.

[608] K.H. Tang, A. Harms, and P.A. Frey. Identification of a novel pyridoxal 5′-phosphate binding site in adenosylcobalamin-dependent lysine 5,6-aminomutase from *Porphyromonas gingivalis*. *Biochemistry*, 41:8767–8776, 2002.

[609] K.H. Tang, S.O. Mansoorabadi, G.H. Reed, and P.A. Frey. Radical triplets and suicide inhibition in reactions of 4-thia-D- and 4-thia-L-lysine with lysine 5,6-aminomutase. *Biochemistry*, 48:8151–8160, 2009.

[610] E.J. Taylor, S.J. Charnock, J. Colby, G.J. Davies, and G.W. Black. Cloning, purification and characterization of the 6-phospho-3-hexulose isomerase YckF from *Bacillus subtilis*. *Acta Crystallogr. D Biol. Crystallogr.*, 57:1138–1140, 2001.

[611] M.B. Taylor and E. Juni. Stereoisomeric specificities of 2,3-butanediol dehydrogenase. *Biochim. Biophys. Acta*, 39:448–457, 1960.

[612] P.L. Taylor, K.M. Blakely, G.P. de Leon, J.R. Walker, F. McArthur, E. Evdokimova, K. Zhang, M.A. Valvano, G.D. Wright, and M.S. Junop. Structure and function of sedoheptulose-7-phosphate isomerase, a critical enzyme for lipopolysaccharide biosynthesis and a target for antibiotic adjuvants. *J. Biol. Chem.*, 283:2835–2845, 2008.

[613] H. Terada, K. Mukae, S. Hosomi, T. Mizoguchi, and K. Uehara. Characterization of an enzyme which catalyzes isomerization and epimerization of D-erythrose 4-phosphate. *Eur. J. Biochem.*, 148:345–351, 1985.

[614] R. Teufel, V. Mascaraque, W. Ismail, M. Voss, J. Perera, W. Eisenreich, W. Haehnel, and G. Fuchs. Bacterial phenylalanine and phenylacetate catabolic pathway revealed. *Proc. Natl. Acad. Sci. USA*, 107:14390–14395, 2010.

[615] W. Thamer, I. Cirpus, M. Hans, A.J. Pierik, T. Selmer, E. Bill, D. Linder, and W. Buckel. A two [4Fe-4S]-cluster-containing ferredoxin as an alternative electron donor for 2-hydroxyglutaryl-CoA dehydratase from *Acidaminococcus fermentans*. *Arch. Microbiol.*, 179:197–204, 2003.

[616] D. Thibaut, M. Couder, A. Famechon, L. Debussche, B. Cameron, J. Crouzet, , and F. The final step in the biosynthesis of hydrogenobyrinic acid is catalyzed by the cobH gene product with precorrin-8X as the substrate. *J. Bacteriol.*, 174:1043–1049, 1992.

[617] J.B. Thoden, J. Kim, F.M. Raushel, and H.M. Holden. The catalytic mechanism of galactose mutarotase. *Protein Sci.*, 12:1051–1059, 2003.

[618] J.B. Thoden, D.J. Timson, R.J. Reece, and H.M. Holden. Molecular structure of human galactose mutarotase. *J. Biol. Chem.*, 279:23431–23437, 2004.

[619] L.C. Thompson, J.E. Ladner, S.G. Codreanu, J. Harp, G.L. Gilliland, and R.N. Armstrong. 2-Hydroxychromene-2-carboxylic acid isomerase: a kappa class glutathione transferase from *Pseudomonas putida*. *Biochemistry*, 46:6710–6722, 2007.

[620] T.T. Thuy, K. Liou, T.J. Oh, D.H. Kim, D.H. Nam, J.C. Yoo, and J.K. Sohng. Biosynthesis of dTDP-6-deoxy-β-D-allose, biochemical characterization of dTDP-4-keto-6-deoxyglucose reductase (GerKI) from *Streptomyces* sp. KCTC 0041BP. *Glycobiology*, 17:119–126, 2007.

