New York State Integrated Pest Management Program | Cornell Cooperative Extension

Malic Acid Profile

Active Ingredient Eligible for Minimum Risk Pesticide Use

Brian P. Baker and Jennifer A. Grant
New York State Integrated Pest Management, Cornell University, Geneva NY

Label Display Name: Malic acid

Active Components: Malic acid

CAS Registry #: DL-Malic acid: 6915-15-7
L-Malic acid: 97-67-6
D-Malic acid: 636-61-3

U.S. EPA PC Code: 051101

CA DPR Chem Code: 1364

Other Names: 2-Hydroxybutanedioic acid; α-Hydroxysuccinic acid; Hydroxysuccinic acid; 2-hydroxyethane-1,2-dicarboxylic acid; Apple acid; TEO; d,l-Malic acid; DL-Malic acid; Deoxytetraric acid; R,S-Malic acid; Maleinsäure (German)

Other Codes: BRN 1723539, 1723540; EINECS 230-022-8; INS: 296; Caswell 537; CRC: DCG74-V; FEMA 2655; HSDB 1202; ChEBI 6650

Summary: Malic acid is a common, naturally occurring ingredient in many foods. It is the main acid found in apples and other fruits. The main pesticidal use of malic acid is as an antimicrobial disinfectant, but most of its uses in pesticide formulations are as an inert ingredient, where it serves as a pH adjuster, buffering agent, and sequestrant. While it has no record of safety concerns, malic acid is not permitted for use on food as a pesticide and there are no EPA-registered products. A national search did not discover any currently marketed commercial products.

Pesticidal Uses: The main pesticidal use of malic acid is as an antimicrobial disinfectant.

Formulations and Combinations: Malic acid is combined with citric acid as an antimicrobial. It is also used as an inert ingredient in many pesticide formulations, serving as a pH adjuster and buffering agent.

Basic Manufacturers: Bartek; Brenntag Pacific; US Chemical Co.; Fluka; Fuso; Haarmann & Reimer; Miles; Tate & Lyle.

Safety Overview: Malic acid is a weak acid that is readily biodegradable and has no record of any adverse incidents.

Background

Malic acid is a dicarboxylic acid that occurs in nature as L-malic acid. Another optically active isomer is D-malic acid which can be synthesized as the racemic mixture of DL-malic acid. Malic acid is commonly referred to as 'apple acid' because of its high concentration in apples (*Malus domestica*). Other natural sources of malic acid include acerola (*Malpighia emarginata*), alfalfa (*Medicago sativa*), angelica (*Angelica archangelica*), black haw (*Viburnum prunifolium*), bloodroot (*Sanguinaria Canadensis*), cherries and other stone fruit (*Prunus* spp.), cranberries (*Vaccinium macrocarpon*), horsetail (*Equisetum arvense*), jujube (*Ziziphus jujube*), marigolds (*Tagates* spp.), rose hips (*Rosa canina*), schisandra (*Schisandra chinensis*), and tamarind (*Tamarindus indica*) (Khan and Abourashed 2010).

Malic acid is produced in the metabolic cycles of humans, plants, and animals. In the Krebs and glyoxylate cycles, malic acid provides cells with the carbon skeleton and energy necessary for amino acid formation. There are two enantiomers, the L-, which sometimes is referred to as S-, and the D-, which is sometimes referred to as R-. Racemic DL-malic acid was first synthesized in 1923 (McKenzie et al. 1923). Biological production of L-malic acid from bacteria, including *Lactobacillus* L-malic acid is produced by the fermentation of fumaric acid. Fumaric acid can be produced by the fermentation from glucose. Yeast (*Aureobasidium pullulans*) can also be used to produce L-malic acid by fermentation (Zou et al. 2013).

DL-Malic acid can be commercially produced by several different synthetic processes. Most involve either maleic anhydride or fumaric acid hydrated at high temperatures (Felthouse et al. 2000). Maleic anhydride is converted to maleic acid, which in turn is converted to malic acid. Another process involves the mixing of maleic acid, fumaric acid, and sodium hydrogen maleate in an aqueous solution (Ramsey and Schultz 1993).

