Article

The Oxidation of Red and White Wines and its Impact on Wine Aroma

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Introduction

The oxidation of wines has quite different consequences for red and white varieties, although the underlying chemistry is similar.[1,2] Oxygen additions are usually required in the maturation of red wines prior to bottling, to enhance wine quality (through the removal of unwanted aromas), to stabilize colour and to improve mouth feel, but it is difficult to predict the optimum level of oxygen exposure. On the other hand, oxygen additions seldom improve white wines where preservation of fruity aromas is sought, and where oxidative browning can detract from the appearance of the wine. This article summarizes the chemistry behind wine oxidation with a focus upon polyphenol-mediated processes and how these impact upon aromas in red and white wines.

Oxygen in Wine

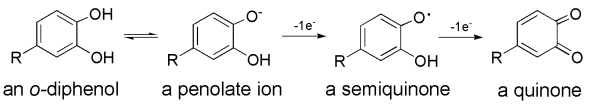
It is inevitable that wines are exposed to O_2 at various stages of production. Air-saturated wine can take up to 6 mL/L (8.6 mg/L) of O_2 at room temperature, with greater solubility at a lower temperature. Larger doses are supplied to red wines during deliberate pump-overs, while slower rates of O_2 ingress occur for wines in barrels. For example, while mixing wines from different casks was found to raise the O_2 concentration to around 1.8 mg/L, racking of a wine at 15-20 °C produced an O_2 concentration of 0.4 mg/L, but this value increased three-fold when the temperature of racking was lowered to 10 °C.[3] An alternative to barrel aging is the new technology of micro-oxygenation now commonly used with red wines. This involves continuous, slow bubbling of oxygen into the wine for several weeks at a rate of a few mL of O_2/L of wine per month. Under these conditions the dissolved O_2 has been measured at 0.2 to 0.25 mg/L.[4]

Once a wine is bottled it might be expected that oxygen is largely excluded, but wine closures vary considerably in how much O_2 they allow into the wine. Synthetic plastic corks allow the entry of larger amounts of O_2 to enter the wine than natural corks and screw caps and are thus best suited for wines that are to be consumed soon after bottling. The effects of closure type upon the colour and aroma in trials on red and white wines are referred to below. The conditions used for bottling are also very important, as the small headspace above the bottled wine can contain a few mg of O_2,[5] equivalent to several months of the oxygen entry through the closure, unless a special vacuum or inert gas system is used on the bottling line.

The Oxidation of Wine Polyphenols

There are many organic compounds in wine that are potential targets for oxidation processes. These range from ethanol itself through to various acids [tartaric acid (**1**) being the major wine acid – see Chart 1 and aroma compounds, but these are not, in fact, the main initial substrates of oxidation. An important finding in the research undertaken by Vernon Singleton (UC Davis) in the 1970s, was that ethanol oxidizes to acetaldehyde at a significant rate only through the coupled oxidation of readily oxidizable polyphenols such as caffeic acid (**2**, typical of white wine hydroxycinnamic acids) and catechin (**3**, a flavanol at high levels in red wine – see Chart 1).[6] Without these polyphenols ethanol and tartaric acid are remarkably stable to oxidation. The oxidation of polyphenols generates a strong oxidant, presumed to be H_2O_2, that can oxidize other substances in wine such as ethanol.

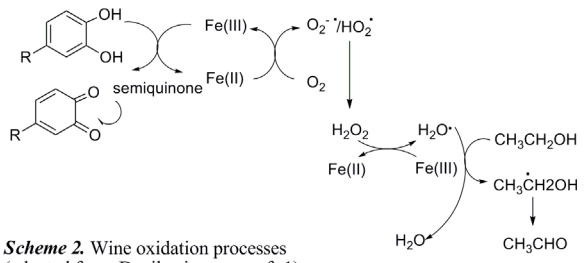
Wine polyphenols containing a 1,2-diphenol (an *o*-catechol group), such as **2** and **3**, can be oxidized through to quinone forms easily as shown in Scheme 1. Model studies have shown that in solution this process is more rapid at a higher pH, due to a higher percentage of the phenolate that reacts with oxygen.[7] Only a small proportion of phenolate ions are expected at wine pH (pK_a polyphenols *ca*. 9-10), but many more will be present in a pH 4 wine than a pH 3 wine, consistent with higher pH wines being more susceptible to oxidation problems. It has also been shown that one of the subsequent reactions of the quinones formed is with remaining polyphenols and leads to brown products, but the process regenerates the catechol group making it available for further oxidation. Overall, more oxygen is taken up than would be expected given the original number of polyphenol molecules present.



