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Oxygen management during vinification and storage of Shiraz wine

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This article reviews the key characteristics of Shiraz wines from a molecular point of view discusses the important role of oxygen in the development of the Shiraz aroma, colour and taste.

The importance of controlled oxygen supply for Shiraz wine during vinification processes and storage is explained through the key chemical processes. Emphasis is on expressing the maximum potential of the wine and avoiding the risk of development of reductive characters caused by smelly sulfur compounds. Post-bottling, the right level of oxygen ingress is managed through a closure with controlled oxygen transfer rate (OTR).

EXECUTIVE SUMMARY

Oxygen management in wines is one of the keys to ensure high quality and the most suitable wines for different types of markets and consumers. When it comes to wine quality, basic consumer expectations are centred on the absence of faults including corked wines, oxidation, reduction or wines with organoleptic deviations of microbiological origin. Results for around 14,000 bottles tasted by experts during the 2006 International Wine Challenge show that 7% were regarded to be defective. Among the defective bottles, those judged as oxidised or reduced were twice as numerous as those judged as corked. This illustrates how bad oxygen management during the phases of wine production or during storage after bottling can potentially cause severe problems in wine quality.

Among the most popular grape varieties, Shiraz possesses obvious qualitative advantages, such as a strong colour with violet undertones, supple tannins and a complex, elegant aromatic nose and palate. However, Shiraz has a pronounced tendency to develop reductive notes, and its vinification and storage consequently require well-controlled management of the oxygen supply.

POLYPHENOLIC AND AROMATIC COMPOSITION OF SHIRAZ

The quality of red wines depends on a balance that combines a variety of aromatic notes with a complex perception on the palate. In this context, the aromatic and polyphenolic compounds are extremely important for the winemaker. The quality of the harvest will be determined by the grapes' aromatic and polyphenolic potential, and the vinification processes should be chosen in view of an expression of this potential, adapted to the type of wine desired. As Shiraz has a tendency to become reductive, particular attention should be paid to oxygen management.

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AROMAS

There are two large families of grape aroma compounds. First, free aromatic aromas; and secondly, aroma precursors that represent a variety of aromas, revealed during the different phases of wine vinification and maturation. Free aromas can be classified into different families, especially terpenes, phenols, aldehydes, norisoprenoïds, esters, higher alcohols, pyrazines and sulfur compounds. Shiraz is low in free aromatic compounds but contains numerous aroma precursors.

Free aroma: the particular case of black pepper aroma in Australian Shiraz

Top-quality Australian Shiraz wines are often described as presenting black pepper aromas. The Australian Wine Research Institute (AWRI) has established an ambitious research program over several years to discover which molecule is responsible for this olfactory characteristic. At the Australian Wine Industry Technical Conference in July 2007, the AWRI's Alan Pollnitz revealed the identity of this molecule (Pollnitz *et al.* 2007). His team was able to establish, with the assistance of gas chromatography coupled with a mass spectrometer, and an olfactometric detector. It was revealed that rotundone, a bicyclic sesquiterpene, is responsible for the black pepper character of Shiraz grapes and wine. This molecule has a very low perception threshold of 16ng/L in wine. For more information about the AWRI's discovery of the black pepper aroma, refer to the article by Markus Herderich and Isak Pretorius in the July/August 2008 issue of the *Wine Industry Journal*, 23 (4): 21-23.

Shiraz aromatic precursors

Despite being present throughout the grape berry, the aroma compounds are more abundant in the skin. Of these different molecules, glycosidic precursors are among those that have been studied the most (Schneider 2003). In general, glycosides are made up of glycosidic and aglycone components.