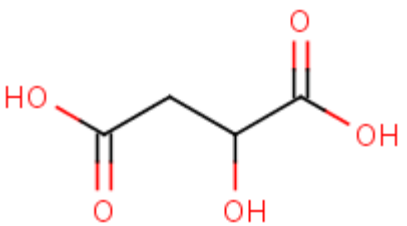
Malic acid is an ingredient in foods and beverages. It acts as a chelating and buffering agent (Merck 2015). Use of the less common D– and racemic forms are restricted in infant foods, because small children lack the capacity to metabolize the D-form.

Chemical and Physical Properties

The molecular structure of malic acid is presented in Figure 1.

Figure 1

Molecular Structure of Malic Acid



Source: EMBL 2015

The physical and chemical properties of malic acid are summarized in Table 1.

Table 1

Physical and Chemical Properties of Malic Acid

Property	Characteristic/Value	Source
Molecular Formula:	$C_4H_6O_5$	(Merck 2015)
Molecular Weight:	134.09	(Merck 2015)
Percent Composition:	C 35.83%, H 4.51%, O 59.66%	(Merck 2015)
Physical state at 25°C/1 Atm.	Crystal (solid)	(Merck 2015)
Color	White	(Royal Society of Chemistry 2015)
Odor	Odorless	(US NLM 2016)
Density/Specific Gravity	1.6 g/cm3 at 20 °C	(Sigma-Aldrich 2015)
Melting point	130-131°C	(Merck 2015)
Boiling point	150°C	(US NLM 2016)
Solubility	Solubility in g/100 g solvent at 20°: methanol 82.70, diethyl ether 0.84, ethanol 45.53, acetone 17.75, dioxane 22.70, water 55.8. Practically insoluble in benzene.	(Merck 2015)
Vapor pressure	< 0.1 hPa (< 0.1 mmHg) at 20 °C	(Sigma-Aldrich 2015)
pH	1.95	
Octonol/Water (K_{ow}) coefficient	-1.26	(EPI 2012)
Viscosity	Aqueous: 6.5 mPa·s at 25°C	(Blair and DeFraties 2000)
Miscibility	N/A	
Flammability	Non-flammable	(Bartek 2013)
Storage stability	Stable at normal temperatures	(Bartek 2013)
Corrosion characteristics	Corrosive to carbon steel; mildly corrosive to aluminum and stainless steel.	(Blair and DeFraties 2000)
Air half life	30.9 hrs	(EPI 2012)
Soil half life	112.0 hrs	(EPI 2012)
Water half life	55.9 hrs	(EPI 2012)
Persistence	124.0 hrs	(EPI 2012)

Human Health Information

Malic acid is naturally present in many foods including apples, pears, blueberries, and many other fruits. Occupational exposure occurs primarily through inhalation and dermal contact (HSDB 2015).

Acute Toxicity

Results and values for acute toxicity tests reported in Table 2 are for DL-malic acid, unless reported otherwise.

Table 2

Acute Toxicity of Malic Acid

Study	Results	Source
Acute oral toxicity	Mouse: LD_{50} 1600-3200 mg/kg Rat: > 3200 mg/kg	(HSDB 2015)
Acute dermal toxicity	Strong skin irritant to guinea pig and moderately irritating to rabbits at 500 mg/24 hr	(HSDB 2015)
Acute inhalation	Not found	
Acute eye irritation	Rabbit: Severe irritation at 750µg	(HSDB 2015)
Acute dermal irritation	Strong skin irritant to guinea pig and moderately irritating to rabbits at 500 mg/24 hr	(HSDB 2015)
Skin sensitization	Reactive in 18% of the subjects	(Fiume 2001)

Symptoms of acute toxicity in rats and mice are weakness, retraction of abdomen, respiratory distress, and cyanosis (HSDB 2015). When DL-malic acid is consumed by rats, both L- and DL-malic acid are almost entirely metabolized, with slightly more unmetabolized DL-malic acid excreted in the urine (Daniel 1969).

Sub-chronic Toxicity

Results and values for sub-chronic toxicity tests reported in Table 3 are for DL-malic acid, unless reported otherwise. The 90 day oral toxicity study on rats noted deformities in the test subjects, including changes in organ weights, decreased growth, and a hunched appearance (HSDB 2015).

