Oak Tannin Selection and Barrel Toasting

Impact on dry white wine oxidative stability

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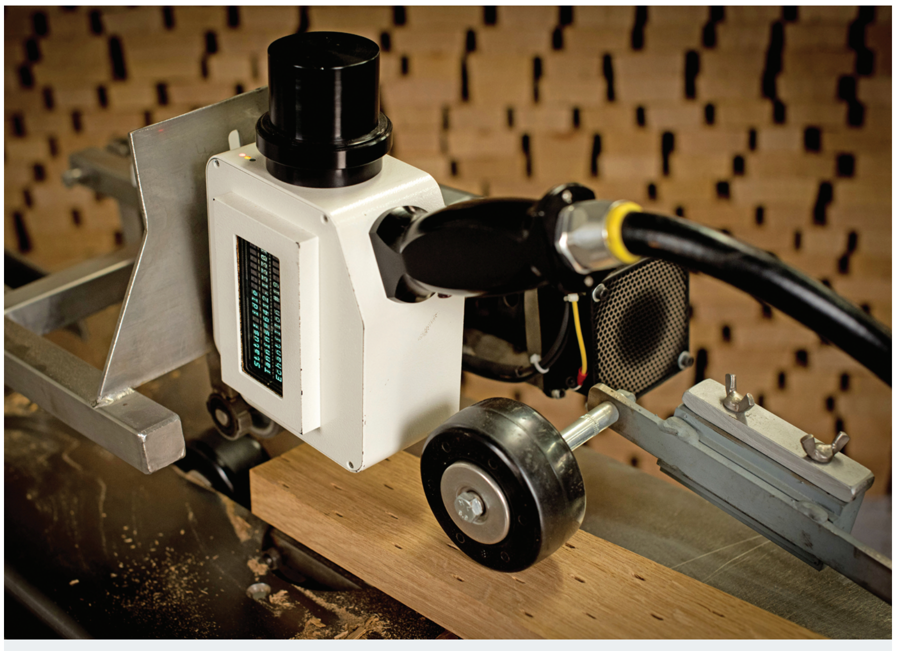
Key Points

- The signature of great dry white wines, besides their organoleptic complexity, is their ability to improve with age.
- Élevage improves white wine's oxidative stability.
- Independent of the vintage and wine matrix, there is a positive correlation between a wine's oxidative stability and oak barrel tannin potential measured by Near Infrared Spectroscopy on the untoasted wood.



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Near Infrared Spectroscopy (NIRS) measurement of tannin potential (TP) along the length of untoasted French oak staves

GREAT DRY WHITE WINES, besides their organoleptic complexity, have an ability to improve with age. Oxidative instability was first observed at the beginning of the 1990s; and since then, winemakers have taken greater precautions to avoid premature aging.

Management of élevage (barrel aging), an intrinsic step in the production of premium quality wines, plays a major role. In addition to its role in micro-oxygenation and the enrichment in phenolic and odorant compounds, oak wood has an antioxidant capacity, which influences wine's redox potential and thus its oxidative stability. Oak wood's antioxidant capacity depends on its ellagitannin content,[1,3] demonstrating a strong correlation between wine's antioxidant capacity and its concentration in ellagitannins.

This study confirms that hydrolyzable tannins play a role in the phenomenon of oxidation in wine. Ellagitannins are extremely reactive with oxygen. Their concentration in wine increases rapidly in the first three months of élevage.[6] Numerous physico-chemical factors can explain their subsequent decrease in the wine.

Ellagitannins' high reactivity in the presence of oxygen is one explanation for the decrease in their concentration. The oxidation of these ellagitannins leads to the formation of quinones which can undergo a nucleophilic attack from ethanol to form hemiacetal derivatives that, in turn, undergo another attack from ethanol to form acetal derivatives.

Another explanation may be the hydrolysis of C-glycosidic ellagitannins, leading to the formation of ellagic acid and vescalin for vescalagin, and formation of castalin for castalagin.

While the interaction between wine and oak barrel has been the subject of many studies over the past decades, until now there have been almost no data on the stabilizing capacity of the oak extractable compounds with regard to the oxidation of wines and white wines, in particular.

