MAXIMISING AROMA PRESERVATION IN WHITE AND ROSÉ WINES

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INTRODUCTION

All winemakers are concerned with quality, to greater or lesser extents within budget constraints. In terms of white winemaking, the appearance of the wine is secondary to the nose of the wine, so it is critical that a wine of quality be expressive of both varietal characters and terroir. For aromatic wines such as Sauvignon blanc, which typically do not improve with bottle age, saleability relies heavily on freshness and maintenance of the wine's aroma profile. It is widely known that wine aroma changes over time, and that the first aromatic compounds to be lost are those that are most susceptible to oxidation, such as the volatile thiols in Sauvignon blanc (and other varieties such as Riesling, Colombard, Gros Manseng, Verdelho) 4MMP, 3MH and, particularly, 3MHA (figure 1; Bowyer et al., 2008).

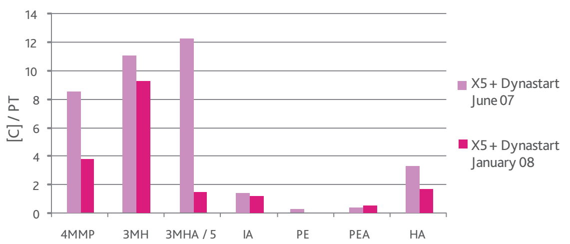

Fig.1. *A comparison of the aroma profiles of one wine fermented with Zymaflore X5 rehydrated with* DYNASTART®, *analysed at two time points (June 2007 and January 2008) separated by 7 months with cellaring at 15 °C under screwcap. Aroma intensity is expressed as Concentration/Perception Threshold, where a value of ≥1 indicates contribution to wine aroma. 4MMP = 4-methoxymercaptopentanone, broom/boxtree; 3MH = 3-mercaptohexanol, grapefruit; 3MHA = 3-mercaptohexyl acetate, passionfruit; IA = isoamyl acetate, banana; PE = phenyl ethanol, rose; PEA = phenyl ethyl acetate, tea; HA = hexyl acetate, pear.*

Methods of preserving wine aroma encompass several approaches, from reductive handling of fruit and juice to the addition of tannin, though all preservation methods have their drawbacks. For example, reductive handling requires the use of inert gases, whilst tannin additions, if done excessively, can alter the palate of the subsequent wine.

GLUTATHIONE

A more recent approach to aroma preservation is through the use of the protective power of glutathione (Lavigne et al. 2002). Glutathione (GSH) is a plant-derived natural anti-oxidant, which is superior in action to both ascorbic acid and sulphur dioxide. It has been known for many years that is a more potent anti-oxidant than ascorbic acid, and that it is thus preferentially consumed ahead of ascorbic acid under oxidative conditions (Hopkins and Morgan, 1936). Indeed, it is thought that one purpose of GSH in plant systems is to maintain ascorbic acid in its reduced form for improved physiological activity (Saetre and Rabenstein, 1978). In grapes, GSH accumulates during ripening (Adams and Liyanage, 1993) and levels vary considerably, ranging from 17 – 114 ppm (Cheynier et al., 1989), whereas in yeast GSH constitutes about 1 % of the dry mass (Park et al., 2000; Elskens et al., 1991).

The glutathione content of wine is known to correlate with the YAN content of the juice (Lavigne et al., 2007), for the simple reason that if juice YAN is low then GSH is consumed by the yeast as a nitrogen source. For example, in figure 2 one can see that when juice YAN is sufficient the GSH content of juice and subsequent wine is approximately equal, yet when juice YAN < 100 ppm there is very little GSH remaining in the corresponding wines. Additionally, yeast assimilate GSH in the early stages of fermentation, and release it in the latter stages, particularly during autolysis (figure 3).

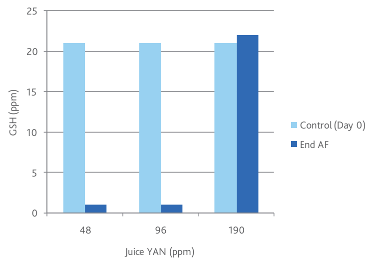

Fig. 2. *Correlation between juice YAN and subsequent GSH content of wine.*

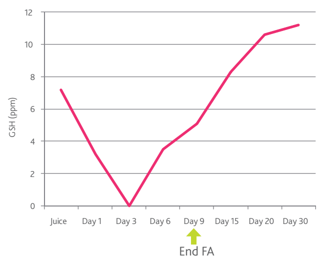

Fig. 3. *Concentration of GSH during fermentation and lees ageing with sufficient YAN*

Given the potency of GSH, it is clear that winemakers can use this compound to great effect in winemaking as a natural anti-oxidant for the preservation of wine aromas that are susceptible to oxidation, and concurrently delay the appearance of developed characters. In this way wine freshness can be retained through maximum aromatic preservation, therefore with increased maintenance of wine quality and consumer appeal.