[621] S.M. Toh and A.S. Mankin. An indigenous posttranscriptional modification in the ribosomal peptidyl transferase center confers resistance to an array of protein synthesis inhibitors. *J. Mol. Biol.*, 380:593–597, 2008.

[622] M. Tomoeda and R. Kitamura. A *cis-trans* isomerising activity of *Escherichia coli*. Isomerization from 2-(2-furyl)-3-*cis*-(5-nitro-2-furyl) acrylamide (furylfuramide) to its *trans* isomer. *Biochim. Biophys. Acta*, 480:315–325, 1977.

[623] C.P. Toseland and M.R. Webb. ATPase mechanism of the 5′-3′ DNA helicase, RecD2: evidence for a pre-hydrolysis conformation change. *J. Biol. Chem.*, 288:25183–25193, 2013.

[624] 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.

[625] P.C. Trackman and R.H. Abeles. Methionine synthesis from 5′-*S*-methylthioadenosine. Resolution of enzyme activities and identification of 1-phospho-5-*S*-methylthioribulose. *J. Biol. Chem.*, 258:6717–6720, 1983.

[626] A.G. Trejo, G.J.F. Chittenden, J.G. Buchanan, and J. Baddiley. Uridine diphosphate α-D-galactofuranose, an intermediate in the biosynthesis of galactofuranosyl residues. *Biochem. J.*, 117:637–639, 1970.

[627] K.K. Tsuboi, J. Estrada, and P.B. Hudson. Enzymes of the human erythrocytes. IV. Phosphoglucose isomerase, purification and properties. *J. Biol. Chem.*, 231:19–29, 1958.

[628] C.L. Turnbough, Neill Jr., Landsberg R.J., Ames R., and B.N. Pseudouridylation of tRNAs and its role in regulation in *Salmonella typhimurium*. *J. Biol. Chem.*, 254:5111–5119, 1979.

[629] G.E. Tusnady, E. Bakos, A. Varadi, and B. Sarkadi. Membrane topology distinguishes a subfamily of the ATP-binding cassette (ABC) transporters. *FEBS Lett.*, 402:1–3, 1997.

[630] T.R. Tyler and J.M. Leatherwood. Epimerization of disaccharides by enzyme preparations from *Ruminococcus albus*. *Arch. Biochem. Biophys.*, 119:363–367, 1967.

[631] K. Uechi, G. Takata, Y. Fukai, A. Yoshihara, and K. Morimoto. Gene cloning and characterization of L-ribulose 3-epimerase from *Mesorhizobium loti* and its application to rare sugar production. *Biosci. Biotechnol. Biochem.*, 77:511–515, 2013.

[632] V. Ullrich, L. Castle, and P. Weber. Spectral evidence for the cytochrome P_{450} nature of prostacyclin synthetase. *Biochem. Pharmacol.*, 30:2033–2036, 1981.

[633] V. Ullrich and M. Haurand. Thromboxane synthase as a cytochrome P_{450} enzyme. *Adv. Prostaglandin Thromboxane Res.*, 11:105–110, 1983.

[634] A. Urban, I. Behm-Ansmant, C. Branlant, and Y. Motorin. RNA sequence and two-dimensional structure features required for efficient substrate modification by the *Saccharomyces cerevisiae* RNA:Ψ-synthase Pus7p. *J. Biol. Chem.*, 284:5845–5858, 2009.

[635] S. Usui and C.-A. Yu. Purification and properties of isopenicillin-N epimerase from *Streptomyces clavuligerus*. *Biochim. Biophys. Acta*, 999:78–85, 1989.

[636] M. Uziel and D.J. Hanahan. An enzyme-catalyzed acyl migration: a lysolecithin migratase. *J. Biol. Chem.*, 226:789–798, 1957.

[637] R.D. Vale, T.S. Reese, and M.P. Sheetz. Identification of a novel force-generating protein, kinesin, in microtubule-based motility. *Cell*, 42:39–50, 1985.

