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How esters and aldehydes impact on key wine aromas

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Introduction

This article is one of a series which covers the fungal and bacterial origins of wine aromas. These articles detail esters, aldehydes, volatile fatty acids, volatile phenols, sulphurous compounds and higher alcohols. The old adage "one man's trash is another man's treasure", holds true with these compounds.

Russell Moss

A winemaker may make a Sauvignon blanc table wine within which they would like to have dominant aromas of grapefruit, gooseberry and passion-fruit and perceptible acetaldehyde would be viewed as a fault. However, another winemaker may wish to make a wine that emulates sherry, at which point maximising acetaldehyde production would be intrinsic to the style of the wine.

The same is also true with esters. A winemaker may wish to create a young wine that is similar to Beaujolais Nouveau or a fresh white wine that is meant for immediate sale. In these cases, the formation and retention of esters during fermentation will be critical to wine style. Another *vigneron* may wish to make a Pinotage table wine that has deep flavours of smoke, earth and a varied assortment of berries. In this case, the winemaker might view isoamyl acetate (an ester) as a fault and attempt to minimise its impact on their wine by controlling viticultural and winemaking practices which will influence this compound.

Esters

Esters are the class of volatile compounds that are responsible for a general “fruity” smell in wines. They are some of the most abundant aromatic compounds within wine (Pretorius & Lambrechts, 2000). Esters are found in grapes in small amounts, but most of the esters in wine are formed during fermentation or during wine ageing. Esters can be classified as either volatile esters (or neutral esters) and acid esters (or non-volatile esters). The neutral esters are produced through enzymatic reactions; acid esters are formed in simple hydrogen-ion-catalysed esterification (Margalit, 2004). This simple acid catalysed reaction is slower than enzymatic esterification, but may be responsible for aged characters of wine. Additionally, acid catalysed esterification may occur faster in wines of a lower pH (Edwards *et al*., 1985). Therefore, esters not only contribute significantly to the sensory impact of newly fermented wine, but the aged product as well.

Volatile esters are produced in such high quantities during fermentation that the concentration surpasses the synthesis/hydrolysis equilibrium point, and they cannot be maintained. During ageing, volatile esters decrease as they react hydrolytically and finally achieve equilibrium (Pretorius & Lambrechts, 2000). Non-volatile esters contribute relatively negligible aromas and flavours in wine; however they may somewhat soften the tartness of highly acidic white wines such as those hailing from Chablis (Margalit, 2004). Volatile esters are a major component of fermentation bouquet and rapidly dissipate after fermentation (Boulton *et al*., 1996). Therefore, wines such as those famous in Germany around fall, *Federweißer* also known as *neu wein*, rely heavily on fermentation esters as they are wines in which fermentation was stopped and bottled for quick sale.

There are two groups of esters, namely aliphatic and phenolic. Only the aliphatic monocarboxylic esters make a significant impact in wine. The monocarboxylic acid esters can be further broken down into those formed from ethanol and saturated fatty acids. The second group are those formed from acetic acid and higher alcohols. It is true that the monocarboxylic acids are the most significant esters for most wines, however meth- and ethanolic esters have been found to be associated in the aroma of Muscadine wines (Lamikanra *et al*., 1996). The physiological function of esters formed during fermentation is unclear (Pretorius & Lambrechts, 2000).

Esters can arise in two ways: from acetates, ethanol and higher alcohols or from ethanol and straight chained fatty acids. Esters which form from acetates, ethanol and higher alcohols include:

- Ethyl acetate, isobutyl acetate, isoamyl acetate and 2 phenethyl acetate.
- Esters which form from ethanol and straight chain fatty acids include: Ethyl hexanoic acid, ethyl octanoic acid and ethyl decanoid acid.

The esters formed from fatty acids are not nearly as important in wine production as the acetate esters. They are more significant in products of distillation (Zoecklein *et al*., 1999).

The mechanism by which yeasts form esters has been theorised by many, but a consensus has not been reached. Some believe that the reaction is catalysed by an enzyme called alcohol acetyltransferase (AAT). This reaction uses alcohol (as a substrate), co-enzyme A and ATP to form an ester (Boulton *et al*., 1996; Mason & Dufour, 2000; Zoecklein *et al*., 1999). Esters may also be formed through simple hydrogen-ion-catalysed reactions.

Oenoccoccus oeni and other lactic acid bacteria have esterases and can affect the ester concentration of a wine during malolactic fermentation. This is done through either ester synthesis or hydrolysis, which will complement or detract from wine aroma, depending on the esters produced or metabolised by the strain (Davis *et al.*, 1985).

Esters are usually associated with "general fruit" rather than attributing a specific aroma; however, they are not always pleasant (e.g. ethyl acetate) (Pretorius & Lambrechts, 2000; Zoecklein *et al*., 1999). Ethyl acetate, which has a detection threshold of 12 – 14 ppm, is also present in acetic acid and contributes to the vinegar (or nail polish) aroma at 120 – 160 mg/ℓ. The perception of VA as a fault is a function of the ethyl acetate:acetic acid ratio (Margalit, 2004; Pretorius & Lambrechts, 2000).