The glycosidic component comprises at least one glucose molecule, one apiose, rhamnose or arabinose molecule that can contribute to the complexity of the structure of this subsection. Aglycones are made up of volatile compounds grouped into different classes according to their structure (aromatic alcohols, aliphatics and C6 aliphatics, phenols, terpenes and C13 norisoprenoïds). The limitations of current analytical methods for glycosidic precursors only give access to a small quantity of information concerning this important parameter for the quality of the harvest. The analysis combines tedious sample preparation (extraction, separation, enzymatic treatment) and uses gas chromatography coupled with a mass spectrometer. Faster methods have been developed, notably a promising method using fourier transform infrared spectroscopy (FTIR), which requires further development. Different grape varieties can be distinguished not only by their different glycosidic precursor content, but also through the differential distribution into different categories of aglycones within the glycosidic precursors. A thesis financed by Inter Rhône has enabled the aromatic potential of Shiraz to be better characterised. Shiraz can be distinguished by a relatively high C-13 glycosylated norisoprenoïd content and a lower glycosylated phenol content.

Compounds causing reductive characters

In general, the molecules responsible for reductive aromas are low weight sulfur molecules. The AWRI recently developed a method allowing around 10 sulfur molecules to be quantified (Siebert 2007). The analysed molecules are listed in Table 1. These molecules are formed mainly during fermentation phases from precursors (cysteine and S-methyl methionine).

Stressful conditions (nutrient deficiency or absence of oxygen) and excess quantities of sulfur (especially in the form of sulfur dioxide) are possible causes for the production of these bad-smelling molecules.

The particular case of DMS

Dimethyl sulfide (DMS) is one of the sulfur molecules we have just discussed. It is formed during fermentation and wine ageing. A thesis financed by Inter Rhône and carried out in partnership with INRA in Montpellier has proved that this molecule is particularly abundant in Shiraz wines. Its contribution to the wine's aroma can vary radically depending on its concentration.

When present in high concentrations, DMS contributes reductive characters to wines (especially cabbage odours), while at lower concentrations it contributes towards the aromatic complexity of the Shiraz by modifying the aromatic perception; revealing notes of red fruit or truffle.

Likewise, it has been shown that in Shiraz musts, a DMS reserve exists in the form of potential DMS. This precursor has been identified as S-methyl methionine. Depending on the storage conditions of Shiraz wines, DMS will be released from this potential which could modify the wine's aromatic perception.

POLYPHENOLS

Grape polyphenols can be classified into two categories; flavonoids (essentially proanthocyanidins or condensed tannins, anthocyanins, flavonols) and non-flavonoids (phenolic acids and stilbenes). Anthocyanins and tannins are the main polyphenols of interest in red wines due to their respective contribution to colour and astringency in wines, but equally due to their propensity to react and produce derived compounds, which ensure colour stability and suppleness in the wine.

Anthocyanins

Anthocyanins are pigments located in the vacuoles of the grape berry's hypodermal cells, and in the pulp of teinturier grapes. The anthocyanin content and composition varies between different grape varieties. Shiraz anthocyanins are glucosides of malvidin, peonidin, petunidin, delphinidin and cyanidin.

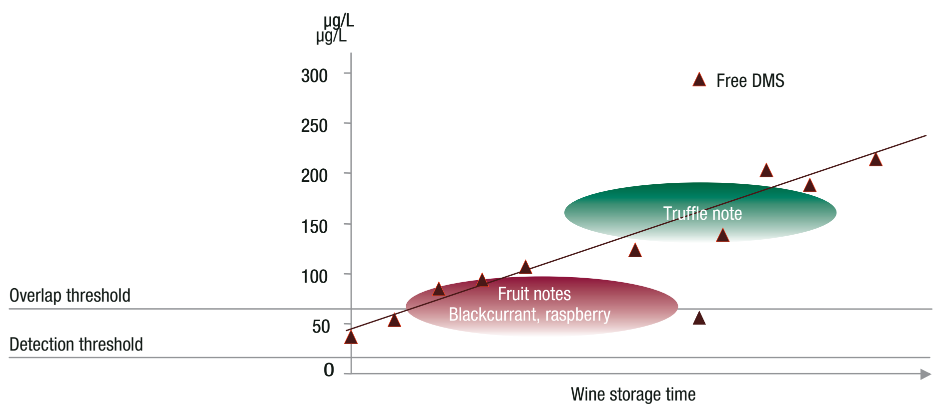


Figure 1. Development of free DMS over time in Shiraz wine when stored under low oxygen ingress conditions.

