Handbook of Enology
Volume 2
The Chemistry of Wine
Stabilization and Treatments
2nd Edition

P. Ribéreau-Gayon, Y. Glories

Faculty of Enology
Victor Segalen University of Bordeaux II, France

A. Maujean

Laboratory of Enology
University of Reims-Champagne-Ardennes

D. Dubourdieu

Faculty of Enology
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John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester,
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Contents

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March 17, 2005

Professor Pascal RIBEREAU-GAYON
Corresponding Member of the Institute
Member of the French Academy of Agriculture

PART ONE

The Chemistry of Wine

1

Organic Acids in Wine

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.

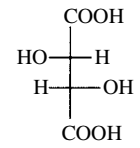
1.2 THE MAIN ORGANIC ACIDS

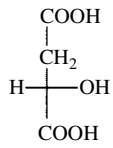
1.2.1 Steric Configuration of Organic Acids

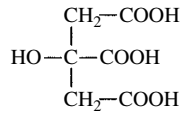
Most organic acids in must and wine have one or more chiral centers. The absolute configuration of the asymmetrical carbons is deduced from that of the sugars from which they are directly

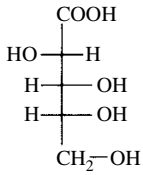
Handbook of Enology Volume 2: The Chemistry of Wine and Stabilization and Treatments P. Ribéreau-Gayon, Y. Glories, A. Maujean and D. Dubourdieu

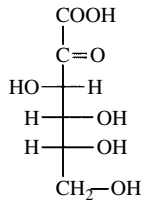
Table 1.1. The main organic acids in grapes

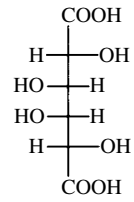

L(+)-Tartaric acid

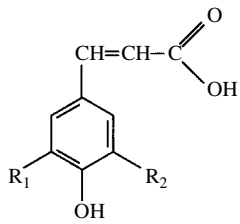

L(−)-Malic acid

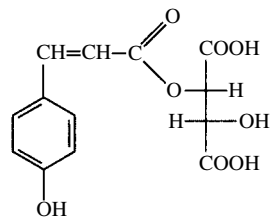

Citric acid


D-Gluconic acid


2-keto D-Gluconic acid


Mucic acid


Coumaric acid
($R_1 = R_2 = H$)
Caffeic acid
($R_1 = OH$; $R_2 = H$)


Coumaryl tartaric acid

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 stereoisomerism.

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 *Àpfelsäure*, 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

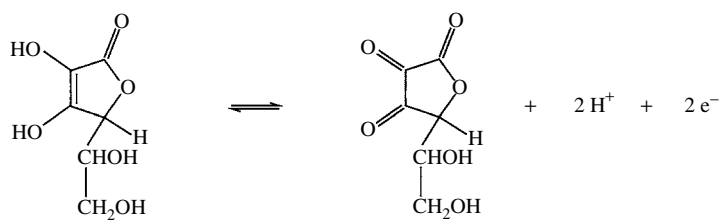


Fig. 1.1. Oxidation–reduction equilibrium of ascorbic acid

an onic and uronic acid. The presence of a plane of symmetry in its structure between carbons 3 and 4 makes it a meso-type stereoisomer. Mucic acid has no optical activity. Its presence has been observed in the crystalline deposits formed throughout the aging of sweet white wines made from grapes with noble rot.

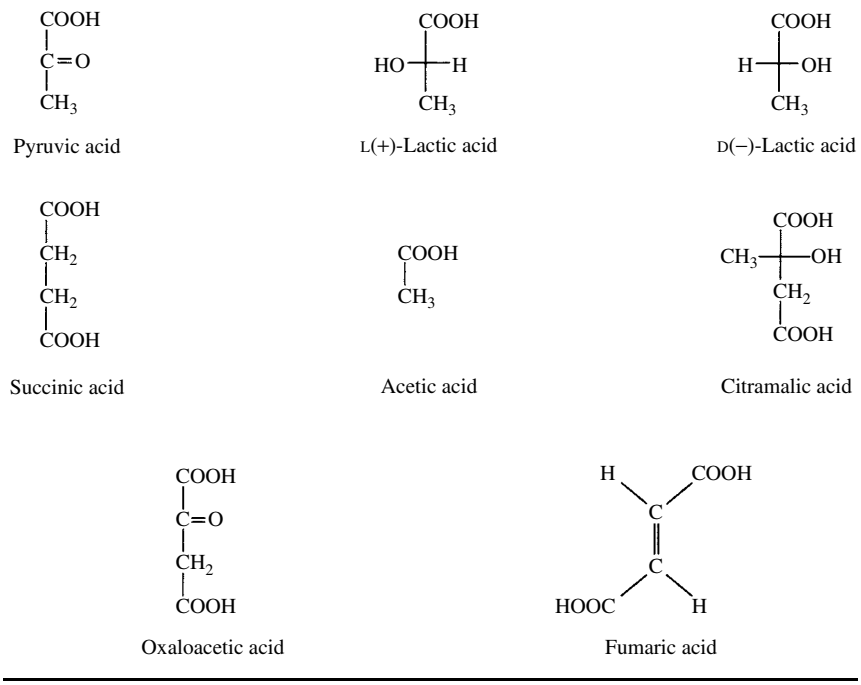
1.2.3 Organic Acids from Fermentation

The main acids produced during fermentation are described in Table 1.2. The first to be described is pyruvic acid, due to its meeting function in the cell metabolism, although concentrations in wine are low, or even non-existent. Following reduction by a hydride H^- ion—from aluminum or sodium borohydride, or a co-enzyme (NADH) from L and D lactate dehydrogenases—pyruvic acid produces two stereoisomers of lactic acid, L and D. The first, 'clockwise', form is mainly of bacterial origin and the second, 'counter-clockwise', mainly originates from yeasts.

The activated, enolic form of the same acid, phosphoenol pyruvate (Figure 1.2), adds a nucleophile to carbon dioxide, producing oxaloacetic acid, a precursor by transamination of aspartic acid.

