JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

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Scalping of Light Volatile Sulfur Compounds by Wine Closures

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ABSTRACT: Closures have an important influence on wine quality during aging in a bottle. Closures have a direct impact on oxygen exposure and on volatiles scavenging in wine. Model wine solution soaking assays of several types of closures (i.e., natural and technical cork stoppers, synthetic closures, screw caps) with two important wine volatile sulfur compounds led to a considerable reduction in their levels. After 25 days, cork closures and synthetic closures, to a lesser extent, have significantly scavenged hydrogen sulfide and dimethyl sulfide. These compounds have a determinant impact on wine aging bouquet, being largely responsible for "reduced off-flavors". Hydrogen sulfide levels are often not well correlated with the exposure of wine to oxygen or with the permeability of the closure. Its preferential sorption by some types of closures may explain that behavior. Scalping phenomenon should be taken into account when studying wine post-bottling development.

KEYWORDS: *Cork closures, reduction off-flavors, scalping, wine evolution*

INTRODUCTION

Wine post-bottling evolution has been an extensively studied subject, especially over the last decades. While storage conditions like cellar temperature and relative humidity or light exposure are certainly determinant for the conservation of wine organoleptic properties, closures play a key role on wine quality evolution during aging in a bottle.[1−9] This impact may be double since closures are related both with oxygen exposure[6,10−12] and with the scalping of flavor compounds.[13−17] Indeed, wine oxygen intake after bottling depends on (i) barrier properties exhibited by each closure type,[11] (ii) oxygen present in the headspace at bottling,[5] and also, to some extent, (iii) the amount of oxygen contained by the closure itself.[6] In general, oxygen exposure is greater for wines bottled under synthetic stoppers and smaller for those bottled under screw caps and technical corks, while natural cork stoppers present an intermediate behavior.[10,11] It is commonly accepted that an exaggerated exposition to oxygen leads to depletion of wine's organoleptic properties (i.e., oxidative aromas). However, on the other hand, the lack of a small amount of oxygen, either at bottling or as a result of oxygen permeation through the closures, results in undesirable reductive aromas, such as cabbage-, garlic-, onion-, or rubber-like aromas. Reduced character in wine is generally associated with the presence of highly volatile sulfur compounds (VSC) (bp <90 °C), such as hydrogen sulfide (H_2S), methanethiol (MeSH), ethanethiol (EtSH), dimethyl sulfide (DMS), diethyl sulfide (DES), or dimethyl disulfide (DMDS). These sulfur compounds have a strong impact on wine aroma, due to their high volatility and low odor thresholds. Their odor can be described as cabbage-, garlic-, onion-, or rubber-like, usually having negative effects on wine aroma (Table 1). The control of oxygen level during the wine-making process (i.e., micro-oxygenation) or during the wine aging in bottle (i.e., oxygen permeation through the closures) is the main parameters used to control the formation of such compounds in wine. However, several studies have pointed out that stoppers with similar oxygen permeation[11] but made of different polymeric materials (i.e., suberin, lignin, and polysaccharides for natural cork or polyethylene for synthetic cork) result in different levels of reduced off-flavor aromas in wines.[1,2,4,9] Thus, the question of the influences of the stopper polymeric material on the level of off-flavor aromas rises.

Table 1. Aroma Descriptors and Thresholds for Some Volatile Sulfur Compounds in Wine

compound	content in wines (μg L^{-1})[18] [a]	threshold (μg L^{-1})[18]	descriptors[18]
hydrogen sulfide	nd[b]−370	0.1−150	rotten egg
methanethiol	nd−16	0.3 (ethanol/water)	cooked cabbage, putrefaction
ethanethiol	nd−5	1.1	onion, fecal, rubber, garlic
dimethyl sulfide	nd−474	10−160	asparagus, cabbage
dimethyl disulfide	nd−22	20−45	cooked cabbage, onion
diethyl sulfide	nd−10	0.93−18	garlic
diethyl disulfide	nd−85	4.3−40	onion

[a]And references therein. [b]nd: not detected.