Scheme 1. Oxidation of polyphenols

Oxygen itself is a triplet, and requires activation of some form before it can be reduced progressively to hydroperoxyl radical ($HO_2^{\bullet}$), hydrogen peroxide (H_2O_2), the hydroxyl radical ($OH^{\bullet}$), and eventually H_2O. In wines, the activation of oxygen is thought to involve catalysts, particularly iron and copper as these complex O_2 and facilitate the oxidation process with polyphenols (Scheme 2).[8] In the coupled oxidation process, Fe(II) converts H_2O_2 to the very reactive $OH^{\bullet}$ (the Fenton reaction) that oxidizes most organic compounds, including ethanol to acetaldehyde and glycerol to glyceraldehyde, *etc*.[9]

Polyphenols containing a 1,2-diphenol (an *o*-catechol moiety) or a 1,2,3-triphenol (a galloyl group) are the most easily oxidized, and show the lowest oxidation-reduction potentials in a model wine solution measured at a glassy carbon electrode.[10] The current peak in cyclic voltam-



Scheme 2. Wine oxidation processes (adapted from Danilewicz - see ref. 1)

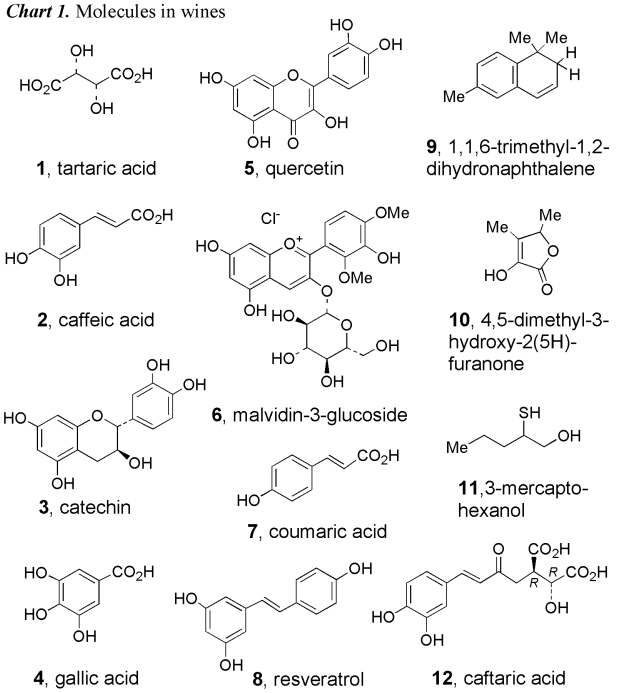
mograms for common wine polyphenols such as **2**, **3**, or gallic acid (**4**), and quercetin (**5**; Chart 1) is seen at a similar potential, *ca*. 0.4 V (*vs*. Ag/AgCl), as is the main current peak for diluted red and white wines. This further confirms that such polyphenols are the main initial substrates in wine oxidation.[11] Integration of the current peak can quantify the level of catechol- and galloyl-containing polyphenols in wine.[10-12] Further compounds, such as the malvidin anthocyanins (see **6**), the major coloured species in red wines, and compounds with more isolated phenolic groups, such as *p*-coumaric acid (**7**) and resveratrol (**8**; Chart 1), are oxidized at higher potentials. However, despite their lower ease-of-oxidation, anthocyanins such as malvidin-3-glucoside (**6**) degrade faster in wine than, *e.g.* **2** or **7**, the catechol-containing hydroxycinnamic acids,[13,14] as other reactions involving the anthocyanins come into play, including the formation of bridges between the polyphenol moieties.

