

Research Note

Impact of Oak-Derived Compounds on the Olfactory Perception of Barrel-Aged Wines

Andrei Prida^{1*} and Pascal Chatonnet²

Abstract: Barrel-aged wine is a complex mixture and its olfactory perception results from the interaction of many flavors. To estimate the role of oak-derived flavor compounds, it is necessary to consider odor activity values (OAV) and to perform a correlation study to assess the impact of flavor compounds on the flavor attributes. Twenty Spanish and French wines, each aged in different types of barrels, were studied using both sensory (descriptive) and chemical (GC-MS) analysis. Paired-sample *t*-tests were used to assess whether there were systematic differences in the concentrations of oak-derived compounds between wines aged in different barrels and evaluated differently in the sensory tests. Regardless of their low OAVs, furanic compounds (furfural, furfuryl alcohol, and 5-methylfurfural) increased the “overall oak” intensity rating and decreased the “fruity” intensity rating. It is hypothesized that these compounds indirectly impacted the respective intensities. The presence of *cis*- and *trans*-whisky lactones, eugenol, and vanillin increased the intensity rating of the vanilla/pastry descriptor, while furfural and 5-methylfurfural diminished it. Regardless of the volatile phenols (guaiacol, 4-methylguaiacol, eugenol) described as smoky and spicy in their pure state, no reliable links were found between these compounds and the respective sensory descriptors in wines. Samples described as having higher olfactory persistence were richer in relatively high-boiling wood compounds, such as *trans*- and *cis*-whisky lactone, maltol, eugenol, and vanillin, than their paired samples, explaining their retronasal persistence.

Key words: oak, wine, sensory analysis, chemical analysis

Research on the compounds responsible for specific aromas in wine begins by identifying the key compounds that remind the taster of these odors. However, among the chemicals in the aromas in the pure state, only a few can be perceived in wine. Wine has been characterized as a sensory buffer that can compensate for the addition or omission of several odorant compounds without any significant changes in the overall aroma perception (Ferreira et al. 2008). Sensory buffer components include ethanol, fermentation products, and odor compounds that could not break through this buffer. Together these components provide wine with a generic “wine” flavor with no specific notes. The compounds that can break through this buffer, referred to as “impact compounds,” confer certain specific aromas to wine, such as raspberry, grapefruit, and smoke. The odor activity value (OAV) of the flavor compound (i.e., the ratio between the amount in the wine/sensory threshold) indicates the possibility of the compound being an “impact” compound. A taster cannot predict the real intensity of the aroma, as the effects of the matrix can strongly affect the volatilization of odor components, depending on their chemical structure (Pangborn et al. 1978, Mälkki et al. 1993).

Barrel maturation adds more complexity to wine because of the leaching of several strong odorant chemicals from the wood and their subsequent transformation in the wine. Important wood chemicals, which might be impact molecules, include the naturally present *cis*- and *trans*-methyl-octalactone (whisky lactones, with a coconut flavor in their pure state), *trans*-2-nonenal (sawdust smell), volatile phenols released via toasting such as guaiacol, 4-methylguaiacol, and eugenol (spicy and smoky smells), and vanillin (vanilla smell). All of these compounds can be present in barrel-aged wines in concentrations above the sensory threshold; their concentrations depend on the chemical composition of the barrel’s wood. Some of them undergo modification in a wine medium. Decreased vanillin concentration during barrel fermentation and maturation in the presence of yeast lees has been reported (Chatonnet et al. 1992, Spillman et al. 1997, 1998); the products of transformation were low odorant vanillyl alcohol and vanillyl ethyl ester. The *trans*-2-nonenal concentration decreases during stave maturation and more dramatically during toasting (Chatonnet and Dubourdiou 1998). In a wine medium, this compound, as any other aliphatic aldehyde, can interact with tannins and sulfur dioxide. Thus, its contribution is perceived only in wines characterized by pronounced green sawdust off-flavors. Furfurylthiol and 5-methyl-2-furanmethanthiol (coffee-smelling compounds with very low odor thresholds of 0.4 and 50 ng/L, respectively) have been identified as products of transformation of furfural and 5-methylfurfural, respectively, in a wine medium (Blanchard et al. 2001, Tominaga et al. 2004, Tominaga and Dubourdiou 2006).

¹Tonnellerie Seguin Moreau, Z.I. Merpins, B.P. 94, 16103, Cognac, France, and

²Laboratoire Excell, Parc Innolin, 10, rue du Golf, 33700 Mérignac, France.