Considering flavor scalping or flavor scavenging phenomenon, it can be described as the direct sorption of volatile compounds and other food constituents by polymeric constituents in packaging.[19] While numerous studies have focused on the scalping of a volatile, namely, of D-limonene in citrus juice, by polymeric packaging,[19−22] few studies have considered volatile scavenging by wine closures. Research on the interaction of the latter with flavor compounds started with the evaluation of sorption of chloroanisoles by cork stoppers.[23] The broadening of the subject was undertaken by other studies, which considered a wider range of compounds (from TDN to

Received: March 1, 2012
Revised: October 17, 2012
Accepted: October 17, 2012
Published: October 17, 2012

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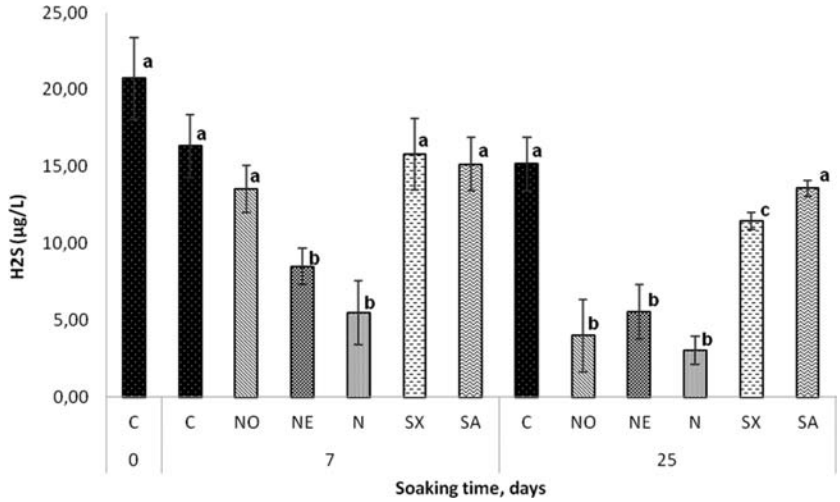

Figure 1. Evolution of hydrogen sulfide with soaking time for each type of closure (one-piece closures): C, control (no closure); NO, synthetic closure; NE, microagglomerate cork closure; N, natural cork closure; SX, screw cap Saranex; SA, screw cap Saran. ANOVA to compare data; values with different letters within each row are significantly different (Tukey's test, $p < 0.05$).

ethyl esters) and their interaction with several types of wine closures, concluding that relatively nonpolar compounds were the most affected.[13] Others decided to focus on specific families of wine compounds, like volatile phenols[15] and methoxypyrazines.[14]

Consequently, scalping of low VSC could explain why closures allowing wine to be exposed to similar quantities of oxygen lead to different levels of reduced off-flavors. Therefore, the aim of this study was to investigate the existence of scalping of low volatile sulfur compounds normally present in wine by cork stoppers and other types of closures.

MATERIALS AND METHODS

General. Hydrogen sulfide (>99%) and dimethyl sulfide (>99.9%) were purchased from Sigma Aldrich (St. Quentin Fallavier, France). These standards were of the highest purity available, and no further purification was performed. Hydrogen sulfide stock solution was prepared by bubbling the gas into previously degassed water with low flow in order to prevent water evaporation. Concentration was determined by weighting the solution before and after the contact with the gas, thus obtaining the mass of the latter. Stock solutions of the standards were prepared using degassed water to prevent oxidation and kept in the dark at −20 °C under nitrogen, before immediate use. All other stock solutions were prepared by diluting each compound in ethanol. Five sealing systems were tested in the trial: a natural cork stopper (reference "natural superior", 44 mm length, 24 mm diameter) and a microagglomerate cork stopper (44 mm length, 24 mm diameter) both obtained from Amorim SA; a synthetic closure (Nomacorc classic, 43 mm length, 22.5 mm diameter); and two Stelvin screw cap closures, Saran tinfoil and Saranex, respectively. Before being used, stoppers (i.e., screw cap, cork and synthetic) were kept in a closed container for 2 weeks under nitrogen atmosphere which was periodically flush and refilled in order to remove and limit the presence of oxygen inside the polymeric structures of the studied stoppers, as is usually performed.[24]