The aldehydes produced by coupled polyphenol oxidation, and through yeast activity, have important roles in wine aging. They provide links between various flavonoid polyphenols (including anthocyanins) to produce new polymeric pigments that, explain the change in red wine hue with age.[15] These components are often more stable than the anthocyanins that they are formed from and are resistant to bleaching by the bisulfite added as a wine preservative. There is considerable current interest in the way in which anthocyanins combine with wine tannins (larger oligomeric and polymeric polyphenols made up of catechin-type units) and lower the astringent effect of the tannins. Such studies help explain the *softening* of red wine astringency with age, an important area of sensory science where the underlying chemistry is still poorly understood.

Oxidation and Effects on Wine Aroma

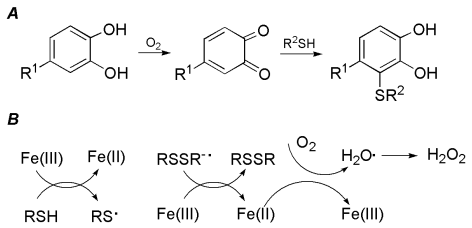
A range of off-odours can be formed from wine oxidation.[16-18] At low concentrations these may add to the complexity of a wine, but as these increase they begin to detract from wine quality. Some examples of the compounds associated with sensory terms for aged wines such as *farm-feed* and *woody-like* include phenylacetaldehyde ($PhCH_2CHO$), 3-(methylthio)propionaldehyde ($MeSCH_2CH_2CHO$), 1,1,6-trimethyl-1,2-dihydronaphthalene (**9**; responsible for the *kerosene* odour in aged Riesling) and 4,5-dimethyl-3-hydroxy-2(5*H*)-furanone (**10**).[17] At the same time, the concentration of acetaldehyde itself does not always increase markedly during wine oxidation experiments, and it is recognised that many important wine oxidation aromas remain to be identified.[16]

Chart 1. Molecules in wines



Alongside the production of new odours, wine oxidation can lead to the removal of existing aroma compounds, particularly those containing sulfur. This can be a positive development, as many sulfur-containing compounds produce unwanted aromas reminiscent of rubber or cooked cabbage.[19] Winemaking processes involving the introduction of O_2 to wine (as in racking) provide the first means for their removal, while fining with copper salts is also used. At the same time, there are sulfur-containing compounds present that add to the varietal character of the wine, but these may be lost through oxidation processes. These include 3-mercaptohexanol (3MH, **11**) which provides important grapefruit and passion fruit-type aromas in Sauvignon Blanc and other wines.[20]

One mechanism proposed for the removal of sulfur-containing compounds is by reaction with the quinones formed during polyphenol oxidation (Scheme 3A). Experiments exposing catechol-containing polyphenols to oxygen show losses of **11** consistent with a polyphenol-mediated oxidation mechanism.[21,22] The oxidation of thiols to disulfides (Scheme 3B) has also been suggested as a possible pathway.[19,23,24] In one recent survey of wines of different ages, the tendency towards higher levels of dimethyl disulfide (MeSSMe) and diethyl disulfide (EtSSEt) in the older wines was seen as implicating disulfide formation during aging.[25] The rapid reaction of the thiol-containing amino acid cysteine in the presence of O_2, Fe(II) and Cu(II) has also been ascribed to the metal-catalysed oxidation of thiols as shown in Scheme 3B.[22] However, while the addition of O_2 was seen to lower the concentrations of methane and ethane thiols in a micro-oxygenation study, no disulfides were seen.[26] Thiols with low sensory thresholds potentially can be released from disulfide forms by reduction with bisulfites in wine,[27] or through the hydrolysis of thioacetates.[24] However, there is a lack of experimental data on the effects of oxidation upon sulfur-containing compounds, and research is being undertaken in this area at the University of Auckland.