*Corresponding author (email: aprida@seguin-moreau.fr; tel. (33) 5 45 82 62 22)

Manuscript submitted Sep 2009, revised Oct 2009, Jan 2010, accepted Mar 2010

Copyright © 2010 by the American Society for Enology and Viticulture. All rights reserved.

However, the importance of these compounds in matured wine is difficult to measure as they are very unstable.

Wine is a complex mixture and its olfactory perception is the result of the interaction of odors. Therefore, to estimate the role of a particular odor compound, it is important to consider both the OAVs and to perform a correlation study to discern the impact of flavor compounds on aroma attributes. Several studies dealing with wood-derived compounds have already been undertaken. In Pinot noir wine, either a positive correlation between *cis*-methyl-octalactone and sensory descriptors such as toasty, coconut, woody, and vanilla or a negative correlation with the pharmaceutical, hay, and clove descriptors was observed (Sauvageot and Feuillat 1999). In another study, a partial least squares model was applied to the sensory and chemical results of 57 Spanish wines and an excellent correlation between the woody-vanilla-cinnamon descriptor and *cis*-methyl-octalactone was found (Aznar et al. 2003). This correlation was less pronounced with vanillin and eugenol. In addition, *cis*-methyl-octalactone contributed to the intensity of the sweet-candy-cocoa descriptor and vanillin to the fruity descriptor.

In a more recent study on white (Chardonnay) and red (Cabernet Sauvignon) wine aged in different barrels, *cis*-methyl-octalactone concentration correlated positively with the coconut, berry, coffee, and dark chocolate descriptors in red wine but only with coconut in white wine (Spillman et al. 2004). The vanillin concentration in white wine was not directly correlated to the vanilla descriptor; however, it was correlated to the cinnamon and smoky descriptors. Some other compounds, including guaiacol, 4-methylguaiacol, 4-ethylphenol, furfural, and 5-methylfurfural, contributed to the intensity of the latter descriptor. In red wine, the vanilla descriptor is linked to numerous wood compounds such as volatile phenols, γ -lactones, and furanic compounds while the smoky descriptor is correlated to furfuryl alcohol.

The above studies highlight several important phenomena. Odorant molecules often enhanced the intensity of a descriptor differently from the aroma of the respective chemicals in their pure state. One can also observe the sensory impact of other compounds, such as furanic compounds, which were judged unimportant because of their low OAVs. However, the conclusions of these studies cannot be widely extended. Two were characterized by small sample sizes of only one (Sauvageot and Feuillat 1999) and two (Spillman et al. 2004) wines. Therefore, the scientifically rigorous conclusions reached in their studies apply only to those wines. With a different wine matrix, the conclusions could be different. The third study used a much broader experimental design (57 wines), which allowed for more general conclusions about the correlations (Aznar et al. 2003).

A statistically different approach was used here to complete the above studies. A range of different wines, each aged in different types of barrels, was compared using both sensory and chemical analysis. Paired-samples *t*-tests were used to assess whether there is any evidence of systematic differences in the concentrations of aroma compounds

between wines aged in different barrels and which were evaluated differently in the sensory tests. This study is limited to only wood-derived compounds and descriptors directly linked to characteristics of these compounds.

Materials and Methods

Wines. Twenty different French and Spanish wines were selected and aged in barrels for 6 to 12 months (Table 1). Each wine was aged in new barrels of various types produced from French oak wood (Seguin-Moreau Cooperage, Merpins, France) that according to grain, bending, and toasting technique (barrel body and barrel heads). The aim of the study was to compare the sensory perceptions of wines that were initially identical but aged in different barrel types that contribute different wood-derived compounds. The origin of the differences in chemical composition of wood-derived compounds among wines was not examined.

Sensory analysis. Sensory analyses were performed by a tasting panel of 10 to 14 people comprising professional enologists from the internal staff of the Seguin Moreau Cooperage and invited winemakers. Panelists were asked to assign quantitative marks from 0 to 10 (0 as lowest and 10 as highest) to the following descriptors: fruity, vanilla/pastry, toasty/smoky, spicy, overall woody, and olfactory persistence. Training sessions were carried out using wines characterized by different intensities of individual descriptors (e.g., fruity) after a panel consensus on these wines. The “overall oaky” descriptor was chosen by tasters to describe all olfactory sensations brought about by the wood.

The sensory sessions were organized by series, with the same wine aged in different barrel types. Either one single session per day or a maximum of three sessions per day were organized for the long (eight to nine different barrel types per wine) and short series (two to three different barrel types per wine), respectively. Twenty sessions were performed, corresponding to the 20 different wine matrixes used in the study. The tasting sessions were conducted in standard tasting rooms by a session observer. Before the sensory analysis, the bottle was examined for possible off-flavors and rejected if there was an abnormal odor.