Soaking Assays. Final standards were prepared from dilutions of stock solutions in previous degasified model wine solution (5 g/L of tartaric acid, 12% of ethanol with a pH adjusted to 3.5 by NaOH) thus obtaining solutions of volatiles with concentrations close to the maximum concentration found in wines. When preparing the soaking solutions in 100 mL Erlenmeyer flasks, each batch of replicates of closures soaked in the solution of volatile sulfur compounds was followed by three control flasks (C) (containing the VSC solution without the closures) to ensure that the hypothetic amount of VSC volatilized with time could be measured. This allowed the correction of the quantities of VSC found to be sorbed by the closure. Trials were executed using both one piece and 10 mm cuts of cork and 10 mm cuts of synthetic stoppers. The latter assay was performed as an attempt to reproduce a surface exposition which generally occurs during wine aging in bottles. Closures were soaked in 100 mL Erlenmeyer using a solution with a concentration of 20 $\mu g \cdot L^{-1}$ for each compound, in the dark and at room temperature (i.e., set at 22 °C). Analysis of each soaking solution and the respective control (VSC only) was performed at the beginning of the trial (t0), after 7 days (t7) and after 25 days (t25) of soaking. The experiment was conducted separately for each compound and for each type of closure; all samples were tested in triplicate and separately submitted to headspace analysis.

As a consequence of their extreme reactivity and their tendency to oxidation, the quantification of the VSC constitutes a challenge, especially at the low levels in which they exist in wines. In order to avoid oxidation of the sulfur compounds in model wine solutions, samples were prepared under nitrogen, Erlenmeyer flask were flush with N_2 prior to adding the soaking solution in order to limit oxygen to its minimum in the head space, and then each flask was closed as tightly as possible, using proper glass stoppers that had been seal with Parafilm.

Headspace Method. Sample preparation and headspace analysis procedures were performed as described.[25] VSC soaking solution (10 mL) was pipetted using a 10 mL micropipet into 20-mL glass crimp-top deactivated vials (Restek) containing 1 g of NaCl before addition of the internal standard (thiophene, 100 $\mu g\ L^{-1}$). To decrease the risk of oxidation, the vials were previously flushed with nitrogen and temporarily sealed with Parafilm. Immediately after crimping, samples were stirred for 60 min at room temperature. One milliliter of headspace was then injected into the gas chromatographic apparatus.

GC Analysis. GC analyses followed the method described by Lavigne[26] and were performed on a Hewlett-Packard 5980-I coupled with a HP 19256-A flame photometric detector at λ = 393 nm, on a Chromosorb WHP (4 m × 3 mm) packed column. The oven temperature was kept at 65 °C for 5 min and then increased to 110 °C at a rate of 6 °C min^{-1}. The carrier gas was hydrogen with a flow rate of 15.5 mL min^{-1}, and the flame detector was also supplied with hydrogen gas at a flow rate of 93 mL min^{-1} and a mixture of nitrogen/oxygen (80/20) at a flow rate of 100 mL min^{-1}. The makeup gas was nitrogen at 55 mL min^{-1}.

Calibration and Quantification. Peaks corresponding to the different compounds were integrated using the data analysis package included in ChemStation (Agilent). Calibration curves were achieved by adding separately growing concentrations of pure H_2S or DMS in

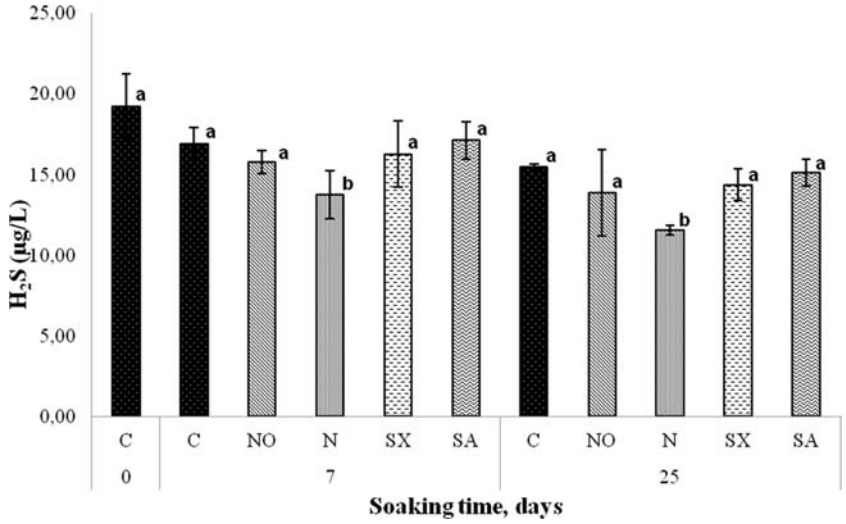

Figure 2. Evolution of hydrogen sulfide with soaking time for each type of closure (10 mm cuts): C, control (no closure); NO, synthetic closure; NE, microagglomerate cork closure; N, natural cork closure; SX, screw cap Saranex; SA, screw cap Saran. ANOVA to compare data; values with different letters within each row are significantly different (Tukey's test, $p < 0.05$).