The enzymic decarboxylation of pyruvic acid, assisted by thiamin pyrophosphate (TPP) or vitamin B1, produces ethanal, which is reduced

Table 1.2. The main acids produced during fermentation



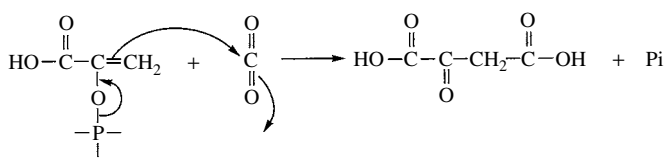


Fig. 1.2. Biosynthesis of oxaloacetic acid from phosphophenolpyruvic acid

Table 1.3. State of salification of the main inorganic and organic acids (Ribéreau-Gayon *et al.*, 1972)

Category	Name	pK_a	Form in wine
Strong inorganic acids	Hydrochloric	Less than 1	Completely dissociated salts
	Sulfuric 1	Approx. 1	
	Sulfuric 2	1.6	
	Sulfurous 1	1.77	Bisulfite acid
	Phosphoric 1	1.96	Phosphate acid
Strongest organic acids	Salicylic	2.97	Acid functions partly neutralized and partly free (not highly dissociated)
	Tartaric 1	3.01	
	Citric 1	3.09	
	Malic 1	3.46	
	Formic	3.69	
	Lactic	3.81	
	Tartaric 2	4.05	
Weakest organic acids	Benzoic	4.16	Free acid functions (very little dissociated)
	Succinic 1	4.18	
	Citric 2	4.39	
	Acetic	4.73	
	Butyric	4.82	
	Propionic	4.85	
	Malic 2	5.05	
	Succinic 2	5.23	
	Citric 3	5.74	
Weak inorganic acids	Phosphoric 2	6.70	Free acid functions (almost entirely non-dissociated)
	Carbonic 1	6.52	
	Sulfurous 2	7.00	
	Hydrogen sulfide 1	7.24	
	Carbonic 2	10.22	
	Phosphoric 3	12.44	
Phenols	Polyphenols (tannin and coloring)	7–10	Free (non-dissociated)

to form ethanol during alcoholic fermentation. Its enzymic, microbial or even chemical oxidation produces acetic acid.

Another acid that develops during fermentation due to the action of yeast is succinic or 1-4-butanedioic acid. Concentrations in wine average 1 g/l. This acid is produced by all living organisms and is involved in the lipid metabolism and the Krebs cycle, in conjunction with fumaric acid. It is a di-acid with a high pK_a (Table 1.3). Succinic acid has an intensely bitter, salty taste that causes salivation and accentuates a wine's flavor and vinous character (Peynaud and Blouin, 1996).

Like succinic acid, citramalic or α-methylmalic acid, confused with citric acid in chromatography for many years, is of yeast origin.

In conclusion, it is apparent from this description that, independently of their origins, most of the main organic acids in must and wine consist of poly-functional molecules, and many are hydroxy acids. These two radicals give these acids polar and hydrophilic characteristics. As a result, they are soluble in water, and even in dilute alcohol solutions, such as wine. Their polyfunctional character is also responsible for the chemical reactivity that enables them to develop over time as wine ages. In this connection, results obtained by monitoring ethyl lactate levels in Champagne for 2 years after malolactic fermentation are highly convincing. Indeed, after 2 years aging on the lees, concentrations reach 2 g/l and then decrease. The degree of acidity, indicated by their pK_a values,

controls the extent to which these acids are present in partial salt form in wine (Table 1.3).

A final property of the majority of organic acids in wine is that they have one or more asymmetrical carbons. This is characteristic of biologically significant molecules.

1.3 DIFFERENT TYPES OF ACIDITY

The fact that enologists need to distinguish between total acidity, pH and volatile acidity demonstrates the importance of the concept of acidity in wine. This is due to the different organoleptic effects of these three types of acidity. Indeed, in any professional tasting, the total acidity, pH and volatile acidity of the wine samples are always specified, together with the alcohol and residual sugar contents.

The importance of total acidity is obvious in connection with flavor balance:

$$\text{sweet taste (sugars, alcohols)} \rightleftharpoons \text{acid taste (organic and inorganic acids)} + \text{bitter taste (phenols)}$$

Looking at this balance, it is understandable that dry white wines have a higher total acidity than red wines, where phenols combine with acids to balance the sweet taste of the alcohols. Volatile acidity indicates possible microbial spoilage.

1.3.1 Total Acidity

Total acidity in must or wine, also known as 'titratable acidity', is determined by neutralization, using a sodium hydroxide solution of known normality. The end point of the assay is still often determined by means of a colored reagent, such as bromothymol blue, which changes color at pH 7, or phenolphthalein, which changes color at pH 9. Using one colored reagent to define the end point of the assay rather than the other is a matter of choice. It is also perfectly conventional to use a pH meter and stop the total acidity assay of a wine at pH 7, and, indeed, this is mandatory in official analyses. At this pH, the conversion into salts of the second acid function of the di-acids (malic and succinic) is not completed, while the neutralization of the phenol functions starts at pH 9.

The total acidity of must or wine takes into account all types of acids, i.e. inorganic acids such as phosphoric acid, organic acids including the main types described above, as well as amino acids whose contribution to titratable acidity is not very well known. The contribution of each type of acid to total acidity is determined by its strength, which defines its state of dissociation, as well as the degree to which it has combined to form salts. Among the organic acids, tartaric acid is mainly present in must and wine as monopotassium acid salt, which still contributes towards total acidity. It should, however, be noted that must (an aqueous medium) and wine (a dilute alcohol medium), with the same acid composition and thus the same total acidity, do not have the same titration curve and, consequently, their acid–alkaline buffer capacity is different.

Even using the latest techniques, it is difficult to predict the total acidity of a wine on the basis of the acidity of the must from which it is made, for a number of reasons.

Part of the original fruit acids may be consumed by yeasts and, especially, bacteria (see 'malolactic fermentation'). On the other hand, yeasts and bacteria produce acids, e.g. succinic and lactic acids. Furthermore, acid salts become less soluble as a result of the increase in alcohol content. This is the case, in particular, of the monopotassium form of tartaric acid, which causes a decrease in total acidity on crystallization, as potassium bitartrate still has a carboxylic acid function.

In calculating total acidity, a correction should be made to allow for the acidity contributed by sulfur dioxide and carbon dioxide. Sulfuric acid is much stronger ($pK_{a_1} = 1.77$) than carbonic acid ($pK_{a_1} = 6.6$).

In fact, high concentrations of carbon dioxide tend to lead to overestimation of total acidity, especially in slightly sparkling wines, and even more so in sparkling wines. This is also true

of young wines, which always have a high CO_2 content just after fermentation.

Wines must, therefore, be degassed prior to analyses of both total and volatile acidity.

1.3.2 Volatile Acidity

Volatile acidity in wine is considered to be a highly important physicochemical parameter, to be monitored by analysis throughout the winemaking process. Although it is an integral part of total acidity, volatile acidity is clearly considered separately, even if it only represents a small fraction in quantitative terms.

