Impact of oxygen permeability of stoppers on the aging of wines over a 10-year period

Part 3/3: The case of Merlot and Cabernet-Sauvignon

Alexandre Pons[1,2], Valérie Lavigne[1,2], Cécile Thibon[2], Pascaline Redon[2], Christophe Loisel[3], Véronique Chevalier[3], Denis Dubourdieu[2], Philippe Darriet[2]

[1] *Tonnellerie Seguin Moreau – Cognac France – France.*
[2] *Unité de recherche œnologie – EA 4577 – USC 1366 INRA – ISVV – Univ. de Bordeaux Villenave-d'Ornon – France.* [3] *Diam Bouchage – Céret – France.*

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Stopper quality is essential for the proper aging of wines in the bottle. The stopper must ensure ideal sealing of liquid in the bottle, have no sensory impact on the wine and enable control of the gas permeability level. It is now accepted that the closures used on wine bottles have two essential characteristics in terms of oxygen contribution: OIR and OTR. The first two articles in this series were the opportunity to introduce the concept of OIR (Oxygen Initial Release) for micro-agglomerated cork stoppers *(Chevalier et al., 2019)*, while also specifying the impact of the stopper's OTR (Oxygen Transfer Rate) on the aroma evolution of white wines made from Sauvignon Blanc *(Pons et al., 2019)*.

Thanks to the analysis of specific markers and the application of an appropriate sensory analysis protocol, we showed how the stopper's oxygen transfer rate (OTR) significantly impacts the aroma evolution of various white Sauvignon Blanc wines over the long term. This value is a key parameter in preserving the fruitiness of young wines. Controlling this parameter also delays the manifestation of premature aging symptoms. We have shown that the choice of a stopper with controlled oxygen transfer is a precious tool for enologists, helping them preserve the fruits of their labor.

The third part of this project is an examination of the aroma and analytical evolution of three red Bordeaux wines (Merlot and Cabernet-Sauvignon) over a period of 10 years, as a function of the oxygen transfer level of different stoppers.

Materials and Methods

Three red wines, made from a blend of mostly Merlot and Cabernet-Sauvignon grapes (2006 vintage), were corked either with traditional stoppers (natural cork of different quality levels depending on wine quality), or with several families of stoppers with different oxygen permeability values (OTR). As such, three Diam stoppers with increasing OTR values were selected. This selection is accompanied by three synthetic stoppers and two screw caps whose theoretical OTR values, as found in the literature, are presented in ***Table 1.***

The red wines from the 2006 vintage were selected based on their aging potential. It is evaluated on the basis of historical knowledge of wines from each growth. They come from appellations in the Bordeaux region. As part of this study, they are referred to as follows: "low aging potential" (l-ap), "Medium aging potential" (M-ap) and "Long aging potential" (L-ap). The l-ap wine is a Merlot wine aged in stainless steel tanks. It comes from the Bordeaux appellation. The M-ap wine is from the Côtes de Bordeaux appellation. It is a balanced blend of Cabernet-Sauvignon and Merlot, which is aged for 10 months in oak barrels. The L-ap wine is from the Graves appellation. It is a blend in which Cabernet-Sauvignon dominates, aged for 10 months in oak barrels.

Table 1: Selected stoppers (X) **for each wine, ranked according to their OTR value.**

	OTR mg/year	l-ap	M-ap	L-ap
Saran capsule	< 0.1 [1]	X	-	-
DIAM 30 P0.07	0.3	X	X	X
DIAM 5 P0.15	0.4	X	X	X
Saranex capsule	0.5 [1]	X	-	-
DIAM 5 P0,35	0.6	X	X	-
Synthetic 3	0.6 [1]	X	X	-
Synthetic 1	1.5 [1]	X	-	X
Synthetic 2	4.6 [1]	-	X	-
Natural cork	0.1 – 40 [1]	X	X	X