[638] M.A. Valvano, P. Messner, and P. Kosma. Novel pathways for biosynthesis of nucleotide-activated *glycero-manno*-heptose precursors of bacterial glycoproteins and cell surface polysaccharides. *Microbiology*, 148:1979–1989, 2002.

[639] L. van der Drift, G.D. Vogels, and C. van der Drift. Allantoin racemase: a new enzyme from *Pseudomonas* species. *Biochim. Biophys. Acta*, 391:240–248, 1975.

[640] K.E. van Straaten, F.H. Routier, and D.A. Sanders. Towards the crystal structure elucidation of eukaryotic UDP-galactopyranose mutase. *Acta Crystallogr. Sect. F Struct. Biol. Cryst. Commun.*, 68:455–459, 2012.

[641] L.J. van Tegelen, P.R. Moreno, A.F. Croes, R. Verpoorte, and G.J. Wullems. Purification and cDNA cloning of isochorismate synthase from elicited cell cultures of *Catharanthus roseus*. *Plant Physiol.*, 119:705–712, 1999.

[642] A.I. Virtanen. On enzymic and chemical reactions in crushed plants. *Arch. Biochem. Biophys. Suppl.*, 1:200–208, 1962.

[643] W.A. Volk. Purification and properties of phosphoarabinoisomerase from *Propionibacterium pentosaceum*. *J. Biol. Chem.*, 235:1550–1553, 1960.

[644] W.M. De Vos, I. Boerrigter, R.J. Van Rooijen, B. Reiche, , and W. Characterization of the lactose-specific enzymes of the phosphotransferase system in *Lactococcus lactis*. *J. Biol. Chem.*, 265:22554–22560, 1990.

[645] S.J. Wakil. D(-)β-Hydroxybutyryl CoA dehydrogenase. *Biochim. Biophys. Acta*, 18:314–315, 1955.

[646] Q. Wang, P. Ding, A.V. Perepelov, Y. Xu, Y. Wang, Y.A. Knirel, L. Wang, and L. Feng. Characterization of the dTDP-D-fucofuranose biosynthetic pathway in *Escherichia coli* O52. *Mol. Microbiol.*, 70:1358–1367, 2008.

[647] 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.

[648] W. Wang, L. Cao, C. Wang, B. Gigant, and M. Knossow. Kinesin, 30 years later: Recent insights from structural studies. *Protein Sci.*, 24:1047–1056, 2015.

[649] Z. Wang, O. Guhling, R. Yao, F. Li, T.H. Yeats, J.K. Rose, and R. Jetter. Two oxidosqualene cyclases responsible for biosynthesis of tomato fruit cuticular triterpenoids. *Plant Physiol.*, 155:540–552, 2011.

[650] Z. Wang, T. Yeats, H. Han, and R. Jetter. Cloning and characterization of oxidosqualene cyclases from *Kalanchoe daigremontiana*: enzymes catalyzing up to 10 rearrangement steps yielding friedelin and other triterpenoids. *J. Biol. Chem.*, 285:29703–29712, 2010.

[651] K. Watabe, T. Ishikawa, Y. Mukohara, and H. Nakamura. Purification and characterization of the hydantoin racemase of *Pseudomonas* sp. strain NS671 expressed in *Escherichia coli*. *J. Bacteriol.*, 174:7989–7995, 1992.

[652] K. Watanabe, K. Suzuki, and S. Kitamura. Characterization of a GDP-D-mannose 3″,5″-epimerase from rice. *Phytochemistry*, 67:338–346, 2006.

[653] H. Weissbach, J. Toohey, and H.A. Barker. Isolation and properties of B_{12} coenzymes containing benzimidazole or dimethylbenzimidazole. *Proc. Natl. Acad. Sci. USA*, 45:521–528, 1959.

[654] E.L. Westman, D.J. McNally, M. Rejzek, W.L. Miller, V.S. Kannathasan, A. Preston, D.J. Maskell, R.A. Field, J.R. Brisson, and J.S. Lam. Erratum report: Identification and biochemical characterization of two novel UDP-2,3-diacetamido-2,3-dideoxy-α-D-glucuronic acid 2-epimerases from respiratory pathogens. *Biochem. J.*, 405:625–625, 2007.