On the other hand, from a qualitative standpoint, this value has always been, quite justifiably, linked to quality. Indeed, when an enologist tastes a wine and decides there is excessive volatile acidity, this derogatory assessment has a negative effect on the wine's value. This organoleptic characteristic is related to an abnormally high concentration of acetic acid, in particular, as well as a few homologous carboxylic acids. These compounds are distilled when wine is evaporated. Those which, on the contrary, remain in the residue constitute fixed acidity.

Volatile acidity in wine consists of free and combined forms of volatile acids. This explains why the official assay method for volatile acidity, by steam distillation, requires combined fractions to be rendered free and volatile by acidifying the wine with tartaric acid (approximately 0.5 g per 20 ml). Tartaric acid is stronger than the volatile acids, so it displaces them from their salts.

In France, both total and volatile acidity are usually expressed in g/l of sulfuric acid. An *appellation d'origine contrôlée* wine is said to be 'of commercial quality' if volatile acidity does not exceed 0.9 g/l of H_2SO_4, 1.35 g/l of tartaric acid or 1.1 g/l of acetic acid. Acetic acid, the principal component of volatile acidity, is mainly formed during fermentation.

Alcoholic fermentation of grapes normally leads to the formation of 0.2–0.3 g/l of H_2SO_4 of volatile acidity in the corresponding wine. The presence of oxygen always promotes the formation of acetic acid. Thus, this acid is formed both at the beginning of alcoholic fermentation and towards the end, when the process slows down. In the same way, an increase in volatile acidity of 0.1–0.2 g/l of H_2SO_4 is observed during malolactic fermentation. Work by Chauvet and Brechot (1982) established that acetic acid was formed during malolactic fermentation due to the breakdown of citric acid by lactic bacteria.

Abnormally high volatile acidity levels, however, are due to the breakdown of residual sugars, tartaric acid and glycerol by anaerobic lactic bacteria. Aerobic acetic bacteria also produce acetic acid by oxidizing ethanol.

Finally, acescence in wine is linked to the presence of ethyl acetate, the ethyl ester of acetic acid, formed by the metabolism of aerobic acetic bacteria (Section 2.5.1).

1.3.3 Fixed Acidity

The fixed acidity content of a wine is obtained by subtracting volatile acidity from total acidity. Total acidity represents all of the free acid functions and volatile acidity includes the free and combined volatile acid functions. Strictly speaking, therefore, fixed acidity represents the free fixed acid functions plus the combined volatile acid functions.

When fixed acidity is analyzed, there is a legal obligation to correct for sulfur dioxide and carbon dioxide. In practice, these two molecules have a similar effect on total acidity and volatile acidity, so the difference between total acidity and volatile acidity is approximately the same, with or without correction (Ribéreau-Gayon *et al*., 1982).

1.4 THE CONCEPT OF pH AND ITS APPLICATIONS

1.4.1 Definition

The concept of pH often appears to be an abstract, theoretical concept, defined mathematically as log subscript ten of the concentration of hydroxonium ions in an electrically conductive solution, such as must or wine:

$$pH = -\log_{10}[H_3O^+]$$

Furthermore, the expression of pH shows that it is an abstract measure with no units, i.e. with no apparent concrete physical significance.

The concepts of total or volatile acidity seem to be easier to understand, as they are measured in milliliters of sodium hydroxide and expressed in g/l of sulfuric or tartaric acid. This is rather paradoxical, as the total acidity in a wine is, in fact, a complex function with several variables, unlike pH which refers to only one variable, the true concentration of hydroxonium ions in must and wine.

The abstract character generally attributed to pH is even less justified as this physicochemical parameter is based on the dissociation equilibrium of the various acids, AH, in wine, at fixed temperature and pressure, as shown below:

$$AH + H_2O \rightleftharpoons A^- + H_3{}^+O$$

The emission of $H_3{}^+O$ ions defines the acidity of the AH molecule. Dissociation depends on the value of the equilibrium constant, K_a, of the acid:

$$K_a = \frac{[A^-][H_3{}^+O]}{[AH]} \qquad (1.1)$$

To the credit of the concept of pH, otherwise known as true acidity, it should be added that its value fairly accurately matches the impressions due to acidity frequently described as 'freshness' or even 'greenness' and 'thinness', especially in white wines.

A wine's pH is measured using a pH meter equipped with a glass electrode after calibration with two buffer solutions. It is vital to check the temperature.

The pH values of wines range from 2.8 to 4.0. It is surprising to find such low, non-physiological values in a biological, fermentation medium such as wine. Indeed, life is only possible thanks to enzymes in living cells, and the optimum activity of the vast majority of enzymes occurs at much higher intra-cellular pH values, close to neutral, rather than those prevailing in extra-cellular media, i.e. must and wine. This provides some insight into the role of cell membranes and their ATPases in regulating proton input and output.

On the other hand, it is a good thing that wines have such low pH values, as this enhances their microbiological and physicochemical stability. Low pH hinders the development of microorganisms, while increasing the antiseptic fraction of sulfur dioxide. The influence of pH on physicochemical stability is due to its effect on the solubility of tartrates, in particular potassium bitartrate but, above all, calcium tartrate and the double salt calcium tartromalate.

Ferric casse is also affected by pH. Indeed, iron has a degree of oxidation of three and produces soluble complexes with molecules such as citric acid. These complexes are destabilized by increasing pH to produce insoluble salts, such as ferric phosphates (see 'white casse') or even ferric hydroxide, $Fe(OH)_3$.

1.4.2 Expression of pH in Wine

Wines are mixtures of weak acids, combined to form salts to a greater or lesser extent according to their pK_a (Table 1.3). The proportion of salts also depends on geographical origin, grape variety, the way the vines are trained, and the types of winepress and winemaking methods used.

Due to their composition, musts and wines are acidobasic 'buffer' solutions, i.e. a modification in their chemical composition produces only a limited variation in pH. This explains the relatively small variations in the pH of must during alcoholic and malolactic fermentation.

The pH of a solution containing a weak monoprotic acid and its strong basic salt proves the Anderson Hasselbach equation:

$$\begin{aligned} pH &= pK_a + \log \frac{[\text{salt formed}]}{[\text{remaining acid}]} \\ &= pK_a + \log \frac{[A^-]}{[AH]} \end{aligned} \qquad (1.2)$$

This equation is applicable to must and wine, where the strongest acids are di-acids. It is an approximation, assuming the additivity of the acidity contributed by each acid to the total. The application of Eqn (1.2) also makes the 'simplifying' assumption that the degree to which the acids are combined in salts is independent.