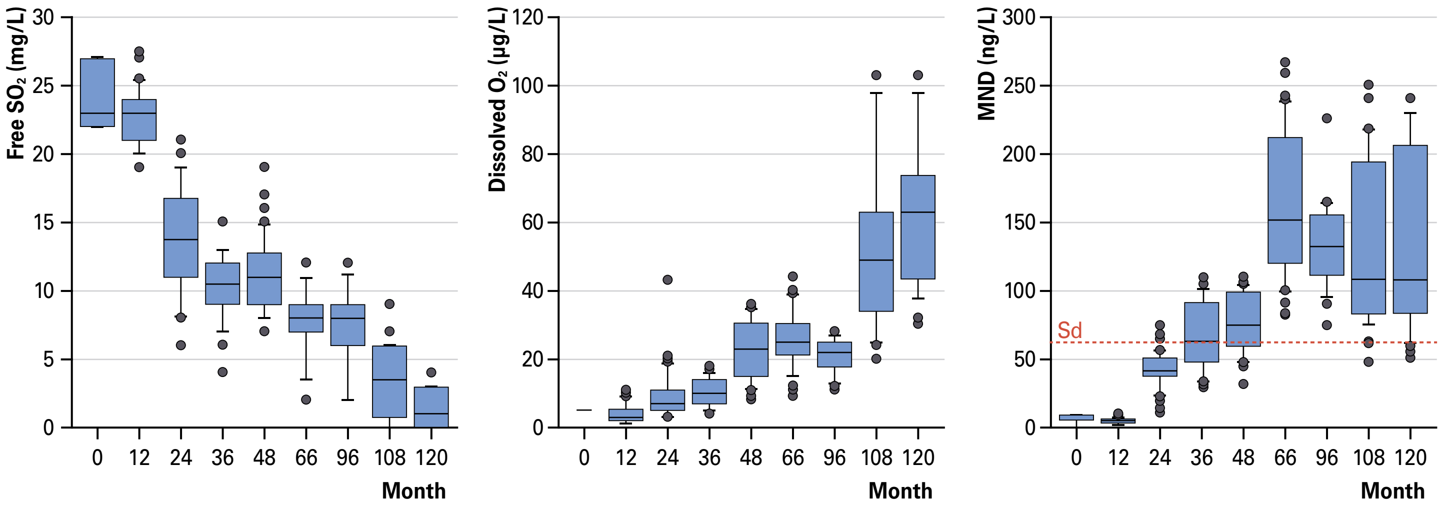
[1] *Roberston, 2009.*

The evolution of the wines was monitored from an analytical and sensory point of view. To do this, an aroma compound which is a chemical marker of oxidation was measured: 3-methyl-2,4-nonanedione (MND), which has a prune aroma. Other markers of the oxidative evolution of red wines completed the study: free SO_2 and the dissolved oxygen level (as assessed by Orbisphere oxygen sensor). Each measurement corresponds to analysis of three bottles.

At the end of this project, after 10 years of bottle aging, we completed the analytical characterization of the wines by determining the content of a compound responsible for the varietal aroma of the wines: 3-sulfanylhexanol, with grapefruit notes. Its contribution to the fruity aromas of red wines has already been established, along with other varietal thiols, enhancing the black currant aroma of these wines *(Blanchard et al., 1999; 2004; Rigou et al., 2014).*

The wines were tasted at regular intervals. A panel of internal tasters from the Enology research unit of the Institut des Sciences de la Vigne et du Vin (ISVV) evaluated the intensity of oxidation in the samples as well as their preference for the samples.

■ **Figure 1: Box-plot representation of the evolution of free SO_2, dissolved oxygen, and MND content during the bottle aging of three red wines stoppered with all closures** (n = 3).



Analytical characterization and evolution of red wines during bottle aging

We tracked the evolution of several markers of the oxidative aging of red wines: free SO_2, dissolved oxygen and MND. We thus present all of the analytical results obtained for the three wines closed with the six stoppers in ***Figure 1.*** First of all, we show that free SO_2 decreases in a highly variable manner during bottle aging. This evolution is accompanied by a large scatter in the data, expressing the impact of the stopper on the various quality levels of wine. Similar results are obtained for the evolution of dissolved oxygen content. Once the oxygen introduced during bottling is consumed, the dissolved oxygen contents measured after three weeks of bottle aging are less than 5 µg/L. During the first eight years of aging, dissolved O_2 levels remained less than 50 µg/L, regardless of wines and stopper type. After 10 years of bottle aging, dissolved oxygen contents are between 25 µg/L and 100 µg/L, depending on stopper type. It is known that a young red wine, owing to its phenolic composition, is apt to consume a great deal of dissolved oxygen (~2-4 mg/L/day). Our measurements on older red wines show non-negligible levels of dissolved oxygen in the bottles. It is thus likely that such ranges can lead to oxidative evolution of the aroma of some of these wines.

