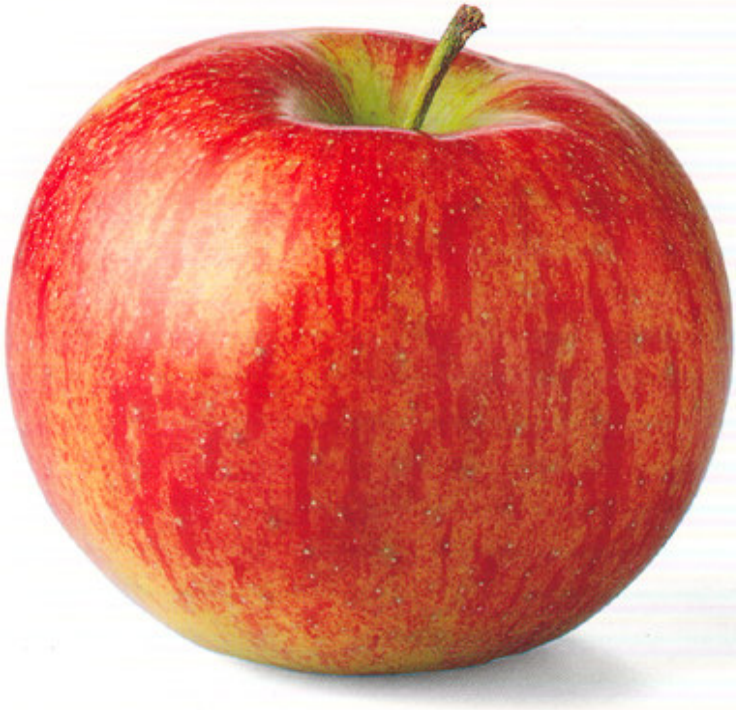
Lonza group



Malic Acid

General information

Malic Acid is manufactured by Lonza SpA by hydration of Maleic Anhydride (at high temperature and pressure) in their factory at Scanzorosciate (Bergamo), in a very modern plant with 10,000 tons spare capacity.

Malic Acid is widely found in nature and is the predominant organic acid in many fruits and berries, far more than citric acid (Fig. 1).

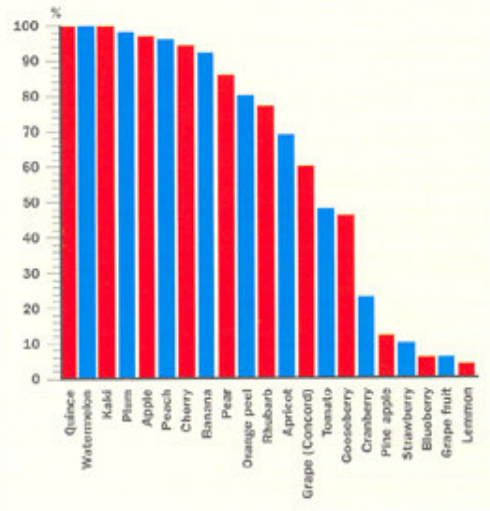
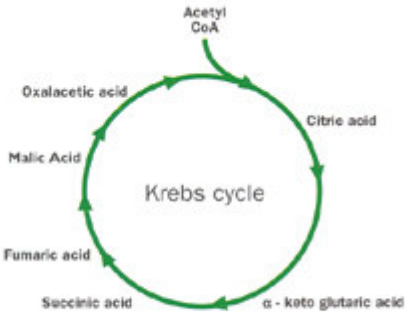


Figure 1 - Malic Acid in Fruits and Berries (Malic as percentage of total acids)

Lonza SpA. Scanzorosciate factory. Malic Acid plant.

In the animal kingdom and in humans too, Malic Acid plays an essential role in carbohydrate metabolism and, therefore, in the production of basic energy for cellular processes. It is, in fact, the precursor of oxalacetic acid and an important step in the Krebs cycle.

Malic Acid cristallizes from aqueous solutions as white, translucent crystals which are anhydrous, non-hygroscopic (in normal conditions) and non-volatile, with a melting point of around 130°C.
Its first dissociation constant (K_1 = 4,0 x 10^{-4} at 25°C) gives it relatively strong acid properties, strong enough in solution to give a fairly high hydrogen ion concentration, but, at the same time, weak enough to create an effective buffer solution.