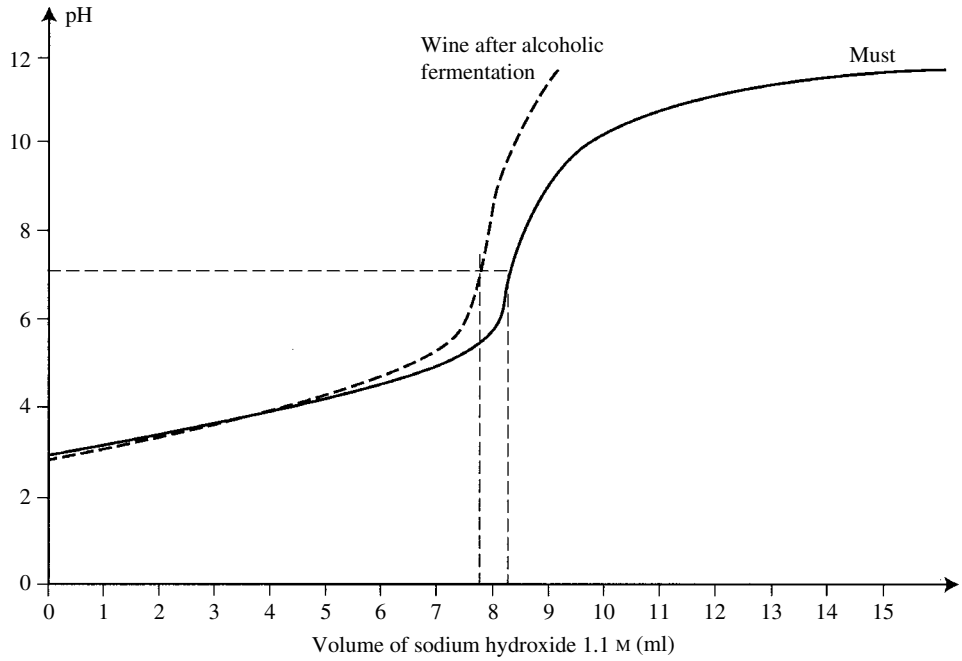


Fig. 1.3. Comparison of the titration curves of a must and the corresponding wine

These assumptions are currently being challenged. Indeed, recent research has shown that organic acids react among themselves, as well as with amino acids (Dartiguenave *et al.*, 2000).

Comparison (Table 1.3) of the pK_a of tartaric (3.01), malic (3.46), lactic (3.81) and succinic (4.18) acids leads to the conclusion that tartaric acid is the 'strongest', so it will take priority in forming salts, displacing, at least partially, the weaker acids. In reality, all of the acids interact. Experimental proof of this is given by the neutralization curve of a must, or the corresponding wine, obtained using sodium or potassium hydroxide (Figure 1.3). These curves have no inflection points corresponding to the pH of the pK of the various acids, as there is at least partial overlapping of the maximum 'buffer' zones (p$K_a \pm 1$). Thus, the neutralization curves are quasi-linear for pH values ranging from 10 to 90% neutralized acidity, so they indicate a constant buffer capacity in this zone. From a more quantitative standpoint, a comparison of the neutralization curves of must and the corresponding wine shows that the total acidity, assessed by the volume of sodium hydroxide added to obtain pH 7, differs by 0.55 meq. In the example described above, both must and wine samples contained 50 ml and the total acidity of the wine was 11 meq/l (0.54 g/l of H_2SO_4) lower than that of the must. This drop in total acidity in wine may be attributed to a slight consumption of malic acid by the yeast during alcoholic fermentation, as well as a partial precipitation of potassium bitartrate.

The slope of the linear segment of the two neutralization curves differs noticeably. The curve corresponding to the must has a gentler slope, showing that it has a greater buffer capacity than the wine.

The next paragraph gives an in-depth description of this important physicochemical parameter of wine.

1.4.3 The "Buffer" Capacity of Musts and Wines

Wines' acidobasic buffer capacity is largely responsible for their physicochemical and microbiological stability, as well as their flavor balance.

For example, the length of time a wine leaves a fresh impression on the palate is directly related to the salification of acids by alkaline proteins in saliva, i.e. the expression of the buffer phenomenon and its capacity. On the contrary, a wine that tastes "flat" has a low buffer capacity, but this does not necessarily mean that it has a low acidity level. At a given total acidity level, buffer capacity varies according to the composition and type of acids present. This point will be developed later in this chapter.

In a particular year, a must's total acidity and acid composition depend mainly on geography, soil conditions, and climate, including soil humidity and permeability, as well as rainfall patterns, and, above all, temperature. Temperature determines the respiration rate, i.e. the combustion of tartaric and, especially, malic acid in grape flesh cells. The predominance of malic acid in must from cool-climate vineyards is directly related to temperature, while malic acid is eliminated from grapes in hotter regions by combustion.

Independently of climate, grape growers and winemakers have some control over total acidity and even the acid composition of the grape juice during ripening. Leaf-thinning and trimming the vine shoots restrict biosynthesis and, above all, combustion, by reducing the greenhouse effect of the leaf canopy. Another way of controlling total acidity levels is by choosing the harvesting date. Grapes intended for champagne or other sparkling wines must be picked at the correct level of technological ripeness to produce must with a total acidity of 9–10 g/l H_2SO_4. This acidity level is necessary to maintain the wines' freshness and, especially, to minimize color leaching from the red-wine grape varieties, Pinot Noir and Pinot Meunier, used in champagne. At this stage in the ripening process, the grape skins are much less fragile than they are when completely ripe. The last method for controlling the total acidity of must is by taking great care in pressing the grapes and keeping the juice from each pressing separate (Volume 1, Section 14.3.2). In champagne, the *cuvée* corresponds to cell sap from the mid-part of the flesh, furthest from the skin and seeds, where it has the highest sugar and acidity levels.

Once the grapes have been pressed, winemakers have other means of raising or lowering the acidity of a must or wine. It may be necessary to acidify "flat" white wines by adding tartaric acid after malolactic fermentation in years when the grapes have a high malic acid content. This is mainly the case in cool-climate vineyards, where the malic acid is not consumed during ripening. The disadvantage is that it causes an imbalance in the remaining total acidity, which, then, consists exclusively of a di-acid, tartaric acid, and its monopotassium salt.

One method that is little-known, or at least rarely used to avoid this total acidity imbalance, consists of partially or completely eliminating the malic acid by chemical means, using a mixture of calcium tartrate and calcium carbonate. This method precipitates the double calcium salt, tartromalate, (Section 1.4.4, Figure 1.9) and is a very flexible process. When the malic acid is partially eliminated, the wine has a buffer capacity based on those of both tartaric and malic acids, and not just on that of the former. Tartrate buffer capacity is less stable over time, as it decreases due to the precipitation of monopotassium and calcium salts during aging, whereas the malic acid salts are much more soluble.