To verify this hypothesis, we determined the content of MND, a marker of the oxidative evolution of red wine aroma throughout aging. Concentration of this compound increases during bottle aging. At bottling, its content is less than 10 ng/L, regardless of wine type. After 24 months of aging, it is possible to distinguish between the different conditions, with extreme contents ranging from 12 to 72 ng/l. Thus, some wines have contents above the detection threshold for this compound (Sdwine 60 ng/l). However, it is only at 66 months of bottle aging that more significant deviations are observed. After this aging time, all of the wines have MND contents above the detection threshold. Depending on the wine and stopper type, contents are between 76 and 264 ng/L. The scatter of these values during bottle aging may be interpreted as revealing the combined impact of the stopper and the intrinsic quality of the wine and its aging potential. Depending on wine type, the stopper may significantly but temporarily slow down the kinetics of increased MND content in wines. This scatter in MND contents in wines occurs throughout the period of bottle aging.

Effect of stopper oxygen permeability on the evolution of free SO_2 content during bottle aging

As an example, the free SO_2 contents found in the l-ap and L-ap wines are presented in ***Figure 2.*** In general, the contents found in wines after five years of aging do not seem to be affected by stopper type. However, after 10 years, they are lower when the stopper's OTR value is higher, regardless of the intrinsic quality of the wine under study. After 10 years of bottle aging, almost all of the samples no longer contain any free SO_2, except for the Diam30 P0.07 wine, which has low, but non-negligible, levels (< 5 mg/L).

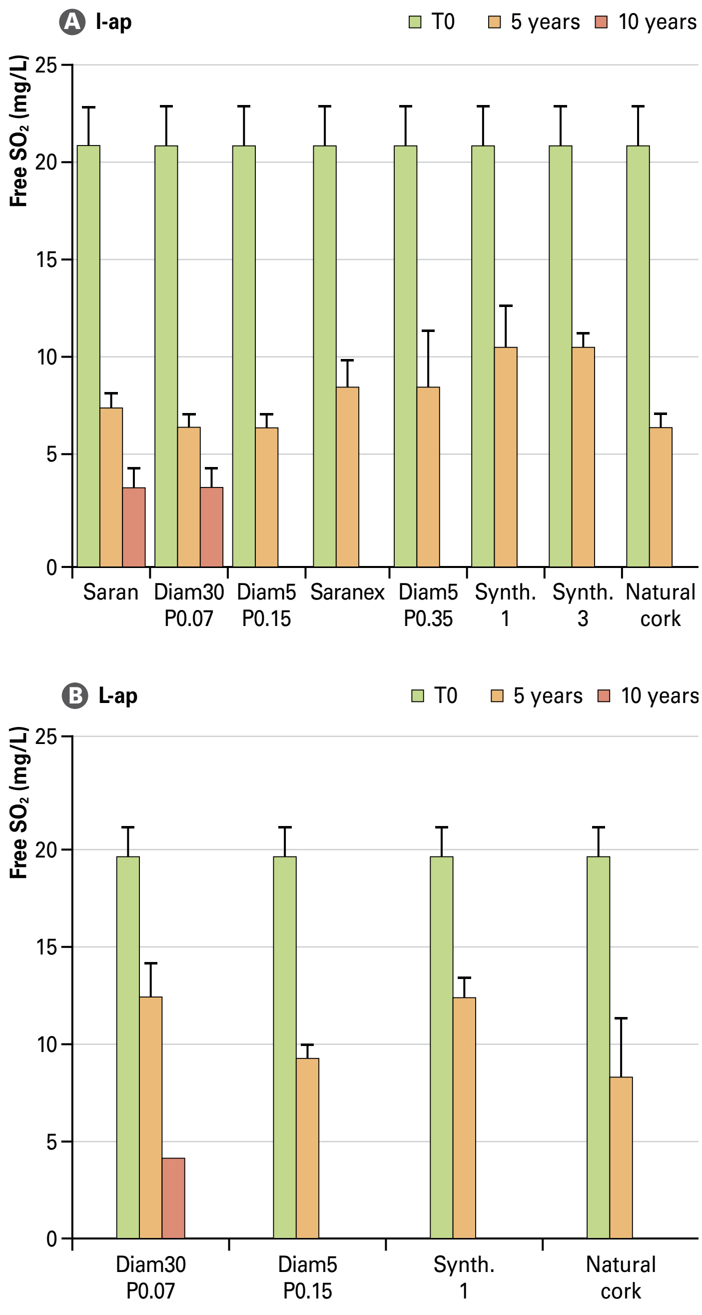
Evolution of MND content during bottle aging as a function of wine quality

