Food Research International xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

# Study of Chardonnay and Sauvignon blanc wines from D.O.Ca Rioja (Spain) aged in different French oak wood barrels: Chemical and aroma quality aspects

Paula Herrero [a], María Pilar Sáenz-Navajas [a], José Miguel Avizcuri [a,c], Laura Culleré [a], Pedro Balda [c], Elena C. Antón [b], Vicente Ferreira [a], Ana Escudero [a,*]

[a] Laboratory for Aroma Analysis and Enology. Instituto Agroalimentario de Aragón (IA2). Associate unit to Instituto de las Ciencias de la Vid y el Vino (ICVV), (UR-CSIC-GR), Department of Analytical Chemistry, Faculty of Sciences, University of Zaragoza, 50009 Zaragoza, Spain
[b] Tonelería Murua S. A., 26006 Logroño, La Rioja, Spain
[c] Instituto de las Ciencias de la Vid y el Vino (ICVV), Universidad de La Rioja-CSIC-Gobierno de La Rioja. Carretera de Burgos, km.6, Finca de la Grajera, 26007 Logroño, Spain

ARTICLE INFO

*Article history:*
Received 2 June 2016
Received in revised form 3 August 2016
Accepted 7 August 2016
Available online xxxx

*Keywords:*
Sensory analysis
French oak barrels
Sauvignon blanc
Chardonnay
Aromatic compounds
Orthonasal quality

ABSTRACT

This study discusses chemical data corresponding to the analysis of twenty-one wood-extractable aromatic compounds in twenty-four different barrels varying in the toasting level at three sampling times: at the end of the alcoholic fermentation and after 5 and 12 months of aging. Twelve barrels contained monovarietal Chardonnay wine while the other twelve barrels contained Sauvignon blanc wine. The levels of nearly all the analyzed compounds increased with the aging time, with the exception of vinylphenols and methyl vanillate, which decreased. These latter compounds had significantly higher levels in the Chardonnay wines than in the Sauvignon blanc. Furfural, guaiacol and vanillin derivatives increased with the toasting level. ANOVA study showed significant interactions between the toasting level and aging time as well as between the variety and aging time, which revealed significant differences in the levels of the compounds studied in the wines dependent on the toasting level, variety and aging time.
Quality perception based exclusively on orthonasal aroma stimuli was evaluated by a panel of Spanish wine professionals in 12-month aged wines belonging to both grape varieties. Experts from D.O.Ca Rioja aroma did not share a common aroma quality concept for aged Chardonnay and Sauvignon blanc wines. Considering the cluster formed by the majority of experts (76%) for the Chardonnay and cluster 1 (56%) for Sauvignon blanc, quality scores were negatively correlated with the concentration level of 4-vinylphenol and positively with the concentration level of *(E)*-isoeugenol. The opposite was observed for cluster 2 (44%) identified for Sauvignon blanc wines.


## 1. Introduction

Fermentation and barrel aging help to improve wine in terms of color, aroma and flavor. The quality is affected by the wood type, toasting level, aging time (Aiken & Noble, 1984; Gutiérrez Alfonso, 2002) and the grape variety used in the production of wine which is subsequently aged in barrels.

Intrinsic quality (i.e. sensory properties of the wine itself) is influenced by the presence of sensory-active compounds formed as a result of the processes carried out during barrel aging. Jarauta, Cacho, and Ferreira (2005) distinguished between those processes that stimulate an increase or a decrease in the concentration of particular compounds.

The main factors affecting wood composition and therefore the concentrations of wood-extractable compounds are on the one hand the specie, the geographical origin and the silvo-cultural treatment of the tree (Ibern-Gómez et al., 2001; Pérez-Coello, Sanz, & Cabezudo, 1999; Puech, Feuillat, & Mosedale, 1999) and on the other hand the method used for the seasoning, the degree of toasting and the age of the barrel (Cadahía, Fernández de Simón, & Jalocha, 2003; Cerdán, Rodríguez Mozaz, & Ancín Azpilicueta, 2002; Chatonnet & Dubourdieu, 1998; Fernández de Simón, Cadahía, Hernández, & Estrella, 2006). Some compounds are already present in significant quantities even in untoasted wood barrels, such as *(Z)*- and *(E)*-whiskylactone, but others are formed from polymeric compounds present in wood that are broken down during heating processes (Campbell, Polnitz, Sefton, Herderich, & Pretorius, 2006; Hale, Mccafferty, Larmie, Newton, & Swan, 1999; Reazin, 1981). During wood seasoning, some phenolic compounds and whiskylactones increase their concentration (Cadahía, Muñoz, Fernández de Simón, & García-Vallejo, 2001; P. Chatonnet, Boidron, Dubourdieu, & Pons, 1994). Once wood is seasoned, the degree of toasting varies depending on the company but can be globally classified as light, medium or high.