Another advantage of partial elimination of malic acid followed by the addition of tartrate over malolactic fermentation is that, due to the low acidification rate, it does not produce wines with too low a pH, which can be responsible for difficult or stuck second fermentation in the bottle during the champagne process, leaving residual sugar in the wine.

Standard acidification and deacidification methods are aimed solely at changing total acidity levels, with no concern for the impact on pH and even less for the buffer capacity of the wine, with all the unfortunate consequences this may have on flavor and aging potential.

This is certainly due to the lack of awareness of the importance of the acid-alkali buffer capacity in winemaking. Changes in the acid-alkaline characteristics of a wine require knowledge of not only its total acidity and real acidity (pH), but also of its buffer capacity. These three parameters

may be measured using a pH meter. Few articles in the literature deal with the buffer capacity of wine: Genevois and Ribéreau-Gayon, 1935; Vergnes, 1940; Hochli, 1997; and Dartiguenave *et al*., 2000. This lack of knowledge is probably related to the fact that buffer capacity cannot be measured directly, but requires recordings of 4 or 5 points on a neutralization curve (Figure 1.3), and this is not one of the regular analyses carried out by winemakers.

It is now possible to automate plotting a neutralization curve, with access to the wine's initial pH and total acidity, so measuring buffer capacity at the main stages in winemaking should become a routine.

Mathematically and geometrically, buffer capacity, β, is deduced from the Henderson-Hasselbach equation [equation (1.2), (Section 1.4.2)]. Buffer capacity is defined by equation (1.3).

$$\beta = \frac{\Delta B}{\delta pH} \tag{1.3}$$

where ΔB is the strong base equivalent number that causes an increase in pH equal to ΔpH. Buffer capacity is a way of assessing buffer strength. For an organic acid alone, with its salt in solution, it may be defined as the pH interval in which the buffer effect is optimum [equation (1.4)].

$$pH = pK_a \pm 1 \tag{1.4}$$

Buffer capacity is normally defined in relation to a strong base, but it could clearly be defined in the same way in relation to a strong acid. In this case, the $pH = f$ (strong acid) function decreases and its β differential is negative, i.e.:

$$B = -\frac{\Delta(\text{acid})}{\Delta pH}$$

Strictly speaking, buffer capacity is obtained from the differential of the Henderson-Hasselbach expression, i.e. from the following derived formula:

$$pH = pK_a + \frac{1}{2.303} \cdot \text{Log}_e[A^-] - \frac{1}{2.303} \cdot \text{Log}_e[HA]$$

as only the Naperian logarithm is geometrically significant, and provides access to the slope of the titration curve around its pK_a (Figure 1.4).

Both sides of the equation are then differentiated, as follows:

$$dpH = \frac{1}{2.303} \cdot \frac{d[A^-]}{[A^-]} - \frac{1}{2.303} \cdot \frac{d[HA]}{[HA]}$$

Making the assumption that the quantity of strong base added, d[B], generates the same variation in acidity combined as salts, $d[A^-]$, and leads to an equal decrease in free acidity d[HA], per unit, now

$$d[B] = d[A^-] = d[HA]$$

the differential equation for pH is then:

$$dpH = \frac{1}{2.303} \cdot \frac{d[B]}{[A^-]} + \frac{1}{2.303} \cdot \frac{d[B]}{[HA]} = \frac{1}{2.303} \cdot d[B] \left\{ \frac{1}{[A^-]} + \frac{1}{[HA]} \right\}$$

or,

$$dpH = \frac{d[B]}{2.303} \cdot \left\{ \frac{[HA] + [A^-]}{[A^-] \cdot [HA]} \right\}$$

Dividing both sides of the equation by d[B] gives the reverse of equation (1.3), defining the buffer capacity. Equations (1.2) and (1.3) have been defined for monoproteic acids, but are also applicable as an initial approximation to di-acids, such as tartaric and malic acids.

Theoretically, variations ΔB and ΔpH must be infinitely small, as the value of the $\Delta B/\Delta pH$ ratio at a fixed pH corresponds geometrically to the tangent on each point on the titration curve (Figure 1.4). More practically, buffer capacity can be defined as the number of strong base equivalents required to cause an increase in pH of 1 unit per liter of must or wine. It is even more practical to calculate smaller pH variations in much smaller samples (e.g. 30 ml). Figure 1.4 clearly shows the difference in buffer capacity of a model solution between pH 3 and 4, as well as between pH 4 and 5.

This raises the issue of the pH and pK_a at which buffer capacity should be assessed. Champagnol (1986) suggested that pH should be taken as the mean of the pK_a of the organic acids in the must

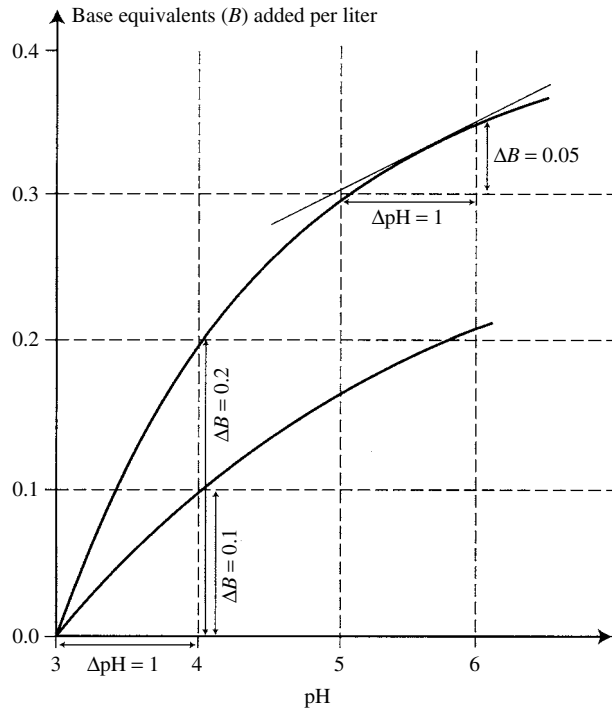


Fig. 1.4. Determining the buffer capacity β from the titration curves of two model buffer solutions

or wine, i.e. the mean pK_a of tartaric and malic acids in must and tartaric and lactic acids in wine that has completed malolactic fermentation.

This convention is justified by its convenience, provided that (Section 1.4.2) there are no sudden inflection points in the neutralization curve of the must or wine at the pK_a of the organic acids present, as their buffer capacities overlap, at least partially. In addition to these somewhat theoretical considerations, there are also some more practical issues. An aqueous solution of sodium hydroxide is used to determine the titration curve of a must or wine, in order to measure total acidity and buffer capacity. Sodium, rather than potassium, hydroxide is used as the sodium salts of tartaric acid are soluble, while potassium bitartrate would be likely to precipitate out during titration. It is, however, questionable to use the same aqueous sodium hydroxide solution, which is a dilute alcohol solution, for both must and wine.