The evolution of this oxidation marker for red wines is described for the first time here over such a long period of time. It is known that MND content at the end of alcoholic fermentation is often quite low (< 10 ng/L) *(Allamy et al., 2018; Pons et al., 2018).* Barrel aging can, as a function of aging techniques and varietal selection, lead to contents between 10 and 80 ng/L. The highest contents at the end of aging are most often associated with late-harvest Merlot wines that are made without any special protections against oxygen. Lastly, it is also known that the presence of molecular oxygen and, more generally, oxidative phenomena are the source of MND formation in red wines from precursors which are currently being studied *(Peterson et al., 2019; Pons, 2019).* This diketone can be found at contents up to and even exceeding 350 ng/L, depending on wines and the quality of their conservation in bottle. At present, we do not precisely know the kinetics of formation of this compound during bottle aging.

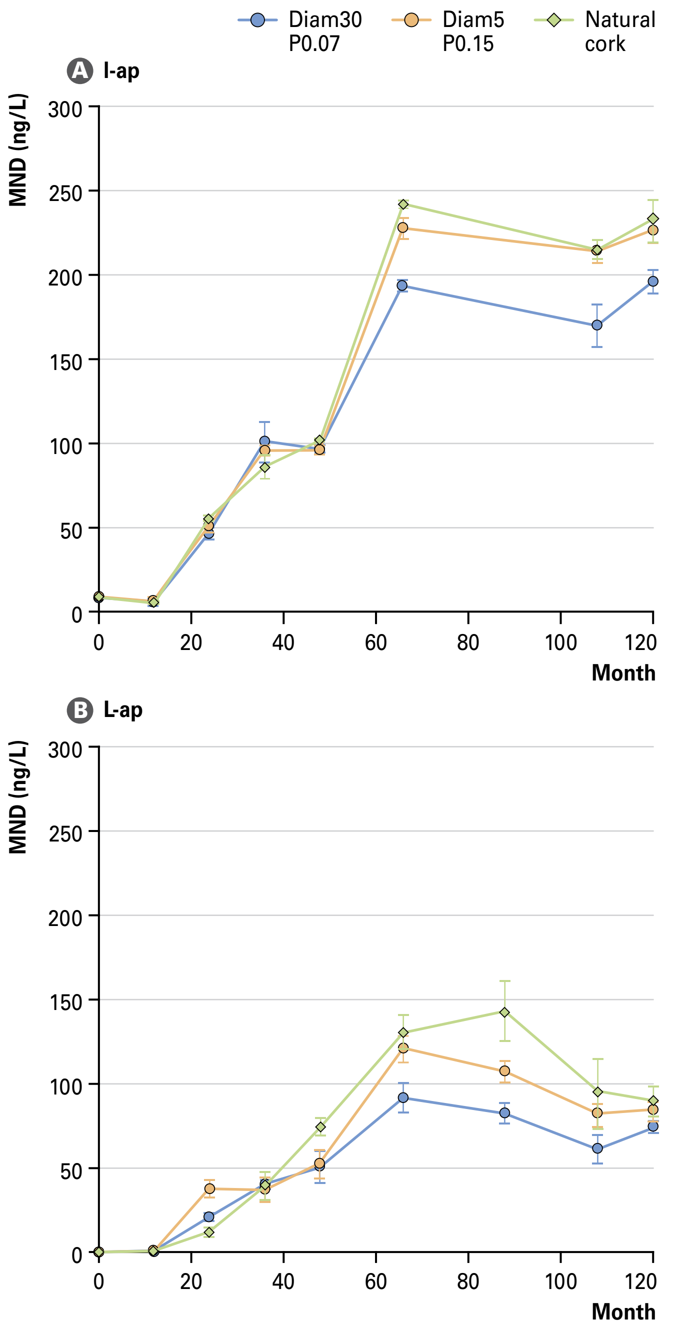
As an example, we present the results obtained for three cork stoppers, with the low aging potential wine (l-ap) and Long aging potential wine (L-ap): a natural cork stopper and new micro-agglomerated cork stoppers: Diam5 P0.15 and Diam30 P0.07 ***(Figure 3).***