Table 1. The AWRI's 10 analysed molecules responsible for reductive aromas.					
Low MW sulfur compound		Odour descriptor	Aroma threshold (ppb)	Detected (ppb)	
				Literature review	AWRI
Hydrogen Sulfide	H2S	Rotten egg, sewage-like	1	nd – 370	nd – 56
Methanethiol	MeSH	Rotten cabbage, burnt rubber, putrefacation	1.5	nd – 16	nd – 11
Ethanethiol	EtSH	Onion, rubbery, burnt match, sulfidy, earthy	1.5	nd – 50	nd – 3
Dimethyl sulfide	DMS	Blackcurrant , cooked cabbage, asparagus, canned corn, molasses	25	nd – 474	nd – 980
Diethyl sulfide	DES	Garlic, rubbery	1	nd – 10	nd
Carbon disulfide	CS2	Sweet, ethereal, slight green, rubber, sulfidy, chokingly repulsive	5	nd – 18	nd – 140
Dimethyl disulfide	DMDS	Vegetal, cabbage, intense onion-like (at high levels)	10	nd – 22	nd – 2
Diethyl disulfide	DEDS	Bad smelling, onion	4	nd – 85	nd – 1.5
Methyl thioacetate	MeSAc	Sulfurous, cheesy, egg	40	nd – 115	nd – 53

Shiraz also contains significant quantities of acetylated and coumaroylated anthocyanins, resulting from the esterification of the glucoside forms respectively by acetic and *p*-coumaric acid acids (Figure 2). Coumaroylated anthocyanins, when present in significant quantities, contribute to intense violet notes in Shiraz wines.

This structural complexity is complemented by the anthocyanins' property of existing under several isoforms in equilibrium in solution and the pH dependency. It is interesting that at red wine pH (around 3.7 for Shiraz) only approximately 20% of the anthocyanins are in the red coloured flavylium form, the colourless hemiacetal form being predominant. Different average total anthocyanin contents have been established for different grape varieties. Shiraz contains high quantities of anthocyanins and is characterised by a low proportion of malvidin 3-glucoside (around 50%), while it is frequent to find this dominant anthocyanin in proportions of 65-75% (Puech 2000). This observation confirms the importance of acetylated anthocyanins in Shiraz.

Tannins

Proanthocyanidins, or condensed tannins are polymers made up of monomer flavanols. In grapes, these are catechin, epicatechin, epicatechin gallate and epigallocatechin, located in the seeds or in the skins. The stalk also contains tannins, but in quantities that do not exceed 5% of the grapes' total tannins (Souquet *et al.* 2000). Tannins are present in the cells either in free form or in aggregate form, two states of organisation that evolve during ripening (Cadot 2004).

Tannins differ at structural levels according to their tissular origin. Seed tannins are characterised by the presence of an epicatechin gallate content exceeding 20% (Prieur *et al.* 1994) in their composition and by an average size (or degree of polymerisation = dp) of under 10 units. Skin tannins are characterised by lower epicatechin gallate content (around 5%), but has an epigallocatechin content of around 20% (Souquet *et al.* 1996). In regard to their size, skin tannins are generally larger than seed tannins, with an average dp of 30.

Structural analysis of tannins remains the privilege of a few selected fundamental research laboratories, which makes access to information problematic, but a few differences between grape varieties have been demonstrated. Interestingly, it has been proven that Shiraz skin tannins are rather short (an average degree of polymerisation of 30) and that Shiraz seed tannins are not very galloylated (5% epicatechin gallate) (Vidal *et al.* 2003). Taking into account that the longer and more galloylated the tannins, the greater the astringency. The structural organisation of Shiraz tannins can explain their relative suppleness and elegance.