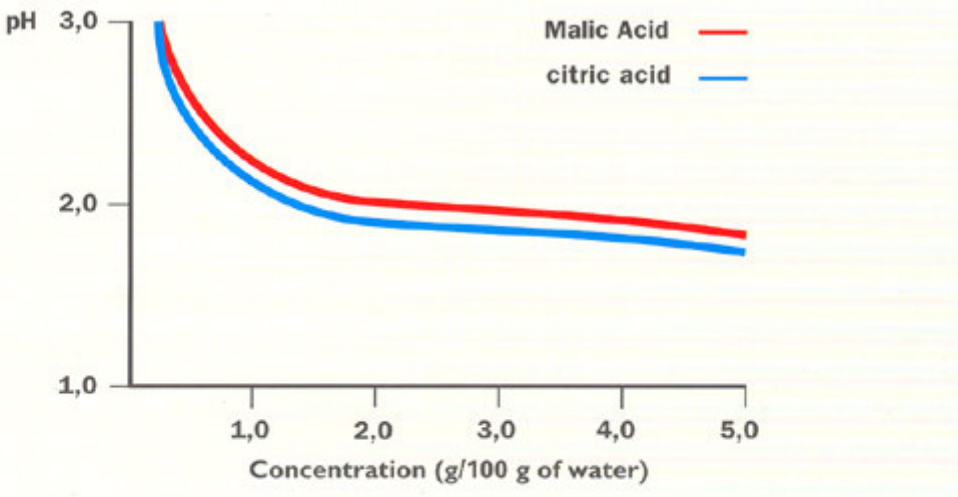


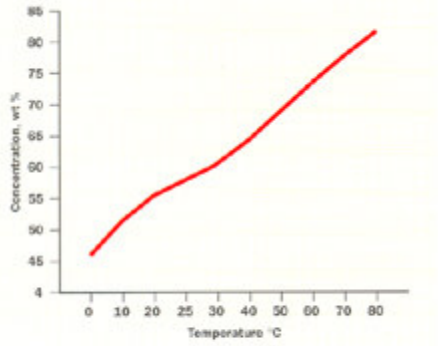
Figure 2 - pH of aqueous solutions at 25°C

By comparing the buffering indeces of the commonest food organic acidulants (Fig. 3) it is clear that the Malic Acid index rates high (certainly higher than that of citric acid) and it is well known that the bigger the value, the better the buffering action of the acid.

Figure 3 - Buffering indices

Tartaric acid	3.53
Fumaric acid	3.46
Malic Acid	**3.26**
Adipic acid	3.26
Succinic acid	2.90
Citric acid	2.46

Figure 4 - Solubility of Malic Acid in water



Malic Acid has very good solubility in water: at 25°C the saturated solution contains 58% of Malic Acid by weight and its solubility grows very rapidly when the temperature is increased (Fig. 4).

Lonza SpA. Scanzorosciate factory. Malic Acid Plant.

Properties and advantages of Malic Acid

Flavour enhancement

Malic Acid blends very well with a wide range of essences and flavours; its acid taste builds up slowly at the beginning, but persists for a very long period.
With citric acid, on the other hand, the acid taste builds up more rapidly to start with, but taste stimulation is of short duration (Fig. 5).

The final effect of this is to give the sensation of a stronger taste in the case of Malic Acid. Understandably, therefore, this property makes Malic Acid particularly desirable in the formulations of many beverages.

Storage prolongation

Since Malic Acid is anhydrous and not particularly hygroscopic, it can be stored, in normal conditions, for a very long time without any caking problems. Due to this characteristic end products, in powder or in granular form, blended with Malic Acid also have a longer shelf life.

Advantage of a lower melting point

The melting point of Malic Acid is about 130°C, a temperature clearly lower than that of citric acid (153°C).
This difference is particularly interesting and important, especially in the production of hard candies.