The first step involves distinguishing the wines aged in barrels with different toasting and tannin potential, according to their capacity to resist oxidation, using electronic paramagnetic resonance (EPR) after free radical initiation. Furthermore, in order to understand the nature of the wood compounds that contribute to wine's oxidative stability, specific molecular analyses (ellagitannins and grape phenolic compounds and glutathione), as well as non-specific analyses, were carried out on the same samples.

Experimental Set-up

In order to study the impact of élevage on the oxidative stability of dry white wines, we combined two innovative approaches. Wines aged in barrels with various uniform tannin potential (which were classified according to their total ellagitannin content as measured by near infrared spectroscopy on the untoasted wood) and different toasting levels (high precision toasting by radiant heat)[2] were distinguished by their overall ability to resist oxidation. Trials were carried out on different vintages (2015 and 2016) and varieties (Sauvignon Blanc from Bordeaux and Chardonnay from Burgundy).

The wines' ability to resist oxidation was estimated by electronic paramagnetic resonance (EPR) after free radical initiation of oxidation. Analyses of the ellagitannins, grape phenolic compounds and glutathione were carried out on the same samples throughout the wines' eight months in barrel.

Table 1: Wine Trials

WINES AND VINTAGE		VARIETY	TOASTING*	LTP**	MTP**	CONTROL***
A	2016	Chardonnay	Blanche	X	X	X
B	2015	Sauvignon blanc	Blanche	X	X	X
C	2016	Chardonnay	Blanche	X	X	X

Toasting*: Blanche = 150° C for one hour
LTP and MTP**: Tannin Potential corresponding to different ellagitannin content in untoasted wood: Low or LTP from 2,000 to 4,000, Medium or MTP from 4,001 to 6,000 of ellagic acid equivalent per gram of dry wood
Control*** = one-year-old barrel

Analysis of the Wines' Oxidative Stability

EPR was used to discern resistance to oxidation of the white wines aged in barrels with different tannin potential and toasting level. The method for analyzing wine's oxidative stability is based on assessment of the kinetics of 1-hydroxyethyl radical formation, after free radical initiation in the wine, which is then captured by a POBN paramagnetic probe. The free radical initiation is chemically-initiated (Fenton reaction), which leads to the formation of very unstable radicals that will react with the POBN probe.

The kinetic curve's gradient (K) and the value of the maximal intensity (Imax) are chosen as representative values to distinguish the different wines. On the basis of our analytic approach, wines with low Imax and K values are considered to be more stable against oxidation.[5] In all of our experiments, élevage improves the wines' oxidative stability (FIGURE 1A). Furthermore, the wines' distribution according to their Imax and K values, enabled us to demonstrate a positive correlation between a barrel's tannin potential (TP) and wine oxidative stability.

Independent of the wine matrix (See FIGURE 1B), the medium tannin potential modalities show better stability at the end of élevage than low tannin potential modalities, which have similar characteristics to the control modalities (one-year-old barrels). This phenomenon, confirmed for the three matrices tested, demonstrates the positive impact of extractible ellagitannins on wine resistance to oxidation.

This set of experiments also investigated wines aged in low tannin potential barrels associated with two types of light toasts: Blanche (150° C for one hour) and Ivoire (160° C to 170° C for 1.5 hours). At the end of élevage, no significant difference was found between these two toasting profiles (data not shown). It is important to note that the toasting tested in our study was very low and close in terms of intensity (light). We can hypothesize that a higher toasting level would have an impact.

FIGURE 1A: Wine classification (A) during aging in barrels with different tannin potential, according to the maximum intensity and kinetic curve's gradient K of formation of radicals POBN-1-HER (arbitrary units) measured by EPR after chemical initiation by Fenton reaction. Analysis carried out just after alcoholic fermentation (T0) and end of aging (T8).

