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Review

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Oxygen Contribution to Wine Aroma Evolution during Bottle Aging

Maurizio Ugliano*

Nomacorc France, Domaine de Donadille, Avenue Yves Cazeaux, 30230 Rodilhan, France

ABSTRACT: Wine aroma undergoes major changes during bottle aging, which are deeply influenced by the degree of oxygen exposure in the bottle. This review discusses the involvement of oxygen in the main chemical transformations occurring in wine aroma composition during bottle aging, with particular emphasis on the formation of oxidative aroma compounds and formation/degradation of sulfur-containing volatile compounds. The implications for wine sensory properties are discussed, as well as some practical aspects of oxygen management during bottle aging, including the role of closure oxygen permeability.

KEYWORDS: *oxygen, wine aging, wine aroma, aldehydes, polyfunctional thiols, mercaptans, hydrogen sulfide, wine closures*

INTRODUCTION

Unlike many other foods, which normally experience a decline in sensory properties during their shelf life, the evolution of wine sensory quality is thought to reach a peak after a period in the bottle. The length of this time frame can vary enormously depending on the wine, meaning that some wines evolve very rapidly toward an optimum followed by a decline, whereas others can stand several years of aging during which their overall sensory characters evolve favorably. In certain wine regions, a minimum period of bottle aging is prescribed by the regulation of specific appellations.

In his studies on wine, Pasteur theorized that only when a wine is exposed to oxygen can it develop the pleasant aroma and mouthfeel attributes of finely aged high-quality wines.[1] During bottle maturation, wine is exposed to relatively low quantities of oxygen, which are nevertheless sufficient to influence the outcomes of bottle aging.[2] In particular, oxygen modulates the extent of different reactions involving volatile and nonvolatile components, resulting in the formation/degradation of a number of powerful aroma compounds, with major consequences on the process of aroma evolution during bottle aging.[3−8] In addition, other chemical reactions taking place during bottle aging do not involve oxygen, meaning that, even in an environment completely devoid of oxygen, a certain form of aging will occur.[3]

In recent years, the development of procedures allowing the quantification of the oxygen present in a bottle at different times during aging has greatly improved our understanding of how oxygen contributes to aroma development during bottle maturation.[4−11] Nevertheless, the chemical mechanisms involved in the formation of many key aging aroma compounds remain to be established, and key factors are yet to be properly identified and rationalized.

In this review, the process of aroma evolution during wine bottle aging is discussed from the point of view of the contribution of oxygen both as driver of quality improvements and as a vector of wine spoilage. The practical implications of different oxygen-related chemical transformations are evluated with regard to their role in the production of wines with improved sensory characteristics.

OXYGEN EXPOSURE IN A WINE BOTTLE

Upon bottling under typical industry conditions, both the wine and the gaseous headspace of the bottle contain substantial amounts of oxygen. The sum of these two components is commonly referred to as total package oxygen (TPO), which can vary over a range of approximately 1−9 mg/L.[9] In the case of cylindrical closures, additional oxygen is released in the bottle in the weeks or months following bottling, due to compression in the bottleneck, increasing oxygen partial pressure inside the closure.[7,10] Because young wines contain large concentrations of oxygen reactive species, the oxygen present at bottling is rapidly consumed by the wine (Figure 1, curves A and B). However, additional oxygen can enter in the bottle, depending on the oxygen permeability of the closure. This oxygen ingress is typically slower than the rate of oxygen consumption of the wine, so that, after consumption of the initial excess of oxygen, dissolved and headspace concentrations of oxygen are usually very low (often in the micrograms per

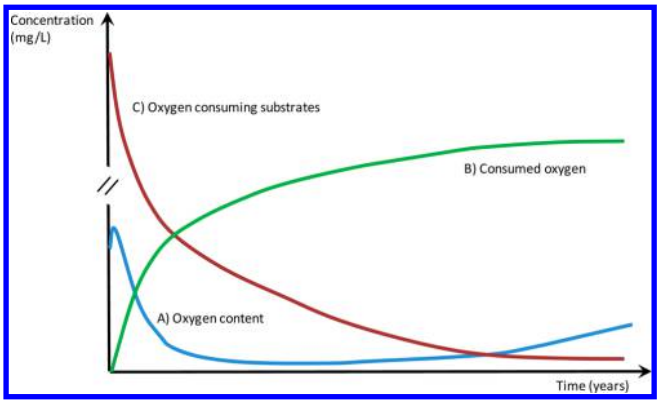

Figure 1. Theoretical representation of the evolution of oxygen content in the bottle, cumulative oxygen consumption, and content of oxidizable substances during bottle aging.

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liter range).[11] As the wine reacts with oxygen, oxidizable substrates are progressively depleted (Figure 1, curve C), with a consequent decrease in wine capacity to consume oxygen. Theoretically, this could eventually lead to the rate of oxygen ingress becoming higher than that of oxygen consumption, resulting in a net accumulation of free oxygen in the bottle. In the case of a substrate such as SO_2, the evolutions of curves B and C have been shown to be closely correlated during longer term bottle aging, whereas curves A and C are well correlated only in the initial period of bottling.[11]

OXYGEN AND PHENOLICS: WINE PRIMARY OXIDATION

Oxygen in wine is in the unreactive triplet state, and its ability to react directly with most wine components is low.[12] This reactivity is largely increased in the presence of an oxidation catalyst, which in the case of wine can be iron. Accordingly, Fe^{2+} can donate an electron to oxygen, resulting in the formation of a superoxide ion $O_2^{\bullet-}$, which at wine pH exists as a hydroperoxyl radical (Figure 2). This radical has relatively low

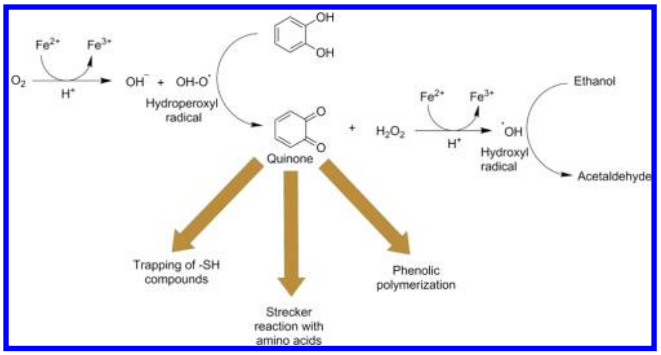

Figure 2. Oxygen-driven formation of quinones and hydrogen peroxide, consequent oxidation of ethanol to acetaldehyde, and main reactions of quinones in the wine environment.