THE ROLE OF OXYGEN IN SHIRAZ WINE EVOLUTION

Oxygen plays a fundamental role in oenology. Oxygen contained in the air can be dissolved into the wine during different manipulations, such as racking, pumping over and lees stirring. In general, any rapid oxygenation will generate a deviation, while slow oxygenation will allow the wine to develop in complexity (such as in the case of barrel maturation and micro-oxygenation). During the different stages of wine production, oxygen intervenes and can either play a beneficial or detrimental role. The principal compounds responsible for oxygen consumption are polyphenols, therefore explaining the different oxidation capacities between white and red wines. For many years, oxidation phenomena that occurred during wine packaging and ageing in bottles were neglected, under the assumption that the main supply took place during the vinification phases.

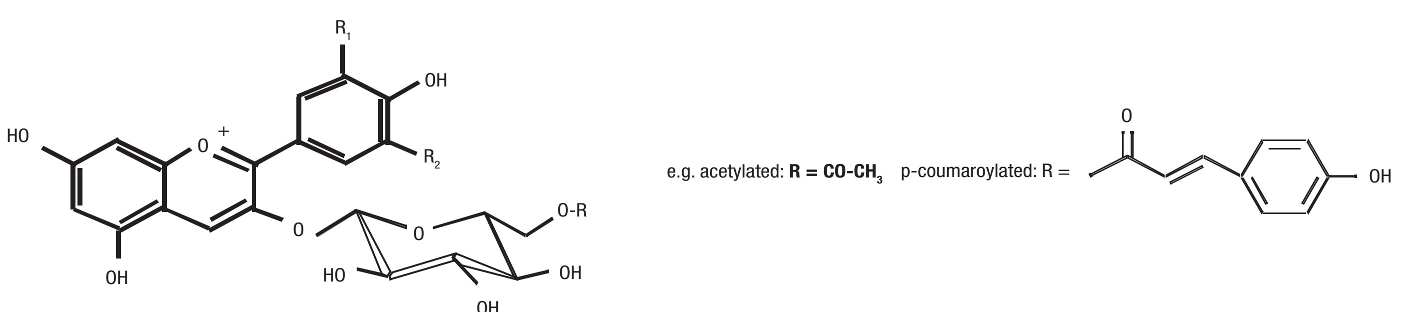
Recent detailed studies have illustrated the possible high introduction of oxygen during the phases of wine preparation (filtration, stabilisation) and bottling (Vidal *et al.* 2001; Vidal *et al.* 2003; Vidal *et al.* 2004). These studies show that a wine can receive, from 1-11mg/L of oxygen during preparation and packaging phases. Controlling these phases, therefore, appears to be unavoidable in the research for wine quality improvement.

Lastly, final oxygen inputs can occur once the wine has been bottled. Following the work of Ribéreau-Gayon in 1931, it was admitted that the quantities of oxygen that enter the bottle via the cork were negligible and were therefore not responsible for the evolutions observed in bottled wine. The arrival of alternative solutions to cork has revived studies on potential oxygen supply via different types of closures. Several recent studies (Godden *et al.* 2001; Skouroumounis *et al.* 2005; Limmer 2005) have shown that different types of closures can have differential influences on the evolution of the wine through, among others, the evolution of the sulfur dioxide content (SO_2) and absorbance at 420nm (OD 420).

Knowing that oxygen can influence the development of aroma, colour and taste characteristics in wines, the importance of providing the required quantities of oxygen at the different phases of the wine's life in order to express the Shiraz's best potential is now evident. In the following section, the mechanisms behind the influence of oxygen are examined in more detail.

The influence of oxygen on aroma development

Aromatic molecules can be classified into different families according to their structural organisation. Due to their chemical structure, these different families present totally different sensitivities to oxygen with some being degraded quickly



through contact with oxygen, while others require the presence of oxygen in order to develop. The Nomacorc research team has summarised the oxygen sensitivity of the main aroma groups in Figure 3.

Shiraz's aromatic pool is essentially present in the form of precursors, and at present it is impossible to predict the evolution of the aromatic precursor pool according to oxygen quantities. This subject requires further detailed research.

