Kirk-Othmer Encyclopedia of Chemical Technology.

HYDROXY DICARBOXYLIC ACIDS

Many natural and synthetic organic compounds are hydroxy dicarboxylic acids (see also Hydroxycarboxylic acids). This article discusses mainly malic and tartaric acids; thiomalic acid is included because of its structural similarity to malic acid.

1. Malic Acid

Malic acid [6915-15-7] (hydroxysuccinic acid, hydroxybutanedioic acid, or 1-hydroxy-1,2-ethanedicarboxylic acid), $C_4H_6O_5$, is a white, crystalline material. The levorotatory isomer, S(−)-malic acid [97-67-6] (L-malic acid), is a natural constituent and common metabolite of plants and animals. The racemic compound, *R,S*-malic acid [617-48-1] (DL-malic acid), is a widely used food acidulant. This material is also used in some industrial applications as a sequestrant and as a buffer for pH control. R(+)-Malic acid [636-61-3] (D-malic acid) is available only as a laboratory chemical. In the United States, *R,S*-malic acid was first produced synthetically in 1923. Until the early 1960s, it was produced batchwise on a small scale and had limited industrial application. Following the introduction of a modern, continuous manufacturing process in the early 1960s, malic acid gradually became a large-volume industrial organic acid.

1.1. Physical Properties

Malic acid crystallizes from aqueous solutions as white, translucent, anhydrous crystal. The S(−) isomer melts at 100–103°C (1) and the R(+) isomer at 98–99°C (2). On heating, D,L-malic acid decomposes at ca 180°C by forming fumaric acid and maleic anhydride. Under normal conditions, malic acid is stable; under conditions of high humidity, it is hygroscopic.

Malic acid is a relatively strong acid. Its dissociation constants are given in Table 1. The pH of a 0.001% aqueous solution is 3.80, that of 0.1% solution is 2.80, and that of a 1.0% solution is 2.34. Many of its physical properties are similar to those of citric acid (qv). Solubility characteristics are shown in Figure 1 and Table 1, densities of aqueous solutions are listed in Table 2, and pH values vs concentration are shown in Figure 2.

1.2. Chemical Properties

Because of its chiral center, malic acid is optically active. In 1896, when tartaric acid was first reduced to malic acid, the levorotatory enantiomer, S(−), was confirmed as having the spatial configuration (**1**) (5, 6). The other enantiomer (**2**) has the R configuration. A detailed discussion of configuration assignment by the sequence rule or the R and S system is available (7).

Table 1. Physical Properties of *R,S*-Malic acid[a]

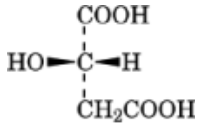
Property	Value
mol wt	134.09
appearance	white, crystalline
crystal system	triclinic
melting point, °C	ca 130
d_4^{20}	1.601
dissociation constant	
K_1	4×10^{-4}
K_2	9×10^{-6}
heat of combustion (at 20°C), MJ/mol[b]	1.340
heat of solution, kJ/mol[b] solute	−20.515
viscosity (50% aqueous solution at 25°C), mPa·s(= cP)	6.5
solubility[c] in nonaqueous solvents, %wt/wt	
ethanol	45.5
acetone	17.8
methanol	82.7

[a] Ref. 3.
[b] To convert J to cal, divide by 4.184.
[c] Ref. 4.

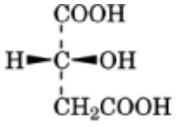
Table 2. Density of Aqueous Malic Acid Solutions at 15°C[a]

Concentration, g/L	d_{15}^{15}, g/ml	(°Bé)	Concentration, g/L	d_{15}^{15}, g/L	(°Bé)
30	1.115	(14.9)	46	1.169	(21.0)
32	1.121	(15.7)	48	1.179	(22.0)
34	1.129	(16.6)	50	1.186	(22.7)
36	1.138	(17.6)	52	1.192	(23.4)
38	1.146	(18.5)	54	1.199	(24.1)
40	1.151	(19.0)	56	1.208	(25.0)
42	1.158	(19.8)	58	1.212	(25.4)
44	1.165	(20.5)	60	1.220	(26.1)

[a] At 25°C specific gravity ranges from 1.04 at 10 wt % to 1.25 at 55 wt %.



(**1**)



(**2**)

The optical activity of malic acid changes with dilution (8). The naturally occurring, levorotatory acid shows a most peculiar behavior in this respect; a 34% solution at 20°C is optically inactive. Dilution results in increasing levo rotation, whereas more concentrated solutions show dextro rotation. The effects of dilution are explained by the postulation that an additional form, the epoxide (**3**), occurs in solution and that the direction

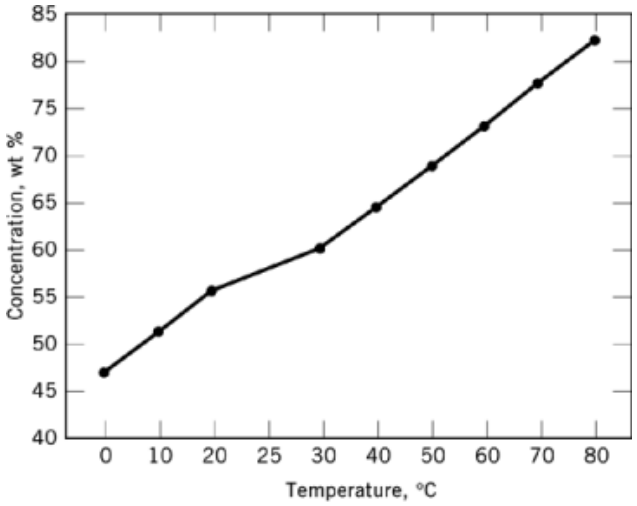


Fig. 1. *R,S*(±)-Malic acid solubility in water, showing maximum solubilities vs temperature (4).