Strictly speaking, a sodium hydroxide solution in dilute alcohol should be used for wine to avoid modifying the alcohol content and, consequently, the dielectric constant, and, thus, the dissociation of the acids in the solution during the assay procedure. It has recently been demonstrated (Dartiguenave *et al.*, 2000) that the buffer capacities of organic acids, singly (Table 1.4 and 1.5) or in binary (Table 1.6) and tertiary (Table 1.7) combinations, are different in water and 11% dilute alcohol solution. However, if the solvent containing the organic acids and the sodium hydroxide is the same, there is a close linear correlation between the buffer capacity and the acid concentrations (Table 1.4).

Table 1.5 shows the values (meq/l) calculated from the regression line of the buffer capacities for acid concentrations varying from 1–6 g/l in water and 11% dilute alcohol solution. The buffer capacity of each acid alone in dilute alcohol solution was lower than in water. Furthermore, the buffer capacity of a 4-carbon organic acid varied more as the number of alcohol functions increased (Table 1.8). Thus, the variation in buffer capacity of malic acid, a di-acid with one alcohol function,

Table 1.4. Equations for calculating buffer capacity (meq/l) depending on the concentration (mM/l) of the organic acid in water or dilute alcohol solution (11% vol.) between 0 and 40 mM/l. (Dartiguenave *et al.*, 2000)

Solvent	Water	Dilute alcohol solution
Tartaric acid	$Y = 0.71\ x + 0.29$; $R^2 = 1$	$Y = 0.60\ x + 1.33$; $R^2 = 1$
Malic acid	$Y = 0.56\ x + 0.43$; $R = 0.998$	$Y = 0.47\ x + 0.33$; $R^2 = 0.987$
Succinic acid	$Y = 0.56\ x - 1.38.10^{-2}$; $R^2 = 0.993$	$Y = 0.53\ x + 0.52$; $R^2 = 0.995$
Citric acid	$Y = 0.57\ x + 0.73$; $R^2 = 1$	$Y = 0.51\ x + 0.62$; $R^2 = 1$

Table 1.5. Buffer capacity (meq/l) depending on the concentration (g/l) of organic acid in water and dilute alcohol solution. (Dartiguenave *et al.*, 2000)

Acid concentration and type of medium		Tartaric acid	Malic acid	Succinic acid	Citric acid
1 g/l	Water	5.0	4.6	4.7	3.7
	Dilute alcohol	5.3	3.8	4.0	3.5
2 g/l	Water	9.7	8.8	9.5	6.7
	Dilute alcohol	9.3	7.3	9.4	5.9
4 g/l	Water	16.4	17.1	19.0	12.6
	Dilute alcohol	14.9	14.3	17.5	11.3
6 g/l	Water	28.7	25.5	28.4	18.5
	Dilute alcohol	25.3	21.3	26.4	16.6

in a dilute alcohol medium, was 1.4 meq/l higher than that of succinic acid. When the hydroxyacid had two alcohol functions, the increase was as high as 5.3 meq/l (17.7%), e.g. between tartaric and malic acids, even if the buffer capacities of the three acids were lower than in water.

However, the fact that the buffer capacities of binary (Table 1.6) or tertiary (Table 1.7) combinations of acids in a dilute alcohol medium were higher than those measured in water was certainly unexpected. This effect was particularly marked when citric acid was included, and reached spectacular proportions in a T.M.C. blend (Table 1.7), where the buffer capacity in dilute alcohol solution was 2.3 times higher than that in water.

These findings indicate that the acids interact among themselves and with alcohol, compensating for the decrease in buffer capacity of each individual acid when must (an aqueous solution) is converted into wine (a dilute alcohol solution). From a purely practical standpoint, the use of citric acid to acidify dosage liqueur for bottle-fermented sparkling wines has the doubly positive effect of enhancing the wine's aging potential, while maintaining its freshness on the palate.

Table 1.6. Demonstration of interactions between organic acids and the effect of alcohol on the buffer capacity of binary combinations (Dartiguenave *et al.*, 2000)

Medium	Buffer capacity (meq/l)	Composition of equimolar mixes of 2 acids Total acid concentration (40 mM/l)		
		Tartaric acid Malic acid	Tartaric acid Succinic acid	Tartaric acid Citric acid
Water	Experimental value	21	20	23.5
	Calculated value	25.7	25.7	26.3
	Difference (Calc. − Exp.)	4.7	5.7	2.8
EtOH (11% vol.)	Experimental value	18.3	20.1	29
	Calculated value	24	23.3	24
	Difference (Calc. − Exp.)	5.7	3.2	−5
Effect of ethanol	(EtOH − H_2O) Exp.	−2.7	0.1	5.5

Table 1.7. Demonstration of interactions between organic acids and the effect of alcohol on the buffer capacity of tertiary combinations (Dartiguenave *et al.*, 2000)

Medium	Buffer capacity (meq/l)	Composition of equimolar mixes of 3 acids (13.3 mM/l) Total acid concentration (40 mM/l)	
		Tartaric acid Malic acid Succinic acid	Tartaric acid Malic acid Citric acid
Water	Experimental value	9.4	11.6
	Calculated value	25.4	25.5
	Difference (Calc. − Exp.)	16.0	13.9
EtOH (11% vol.)	Experimental value	21.7	26.4
	Calculated value	22.8	23.2
	Difference (Calc. − Exp.)	1.1	−3.2
Effect of ethanol	(EtOH − H_2O) Exp.	12.3	14.8

Table 1.8. Effect of hydroxyl groups in the structure of the 4-carbon di-acid on buffer capacity (meq/l) (Dartiguenave *et al.*, 2000)

Medium	1 hydroxyl group			2 hydroxyl groups		
	Malic acid	Succinic acid	Δ (Mal.− Suc.)	Tartaric acid	Malic acid	Δ (Tart.− Mal.)
Water	23.8	23.4	0.4	29	23.8	5.2
11% vol. dilute alcohol solution	22,0	20.6	1.4	25.9	22	3.9

Table 1.9. Changes in the buffer capacity of must from different pressings of Chardonnay grapes at various stages in the winemaking process. (Buffer capacity is expressed in meq/l). (Dartiguenave, 1998)

	Cuvée		Second pressing	
	1995	1996	1995	1996
Initial value of must	77.9	72.6	71.2	65.9
After alcoholic fermentation	60.7	63.6	57.5	ND
After malolactic fermentation	51.1	60.1	48.4	ND
After cold-stabilization	48.1	50.3	ND	42.4

Table 1.9 shows the changes in buffer capacity in successive pressings of a single batch of Chardonnay grapes from the 1995 and 1996 vintages, at the main stages in the winemaking process.