Shiraz wines have a tendency to develop reductive odours. It is, therefore, interesting to study the development of sulfurous compounds in relation to oxygen quantities. As illustrated in Figure 3, sulfurous compounds are oxygen sensitive, meaning supplying oxygen to the wine will reduce their concentration. In fact, in the presence of oxygen, the polyphenols in the wine are converted into quinones, which have the ability of creating a complex with the bad-smelling molecules. Andrew Waterhouse, UC Davis, has recently published a summary table of the principal oxidative reactional pathways that demonstrate how the quinones trap the sulfurous compounds.

However, sulfurous compound precursors exist that can produce bad-smelling sulfurous compounds. It is highly important to ensure moderate oxygen supplies throughout the life of the product and ensure a constant quinone production in order to trap the molecules that are formed, either by hydrolysis or under anaerobic conditions as described in Figure 5 taken from a publication by Limmer 2006.

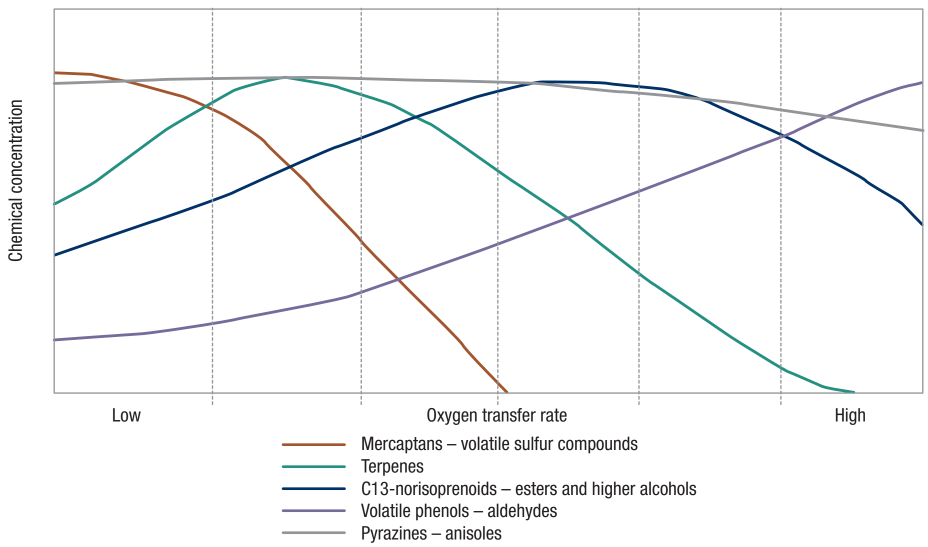
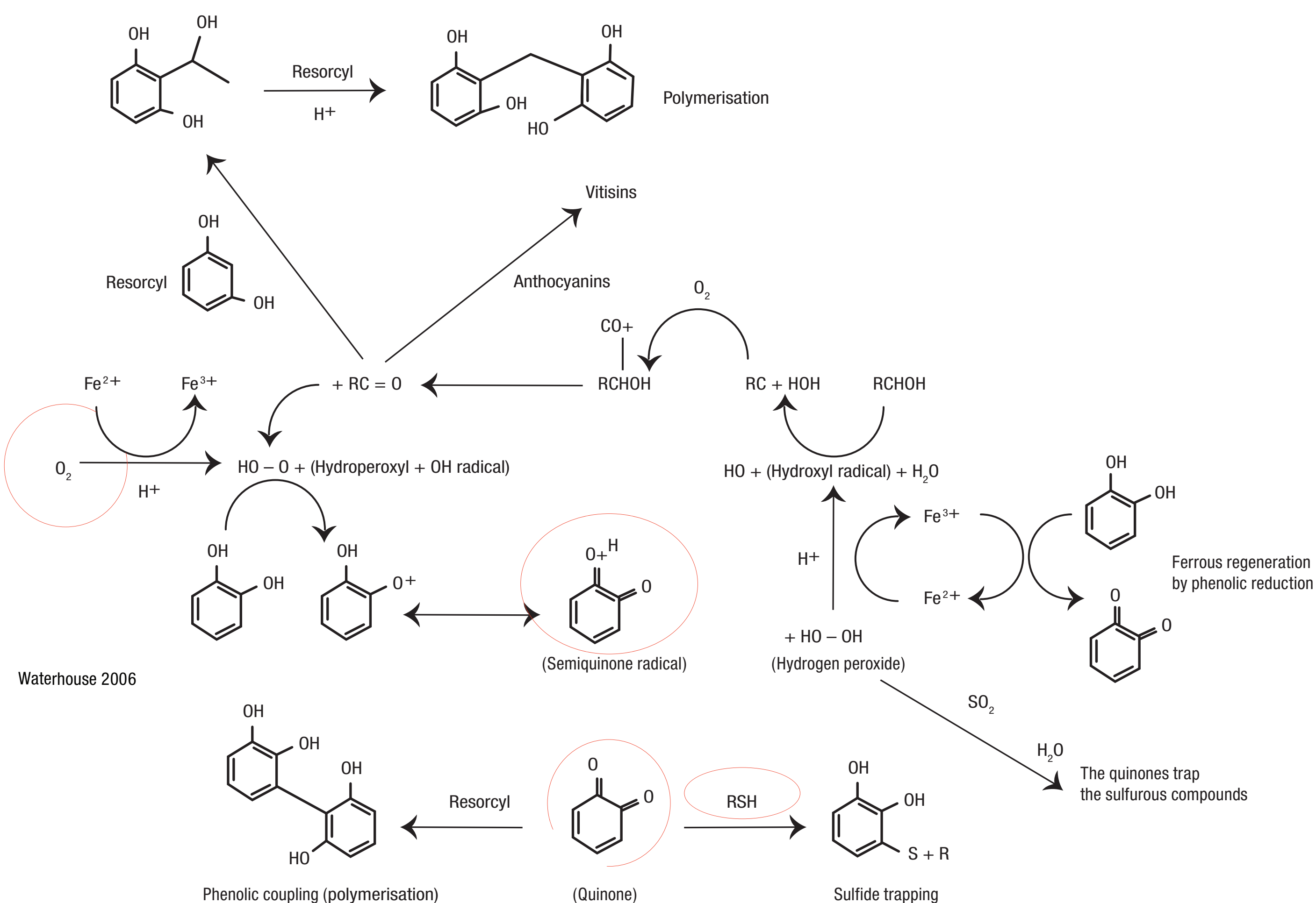