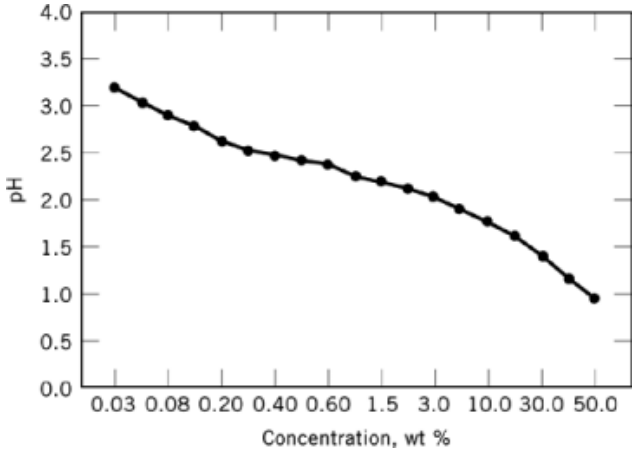
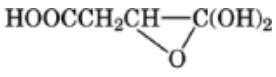


Fig. 2. Malic acid pH values vs concentration for R,S(±)-malic acid (4).

of rotation of the normal (open-chain) and epoxide forms is reversed (8). Synthetic (racemic) *R,S*-malic acid can be resolved into the two enantiomers by crystallization of its cinchonine salts.



(3)

1.3. Reactions

Malic acid undergoes many of the characteristic reactions of dibasic acids, monohydric alcohols, and α-hydroxycarboxylic acids. When heated to 170–180°C, it decomposes to fumaric acid and maleic anhydride

Table 3. Corrosion by 25 wt % Solution of Malic Acid

Metal	Corrosion rate, mm/yr[a]	Temperature, °C
aluminum	<0.5	below 100
carbon steel	>1.3	[b]
stainless steel (304)	<0.05	below 50
stainless steel (316)	<0.05	below 120

[a] To convert mm/yr to mils penetration/yr (Mpy), divide by 2.54×10^{-2}.
[b] At all temperatures.

which sublimes on further heating (see Maleic anhydride, maleic acid, and fumaric acid). Malic acid forms two types of condensation products: linear malomalic acids and the cyclic dilactone or malide; it does not form an anhydride.

As a dibasic acid, malic acid forms the usual salts, esters, amides, and acyl chlorides. Monoesters can be prepared easily by refluxing malic acid, an alcohol, and boron trifluoride as a catalyst (9). With polyhydric alcohols and polycarboxylic aromatic acids, malic acid yields alkyd polyester resins (10) (see Alcohols, polyhydric; Alkyd resins). Complete esterification results from the reaction of the diester of malic acid with an acid chloride, eg, acetyl or stearoyl chloride (11).

Alkyl halides in the presence of silver oxide react with alkyl malates to yield alkoxy derivatives of succinic acid, eg, 2-ethoxysuccinic acid, $HOOCCH_2CH(OC_2H_5)COOH$ (12, 13). A synthetic approach to produce ethers of malic acid is the reaction of malic esters and sodium alkoxides which affords 2-alkoxysuccinic esters (14).

Amides are obtained when alkyl esters of malic acid are treated with ammonia in alcoholic solution. Hydrazine reacts in a similar manner to yield malic dihydrazide (15) (see Hydrazine and its derivatives). Depending on the proportions of water that are present in the reaction, aniline and malic acid form *N,N′*-diphenylmalamide or the cyclic compound, *N*-phenylmalanil (16). When monoanilinium malate is distilled under reduced pressure, a mixture of *C*-anilino-*N*-phenylsuccinimide, *N*-phenylmalanil, and *N*-phenylsuccinimide is obtained (17, 18).

Malic acid yields coumalic acid when treated with fuming sulfuric acid (19). Similar treatment of malic acid in the presence of phenol and substituted phenols is a facile method of synthesizing coumarins that are substituted in the aromatic nucleus (20, 21) (see Coumarin). Similar reactions take place with thiophenol and substituted thiophenols, yielding, among other compounds, a red dye (22) (see Dyes and dye intermediates). Oxidation of an aqueous solution of malic acid with hydrogen peroxide (qv) catalyzed by ferrous ions yields oxalacetic acid (23). If this oxidation is performed in the presence of chromium, ferric, or titanium ions, or mixtures of these, the product is tartaric acid (24). Chlorals react with malic acid in the presence of sulfuric acid or other acidic catalysts to produce 4-ketodioxolones (25, 26).

In aqueous solution, malic acid can be mildly corrosive toward aluminum and corrosive to carbon steel. Under normal conditions, it is not corrosive to stainless steels, which usually are the construction materials for processes involving malic acid. Malic acid is also virtually noncorrosive to tinplate and other materials used to package acidulated foods and beverages (Table 3) (27).

At proper pH in aqueous media, malic acid forms complexes or chelates with metal ions (see Chelating agents). These chelating reactions are useful in industrial processes requiring elimination or control of metal-ion catalysis (eg, of oxidation), removal of corrosion products (eg, rust), lowering of metal oxidation potentials (electroplating), etc. The chelating properties of malic acid vary with different metal cations, ionic strength, pH, etc, and in many cases approximate those of other hydroxy carboxylic acids (28). Formation constants for malic acid chelates with various metal ions are as follows:Ca, 1.8;Cu, 3.4;Mg, 2.2; andZn, 2.8. Malic acid forms a weak buffer from approximately pH 3.0 to 6.0 (Fig. 3).