Upon bottling, the L-ap wine, mainly made from Cabernet-Sauvignon, did not contain any MND, whereas the l-ap wine, which has a high proportion of

■ **Figure 2: Example of free SO_2 contents found in the l-ap Ⓐ and L-ap Ⓑ wines after 5 years and 10 years of bottle aging as a function of stopper type** (n = 3).



■ **Figure 3: Example of evolution of MND contents during bottle aging, as a function of cork stopper type for the l-ap wine Ⓐ and L-ap wine Ⓑ** (n = 3).



Merlot, already had non-negligible concentrations of close to 9 ng/L.

Regardless of the aging potential of wines, MND contents increase during aging. It is interesting to note that kinetics are greater for the low aging potential wine (l-ap) than for the Long aging potential wine (L-ap). It is also remarkable to observe that for these two wines, 48 months of aging are needed in order to distinguish a closure effect on MND concentration. Beyond that period, lower contents are systematically found in wines closed with the least oxygen-permeable stopper: Diam30 P0.07. The impact of the stopper is more marked on the l-ap wine than on the L-ap wine. This can be explained by the greater resistance of the L-ap wine to oxidative phenomena. This intrinsic quality corresponds to a lower capacity of this red wine to produce MND during bottle aging.

To illustrate the aging potential of a red wine analytically, we present the distribution of MND contents found in the l-ap, M-ap and L-ap wines after 10 years of bottle aging in ***Figure 4.*** For the l-ap wine, MND concentrations are highly affected by stopper type. The mean contents found in these samples are much higher (211 ng/L) than those found in the M-ap and L-ap wines. The mean MND contents are found at intermediate levels for the M-ap wine (97 ng/L) and at low levels in the L-ap wine (62 ng/L). Thus, after 10 years of bottle aging, we show for these three red wines that the higher the ability to keep the wine is, the lower its MND concentration will be. These results confirm the relevance of this quantification, which illustrates the oxidative evolution of red wines. In addition, it provides a posteriori validation of our selection of the wines based on empirical evaluation of their aging potential via tasting. Thus, by means of quantifying this compound, our study provides new information to specify to what degree the closure can affect the quality of wine aging in the bottle.

Effect of stopper OTR on 3-sulfanylhexanol contents after 10 years of bottle aging

3-sulfanylhexanol is a thiol whose aroma is reminiscent of grapefruit and passion fruit. Its contribution to the aroma of Sauvignon Blanc wines has been widely described. Its aroma detection threshold is 60 ng/L. It can also be found at high concentrations in young red wines (several µg/L) *(Bouchilloux et al., 1998; Blanchard et al., 1999; Blanchard et al., 2004).* Several studies have shown its contribution, as with other thiols of varietal origin, to the fruitiness of red wines, in particular black fruit notes. This thiol is rather stable, and its concentration decreases quickly during tank/barrel aging, particularly when the oxygenation level is high *(Blanchard et al., 2004).* Recent studies have shown that it is involved in the fruity notes in the bottle bouquet of great red wines aged for several years in the bottle *(Picard et al., 2015).*