Scheme 3. Oxidation of S-containing compounds in wine; ***A:*** polyphenol-mediated; ***B:*** metal-catalyzed thiol oxidation (adapted from Danilewicz - see ref. 24)

Influence of Wine Antioxidants

In addition to controlling the rate of O_2 entry into a wine, winemakers can make use of antioxidants to control oxidation, using those already present in the grape juice, such as glutathione, or through added SO_2 (bisulfite in solution) and ascorbic acid. SO_2 is almost universally used in modern winemaking at levels of 20 mg/L or more of free SO_2 (and to 100 mg/L or more of total SO_2 once forms bound to acetaldehyde and other compounds are included). Sulfites are added to grape juice to inhibit the rapid oxidation caused by polyphenol oxidase activity.[28] Here it can act as a scavenger of H_2O_2 formed from further oxidation processes, but it does not react rapidly with O_2 itself.[1] On the other hand, SO_2 has a further role in the rapid reduction of oxidized polyphenols,[29] thus removing polyphenol quinones from further browning and aroma degradation processes.

Related protection is provided in grape juice and young wines by the presence of free glutathione at 30 to 100 mg/L with the actual concentration being dependent upon the pressing conditions used.[30] An important role for glutathione in white grape juice is to react with the quinone formed from the main hydroxycinnamic acid, caftaric acid (**12**), to produce an S glutathionyl caftaric acid, which is more stable to enzymatic oxidation and limits the browning of the juice.[28] Glutathione also appears to have a protective role in wines by reacting with oxidized polyphenols in preference to varietal aroma compounds such as thiol **11**, or other polyphenols.[31]

There has been some interest in finding replacements for SO_2 additions in winemaking owing to potential health-problems in sensitive individuals and ascorbic acid has been considered. As the dienol moiety is readily oxidized[1] by O_2, it can be used for its direct removal, a role that is not ascribed to SO_2 or glutathione. However, ascorbic acid additions to wine have a controversial history in that certain pro-oxidative effects have been observed and ascribed to the formation of H_2O_2 or other reactive oxygen species following the initial antioxidant activity. This is analogous to the polyphenol oxidation of Scheme 2. In model studies, ascorbic acid was shown to rapidly form acetaldehyde in ethanolic solutions, a process that could be slowed but not completely eliminated through SO_2 additions,[6] and a change from anti-oxidative to pro-oxidative activity has been seen after a certain time in accelerated aging trials.[32] On the other hand, wine storage trials have shown mixed results regarding added ascorbic acid, with some trials showing little benefit to wine browning from the addition.[33] In other trials, such as a three year trial on Chardonnay and Riesling at the Australian Wine Research Institute (AWRI) in Adelaide, wines without ascorbic acid additions were browner, and the additions either led to no difference in aroma or to less oxidized and more fruity aromas, with little change in SO_2 levels.

Red Wine Oxidation

Red wines contain polyphenols at a higher concentration (1 to 5 g/L) than white wines, particularly much higher levels of the anthocyanin flavonoids responsible for colour and astringency (flavanol oligomers and polymers). Some of the established effects of O_2 additions to red wine include a decrease in certain smaller polyphenols and an increase in red polymeric pigments, alongside a loss of sulfites.[34] Several recent reports on the effects of micro-oxygenation in red wines have confirmed the loss of monomeric anthocyanins and other polyphenols, along with the enhanced formation of polymeric pigments (resistant to SO_2 bleaching), often with an increase in wine colour density.[13,14,35,36] Further changes in red wine pigments have included the formation of ethyl-bridged compounds associated with the acetaldehyde released during wine oxidation processes,[35,37] while a build up of acetaldehyde has been recorded in the later stages of regular micro-oxygenation,[38] and during an electrochemical micro-oxygenation approach.[39] Overall, micro-oxygenation has been shown to increase the rate of a range of red wine aging processes, allowing wines to be prepared for bottling in a shorter period.[40] A further influence on the rate of oxidative changes during micro-oxygenation is the level of SO_2 in the wine. We have tracked the development of polymeric pigments from monomeric anthocyanins during a sixteen week treatment of a Merlot wine at an O_2 exposure of 10 mL/L/month, and observed that these processes are severely restricted as more SO_2 is added to the wines (Fig. 1).[14]