Table 3

Sub-chronic Toxicity of Malic Acid

Study	Results	Source
Repeated Dose 28-day Oral Toxicity Study in Rodents	Not found	
90 day oral toxicity in rodents	(24 mo) Changes in organ weights, decreased growth, hunched appearance in rats @ 200 mg/kg	(HSDB 2015)
90 day oral toxicity in non-rodents	Not found	
90 Day dermal toxicity	Not found	
90 Day inhalation toxicity	Not found	
Reproduction/development toxicity screening test	No significant differences between test and control groups.	(Fiume 2001)
Combined repeated dose toxicity with reproduction/development toxicity screening test	Negative in rats at up to 350 mg/kg bw	(Weinberg Group 2003)
Prenatal developmental toxicity study	Non-teratogenic to chick embryos	(Weinberg Group 2003)
Reproduction and fertility effects	Slight differences in developmental indices of rats between test and control groups were considered within the range of normal variation.	(Fiume 2001)

Chronic Toxicity

Chronic toxicity and carcinogenicity for DL-malic acid are reported in Table 4.

Table 4

Chronic Toxicity of Malic Acid

Study	Results	Source
Chronic toxicity	Negative	(Weinberg Group 2003)
Carcinogenicity	Not found	
Combined chronic toxicity & carcinogenicity	Not found	

Malic acid is not identified as a carcinogen by the International Agency for Research on Cancer (IARC 2014), is not on the California Proposition 65 list of known carcinogens (Cal-EPA 1997), and does not appear on the Toxics Release Inventory (TRI) Basis of OSHA Carcinogens (US EPA Toxics Release Inventory Program 2015). Various safety assessments for malic acid were searched, and no studies that investigated the carcinogenicity of malic acid were found (Fiume 2001; Weinberg Group 2003).

Human Health Incidents

No human health incidents involving malic acid as a pesticide active ingredient were reported to the National Pesticide Information Center (NPIC) between April 1, 1996 and March 30, 2016 (NPIC 2016).

Environmental Effects Information

Effects on Non-target Organisms

Malic acid's effects on non-target organisms are summarized in Table 5.

Table 5

Effects of Malic Acid on Non-target Organisms

Study	Results	Source
Avian Oral, Tier I	Not found	
Non-target plant studies	Not found	
Non-target insect studies	Not found	
Aquatic vertebrates	Not found	
Aquatic invertebrates	*Daphnia magna* 48 hr LC_{50}: 240 mg/L	(Weinberg Group 2003)

No animal incidents involving malic acid as a pesticide active ingredient were reported to NPIC between April 1, 1996 and March 30, 2016 (NPIC 2016).

Environmental Fate, Ecological Exposure, and Environmental Expression

Photodegradation and biodegradation data for malic acid show that it dissociates into H^+ and malate ($H_5C_4O_5^-$) (Weinberg Group 2003). A series of screening tests show that malate readily biodegrades in soil and water. Level III fugacity modeling predicts that about 38% of any malic acid released to the environment would partition to water, <1% to air, 62% to soil, and <1% to sediments.

Table 6

Environmental Fate, Ecological Exposure, and Environmental Expression

Study	Results	Source
Leaching series	Not found	
Photodegradation in water	Not found	
Photodegradation in air	Photolysis rate of 7.76 x 10^{12} cm^3/mole*sec at 25°C after 2 days	(Weinberg Group 2003)
Photodegradation in soil	Not found	
Ready biodegradability	Readily biodegradable in water	(Weinberg Group 2003)

Because malic acid occurs naturally in apples and many other fruits and plants, it is widely distributed from natural sources in the environment. Malic acid may occur in atmospheric samples as a result of volatilization from naturally occurring sources, or from the atmospheric oxidation of precursor aldehydes. Malic acid and other dicarboxylic acids are probably formed when oxidation of cyclic olefins or other hydrocarbons cause photochemical reactions (HSDB 2015). If released to the atmosphere, it will degrade in the vapor phase by reaction with photochemically produced hydroxyl radicals having an estimated half-life of about 2 days. Particulate phase malic acid also occurs from natural sources and has been monitored in ambient air. These particulates will be physically removed through wet and dry deposition. If released to soil or water, malic acid is expected to biodegrade. Various biological screening studies have demonstrated that malic acid biodegrades (HSDB 2015).

Environmental Incidents

No environmental incidents involving malic acid as a pesticide active ingredient were reported to NPIC between April 1, 1996 and March 30, 2016 (NPIC 2016).