The taster's marks were normalized by subtracting the average intensity mark of a specific descriptor among the individual series for the same taster from the mark of the same descriptor intensity for the specific wine. The normalized values were used for statistical analysis. Independent samples *t*-tests were performed to find the statistical difference between the intensity rating for each descriptor when the same wine was aged in different barrels. Thus, in a three-sample experiment, three comparisons were possible (barrel type A versus barrel type B, barrel type A versus barrel type C, and barrel type B versus barrel type C). In all, 161 pair comparisons were performed.

Chemical analysis. Nineteen wood-derived volatile compounds found in wines were quantified by gas phase chromatography–mass spectrometry. These included furanic and pyranic compounds (furfural, 5-hydroxymethylfurfural [5HMF], 5-methylfurfural [5MF], furfuryl alcohol,

maltol, and ethylmaltol). When wine is aged in a barrel, furfural can be converted into furfuryl alcohol. Therefore, we calculated the total furfural concentration as the sum of furfural and furfuryl alcohol. In addition, two aromatic aldehydes (vanillin and syringaldehyde), nine volatile phenols (guaiacol, 4-methylguaiacol, eugenol, isoeugenol, *o*-cresol, *m*-cresol, phenol, syringol, and allylsyringol), and two whisky lactone isomers (*trans*- and *cis*-whisky lactones) were examined.

For analysis, 100 mL wine was supplemented with 100 µL internal standard solution (100 mg/L octan-3-ol in absolute ethanol). The wine was extracted three times using 5 mL dichloromethane for 5 min on a magnetic stirrer and the organic phases were combined after static decantation. Sodium bicarbonate (0.2 g) was added to the organic phases and stirred for 5 min to remove excess fatty organic acids. Finally, the organic extract was dried over anhydrous sodium sulfate and concentrated under a nitrogen flux (100 mL/min) to a final volume of 0.5 mL. The extract was stored at 5°C in a refrigerator until injection.

The organic extract (1 µL) was injected automatically (Gerstel automatic sampler; Mülheim an der Ruhr, Germany) in splitless mode (split rate: 100 mL/min) on an 6890 gas chromatograph coupled to an 5973 inert mass selective detector (Agilent Technologies, Santa Clara, CA). The chromatographic separation was done by a SGE Solgel-Wax capillary column (Scientific Instrument Services, Ringoes, NJ) of 30 m x 0.25 mm x 0.25 µm thick stationary phase

using helium with a constant gas flow of 1.5 mL/min. The oven temperature was ramped from 40°C to 130°C at 20°C/min, then from 130°C to 180°C at 2°C/min, and finally from 180°C to 240°C at 5°C/min, with a final isotherm at 240°C for 15 min.

Detection was by a mass selective detector using an electronic impact (ionization energy 70 KeV, source temperature 230°C, quadrupole temperature 150°C, transfer line temperature 260°C) and selective ion monitoring for specific detection of targeted compounds. The quantitative analysis was obtained from a calibration curve made for each compound in a model wine solution (13% by volume ethanol, 5 g/L tartaric acid, pH adjusted to 3.6 using 10 NaOH) and supplemented with the different targeted compounds at different concentrations in relation to the internal standard.

The following *m/z* ions were used for the simultaneous identification and quantification (underlined) of the various compounds: octan-3-ol, 83/101 (internal generic standard); guaiacol, 124/109; 4-methylguaiacol, 152/137; phenol, 94/66; eugenol, 122/107; syringol, 154/139; 4-allylsyringol, 194/119; maltol, 126/71; furfural, 96/95; furfuryl alcohol, 98/97; 5-methylfurfural, 110/109; 5-hydroxymethylfurfural, 126/97; vanillin, 151/152; syringaldehyde, 181/182; *cis*-/*trans*-whisky lactone, 99/71, *m*, *p*, *o*-cresol, 108/107; isoeugenol, 164/149; ethylmaltol, 140/139. Performances of the quantitative analysis obtained are shown (Table 2).