reactivity in the wine environment, therefore reacting only with strong hydrogen-donating species such as wine phenolics.[13] Reaction of superoxide ion with *o*-diphenols present in wine will lead to the formation of quinones and H_2O_2 at wine pH (Figure 2). Both of these species play a crucial role in several of the chemical reactions influencing wine aroma during bottle aging. Indeed, hydrogen peroxide can react with ferrous ions via a Fenton reaction mechanism to give hydroxyl radical, an extremely reactive species capable of oxidizing indiscriminately wine components to an extent proportional to their concentration.[12] Following this pathway, ethanol, which is the most abundant nonwater component of wine, will be oxidized to acetaldehyde, whereas other aldehydes can be formed from the oxidation of tartaric acid or other alcohols.[12−15]

Quinones, on the other hand, can participate in an array of reactions involving aroma compounds or aroma precursors, which will be discussed later in this review. However, quinones and their *o*-diphenol precursors can also react with several other substrates typically present in wine (for example, other phenolic compounds), and these reactions will be in competition with the ones involving aroma-related components.[16]

In addition, wine typically contains several antioxidants that are able to modulate the extent of oxidative damage. Among these, sulfur dioxide (SO_2) is naturally present as a result of yeast metabolism and can be further added as antioxidant and antimicrobial. Direct reaction of SO_2 with oxygen is slow and has a marginal role in SO_2 antioxidant activity. However, the ability of SO_2 to reduce the powerful oxidant hydrogen peroxide to water, as well as to reconvert quinones to phenols,[14] makes it a very effective antioxidant for wine (Figure 3). Recent observation also highlighted the ability of SO_2 to

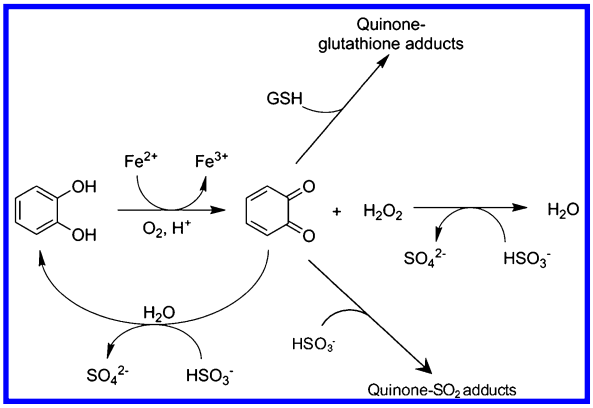

Figure 3. Proposed mechanisms illustrating SO_2 and GSH antioxidant protection in wine (adapted from refs 14, 15, and 17−19).

form stable adducts with quinone.[17] Wines can also contain significant amounts of glutathione (GSH), a naturally occurring antioxidant from grapes and yeast metabolism, with high affinity for quinones[18,19] (Figure 3). Ascorbic acid is also added often to white wine as an antioxidant. The chemistry of this compound in wine has been reviewed elsewhere.[20]

Finally, pH is known to deeply affect the rate of oxygen consumption of a wine and its rate of oxidation. Oxygen uptake is faster at higher pH, and for this reason several studies on the oxidation of wine phenolics have been carried out at alkaline pH.[19] However, it was shown that global oxygen consumption of a wine, albeit slower, is greater at acidic pH than at alkaline.[19] No correlation was observed between pH and browning susceptibility of white wines.[21]

EVOLUTION OF WINE AROMA COMPOSITION DURING BOTTLE AGING

Wine aroma changes dramatically during bottle aging, through a complex array of chemical reactions that are only partly understood. Table 1 summarizes the main changes occurring in key wine aroma compounds during aging, highlighting the possible contribution of oxygen. In most cases, oxygen contributes to the evolution of these key aroma compounds. Some cases exist that do not involve oxygen, for example, the acid-catalyzed reactions of fermentation-derived aroma compounds and their precursors.[22,23] In some other cases, the role of oxygen remains to be established, for example, for methoxypyrazines.[24] Overall, the major areas of influence of oxygen appear to be linked to the formation of certain oxidative aromas compounds (e.g., aldehydes or sotolon) and the formation/degradation of sulfur-containing volatile compounds, which are largely discussed in this review.

Oxidative Phenomena Affecting Wine Aroma. Under typical industry conditions, a certain degree of oxygen exposure will inevitably occur during bottle aging. Early work on oxidative spoilage of white wines indicated that oxidation brought about sensory characters described as honey, farm-feed, and hay,[25] as well as cooked vegetables, woody, liquor, and cider,[26] with a concomitant decrease in wine floral and fruity attributes. A number of trace aroma compounds (Figure

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Table 1. Chemical Compounds Implicated in Aroma Evolution during Wine Bottle Aging

compound(s)	examples	trend during aging	contribution of oxygen[a]	ref
polyfunctional thiols	3SH, 3SHA, 4SMP	decrease	yes	4, 7, 51, 54, 55, 71
	benzyl mercaptan	possible increase	yes	65
H_2S		possible increase	yes	4, 7, 8
MeSH		possible increase	yes	7, 8
DMS		increase	no	8, 72, 74, 75
C_3–C_{10} fatty acid esters	ethyl hexanoate	decrease	not known	22, 23
ethyl acetate		variable	not known	22
acetate esters	3-methylbutyl acetate	decrease	not known	22, 23
branched-chain ethyl esters	ethyl 3-methylbutanoate	increase	not known	22, 23
acetaldehyde		increase	yes	16
aliphatic aldehydes	*trans*-2-nonenal	increase	yes	28, 30
higher alcohols	3-methyl-1-butanol	generally stable but small amounts can be converted to aldehydes	yes	28, 30, 34
Strecker aldehydes	methional	increase	yes	28, 30
sotolon		increase	yes	4
3-methyl-2,4-nonadione		increase	possible	38, 39
aliphatic lactones	nonalactone	increase	possible	39
norisoprenoids	TDN, damascenone	increase	not known	22, 23
monoterpenes	linalool	increase, then decrease	not known	23
methoxypyrazines	3-isobutyl-2-methoxypyrazine	decrease	not known	24

[a]Refers only to chemical reactions, without considering microbial metabolism.