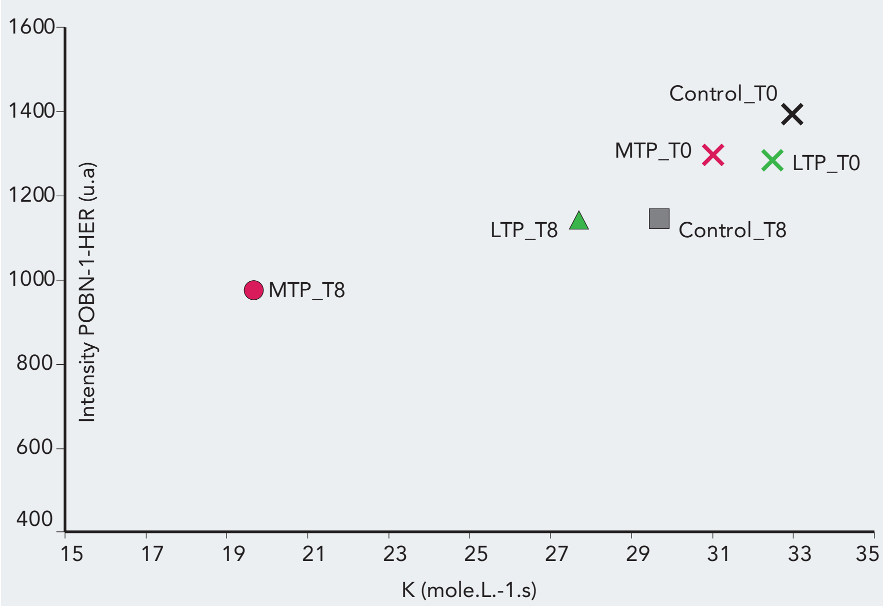


FIGURE 1B: Wine classification (A, B) during aging in barrels with different tannin potential, according to the maximum intensity and kinetic curve's gradient K of formation of radicals POBN-1-HER (arbitrary units) measured by EPR after chemical initiation by Fenton reaction. Analysis carried out at the end of aging (eight months).

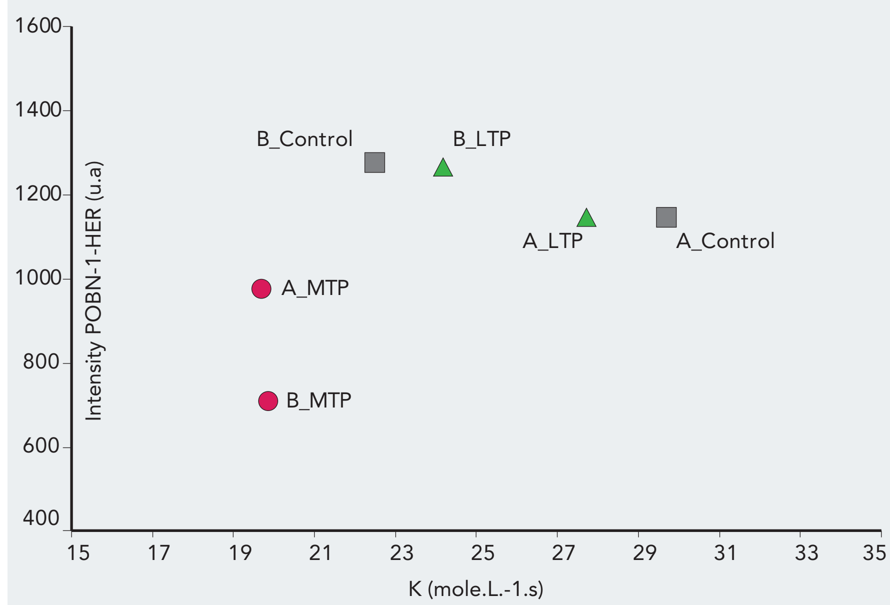


FIGURE 2: Evolution of ellagitanin content in wines (A, B, C) during élevage, according to oak tannin potential.

