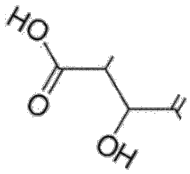

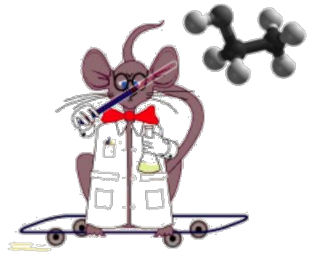

WINE CHEM 101 Part B

By Bob Peak

In last year's catalog and newsletter, we began a discussion of the chemistry of wine and winemaking—Wine Chem 101, Part A—with details about conversion of sugars to alcohol. (That article is still available at thebeveragepeople. com). At the end of the article, I credited wine acids for the "zing" in wine flavor that lifts it above ordinary bever-ages. So, in this issue, I will tackle that part of Wine Chem: Acid. The two major organic acid components of grapes and grape juice are tartaric and malic acids, usually starting at about a 50-50 ratio. Together, they create the low pH conditions that help make wine a stable beverage and provide the pleasant tartness we all associate with it. The combined range of these acids in fresh grape juice will usually fall between 3 and 15 grams per liter (or 0.3 to 1.5%). Although this wide range of acid levels—measured as TA or Titratable Acidity—can be seen around the world, most North Coast grape juice comes in between 0.4 and 0.7% TA, with about 0.65% preferred. There is also a trace of citric acid in grapes, but it is not a significant contributor to TA. Together, these acids are the "fixed" acids of grape juice, joined in some wines by lactic acid from malolactic fermentation. The term "fixed" is used to distinguish from the spoilage acids of wine, the volatile acids. Those acids—mostly acetic acid—are the products of vinegar fermenta-tion and will introduce unpleasant aromas to wine at very low levels.

Although malic and tartaric acids begin at near equal levels, it is tartaric that dominates the acid flavor profile in most wines. Like the other fixed acids, it belongs to a chemical class called the carboxylic acids. The structure can be represented as: HOOC-HCOH-HOCH-COOH

Those "H's" on each end of the molecule identify this particular acid as a dicarboxylic acid—there are two active "acid" locations (protons) on every molecule. That is twice as much available acid activity as in a like amount of a monocarboxylic acid. Like all the wine acids, tartaric is considered "weak" chemically. It has a native dissociation constant or natural pH level of 4.3 for the first proton and 3.0 for the second one. For an acid, the dissociation constant is written as pKa—the negative logarithm (p) of the constant (K) for dissociation of the acid (a).

Tartaric acid passes through fermen-tation and aging mostly unchanged. The main exception is cold stabili-zation. That is a process by which wine during aging is allowed—or induced—to get very cold (near freez-ing). The presence of much higher alcohol in wine, as compared with juice, reduces the solubility of tartaric acid. The tartaric acid combines with potassium that is naturally present in the wine, cold temperatures fur-ther drive down that solubility, and crystals of potassium bitartrate (KHT) appear on the interior surfaces of the carboy, tank, or barrel. If your wine is too tart when you make it, you can utilize this process to remove some of the tartaric acid and lower the overall acidity, mellowing the flavor. You may occasionally find a commercial wine that has not been adequately cold sta-bilized. In white wines, after chilling, it may look like there are crystals of glass on the bottom of the bottle. In reds, the crystals usually stick to the cork and are dyed red by the wine. In either case, potassium bitartrate is non-toxic and harmless, although it feels a little gritty on the tongue if you accidentally drink the dregs of the last glass from the bottle!

The other large acid component of grape juice—malic acid—is much more reactive than tartaric during winemaking. Like tartaric, it is a di-carboxylic acid, this time with pKa's of 5.1 and 3.4. These higher num-bers indicate that malic is an even weaker acid than tartaric. Interest-ingly, though, to human taste malic acid is much sharper than tartaric. If you have teenage children (or have recently been a teenager), you may be aware of Warheads candies or Jones Green Apple soda. Both producers use malic acid for extremely sour food-grade tastes. In nature, malic is the acid of apples and gets its name from malus, the genus name for apple trees.

In most whites and rosés, the malic acid proceeds unchanged through fermentation and is present in the crisp "appley" flavor you sometimes get in these wines. With malic acid accounting for about half of the 0.4 to 0.7% TA, we can express that 0.2 to 0.35% instead as 2,000 to 3,500 milligrams per liter (mg/L) or ppm (parts per million). In wine styles other than these crisp ones, those malic acid levels would taste un-pleasantly sour.

For most red wines, as well as big whites like Chardonnay, the malic acid concentration is deliberately lowered during fermentation. The process, malolactic fermentation, is carried out by bacteria, either with or after primary fermentation. The bacteria—oenococcus oeni—convert each molecule of malic acid into a corresponding molecule of lactic acid. Favorable conditions for this fermenta-tion include:

Temperature 65 to 75 degrees F
pH above 3.2 (above 3.4 is even easier)
Alcohol below 14%
Total SO_2 below 30 ppm
Free SO_2 below 10 ppm

The safest way to carry out malolactic fermentation is after primary fermen-tation, although the conditions for the bacteria are more favorable prior to completion. The safety factor enters because oenococcus oeni, in the pres-ence of sugar, can produce the volatile acids of vinegar mentioned above. But what about the chemistry?

The reaction is:

$C_4H_6O_5$ (malic acid)$\rightarrow C_3H_6O_3 + CO_2$ (lactic acid and carbon dioxide)

The process is generally considered complete when the residual malic acid level drops below about 30 ppm. At that level, most authorities consider it highly unlikely that spontaneous malolactic fermentation will restart after bottling. (If it did, the wine would turn fizzy and cloudy, also developing off aromas). It is important for home winemakers to note that this is just a “generally accepted” level for com-mercial wine and is not some absolute barrier. At 30 ppm, a wine that started with 2500 ppm will be 98.8% complete. If instead your wine has 35 or 40 ppm left, it is just a matter of having perhaps 1.3% remaining instead of 1.2%. That is not a very big difference to be con-cerned about. If you keep your wine under good cellar conditions and bottle with adequate SO_2, there is very little risk of spontaneous refermentation of a tiny amount of malic acid.

And what about that lactic acid? You now have just as much of that as you had malic acid to start. Lactic, however, is a monocarboxylic acid:

CH_3-HCOH-COOH

There is just one active proton at one end of the molecule. Since we get one lactic acid molecule for every malic molecule, but it only has half the ac-tive protons, it drops the malic acid contribution to TA by half. Effectively, the 0.2 to 0.35% goes to 0.1 to 0.18%. Furthermore, lactic acid has a much milder flavor than malic acid. In con-trast to apples, lactic acid is the acid of yogurt and cheese—smooth and creamy! The pKa is 3.08, keeping us in the general pH range of wine. If you submit juice or wine to a laboratory for a complete acid analysis, two more fixed acids may show up. As mentioned before, citric acid is a minor contributor to TA. In grapes affected by the “noble rot” botrytis, however, citric acid can be very high and may contribute to the racy flavors of some late-harvest wines. Succinic acid is also sometimes present as a fermentation product, but gener-ally at levels well below 0.1%.

So that’s it for the acids. But several times I have mentioned pH, which everybody knows is somehow related to acid.

I love talking about pH and can go on for hours about it. But this is all the column inches I could coax out of Editor Robyn this year, so you’ll have to wait until summer 2010 for Part C of Wine Chem 101: All About pH!