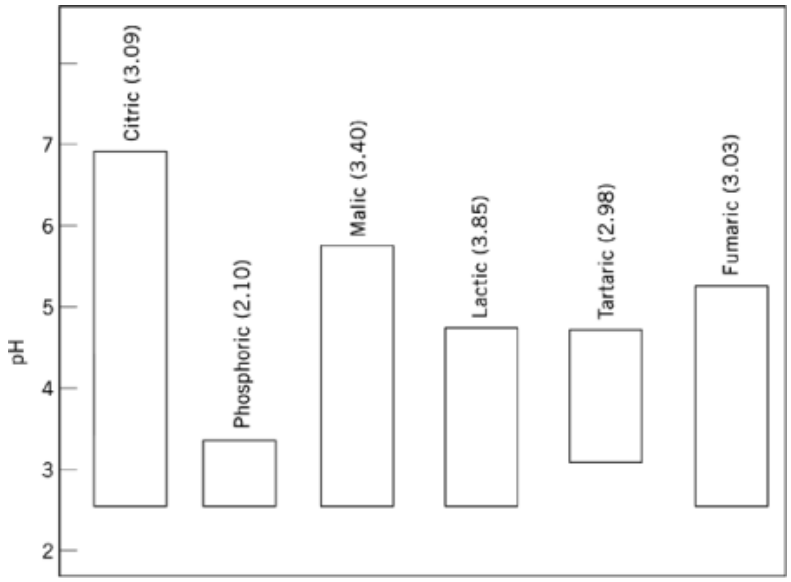


Fig. 3. Effective buffer ranges for food acidulants; pK_a values are given in parentheses.

Table 4. Malic Acid in Fruits[a]

Fruit	Total acid, %	Fruit	Total acid, %
apple	97.2	orange pulp	trace
apricot	23.7–69.8	peach	50.0–96.2
banana	53.7–92.3	pear	33.0–86.6
blueberry	6.0	persimmon	100.0
cherry	94.2	pineapple	12.5
cranberry	19.1–23.5	plum	98.5
gooseberry	46.2	quince	100.0
grape (Concord)	60.0	rhubarb	77.0
grapefruit	5.6	strawberry	9.9–11.0
lemon	4.5	watermelon	100.0
orange peel	59.6–80.0		

[a] Refs. (29–31).

1.4. Occurrence

S(−)-Malic acid occurs widely in biological systems. It is the predominant acid in many fruits (Table 4). However, malic acid occurs in relatively low concentrations, thus making its isolation from natural sources expensive and impractical.

In addition to its presence in fruits, S(−)-malic acid has been found in cultures of a variety of microorganisms including the aspergilli, yeasts, species of *Sclerotinia,* and *Penicillium brevicompactum.* Yields of levorotatory malic acid as high as 74% of theoretical have been reported. Iron, manganese, chromium, or aluminum ions reportedly enhance malic acid production. S(−)-Malic acid is involved in two respiratory metabolic cycles: the Krebs tricarboxylic acid cycle (see Citric acid) and the glyoxylic acid cycle. These metabolic cycles account for the terminal oxidation system which supplies energy and provides the carbon skeletons from which many of the amino acids of proteins are derived.

1.5. Manufacture

In the United States, Canada, and Europe, only the synthetic *R,S*-malic acid is produced commercially, whereas both the S and R,S forms are produced in Japan.

1.5.1. Biosynthesis of S(−)-Malic Acid

Aqueous fumaric acid is converted to levorotatory malic acid by the intracellular enzyme, fumarase, which is produced by various microorganisms. A Japanese process for continuous commercial production of S(−)-malic acid from fumaric acid is based on the use of immobilized *Brevibacterium flavum* cells in carrageenan (32). The yield of pyrogen-free S(−)-malic acid that is suitable for pharmaceutical use is ca 70% of the theoretical.

1.5.2. Commercial Synthesis of R,S-Malic Acid

The commercial synthesis of *R,S*-malic acid involves hydration of maleic acid [110-16-7] or fumaric acid [110-17-8] at elevated temperature and pressure. A Japanese patent (33) describing a manufacturing procedure for malic acid claims the direct hydration of maleic acid at 180°C and 1.03–1.21 MPa (150–175 psi).

The conventional commercial processes are commonly carried out on maleic anhydride in aqueous solution at elevated temperatures above 150°C, at pressures above 1.4 MPa (200 psi), and for a residence time of 3–5 h (34). The resulting mixture contains primarily malic acid and fumaric acid in equilibrium with a small percentage of maleic acid. The purification of the malic acid that is obtained can be accomplished by a two-stage crystallization process (35) involving the following steps: (*1*) adjusting the aqueous solution to a malic acid concentration of 40% by weight at 40°C; (*2*) cooling the solution to ca 15°C until equilibrium is reached; (*3*) separating solid fumaric acid from the slurry, preferably by filtration; (*4*) concentrating the mother liquor from the previous step to a malic acid concentration of at least 62% by weight at a temperature of at least 40°C to effect the crystallization of malic acid; (*5*) separating solid malic acid from the resulting slurry at about 40°C; (*6*) washing the malic acid with an aqueous solution that is substantially free from maleic and fumaric acids; (*7*) redissolving the washed malic acid crystals in water; (*8*) removing insolubles, principally fumaric acid, by filtration; (*9*) passing the mother liquor through a carbon column to remove colored contaminants; (*10*) adjusting the resulting solution to a malic acid concentration of 62% by weight at about 40°C and maintaining this temperature to effect the crystallization of malic acid; (*11*) separating solid malic acid at ca 40°C; and (*12*) washing the solid malic acid with an aqueous solution that is substantially free of maleic and fumaric acids. The purified malic acid contains less than 0.05% maleic acid and less than 1% fumaric acid. Additional purification can be achieved by use of cation- and anion-exchange columns after the carbon treatment and before the second-stage crystallization, ie, between steps (*9*) and (*10*) (36) (see Ion exchange). The cation exchange removes heavy-metal ions that were introduced into the system and the anion exchange removes unsaturated organic acids, primarily maleic and fumaric acids. The purified malic acid crystals that are obtained after the final washing step are dried and classified before packaging.

