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Improving the Flavor of Fruit Products with Acidulants

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Acidulants are sometimes overlooked when developing fruit-flavored products such as beverages, gelatin desserts, jams, jellies or candies. The flavors and sweeteners are adjusted to achieve the flavor profile desired and the acidulant which is available in inventory, for example, citric acid, is commonly used.

However, the flavor profile of most products can be significantly improved by using a mixture of acidulants or a different acidulant. The use of a mixture of acidulants makes the flavor profile more authentic. As shown in Table I, fruits naturally contain mixtures of acidulants, not only one acidulant. These fruits typically contain 0.5-2.0% total acid, with the exception of tamarind, whose pulp contains more than 10% total acid.

Table I. Acids Naturally Present in Fruits

Fruit	Predominant Acid	Secondary Acids
Apple	Malic Acid (95%*)	Tartaric Acid, Fumaric Acid
Apricot	Malic Acid (70%*)	Citric Acid, Tartaric Acid
Cherry	Malic Acid (94%*)	Tartaric Acid
Grape	Malic Acid (60%*)	Tartaric Acid
Grapefruit	Citric Acid	Malic Acid
Guava	Citric Acid	Malic Acid
Lime, Lemon	Citric Acid	Malic Acid
Mango	Citric Acid	Malic Acid, Tartaric Acid
Orange	Citric Acid	Malic Acid
Peach	Malic Acid (73%*)	Citric Acid
Pear	Malic Acid (77%*)	Citric Acid
Pineapple	Citric Acid	Malic Acid
Raspberry	Citric Acid	Malic Acid, Tartaric Acid
Strawberry	Citric Acid	Malic Acid, Tartaric Acid
Tamarind	Tartaric Acid	Citric Acid, Malic Acid
Watermelon	Malic Acid (99%*)	Fumaric Acid

*% of the total acid in the fruit

As shown in Table I, malic acid and citric acid are the predominant acids in most fruits. What is interesting is how prevalent malic acid is. Even in grapes, which most people associate with tartaric acid, most of the acid present is malic acid. In oranges, which most people associate with citric acid, approximately 15% of the total acid present is malic acid.

In this presentation, I will discuss the use of acidulants to improve the flavor of fruit-flavored products. I will discuss those acidulants normally used in fruit-flavored products, that is; citric acid, fumaric acid, malic acid and tartaric acid.

Physicochemical Properties of the Acidulants

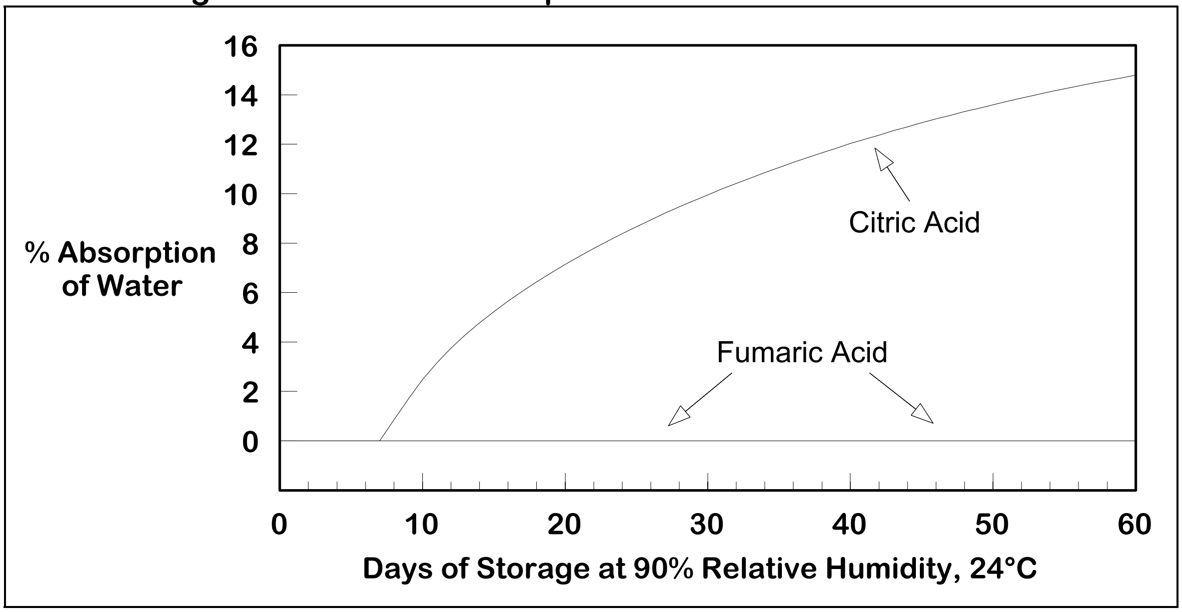
As shown in Table II, citric, malic and tartaric acids are all very soluble in water. Fumaric acid, on the other hand, has a solubility of 0.5% at 20°C. This is sufficient for many applications, although more time must be allowed to dissolve the fumaric acid. In chewing gum, the slow dissolution of fumaric acid is an advantage because it means that the sensation of sourness in the mouth will be prolonged. This enhances the flavor impact of some chewing gums.