4) have been identified as major contributors to the aroma of oxidation-spoiled white wines, including 3-(methylthio)-propionaldehyde (methional), phenylacetaldehyde, 2,4,5-trimethyldioxolane, aliphatic aldehydes such as *trans*-2-nonenal, and sotolon (3-hydroxy-4,5-dimethylfurnan-2(5*H*)-one).[25−29] The aldehydes, methional and phenylacetaldehyde, are among the oxidation-related aroma compounds that have drawn the most attention, due to their supposedly greater aroma impact and possible contribution to the aroma of red and white wines.[25,28,30] For these aldehydes, formation from the amino acids methionine and phenylalanine, respectively, via Strecker reaction involving the presence of a dicarbonyl compound has been proposed[28,29,31,32] (Figure 5A,B). In theory, other aldehydes can be formed following this mechanism, for example, branched-chain aldehydes such as 2-methylpropanal from valine and 2- and 3-methylbutanal from isoleucine and leucine, respectively. Wine contains several types of dicarbonyl compounds, some of which derive from oxygen exposure. For example, as previously discussed, highly reactive quinones will be formed from oxidation of wine *o*-diphenols, which can then react with amino acids through a Strecker mechanism (Figure 5A).[32] This would be in agreement with the observation that large amounts of methional and phenylacetaldehyde are present in wines deliberately exposed to an excess of oxygen.[25,27] However, when dry wines were exposed to air in the laboratory, increases in the concentrations of methional and phenylacetaldehyde were observed, but the concentration of branched-chain aldehydes remained unchanged.[30] Conversely, the same wines submitted to long bottle aging showed increased concentrations of both types of aldehydes.[30] These observations remain difficult to interpret without any data on the kinetics of reaction of different amino acids with dicarbonyls under wine conditions. Different *o*-diphenols were shown to form different quantities of aldehydes, with caffeic acid giving higher methional and phenylacetaldehyde compared to catechin and epicatechin,[32] but this was observed at pH much higher than that of wine. More recently, it was shown that in wine-like conditions methionine and phenylalanine were not capable of reacting with a model quinone.[33] On the other hand, wine contains also other dicarbonyls, arising from microbial metabolism. These include diacetyl, glyoxal, and methylglyoxal.[31] Formation of aldehydes involving these carbonyls and the corresponding amino acids has been demonstrated in wine-like medium[31] and might play a role in the formation of aldehydes during bottle aging (Figure 5B). Finally, wine contains also relatively large amounts of higher alcohols derived from yeast metabolism, such as 2- and 3-methylbutanol, phenylethanol, and 3-(methylthio)-1-propanol (methionol). The possibility that aldehydes could be formed from the oxidation of the corresponding alcohols has been previously suggested[28,33,34] (Figure 5C), and a good correlation between the precursor−final compound couples methionol−methional and phenylethanol−phenylacetaldehyde was re-

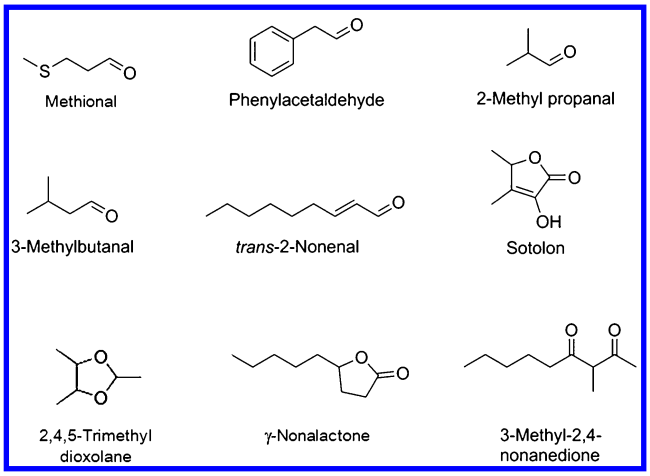

Figure 4. Aroma compounds observed in oxidation-spoiled wines.

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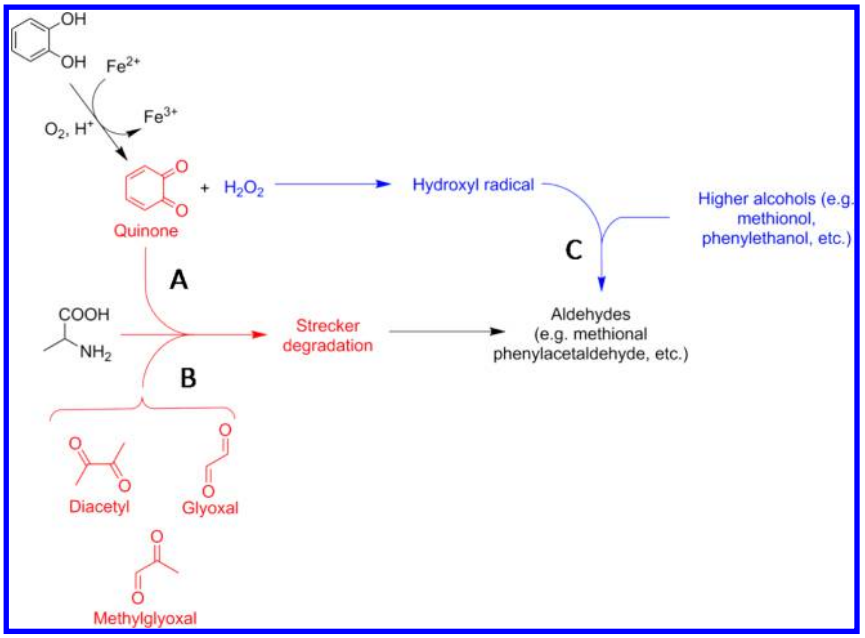

Figure 5. Mechanisms of formation of branched-chain aldehydes in wines via (A) Strecker degradation of amino acids involving nonenzymatic formation of quinones, (B) Strecker degradation of amino acids involving dicarbonyl compounds of microbial origin, or (C) oxidation of higher alcohols by hydroxyl radical (adapted from refs 12, 13, 26, 29, and 30).

ported in aged wines.[35] Such a mechanism would be analogous to the one generating acetaldehyde from ethanol and could potentially be involved in the formation of several aldehydes from the corresponding alcohols. It should be noted that the different mechanisms described are not mutually exclusive, and therefore they could all be actively contributing to aldehyde formation during wine bottle aging, albeit at different rates. For example, Escudero et al. observed increased formation of methional in wines with both added methionine and methionol.[28] In addition to formation mechanisms, the actual occurrence of aldehydes at different stages of wine bottle aging might also depend on their reactivity in the wine environment. Acetaldehyde can be involved in condensation reactions with flavanols and anthocyanins, potentially resulting in its decrease of acetaldehyde.[36] The involvement of other aldehydes in these reactions remains to be demonstrated.