* Corresponding author.
*E-mail address:* escudero@unizar.es (A. Escudero).

http://dx.doi.org/10.1016/j.foodres.2016.08.002

Hydrothermolysis and pyrolysis reactions take place during the toasting process, inducing the degradation of biopolymers such as lignin, polysaccharides, polyphenols and lipids. Thermal degradation of lignin leads to the formation of volatile phenols (such as guaiacol or eugenol) and phenolic aldehydes (such as vanillin or syringaldehyde) (Faix, Meier, & Fortmann, 1990). Furanic compounds are derived from polysaccharides and furfural is produced when pentoses (xylose) coming from the hemicellulose are heated. 5-hydroxymethylfurfural and 5-methylfurfural are produced when hexoses (rhamnose), present in cellulose, are heated during the toasting process. Furfuryl alcohol is formed by the enzymatic reduction of furfural during barrel aging (Boidron, Chatonnet, & Pons, 1988; Chatonnet, 1998; Chatonnet, Boidron, & Pons, 1989).

Barrels made of oak are the most appreciated for the fermentation and aging processes. The most widely used species are *Quercus alba*, from North America, and *Quercus petraea* and *Quercus robur* from Europe, mainly from France. French oak has lower concentrations of *(Z)*-whiskylactone (Jarauta et al., 2005; Rodríguez-Bencomo, Ortega-Heras, Pérez-Magariño, & González-Huerta, 2009; Waterhouse & Towey, 1994), making the woody aroma nuance in wines more subtle. For this reason, French oak has been selected for the aging of white wines.

Several chemical studies relating to differences among wood barrels have been published, and different extraction methods have been used such as solvent extraction (Culleré et al., 2013; Díaz-Maroto, Guchu, Castro-Vázquez, de Torres, & Pérez-Coello, 2008; Fernández de Simón, Muiño, & Cadahía, 2010; Flamini, Vedova, Cancian, Panighel, & De Rosso, 2007; Vichi et al., 2007) or solid phase microextraction (Bozalongo, David Carrillo, Fernández Torroba, & Tena, 2007; Díaz-Maroto, Sánchez-Palomo, & Pérez-Coello, 2004). There are also several studies in the literature addressing the effect of the interaction between wood type and toasting level on red wines (fermented or aged in wood barrels) (Cerdán, Goñi, & Azpilicueta, 2004; Cerdán et al., 2002; De Rosso, Panighel, Dalla Vedova, Stella, & Flamini, 2009; Fernández de Simón, Cadahía, & Jalocha, 2003; Fernández de Simón et al., 2006; Fernández de Simón et al., 2014; Gómez García-Carpintero, Gómez Gallego, Sánchez-Palomo, & González Viñas, 2012; Jarauta et al., 2005; Prida & Chatonnet, 2010; Rodríguez-Bencomo et al., 2009; Spillman, Sefton, & Gawel, 2004). However, there are few works about white wines aged either in wood barrels or with chips. Chardonnay is the most widely studied variety (Guchu, Díaz-Maroto, Pérez-Coello, González-Viñas, & Ibáñez, 2006; Liberatore, Pati, Nobile, & Notte, 2010; Prida & Chatonnet, 2010; Spillman et al., 2004; Towey & Waterhouse, 1996), although Verdejo (Rodríguez-Nogales, Fernández-Fernández, & Vila-Crespo, 2009) and white Listán have also been studied (Gutiérrez Alfonso, 2002). Classical sensory descriptive analysis is reported in the two latter studies, but there are only a few works in which the perceived intrinsic quality of aged white wines is studied (Herjavec, Jeromel, Da Silva, Orlic, & Redzepovic, 2007; Kozlovic, Jeromel, Maslov, Pollnitz, & Orlić, 2010; Liberatore et al., 2010).

The main objective of this work was to carry out different experiments to evaluate how monovarietal Chardonnay and Sauvignon blanc wines aged in French oak barrels were influenced by different toasting levels and aging times. Three important goals were pursued: to study the influence of these factors on the concentrations of 21 aroma compounds released during barrel aging (volatile phenols, lactones, furanic compounds, phenolic aldehydes and their derivatives), to evaluate the perceived aroma quality of 12-month aged white wines, and to examine the relationships established between sensory quality and chemical composition.

## 2. Materials and methods

### 2.1. Reagent and standards

The twenty-one aromatic compounds analyzed were purchased from Sigma-Aldrich (Darmstadt, Germany), Lancaster (Morecambe, Lancashire, UK) and Panreac (Barcelona, Spain). The internal standards, 2-octanol and 3,4-dimethylphenol, were supplied by Sigma-Aldrich (Darmstadt, Germany). The purity of all these standards were above 97%, as can be seen in Table 1 (Supplementary material).

Dichloromethane was obtained from Fisher Scientific (Loughborough, UK). LiChrosolv ethanol was obtained from Merck (Darmstadt, Germany). Ammonium sulfate was supplied by Panreac (Barcelona, Spain). Pure water was obtained from a Milli-Q purification system (Millipore, Bedford, USA).

### 2.2. Samples

The Chardonnay and Sauvignon blanc wines were elaborated by Bodegas Tobía (La Rioja, Spain), while the French oak wood barrels with different toasting levels used for this study were supplied by Tonelería Murua, S.A. (La Rioja, Spain). Four different toasting levels were chosen: three light toasted samples (TL1, TL2, TL3) and a medium toasted sample (TM1). Three wood barrels of each type were provided. The study was thus carried out in triplicate.