Table II. Solubility and Hygroscopicity of Acidulants

Acidulant	Solubility in water at 20°C	Hygroscopicity
Citric	62%	hygroscopic
Fumaric	0.5%	non-hygroscopic
Malic	56%	hygroscopic
Tartaric	60%	hygroscopic

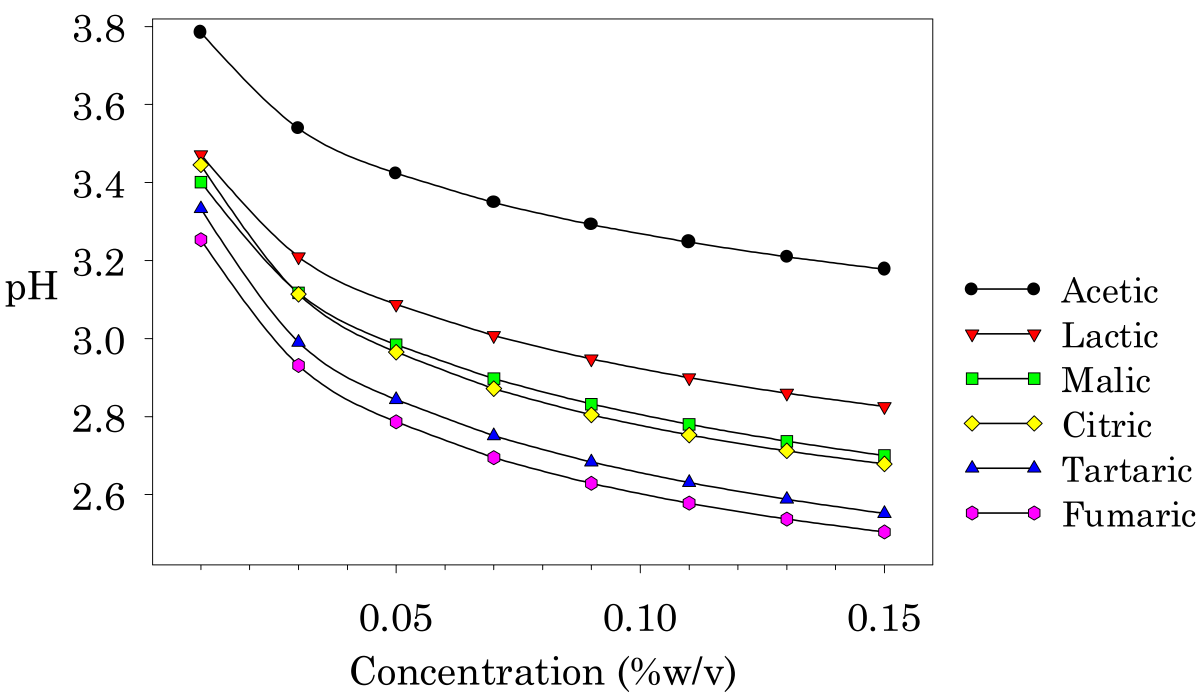
As shown in Table II and Figure I, fumaric acid is non-hygroscopic when compared to other acidulants like citric acid. Fumaric acid is used extensively in dry mix products to avoid moisture absorption and the product degradation associated with it.