SO_2 is likely to have a strong modulation role in aldehyde-related reactions. Formation of quinone–SO_2 adducts[17,33] as well as quinone recycling to the parent *o*-diphenols by SO_2[14,15] would indeed prevent reaction with amino acids. Oxidation of alcohols would be also prevented as SO_2 can reduce H_2O_2 to water (Figure 3). Also, SO_2 can reversibly combine with microbial-derived dicarbonyls to prevent their reaction with amino acids, but these will become available as SO_2 levels drop, for example, as a result of oxygen exposure. Diacetyl availability for oxidative reactions is also influenced by the reduced/oxidized glutathione redox couple, which could further contribute to modulate formation of aldehydes from amino acid–dicarbonyl reactions.[37] In the presence of sufficient SO_2, aldehydes will be in combined form, but might be released if SO_2 is depleted.

In some recent studies the compound 3-methyl-2,4-nonadione was identified as a potential contributor to prune and dry fig oxidative off-odors in red wines, either alone or potentially in conjunction with γ-nonalactone and massoia lactone (5,6-dihydro-6-pentyl-2*H*-pyran-2-one).[38−40] It was suggested that oxygen might play a role in the formation of 3-methyl-2,4-nonadione.[39] Other authors also observed the presence of 3-methyl-2,4-nonadione in Spanish aged red wines,[41] although in that case it was not negatively correlated with wine sensory quality.

Finally, sotolon has also been associated with oxidative spoilage of dry white wine,[25−27,42] presumably originating from aldol condensation between α-ketobutyrate and acetaldehyde.[43] Under conditions of bottle aging, a positive relationship between the degree of oxygen exposure and the concentration of sotolon has been observed.[4,42]

Overall, although many aroma compounds relevant to wine oxidation have been identified, most studies were aimed at understanding wine oxidative spoilage and were often carried out under conditions of extreme oxygen exposure. Conversely, oxidative processes taking place during bottle aging under normal conditions are rather "mild", and the significance of such levels of oxidation to the aroma quality of wines remains to be established. For example, some aroma characteristics of long-aged red wines, such as sweet orange and dry fruit, could be linked to the presence of increased concentrations of branched-chain aldehydes in combination with β-damascenone.[30]

As well as contributing to increased levels of oxidative compounds, oxygen-related reactions can also result in the loss of aroma compounds associated with fresh and fruity aromas. Certain white wines made with grapes such as Sauvignon blanc, Verdejo, Petit, and Gros Manseng are characterized by intense aromas of passion fruit, grapefruit, and box tree. These aromas are part of the typicality of these wines and are highly sought by consumers. From a chemical point of view, they are linked to the occurrence of certain polyfunctional thiols, particularly the compounds 3-sulfanylhexanol (3SH), 4-sulfanyl-4-methylpentanone (4SMP), and 3-sulfanylhexyl acetate (3SHA)[44−47] (Figure 6). In other red and white wines these aroma compounds have probably a less prominent sensory role, although they still contribute to fresh fruity aromas.[46,48−50] Polyfuctional thiols such as 3SH and 4SMP are present in

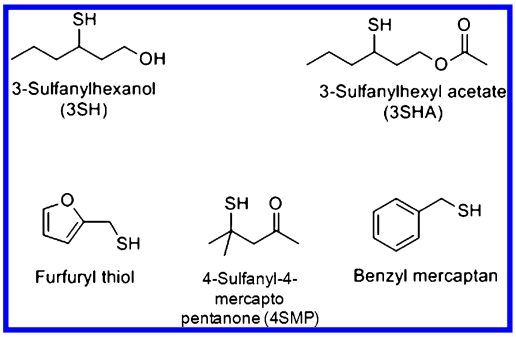

Figure 6. Polyfunctional thiols implicated in wine aroma evolution during bottle aging.

grapes in the form of nonvolatile odorless precursors, which are transformed into fragrant compounds by the action of yeast.[47] Although precursors are still present in the wine at the end of fermentation, these appear to be stable at wine pH, so that free forms of these compounds should not be formed during aging, and indeed they are more likely to decline.[7] The observation[4,7] that higher losses of polyfunctional thiols occur under conditions of higher oxygen exposure suggested that such a decline is linked to oxidative phenomena. Polyfunctional thiols are strong nucleophiles, and therefore they can rapidly react with the quinones formed from oxidation of *o*-diphenols via a Michael addition.[15−17,51] It was shown that (−)-epicatechin was more reactive with volatile thiols than (+)-catechin and that 3SH was generally more reactive than 4SMP with their quinones.[51] Anthocyanins can protect polyfuctional thiols from this type of degradation, and therefore polyfunctional thiols should be better preserved in red wines.[52] SO_2 also prevents loss of polyfunctional thiols, as it can recycle quinones to the original diphenols, bind them directly, or reduce hydrogen peroxide to water.[15,17,51] However, formation of quinone−3SH adducts was shown to occur even in the presence of SO_2, although to a lower extent.[53] Recent observations support the view that quinone trapping is the main mechanism accounting for 3SH loss in wine under oxidative conditions, whereas other mechanisms, for example, the reaction of thiols with Fenton radicals and consequent formation of a disulfide, appear to contribute marginally.[16] The polyfunctional thiol 3SHA represents a different case. The ester structure of this molecule, resulting from yeast-driven acetylation of 3SH, makes it also prone to acid-catalyzed hydrolysis at wine pH, with consequent formation of 3SH. As 3SH has a higher odor threshold than 3SHA, this process is expected to result in lower aromatic intensity and possibly different aroma nuances. Acid hydrolysis was found to have a stronger influence than quinone trapping on the decline of 3SHA during bottle aging of Sauvignon blanc wines under highly hermetic closures such as screw caps.[54,55] In a recent study, the polyfunctional thiol 3-ethylsulfanyl acetate was identified for the first time as a key contributor to off-flavors in Sauvignon blanc wines.[56] This compound was observed at higher levels in aged wines and in wines obtained from juices exposed to air, but the effect of postbottling oxygen exposure on its concentration remains to be investigated.