The wines underwent alcoholic fermentation inside the different wood barrels and were later aged for 12 months. Samples for analysis were taken from each barrel at the end of the alcoholic fermentation period, and at 5 and at 12 months of aging. A set of 72 samples was finally obtained, barrels with 4 different toasting levels in triplicate for the 2 different grape varieties (see Table 1). Twenty-one wood-related aroma compounds were analyzed in the complete set of samples.

### 2.3. Sensory analysis

The sensory assessment was carried out by a panel of 25 expert judges, at the Instituto de Ciencias de la Vid y el Vino (Logroño, La Rioja, Spain). The experts had extensive wine tasting experience (all being oenologists and wine researchers). The panel was composed of 14 women and 11 men with ages raging between 28 and 56 years (with an average of 36 years). Only those wines with 12 months of aging were tasted. Twenty milliliters of wine were served at room temperature in dark ISO glasses (ISO 3591, 1977) coded with three-digit numbers and covered with plastic Petri dishes according to a sequential monadic random arrangement. Each sample was a mixture of wine taken from 3 wine barrels with the same toasting level. The sessions took place in a ventilated and air-conditioned tasting room (around 20 °C).

Each variety was evaluated independently. Judges were presented with five wine samples (TL1, TL2, TL3 and TM1 together with one sample in duplicate in order to control individual repeatability). They were asked to firstly smell all samples and identify the two samples representing the extremes in the sample set (highest and lowest quality) based on aroma quality perception. They had to anchor these samples in the extremes of a 10 cm structured linear scale. The remaining samples were ranked and scored in the scale, as a measure of the relative degree of quality difference perceived among the set of samples presented. Just after participants had scored wine quality, they were

**Table 1**
Studied samples: variety, toasting and sampling time.

| Sample | Variety | Toasting | Sampling times |
|---|---|---|---|
| CH-T1 | Chardonnay | TL1 | FFA, 5M, 12M |
| CH-TL2 | Chardonnay | TL2 | FFA, 5M, 12M |
| CH-TL3 | Chardonnay | TL3 | FFA, 5M, 12M |
| CH-TM1 | Chardonnay | TM1 | FFA, 5M, 12M |
| SB-TL1 | Sauvignon blanc | TL1 | FFA, 5M, 12M |
| SB-TL2 | Sauvignon blanc | TL2 | FFA, 5M, 12M |
| SB-TL3 | Sauvignon blanc | TL3 | FFA, 5M, 12M |
| SB-TM1 | Sauvignon blanc | TM1 | FFA, 5M, 12M |

TL1: light toasting type 1, TL2: light toasting type 2, TL3: light toasting type 3, TM1: medium toasting type 1, FFA: end of alcoholic fermentation, 5M: 5 months of barrel aging, 12M: 12 months of barrel aging.

asked to freely elicit a maximum of two aroma attributes linked to high and low quality wines according to their own criteria.

### 2.4. Quantification of wood-related compounds through liquid-liquid extraction further gas chromatography-mass spectrometry detection analysis

Wood-related compound analysis was carried out through liquid-liquid extraction further gas chromatography-mass spectrometry detection analysis. Twenty-one compounds were quantified following this methodology: guaiacol, 4-ethylguaiacol, 4-propylguaiacol, 4-vinylguaiacol, 4-methylguaiacol, *(Z)*- and *(E)*-whiskylactone, eugenol, *(E)*-isoeugenol, 4-ethylphenol, 4-vinylphenol, 2,6-dimethoxyphenol, vanillin, methyl vanillate, ethyl vanillate, acetovanillone, syringaldehyde, furfural, 5-methylfurfural, 5-hydroxymethylfurfural and furfuryl alcohol.

The wine samples were previously spiked with internal standards (2-octanol, 3,4-dimethylphenol at approximately 75 mg $L^{-1}$ in ethanol). A mass of 4.1 g of ammonium sulfate was added to 10 mL flasks, followed by 2.7 mL of wine, 6.3 mL of Milli Q water and 250 μL of dichloromethane. The flasks were stirred for 90 min and finally centrifuged at 2500 r.p.m. for 10 min. The aqueous phase was discarded and 2 μL of organic phase was then analyzed through GC-MS.

#### 2.4.1. Gas chromatography-mass spectrometry conditions

The aromatic compounds were analyzed using a Varian GC-450 gas chromatograph (Walnut Creek, CA, USA), coupled to a Varian Saturn 2200 ion-trap detector. The column used was a DB-WAXEtr (J & W Scientific, Folsom, CA, USA) of 60 m × 0.25 mm i.d. and with 0.25 μm film thickness, preceded by a 3 m × 0.25 mm i.d uncoated precolumn. The carrier gas was helium at a flow rate of 1.5 mL $min^{-1}$. The GC oven temperature program was as follows: 40 °C for 3 min, raised at 2 °C $min^{-1}$ up to 220 °C, then ramped at 20 °C $min^{-1}$ up to 240 °C for 30 min. A 2 mm wide glass liner from Supelco (Bellefonte, PA, USA) was used in the injector. The splitless time was 2.4 min, and a pressure pulse (30 psi) was applied during 2.3 min. Injection, assisted with an autosampler provided by CombiPAL from CTS Analytics (Zwingen, Switzerland), was carried out with the following temperature program: 55 °C for 0.40 min, raised at 200 °C $min^{-1}$ up to 300 °C during all the chromatographic run.