Table 1 Origin of the 20 wine samples studied.

| Wine | Vine origin ^a | Variety | Vintage | Barrel types (n) | Comparison pairs (n) | Barrel wood ^b |
|-------|--------------------------|------------------------------------|---------|------------------|----------------------|---|
| 1 | Rhone Valley | Syrah | 2004 | 3 | 3 | M, M+, and ML |
| 2 | Bordeaux | Cabernet Sauvignon | 2005 | 9 | 36 | M, M+, and ML; toasted and nontoasted heads, medium and tight grain |
| 3 | Bordeaux | Cabernet Sauvignon | 2005 | 9 | 36 | M, M+, and ML; toasted and nontoasted heads, medium and tight grain |
| 4 | Bordeaux | Cabernet Sauvignon | 2005 | 3 | 3 | M, M+, and ML |
| 5 | Bordeaux | Cabernet Sauvignon | 2005 | 3 | 3 | M, M+, and ML |
| 6 | Bordeaux | Cabernet Sauvignon | 2006 | 3 | 3 | M, M+, and ML |
| 7 | Bordeaux | Cabernet Sauvignon/Merlot | 2007 | 3 | 3 | M, M+, and ML |
| 8 | Languedoc | Chardonnay | 2006 | 2 | 1 | Water bending and fire bending |
| 9 | Languedoc | Chardonnay | 2006 | 2 | 1 | Water bending and fire bending |
| 10 | Southwest | Merlot/Tannat | 2006 | 4 | 6 | M, M+, and ML; toasted and nontoasted heads |
| 11 | Southwest | Merlot/Tannat | 2007 | 4 | 6 | M, M+, and ML; toasted and nontoasted heads |
| 12 | Somontano | Cabernet Sauvignon/ Tempranillo | 2006 | 8 | 28 | M, M+, and ML; toasted and nontoasted heads |
| 13 | Southwest | Merlot | 2006 | 5 | 10 | M, M+, and ML; medium and tight grain |
| 14 | Bordeaux | Merlot | 2007 | 3 | 3 | M, M+, and ML |
| 15 | Bordeaux | Merlot | 2007 | 4 | 6 | M, M+, and ML; medium and tight grain |
| 16 | Bordeaux | Merlot | 2007 | 2 | 1 | M and ML |
| 17 | Burgundy | Chardonnay | 2007 | 3 | 3 | M and ML; water and fire bending |
| 18 | Burgundy | Chardonnay | 2007 | 3 | 3 | M and ML; water and fire bending |
| 19 | Burgundy | Chardonnay | 2007 | 3 | 3 | M and ML; water and fire bending |
| 20 | Burgundy | Pinot noir | 2007 | 3 | 3 | M and ML; water and fire bending |
| Total | | | | 79 | 161 | |

^aAll wines from France, excepting Somontano, which was from Spain.

^bToasting level: M, medium; M+, medium plus; ML, medium long.

Results and Discussion

Seventy-nine different wine samples were analyzed throughout the study (Table 3). The high variability reflects differences in chemical composition of barrel wood and in extraction and transformation of wood compounds during wine maturation. The wine matrix (alcohol concentration and pH) and maturation conditions (temperature, dissolved oxygen, and redox potential) can affect the extraction of oak compounds (Garde Cerdan et al. 2004). In addition, the wines in different series were sampled at different stages of their maturation, from 6 to 12 months).

The independent samples *t*-tests performed for each pair of samples examined during the sensory sessions allowed us to find pairs with different intensity ratings for descriptors at $p < 0.05$ (Table 4). Thus, one sample had a significantly higher intensity rating ($p < 0.05$) for a certain descriptor (e.g., fruity) than the other sample found in the same pair. Both samples in the pair represented the same wine aged in different barrels; therefore, the difference in the sensory perception and chemical composition was due solely to the barrel and not to the wine itself.

Paired-samples *t*-tests were run for all chemical variables measured for the paired samples to check whether there were any systematic differences in the chemical composition of wines aged in different barrels and with different perceived sensory character. This design allowed the effect of the starting wine to be isolated from the effect of the wood on flavor and allowed a degree of generalization because a range of different wines were used. The concentrations of specific compounds in samples with higher perceived intensity of a specific descriptor were subtracted from those in their paired samples where this intensity was

lower. Thus, the values of differences could be positive or negative. A positive difference indicates that a higher concentration of that chemical increased the perception of the respective descriptor, while a negative difference decreased it. The standard deviations of differences between samples and their statistical significance were calculated to check whether the differences were systematic across all pairs.

Relatively few pairs (17 to 28 out of 161 possible pairs) were judged different for any descriptor. Thus, regardless of the variation in oak-derived chemical composition between wine samples, only certain pairs were different enough to be distinguished in sensory analysis.