The initial step of production is carried out in a titanium reactor (34) because of the high corrosivity of maleic acid to most metals under the drastic reaction conditions used. The other steps are performed in stainless steel equipment. Improved purification processes for malic acid have been patented (37, 38).

1.6. Energy and Environmental Considerations

The energy requirements to produce malic acid via conventional processes are fairly moderate. Hydration of malic acid is exothermic. This heat is recovered and helps preheat the reaction. Steam is also used for concentration and purification of the malic acid stream. Steam usage is in the range of 2.5–5.0 kg steam per 1 kg malic acid produced. Electricity is used in the range of $0.5\ \mathrm{kW{\cdot}h}$ per kg malic acid. Malic acid production generates low levels of solid, airborne, and liquid waste. Solid waste is primarily nontoxic malic acid salts resulting from

regenerating carbon cells and ion-exchange resins. Airborne emissions are primarily particulates. A 1% malic acid solution is readily biodegradable, with a BOD (5) of5300 mg/L.

1.7. Shipping and Storage

Malic acid is shipped in 50-lb, 100-lb, and 25-kg, multiwall paper bags or 100-lb (45.5 kg) fiber drums. A technical-grade, 50% solution may be shipped in tank cars or tank trucks. Malic acid can be stored in dry form without difficulty, although conditions of high humidity and elevated temperatures should be avoided to prevent caking.

1.8. Economic Aspects

Malic acid is manufactured in over 10 countries, with 1992 worldwide production estimated at approximately 33,000 t, distributed as follows: 44.4%, North America; 52.1%, Far East; and 3.5%, Africa.

The production is primarily used for food (26.6%) and beverages (54.7%); however, some industrial applications (18.7%) exist, eg, coatings, polymers, and resins. (Historical patterns of use in the United States have been stable and are as noted in parentheses.) Over the past few years, the list price of malic acid has been stable. In the United States, the current list price for malic acid is$1.79/kg , delivered and packaged in 50-lb (22.7-kg) bags (39).

1.9. Specifications and Analysis

R,S-Malic acid that is sold in the United States meets the specifications of the *Food Chemicals Codex* and *National Formulary,* which are listed in Table 5 (40, 41). Malic acid is available in the following U.S. standard sieve sizes:

Granular	min	100 wt % through 2.00 mm (10 mesh) sieve
	max	10 wt % through 0.30 mm (50 mesh) sieve
Fine granular	min	99 wt % through 0.71 mm (25 mesh) sieve
	max	5 wt % through 0.15 mm (100 mesh) sieve
Powder	min	2 wt % through 0.18 mm (80 mesh) sieve
	max	5 wt % through 0.15 mm (100 mesh) sieve

Aqueous titration with 1*N* sodium hydroxide is the usual malic acid assay. Maleic and fumaric acid are determined by a polarographic method. Analytical methods have been described (40).

1.10. Health and Safety

The U.S. FDA has affirmed *R,S*- and S(−)-malic acid as substances that are generally recognized as safe (GRAS) as flavor enhancers, flavoring agents and adjuvants, and as pH control agents at levels ranging from 6.9% for hard candy to 0.7% for miscellaneous food uses (42). *R,S*- and *S*(−)-malic acid may not be used in baby foods. Malic acid is also cleared to correct natural acid deficiencies in juice or wine (43).

Table 5. Malic Acid Specifications

Parameter or substance	*Food Chemicals Codex*[a]	*National Formulary*[a]
assay	not less than 99.0% as $C_4H_6O_5$	99.0%–100.5%
arsenic	≤3 ppm	
fumaric acid	≤1.0%	≤1.0%
heavy metals (as Pb)	≤0.002%	≤0.002%
lead	≤10 ppm	
maleic acid	≤0.05%	≤0.05%
residue on ignition	≤0.1%	≤0.1%
water-insoluble matter	≤0.1%	≤0.1%
specific rotation		−0.10 – 0.10°
organic volatile impurities		meets requirements of NF method I

[a] Ref. 40.
[b] Ref. 41

1.11. Uses

R,S-Malic acid is utilized in a variety of food and beverage and some industrial applications because of its unique combination of properties. These include having unusual taste-blending characteristics, flavor-fixing qualities, the ability to retain sour taste longer, high water solubility, and chelating and buffering properties. Malic acid is also a reactive intermediate in chemical synthesis.

1.11.1. Beverages

Malic acid is increasingly being employed in both liquid and powder drinks as a flavor enhancer, pH buffer, and to increase the effectiveness of antimicrobial preservatives. Having a greater acid taste than citric acid, malic acid is often substituted for citric acid and contributes to the beverage formulation by intensifying and imparting improved taste to fruit flavors. In low calorie drink formulations, malic acid suppresses the bitter aftertaste that saccharin can often impart. This is attributed to the flavor profile of malic acid, which provides a stronger, yet slower and longer flavor release in comparison to citric acid.

1.11.2. Candy

Its low melting point and sugar inversion properties make malic acid a desirable acidulant, especially in hard candy products (44, 45). Due to their insolubility, hard water salts can cause clouding of the finished product. However, because of the higher solubility of calcium malate [17482-42-7] relative to alternative acidulants, clarity of the finished product is enhanced. Additionally, in sugar confectionery products where acidulation may exceed 2.0%, malic acid can provide economic benefits.

1.11.3. Other Food Uses

Jellies, jams, and preserves use malic acid to balance flavor and adjust pH for pectin set. Canned fruits and vegetables employ malic acid in combination with ascorbic acid to produce a synergistic effect that aids in the reduction of browning. Wine and cider producers use malic acid in malolactic fermentation to provide bouquet and for pH adjustment.

1.11.4. Miscellaneous

Malic acid is used in pharmaceuticals (qv), cosmetics (qv), dentifrices (qv), metal cleaning, electroless plating (46), wash-and-wear textile finishing (47–49), for stabilization of heat-sensitive copying paper (50), as an inhibitor of gelation, livering, and agglomeration in cellulose nitrate liqueurs, and in many other applications.