Previously, we have demonstrated the large reduction in GSH levels observed during the oxidative handling of juice, and also that selected fining practices do not remove GSH from juice (Bowyer et al., 2009). In this article we demonstrate how the manipulation of GSH during fermentation can increase aroma longevity in aromatic wines.

ANTI-OXIDANTS

Anti-oxidants behave in a manner similar to electrochemically-active species, because they respond to the potential for oxidation or reduction in their environment. For example, examining a series of chemicals that are thought of as anti-oxidants (figure 4), one can see that in comparison with tannins, SO_2 is not as effective an anti-oxidant. In the case of white and rosé wines, no significant amounts of tannin are present, and the next most effective anti-oxidant in such wines is thus glutathione. Clearly, maximisation of GSH will lead to better wine preservation, and so the goal of winemakers should be to maximise the concentration of GSH in these wines.

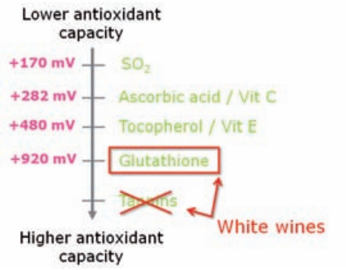

Fig. 4. *A comparison in the reduction potential of various anti-oxidants.*

What then is it about GSH that makes it an effective anti-oxidant? In essence, it is the presence of a thiol group in the molecule. Thiols provide many of the strongest fruity characters found in certain wines (such as Sauvignon blanc), and these aromas can be susceptible to oxidation precisely because they are good anti-oxidants, like GSH. The problem is that when they react in this manner their contribution to wine aroma is lost or altered, hence wine quality deteriorates. The thiol group (-SH) is a reduced form of sulphur (S). S is able to react with oxygen to form oxides (as in SO_2), sulfites (SO_3^{2-}) and, ultimately, sulphate (SO_4^{2-}). Since an informal definition of oxidation is "combination with oxygen", the progression of sulfur from –SH to SO_4^{2-} constitutes the behaviour of an anti-oxidant (figure 5).

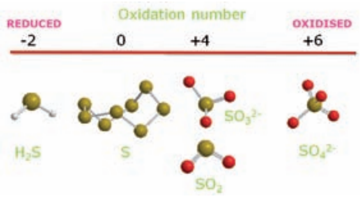

Fig. 5. *The progression of sulphur through a series of oxidation states, from reduced (H_2S) to elemental sulphur (S8), then sulphur dioxide (SO_2) and sulfite (SO_3^{2-}), finishing with the (SO_4^{2-}) form.*

In the specific case of glutathione the situation can be slightly more complicated in that, for the more chemically-minded, GSH acts as a nucleophile and regenerates hydroquinone and quinone species, which are oxidised forms of phenols, as shown in figure 6. The end result is typical anti-oxidant behaviour, since the oxidised form of the molecule is reduced to the original phenolic form, with the glutathione now bound to the phenolic core to form the "grape reaction product".

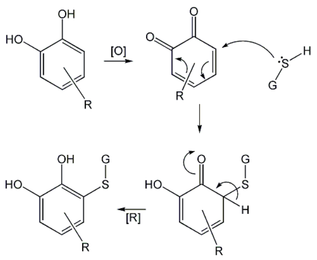

Fig. 4. *Schematic of the anti-oxidant behaviour of GSH in the presence of oxidised phenolic compounds. Oxidation [O] of the phenolic compound generates a quinone, which the GSH nucleophile targets to form the "grape reaction product", and in so doing restoration of the aromatic structure occurs.*

PRESERVING WINE AROMA

Some simple practical adaptations can be made to preserve the glutathione content of wines. Maintenance of SO_2 levels is essential, remembering that it plays both anti-microbial and anti-oxidant roles. Lees ageing, provided the lees are clean and free of contaminant organisms, can clearly improve wine GSH content, since GSH is released by yeast during the start of autolysis. Excessive racking should be avoided, as this process always introduces some oxygen, which promotes oxidation and GSH depletion. Additionally, the capacity of yeast lees to absorb oxygen is higher and this limits glutathione oxidation. Paradoxically, older barrels appear to preserve GSH better than new barrels, because the levels of oxygen found in wine in older barrels is lower than those found in newer barrels as a result of lower porosity in the used wood. These two latter points are illustrated in figure 7 (Lavigne et al., 2002).