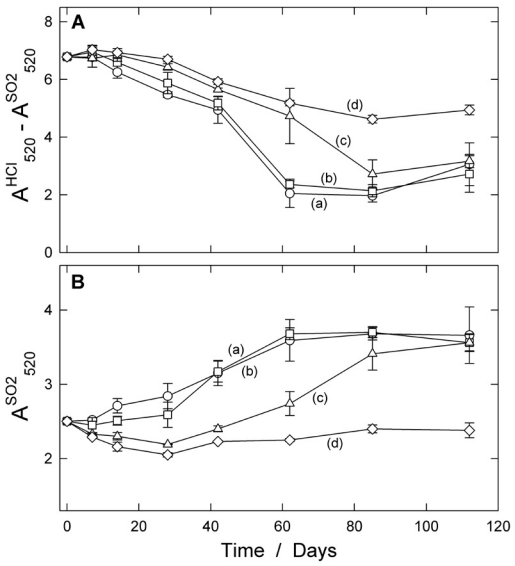


Fig. 1. Loss of monomeric anthocyanins given by the spectrophotometric measure (A^{HCl}_{520} - $A^{SO_2}_{520}$), and increase in non-bleachable (mainly polymeric) pigments ($A^{SO_2}_{520}$) during the micro-oxygenation of a red wine with different SO_2 additions: (a) 0, (b) 50, (c) 100, (d) 200 mg/L (n = 3).

The influence of red wine oxygenation upon aroma compounds and wine sensory properties has been more difficult to confirm compared to effects on wine colour. Micro-oxygenation is promoted as a technique that lowers unwanted vegetative characters in wines and elevates varietal, fruity aromas,[41] but the limited reports in this area show little change in levels of fruity esters, short chain fatty acids, or floral terpenes[42] while, in a separate report, the intensity of the berry/plum character and overall wine quality both fell in the micro-oxygenated wines.[13] Trends in aroma profiles have also been observed in wine closure trials with both white and red wines undertaken at the AWRI. In a three year closure trial on a Cabernet Sauvignon wine, that with the greatest air headspace showed significant losses of SO_2 soon after bottling and developed a higher *oxidized* aroma score.[43] Conversely, the wine under screw cap with the smallest air headspace showed the smallest loss of SO_2 and recorded higher, but not dominating, *struck flint/rubber* aromas. This shows how different wines can develop in the bottle according to the choice of wine closure and bottling procedures.

White Wine Oxidation

White wines contain lower levels of polyphenols (0.2-0.5 g/L), mainly hydroxycinnamic acids, *e.g.* **2** and **7**, but these remain very important for oxidation issues centred around wine browning and losses in varietal aroma. The low concentrations of flavonoids such as catechin (**3**) and quercetin (**5**) glycoside remain important particularly for wine browning and are more prevalent in musts exposed to longer skin contact times and harder pressings.[7,30] Tests on browning rates with different wines have shown varying results with respect to the importance of phenolic content, SO_2 level, pH, and metal content.[44]

Wine closure trials at the AWRI have again shown interesting trends in aroma development in the bottle. In the trial on the Chardonnay and Riesling wines referred to above, a higher rate of O_2 ingress through a synthetic closure led to lower levels of SO_2, higher browning and more advanced oxidized aromas.[45] By contrast, the limited O_2 ingress for wines under screw cap and cork, or for storage in glass ampoules, led to lower rates of browning and lower SO_2 levels, low oxidized characters, but again a discernable *struck flint/rubber* aroma for the screw cap and ampoule wines. This relates to the low oxygen ingress combined with the presence of certain sulfur-containing precursors at bottling.

For NZ Sauvignon Blanc, we have examined the effect of storage conditions on the decline in compounds responsible for the passion fruit and citrus aromas, particularly 3MH (**11**) and its acetate 3MHA.[20,46] Across sixteen Sauvignon Blanc wines bottled at the wine research hall in Auckland, under both cork and screw cap closures, a steady increase in absorbance at 420 nm (a widely used measure of wine browning) was seen (Fig. 2).[47] The rate of browning was greater under the cork closure, but this can be related more to the method of bottling at the University (which allows more O_2 into the wine than does a commercial operation) rather than to properties of the closure. The development of the two aroma compounds was very different, with 3MHA declining to very low levels over the first year in the bottle (Fig. 3), regardless of the closure type. This confirms the need to drink this wine young while such fruity aromas are at their most intense. A different aging pattern is shown by 3MH (**11**) and, in many cases, its concentration increased over the first three months in the bottle, likely due to hydrolysis of its acetate. A decline in level then follows with longer storage (Fig. 4). The 32% average decrease in **11** under cork versus a 21% average decrease under screw cap across the sixteen wines, matched the higher level of (oxidative) browning under the cork closure, related to conditions at bottling for this particular trial.