Efficacy

Anti-microbial Activity

Fruits that are high in malic acid are noted to have bacteriostatic properties (Khan and Abourashed 2010). Acidic substances reduce pH to levels where bacterial growth is inhibited, thus preventing spoilage and its associated ill effects on human health (Eswaranandam et al. 2004; Lu et al. 2011). Malic acid was more effective than citric, lactic, or tartaric acid against *Listeria monocytogenes, Escherichia coli* O157:H7 and *Salmonella gaminara* cultured on soy protein (Eswaranandam et al. 2004). A 2.6% solution of malic acid incorporated in soy film proteins decreased the colony forming units from 8.3 to 5.5 CFU/ml for *L. monocytogenes,* from 9.0 to 3.0 CFU/ml for *S. gaminara*, and from 8.9 to 6.8 CFU/ml for *E. coli* O157:H7.

The EPA reviewed efficacy data for formulated products that contained malic acid as an active ingredient and applied for registration to make public health claims on their labels. A combination of 5% malic acid, 10% citric acid, and 2% sodium lauryl sulfate impregnated in a facial tissue effectively deactivated human rhinovirus in a contact time of 1 minute (Guse 1983). A subsequent study showed that even with a reduced dose of 1.6% malic acid, 3.2% citric acid, and 0.5% sodium lauryl sulfate, the facial tissue showed sufficient efficacy to reduce not only rhinovirus, but also influenza, parainfluenza, adenovirus, reovirus, and herpes simplex viruses as well (Guse 1986).

Malic acid added to apple, pear, and melon juices inhibited the growth of *Listeria monocytogenes, Escherichia coli* O157:H7 and *Salmonella enteritidis* (Raybaudi-Massilia et al. 2006). However, malic acid was the least effective of the various weak acids tested on *Escherichia coli* O157:H7 under anaerobic conditions (Lu et al. 2011). The comparison included benzoic, sorbic, fumaric, lactic, and acetic acid, as well as sulfite. The amount of malic acid required to achieve a 5-log reduction in *E. coli* O157:H7 was greater than the ionic strength of 0.342, the equivalent of 2% NaCl (salt), and nearly half as effective as acetic acid, the second least effective acid tested.

Malic and citric acid are claimed in a patent to enhance the efficacy of copper-based fungicides (Tate 1996). Another patent claimed that malic acid used with various surfactants can increase the efficacy of petroleum distillates as dormant oil insecticides (Roberts 1995).

Malic acid as an adjuvant ingredient was studied along with various other complexing agents thought to increase the efficacy of the herbicides dichlorprop and glyphosate on common bean (*Phaseolus vulgaris*), quackgrass (*Agropyron repens*), and chickweed (*Stellaria media*). Malic acid enhanced herbicidal activity more than acetic, succinic, propionic, sulfuric, or formic acids (Turner and Loader 1978). However, orthophosphoric acid was the most effective acid at enhancing herbicidal effects, and citric, oxalic, tartaric, and glycolic acid all were comparable to malic in their efficacy.

Standards and Regulations

EPA Requirements

Malic acid is not explicitly exempt from the requirement of a tolerance and is allowed only for non-food uses (US EPA 2015).

FDA Requirements

The Food and Drug Administration has affirmed malic acid as generally recognized as safe (GRAS) when used in foods in accordance with the levels and uses for various products, except for use in infant foods [21 CFR 184.1069]. The restriction on baby food relates to the slow rate of metabolism of the unnatural D-malic acid, which is half of DL-malic acid. Slowly metabolized D-malic acid can cause acidosis in infants. The upper limit of DL-malic acid is established based on the amount of D-lactic acid that may not be metabolized by mammals. The current Good Manufacturing Practice limits for malic acid are contained in Table 7. Despite its GRAS status, malic acid may not be used as a pesticide on food crops (US EPA 2015).

Table 7

Current Good Manufacturing Practice Maximum Levels for Malic Acid, as served

Food Group	Pct
Non-alcoholic beverages	3.4%
Chewing gum	3.0%
Gelatins, puddings and fillings	0.8%
Jams & jellies	2.6%
Processed fruits and fruit juices	3.5%
Soft candy	3.0%
All other food categories	0.7%

Source: 21 CFR 180.1069(d)

Other Regulatory Requirements

The status of malic acid for use as a pesticide in organic production depends on the source and manufacturing process. Synthetic malic acid does not appear on the National List of allowed synthetic substances allowed for crop production [7 CFR 205.601] and is therefore prohibited for organic production [7 CFR 205.105(a)]. However, L-malic acid derived from fermentation or extracted from fruit is non-synthetic and does not appear on the prohibited non-synthetic list [7 CFR 205.602], therefore it is allowed for organic production.

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