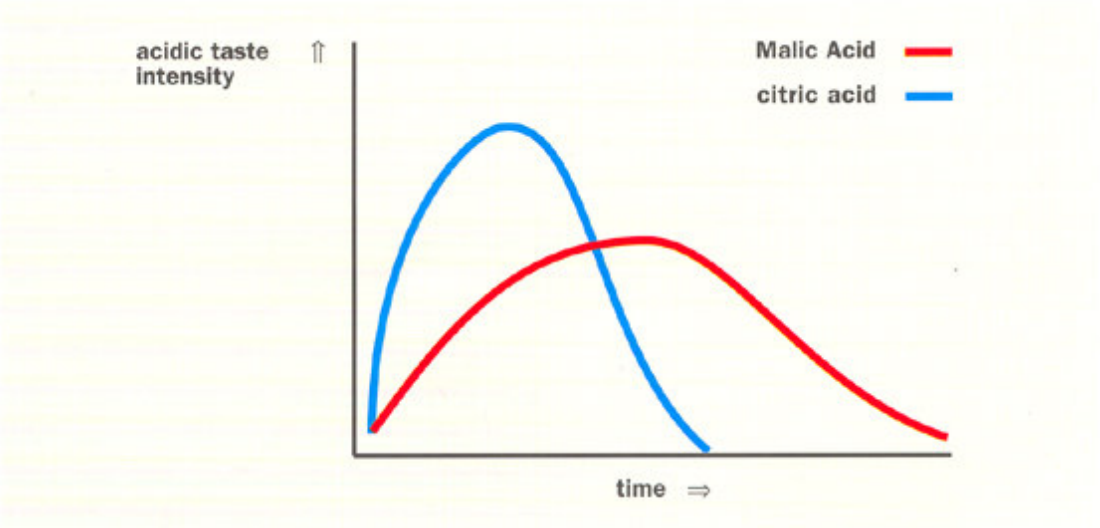


Figure 5 - Taste retention curves of Malic Acid and citric acid

Figure 6 - Solubility

	Maximum concentration in aqueous solution at room temperature	Solubility of calcium salts at room temperature
	g/100 g solutions	g anhydrous salt/ 100 g water
Citric acid	64.0	0.09
Malic Acid	**58.0**	**0.30**
Tartaric acid	125.0	0.30
Succinic acid	6.5	1.28
Lactic acid	100.0	3.50

Better solubility of its salts

The calcium salts of Malic Acid are much more soluble in water than those of citric acid for instance (Fig. 6), which avoids cloudiness in the end product even when only moderately hard water is used.

Chelating power

Malic Acid has good chelating properties which permit the formation of stable complexes with many heavy metals. Due to this property Malic Acid can replace citric acid in the processing and refining of edible oils and in protection against food deterioration.

Synergy with artificial sweeteners

Recent studies have shown that the longer taste retention of Malic Acid helps to mask the bitter aftertaste of many artificial sweeteners, at the same time enhancing sweetening power.

The following three points, which are some of the results obtained in a study carried out by the Experimental Station for the Food Preservatives Industry of Parma on behalf of Lonza SpA, confirm without any doubt that Malic Acid:

- enhances the sweetening power of Aspartame and this action is even more marked in the case of K.acesulfame (Fig. 7)