Esters are generally thought to be more important to the aroma of white wines; their significance in red wine aroma is less understood. Esters are critical in the production of Pinotage wine. If uncontrolled, this variety develops a pungent, banana aroma from isoamyl acetate, which is not only produced during fermentation, but also found within the grape itself (Van Wyk *et al.*, 1979). Esters can be a major contributor to varietal aroma as well. This is especially true in Pinot noir from Burgundy, which contains four particular esters that contribute to its characteristically fruity aroma (Moio & Etievant, 1995).

Native yeasts such as *Hansenula anomala* and *Kloeckera apiculate* produce an abundance of ethyl acetate. Therefore, yeast strain can affect the formation of certain esters. Lema *et al*. (1996) found that the concentration of total esters was more dependent on the size of the initial yeast culture, rather than the yeast strain itself. However, the concentration of the esters produced was different from strain to strain. *Saccharomyces* yeast generally produce roughly the same concentrations of esters, but their distribution differs. Non-*Saccharomyces* yeast can produce many more esters than *Saccharomyces*, but may not always be pleasant. Nonetheless, this may be a reason why natural fermentations produce wines of greater complexity (Boulton *et al*., 1996).

Volatile esters are an important component of the fermentation bouquet, and they rapidly dissipate after fermentation (Boulton *et al*., 1996). Further, must conditions, such as high solids and high fermentation temperatures (>15°C), can decrease the amount of potential esters formed during fermentation (Boulton *et al*., 1996; Margalit, 2004).

Aldehydes

Acetaldehyde constitutes around 90% of all the aldehydes found in wine. It is a normal yeast fermentation by-product and is an intermediary in the process of diacetyl forming from pyruvic acid (Pretorius & Lambrechts, 2000).

Acetaldehyde is the penultimate compound produced during the conversion of sugar to ethanol. Sugar is metabolised through glycolysis, which allows for the formation of ATP and NADH, providing cellular energy. The end product of glycolysis is two pyruvate molecules. Pyruvate is then enzymatically decarboxylated to form acetaldehyde. Acetaldehyde is then enzymatically converted to ethanol. Not all the acetaldehyde produced by the yeast cell is converted to ethanol, as it is used to maintain a redox balance within the cell. Therefore, some of the acetaldehyde remains in the cell, some is excreted, and the rest is converted into alcohol. Notably, ethanol is able to oxidise back into an aldehyde (Swiegers *et al*., 2005). Acetaldehyde can also increase in wine through enzymatic oxidation of ethanol by film yeast. These yeasts utilise ethanol as their primary carbon source for growth. Film yeast are regularly exploited in the production of sherry, but must be controlled when creating table wine. Further, yeast differ widely in their ability to produce acetaldehyde. In general, low acetaldehyde-producing yeast generate less acetic acid and acetoin than their higher-producing cousins (Romano *et al*., 1994). Therefore, these yeast can be selected in order to create a more "fresh" wine style. Cellar temperature during bulk wine storage is critical for the control of film yeast. Temperatures of 8 – 12°C are ideal for restraining oxidative yeast film formation (Zoecklein *et al*., 1999).

Aldehydes commonly convey a nutty or bruised apple aroma (Swiegers *et al*., 2005). This compound is intrinsic to oxidative wine styles, such as sherry and *Vin jaune* (yellow wine); however, where these characteristics are desired in the aforementioned styles, they are viewed as a fault in typical table wines. In fact, where aldehydes are intrinsic to the Savagnin dominant *Vin jaune* wines of Jura, aldehydes in the *Vin de paille* (also Savagnin dominant) wines from this region, would be viewed as a fault.

Besides affecting wine aroma, aldehydes may be intricately linked to colour development of red wines. Aldehydes interact with phenolic compounds during wine ageing, which promotes the formation of tannin-anthocyanin polymerisation. The role of acetaldehyde in wine colour stability may be of little to no significance (Somers & Wescombe, 1987; Timberlake & Bridle, 1976; Swiegers *et al*., 2005).

Free acetaldehyde in young wine is usually less than 75 ppm. Although, if oxidative reactions induce higher acetaldehyde concentrations then SO2 is used to neutralise the aromatic impact of acetaldehyde and form the less aromatic product, acetaldehyde-α-hydroxysulfonate (Zoecklein *et al*., 1999). It requires 1.45 mg of SO2/mg of acetaldehyde for the latter to be completely "bound" (Hornsey, 2007). Unfortunately, SO2 is not always a positive tool in decreasing the sensory impact of acetaldehyde. Increasing amounts of pre-fermentative SO2 correlates with higher acetaldehyde production, since SO2 inhibits aldehyde dehydrogenase, which converts acetaldehyde to ethanol (Frivik & Ebeler, 2003; Ribereau-Gayon *et al*., 2006). Further, incorrect timing of the SO2 addition leads to the degradation of acetaldehyde-α-hydroxysulfonate by lactic acid bacteria, thereby releasing SO2 and halting, or prolonging, malolactic fermentation (Osborne *et al*., 2000).

Conclusion

Wine is commonly referred to as a “complex matrix” and this is certainly true. However, by breaking wine down into its fundamental components, we can begin to understand how to better manage our vineyards and wineries to attain the wine styles that our markets desire. Esters and aldehydes could be considered a fault or aromas that are intrinsically valuable to our wine style, depending upon what we are trying to achieve. To this end, it is crucial to understand how these compounds arise and how vintners can manage them effectively and efficiently.

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