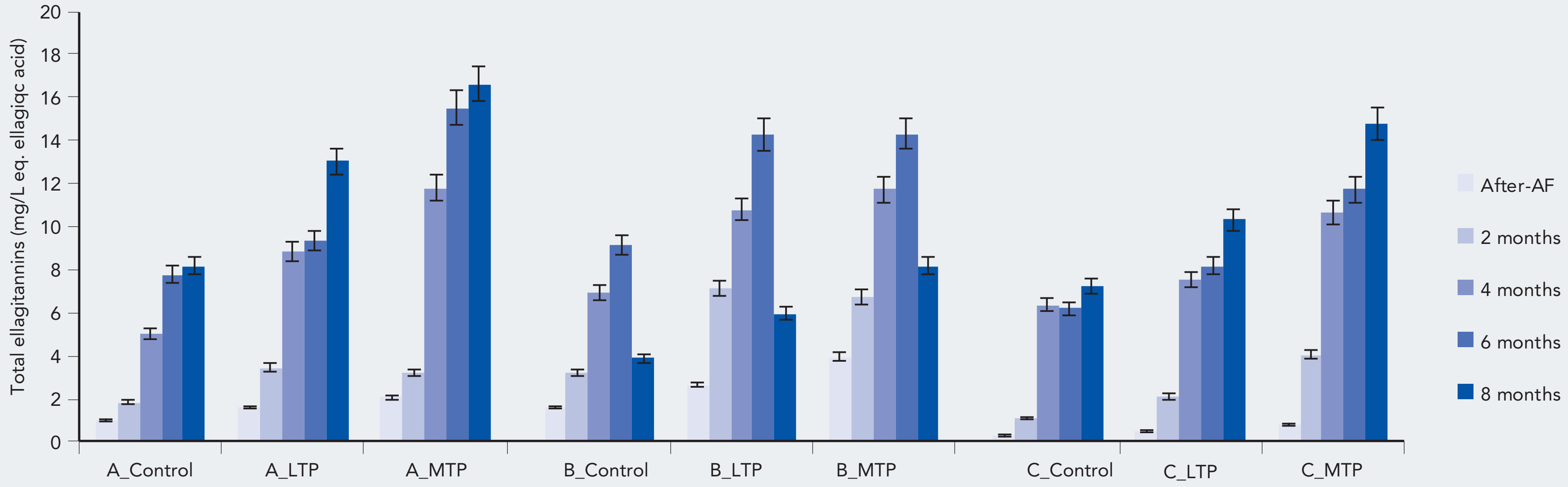
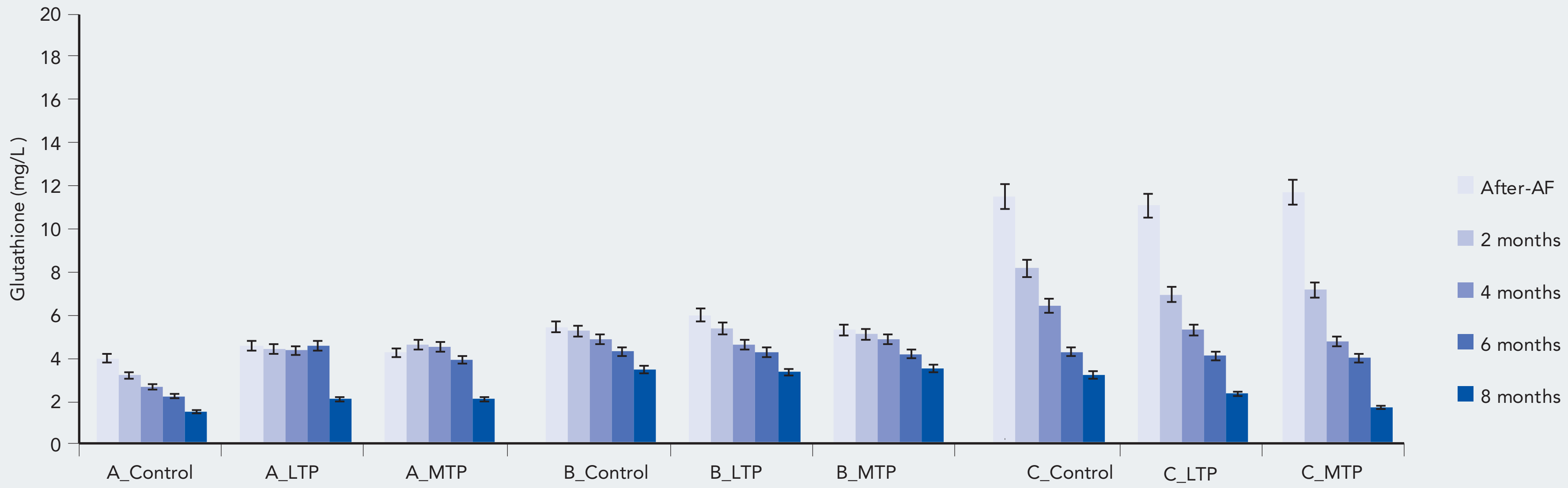


FIGURE 3: Evolution of glutathione content in wines (A, B, C) during élevage, according to oak tannin potential.