Figure I. Moisture Absorption of Citric vs. Fumaric Acid



Shown in Figure II are the pH curves of the acidulants. The acidulant with the lowest pH, fumaric acid, is also the strongest of the acidulants. To provide equivalent sourness, smaller quantities of fumaric acid are needed than of other acidulants. Fumaric acid is therefore said to have a

Figure II. Acidulants: pH vs. Conc. (%w/v)



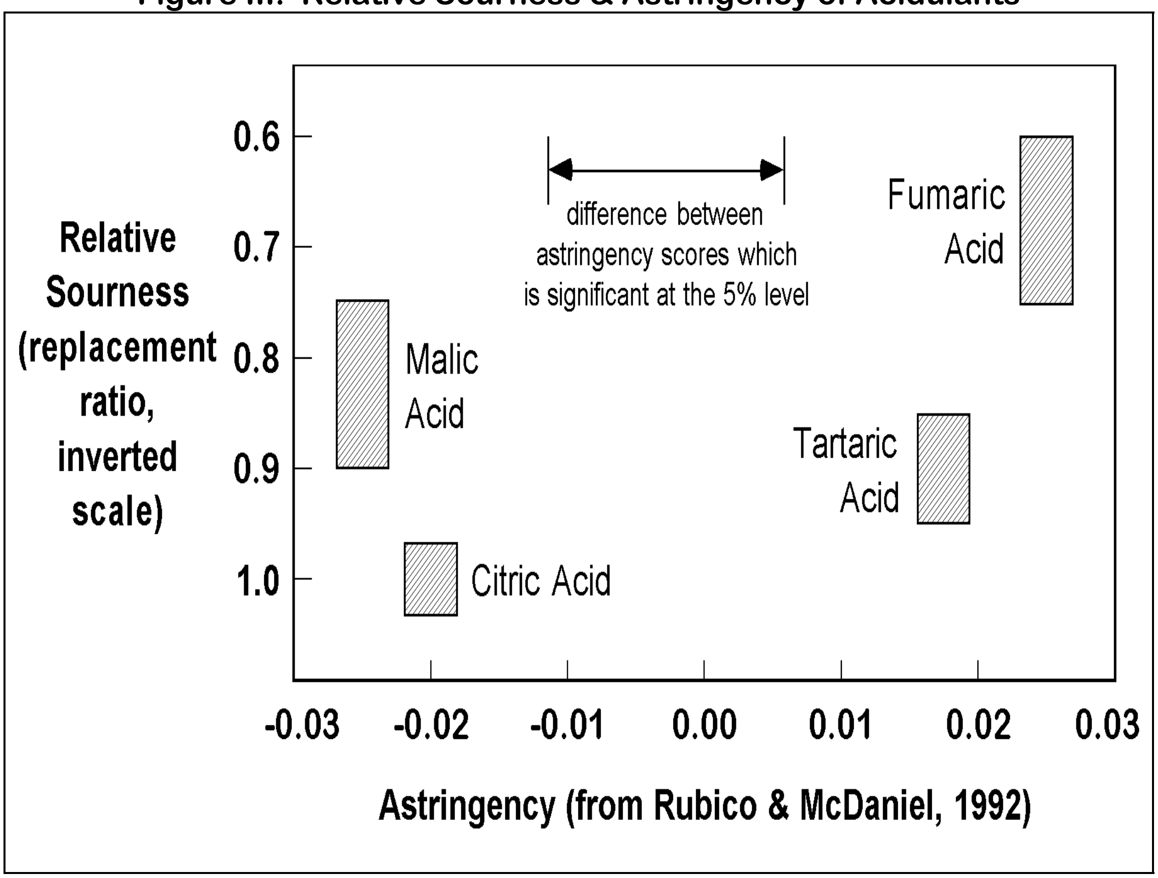
Source: NutriQuim, S.A. de C.V. and Bartek Ingredients, Inc.

higher relative sourness. Malic acid has a higher relative sourness than citric acid, even though its pH is higher, as shown in Figure II. Malic acid has a more prolonged sour sensation in the mouth than citric acid and for this reason a higher relative sourness.

Relative Sourness & Astringency of the Acidulants

Shown in Figure III are the relative sourness and astringency of the acidulants. The relative sourness is expressed as the replacement ratio on an inverted scale. For example, since 0.60-0.75 Kg. of fumaric acid can be used to provide approximately the same sourness as 1 Kg. of citric acid, the replacement ratio in this case is 0.60-0.75. In the case of malic acid, the replacement ratio is 0.75-0.90. For tartaric acid, it is 0.85-0.95. These replacement ratios are based on various comparative studies of acidulants as well as experience in using these acidulants in different product formulas. The replacement ratios shown here are ranges which take into account all possible uses. The exact replacement ratio for a particular product formula must be determined by experimentation, since the sensation of sourness is influenced by many factors.