[655] E.L. Westman, D.J. McNally, M. Rejzek, W.L. Miller, V.S. Kannathasan, A. Preston, D.J. Maskell, R.A. Field, J.R. Brisson, and J.S. Lam. Identification and biochemical characterization of two novel UDP-2,3-diacetamido-2,3-dideoxy-α-D-glucuronic acid 2-epimerases from respiratory pathogens. *Biochem. J.*, 405:123–130, 2007.

[656] M. Whitlow, A.J. Howard, B.C. Finzel, T.L. Poulos, E. Winborne, and G.L. Gilliland. A metal-mediated hydride shift mechanism for xylose isomerase based on the 1.6 Å *Streptomyces* rubiginosus structures with xylitol and D-xylose. *Proteins*, 9:153–173, 1991.

[657] C.P. Whitman, B.A. Aird, W.R. Gillespie, and N.J. Stolowich. Chemical and enzymatic ketonization of 2-hydroxymuconate, a conjugated enol. *J. Am. Chem. Soc.*, 113:3154–3162, 1991.

[658] C.P. Whitman, G. Hajipour, R.J. Watson, W.H. Johnson, Bembenek Jr., Stolowich M.E., and N.J. Stereospecific ketonization of 2-hydroxymuconate by 4-oxalocrotonate tautomerase and 5-(carboxymethyl)-2-hydroxymuconate isomerase. *J. Am. Chem. Soc.*, 114:10104–10110, 1992.

[659] D.A. Whittington, M.L. Wise, M. Urbansky, R.M. Coates, R.B. Croteau, and D.W. Christianson. Bornyl diphosphate synthase: structure and strategy for carbocation manipulation by a terpenoid cyclase. *Proc. Natl. Acad. Sci. USA*, 99:15375–15380, 2002.

[660] E. Wiame and E. Van Schaftingen. Fructoselysine 3-epimerase, an enzyme involved in the metabolism of the unusual Amadori compound psicoselysine in *Escherichia coli*. *Biochem. J.*, 378:1047–1052, 2004.

[661] D.J. Wichelecki, M.W. Vetting, L. Chou, N. Al-Obaidi, J.T. Bouvier, S.C. Almo, and J.A. Gerlt. ATP-binding cassette (ABC) transport system solute-binding protein-guided identification of novel D-altritol and galactitol catabolic pathways in *Agrobacterium tumefaciens* C58. *J. Biol. Chem.*, 290:28963–28976, 2015.

[662] A. Wiese, M. Pietzsch, C. Syldatk, R. Mattes, and J. Altenbuchner. Hydantoin racemase from *Arthrobacter aurescens* DSM 3747: heterologous expression, purification and characterization. *J. Biotechnol.*, 80:217–230, 2000.

[663] R. Willem, M. Biesemans, K. Hallenga, G. Lippens, F. Malaisse-Lagae, and W.J. Malaisse. Dual anomeric specificity and dual anomerase activity of phosphoglucoisomerase quantified by two-dimensional phase-sensitive ^{13}C EXSY NMR. *J. Biol. Chem.*, 267:210–217, 1992.

[664] B.A. Wilson, S. Bantia, G.M. Salituro, A.M. Reeve, and C.A. Townsend. Cell-free biosynthesis of nocardicin A from nocardicin E and *S*-adenosylmethionine. *J. Am. Chem. Soc.*, 110:8238–8239, 1988.

[665] D.B. Wilson and D.S. Hogness. The enzymes of the galactose operon in *Escherichia coli*. I. Purification and characterization of uridine diphosphogalactose 4-epimerase. *J. Biol. Chem.*, 239:2469–2481, 1964.

[666] D.C. Wilton, A.D. Rahimtula, and M. Akhtar. The reversibility of the Δ^8-cholestenol-Δ^7-cholestenol isomerase reaction in cholesterol biosynthesis. *Biochem. J.*, 114:71–73, 1969.