The mass detector operated in electronic impact mode and the acquisition was made in scanning mode in the mass range of 35–220 *m*/*z*. The ion-trap, manifold and auxiliary temperatures were 170 °C, 80 °C and 220 °C, respectively. The analytes and internal standard areas were measured with selective masses (determined for maximum sensitivity and selectivity). The mass to charge ratio (*m*/*z*) for each analyte is shown in Table 1 in the Supplementary material.

### 2.5. Data analysis

#### 2.5.1. Sensory analysis

Quality scores were calculated by measuring the distance between the origin of the scale and the mark indicated by the participants, ranging from 0 to 10. Principal Component Analysis (PCA) was run on individual quality scores (judges in columns and wines in rows) derived from assessments in order to evaluate inter-individual consistency and thus judges' agreement. When no agreement among judges was observed, quality scores were grouped in a wine-by-participant matrix and submitted to hierarchical cluster analysis (HCA) with the Ward criteria in order to identify groups of participants scoring wines similarly. Analyses were performed with SPAD software (5.5 version, CISIA-CESRESTA, Montreuil, France).

Two-way analysis of variance (ANOVA) with replicate and wine as fix factors was calculated on quality scores in order to evaluate panel repeatability.

Two-way analysis of variance (ANOVA) with judges as random factor and wine as fix factor was calculated on quality scores. When significant effect of wine was observed, pairwise comparisons were carried out using a SNK (Student-Newman-Keuls) ($p < 0.05$). This data treatment was done with SPSS 19.0 software (SPSS Inc., Chicago, IL, USA).

#### 2.5.2. Chemical data

For all the chemical variables, three-way ANOVA considering all main effects and interactions (variety, aging time and toasting level as fix factors) was calculated on concentration data. For significant effects, post-hoc Student-Newman-Keuls ($p < 0.05$) pairwise comparison post-hoc test were calculated using SPSS software. One-way ANOVA (aging time or toasting level) was also carried out only for those compounds or aroma families for which significant interactions were found between factors.

#### 2.5.3. Relationships between chemical variables and aroma quality

Principal component analysis (PCA) was calculated with chemical parameters as active variables and quality scores as illustrative variable. This analysis was carried out with SPAD 5.5. software. Only those compounds with an odor activity value (OAV) above 0.2 were taken into account for this analysis.

Odor activity values were calculated by dividing the individual concentration by the corresponding odor threshold in wine (Tables 2 and 3).

This analysis was also carried out for the whole set of judges (data not shown) but as the criteria used for the evaluation were heterogeneous we could not consider the relationships found meaningful.

## 3. Results and discussion

The results (average and standard deviation, $n = 3$) for the analyses carried out for the wines aged in 24 different barrels at 3 sampling times are presented in Tables 2 and 3 for Chardonnay and Sauvignon blanc, respectively.

### 3.1. Wood-related compounds

The high variability found among replicates (Tables 2 and 3) reflects the differences between equivalent barrels, regarding toasting level and wood type, as well as differences between extraction and wine maturity. This fact has also been remarked in other works (Fernández de Simón et al., 2003; Prida & Chatonnet, 2010).

Twenty-one compounds were quantified and grouped according to aroma similitude: the vanillins comprised vanillin, acetovanillone, methyl and ethyl vanillate and syringaldehyde; the guaiacols included guaiacol, 4-propylguaiacol and 4-methylguaiacol, and finally the furfurals were made up of furfural, 5-methylfurfural, 5-hydroxymethylfurfural and furfuryl alcohol. The syringaldehyde, furfuryl alcohol, furfural and 5-hydroxymethylfurfural levels found in both varieties were very high, as Tables 2 and Table 3 show. These concentrations were much higher than the levels found in other barrel-aged wines (Jarauta, 2004; Jarauta et al., 2005). The real reason for these huge amounts of the four compounds cited above is not known. However, one hypothesis may be that either the kind of wood or barrel or toasting level used in this study are responsible for these unexpected levels. Furfuryl alcohol was above its odor threshold (OT) even at the end of alcoholic fermentation (before aging), and reached its maximum level at 12 months of aging at as much as 10 times its OT for Chardonnay wines or 24 times for Sauvignon blanc wines. *(Z)*-whiskylactone was present at 5 times its OT for both varieties at 12 months of aging, while *(E)*-whiskylactone remained below its OT. Wines with a medium toasting level had the lowest concentrations of this compound, which has also been reported by other authors (Bozalongo et al., 2007; Díaz-Maroto et al., 2008; Guchu et al., 2006). In both cases, ethylphenols were below their OT, a fact that exemplifies the absence of defects of these wine samples (Chatonnet, Dubourdie, Boidron, & Pons, 1992).