The demonstration of the effect of alcohol and interactions among organic acids (Table 1.6, 1.7, and 1.8) led researchers to investigate the precise contribution of each of the three main acids to a wine's buffer capacity, in order to determine whether other compounds were involved. The method consisted of completely deacidifying a wine by precipitating the double calcium tartromalate salt. After this deacidification, the champagne-base wine had a residual total acidity of only approximately 0.5 g/l H_2SO_4, whereas the buffer capacity was still 30% of the original value. This shows that organic acids are not the only compounds involved in buffer capacity, although they represent 90% of total acidity.

Among the many other compounds in must and wine, amino acids have been singled out for two reasons: (1) in champagne must and wine, the total concentration is always over 1 g/l and may even exceed 2 g/l, and (2) their at least bi-functional character gives them a double-buffer effect. They form salts with carboxylic acids via their ammonium group and can become associated with a non-dissociated acid function of an organic

acid via their carboxyl function, largely dissociated from wine pH, thus creating two buffer couples (Figure 1.5).

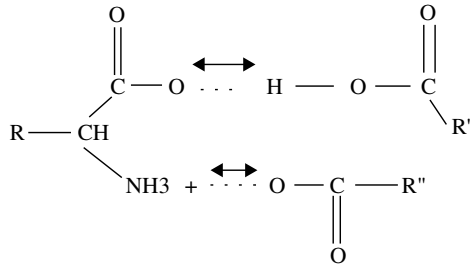


Fig. 1.5. Diagram of interactions between amino acids and organic acids that result in the buffer effect

An in-depth study of the interactions between amino acids and tartaric and malic acids focused on alanine, arginine, and proline, present in the highest concentrations in wine, as well as on amino acids with alcohol functions, i.e. serine and threonine (Dartiguenave *et al*., 2000).

The findings are presented in Figures 1.6 and 1.7. Hydrophobic amino acids like alanine were found to have only a minor effect, while amino acids with alcohol functions had a significant impact on the buffer capacity of an aqueous tartaric acid solution (40 mM/l). An increase of 0.6 meq/l was obtained by adding 6.7 mM/l alanine, while addition of as little as 1.9 mM/l produced an increase of 0.7 meq/l and addition of 4.1 mM/l resulted in a rise of 2.3 meq/l.

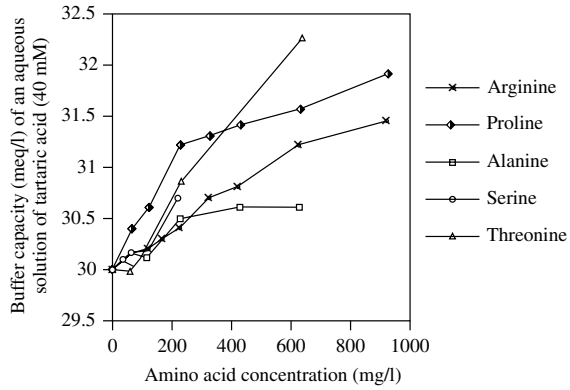


Fig. 1.6. Variations in the buffer capacity of an aqueous solution of tartaric acid (40 mM) in the presence of several amino acids. (Dartiguenave *et al*., 2000)

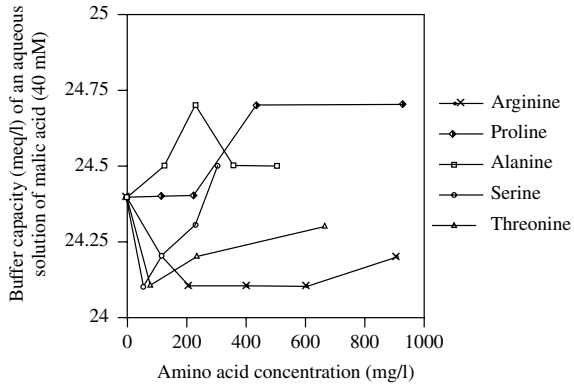


Fig. 1.7. Variations in the buffer capacity of an aqueous solution of malic acid (40 mM in the presence of several amino acids. (Dartiguenave *et al*., 2000))

The impact of amino acids with alcohol functions was even more spectacular in dilute alcohol solutions (11% by volume). With only 200 mg/l serine, there was a 1.8 meq/l increase in buffer capacity, compared to only 0.8 meq/l in water. It was also observed that adding 400 mg/l of each of the five amino acids led to a 10.4 meq/l (36.8%) increase in the buffer capacity of a dilute alcohol solution containing 40 mM/l tartaric acid.

It is surprising to note that, on the contrary, amino acids had no significant effect on the buffer capacity of a 40 mM/l malic acid solution (Figure 1.7).

All these observations highlight the role of the alcohol function, both in the solvent and the amino acids, in interactions with organic acids, particularly tartaric acid with its two alcohol functions.

The lack of interaction between amino acids and malic acid, both in water and dilute alcohol solution, can be interpreted as being due to the fact that it has one alcohol function, as compared to the two functions of tartaric acid. This factor is important for stabilizing interactions between organic acids and amino acids via hydrogen bonds (Figure 1.8).

1.4.4 Applying Buffer Capacity to the Acidification and Deacidification of Wine

The use of tartaric acid (known as 'tartrating') is permitted under European Community (EC) legislation, up to a maximum of 1.5 g/l in must and 2.5 g/l in wine. In the USA, acidification is permitted, using tartrates combined with gypsum ($CaSO_4$) (Gomez-Benitez, 1993). This practice seems justified if the buffer capacity expression (Eqn 1.3) is considered. The addition of tartaric acid (HA) increases the buffer capacity by increasing the numerator of Eqn (1.3) more than the denominator. However, the addition of $CaSO_4$ leads to the precipitation of calcium tartrate, as this salt is relatively insoluble. This reduces the buffer capacity and, as a result, ensures that acidification will be more effective.

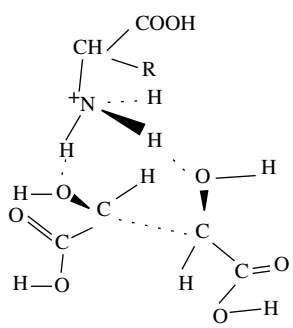


Fig. 1.8. Assumed structure of interactions between tartaric acid and amino acids. (Dartiguenave *et al.*, 2000)

Whenever tartrating is carried out, the effect on the pH of the medium must also be taken into account in calculating the desired increase in total acidity of the must or wine. Unfortunately, however, there is no simple relationship between total acidity and true acidity.