Figure 7 **Sweetness**

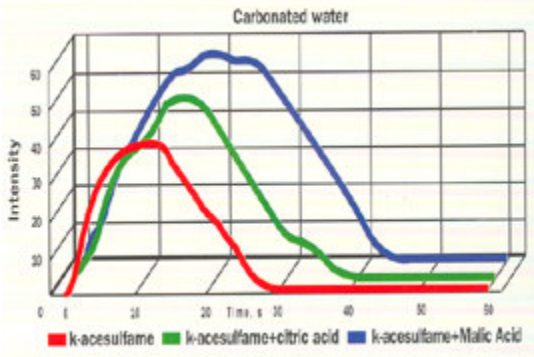
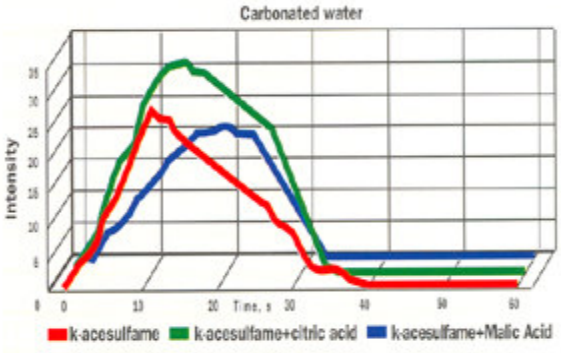
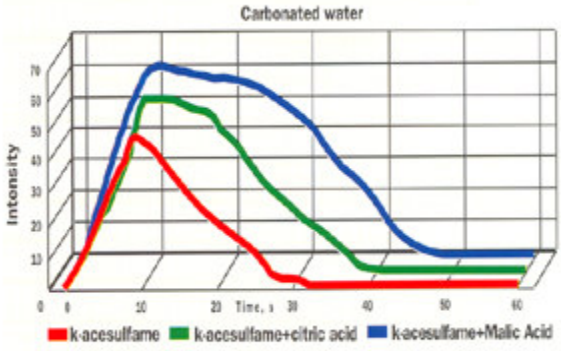


Figure 8 **Bitterness**



• masks the inevitable bitter aftertaste that is generally present in artificial sweeteners and particularly in K-acesulfame (Fig. 8).

Figure 9 **Fruitiness**



• increases the efficacy of flavouring agents (Fig. 9).

Greater economy

The use of Malic Acid, in substitution for or combination with citric acid, has three cost advantages:

• Food technology studies confirm that by using Malic Acid it is possible to achieve the same acid taste as with citric acid, but with a smaller quantity. This is due to the longer taste retention of Malic Acid and therefore, in the final analysis, to its stronger taste. Experiments have borne out these facts by showing that with a wide range of foods and beverages the same acid taste obtained with anhydrous citric acid can be achieved by using about 10% less Malic Acid (as compared with about 20% for monohydrate citric acid).

• The ability of Malic Acid to enhance, and then to strengthen, the effect of flavours and fragrances very often makes it possible to reduce their quantities thus achieving a significant saving.

• In the case of formulations containing artificial sweeteners (low calorie beverages, for instance) the synergic effect of Malic Acid quite often enables smaller quantities to be used.

Application of Malic Acid

Lonza SpA Malic Acid thanks to its properties, has a wide range of applications in the food industry (beverages, candies, chewing gums, jellies, jams, frozen confectionery), in animal foodstuffs (petfood, mixtures of acidifiers for pigs), in the treatment of metals, in metal plating, in the pharmaceutical and cosmetic industry, and in building materials.

Beverages

• Malic Acid is increasingly used in both liquid beverages and powder drinks as a flavour enhancer, because of its buffer power and to increase the efficacy of antimicrobial preservatives.
Due to its acid taste, which is stronger than that of citric acid, Malic Acid is more than often used as a substitute for or in combination with it in the formulation of beverages, thus substantially contributing to the intensification and the improvement of the taste of the fruits flavours used.

• In sports drinks, in their derivatives, "life style" drinks, and in enriched drinks, which are very often rich in calcium salts, Lonza SpA Malic Acid always enables clear solutions to be obtained, without any undesirable cloudiness, because of the high solubility of its salts.

• In low calorie drinks, Lonza SpA Malic Acid is increasingly used to mask the unpleasant aftertaste of many artificial sweeteners, thanks to its longer taste retention, which makes the final flavour much smoother and more balanced.
From the cost angle, this synergy between Malic Acid and synthetic sweeteners makes possible a some reduction in the quantity of sweetener required, with a substancial saving in the cost of the formula.
Moreover, it must be remembered, that by replacing citric with Malic Acid 10-20% can be saved on the acidulant.

• Powdered drinks containing Malic Acid, instead of other acidulants, such as citric acid, can be stored a long time without any caking problem, since it is anhydrous and non-hygroscopic.