Wines' Chemical Profiles

The evolution kinetics of overall hydrolyzable tannin content for the different modalities are shown in FIGURE 2. The measurements were carried out, starting from the end of the alcoholic fermentation up until eight months of élevage. A positive correlation is demonstrated, independent of the matrix and the oak's tannin content, between the tannin potential of the oak wood and concentration of total ellagitannin in the wine. The higher the tannin potential of the barrel, the greater the ellagitannin content in the wine. As previously described by **A.A. Watrelot** on red wine,[6] a very sharp increase is noted in the first three months, which implies significantly higher extraction kinetics at the beginning of élevage. It is also important to note that very little ellagitannins are extracted during alcoholic fermentation.

After two months of élevage, the average ellagitannin concentration in the wines was 4.2 and 4.6 mg/L ellagic acid equivalents for the low and medium tannin potential modalities, respectively; a rapid increase was then observed after four months (9.07 and 11.4 mg/L ellagic acid equivalents for low and medium tannin potential, respectively) and after six months of élevage (10.59 and 13.85 mg/L ellagic acid equivalents for low and medium tannin potential, respectively).

The results in FIGURE 2 show that the time necessary to reach the maximum ellagitannin concentration in the wines is related to the wine matrix and not to the oak tannin potential. For wine B, ellagitannin extraction peaks at six months of élevage (14.28 mg/L ellagic acid equivalents for low tannin potential, 14.30 mg/L ellagic acid equivalents for medium tannin potential), which is followed by a decrease after eight months whereas ellagitannin extraction is constant throughout élevage for wines A and C.

Various physico-chemical parameters, such as pH, alcohol content (ABV) and temperature, can modify the ellagitannin extraction rate in wine.[4] In our experimental conditions, wines A, B and C showed similar pH and ABV, and were aged in cellars with mild temperatures (15° C to 18° C). Thus, we can hypothesize that wine B's greater rate of ellagitannin consumption during élevage could be linked to its higher oxidation resistance, as measured by the EPR method. Indeed, ellagitannin reacts first with oxygen and thus leads to a better protection toward oxidation.

Trials combining low tannin potential with the light toasts (Blanche and Ivoire) did not demonstrate an impact on the ellagitannin extraction kinetics (data not shown). However, the wine matrix effect on the extraction kinetics was confirmed for this series of trials for three distinct wines.

The evolution in glutathione content, a known antioxidant, according to oak tannin potential, was also monitored throughout élevage (see FIGURE 3). It should be noted that no significant difference in the fermentation kinetics, during alcoholic fermentation, was observed. At the end of alcoholic fermentation, the glutathione concentration is identical for the different modalities of each type of wine. Identical results were obtained for wines aged in low tannin potential barrels coupled with Blanche and Ivoire toasts.

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Near Infrared Spectroscopy scanner analyzes wood with an acoustooptic tunable filter to make mathematical correlation to yield tannin level.

We can thus deduce that a low tannin potential, combined with a light toast has no influence on the glutathione concentration after alcoholic fermentation. Afterwards, during élevage, the glutathione concentration decreases progressively, depending on the tannin potential and the type of wine (see FIGURE 3). It should be noted that for wine A, the new barrel had a significant positive effect on glutathione preservation whereas for wine C, this was not the case.

Élevage Increases Wine Shelf Life

The objective of this research was to assess the impact of oak tannin selection and barrel toasting on dry white wine oxidative stability.

The results indicate that wine oxidative stability increases during élevage, independent of the grape variety (Sauvignon Blanc and Chardonnay). At the end of élevage, wines aged under medium oak tannin potential show better antioxidant stability.

Concerning the ellagitannins, our analyses demonstrate a high level of homogeneity in the tested barrels, and a concordance between the total content in the wines and the barrel classification. Wine ellagitannin kinetic extraction is linear during élevage and achieves a maximum at six or eight months in a grape variety-dependent manner.

Oak wood barrel tannin potential and toasting have no effect on the glutathione and grape polyphenol content of a wine.

At this stage, the specific analytic approach seems unable to explain the variabilities in wine oxidative stability. There is no clear correlation between glutathione levels and wine oxidative stability at the end of aging. We will continue our research in order to better understand the wood compounds conducive to better oxidative stability. These studies of the wood's metabolomics will be the subject of a later publication. **WBM**

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