An increase in true acidity, i.e. a decrease in pH, may occur during bitartrate stabilization, in spite of the decrease in total acidity caused by this process. This may also occur when must and, in particular, wine is tartrated, due to the crystallization of potassium bitartrate, which becomes less soluble in the presence of alcohol.

The major difficulty in tartrating is predicting the decrease in pH of the must or wine. Indeed, it is important that this decrease in pH should not be incompatible with the wine's organoleptic qualities, or with a second alcoholic fermentation in the case of sparkling wines. To our knowledge, there is currently no reliable model capable of accurately predicting the drop in pH for a given level of tartrating. The problem is not simple, as it depends on a number of parameters. In order to achieve the required acidification of a wine, it is necessary to know the ratio of the initial concentrations of tartaric acid and potassium, i.e. crystallizable potassium bitartrate.

It is also necessary to know the wine's acido-basic buffer capacity. Thus, in the case of wines from northerly regions, initially containing 6 g/l of malic acid after malolactic fermentation, tartrating may be necessary to correct an impression of 'flatness' on the palate. Great care must be taken in acidifying this type of wine, otherwise it may have

a final pH lower than 2.9, which certainly cures the 'flatness' but produces excessive dryness or even greenness. White wines made from red grape varieties may even take on some red color. The fact that wine has an acidobasic buffer capacity also makes deacidification possible.

Table 1.10 shows the values of the physicochemical parameters of the acidity in champagne-base wines, made from the *cuvée* or second pressing of Chardonnay grapes in the 1995 and 1996 vintages. They were acidified with 1 g/l and 1.5 g/l tartaric acid, respectively, after the must had been clarified.

Examination of the results shows that adding 100 g/hl to a *cuvée* must or wine only resulted in 10–15% acidification, corresponding to an increase in total acidity of approximately 0.5 g/l (H_2SO_4). Evaluating the acidification rate from the buffer capacity gave a similar result. The operation was even less effective when there was a high potassium level, and potassium bitartrate precipitated out when the tartaric acid was added.

Adding the maximum permitted dose of tartaric acid (150 g/hl) to second pressing must or wine was apparently more effective, as total acidity increased by 35% and pH decreased significantly (−0.14), producing a positive impact on wine stability and flavor. The effect on pH of acidifying *cuvée* wines shows the limitations of adding tartaric acid, and there may also be problems with the second fermentation in bottle, sometimes resulting in "hard" wines with a metallic mouth feel.

It would be possible to avoid these negative aspects of acidification by using L(-)lactic acid. This is listed as a food additive (E270) and meets the requirements of both the Food chemical Codex and the European Pharmacopoeia. Lactic acid is commonly used in the food and beverage industry, particularly as a substitute for citric acid in carbonated soft drinks, and is even added to some South African wines.

Its advantages compared to tartaric acid are the pK_a of 3.81 (tartaric acid: 3.01), and the fact that both its potassium and calcium salts are soluble. This enhances the acidification rate while minimizing the decrease in pH. Finally, lactic acid is microbiologically stable, unlike tartaric, malic, and citric acids. Until recently, one disadvantage of industrial lactic acid was a rather nauseating odor, which justified its prohibition in winemaking. The lactic acid now produced by fermenting sugar industry residues with selected bacteria no longer has this odor.

Current production quality, combined with low prices, should make it possible to allow experimentation in the near future, and, perhaps, even a lifting of the current ban on the use of lactic acid in winemaking.

The additives authorized for deacidifying wines are potassium bicarbonate ($KHCO_3$) and calcium carbonate ($CaCO_3$). They both form insoluble salts with tartaric acid and the corresponding acidity is eliminated in the form of carbonic acid (H_2CO_3) which breaks down into CO_2 and H_2O. A comparison of the molecular weights of these two salts and the stoichiometry of the neutralization reactions leads to the conclusion that, in general, one gram of $KHCO_3$(PM = 100) added to one liter of wine produces a drop in acidity of 0.49 g/l, expressed in grams of H_2SO_4(PM = 98). Adding one gram of $CaCO_3$(PM = 100) to a liter of wine produces a decrease in acidity equal to its own weight (exactly 0.98 g/l), expressed in grams of sulfuric acid.

In fact, this is a rather simplistic explanation, as it disregards the side-effects of the precipitation of insoluble potassium bitartrate salts and, especially, calcium tartrate, on total acidity as well as pH. These side-effects of deacidification are only fully expressed in wines with a pH of 3.6 or lower after cold stabilization to remove tartrates. It is obvious from the pH expression (Eqn 1.2) that, paradoxically, after removal of the precipitated tartrates, deacidification using $CaCO_3$ and, more particularly, $KHCO_3$ is found to have reduced the [salt]/[acid] ratio, i.e. increased true acidity. Fortunately, the increase in pH observed during neutralization is not totally reversed.

According to the results described by Usseglio-Tomasset (1989), a comparison of the deacidifying capacities of potassium bicarbonate and calcium carbonate shows that, in wine, the maximum deacidifying capacity of the calcium salt is only 85% of that of the potassium salt. Consequently, to bring a wine to the desired pH, a larger

Table 1.10. Composition of Chardonnay wines after tartaric stabilization, depending on the time of acidification (addition to must or wine after malolactic fermentation). *Cuvées* were acidified with 1 g/l tartaric acid and second pressings with 1.5 g/l. (Dartiguenave, 1998)

	Cuvée						Second pressing		
	1995			1996			1996		
	Control	Acidified must	Acidified wine	Control	Acidified must	Acidified wine	Control	Acidified must	Acidified wine
pH	3.06	2.97	2.97	3.06	2.99	2.97	3.18	3.04	3.00
Total acidity (g/l, H_2SO_4)	5.2	6.0	5.6	5.4	5.9	5.8	4.1	4.9	5.0
Tartaric acid (g/l)	3.6	4.0	4.3	4.4	5.2	5.0	3.4	4.6	4.8
Malic acid (g/l)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Lactic acid (g/l)	4	4.3	4.4	4.2	4.1	4.1	3	3	2.7
Total nitrogen (mg/l)	274.7	221.9	271	251.6	280.3	289.8	245.9	250.4	254.4
Amino acids (mg/l)	1051.4	703.7	1322.6	1254.2	1422.7	1471.7	1177.5	1350.4	1145
Potassium (mg/l)	390	345	320	345	290	285	380	305	300
Calcium (mg/l)	71.5	90	79	60	64	61	50	55	48
Buffer capacity (NAOH, H_2O)	48.1	56.6	56.2	50.3	55.5	56.9	42.4	49.1	47.7
Buffer capacity (NAOH.EtOH 11% vol)	55.6	59.2	55.9	47.1	51.9	50.2	37.9	44.3	42