2. Thiomalic Acid

Thiomalic acid [70-49-5] (mercaptosuccinic acid), $C_4H_6O_4S$, mol wt = 150.2, is a sulfur analogue of malic acid. The properties of the crystalline, solid thiomalic acids are given in Table 6. The racemic acid has the following acid dissociation constants at 25°C: $pK_{a1} = 3.30$; $pK_{a2} = 4.94$.

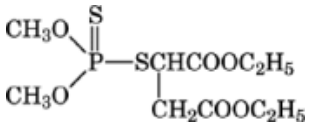
Table 6. Properties of Thiomalic Acids

Acid	CAS Registry Number	Mp, °C	Solubility		$[\alpha]_D^{17}$[a]
			Water	Ethanol	
R,S-	[644-87-1]	151	very sol	very sol	
R	[20182-99-4]	154	sol	sol	+64.4°
S	[74708-34-2]	152–153	sol	slightly sol	−64.8°

[a] 5% acid in ethanol.

R,S-Thiomalic acid [644-87-1] can be prepared from bromosuccinic acid by reaction with K_2S (51, 52). The two enantiomers can be obtained from the corresponding optically active potassium bromosuccinates (52, 53). Salts or amides of maleic acid react with NaSH to give the thiomalic derivatives (54). In the presence of a ferric salt in aqueous ammoniacal solution, thiomalic acid is oxidized to the disulfide (55). Oxidation with diluted HNO_3 gives sulfosuccinic acid (56). The thiomalic acids form salts, chelates, and esters. *R,S*-Thiomalic acid gives a red color with $FeCl_3 + NH_4OH$ (57). Reaction with aqueous AuCN gives aurothiomalic acid (58).

Thiomalic acid is a skin sensitizer (59) and an antidote in heavy-metal poisoning (60). Traditionally, it was a component of cold permanent hair-waving solutions (see Hair preparations) (61, 62) and of rust-removing (63) and corrosion-inhibiting compositions (see Corrosion and corrosion control) (64). Sodium aurothiomalate [12244-57-4] (Myochrisin) and other gold thiomalate complexes have antiarthritic properties (65) (see Gold and gold compounds). The well-known insecticide, malathion [121-75-5], is the thiomalate *S*-ethyl ester of *O,O*-dimethylphosphonodithioic acid (see Insect control technology).



3. Tartaric Acid

Tartaric acid [526-83-0] (2,3-dihydroxybutanedioic acid, 2,3-dihydroxysuccinic acid), $C_4H_6O_6$, is a dihydroxy dicarboxylic acid with two chiral centers. It exists as the dextro- and levorotatory acid: the meso form (which is inactive owing to internal compensation), and the racemic mixture (which is commonly known as racemic acid). The commercial product in the United States is the natural, dextrorotatory form, (*R*-*R**,*R**)-tartaric acid (L(+)-tartaric acid) [87-69-4]. This enantiomer occurs in grapes as its acid potassium salt (cream of tartar). In the fermentation of wine (qv), this salt forms deposits in the vats; free crystallized tartaric acid was first obtained from such fermentation residues by Scheele in 1769.

In Europe, South Africa, and Japan, racemic (*R**,*R**)-tartaric acid [13337-9] (DL-tartaric acid) is also produced commercially via maleic anhydride oxidation.

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3.1. Physical Properties

When crystallized from aqueous solutions above 5°C, natural (*R*-*R**,*R**)-tartaric acid is obtained in the anhydrous form. Below 5°C, tartaric acid forms a monohydrate which is unstable at room temperature. The optical rotation of an aqueous solution varies with concentration. It is stable in air and racemizes with great ease on heating. Some of the physical properties of (*R*-*R**,*R**)-tartaric acid are listed in Table 7.

Table 7. Physical Properties of (*R*-*R*R**)-Tartaric Acid**

Property	Value
mol wt	150.086
appearance	colorless or translucent crystals
crystal system	monoclinic
mp, °C (anhydrous)	169–170
d^{20}, g/cm^3	1.76
$[\alpha]_D^{20}$ (for concentration, *c*, from 20–50%)	15.050–0.1535*c*
K_{a1} at 25°C	1.04×10^{-3}
K_{a2} at 25°C	4.55×10^{-5}
heat of combustion, kJ/mol[a]	1080[b]
heat of solution, kJ/mol[a]	−13.8[c]

[a] To convert kJ to kcal, divide by 4.184.
[b] Ref. 66.
[c] Ref. 3.

The solubility of (*R*-*R**,*R**)-tartaric acid in water varies from 115 g/100 g H_2O at 0°C to 343 g/100 g H_2O at 100°C. One hundred grams of absolute ethanol dissolves 20.4 g of tartaric acid at 18°C, and 100 g of ethyl ether dissolves 0.3 g at 18°C. Densities ($d^{15}{}_4$) of (*R*-*R**,*R**)-tartaric acid solutions at 15°C range from 1.0045 for a 1 wt % solution to 1.296 for a 50 wt % solution (67).

Some physical properties of the four enantiomeric tartaric acids are compared in Table 8.

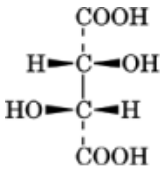
Table 8. Physical Properties of Tartaric Acids

Properties	Natural	Levorotatory	Racemic	Meso
mp, °C (anhydrous)	169–170	169–170	205–206	159–160
soly, g/100 g H_2O (in water, at 20°C)	139	139	20.6	125
soly of acid potassium salt, g/100 g H_2O (at 25°C)	0.84	0.84	0.72	16.7
soly of Ca salt, g/100 g	0.020[a]	0.025[b]	0.004[a]	0.034[b]
mol water in hydrate of calcium salt	4	4	8	3

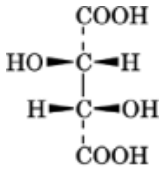
[a] At 25°C.
[b] At 20°C.