Figure III. Relative Sourness & Astringency of Acidulants



The most obvious factor influencing relative sourness is pH. The higher the level of hydrogen ions, or the lower the pH, usually the more sour will be the sample. This is true for fumaric acid, which as shown in Figure III has the highest relative sourness of the acidulants. However, this is not always true. For example, comparing malic acid with citric acid at the same concentration, malic acid has a higher pH but tastes more sour. As I mentioned earlier, malic acid has a more prolonged sour sensation and for this reason a higher relative sourness. Each acidulant has different sensory characteristics. It is not possible to simply replace one acidulant with another in a product formula, even taking into account the replacement ratio, and expect that the product will taste the same. The idea is to use an acidulant or mixture of acidulants which results in the optimum flavor profile for the product.

A sensory aspect of acidulants which must be considered is astringency. This is the sensation of puckering or shrinking throughout the mouth. In the case of acidulants, the sensation of astringency occurs after the sensation of sourness and lasts longer (Straub, 1992). The astringency of tamarind is due to its high level of tartaric acid. Astringency is also associated with tannins, for example; in tea, coffee, grapes, cherries and unripe fruit.

The values used for astringency in Figure III are taken from the comparative study of Rubico & McDaniel (1992), in which (12) trained panelists evaluated different acidulants at 0.08%w/v. The panelists were asked to rate different acidulants in terms of various sensory attributes, including astringency. The average scores for astringency are used in Figure III. Tartaric acid and fumaric acid are more astringent than citric acid or malic acid, as shown in Figure III. At the 5% level of significance, fumaric and tartaric acids have the same astringency, as do citric and malic acids. Based on Figure III, we would expect fumaric acid to be useful in replacing tartaric acid in flavors where astringency is present, for example, in tamarind or grape. In fact, fumaric acid is very effective in these applications.

Using Acidulants in Fruit-Flavored Products: Consumer Preference

1. The use of malic acid to improve the flavor of aspartame-sweetened beverages (Anon., 1986).

Panelists in the United States were asked to compare non-carbonated beverages sweetened with aspartame and made with 100% malic acid vs. 100% citric acid. They were asked to identify which acidulant they preferred. The results were as follows:

Beverage flavor	# of panelists	# of panelists preferring malic acid	Probability of error in concluding that there was a preference for malic acid*
Fruit Punch	25	17	10.8%
Orange	31	21	7.1%
Grape	22	15	13.4%

*O'Mahoney (1986), Paired-Comparison Preference Test

In all beverage flavors, malic acid was preferred over citric acid. Malic acid is preferred for aspartame-sweetened products because the prolonged sour sensation of malic acid matches the sweet aftertaste of aspartame. If citric acid is used instead of malic acid, the sweet aftertaste of aspartame is more noticeable and the product does not taste as good.

2. The use of malic acid to enhance the flavor of an orange-flavored beverage.

14 panelists in Mexico were asked to compare two non-carbonated, orange-flavored beverages made with A) 100% citric acid, and B) 95% citric acid with 5% malic acid. The beverages were sweetened with sugar. The formulas for the two beverages are shown below. The panelists were asked which beverage they preferred. 10 out of 14 panelists preferred Formula B (citric acid and malic acid). Of the panelists who preferred Formula B, many commented that this sample had a stronger flavor. There is a probability of error of 18% in concluding that there exists a preference for Formula B over Formula A (O'Mahoney, 1986, Paired-Comparison Preference Test).

Formula 2A (with 100% Citric Acid)

Ingredient	Level of Use
Water	to 100%
Sodium Benzoate (Kalama)	0.03% w/v
Sodium Citrate	0.04% w/v
Citric Acid	0.30% w/v
Sugar	12.50% w/v
PC35 Orange flavor with color (Virginia Dare)	0.07% v/v
pH=2.6 Ingredients with **boldface** letters are available from NutriQuim, S.A. de C.V.	

Formula 2B (with Citric Acid and Malic Acid)

Ingredient	Level of Use
Water	to 100%
Sodium Benzoate (Kalama)	0.03% w/v
Sodium Citrate	0.035% w/v
Malic Acid (Bartek)	0.015% w/v
Citric Acid	0.28% w/v
Sugar	12.50% w/v
PC35 Orange flavor with color (Virginia Dare)	0.07% v/v
pH=2.6 Ingredients with **boldface** letters are available from NutriQuim, S.A. de C.V.	