Please cite this article as: Herrero, P., et al., Study of Chardonnay and Sauvignon blanc wines from D.O.Ca Rioja (Spain) aged in different French oak wood barrels: Chemical and ar..., *Food Research International* (2016), http://dx.doi.org/10.1016/j.foodres.2016.08.002

**Table 2**
Average concentration (μg L$^{-1}$) for Chardonnay wine samples (in brackets standard deviation, for 3 samples) and individual odor threshold.

| Furfurals | O.T.* | TL1 | | | TL2 | | | TL3 | | | TM1 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | FFA | 5M | 12M | FFA | 5M | 12M | FFA | 5M | 12M | FFA | 5M | 12M |
| Furfural | 14,100 | 501 (76) | 4567 (3161) | 6444 (1619) | 340 (60) | 1446 (1063) | 1966 (561) | 693 (302) | 1966 (989) | 3674 (646) | 779 (92) | 9015 (5392) | 8995 (2742) |
| 5-Methylfurfural | 20,000 | 14 (2.6) | 287 (180) | 353 (91) | 4.8 (1.3) | 65 (26) | 105 (14) | 30 (26) | 191 (84) | 192 (55) | 25 (6.6) | 1011 (764) | 885 (385) |
| 5-Hydroxymethylfurfural | 100,000 | 231 (19) | 4285 (1955) | 9792 (987) | 58 (100) | 1561 (847) | 2039 (474) | 339 (164) | 4162 (2030) | 3157 (1097) | 175 (41) | 5038 (4883) | 6973 (2462) |
| Furfuryl alcohol | 2000 | 3372 (535) | 3029 (530) | 25,012 (532) | 2101 (440) | 2563 (1009) | 3287 (724) | 5002 (2333) | 3101 (495) | 8133 (1414) | 5927 (281) | 4195 (825) | 35,231 (553) |
| Whiskylactone | | | | | | | | | | | | | |
| (E)-Whiskylactone | 790 | 29 (2.3) | 87 (10) | 116 (6.3) | 31 (2.4) | 98 (48) | 160 (25) | 41 (21) | 114 (62) | 78 (41) | 31 (1.1) | 101 (14) | 108 (7.8) |
| (Z)-Whiskylactone | 67 | 66 (13) | 209 (7.2) | 261 (10) | 71 (17) | 238 (60) | 281 (38) | 50 (11) | 187 (17) | 319 (14) | 44 (6.2) | 194 (24) | 187 (15) |
| Ehylphenols | | | | | | | | | | | | | |
| 4-Ethylphenol | 35 | 0.62 (0.47) | 0.74 (0.19) | 0.6 (0.33) | 0.64 (0.21) | 1.2 (1.2) | 0.4 (0.73) | 0.56 (0.27) | 0.70 (0.28) | 0.30 (0.27) | 0.62 (0.40) | 0.71 (0.36) | 0.36 (0.38) |
| 4-Ethylguaiacol | 33 | 0.73 (0.20) | 1.2 (0.12) | 2.6 (0.16) | 0.71 (0.08) | 1.2 (0.42) | 1.6 (0.25) | 0.61 (0.11) | 1.2 (0.29) | 1.6 (0.25) | 1.3 (0.12) | 2.1 (0.15) | 2.7 (0.14) |
| Eugenols | | | | | | | | | | | | | |
| Eugenol | 6 | 6.3 (0.14) | 17 (0.97) | 20 (0.56) | 5.9 (0.47) | 16 (4.2) | 20 (2.3) | 5.5 (0.24) | 15 (1.8) | 18 (1.0) | 5.5 (0.21) | 17 (4) | 19 (2.1) |
| (E)-Isoeugenol | 6 | <0.30 (−) | 4.9 (4.3) | 4.8 (2.1) | <0.30 (−) | 5.4 (4.1) | 2.6 (2.0) | <0.30 (−) | 3.9 (2.8) | <0.30 (−) | <0.30 (−) | 7.4 (2.8) | 5.1 (1.4) |
| Vinylphenols | | | | | | | | | | | | | |
| 4-Vinylphenol | 180 | 672 (37) | 288 (52) | 148 (44) | 714 (17) | 275 (89) | 141 (53) | 678 (63) | 285 (48) | 151 (55) | 713 (104) | 293 (46) | 111 (75) |
| 4-Vinylguaiacol | 40 | 495 (47) | 306 (46) | 229 (47) | 573 (99) | 310 (68) | 257 (84) | 499 (33) | 295 (44) | 236 (38) | 623 (74) | 340 (35) | 294 (55) |
| Guaiacols | | | | | | | | | | | | | |
| Guaiacol | 9.5 | 2.7 (0.33) | 6.8 (1.3) | 14 (0.8) | 2.2 (0.40) | 4.2 (2.2) | 4.6 (1.3) | 2.6 (0.74) | 5.9 (1.8) | 8.4 (1.3) | 4.6 (0.27) | 12 (2.9) | 17 (1.6) |
| 4-Propylguaiacol | 10 | <0.02 (−) | 0.15 (0.13) | <0.02 (−) | <0.02 (−) | 0.23 (0.07) | 0.16 (0.03) | <0.02 (−) | 0.14 (0.12) | 0.15 (0.06) | 0.05 (0.09) | 0.34 (0.06) | 0.37 (0.08) |
| 4-Methylguaiacol | 20 | 3.1 (1.1) | 7.1 (2.9) | 10 (2.0) | 2.8 (0.58) | 5.5 (1.9) | 6.5 (1.2) | 3.2 (0.84) | 6.0 (1.5) | 6.3 (1.1) | 9.3 (0.82) | 15 (3.5) | 21 (2.2) |
| Vanillins | | | | | | | | | | | | | |
| Vanillin | 995 | 9.6 (0.78) | 166 (39) | 498 (20) | 8 (2.6) | 109 (46) | 187 (25) | 11 (2.4) | 145 (56) | 214 (29) | 13 (2.9) | 307 (246) | 611 (124) |
| Methyl vanillate | 990 | 20 (2.8) | 13 (4.6) | 12 (3.7) | 22 (2.2) | 13 (6.4) | 15 (4.3) | 21 (3.3) | 13 (4.7) | 13 (4) | 23 (3.8) | 15 (5.7) | 15 (4.8) |
| Ethyl vanillate | 3000 | 5.8 (0.84) | 7.7 (2.8) | 8.2 (1.8) | 5.7 (0.14) | 6.9 (3.6) | 10 (1.9) | 5.5 (0.89) | 6.6 (1.4) | 8.5 (1.1) | 6.0 (0.88) | 6.4 (1.4) | 8.4 (1.1) |
| Acetovanillone | 1000 | 22 (3) | 23 (5.3) | 33 (4.2) | 20 (1.9) | 19 (7.7) | 24 (4.8) | 22 (2.8) | 21 (7.2) | 25 (5) | 30 (3.3) | 34 (11) | 46 (7.3) |
| Syringaldehyde | 50,000 | 32 (0.94) | 990 (340) | 2527 (170) | 12 (3.2) | 391 (157) | 791 (80) | 35 (14) | 874 (494) | 1146 (254) | 48 (5.8) | 1593 (1298) | 3177 (652) |
| Others | | | | | | | | | | | | | |
| 2,6-Dimethoxyphenol | 570 | 3.1 (2.7) | 12 (5.2) | 20 (3.9) | 2.1 (1.9) | 10 (3.5) | 11 (2.7) | 2.1 (1.9) | 12 (4.3) | 18 (3.1) | 7.7 (6.9) | 36 (2) | 50 (4.5) |