[667] F.E. De Windt and D. van der Drift. Purification and some properties of hydroxypyruvate isomerase of *Bacillus fastidiosus*. *Biochim. Biophys. Acta*, 613:556–562, 1980.

[668] M.L. Wise, M. Hamberg, and W.H. Gerwick. Biosynthesis of conjugated fatty acids by a novel isomerase from the red marine alga *Ptilota filicina*. *Biochemistry*, 33:15223–15232, 1994.

[669] M.L. Wise, J. Rossi, and W.H. Gerwick. Binding site characterization of polyenoic fatty-acid isomerase from the marine alga *Ptilota filicina*. *Biochemistry*, 36:2985–2992, 1997.

[670] 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.

[671] M.L. Wise, K. Soderstrom, T.F. Murray, and W.H. Gerwick. Synthesis and cannabinoid receptor binding activity of conjugated triene anandamide, a novel eicosanoid. *Experientia*, 52:88–92, 1996.

[672] F. Wolfram, E.N. Kitova, H. Robinson, M.T. Walvoort, J.D. Codee, J.S. Klassen, and P.L. Howell. Catalytic mechanism and mode of action of the periplasmic alginate epimerase AlgG. *J. Biol. Chem.*, 289:6006–6019, 2014.

[673] M.J. Wolin, F.J. Simpson, and W.A. Wood. Degradation of L-arabinose by *Aerobacter aerogenes*. III. Identification and properties of L-ribulose-5-phosphate 4-epimerase. *J. Biol. Chem.*, 232:559–575, 1958.

[674] H. Wolosker, S. Blackshaw, and S.H. Snyder. Serine racemase: a glial enzyme synthesizing D-serine to regulate glutamate-*N*-methyl-D-aspartate neurotransmission. *Proc. Natl. Acad. Sci. USA*, 96:13409–13414, 1999.

[675] H. Wolosker, K.N. Sheth, M. Takahashi, J.P. Mothet, R.O. Brady, Ferris Jr., Snyder C.D., and S.H. Purification of serine racemase: biosynthesis of the neuromodulator D-serine. *Proc. Natl. Acad. Sci. USA*, 96:721–725, 1999.

[676] B.A. Wolucka, G. Persiau, J. Van Doorsselaere, M.W. Davey, H. Demol, J. Vandekerckhove, M. Van Montagu, M. Zabeau, and W. Boerjan. Partial purification and identification of GDP-mannose 3",5"-epimerase of *Arabidopsis thaliana*, a key enzyme of the plant vitamin C pathway. *Proc. Natl. Acad. Sci. USA*, 98:14843–14848, 2001.

[677] W.A. Wood. Amino acid racemases. *Methods Enzymol.*, 2:212–217, 1955.

[678] W.A. Wood and I.C. Gunsalus. D-Alanine formation: a racemase in *Streptococcus faecalis*. *J. Biol. Chem.*, 190:403–416, 1951.

[679] T.S. Woodin and L. Nishioka. Evidence for three isozymes of chorismate mutase in alfalfa. *Biochim. Biophys. Acta*, 309:211–223, 1973.

[680] J. Wrzesinski, A. Bakin, K. Nurse, B.G. Lane, and J. Ofengand. Purification, cloning, and properties of the 16*S* RNA pseudouridine 516 synthase from *Escherichia coli*. *Biochemistry*, 34:8904–8913, 1995.

[681] J. Wrzesinski, A. Bakin, J. Ofengand, and B.G. Lane. Isolation and properties of *Escherichia coli* 23*S*-RNA pseudouridine 1911, 1915, 1917 synthase (RluD). *IUBMB Life*, 50:33–37, 2000.

[682] J. Wrzesinski, K. Nurse, A. Bakin, B.G. Lane, and J. Ofengand. A dual-specificity pseudouridine synthase: an *Escherichia coli* synthase purified and cloned on the basis of its specificity for Ψ^{746} in 23S RNA is also specific for Ψ^{32} in $tRNA^{Phe}$. *RNA*, 1:437–448, 1995.