Fruity descriptor. There were no wood-derived compounds that reminded the tasters of a strictly fruit aroma. Thus, it was not surprising that no wood-derived compounds enhanced the fruity expression. On the contrary, the more fruity samples were characterized by systematically lower concentrations of furfural, total furfural, furfuryl alcohol, and 5-methylfurfural, all typically released through barrel toasting. These compounds have relatively high sensory thresholds: 20 to 65 mg/L for furfural; 35 to 45 mg/L for furfuryl alcohol, and 45 to 52 mg/L for 5-methylfurfural in white and red wines (Chatonnet 1995). The differences in these compounds found between more or less fruity samples, when compared to their perception thresholds, could not be explained by their direct sensory impact. There are several possible explanations. First, regardless of the low probability of a direct impact by these compounds, they could enhance the action of other compounds acting as masking agents for the fruity character. Second, the aforementioned compounds could be markers for either some unknown potent odorant that masks the fruity character or

Table 2 Characteristics of the quantitative analysis of the volatile compounds.

| | Detection limit (µg/L) | Quantification limit (µg/L) | Variability (%) |
|------------------------------|------------------------|-----------------------------|-----------------|
| Guaiacol | 0.019 | 0.063 | 4 |
| 4-Methylguaiacol | 0.023 | 0.078 | 4 |
| Phenol | 0.009 | 0.031 | 5 |
| Eugenol | 0.010 | 0.033 | 5 |
| Syringol | 0.034 | 0.115 | 5 |
| 4-Allylsyringol | 0.012 | 0.040 | 4 |
| Maltol | 0.076 | 0.254 | 13 |
| Furfural | 0.043 | 0.145 | 4 |
| Furfuryl alcohol | 0.112 | 0.372 | 5 |
| 5-Methylfurfural | 0.026 | 0.086 | 4 |
| 5-Hydroxymethylfurfural | 0.659 | 2.196 | 6 |
| Vanillin | 0.059 | 0.196 | 5 |
| Syringaldehyde | 0.213 | 0.711 | 14 |
| <i>cis</i> -Whisky lactone | 0.020 | 0.067 | 6 |
| <i>trans</i> -Whisky lactone | 0.011 | 0.037 | 4 |
| <i>o</i> -Cresol | 0.015 | 0.049 | 4 |
| <i>m</i> -Cresol | 0.020 | 0.066 | 5 |
| Isoeugenol | 0.018 | 0.060 | 5 |
| Ethylmaltol | 0.025 | 0.084 | 4 |

Table 3 Concentration ranges of 19 of oak-derived compounds in 79 wine samples.

| | Concentration (µg/L) | | | |
|------------------------------|----------------------|-------|------|------|
| | Min | Max | Avg | SD |
| Furfural | 6 | 5967 | 1043 | 1753 |
| 5-Methylfurfural | 1 | 822 | 179 | 185 |
| Furfuryl alcohol | 80 | 23536 | 2840 | 3425 |
| Guaiacol | 6 | 40 | 17 | 7 |
| <i>trans</i> -Whisky lactone | 1 | 186 | 30 | 37 |
| <i>cis</i> -Whisky lactone | 48 | 1001 | 255 | 160 |
| Maltol | 0 | 169 | 71 | 39 |
| 4-Methylguaiacol | 3 | 22 | 10 | 5 |
| Phenol | 3 | 122 | 13 | 17 |
| Ethylmaltol | 0 | 7 | 2 | 2 |
| <i>o</i> -Cresol | 0 | 4 | 2 | 1 |
| <i>m</i> -Cresol | 1 | 158 | 7 | 21 |
| Eugenol | 4 | 60 | 28 | 14 |
| Isoeugenol | 1 | 127 | 17 | 21 |
| Syringol | 11 | 488 | 65 | 74 |
| 5-Hydroxymethylfurfural | 19 | 3979 | 665 | 838 |
| 4-Allylsyringol | 4 | 300 | 46 | 52 |
| Vanillin | 13 | 506 | 201 | 104 |
| Syringaldehyde | 71 | 1441 | 612 | 337 |
| Total furfural | 187 | 15770 | 3882 | 4728 |

Table 4 Mean differences in concentrations of wood-derived compounds in paired wine samples with significantly different ratings for six sensory descriptors. (Significant differences ($p < 0.05$ by Student's t -test) are in bold font; ns, not significant.)