Formation of Volatile Sulfur Compounds during Bottle Aging of Wine. "Reduction" is a term often used in wine tasting to identify unpleasant aroma properties reminiscent of rotten egg, cabbage, garlic, and putrefaction. These aroma attributes have been associated with the occurrence of different low molecular weight sulfur compounds (LMWSCs), including H_2S, methyl mercaptan (MeSH), ethyl mercaptan (EtSH), and dimethyl sulfide (DMS)[57−62] (Figure 7).

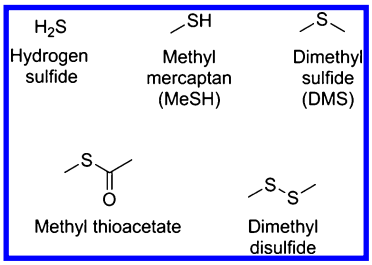

Figure 7. "Reductive" low molecular weight sulfur compounds.

'Reduction' characters are often found to appear after a period of bottle maturation, even in the case of wines that have been bottled "clean". H_2S and MeSH have been indicated by several authors as LMWSC primarily responsible for postbottling reduction.[4,7,8,63] Investigations on the evolution of H_2S during bottle maturation of a white wine showed that this compound can accumulate relatively rapidly, and depending on wine composition, concentrations 3−4 times higher than its odor threshold can be achieved after 6 months in bottle.[7] Wine probably contains precursors that are able to generate H_2S, although these have not been clearly identified to date. Studies in wine-like systems have shown that H_2S can be generated from cysteine in the presence of a dicarbonyl compound.[31] Other authors have hypothesized that H_2S can form from direct reduction of sulfate or sufite.[4] Interestingly, increased accumulation of H_2S was reported during bottle aging of wines with copper sulfate added upon bottling, a common winery practice to reduce the risk of formation of 'reductive' off-odors.[7]

In addition to a direct contribution to wine aroma, H_2S accumulation during bottle aging might represent also a key step in the formation of other aging-related aroma compounds. Reaction of H_2S with furfural can result in formation of the potent roasted coffee aroma furfuryl thiol[64] (Figure 6), whereas formation of the smoky/empyreumatic polyfunctional thiol methyl mercaptan from the reaction of benzaldehyde and H_2S has been suggested but not conclusively demonstrated.[65,66] According to Marchand et al.[67] H_2S is an intermediate in the formation of other powerful odorants such as thiazoles, characterized by roasted aromas. In model solutions containing 20% ethanol, H_2S can react with other −SH compounds in the presence of copper to form mixed di- and trisulfides, which may further contribute to 'reductive' off-odors.[68] The role of H_2S as intermediate in the formation of other sulfur-containing odorants during wine aging deserves further investigation.

Methyl mercaptan (MeSH), a powerful odorant characterized by cabbage and sewage odors, also accumulates during bottle aging. Origins of this compound remain to be established, as no correlation with possible precursors such as methythio acetate or dimethyl disulfide was observed.[8,34] Formation of MeSH from methional and methionine was also reported at wine-like conditions,[31] but this pathway should be verified in real wines. MeSH formation during wine bottle aging remains a complex topic, and more specific studies are needed in this area.

The influence of oxygen exposure on the levels of H_2S and MeSH has been documented by several studies,[4,7,8] and one example is shown in Figure 8 for MeSH. Accumulation of this compound was found to occur mainly between 6 and 12

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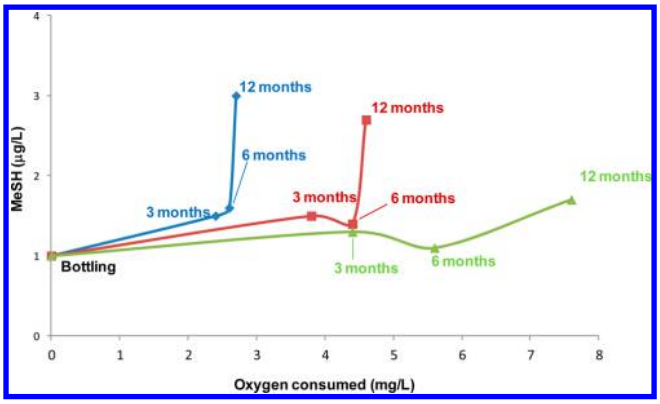

Figure 8. Evolution of MeSH during bottle maturation under three regimens of oxygen exposure in Shiraz wine (adapted from ref 8).

months of bottle storage. In this time frame, the amount of oxygen consumed by the wine was found to be particularly critical to MeSH concentration, with low levels of oxygen consumption corresponding to larger accumulation of MeSH.[8] Specifically, a considerable decrease in the accumulation of MeSH was observed only when oxygen consumption reached approximately 7 mg/L during one year in the bottle.[8] Several hypotheses have been formulated regarding the mechanisms accounting for the loss of H_2S and MeSH in the presence of sufficient oxygen exposure. Oxidation of mercaptans to the corresponding disulfides has been proposed to explain the lower levels of mercaptans observed in wines aged under closures allowing higher oxygen ingress,[69] but this has not been proven. Recent data indicate that, under conditions of controlled oxygen exposure, MeSH decrease is not accompanied by a concomitant increase in the concentration of dimethyl disulfide.[8,70] As previously discussed for polyfunctional thiols, H_2S and MeSH are strong nucleophiles, and they can react with electrophilic oxidation intermediates resulting from phenolic compounds, such as quinones. This hypothesis is supported by the observation that the presence of GSH, a powerful quinone trapping agent, increased accumulation of H_2S and MeSH[7] during bottle maturation. The high reactivity of H_2S toward a model quinone in wine-like solutions was recently shown,[33] whereas others have suggested that formation of disulfides through oxidation of corresponding mercaptan is likely to occur only in wines having low potential to form quinones.[71] It appears therefore plausible that quinone scavenging is responsible for the lower concentrations of H_2S and MeSH observed in wines exposed to more oxygen.