[683] X. Wu, P.M. Flatt, H. Xu, and T. Mahmud. Biosynthetic gene cluster of cetoniacytone A, an unusual aminocyclitol from the endosymbiotic Bacterium *Actinomyces* sp. Lu 9419. *ChemBioChem*, 10:304–314, 2009.

[684] B. Wurster and B. Hess. Glucose-6-phosphate-1-epimerase from baker's yeast. A new enzyme. *FEBS Lett.*, 23:341–348, 1972.

[685] K.B. Xavier, S.T. Miller, W. Lu, J.H. Kim, J. Rabinowitz, I. Pelczer, M.F. Semmelhack, and B.L. Bassler. Phosphorylation and processing of the quorum-sensing molecule autoinducer-2 in enteric bacteria. *ACS Chem. Biol.*, 2:128–136, 2007.

[686] Q. Xiong, W.K. Wilson, and S.P.T. Matsuda. An *Arabidopsis* oxidosqualene cyclase catalyzes iridal skeleton formation by Grob fragmentation. *Angew. Chem. Int. Ed. Engl.*, 45:1285–1288, 2006.

[687] C.J. Xu, D.M. Chen, and S.L. Zhang. [Molecular cloning of full length capsanthin/capsorubin synthase homologous gene from orange (*Citrus sinensis*)]. *Shi Yan Sheng Wu Xue Bao*, 34:147–150, 2001.

[688] M. Xu, M.L. Hillwig, S. Prisic, R.M. Coates, and R.J. Peters. Functional identification of rice *syn*-copalyl diphosphate synthase and its role in initiating biosynthesis of diterpenoid phytoalexin/allelopathic natural products. *Plant J.*, 39:309–318, 2004.

[689] Y. Xue, Z. Wei, X. Li, and W. Gong. The crystal structure of putative precorrin isomerase CbiC in cobalamin biosynthesis. *J. Struct. Biol.*, 153:307–311, 2006.

[690] M. Yamada and K. Kurahashi. Further purification and properties of adenosine triphosphate-dependent phenylalanine racemase of *Bacillus brevis* Nagano. *J. Biochem. (Tokyo)*, 66:529–540, 1969.

[691] 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.

[692] K. Yamanaka. Purification, crystallization and properties of the D-xylose isomerase from *Lactobacillus brevis*. *Biochim. Biophys. Acta*, 151:670–680, 1968.

[693] T. Yamashita, M. Ashiuchi, K. Ohnishi, S. Kato, S. Nagata, and H. Misono. Molecular identification of monomeric aspartate racemase from *Bifidobacterium bifidum*. *Eur. J. Biochem.*, 271:4798–4803, 2004.

[694] T. Yamauchi, S.Y. Choi, H. Okada, M. Yohda, H. Kumagai, N. Esaki, and K. Soda. Properties of aspartate racemase, a pyridoxal 5′-phosphate-independent amino acid racemase. *J. Biol. Chem.*, 267:18361–18364, 1992.

[695] N. Yaneva, J. Schuster, F. Schafer, V. Lede, D. Przybylski, T. Paproth, H. Harms, R.H. Muller, and T. Rohwerder. Bacterial acyl-CoA mutase specifically catalyzes coenzyme B_{12}-dependent isomerization of 2-hydroxyisobutyryl-CoA and (*S*)-3-hydroxybutyryl-CoA. *J. Biol. Chem.*, 287:15502–15511, 2012.

[696] W.K. Yeh, S.K. Ghag, and S.W. Queener. Enzymes for epimerization of isopenicillin N, ring expansion of penicillin N, and 3′-hydroxylation of deacetoxycephalosporin C. Function, evolution, refolding, and enzyme engineering. *Ann. N.Y. Acad. Sci.*, 672:396–408, 1992.

[697] 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.