Figure 3. The oxygen sensitivity of the main aroma groups expressed as the amount of oxygen ingress into the wine.



The influence of oxygen on colour development

Anthocyanins are the red pigments in red grape varieties. When these molecules are extracted during the first phases of fermentation and maceration, they are involved in the reactions that give rise to new pigment types responsible for wine colour.

It is sufficient to observe the colour differences in wine during its lifetime in order to understand that the molecules responsible for colour are indeed reacting.

Several types of reactions exist that underlie these colour developments. Among these, the pathways involving molecules produced by the action of active oxygen forms have been well researched. This is notably the case in the anthocyanin reaction with acetaldehyde, produced from ethyl alcohol, which produces pyranoanthocyanins (Fulcrand 1996).

The new pigments possess different spectral characteristics to indigenous anthocyanins, which will influence the tint and the intensity of the wine colour. This is how the brick-red tint in red wines is able to develop.

The powerful violet pigments contained in Shiraz enable it to tolerate high oxygen supplies relatively well during vinification, as the violet pigments partially conceal the brown pigments that are formed.

Tannin development

Wine tannins are highly reactive molecules, responsible for astringency, and to a lesser extent, bitterness in wines. Small tannin molecules (monomers and oligomers) are more bitter than astringent, while the large molecules (polymers) are highly astringent and only slightly bitter. Tannins change in size and structure during wine ageing. These transformations can occur in the presence or absence of oxygen, however the resulting structures will differ depending on the reactional pathways taken. In all cases, condensed tannins can 'depolymerise' in acidic conditions, that is to say, that the large molecules can break up into several small molecules. These small molecules contribute to an increase in wine's bitterness. The second important reaction to take into account is that tannins can react between each other to produce larger molecules (re-polymerisation). In

repolymerisation characteristic leads to a wide range of molecule sizes that have different influences on wine astringency and bitterness.

In the presence of oxygen, the situation becomes even more complex. Oxygen brings about the production of different aldehydes, with acetaldehyde being the most abundant. Subsequently, acetaldehyde can react rapidly with the tannins, forming bridges between tannin molecules (copolymerisation). Wines that contain small tannin molecules with structures including ethyl bridges (dimeric, trimeric) are perceived as being more bitter than wines that only contain indigenous tannins. Acetaldehyde can also react with larger tannin molecules to create macromolecular structures (cross-linking) that precipitate and as a result, become inactive in terms of astringency. Consequently, interaction between tannins and oxygen can rapidly increase bitterness (by creating oligomers with ethyl bridges) and can soften tannins (via cross-linking reactions). These evolutions can be depicted in Figure 6.

Regarding tannins, it is important to remember that oxygen supplies must be managed as an integrated process to avoid the development of excess bitterness.

What supply of oxygen is required for Shiraz?

By assessing the previous three paragraphs, it is clear that Shiraz wines require a supply of oxygen throughout their production and storage. Shiraz has a high content of precursors of sulfurous compounds, which can be released throughout the wine ageing process. It would be inaccurate to believe that a supply of oxygen during the vinification phases alone is sufficient to avoid the development of reductive aromas during wine storage.

Supplying oxygen to avoid reductive aromas must not compromise the quality of colour or the sensory characteristics of the wine by causing excess bitterness, for example. The oxygen supply must, therefore, be managed, based on the knowledge of the Shiraz's own potential in aromatic and polyphenolic molecules.

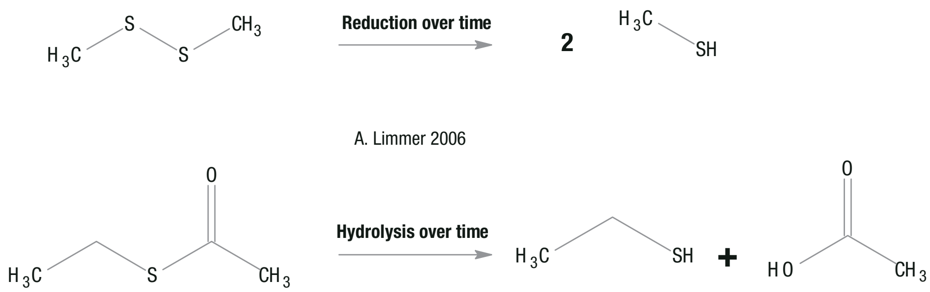


Figure 5. The development of sulfurous compound precursors into bad-smelling sulfurous compounds by reduction or hydrolysis.

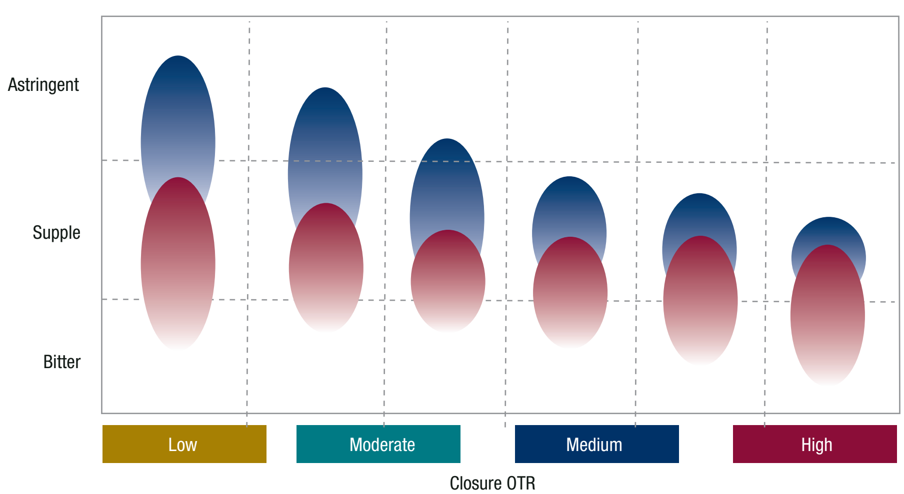


Figure 6. The evolution between tannins and oxygen increasing bitterness and softening