The major pathways potentially involved in the formation and degradation of H_2S and MeSH in wine, as proposed by different authors, are summarized in Figure 9. The balance between formation and consumption reactions will determine the concentration of these compounds at any given time during bottle aging, and this can be modulated by competitive quinone-consuming reactions involving other wine components (for example, glutathione) and levels of oxygen exposure. In addition to reactions directly involving the volatile compound, oxygen exposure could influence reductive compound formation at the level of the precursor(s). For example, a thiol precursor such as cysteine would react with quinones and presumably become unavailable to generate H_2S. Moreover, the patterns of accumulation of H_2S and MeSH during bottle maturation were found to vary considerably among different wines, which might depend on the concentration of individual precursors as well as the presence of reactive species capable of scavenging −SH compounds.[7,8] Further research is needed to clarify the contribution of all these different factors in the context of wine aging.

The concentration of the LMWSC dimethyl sulfide (DMS) also increases during bottle aging, which can have an important role in wine aroma.[72−74] The amount of DMS formed during aging is linked to grape variety, viticultural practices,[74] and fermentation conditions,[75] presumably through an influence on the concentration of the main DMS precursor, *S*-methylmethionine.[72] Under the bottle aging conditions typical of table

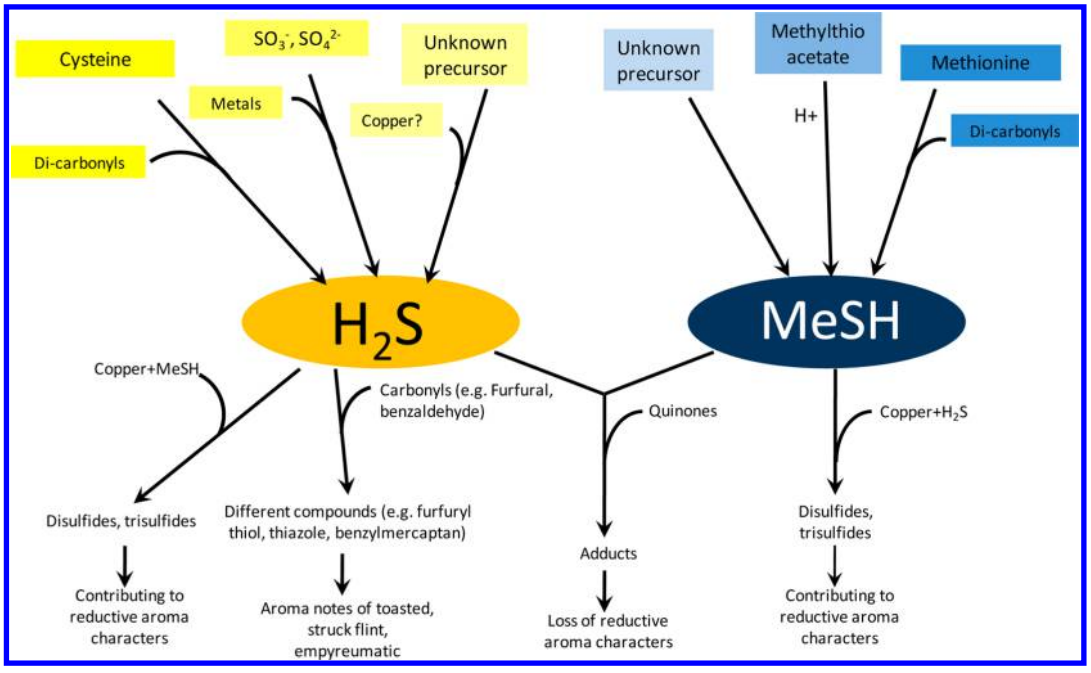

Figure 9. Summary of possible pathways for the formation and degradation of H_2S and MeSH during aging.

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Table 2. Oxygen Permeability Values of Different Commercially Available Closures

	oxygen permeability	ref	comments
natural cork	0.0001−0.1227 mL O_2/day	2	range observed on closures from the same lot, at 36 months after bottling
	2.3 (±0.60); 3.8 (±1.1); 3.2 (±0.4) mg/L/month in the first month	10	oxygen ingress value;[b] different values refer to different lots of similar grade closures
	0.37 (±0.22); 0.5 (±0.3); 0.24 (±0.16) mg/L/month during 2nd−12th months		
	0.27−0.84 mg/month in the first month	79	oxygen ingress value[b]
	0.02−0.16 mg/month during second−third months		
	0.7−27.8 mg/year/cm^2	81	actual OTR value[a]
microagglomerated	1.4 (±0.05) mg/L/month in the first month	10	oxygen ingress value[b]
	0.10 (±0.02) mg/month during 2nd−12th months		
synthetic injected molded	0.27−0.84 mg/month during the first month	79	oxygen ingress value[b]
	0.13−0.63 mg/month during second−third months		
	4.3 (±0.17) mg/L/month during the first month	10	oxygen ingress value[b]
	1.5 (±0.34) mg/L/month during second−third months		
synthetic coextruded	11.9 μg/day	5, 6	actual OTR value;[a] data for two different types of closure from the same manufacturer
	8.0 μg/day		
	11.9 μg/day	98	actual OTR value;[a] data for three different types of closure from the same manufacturer
	7.6 μg/day		
	3.8 μg/day		
	3.6 (±0.17) mg/L/month during the first month	10	oxygen ingress value[b]
	0.85 (±0.25) mg/L/month during second−third months		
	0.017 (±0.0006) cm^3/day in 100% oxygen	78	actual OTR value;[a] data for three different types of closure from the same manufacturer
	0.022 (±0.002) cm^3/day in 100% oxygen		
	0.033 (±0.0006) cm^3/day in 100% oxygen		
screw cap Saran tin	0.0002−0.0008 mL of O_2/day	2, 83	
	0.00005 (±0.0001)−0.00043 (±0.00055) mg/L/day		
screw cap Saranex	0.00008 (±0.00009)−0.02730 (±0.02837) mg/L/day	83	

[a]Defined as the steady state rate at which oxygen permeates through the closure. [b]Also accounting for oxygen released from the closure.

wines, DMS is not affected by oxygen exposure,[8] although in the presence of an excess of oxygen a decrease in DMS has been reported.[34,76] Also, during bottle aging with yeast lees, a common practice for sparkling wine production, increased DMS was observed at lower oxygen exposure regimens. This probably results from increased yeast-driven reduction of dimethyl sulfoxide[77] rather than influence of oxygen on the formation of DMS from *S*-methylmethionine.