| Compound ($\mu\text{g/L}$) | Fruity (22) ^a | | | Overall woody (19) | | | Vanilla/pastry (28) | | | Toasty/smoky (22) | | | Spicy (17) | | | Olfactory persistence (23) | | |
|---------------------------------|--------------------------|--------|-----------|--------------------|--------|-----------|---------------------|--------|-----------|-------------------|--------|-----------|------------|--------|-----------|----------------------------|--------|-----------|
| | Mean | SD | t -test | Mean | SD | t -test | Mean | SD | t -test | Mean | SD | t -test | Mean | SD | t -test | Mean | SD | t -test |
| Furfural | -113.7 | 476.3 | 5% | 393.7 | 956.0 | ns | -215.3 | 405.5 | 1.6% | -95.3 | 2389.9 | ns | 177.0 | 1045.7 | ns | 112.3 | 376.8 | ns |
| 5-Methylfurfural | -76.1 | 122.4 | 5% | 65.4 | 168.5 | ns | -61 | 91.3 | 0.3% | 54.6 | 195.3 | ns | -10.4 | 117.1 | ns | 14.8 | 157.6 | ns |
| Furfuryl alcohol | -1339.9 | 1944.9 | 3.6% | 689.3 | 1926.6 | ns | -286.0 | 1084.5 | ns | 438.7 | 3690.0 | ns | 245.7 | 1441.1 | ns | 548.3 | 1882.1 | ns |
| Guaiacol | 1.2 | 6.2 | ns | 0.9 | 7.9 | ns | -1.5 | 5.5 | ns | -0.5 | 8.6 | ns | -0.1 | 8.1 | ns | -2.8 | 5.6 | ns |
| <i>trans</i> -Whisky lactone | 1.8 | 11.2 | ns | 3.0 | 23.4 | ns | 18.5 | 34.3 | 1.4% | -2.1 | 20.2 | ns | 5.7 | 7.4 | 0.7% | 26.9 | 37.6 | 3% |
| <i>cis</i> -Whisky lactone | 59.1 | 105.9 | ns | 54.7 | 151.1 | 4% | 87.9 | 92.6 | 0.01% | 40.9 | 104.7 | ns | 4.1 | 141.0 | ns | 112.6 | 96.6 | 0.2% |
| Maltol | -7.8 | 21.8 | ns | 13.2 | 30.1 | ns | 2.1 | 15.4 | ns | 12.2 | 22.0 | 3% | -23.6 | 38.8 | 3.3% | 10.7 | 14.2 | 2.5% |
| 4-Methyl-guaiacol | -1.0 | 1.9 | ns | 1.3 | 5.0 | ns | -1.41 | 3.2 | 4% | 1.3 | 4.3 | ns | 0.3 | 4.5 | ns | 0.1 | 3.7 | ns |
| Phenol | 2.4 | 7.0 | ns | -0.4 | 2.4 | ns | -0.3 | 1.3 | ns | 0.1 | 2.8 | ns | -0.4 | 2.1 | ns | -1.2 | 2.3 | ns |
| Ethylmaltol | -0.2 | 0.4 | ns | 0.0 | 0.4 | ns | -0.5 | 1.5 | ns | -0.1 | 0.5 | ns | -0.1 | 0.3 | ns | 0.1 | 0.3 | ns |
| <i>o</i> -Cresol | 0.1 | 0.7 | ns | 0.2 | 0.7 | ns | 0.0 | 0.6 | ns | 0.1 | 0.6 | ns | 0.1 | 0.6 | ns | 0.3 | 0.5 | ns |
| <i>m</i> -Cresol | 0.3 | 0.5 | ns | 0.3 | 0.6 | ns | -0.1 | 0.3 | ns | 0.3 | 0.7 | ns | -4.4 | 17.0 | ns | 0.3 | 0.5 | ns |
| Eugenol | 2.9 | 9.6 | ns | 2.7 | 8.4 | ns | 4.0 | 5.4 | 0.1% | 0.8 | 4.3 | ns | 0.5 | 4.2 | ns | 5.7 | 4.8 | 0.2% |
| Isoeugenol | -2.3 | 4.0 | ns | 12.7 | 29.4 | ns | -0.2 | 2.6 | ns | -0.4 | 12.3 | ns | -1.4 | 5.0 | ns | 0.7 | 3.9 | ns |
| Syringol | -0.8 | 18.9 | ns | 0.9 | 29.2 | ns | -7.3 | 22.9 | ns | 1.7 | 26.6 | ns | -6.5 | 36.3 | ns | -10.7 | 19.2 | ns |
| 5-Hydroxy-methylfurfural | -205.4 | 381.2 | ns | 292.9 | 427.3 | 0.6% | -46.5 | 186.9 | ns | 348.8 | 568.3 | 1.5% | -30.4 | 280.9 | ns | 89.9 | 282.6 | ns |
| 4-Allylsyringol | -7.8 | 14.9 | ns | 1.8 | 28.2 | ns | -4.2 | 19.5 | ns | 0.8 | 16.2 | ns | -4.8 | 13.4 | ns | -2.8 | 15.0 | ns |
| Vanillin | -26.0 | 56.5 | ns | 32.6 | 37.6 | 0.1% | 20.8 | 33.4 | 0.6% | 14.1 | 53.7 | ns | -27.4 | 64.7 | ns | 22.3 | 28.7 | 2% |
| Syringaldehyde | -90.6 | 243.8 | ns | 77.6 | 262.1 | ns | 20.1 | 163.6 | ns | 55.4 | 210.1 | ns | -77.9 | 189.6 | ns | 33.9 | 178.5 | ns |
| Total furfural | -1453.6 | 2274.9 | 4.9% | 1083 | 2698.5 | 0.001% | -490.2 | 1227.2 | ns | 343.4 | 5818.1 | ns | 422.7 | 2337.3 | ns | 660.7 | 2228.6 | ns |