3.2. Chemical Properties

The notation used by *Chemical Abstracts* to reflect the configuration of tartaric acid is as follows: (*R*-*R**,*R**)-tartaric acid [87-69-4](**4**); (**S-R***,*R**)-tartaric acid[147-71-7] (**5**); and *meso*-tartaric acid [147-73-9] (**6**). Racemic acid is an equimolar mixture of the two optically active enantiomers and, hence, like the meso acid, is optically inactive.



(4)



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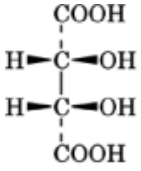
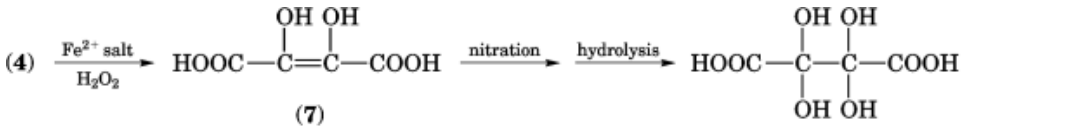


(6)

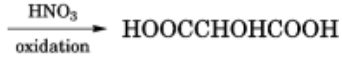
3.2.1. Reactions

When free (*R*-*R**,*R**)-tartaric acid (**4**) is heated above its melting point, amorphous anhydrides are formed which, on boiling with water, regenerate the acid. Further heating causes simultaneous formation of pyruvic acid, $CH_3COCOOH$; pyrotartaric acid, $HOOCCH_2CH(CH_3)COOH$; and, finally, a black, charred residue. In the presence of a ferrous salt and hydrogen peroxide, dihydroxymaleic acid [526-84-1] (**7**) is formed. Nitrating the acid yields a dinitro ester which, on hydrolysis, is converted to dihydroxytartaric acid [617-48-1] (**8**), which upon further oxidation yields tartronic acid [80-69-3] (**9**).



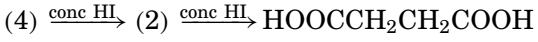
(7)

(8)



(9)

Tartaric acid is reduced stepwise with concentrated hydriodic acid, first to R(+)-malic acid (**2**) and then to succinic acid [110-15-6].



In common with other hydroxy organic acids, tartaric acid complexes many metal ions. Formation constants for tartaric acid chelates with various metal ions are as follows:Ca, 2.9;Cu, 3.2;Mg, 1.4; andZn, 2.7 (68). In aqueous solution, tartaric acid can be mildly corrosive toward carbon steels, but under normal conditions it is noncorrosive to stainless steels (Table 9) (27).

Table 9. Corrosion by 25 wt % Solution of Tartaric Acid

Metal	Corrosion rate, mm/yr[a]	Temperature, °C
aluminum	<0.5	below 30
	>1.3	above 30
carbon steel	>1.3	[b]
stainless steel (304)	<0.05	below 200
stainless steel (316)	<0.05	below 200

[a] To convert mm/yr to mils penetration/yr (Mpy), divide by 2.54×10^{-2}.
[b] At all temperatures.

3.3. Occurrence

(*R-R*,R**)-Tartaric acid occurs in the juice of the grape and in a few other fruits and plants. It is not as widely distributed as citric acid or S(−)-malic acid. The only commercial source is the residues from the wine industry. (*S-R*,R**)-Tartaric acid has been found in the fruit and leaves of *Bauhinia reticulata*, a tree native to Mali (western Africa). Like the dextrorotatory acid, it forms anhydrous monoclinic crystals.

The racemic acid is not a primary product of plant processes but is formed readily from the dextrorotatory acid by heating alone or with strong alkali or strong acid. The methods by which such racemic compounds can be separated into the optically active modifications were devised by Pasteur and were applied first to the racemic acid. Racemic acid crystallizes as the dihydrate $(C_4H_6O_6)_2 \cdot 2H_2O$ in triclinic prisms. It becomes anhydrous on drying at 110°C and melts incongruently at 205°C. Calcium racemate, $(C_4H_4O_6Ca)_2$, is even less soluble in water than calcium tartrate [15808-04-5], thus a dilute racemic acid solution is precipitated by a saturated calcium sulfate solution, whereas active tartaric acid is not.

meso-Tartaric acid is not found in nature. It is obtained from the other isomers by prolonged boiling with caustic alkali. The free acid crystallizes as a monohydrate, $C_4H_6O_6 \cdot H_2O$ in monoclinic prisms. On drying at 110°C, it becomes anhydrous and melts at 159–160°C.

3.4. Synthesis

Racemic acid is obtained synthetically by treatment of maleic acid with hydrogen peroxide in the presence of a catalyst, eg, tungstic acid (69). Other synthetic routes that have been explored include the production of (*R-R*,R**)-tartaric acid by bacterial fermentation of glucose (70) or 5-keto-D-gluconic acid (71), catalytic oxidation of 5-keto-D-gluconic acid with gaseous oxygen (72, 73), and nitric acid oxidation of carbohydrates (qv), eg, glucose (74). Production of (*R*,R**)-tartaric acid by catalytic chlorate oxidation of fumaric or maleic acid also has been described (75).

meso-Tartaric acid can be prepared by microbiological conversion of *trans*-epoxysuccinic acid [22734-83-4] (76). *cis*-Epoxysuccinic acid [16533-72-5] does not undergo this conversion. None of the foregoing processes has achieved commercial significance.