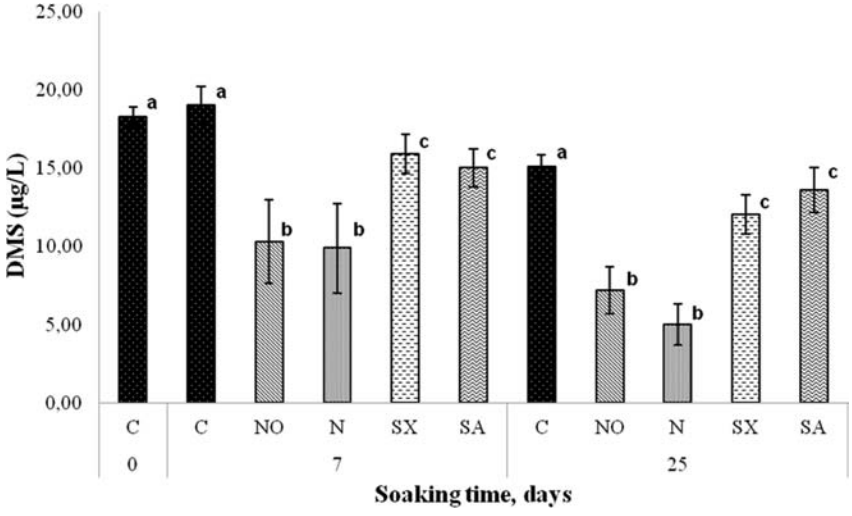

Figure 3. Evolution of dimethyl sulfide with soaking time for each type of closure (one piece): C, control (no closure); NO, synthetic closure; NE, microagglomerate cork closure; N, natural cork closure; SX, screw cap Saranex; SA, screw cap Saran. ANOVA to compare data; values with different letters within each row are significantly different (Tukey's test, $p < 0.05$).

the range from 2 to 100 $\mu g \cdot L^{-1}$ with the internal standard, thiophene at 50 $\mu g\ L^{-1}$, to the model wine solution. The response factors of each compound were established by plotting the concentration ratios versus the peak area ratios of each compound to the internal standard. Concentrations in soaking solutions were determined using the obtained calibration curves. When the concentration of the control diminished with time, the concentrations of H_2S or DMS in soaking solution were corrected in order to minimize the error resulting from the lost of H_2S or DMS not related to the studied closure. Statistical analysis (ANOVA) was conducted using MS Excel 2007 and Statistica 10 software.

RESULTS AND DISCUSSION

Hydrogen Sulfide Scavenging. The concentration in H_2S in the trial with one-piece closures was assessed at the beginning of the experiment and after 7 and 25 days of soaking time (Figure 1). In spite of the efforts undertaken to minimize losses due to volatilization and oxidation, concentration in control flasks was not steady throughout the experiment, namely, during the first 7 days. Still, control was significantly different from other samples, namely from natural cork stoppers. Effectively, sorption seems to exist, especially when comparing the concentrations differences for both natural cork and synthetic closures. Even screw caps provoked a slight decrease in the concentration of hydrogen sulfide, especially those having a polymeric liner (i.e., Saranex). Considering the sorption of hydrogen sulfide by closures, there seems to be a difference between synthetic and natural cork stoppers after the first 7 days, but this tendency disappears after 25 days of soaking. In fact, the sorption mechanism with those two types of stoppers may be different as a consequence of the polymeric material they are made of (i.e., suberin, lignin, and polysaccharides for natural cork and polyethylene for the synthetic cork). It seems that more compact and regular synthetic stoppers need eventually more time to scavenge hydrogen sulfide. Furthermore, the chemical composition of the natural cork may facilitate the disappearance of H_2S, as a consequence of its reaction with cork components. More investigation needs to be performed to better understand its