• In wine production, the right acidity of the must is essential, not only to control the fermentation process, but also the flavour obtained through aging.
The use of Malic Acid, citric acid, or tartaric acid for the pH adjustement before and after fermentation is strictly controlled to a greater or lesser degree by the laws of individual countries which must be complied with when the acidulant to be used is chosen.
An additional advantage in using Malic Acid stems from its ability to form stable iron chelates that prevent the precipitation of iron salts, which in most cases, are the main cause of cloudy wine.

• The production of branded cider, in which the organolepctic properties must remain absolutely constant, requires a high level of standardization both of the production method and of starting materials.
The apple juice used as a starting product has to contain a predetermined percentage of sugar and always constant acidity, which is not always achievable without the addition of acidulants.
In fact, the natural acidity of apples can vary, even considerably, during the year and as well as depending on where the apples come from.
Malic Acid, in view of the fact that it is the main natural acid contained in this fruit is the ideal acid to make up for any natural acidity deficiency.
Moreover malo-lactic fermentation occurs concurrently with the alcoholic fermentation. This is generally considered to be undesirable and necessitates the addition of Malic Acid to restore the characteristic organoleptic properties of the end product.

Confectioneries

• In candies or sweets, the use of Malic Acid is preferable to that of other acidulants because its melting point is lower. Especially in hard candies this a very important point since the acid can easily be incorporated in the cooked syrup on the slub.
Moreover, since the temperature to be reached is rather low, it is possible to avoid caramelization and minimize sugar inversion.
Another characteristic of Malic Acid, which is very

important in these products, is the high solubility of its calcium salts in order to obtain clear, transparent products.

Malic Acid is also used in soft and effervescent candies. In the latter case the Malic Acid blends with the coating of the candy together with other ingredients.

• In chewing-gum, Malic Acid, combined with saccharine, improves saliva stimulation. Moreover by using mixtures of acids with different solubility rates it is possible to make chewing-gum whose taste is more or less prolonged.
The synergism between Malic Acid and artificial sweeteners in this case offers the same advantages we have seen previously in other categories of products.

Desserts

• Acidulants are used in the production of many different kind of desserts: for instance, ices, sherbets, variegated ice creams, jelly dessert powders, milk puddings etc.
Depending on the final product, Malic Acid is used to enhance the taste of the fruit flavours (as in ices and sherbets) or as a pH adjuster in order to obtain the right gelling rate.

Jams and Fruit Jellies

Malic Acid is added in these products to compensate for any deficiencies in natural acid contained in the fruit.
Generally speaking, about 0.5% is enough to obtain a pH that will enable pectin to perform its jelling function correctly and effectively.
Obviously, the properties of the Malic Acid are also used to enhance the taste of the fruit.
In the case of low-calorie jam, in which an artificial sweetener is used, Malic Acid has the same function as in low-calorie drinks.

Fruit and Vegetables

In the conservation of fruit and vegetables,

whether fresh or canned, the use of acidulants is of fundamental importance.

• *Canned fruit and vegetables.*
During sterilization, it is essential that the pH be lower than 5 to enable a mild heat treatment to be used (lower temperature and shorter treatment). Indeed, with a pH exceeding 5, it would be necessary to operate at higher temperatures, which, apart from destroying the micro-organisms, would also destroy the natural structure of the products, leading to deterioration in their appearance and consistency and a reduction in their nutritional value.
The pH is kept under control by means of a food organic acid, and Malic Acid, since it also enhances flavour, is the best one for the purpose.
Fruit and vegetables prepared for canning or freezing very quickly become dark due to the oxidizing action of the air. This can be partially or totally avoided by the addition of ascorbic acid. The combined use of Malic and Ascorbic Acid has a synergic effect and increases the effectiveness of the latter.

• *Fresh vegetables.*
Many vegetables, for example green salads, if treated with solutions containing a preservative and an acidulant such as Malic Acid, will keep fresh much longer.

Edible Oils and Fats

In products of this type, Malic Acid has a synergic effect on the anti-oxidants used to prevent the products from becoming rancid. In addition, during the processing and refining of oils, its chelating properties will eliminate trace elements of metals.

Petfoods

Malic Acid is used in pre-cooked foods for cats and dogs to obtain the pH required for jelling.
Moreover Malic Acid improves the flavour which is a very important point especially in the case of cats-food.
Recent studies have shown that Malic Acid added to petfoods prevents and even treats urinary calculosis, a quite frequent disease in cat and dog.