TL1: light toasting type 1, TL2: light toasting type 2, TL3: light toasting type 3, TM1: medium toasting type 1, FFA: end of alcoholic fermentation, 5 M: 5 months of barrel aging, 12 M: 12 months of barrel aging O.T.: odor threshold.

* Odor threshold values were reported by San Juan, Cacho, Ferreira, and Escudero (2012).

Vanillins were also below their OT. Eugenol was present above its OT for all the samples with at least 5 months of aging, with a maximum of 3.3 OAV (being OAV the ratio between the concentration and the OT) for Chardonnay samples and 6.3 for Sauvignon blanc. In both cases, the concentrations of vinylphenols (4-vinylphenol and 4-vinylguaiacol) decreased their levels over time. Guaiacols, except for 4-propylguaiacol, were above their OT for those samples aged for 12 months in medium toasting level barrels.

Table 4 shows the results obtained from the three-way ANOVA (variety, toasting level and time), especially remarkable being the 4-ethylphenol for which no significant differences were found for any of the studied factors. Just seven compounds showed significant effects for variety. On the one hand, Sauvignon blanc wines had higher concentrations of furfuryl alcohol, eugenol, guaiacol, acetovanillone and syringaldehyde. On the other hand, Chardonnay wines exhibited higher concentrations of 4-vinylphenol and methyl vanillate.

Significant differences among toasting levels were found for 13 out of the 21 analyzed compounds. As can be seen in Table 4, the compounds with the highest significant differences were *(Z)*-whiskylactone, 2,6-dimethoxyphenol and those belonging to the furfural, guaiacol and vanillin families. In all cases, except for *(Z)*-whiskylactone, the maximum was found for samples aged in barrels with a medium toasting level (TM1), as can be seen in Table 5. The effect of toasting level was further calculated on the OAVs of guaiacols (sum of OAVs of individual compounds belonging to this family), 2,6-dimethoxyphenol, vanillins (sum of OAVs of individual compounds), *(Z)*-whiskylactone, and furfurals (sum of OAVs of individual compounds). OAVs were estimated by dividing the concentration level of each compound by its corresponding odor threshold, as discussed below.

With the exception of 2,6-dimethoxyphenol, the OAVs were almost all above 1, which may reflect their sensory importance on the wines studied. Medium toasting level samples were significantly different to all the light toasting level samples for guaiacols and 2,6-dimethoxyphenol. All the light toasting samples can be considered to be similar. The same results for furfurals and guaiacols have been previously reported by other authors. Furfural is a product derived from the degradation of hemicellulose, while 5-methylfurfural and 5-hydroxymethylfurfural come from the degradation of cellulose. Although cellulose is present at higher concentrations than hemicellulose, its crystalline structure provides greater resistance to degradation, which could explain the differences between these compounds

**Table 3**
Average concentration (μg $L^{-1}$) for Sauvignon blanc wine samples (in brackets, standard deviation for 3 samples) and individual odor threshold.