Influence of Oxygen Exposure on Wine Sensory Characters and the Role of Closures. If we leave aside the oxygen resulting from bottling operations, the main factor determining the degree of oxygen exposure in a wine (glass) bottle is represented as the oxygen permeability of the closure. The oxygen transmission rate (OTR), defined as the steady state rate at which oxygen permeates through a given material,[78] has been widely used by the packaging industry to characterize the oxygen barrier properties of films. Although this parameter has been also frequently used for wine closures, comparison of closure performances based on OTR can be misleading. Indeed, the inner cavities of cylindrical closures contain air, which will be released in the bottle as the closure is compressed in the bottleneck, a phenomenon often referred to as "outgassing". Recent studies have shown that the oxygen conveyed inside a bottle through this path can significantly affect wine evolution during bottle aging.[7,8] For this reason, the total value of oxygen ingress should be considered (e.g., outgassing + OTR) rather than OTR alone, especially during the initial period of bottle storage. The degree of oxygen ingress in a bottle can vary largely depending on the type of closure being used, as can be seen in Table 2. Certain production technologies, especially those used for synthetic closures, offer the possibility to obtain a range of closures with preset oxygen permeability values.[76] Different closures also vary for their consistency in oxygen permeability within a single batch as well as across batches,[79,80] with natural cork closures typically exhibiting higher inconsistency due to variations in the structure of the cork material.[10,42,79−82] Inconsistency in oxygen permeability has also been reported for screw caps, which might be due to imperfections in liner[83] or bottle[84] finish.

Since the first closure trials published in the early 2000s, various studies have been carried out on the influence of closure type and oxygen permeability on wine sensory development during bottle aging.[5,10,63,85−89] Generally speaking, the conclusion of these studies is that less permeable closures allow better preservation of fresh fruity aromas, presumably by decreasing oxidative loss of polyfunctional thiols.[4] However, the low degree of oxygen exposure associated with these closures can promote the expression of 'reductive' off-odors.[4,63,85,87,89] Conversely, excessive oxygen exposure in the bottle will result in loss of fruity aromas and oxidative spoilage.[4,85,87,89] The observation has been made that between

the two extremes of too little and too much oxygen, a moderate degree of oxygen exposure allows expression of optimal aroma attributes.[3,4] Unfortunately, only in very few studies has the actual degree of oxygen exposure in the bottle been precisely determined or at least estimated, meaning that it is still rather difficult to define how much oxygen can be beneficial for a wine during bottle aging. Table 3 provides an overview of the results of these studies. Although comparisons should be taken cautiously due to the intrinsic limitations arising from comparing different studies (e.g., different lengths of storage, different bottle volumes, lack of data regarding oxygen at bottling, use of different sensory descriptors), some observations can be made. First, in all cases the ranges of oxygen exposure that can be beneficial to wine development seem much lower than previously indicated. Indeed, from Table 3 it would appear that an exposure to oxygen higher than 12 mg/L over one year (equivalent to less than two saturations of oxygen) can already result in oxidative spoilage, whereas it was previously estimated that 10−25 saturations could result in overall sensory improvement of red wine.[90] One reason for this discrepancy could lie in the difference between the fast oxidation induced by sequential air saturations versus the gentle oxidation taking place during bottle aging, when a synergy exists between the effects of oxygen and that of time. The data in Table 3 also indicate that a certain degree of 'reductive' or 'animal' off-odors (the latter not attributed to volatile phenols and often observed in some Grenache wines[91]), was consistently observed when <1.5 mg/L of oxygen were supplied during one year. On the contrary, improved expression of wine fruity attributes was often observed when going from low (<3 mg/L) to moderate (≈6 mg/L) degrees of oxygen exposure (for example, in the Grenache and Sauvignon blanc studies), in conjunction with a decrease in 'reductive' attributes. This could suggest that certain 'reductive' compounds could possibly mask fruity characters, as proposed by some authors.[35] Overall, further studies are needed to characterize the behavior of different wines in the range of moderate oxygen exposure (e.g., 2−5 mg of O_2/year), where a most balanced aroma evolution of the wine seems to occur. "Scalping" of certain aroma compounds by the closure has also been reported,[92] which should also be considered when investigating the influence of closure on wine aroma

Table 3. Influence of Oxygen Exposure in the Bottle on the Sensory Profile of Wine after a Period of Bottle Aging

wine	time of sensory analysis (months)	degrees of oxygen exposure studied (mg/L)	main trends observed	comments	ref
Grenache red	10	0.6, 1.5, 6, 9.5	'animal' character at 0.6 and 1.5 mg/L; improved expression of red fruit aromas at higher exposures	different degrees of oxygen exposure obtained by varying closure OTR or composition of storage atmosphere	5
Grenache rosé	10	0.3, 0.7, 1.5, 3, 6.1, 9.5	dominant 'animal' character at 0.3 and 0.7 mg/L, progressively decreasing with increasing oxygen; progressive improvement in the expression of 'amyl' and 'strawberry' attributes from 1.5 mg/L onward	different degrees of oxygen exposure obtained by varying closure OTR or composition of storage atmosphere	97
Cabernet Sauvignon	12, 18, and 24	0.8, 3.1, 12.5	sensorially detectable reduction at 0.8 mg/L and 3.1 mg/L; 12.5 mg/L resulted in oxidized wines	different degrees of oxygen exposure obtained by varying bottle filling level	88
Sauvignon blanc	24	1.3, 2.8, 3.8, 4, 4.8, 12	dominant 'reduction' at 1.3 mg/L; moderate to low reduction between 2.8 mg/L and 4.8 mg/L; moderate to high 'overall fruit' between 2.8 and 4.8 mg/L; 'oxidation' at 12 mg/L	different degrees of oxygen exposure obtained by varying closure OTR and headspace oxygen	4

DISCUSSION

Although the first studies on the contribution of oxygen to wine quality date back more than a century, only in the past decade has this area of research drawn major attention.

