

**Handbook of Enology**  
**Volume 2**  
**The Chemistry of Wine**  
**Stabilization and Treatments**  
**2<sup>nd</sup> Edition**

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Original translation by

*Aquitrad Traduction, Bordeaux, France*

Revision translated by

**Christine Rychlewski**

*Aquitaine Traduction, Bordeaux, France*



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March 17, 2005

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## **PART ONE**

### The Chemistry of Wine



# Organic Acids in Wine

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## 1.1 INTRODUCTION

Organic acids make major contributions to the composition, stability and organoleptic qualities of wines, especially white wines (Ribéreau-Gayon *et al.*, 1982); (Jackson, 1994). Their preservative properties also enhance wines' microbiological and physicochemical stability.

Thus, dry white wines not subjected to malolactic fermentation are more stable in terms of bitartrate (KTH) and tartrate (CaT) precipitation. Young white wines with high acidity generally also have greater aging potential.

Red wines are stable at lower acidity, due to the presence of phenols which enhance acidity and help to maintain stability throughout aging.

## 1.2 THE MAIN ORGANIC ACIDS

### 1.2.1 Steric Configuration of Organic Acids

Most organic acids in must and wine have one or more chiral centers. The absolute configuration of the asymmetrical carbons is deduced from that of the sugars from which they are directly

**Table 1.1.** The main organic acids in grapes

$  \begin{array}{c}  \text{COOH} \\    \\  \text{HO} - \text{C} - \text{H} \\    \\  \text{H} - \text{C} - \text{OH} \\    \\  \text{COOH}  \end{array}  $ <p>L(+)-Tartaric acid</p>	$  \begin{array}{c}  \text{COOH} \\    \\  \text{CH}_2 \\    \\  \text{H} - \text{C} - \text{OH} \\    \\  \text{COOH}  \end{array}  $ <p>L(-)-Malic acid</p>	$  \begin{array}{c}  \text{CH}_2 - \text{COOH} \\    \\  \text{HO} - \text{C} - \text{COOH} \\    \\  \text{CH}_2 - \text{COOH}  \end{array}  $ <p>Citric acid</p>
$  \begin{array}{c}  \text{COOH} \\    \\  \text{HO} - \text{C} - \text{H} \\    \\  \text{H} - \text{C} - \text{OH} \\    \\  \text{H} - \text{C} - \text{OH} \\    \\  \text{CH}_2 - \text{OH}  \end{array}  $ <p>D-Gluconic acid</p>	$  \begin{array}{c}  \text{COOH} \\    \\  \text{C} = \text{O} \\    \\  \text{HO} - \text{C} - \text{H} \\    \\  \text{H} - \text{C} - \text{OH} \\    \\  \text{H} - \text{C} - \text{OH} \\    \\  \text{CH}_2 - \text{OH}  \end{array}  $ <p>2-keto D-Gluconic acid</p>	$  \begin{array}{c}  \text{COOH} \\    \\  \text{H} - \text{C} - \text{OH} \\    \\  \text{HO} - \text{C} - \text{H} \\    \\  \text{HO} - \text{C} - \text{H} \\    \\  \text{H} - \text{C} - \text{OH} \\    \\  \text{COOH}  \end{array}  $ <p>Mucic acid</p>
$  \begin{array}{c}  \text{CH} = \text{CH} - \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \end{array} \\    \\  \text{C}_6\text{H}_3(\text{OH})(\text{R}_1)(\text{R}_2)  \end{array}  $ <p>Coumaric acid (<math>\text{R}_1 = \text{R}_2 = \text{H}</math>) Caffeic acid (<math>\text{R}_1 = \text{OH}</math>; <math>\text{R}_2 = \text{H}</math>)</p>	$  \begin{array}{c}  \text{CH} = \text{CH} - \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} - \text{C}(\text{OH})_2 - \text{COOH} \end{array} \\    \\  \text{C}_6\text{H}_4(\text{OH})  \end{array}  $ <p>Coumaryl tartaric acid</p>	

derived. This is especially true of tartaric and malic acids (Table 1.1). The absolute configuration of the asymmetrical carbons is established according to the Prelog rules (1953). Further reference to these rules will be made in the chapter on sugars, which are the reference molecules for stereo-isomerism.

### 1.2.2 Organic Acids in Grapes

The main organic acids in grapes are described (Table 1.1) according to the conventional Fischer system. Besides tartaric acid, grapes also have a stereoisomer in which the absolute configuration of the two asymmetrical carbons is L, but whose optical activity in water, measured on a polarimeter, is d (or +). There is often confusion between these

two notions. The first is theoretical and defines the relative positions of the substituents for the asymmetrical carbon, while the second is purely experimental and expresses the direction in which polarized light deviates from a plane when it passes through the acid in a given solvent.