| | O.T.* | TL1 | | | TL2 | | | TL3 | | | TM1 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | FFA | 5M | 12M | FFA | 5M | 12M | FFA | 5M | 12M | FFA | 5M | 12M |
| Furfurals | | | | | | | | | | | | | |
| Furfural | 14,100 | 184 (24) | 4230 (33) | 3370 (29) | 215 (143) | 2147 (1643) | 891 (893) | 224 (121) | 5209 (4634) | 10,588 (2378) | 230 (127) | 12,534 (1317) | 13,837 (722) |
| 5-Methylfurfural | 20,000 | 8.3 (1.4) | 273 (3.6) | 226 (2.5) | 9.4 (9.2) | 144 (134) | 39 (72) | 15 (6.8) | 489 (508) | 858 (258) | 7.8 (3.3) | 1409 (432) | 1111 (218) |
| 5-Hydroxymethylfurfural | 100,000 | 179 (4.7) | 5059 (1160) | 4401 (583) | 181 (34) | 3457 (2376) | 1444 (1205) | 220 (22) | 5359 (3324) | 13,386 (1673) | 222 (17) | 8613 (695) | 13,149 (356) |
| Furfuryl alcohol | 2000 | 3892 (794) | 7705 (2666) | 12,536 (1730) | 5491 (3722) | 6615 (1001) | 7791 (2361) | 7502 (1528) | 5911 (668) | 36,357 (1098) | 4467 (2409) | 8914 (3273) | 48,623 (2841) |
| Whiskylactone | | | | | | | | | | | | | |
| *(E)*-Whiskylactone | 790 | 25 (8.8) | 79 (14) | 121 (12) | 29 (4.9) | 99 (8.5) | 180 (6.7) | 39 (17) | 98 (22) | 148 (20) | 33 (5.5) | 128 (22) | 162 (14) |
| *(Z)*-Whiskylactone | 67 | 45 (3.2) | 192 (23) | 228 (13) | 50 (17) | 235 (35) | 353 (26) | 62 (18) | 221 (4.5) | 332 (11) | 50 (15) | 220 (16) | 276 (15) |
| Ehylphenols | | | | | | | | | | | | | |
| 4-Ethylphenol | 35 | 0.24 (0.21) | 0.89 (0.37) | 0.38 (0.29) | 0.26 (0.23) | 0.69 (0.29) | 0.46 (0.26) | 0.28 (0.25) | <0.02 (−) | 0.47 (0.12) | 0.32 (0.30) | 0.22 (0.19) | 0.47 (0.24) |
| 4-Ethylguaiacol | 33 | 0.62 (0.13) | 1.5 (0.50) | 1.3 (0.31) | 0.85 (0.23) | 1.4 (0.08) | 1.3 (0.16) | 0.96 (0.30) | 1.3 (0.51) | 2.3 (0.40) | 0.85 (0.19) | 2.2 (0.53) | 2.8 (0.36) |
| Eugenols | | | | | | | | | | | | | |
| Eugenol | 6 | 6.8 (1.2) | 17 (1.6) | 25 (1.4) | 7.3 (1.2) | 19 (1.0) | 30 (1.1) | 9.3 (0.96) | 22 (5.1) | 38 (3.0) | 7.3 (1.3) | 22 (2.6) | 31 (2.0) |
| *(E)*-Isoeugenol | 6 | <0.30 (−) | 4.2 (3.0) | 4.7 (1.5) | <0.30 (−) | 6.9 (6.8) | 7.9 (3.4) | <0.30 (−) | 2.2 (3.8) | 8.5 (1.9) | <0.30 (−) | 7.6 (9.5) | 6.4 (4.8) |
| Vinylphenols | | | | | | | | | | | | | |
| 4-Vinylphenol | 180 | 349 (34) | 209 (26) | 102 (30) | 357 (9.5) | 215 (1.5) | 107 (5.5) | 410 (26) | 214 (46) | 103 (36) | 368 (47) | 203 (18) | 93 (33) |
| 4-Vinylguaiacol | 40 | 538 (86) | 391 (13) | 296 (49) | 498 (71) | 386 (12) | 249 (42) | 605 (143) | 474 (178) | 231 (161) | 500 (50) | 417 (163) | 219 (107) |
| Guaiacols | | | | | | | | | | | | | |
| Guaiacol | 9.5 | 2.6 (0.63) | 6.7 (1.5) | 8.3 (1.1) | 3.3 (1.5) | 8 (1.9) | 9.3 (1.7) | 4.5 (2.7) | 8.7 (4.9) | 20 (3.8) | 3.6 (1.5) | 15 (2.9) | 27 (2.2) |
| 4-Propylguaiacol | 10 | <0.02 (−) | 0.08 (0.12) | <0.02 (−) | <0.02 (−) | 0.03 (0.05) | 0.23 (0.03) | 0.03 (0.05) | <0.02 (−) | 0.36 (0.03) | <0.02 (−) | 0.12 (0.21) | 0.40 (0.10) |
| 4-Methylguaiacol | 20 | 3.3 (0.05) | 7.0 (0.37) | 6.0 (0.21) | 4.0 (2.7) | 5.6 (0.92) | 5.8 (1.8) | 5.2 (1.9) | 8.1 (2.4) | 13 (2.1) | 3.4 (2.1) | 16 (2.3) | 17 (2.2) |
| Vanillins | | | | | | | | | | | | | |
| Vanillin | 995 | 11 (2.6) | 164 (26) | 228 (14) | 9.7 (1.6) | 140 (23) | 173 (12) | 9.3 (0.95) | 270 (224) | 611 (112) | 11 (0.72) | 440 (163) | 678 (82) |
| Methyl vanillate | 990 | 11 (0.13) | 7.7 (1.3) | 7.9 (0.73) | 11 (1.8) | 7.8 (2.3) | 7.3 (2.1) | 13 (2.5) | 9.5 (1.7) | 7.7 (2.1) | 12 (1.9) | 9.8 (3.1) | 8.2 (2.5) |
| Ethyl vanillate | 3000 | 5.1 (0.58) | 6.8 (2.0) | 10 (1.3) | 5.1 (0.31) | 7.8 (2.7) | 11 (1.5) | 5.1 (0.39) | 8.4 (1.2) | 11 (0.81) | 5.3 (0.95) | 8 (1.3) | 12 (1.1) |
| Acetovanillone | 1000 | 26 (0.48) | 26 (0.85) | 31 (0.66) | 28 (5.0) | 26 (2.8) | 28 (3.9) | 32 (1.0) | 32 (9.8) | 42 (5.4) | 29 (5.6) | 45 (8.8) | 47 (7.2) |
| Syringaldehyde | 50,000 | 35 (9.1) | 954 (441) | 1691 (225) | 36 (29) | 722 (76) | 850 (52) | 43 (20) | 879 (671) | 4200 (345) | 38 (28) | 3198 (615) | 6467 (321) |
| Others | | | | | | | | | | | | | |
| 2,6-Dimethoxyphenol | 570 | 4.5 (2.8) | 11 (0.70) | 14 (1.8) | 6.3 (6.4) | 9.6 (3.0) | 13 (4.7) | 3.4 (3.1) | 11 (9.9) | 27 (6.5) | 5.4 (2.1) | 33 (9.8) | 29 (6.0) |