Oxidation remains a major issue in the wine industry, and whereas episodes of obvious oxidative damage might be less frequent, premature loss of fresh, fruity, and varietal characters is still a recurring problem. Improved monitoring of bottling conditions is expected to reduce the incidence of these issues, but more research is needed to better understand the factors determining the high fragility of certain wines toward oxygen. In particular, there is a lack of comparative studies aimed at rationalizing the contribution of different factors involved in oxidation-related reactions. This is the case, for example, for the reactivity of different wine substrates in Strecker-type reactions. Likewise, as the loss of fruity varietal attributes during aging is in good part linked to trapping of polyfunctional varietal thiols by quinones, more studies on the thiol trapping abilities of different quinones could provide valuable insights in this area. Some recent studies on the chemical reaction of quinones with

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different wine nucleophiles represent a first step forward in this direction.[51,53] In addition, *o*-diphenols, their oxidation products quinones, and the radicals generated during such oxidation can react with different phenolic components, including anthocyanins (either directly or through aldehyde mediation, especially acetaldehyde), tannins,[93,94] and hydroxycinnamic acids.[16] One implication of this complex picture is that quinone-mediated reactions that are relevant to wine aroma can be modulated by other concomitant reactions of quinones with other phenolic components. Such pool of "competitive" reactions might represent an intrinsic "buffering" capacity of wine toward oxidation-related transformations potentially contributing to aroma modifications.

'Reductive' characters have been known for a long time in the wine industry and have been historically associated with yeast fermentation. However, the link between fermentation and 'reductive' characters that develop postbottling has yet to be fully demonstrated, and clearly there is a need to better understand the chemical and biochemical mechanisms involved in the occurrence of 'reductive' aromas during bottle aging, rather than during or shortly after fermentation.

'Reductive' aroma characters can compromise wine perceived quality, including lower perception of fruity attributes, and increased 'rotten' aromas. As such, they should be regarded as a negative outcome of bottle aging. However, it was suggested that subthreshold levels of H_2S can increase wine complexity,[61] and this compound can be also implicated in the formation of potentially favorable aroma compounds such as thiazoles, furfuryl thiol, and benzyl mercaptan. Its occurrence during wine aging should be therefore further evaluated. In addition, one highly challenging area is represented by the definition of an optimal balance of reductive versus oxidative winemaking and bottle aging conditions, for the preservation of 'positive' −SH compounds (e.g., polyfunctional thiols) versus accumulation of excessive 'reductive' −SH compounds (e.g., H_2S and MeSH).[3,95] The data in Figure 10 show that these two groups

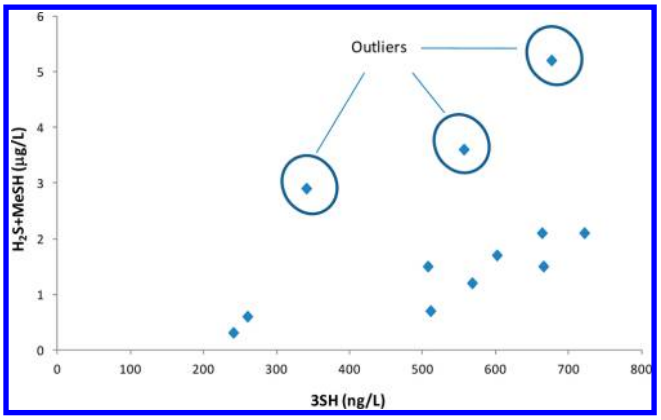

Figure 10. Correlation between the polyfunctional thiol 3SH and the 'reductive' LMWSC H_2S and MeSH after 6 months of bottle storage of a Sauvignon blanc wine under different regimens of oxygen exposure. (Data extracted from ref 7.)

of compounds are often closely connected, meaning that conditions favoring polyfunctional thiols are also likely to favor H_2S and MeSH. Moreover, as shown, outliers also exist, highlighting the underlying complexity due to intrinsic compositional differences existing among wines. These differences might include, for example, GSH and copper concentration at bottling[7] or even oxygen exposure of the wine before bottling.[8] For wines having the same composition, H_2S was shown to be more responsive than 3SH to variations in oxygen exposure.[7] Higher reactivity of H_2S with quinones compared to 3SH was also observed in model wine system.[33]

Moreover, the contribution of oxygen exposure to optimal wine development in the bottle should be also regarded from the point of view of the specific sensory "sensory space" of each wine.[96] For example, it was found that wines of higher price (and longer bottle aging) are richer in both oxidation and reduction compounds,[35] suggesting that, depending on the wine matrix, these compounds might not be drivers of sensory faults but actual contributors to overall complexity.

Sufficient evidence has been provided in recent years to support the view that selection of closures with adequate oxygen permeability can allow effective control of both reduction and oxidation, ultimately delivering wines with improved sensory characteristics. In addition, increased consistency of oxygen permeability is expected to result in improved control on wine evolution during bottle aging, ultimately offering to consumers wines with more consistent sensory properties. Whereas the majority of the studies seem to agree on the fact that moderate oxygen exposure can be beneficial for wine evolution during bottle aging, actual values or even ranges for optimal oxygen exposure are still not available. Given the intrinsic diversity existing across individual wines, the great challenge in this regard remains the ability to predict the tendency of a wine to develop 'reductive' or 'oxidative' characters and, in general, to define how much oxygen a wine might need to express improved sensory characteristics. This information is crucial to select closures with appropriate oxygen permeability, to obtain distinct and specific wine styles.[2,97,98] Moreover, a better understanding of the potential improvements to wine sensory quality associated with oxygen exposure could lead to the development of novel winemaking practices based on improved oxygen management.

Finally, in addition to delivering to consumers more enjoyable wines, it is expected that more rationalized oxygen management strategies will also allow a decrease in the use of SO_2, in line with the current recommendations of the major food and health organizations worldwide.

AUTHOR INFORMATION

Corresponding Author

*Phone: +33 (0)786294104. E-mail: m.ugliano@nomacorc.be.

Notes

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