Tartaric acid is one of the most prevalent acids in unripe grapes and must. Indeed, at the end of the vegetative growth phase, concentrations in unripe grapes may be as high as 15 g/l. In musts from northerly vineyards, concentrations are often over 6 g/l whereas, in the south, they may be as low as 2–3 g/l since combustion is more effective when the grape bunches are maintained at high temperatures.

Tartaric acid is not very widespread in nature, but is specific to grapes. For this reason, it is

called *Weinsäure* in German, or ‘wine acid’. It is a relatively strong acid (see Table 1.3), giving wine a pH on the order of 3.0–3.5.

Tartrates originating from the wine industry are the main source of tartaric acid, widely used in the food and beverage industry (soft drinks, chocolates, cakes, canned foods, etc.). This acid is also used for medical purposes (as a laxative) and in dyeing (for mordanting fabric), as well as for tanning leather. Tartrazine, a diazoic derivative of tartaric acid, is the yellow coloring matter in wool and silk, but is also used as food coloring under the reference number E102.

L(–)-Malic acid is found in all living organisms. It is especially plentiful in green apples, which explains its German name *Äpfelsäure*, or ‘apple acid’. It is also present in white and red currants, rhubarb and, of course, grapes. Indeed, the juice of green grapes, just before color change, may contain as much as 25 g/l. In the two weeks following the first signs of color change, the malic acid content drops by half, partly due to dilution as the grapes grow bigger, and also as a result of combustion. At maturity, musts from northerly regions still contain 4–6.5 g/l malic acid, whereas in southerly regions, concentrations are only 1–2 g/l.

Citric acid, a tri-acid, is very widespread in nature (e.g. lemons). Its very important biochemical and metabolic role (Krebs cycle) requires no further demonstration. Citric acid slows yeast growth but does not block it (Kalathenos *et al.*, 1995). It is used as an acidifying agent in the food and beverage industry (lemonade), while sodium (E331), potassium (E332), and calcium (E333) citrate have many uses in fields ranging from pharmaceuticals to photography. Concentrations in must

and wine, prior to malolactic fermentation, are between 0.5 and 1 g/l.

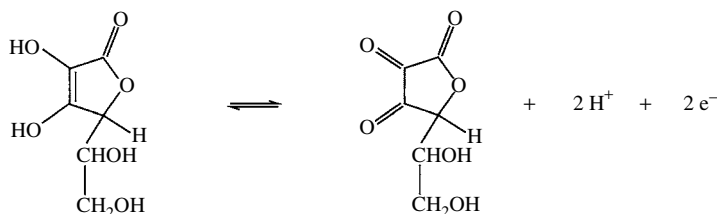
In addition to these three acids, which account for the majority of the acidity in grapes, there are also phenol acids in the cinnamic series (e.g. coumaric acid), often esterified with an alcohol function of tartaric acid (e.g. coumaryltartaric acid).

Ascorbic acid (Figure 1.1) should also be mentioned in connection with these oxidizable phenol acids. It is naturally present in lactone form, i.e. a cyclic ester. Ascorbic acid also constitutes a Redox system in fruit juices, protecting the phenols from oxidation. In winemaking it is used as an adjuvant to sulfur dioxide (Volume 1, Section 9.5).

Must and wine from grapes affected by noble and/or gray rot have higher concentrations of acids produced by oxidation of the aldehyde function (e.g. aldose) or the primary alcohol function of carbon 1 of a ketose (e.g. fructose). Thus, gluconic acid, the compound corresponding to glucose, may reach concentrations of several grams per liter in juice from grapes affected by rot. This concentration is used to identify wines made from grapes affected by noble rot, as they contain less gluconic acid than those made from grapes affected by gray rot (Sections 10.6.4, 10.6.5 and 14.2.3). The compound corresponding to fructose is 2-keto gluconic acid (Table 1.1).

The calcium and iron salts of these acids are used in medicine to treat decalcification and hypochrome anemia, respectively.

Calcium gluconate is well known for its insolubility in wine and the turbidity it causes. Mucic acid, derived from galactose by oxidation, both of the aldehyde function of carbon 1 and the primary alcohol function of carbon 6, is just as undesirable. Also known as galactaric acid, it is therefore both



**Fig. 1.1.** Oxidation–reduction equilibrium of ascorbic acid