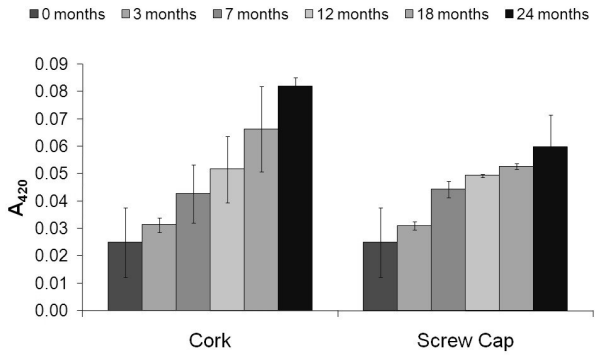


Fig. 2. Typical increase in 420 nm absorbance (browning) for a Marlborough Sauvignon Blanc in the bottle (n = 3).

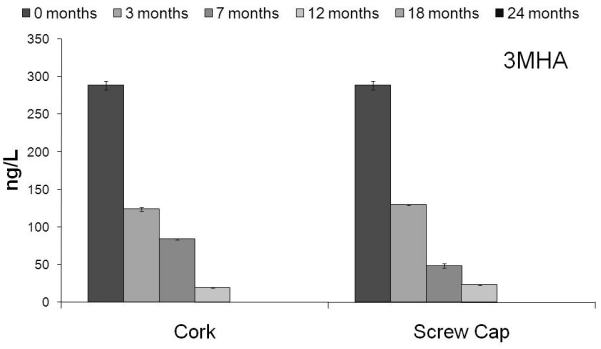


Fig. 3. Typical loss in 3-mercaptohexanol acetate (3MHA) for a Marlborough Sauvignon Blanc in the bottle (n = 3) (same wine as for Figs. 2 and 4).

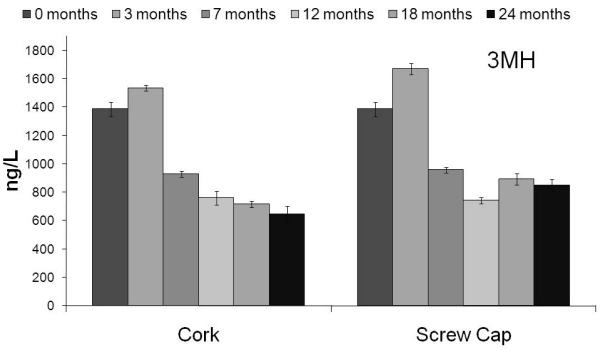


Fig. 4. Typical evolution of 3MH (**11**) for a Marlborough Sauvignon Blanc in the bottle (n = 3).

Final Remarks

The chemistry underlying wine oxidation processes has developed considerably over the past 10-20 years, and the role of polyphenol-mediated oxidation processes is a fea-

ture of this chemistry. The implications for red and white winemaking continue to grow and reveal both positive and negative contributions of O_2 for wine quality. Integrating chemical analyses with sensory studies remains an important area in the study of wine oxidation processes and it needs to progress. At the same time, a more detailed study of the chemical interactions between aroma compounds and oxidized polyphenols is needed to better appreciate the complexity, which makes wine such an interesting, and enjoyable, chemical matrix.