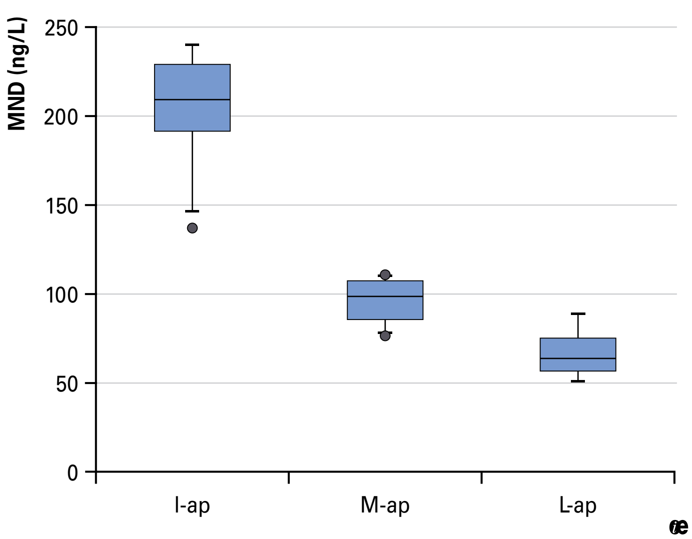
To deepen our knowledge of the exact composition of these red wines after 10 years of bottle aging, we determined 3-sulfanylhexanol (3-SH) content on all of the wines. As an example, we present the results obtained for the wines with low aging potential (l-ap) and Long aging potential (L-ap).

We show that the content of this compound in the l-ap wine reflects the wine's oxidation level as a function of the stopper's OTR value ***(Figure 5).*** The higher OTR is, the lower the 3-SH concentration is. For low OTR stoppers, such as the Saran screw cap and the Diam30 P0.07 stopper, the contents exceed 200 ng/L and thus this thiol contributes to the aroma of these older wines. However, for the stopper that is most permeable to oxygen, Synth. 1, the 3-SH content (55 ng/L) remains below its detection threshold. For this sample, this thiol no longer contributes to wine aroma.

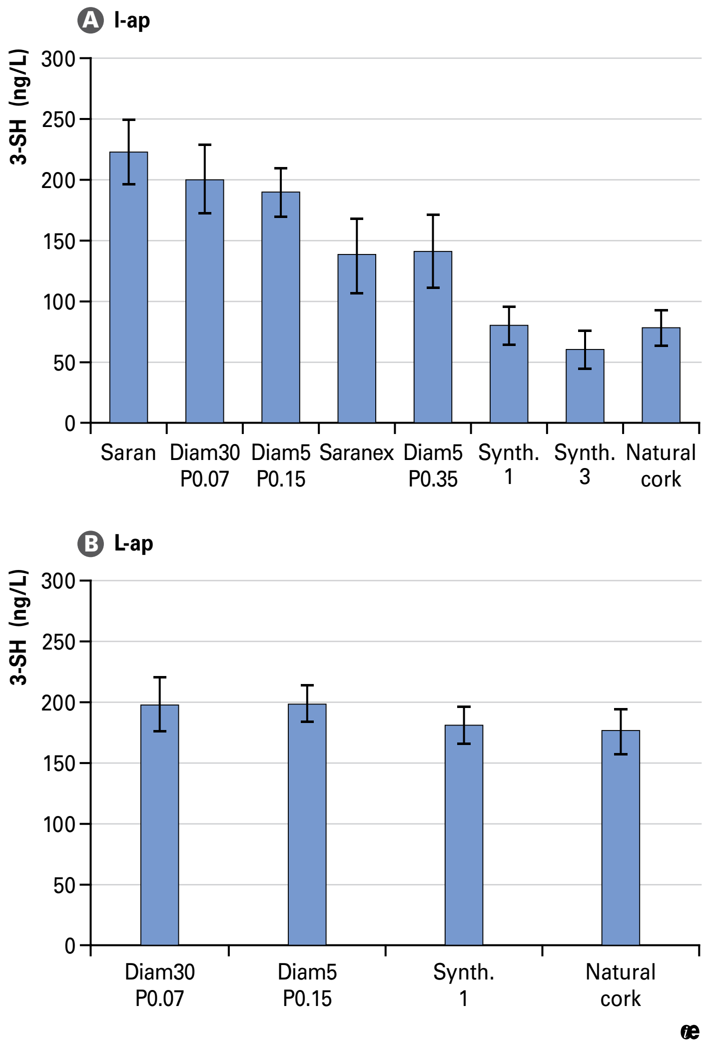
For the Long aging potential wine (L-ap), the average 3-SH contents are on the order of 200 ng/L. They are similar to those found in the l-ap wine closed with low OTR stoppers. However, it is interesting to note that for this L-ap wine, the stopper's OTR value does not have an effect on thiol content. This red wine seems to have a capacity to resist the oxidation reactions initiated during the progressive addition of oxygen by the selected stoppers.