Different formulas with more malic acid and less citric acid were also evaluated but they were preferred less by the panelists. Apparently, the use of 5% malic acid as a percentage of the total acid was enough to enhance the overall flavor profile without changing the citrus character of the flavor.

3. The use of fumaric acid to improve the flavor of a grape-flavored beverage.

17 panelists in Mexico were asked to compare two non-carbonated, grape-flavored beverages made with A) 100% citric acid, and B) 92% fumaric acid and 8% malic acid. The beverages were sweetened with sugar. The formulas for the two beverages are shown below. The panelists were asked which beverage they preferred. 11 out of 17 panelists preferred Formula B (fumaric acid and malic acid). Of the panelists who preferred Formula B, many commented that this sample tasted more like grape.

Formula 3A (with 100% Citric Acid)

Ingredient	Level of Use
Water	to 100%
Sodium Benzoate (Kalama)	0.03% w/v
Sodium Citrate	0.03% w/v
Citric Acid	0.25% w/v
Sugar	12.50% w/v
CL85 Grape flavor with color (Virginia Dare)	0.25% v/v
pH=2.5 Ingredients with **boldface** letters are available from NutriQuim, S.A. de C.V.	

Formula 3B (with Fumaric Acid and Malic Acid)

Ingredient	Level of Use
Water	to 100%
Sodium Benzoate (Kalama)	0.03% w/v
Sodium Citrate	0.04% w/v
Fumaric Acid (Bartek)	0.165% w/v
Malic Acid (Bartek)	0.015% w/v
Sugar	12.50% w/v
CL85 Grape flavor with color (Virginia Dare)	0.25% v/v
pH=2.5 Ingredients with **boldface** letters are available from NutriQuim, S.A. de C.V.	

Grape juice is naturally astringent due to the presence of tannins and tartaric acid. Therefore, fumaric acid is more useful than citric acid as an acidulant in grape-flavored beverages because it has more astringency, as discussed earlier. A low level of malic acid is used to enhance the overall flavor profile.

In this case, there was only a slight preference for the sample with fumaric and malic acids. However, the use of fumaric acid reduced by 40% the total cost of the acidulants, due both to the lower cost of fumaric acid and to its lower level of use.

Using Acidulants in Fruit-Flavored Products: Specific Recommendations

The following recommendations are starting points only. The levels and proportions of acidulants which result in the best flavor profile can only be determined by experimentation.

The composition of the product in which the acidulant is used must be considered when selecting acidulants. The flavor profiles of beverages are generally very sensitive. Since they contain mostly water, a minor change in the ingredients can significantly change the flavor profile. Products which contain fat or hydrocolloids are less sensitive, since fats and hydrocolloids can mask or retard the perception of flavor. Therefore, in products which contain enough fats or hydrocolloids to affect the perception of flavors; such as soft caramels, jams and jellies, and gelatin desserts; the choice of acidulant is less critical than in the case of a beverage.

❑ For fruits where the predominant acid is citric acid (orange, grapefruit, lemon-lime, pineapple, mango, strawberry and others), use citric acid in combination with less than 10% malic acid as a percentage of the total acid. The malic acid enhances the fruit flavor and results in a more blended flavor profile.

❑ For apricot, peach and pear; use a combination of malic acid and citric acid. A starting point would be 2/3 malic acid, 1/3 citric acid.

❑ For flavors with astringency (tamarind, grape, cherry and jamaica), use fumaric acid in combination with less than 10% malic acid as a percentage of the total acid. The astringency from fumaric acid improves the flavor profile of the product.

❑ For apple and watermelon, use 100% malic acid. These fruits contain more than 95% malic acid naturally. Combinations of malic acid and fumaric acid can be used to provide astringency for green apple.

❑ For products where a prolonged sour sensation is needed, use malic acid as the acidulant. For example:
A) In products sweetened with aspartame, malic acid is used to balance the sweet aftertaste of aspartame and enhance the fruit flavor. This is especially effective in carbonated beverages.

B) In hard candy, malic acid's prolonged sourness extends and enhances fruit flavors to give a more fruity, more intense flavor profile.
C) In chewing gum, citric acid can be used to provide the initial sourness and malic and fumaric acids can be used to prolong and extend the sour sensation. Fumaric acid in this case extends the sour sensation due to its slow dissolution.

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