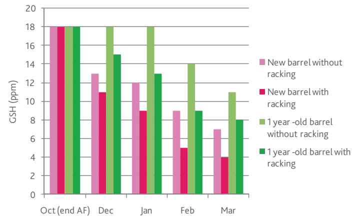

Fig. 7. *A comparison of the glutathione content of wines handled in new and 1 year-old barrels with and without racking.*

Glutathione can also be supplemented during the fermentation through the use of a product like **BIOAROM®**, which is rich in the redox-active compounds glutathione, cysteine and N-acetyl cysteine. Since yeast will simply assimilate GSH prior to 2/3 sugar depletion, supplementation should only be made in the last third of the fermentation (see figure 3). There appears to be a threshold below which GSH supplementation is far less effective at preserving wine aroma, and we estimate this to be approximately 20 ppm of GSH in-bottle. This can be seen clearly in the comparison of the aromatic profiles of wines made from the same juice (2006 Sauvignon blanc, micro-vinification in duplicate) using Product A and **BIOAROM®** as aroma preservatives. The total anti-oxidant contribution of Product A is lower (table 1), and this is demonstrated by aroma preservation that is no better than the control wine (figure 8).

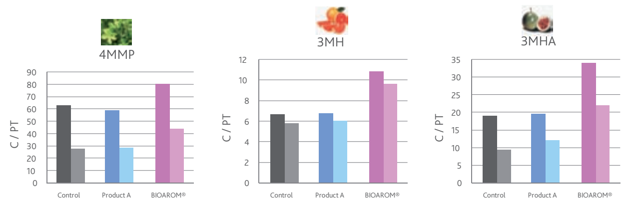

Fig. 8. *A comparison of two products aimed at wine aroma preservation, Product A and BIOAROM. Fermentation was conducted in Sauvignon blanc juice in 2006, with microvinification in duplicate. The two time-points indicated are at bottling and 3 months later with cellaring at 15 °C. Concentration/Perception Threshold, where a value of ≥1 indicates contribution to wine aroma. 4MMP = 4-methoxymercaptopentanone, broom/boxtree; 3MH = 3-mercaptohexanol, grapefruit; 3MHA = 3-mercaptohexyl acetate, passionfruit.*

It is important to understand that GSH supplementation does not enhance the yeast's ability to generate aromas, but rather protects what aromas the yeast does produce. This can be seen clearly in figure 9, where a control wine (Sauvignon blanc) is compared with one made using GSH supplementation (**BIOAROM®**) and another made using **DYNASTART®**, a rehydration nutrient that has been shown to increase yeast aroma production (Bowyer et al., 2008; Swiegers et al., 2008; van der Westhuizen et al., 2008). The most varietal aroma is produced when **DYNASTART®** was used, presumably due to it's stimulation of yeast metabolism, and varietal intensity exceeded the control by some margin. The wine treated with GSH supplementation during fermentation shows better preservation of aromas over the control, particularly for 3MHA (passionfruit), which is very susceptible to oxidation. Importantly, an examination of the GSH concentrations in the wines shows that only the wine treated with **BIOAROM®** had GSH above the nominal threshold of 20 ppm, meaning that this wine is likely to retain these aromas during ageing to a far greater extent that the control or **DYNASTART®**-treated wine.

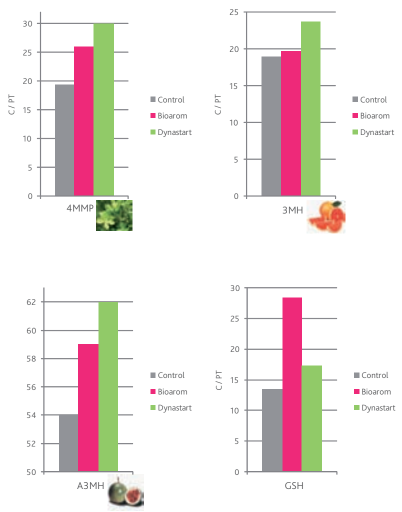

Fig. 8. *A comparison of the glutathione content of wines handled in new and 1 year-old barrels with and without racking.*

SUMMARY

Although glutathione has been known for many years, it is only in recent times that its importance with respect to wine aroma preservation during ageing has become prominent. Supplementation during fermentation is shown to be an effective method of increasing wine glutathione content to ensure that a sufficient amount is available in the final wine to provide adequate aroma protection. Whilst glutathione supplementation is important for all white and rosé wine, it is particularly relevant for wines that rely on strong aromas for consumer appeal, and also for those undergoing export where time is spent in transportation and storage under conditions that may not be ideal for aroma preservation.

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