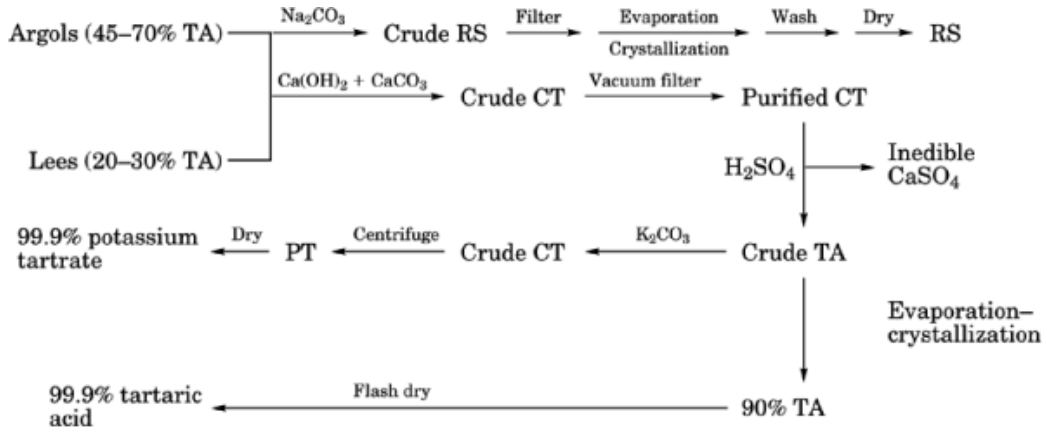


Fig. 4. Manufacturing process for (*R*-*R**,*R**)-tartaric acid (TA) and its salts, calcium tartrate (CT) and potassium tartrate (PT).

3.5. Manufacture

3.5.1. (R-R,R*)-Tartaric Acid and Its Salts*

The raw materials available for the manufacture of tartaric acid and tartrates are by-products of wine making. Crude tartars are recovered from the following sources: (*1*) The press cakes from grape juice, ie, unfermented (marcs) or partly fermented (pomace), are boiled with water, and alcohol, if present, is distilled. The hot mash is settled, decanted, and the clear liquor is cooled to crystallize. The recovered high test crude cream of tartar (vinaccia) has an 85–90% cream of tartar content. (*2*) Lees, which are the dried slimy sediments in the wine fermentation vats, consist of yeast cells, pectinous substances, and tartars. Their content of total tartaric acid equivalent ranges from 16–40%. (*3*) The crystalline crusts that form in the vats in the secondary fermentation period (argols) contain more than 40% tartaric acid; they are high in potassium hydrogen tartrate [868-14-4] and low in the calcium salt.

The chemical reactions involved in tartaric acid production are formation of calcium tartrate from crude potassium acid tartrate,

$$2\ KHC_4H_4O_6 + Ca(OH)_2 + CaSO_4 \longrightarrow 2\ CaC_4H_4O_6 + K_2SO_4 + 2\ H_2O$$

formation of tartaric acid from calcium tartrate,

$$CaC_4H_4O_6 + H_2SO_4 \longrightarrow H_2C_4H_4O_6 + CaSO_4$$

formation of Rochelle salt [304-59-6] from argols,

$$2\ KHC_4H_4O_6 + Na_2CO_3 \longrightarrow 2\ KNaC_4H_4O_6 + CO_2 + H_2O$$

and formation of cream of tartar from tartaric acid and Rochelle salt (RS) liquors,

$$2\ H_6C_4O_6 + 2\ KNaC_4H_4O_6 + K_2SO_4 \longrightarrow 4\ KHC_4H_4O_6 + Na_2SO_4$$

This process is summarized in Figure 4.

Production of the Rochelle salt involves roasting of the blended argols at 160–165°C, mixing with wash liquor from a previous charge, and treatment with sodium carbonate and afterward with potassium oxalate. Evaporation of the resulting filtrate, followed by centrifugation, washing, and drying, yields the finished product.

Cream of tartar [868-14-4] can be produced (*1*) directly from the argol–sodium carbonate cook; (*2*) by combining tartaric acid solutions (which are available from the manufacturer of tartaric acid) with Rochelle salt solution derived from suitable crude potassium bitartrate, eg, high grade argols or recovered cream of tartar; and (*3*) by saturating a water suspension of argols with sulfur dioxide. An accelerated process for removing potassium bitartrate from crude tartaric acid solutions has been described (77).

For the production of tartar emetic (antimony potassium tartrate [28300-74-5]), potassium bitartrate [868-14-4] and antimony oxide, Sb_2O_3, are added simultaneously to water in a stainless-steel reactor. The reaction mixture is diluted, filtered, and collected in jacketed granulators where crystallization takes place after cooling. Centrifuging, washing, and drying complete the process.

(*R*,R**)-Tartaric (racemic) acid is obtained synthetically by epoxidation of maleic acid with hydrogen peroxide in the presence of a catalyst followed by hydrolysis of the resulting *cis*-epoxysuccinic acid (69, 78–84). This commercial process is used in South Africa (83), and it involves the addition of 60%H_2O_2 to 40% aqueous maleic acid. The addition of a molybdenum catalyst permits the reaction to take place at 70°C in 20 h. The resulting *cis*-epoxysuccinic acid is hydrolyzed by boiling, and (*R*,R**)-tartaric acid is isolated by cooling, centrifuging, washing, and drying. A 20% excess of maleic acid is used and the yield (based onH_2O_2) is 84%. Unreacted maleic acid is converted either to fumaric acid or malic acid. The tartaric acid in the mother liquor is recovered.

(*R*,R**)-Tartaric acid also can be produced by racemization of (*R-R*,R**)-tartaric acid in the presence of *meso*-tartaric acid (85). In this process, formation of *meso*-tartaric acid during racemization does not occur.

3.6. Economic Aspects

The estimated total worldwide market for tartaric acid is 58,000 t and potassium bitartrate (acid basis) is 20,000 t. The majority of tartaric acid consumption, represented by beverage, food, and pharmaceutical applications, is shown in Table 10. Potassium bitartrate (cream of tartar) is primarily used in baking powders and mixes.