^aNumber of pairs with significantly different rankings for the descriptor (in parenthesis).

for some process that occurs in wood during heating and which leads to the loss of fruity character. Finally, they are precursors of other, more potent, odorant molecules and could mask the fruity aroma. Examples of such products of transformation include thiols, which possesses a strong coffee aroma (Blanchard et al. 2001, Tominaga et al. 2004, Tominaga and Dubourdieu 2006), and furfuryl ethyl ester, which possesses a kerosene-like aroma (Spillman et al. 1998). Both compounds can mask fruity aromas. It is possible that any or all of these phenomena occur simultaneously.

Overall oak aroma descriptor. The most potent contributors to an overall oak aroma are compounds related to barrel toasting: vanillin, 5-hydroxymethylfurfural, and total furfural. *cis*-Whisky lactone was also among these contributors; however, its concentration was not systematically higher in the more intense oaky samples ($p = 4\%$), unlike the other three compounds. The role of furanic compounds can be explained in the same way as for the fruity descriptor: they enhanced the oaky flavor and acted as markers and/or precursors for potent odorants perceived as an oak barrel aroma. Vanillin and *cis*-whisky lactone can also be regarded as direct contributors and/or possible enhancers of this descriptor.

Vanilla/pastry descriptor. The *cis*- and *trans*-whisky lactones, eugenol, and vanillin are associated the vanilla descriptor. 4-Methylguaiacol, furfural, and 5-methylfurfural concentrations were systematically lower in more intense vanilla samples. Based on its high significance ($p = 0.01$) in the t -test, *cis*-whisky lactone was the most important contributor to this descriptor. As in a previous study (Aznar et al. 2003), vanillin contributed toward the intensity of this descriptor, but less significantly. *trans*-Whisky lactone and eugenol have a high perception threshold in wine: much higher than the average difference found between the paired samples. Their significance may be explained by a co-correlation with *cis*-whisky lactone in wood (Prida and Puech 2007). The role of furfural and 5-methylfurfural was similar as for fruity descriptor: they used different mechanisms to mask the vanilla/pastry flavor.

Toasty/smoky descriptor. Maltol and 5-hydroxymethylfurfural were associated with the toasty/smoky descriptor. The hypothesis of an indirect impact (enhancer, marker, and precursor) seems most plausible here as well, because maltol has a high perception threshold. None of the volatile phenols studied here (such as guaiacol and 4-methylguaiacol) were perceived as

smoky in their pure state. Their weak contribution could be explained by the low variation in their concentrations compared with the perception thresholds in wine.

Spicy descriptor. The impact of wood compounds on the spicy descriptor is rather difficult to explain. However, there was no association between spicy and the concentration of eugenol, described in its pure state as spicy/clove.

Olfactory persistence descriptor. The samples described as having a higher olfactory persistence were richer in *trans*- and *cis*-whisky lactones, maltol, eugenol, and vanillin than their paired samples. This group of compounds was characterized in general by low perception thresholds and a pleasant aroma. In addition, vanillin, whisky lactones, and maltol have relatively high boiling points, which explains their retronasal persistence.

Conclusion

Twenty different wines, each aged in a different barrel type, were studied using both sensory (descriptive) and chemical analysis. Comparisons were made using paired tests on the same wine matrix. Thus, the differences in sensory perception and chemical composition reported in the study were solely due to the impact of different barrels and not to the wine itself.

Furanic compounds (furfural, furfuryl alcohol, and 5-methylfurfural) increased the overall oak intensity and decreased the fruity intensity. The presence of *cis*- and *trans*-whisky lactones, eugenol, and vanillin raised the intensity of the vanilla/pastry descriptor, while furfural and 5-methylfurfural diminished it. Thus, furanic compounds, often judged as unimportant because of their low OAVs, definitely had a strong sensory impact. An indirect impact as markers, enhancers, or precursors of some unknown or known odorants (such as furfuryl thiol, 5-methyl-2-furanmethanethiol, or furfuryl ethyl ester) masked the fruity and vanilla/pastry aromas.