[698] H.G. Yoo, S.Y. Kwon, S. Karki, and H.J. Kwon. A new route to dTDP-6-deoxy-L-talose and dTDP-L-rhamnose: dTDP-L-rhamnose 4-epimerase in *Burkholderia thailandensis*. *Bioorg. Med. Chem. Lett.*, 21:3914–3917, 2011.

[699] T. Yorifuji, K. Ogata, and K. Soda. Crystalline arginine racemase. *Biochem. Biophys. Res. Commun.*, 34:760–764, 1969.

[700] H. Yoshida, M. Yamada, T. Nishitani, G. Takada, K. Izumori, and S. Kamitori. Crystal structures of D-tagatose 3-epimerase from *Pseudomonas cichorii* and its complexes with D-tagatose and D-fructose. *J. Mol. Biol.*, 374:443–453, 2007.

[701] H. Yoshida, M. Yamada, Y. Ohyama, G. Takada, K. Izumori, and S. Kamitori. The structures of L-rhamnose isomerase from *Pseudomonas stutzeri* in complexes with L-rhamnose and D-allose provide insights into broad substrate specificity. *J. Mol. Biol.*, 365:1505–1516, 2007.

[702] K. Yoshida, M. Yamaguchi, T. Morinaga, M. Ikeuchi, M. Kinehara, and H. Ashida. Genetic modification of *Bacillus subtilis* for production of D-*chiro*-inositol, an investigational drug candidate for treatment of type 2 diabetes and polycystic ovary syndrome. *Appl. Environ. Microbiol.*, 72:1310–1315, 2006.

[703] K. Yoshida, M. Yamaguchi, T. Morinaga, M. Kinehara, M. Ikeuchi, H. Ashida, and Y. Fujita. *myo*-Inositol catabolism in *Bacillus subtilis*. *J. Biol. Chem.*, 283:10415–10424, 2008.

[704] I.G. Young and F. Gibson. Regulation of the enzymes involved in the biosynthesis of 2,3-dihydroxybenzoic acid in *Aerobacter aerogenes* and *Escherichia coli*. *Biochim. Biophys. Acta*, 177:401–411, 1969.

[705] M.J. Yu and S.L. Chen. From NAD^+ to nickel pincer complex: a significant cofactor evolution presented by lactate racemase. *Chemistry*, 23:7545–7557, 2017.

[706] Q. Yu, S. Ghisla, J. Hirschberg, V. Mann, and P. Beyer. Plant carotene *cis-trans* isomerase CRTISO: a new member of the FADred-dependent flavoproteins catalyzing non-redox reactions. *J. Biol. Chem.*, 286:8666–8676, 2011.

[707] Q. Yu, P. Schaub, S. Ghisla, S. Al-Babili, A. Krieger-Liszkay, and P. Beyer. The lycopene cyclase CrtY from *Pantoea ananatis* (formerly *Erwinia uredovora*) catalyzes an FADred-dependent non-redox reaction. *J. Biol. Chem.*, 285:12109–12120, 2010.

[708] S. Yu and R. Fiskesund. The anhydrofructose pathway and its possible role in stress response and signaling. *Biochim. Biophys. Acta*, 1760:1314–1322, 2006.

[709] 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.

[710] 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.

[711] 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.

[712] E.J. Yun, S. Lee, H.T. Kim, J.G. Pelton, S. Kim, H.J. Ko, I.G. Choi, and K.H. Kim. The novel catabolic pathway of 3,6-anhydro-L-galactose, the main component of red macroalgae, in a marine bacterium. *Environ. Microbiol.*, 17:1677–1688, 2015.

[713] 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.

[714] V. Zappia and H.A. Barker. Studies on lysine-2,3-aminomutase. Subunit structure and sulfhydryl groups. *Biochim. Biophys. Acta*, 207:505–513, 1970.

[715] 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.

[716] C.S. Zhang, M. Podeschwa, H.J. Altenbach, W. Piepersberg, and U.F. Wehmeier. The acarbose-biosynthetic enzyme AcbO from *Actinoplanes* sp. SE 50/110 is a 2-*epi*-5-*epi*-valiolone-7-phosphate 2-epimerase. *FEBS Lett.*, 540:47–52, 2003.