Table 10. 1991 Worldwide Tartaric Acid MarketSegments[a]

Market	Percent
alcoholic beverages	30
emulsifiers	20
pharmaceuticals	15
foods	10
textiles	10
electrochemicals	10
others	5

[a] Does not include potassium bitartrate.

The 1991 U.S. market for tartaric acid and tartrate was estimated at 3600 t. There is no domestic U.S. producer; therefore, all product is imported from other countries. Imports into the United States for 1991 are summarized in Table 11.

Table 11. 1991 Tartaric/Tartrate U.S. Imports From Other Countries[a]

Country	Tartaric acid imports, %	Potassium bitartrate imports, %
Italy	45.7	36.9
Spain	31.3	51.5
France	3.7	7.0
Argentina	5.9	
the Netherlands	4.3	
Chile	3.5	
other	5.6	4.6

[a] Ref. 86.

In the United States, prices for tartaric acid have ranged from $1.10 to$6.61/kg since the early 1970s with little consistency. The 1993 list price of tartaric acid in the United States was$6.50/kg fob plant packaged in 100-lb (45.5-kg) bags (39). Much of the fluctuation is a result of the availability of raw materials for production.

3.7. Specifications and Analysis

(*R-R*,R**)-Tartaric acid sold in the United States meets the specifications of the *Food Chemicals Codex* (40) and the *National Formulary* (41) (Table 12).

Table 12. Specifications for (*R-R*,R)-Tartaric Acid**

Parameter	*Food Chemicals Codex*[a]	*National Formulatory*[b]
specific rotation	$[\alpha]_D^{25}$ + 12.0° − 13.0°[c]	between 12.0 and 13.0°
assay	not less than 99.7% of $C_4H_6O_6$ after drying	99.7%–100.5%
arsenic (as As)	3 ppm max	
heavy metals (as Pb)	10 ppm max	≤0.001%
loss on drying	0.5% max	≤0.5%
oxalate	passes test	passes test
residue on ignition	0.05% max	≤0.1%
sulfate	passes test	passes test
organic volatile impurities		passes test

[a] Ref. 40.
[b] Ref. 41.
[c] Determined in a solution containing 2 g in each 10 mL sample.

Tartaric acid is supplied as Fine-Granular and Powder in 45-kg bags. It should be stored in tightly closed containers. Test methods for tartaric acid and some tartrates have been described (40, 87).

3.8. Health and Safety

The FDA affirmed (*R-R*,R**)-tartaric acid as a generally-recognized-as-safe (GRAS) food substance (88).

Tartaric acid and tartrates are poorly absorbed from the intestine. Their metabolism is different from that of citric acid in that tartaric acid is only slightly oxidized. The acid that is absorbed is excreted unchanged in the urine. So far as is known, all nutritional and physiological investigations have been made with the dextrorotatory enantiomer.

3.9. Uses

3.9.1. Carbonated Beverages

Tartaric acid has been used like citric acid as an acidulant in carbonated beverages (qv). However, it has almost been completely replaced in the marketplace by less expensive acidulants like phosphoric, citric, malic, and fumaric acids.

3.9.2. Wine Making

Wine making is one of the principal areas of tartaric acid use. There is a relationship between the size of the grape crop and its tartaric acid content when grapes are pressed. In poor harvest years, the tartaric acid content is low; in good harvest years, the tartaric acid content is high. Thus, in poor harvest years, tartaric acid often is added to correct acid deficiencies in wine.

3.9.3. Other Food

Tartaric acid is also used in the manufacture of gelatin (qv) desserts and in fruit jellies, especially in pectin jellies for candies where a low pH is necessary for proper setting. It is used as a starch modifier in starch jelly candies so that the product flows freely while being cast. It is used in hard candy because its melting point permits it to fuse into the "glass" and does not contribute to moisture.

3.9.4. Emulsifiers

A growing application for tartaric acid is in the production of DATEM esters (diacetyl tartaric esters of monoglycerides). These esters are used as dough conditioners in the baking industry. They allow the reduction or elimination of shortening, as well as adding dough strength to free-standing breads.

3.9.5. Pharmaceuticals

Tartaric acid is used in the manufacture of fine drug salts, as in effervescent salts. Tartar emetic [28300-74-5] is used in small doses as an expectorant in cough syrups. It can be used to treat infections caused by *Schistosoma japonium*.

3.9.6. Industrial Uses

Tartaric acid is used in photography, and its iron salts are used in blue copy paper. The diethyl and dibutyl esters are used in paints as lacquer solvents. In the textile industry, tartaric acid acts as a stabilizer in nylon dyeing and in cellusosic fiber bleaching with peroxide. It is used as a chelating agent for boron and other micronutrients in fertilizers. In the plastics industry, tartaric acid is used as a polymerization agent of methyl methacrylate, phenol–formaldehyde resins, PVC, and acrylonitrile. In metals, it is used as a complexing agent in metal cleaning for copper and alloys, aluminum, and ferrous metals. It is used in ceramics as a component in special clays. In the electronics industry, tartaric acid is used in the anodization of semiconductors of gallium arsenide.

3.10. Salts

Rochelle salt is used in the silvering of mirrors. Its properties of piezoelectricity make it valuable in electric oscillators. Medicinally, it is an ingredient of mild saline cathartic preparations, eg, compound effervescing powder. In food, it can be used as an emulsifying agent in the manufacture of process cheese.

Cream of tartar is used in baking powder and in prepared baking mixes (see Bakery processes and leavening agents). Its limited solubility at low temperatures inhibits the reaction with bicarbonate until baking temperature is reached, thus releasing a significant portion of the carbon dioxide at the optimum time.

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GARY T. BLAIR
Haarmann & Reimer Corporation
JEFFREY J. DEFRATIES
Haarmann & Reimer Corporation

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