Some volatile phenols (guaiacol, 4-methylguaiacol, and eugenol) described as smoky and spicy in their pure state and which have low sensory thresholds were not consistently linked to their respective sensory descriptors in wines. Samples described as having a higher olfactory persistence were richer than their paired samples in relatively high-boiling wood compounds such as *trans*- and *cis*-whisky lactone, maltol, eugenol, and vanillin, explaining their retronasal persistence.

Literature Cited

- Aznar, M., R. López, J. Cacho, and V. Ferreira. 2003. Prediction of aged red wine aroma properties from aroma chemical composition. Partial least squares regression models. *J. Agric. Food Chem.* 51:2700-2707.
- Blanchard, L., T. Tominaga, and D. Dubourdieu. 2001. Formation of furfurylthiol exhibiting a strong coffee aroma during oak barrel fermentation from furfural released by toasted staves. *J. Agric. Food Chem.* 49:4833-4835.
- Chatonnet, P. 1995. Influence des procédés de tonnellerie et des conditions d'élevage sur la composition et la qualité des vins élevés en fûts de chêne. Thesis, University of Bordeaux II.
- Chatonnet, P., and D. Dubourdieu. 1998. Identification of substances responsible for the "sawdust" aroma in oak wood. *J. Sci. Food Agric.* 76:179-188.
- Chatonnet, P., D. Dubourdieu, and J.N. Boidon. 1992. Incidence des conditions de fermentation et d'élevage des vins blancs secs en barriques sur leur composition en substances cédées par le bois de chêne. *Sci. Aliments* 12:665-680.
- Ferreira, V., A. Escudero, E. Campo, and J. Cacho. 2008. The chemical foundations of wine aroma—A role game aiming at wine quality, personality and varietal expression. *In* Proceedings of Thirteenth Australian Wine Industry Technical Conference. R. Blair et al. (eds.), pp. 1-9. AWITC, Glen Osmond.
- Garde Cerdan, T., D. Goni, and C. Ancin Azpilicueta. 2004. Accumulation of volatile compounds during ageing of two red wines with different composition. *J. Food Eng.* 65:349-356.
- Mälkki, Y., R.L. Heinö, and K. Autio. 1993. Influence of oat gum, guar gum and carboxymethyl cellulose on the perception of sweetness and flavour. *Food Hydrocolloids* 6:525-532.
- Pangborn, R.M., G.Z. Misaghi, and C. Tassan. 1978. Effect of hydrocolloids on apparent viscosity and sensory properties of selected beverages. *J. Texture Stud.* 9:416-436.
- Prida, A., and J.L. Puech. 2006. Influence of geographical origin and botanical species on the content of extractives in American, French, and East European oak woods. *J. Agric. Food Chem.* 54:8115-8126.
- Sauvageot, F., and F. Feuillat. 1999. The influence of oak wood (*Quercus robur* L., *Q. petraea* Liebl.) on the flavor of Burgundy Pinot noir. An examination of variation among individual trees. *Am. J. Enol. Vitic.* 50:447-455.
- Spillman, P.J., A.P. Pollnitz, D. Liacopoulos, G.K. Skouroumounis, and M.A. Sefton. 1997. Accumulation of vanillin during barrel-aging of white, red, and model wines. *J. Agric. Food Chem.* 45:2584-2589.
- Spillman, P.J., A.P. Pollnitz, D. Liacopoulos, K.H. Pardon, and M.A. Sefton. 1998. Formation and degradation of furfuryl alcohol, 5-methylfurfuryl alcohol, vanillyl alcohol, and their ethyl ethers in barrel-aged wines. *J. Agric. Food Chem.* 46:657-663.
- Spillman, P.J., M.A. Sefton, and R. Gawel. 2004. The contribution of volatile compounds derived during oak barrel maturation to the aroma of Chardonnay and Cabernet Sauvignon wine. *Aust. J. Grape Wine Res.* 10:227-235.
- Tominaga, T., and D. Dubourdieu. 2006. A novel method for quantification of 2-methyl-3-furanthiol and 2-furanmethanethiol in wines made from *Vitis vinifera* grape varieties. *J. Agric. Food Chem.* 54:29-33.
- Tominaga, T., G. Gindreau, and D. Dubourdieu. 2004. Acquisitions récentes sur le caractère torréfié des vins élaborés en fûts de chêne. *In* Rencontres Scientifiques 2 Décembre 2004 l'Art d'innover par Seguin-Moreau, pp. 4-12. Seguin-Moreau, Merpins, France.