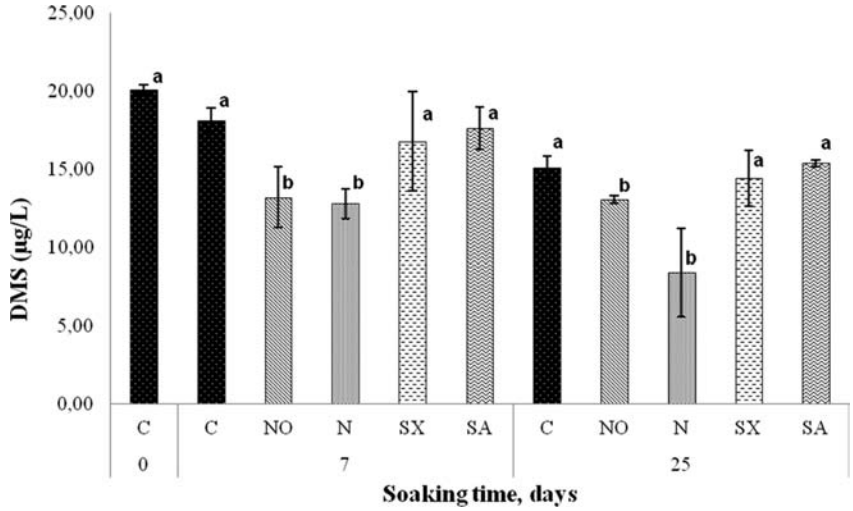

Figure 4. Evolution of dimethyl sulfide with soaking time for each type of closure (10 mm cuts): C, control (no closure); NO, synthetic closure; NE, microagglomerate cork closure; N, natural cork closure; SX, screw cap Saranex; SA, screw cap Saran. ANOVA to compare data; values with different letters within each row are significantly different (Tukey's test, $p < 0.05$).

sorption phenomena. The visible decay in the concentration of H_2S after 25 days of soaking, a relatively short period of time compared to the wine storage time in a bottle, which indicates that the reported differences observed in bottling experiments[1,2,4,9] may be in fact due to differences in scalping or scavenging capacities of different closures used.

Nevertheless, when considering the trial using the 10 mm cuts of the closures' top (Figure 2), the difference between closures had diminished but it was still significant ($p < 0.001$) between natural cork stoppers and screw caps. These results are somehow expected, as a consequence of the considerable decrease of the stopper contact surface with the soaking solution. Still, it is noticeable that in a short period of only 25 days almost 20% of the original amount of H_2S had been sorbed under these conditions, which are more similar to those found in wine.

Dimethyl Sulfide Scavenging. In contrast with H_2S, which has been reported to accumulate in a differentiated manner with bottling time and closure type, DMS seem to be not significantly affected by the type of closure used over time.[2,27] Therefore, it was interesting to evaluate the behavior of these compounds in the same experiment as H_2S. Moreover, their reactivities are different and one can consider these two molecules as extremes when considering the most volatile sulfur compounds in wine. Like in the case of H_2S, control flasks in DMS assay experienced a slight decrease of DMS over time; however, this was more pronounced in the later stage (Figure 3). Nevertheless, the profile obtained with DMS for each type of closure was different since, although a significant decrease in the amounts of DMS for synthetic and natural cork closures was observed, there is no significant difference between these two types of closures in the first 7 days, while after 25 days, natural cork closures seem to decrease the DMS concentration more. The level of DMS with screw caps remains unaltered when compared to the profile exhibited with H_2S.

Moreover, when considering DMS scalping by the top 10 mm of natural cork and synthetic closures (Figure 4), a significant decrease in DMS concentration was again obverved. However, like in the case of H_2S, the decreasing of the concentration was lower compared to the essay with the whole stopper in the soaking solution. These results are somehow expected, as a consequence of considerable diminishing of the stopper contact surface with the soaking solution. Although DMS and H_2S exhibit different reactivities and polarity, they seem to behave in a similar manner regarding the scalping phenomena on the closures material.

The results reported here provide new insight into wine post-bottling evolution, especially when considering the relation between light volatile sulfur compounds and the type of closure. Indeed, as some studies have reported for other types of compounds, VSC scavenging by natural cork or synthetic closures in model wine solution exists. Thus, closures directly impact not only oxygen exposure of wine but also influence concentration of DMS and H_2S by scalping phenomena. This study can be seen as an advance in the exhaustive research of wine post-bottling development, as closures may have impact directly in overall aroma perception by scavenging certain compounds to levels beneath their threshold. Among other studies, more investigations are now in progress in order to understand the sorption mechanism observed in this study and to evaluate which linkage exists between the polymeric structures of the closures (i.e., natural or synthetic) and the studied volatile compounds.

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Funding

The authors thanks Amorim France (Eysines, France) and ANRT [Association Nationale pour la Recherche Technologique] (Paris, France, Cifre Grant No. 1290/2008) for their financial support in this research.

Notes

The authors declare no competing financial interest.

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