References

1. Danilewicz, J. C. *Am. J. Enol. Vitic.* **2003**, *54*, 73-85.
2. Waterhouse, A. L.; Laurie, V. F. *Am. J. Enol. Vitic.* **2006**, *57*, 306-313.
3. Castellari, M.; Simonato, B.; Tornielli, G. B.; Spinelli, P.; Ferrarini, R. *Ital. J. Food Sci.* **2004**, *16*, 387-396.
4. Laurie, V. F.; Law, R.; Joslin, W. S.; Waterhouse, A. L. *Am. J. Enol. Vitic.* **2008**, *59*, 215-219.
5. Vidal, J. C.; Moutounet, M. *J. Int. Sci. Vigne Vin* **2006**, *40*, 35-45; Kontoudakis, N.; Biosca, P.; Canals, R.; Fort, F.; Canals, J.; Zamora, F. *Aust. J. Grape Wine Res.* **2008**, *14*, 116-122.
6. Wildenradt, H. L.; Singleton, V. L. *Amer. J. Enol. Vitic.* **1974**, *25*, 119-26.
7. Singleton, V. L. *Am. J. Enol. Vitic.* **1987**, *38*, 69-77.
8. Danilewicz, J. C. *Am. J. Enol. Vitic.* **2007**, *58*, 53-60.
9. Laurie, V. F.; Waterhouse, A. L. *J. Agric. Food Chem.* **2006**, *54*, 4668-4673.
10. Kilmartin, P. A.; Zou, H.; Waterhouse, A. L. *J. Agric. Food Chem.* **2001**, *49*, 1957-1965.
11. Kilmartin, P. A.; Zou, H.; Waterhouse, A. L. *Am. J. Enol. Vitic.* **2002**, *53*, 294-302.
12. Zou, H.; Kilmartin, P. A.; Inglis, M. J.; Frost, A. *Aust. J. Grape Wine Res.* **2002**, *8*, 163-174; De Beer, D.; Harbertson, J. F.; Kilmartin, P. A.; Roginsky, V. *et al. Am. J. Enol. Vitic.* **2004**, *55*, 389-400.
13. De Beer, D.; Joubert, E.; Marais, J.; Manley, M. *S. Afr. J. Enol. Vitic.* **2008**, *29*, 13-25.
14. Tao, J.; Dykes, S. I.; Kilmartin, P. A. *J. Agric. Food Chem.* **2007**, *55*, 6104-6109.
15. Alcalde-Eon, C.; Escribano-Bailon, M. T.; Santos-Buelga, C.; Rivas-Gonzalo, J. C. *Anal. Chim. Acta* **2006**, *563*, 238-254.
16. Escudero, A.; Asensio, E.; Cacho, J.; Ferreira, V. *Food Chem.* **2002**, *77*, 325-331.
17. Silva Ferreira, A. C.; Hogg, T.; Guedes de Pinho, P. *J. Agric. Food Chem.* **2003**, *51*, 1377-1381.
18. du Toit, W. J.; Marais, J.; Pretorius, I. S.; du Toit, M. *S. Afr. J. Enol. Vitic.* **2006**, *27*, 76-94.
19. Mestres, M.; Busto, O.; Guasch, J. *J. Chromatogr. A* **2000**, *881*, 569-581.
20. Tominaga, T.; Murat, M.-L.; Dubourdieu, D. *J. Agric. Food Chem.* **1998**, *46*, 1044-1048.
21. Blanchard, L.; Darriet, P.; Dubourdieu, D. *Am. J. Enol. Vitic.* **2004**, *55*, 115-120.
22. Danilewicz, J. C.; Seccombe, J. T.; Whelan, J. *Am. J. Enol. Vitic.* **2008**, *59*, 128-136.
23. Limmer, A. *Chem. NZ* **2005**, *69*, 2-5.
24. Rauhut, D.; Kurbel, H.; Dittrich, H. H.; Grossmann, M. *Wein-Wissenschaft, Wiesbaden* **1996**, *51*, 187-192.
25. Fedrizzi, B.; Magno, F.; Badocco, D.; Nicolini, G.; Versini, G. *J. Agric. Food Chem.* **2007**, *55*, 10880-10887.
26. McCord, J. *Austral. NZ Grapegrower Winemaker* **2003**, *July*, 43-53.
27. Bobet, R. A.; Noble, A. C.; Boulton, R. B. *J. Agric. Food Chem.* **1990**, *38*, 449-52.