The analysis of this data has helped us to better interpret the wine preference results from our panel of expert tasters.

■ Figure 4: Box-plot representation of the distribution of MNd contents found in the three wines (l-ap, M-ap and L-ap) **closed with the different stoppers after 10 years of bottle aging.**



■ Figure 5: 3-SH contents found in the l-ap Ⓐ and L-ap Ⓑ red wines after 10 years of bottle aging, ranked as a function of the increasing OTR values of the stoppers (n = 3).



Effect of stopper OTR on the intensity of the oxidized character of wines

In addition to the analytical approach described above, we also evaluated the intensity of the oxidized character of wines by means of tasting by a panel of expert tasters. As an example, we present the results obtained for the l-ap and L-ap wines after 10 years of bottle aging ***(Table 2).*** At the end of this project, owing to the lack of some samples of the l-ap wine, we were not able to conduct the sensory analysis for synthetic stoppers 1 and 3 or for the wines closed with a screw cap (Saranex seal).

We show that the wine with low aging potential (l-ap), made mostly from Merlot and aged in tanks, there is a quite significant impact of the closure on intensity of oxidized character. The wines closed with the least permeable cork stoppers, such as Diam30 P0.07 and Diam5 P0.15, were found to be the least oxidized after 10 years of bottle aging. Similarly, we show that the stopper with the highest OTR is associated with the most oxidized wines.

In contrast, the most age-worthy wine (L-ap), which has a high percentage of Cabernet-Sauvignon in the blend and is oak barrel-aged, there is no impact of the closure on the oxidized character. However, we show, by means of a triangle test, that sensory differences do exist between the wines closed with stoppers of different OTR values from the Diam range ***(Table 3).*** As such,

Table 2: Sum of intensity scores for the oxidized character of the low-ap and Long-ap wines after 10 years of bottle aging.

Wine	Closures						
	Saran	Diam30 P0.07	Diam5 P0.15	Diam5 P0.35	Synth. 1	Natural cork	Results
l-ap	39 b	29 a	29 a	50 c	-	35 ab	P < 0.01 significant
L-ap	-	35 a	29 a	-	38 a	33 a	P = 0.522 (ns)

ns: *not significant.*

Table 3: Results of triangle tests for Diam30 P0.07 and Diam5 P0.15 closures.

	Number of correct responses	Total	Results
Diam30 P0.07/ Diam5 P0.15	10	12	Significant at threshold $\alpha = 0.001$

it is likely that the stopper with a low OTR value orients the aroma evolution of this age-worthy Cabernet-Sauvignon wine towards the development of bottle bouquet.

Conclusion

Started in 2008, this project was intended to provide new insight about the impact of stopper permeability on the quality of red wines during bottle aging. To do this, we put in place an analytical and sensory approach, based on new knowledge about the precise characterization of the aroma fraction of red wines. This work includes not only the impact of the stopper on the traditional marker for red wines (free SO_2) but also on a marker for the oxidative evolution of their aroma (MND) and a marker associated with the preservation of their fruitiness (3-SH).

In the end, we show that the control of oxygen addition during bottle aging of red wines determines the quality of their evolution over time. Our study has identified two different cases for which the stopper contributes to the quality of aging.

For red wines with low aging potential, represented in this study by a tank-aged Merlot wines, we show that a stopper with low oxygen permeability should be chosen. Such a stopper minimizes the oxidative evolution of the wine, which is accompanied by the formation of high MND levels during aging.

For age-worthy red wines, aged in oak barrels and composed predominantly of Cabernet-Sauvignon, a stopper with low oxygen permeability should also be chosen. In effect, under our experimental protocol and for this type of wine, the organoleptic impact of OTR over the long term is different. It does not impact the oxidative evolution of the wine, but rather is probably involved in regulating the expression of bottle bouquet. The latter appears to be promoted by closures with low oxygen permeability. ■

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