OBSERVATIONS AND APPLICATIONS

Vinification in red wine

Shiraz vinification is carried out in very different ways throughout the world. Nevertheless, each wine producer will implement actions aimed at avoiding the development of reductive characters in the wines.

In the case of traditional vinification, fermentations are carried out in open wooden vats. The intention to aerate the wines is evident, even though it remains difficult to control supply during pumping over and cap punching operations. New vinification methods that use stainless steel tanks and regular, controlled oxygen micro-supply (micro-oxygenation), are now frequent. It is important to insist on the fact that oxygen deficiency during fermentation is one of the causes for sluggish fermentation. Delays in completing alcoholic fermentation leave the wine vulnerable for *Brettanomyces* yeasts to develop and produce large quantities of volatile phenols. Therefore, in addition to reductive notes, faults such as 'horse stable' or 'horse sweat' can appear in the wine.

In managing maturation, different itineraries are also followed. It appears that maturing on lees in barrels with no lee stirring or pumping over generates the appearance of strong reductive notes, which can be persistent. In this case, the decision can be made to heavily aerate these wines, but this practice tends to generate the appearance of unwelcome garlic and metallic notes.

It is more judicious to opt for clarified wine maturing methods (elimination of the lees which have a high reduction potential) with more frequent rackings, aiming for wines that are as open as possible at bottling.

The case of vinification in rosé wines

Rosé wines are quite successful on the current market, with the long-criticised wines now appreciated by new types of consumers. The colour of rosé wines is a determining factor in the consumers' choice of purchase and the trend is towards not too strongly coloured, clear wines with no brown hues.

In this context, Shiraz wines have assets as they can provide purple-blue notes at blending which guarantees the rosé wine a shimmering colour.

However, rosé wines are supposed to contain a lot of fruity notes and would suffer from any notes of reduction concealing the fruit. Particular attention should be paid to rosé wines containing Shiraz, possessing a higher risk of developing reductive characters. Oxygen management is in this case much more delicate than for red wines, as the room to manœuvre is much smaller due to the lower concentration of polyphenols in rosé wines.

Oxygen supply management after bottling

Even when particular efforts have been made to produce wines, which are as open as possible prior to bottling, Shiraz wines can still develop reductive characters once bottled. In this context, the choice of closure becomes crucial. It is important to know the oxygen transmission rate (OTR) of the closures and the consistency of their performances to make the right choice in order to ensure the best possible expression of Shiraz wines. On the closure market, numerous solutions exist, but not all are equivalent in delivering an optimal quantity of oxygen to a Nomacorc has given rise to a range of closures, that guarantee a consistent high quality bottle closure, and at the same time, allows for controlled oxygen ingress at different OTRs according to the chosen closure version.

Shiraz wines must not be closed with closures that are too hermetic. As we have seen, these wines require small quantities of oxygen throughout storage to ensure the production of quinones that can trap the progressively produced bad-smelling sulphurous molecules.

Nomacorc leads research programs in partnership with leading oenology research teams throughout the world. These programs aim to gain a better understanding of the influence of the closures' OTR on wine development. Nomacorc is working with Adelaide-based Provisor on Shiraz, and is initiating another key project with the AWRI.

CONCLUSION

Oxygen management during the phases of vinification and storage must be managed according to the knowledge acquired concerning the aromatic and polyphenolic composition of Shiraz. Particular care must be taken to avoid the appearance of reductive notes.

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