28. Singleton, V. L.; Salgues, M.; Zaya, J.; Trousdale, E. *Am. J. Enol. Vitic.* **1985**, *36*, 50-6.
29. Cheynier, V.; Basire, N.; Rigaud, J. *J. Agric. Food Chem.* **1989**, *37*, 1069-71; Cheynier, V.; Masson, G.; Rigaud, J.; Moutounet, M. *Am. J. Enol. Vitic.* **1993**, *44*, 393-9.
30. Maggu, M.; Winz, R.; Kilmartin, P. A.; Trought, M. C. T.; Nicolau, L. *J. Agric. Food Chem.* **2007**, *55*, 10281-10288.
31. Dubourdieu, D.; Moine-Ledoux, V.; Lavigne-Cruege, V.; Blanchard, L.; Tominaga, T. *Recent advances in white wine aging: the key role of the lees*; Proc. ASEV 50th Anniver. Ann., Seattle,WA, June 19-23, 2000. Am. Soc. Enology &Viticulture: Davis, CA 95617-1855, 1966, 196-203.
32. Peng, Z.; Duncan, B.; Pocock, K. F.; Sefton, M. A. *Aust. J. Grape Wine Res.* **1998**, *4*, 127-135; Bradshaw, M. P.; Prenzler, P. D.; Scollary, G. R. *J. Agric. Food Chem.* **2001**, *49*, 934-939.
33. Marks, A. C.; Morris, J. R. *Am. J. Enol. Vitic.* **1993**, *44*, 227-31.
34. Castellari, M.; Matricardi, L.; Arfelli, G.; Galassi, S.; Amati, A. *Food Chem.* **2000**, *69*, 61-67.
35. Cano-Lopez, M.; Pardo-Minguez, F.; Lopez-Roca, J. M.; Gomez-Plaza, E. *Am. J. Enol. Vitic.* **2006**, *57*, 325-331.
36. Perez-Magarino, S.; Sanchez-Iglesias, M.; Ortega-Heras, M.; Gonzalez-Huerta, C.; Gonzalez-Sanjose, M. L. *Food Chem.* **2006**, *101*, 881-893; Sartini, E.; Arfelli, G.; Fabiani, A.; Piva, A. *Food Chem.* **2007**, *104*, 1599-1604.
37. Atanasova, V.; Fulcrand, H.; Cheynier, V.; Moutounet, M. *Anal. Chim. Acta* **2002**, *458*, 15-27.
38. Carlton, W. K.; Gump, B.; Fugelsang, K.; Hasson, A. S. *J. Agric. Food Chem.* **2007**, *55*, 5620-5625.
39. Fell, A. J.; Dykes, S. I.; Nicolau, L.; Kilmartin, P. A. *Am. J. Enol. Vitic.* **2007**, *58*, 443-450.
40. Dykes, S. I.; Kilmartin, P. A. *Wine Ind. J.* **2007**, *22*, 31-45.
41. Moutounet, M.; Ducournau, P.; Chassin, M.; Lemaire, T. *Oenol. 95, 5th Symp. Int. Oenol.,* Bordeaux, June, 1995, Lavoisier Tec et Doc,1996, 411-414 (http://www.tec-et-doc.com/fr/).
42. Heras, M. O.; Rivero-Perez, M. D.; Perez-Magarino, S.; Gonzalez-Huerta, C.; Gonzalez-Sanjose, M. L. *Eur. Food Res. Technol.* **2008**, *226*, 1485-1493.
43. Kwiatkowski, M. J.; Skouroumounis, G. K.; Lattey, K. A.; Waters, E. J. *Aust. J. Grape Wine Res.* **2007**, *13*, 81-94.
44. Simpson, R. F. *Vitis* **1982**, *21*, 233-9; Fernandez-Zurbano, P.; Ferreira, V.; Pena, C. *et al. J. Agric. Food Chem.* **1995**, *43*, 2813-17.
45. Skouroumounis, G. K.; Kwiatkowski, M. J.; Francis, I. L.; Oakey, H. *et al. Aust. J. Grape Wine Res.* **2005**, *11*, 369-384.
46. Dubourdieu, D.; Tominaga, T.; Masneuf, I.; Peyrot des Gachons, C.; Murat, M. L. *Am. J. Enol. Vitic.* **2006**, *57*, 81-88.
47. Herbst, M.; Nicolau, L.; Kilmartin, P. A. *Austral. NZ Grapegrower Winemaker* **2008**, *Technical Issue*, 66-72.