[717] D. Zhang, X. Liang, X.Y. He, O.D. Alipui, S.Y. Yang, and H. Schulz. $\Delta^{3,5}$,$\Delta^{2,4}$-dienoyl-CoA isomerase is a multifunctional isomerase. A structural and mechanistic study. *J. Biol. Chem.*, 276:13622–13627, 2001.

[718] D. Zhang, W. Yu, B.V. Geisbrecht, S.J. Gould, H. Sprecher, and H. Schulz. Functional characterization of Δ^3,Δ^2-enoyl-CoA isomerases from rat liver. *J. Biol. Chem.*, 277:9127–9132, 2002.

[719] H. Zhang, M. Shibuya, S. Yokota, and Y. Ebizuka. Oxidosqualene cyclases from cell suspension cultures of *Betula platyphylla* var. *japonica*: molecular evolution of oxidosqualene cyclases in higher plants. *Biol. Pharm. Bull.*, 26:642–650, 2003.

[720] L. Zhang, W. Mu, B. Jiang, and T. Zhang. Characterization of D-tagatose-3-epimerase from *Rhodobacter sphaeroides* that converts D-fructose into D-psicose. *Biotechnol. Lett.*, 31:857–862, 2009.

[721] R.G. Zhang, I. Dementieva, N. Duke, F. Collart, E. Quaite-Randall, R. Alkire, L. Dieckman, N. Maltsev, O. Korolev, and A. Joachimiak. Crystal structure of *Bacillus subtilis* ioli shows endonuclase IV fold with altered Zn binding. *Proteins*, 48:423–426, 2002.

[722] W. Zhang, D. Fang, Q. Xing, L. Zhou, B. Jiang, and W. Mu. Characterization of a novel metal-dependent D-psicose 3-epimerase from *Clostridium scindens* 35704. *PLoS One*, 8:e62987–e62987, 2013.

[723] 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.

[724] Y. Zhang, J.M. Foster, S. Kumar, M. Fougere, and C.K. Carlow. Cofactor-independent phosphoglycerate mutase has an essential role in *Caenorhabditis elegans* and is conserved in parasitic nematodes. *J. Biol. Chem.*, 279:37185–37190, 2004.

[725] S. Zhao, R. Kumar, A. Sakai, M.W. Vetting, B.M. Wood, S. Brown, J.B. Bonanno, B.S. Hillerich, R.D. Seidel, P.C. Babbitt, S.C. Almo, J.V. Sweedler, J.A. Gerlt, J.E. Cronan, and M.P. Jacobson. Discovery of new enzymes and metabolic pathways by using structure and genome context. *Nature*, 502:698–702, 2013.

[726] X. Zhao and D.A. Horne. The role of cysteine residues in the rearrangement of uridine to pseudouridine catalyzed by pseudouridine synthase I. *J. Biol. Chem.*, 272:1950–1955, 1997.

[727] W. Zheng, M.L. Wise, A. Wyrick, J.G. Metz, L. Yuan, and W.H. Gerwick. Polyenoic fatty-acid isomerase from the marine red alga *Ptilota filicina*: protein characterization and functional expression of the cloned cDNA. *Arch. Biochem. Biophys.*, 401:11–20, 2002.

[728] 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.

[729] J.Q. Zhou, H. Qi, V.P. Schulz, M.K. Mateyak, E.K. Monson, and V.A. Zakian. *Schizosaccharomyces pombe* pfh1+ encodes an essential 5′ to 3′ DNA helicase that is a member of the PIF1 subfamily of DNA helicases. *Mol. Biol. Cell*, 13:2180–2191, 2002.

[730] Y. Zhu, Y. Men, W. Bai, X. Li, L. Zhang, Y. Sun, and Y. Ma. Overexpression of D-psicose 3-epimerase from *Ruminococcus* sp. in *Escherichia coli* and its potential application in D-psicose production. *Biotechnol. Lett.*, 34:1901–1906, 2012.

Index