Pharmaceutical and Cosmetic Products

The use of Malic Acid is worthwhile in this area, because of its ability to enhance the effect of the aromas used to mask the undesirable tastes and smells of medicinals, as in throat lozenges and cough syrups. It is also used in effervescent powders and tablets.

In the area of cosmetics, Malic Acid, like other alpha-hydroxy acids, figures in the formula of creams to prevent wrinkles.

Industrial Uses

The use of Malic Acid is becoming increasingly significant in a number of typically industrial uses:

- In the treatment of metals, such as pickling and descaling, as a substitute for strong inorganic acids, since it has the advantage of being neither corrosive nor toxic. Malic acid is also easily and fully biodegradable.

- In the food industry, especially in the manufacture of drinks, the excellent solubility of its calcium salts make it useful for removing lime deposits from plant and equipment.

- In the textile industry, as a substitute for acetic or formic acid, since it does not damage or corrode machinery. It also has the advantage of not generating any unpleasant smells - which is nice for the workers. It may also be included in the chemicals used in textile finishing.

- In animal feed, it is used, in combination with other acids, for the acidification of pigs feed.

- In plating industry, it is used to correct the pH in plating baths.

- In the manufacture of plasters and cements for the building industry, it is used, combined with tartaric acid, as a setting retardant.

Note
All the data and the information previously mentioned have to be considered as a guide line and the parameters have to be necessary adjusted to each needs and relative end products.

Legislation

In the United States, Malic Acid is considered harmless by the FDA (Food and Drug Administration), which classifies it as GRAS - that is "Generally Recognized as Safe" (the Code of Federal Regulations 21 CFR 184.1069 - 1993 refers), and its use is allowed (without any limitations, except as required by good manufacturing practice) as a flavour enhancer, flavouring agent and adjuvant, and as pH control agent.

In the European Union, the directive on "Food Additives other than Colours and Sweeteners", under No. 95/2/EC of 20th February 1995, permits the general use of Malic Acid (E296) and its salts (E350, E351, E352) in the area of food processing, except for the limitations mentioned in the same directive.

In Italy, the use of Malic Acid in food processing is governed by Ministerial Decree No. 209 of 27th February 1996, which reflects the provisions of European Directive 95/2/EC.

N.B. The use of acidulants, sweeteners, or other additives mentioned in this brochure is governed by the specific legislation of individual states.

Safety and Hygiene

In accordance with the laws of the European Union, all the safety regulations that have to be observed in using the product are contained in the attached safety data sheet.

Chemical and Physical Properties

Chemical description	D,L-Malic Acid (hydroxybutanedioic acid hydroxy-succinic acid)
Molecular formula	$C_4H_6O_5$
Structural formula	HO —CH —COOH CH_2 —COOH
Appearance	White crystalline powder or acid-tasting granules
Molecular weight	134.09
Equivalent weight	67.05
Melting point	130-132°C
d_4^{20}	1.601
Dissociation constants	$K_1=4 \times 10^{-4}$ $K_2=9 \times 10^{-6}$
pH of aqueous solution	(see curve in Figure 2)
Combustion heat (20°C)	320 kcal/mole of solution
Heat of solution	- 4.9 kcal/mole of solution
Viscosity at 20°C (50% aqueous solution)	6.5 CP
Solubility in water	(see curve in Figure 4)
Solubility in ethanol (g/100 ml at 25°C)	39.16
Buffer index	3.26

Microbiological Data

Bacteria	< 10 CFU/g
Yeasts	< 10 CFU/g
Moulds	< 10 CFU/g
Total coliforms	< 10 CFU/g
Salmonella	absent

The information contained in this brochure is correct and accurate and is based on our up-to-date technical and scientific knowledge at the date of publication.

In any case, such information refers exclusively to use of the product in its pure state and for the purposes indicated in this publication.

Nothing contained herein should be construed or interpreted as a reason for any breach of existing patents.

No guarantee, whether explicit or implicit, is given in respect of any results stemming from use of the information given.