TL1: light toasting type 1, TL2: light toasting type 2, TL3: light toasting type 3, TM1: medium toasting type 1, FFA: end of alcoholic fermentation, 5M: 5 months of barrel aging, 12M: 12 months of barrel aging O.T.: odor threshold.

* odor threshold values were reported by San Juan et al. (2012)

(Fernández de Simón, Esteruelas, Muñoz, Cadahía, & Sanz, 2009). Guaiacols come from the degradation of lignin, which helps explain why wines aged in medium toasting level barrels have higher concentrations of this family of compounds. As previously reported in other works, higher toasting levels correspond to higher concentrations of these compounds which come from degradation due to exposure to heat and fire (Gómez García-Carpintero et al., 2012; Guchu et al., 2006; Jackson, 1994; Vichi et al., 2007). It may be interesting to control and to increase the concentration of furanic compounds such as furfurylthiol and 5-methyl-2-furfurylthiol, both with coffee nuances and extremely low OT, come from the conversion of furfural and 5-methylfurfural respectively in a medium such as wine (Blanchard, Tominaga, & Dubourdieu, 2001).

Significant differences were found for 19 out of the 21 compounds with regard to the aging time (Table 4). All the quantified compounds (vanillins, furfurals, guaiacols, eugenols and lactones) increased their concentration over time. Only vinylphenols and ethyl vanillate, with maximum levels found at the end of alcoholic fermentation, decreased over time. Vinylphenols are derived from hydroxycinnamic acids present in grape must which together with the presence of *Bretanomyces*/*Dekkera* yeast, promote their transformation to ethylphenols during the aging period, thus decreasing their concentration levels (Chatonnet, Dubourdieu, & Boidron, 1995; Chatonnet et al., 1992; Dubois, 1983). Methyl vanillate is derived from glycosidic precursors through acid hydrolysis. It decreases over time because it can be easily degraded during aging (Jarauta et al., 2005). The maximum concentrations of 5-Methylfurfural and *(E)*-isoeugenol were found at 5 months of aging.

No significant effect for the variety × toasting level interaction was found, which means that the toasting level exerted an equal effect on the Chardonnay and Sauvignon blanc wines. Differently, significant effects were found for variety × time and toasting × time interactions

**Table 4**
Three-way ANOVA (variety, toasting and time) with the interactions for all the samples.

| | Variety | Toasting | Time | Variety × Toasting | Variety × Time | Toasting × Time |
|---|---|---|---|---|---|---|
| FURFURALS | | | | | | |
| Furfural | ns | *** | *** | ns | ns | ** |
| 5-Methylfurfural | ns | *** | *** | ns | ns | ** |
| 5-Hydroxymethylfurfural | ns | ** | *** | ns | ns | ns |
| Furfuryl alcohol | ** | *** | *** | ns | ns | *** |
| Whiskylactone | | | | | | |
| (E)-Whiskylactone | ns | ns | *** | ns | ns | ns |
| (Z)-Whiskylactone | ns | ** | *** | ns | ns | ns |
| Ethylphenols | | | | | | |
| 4-Ethylphenol | ns | ns | ns | ns | ns | ns |
| 4-Ethylguaiacol | ns | *** | *** | ns | ns | ns |
| Eugenols | | | | | | |
| Eugenol | *** | ns | *** | ns | *** | ns |
| (E)-Isoeugenol | ns | ns | *** | ns | ns | ns |
| Vinylphenols | | | | | | |
| 4-Vinylphenol | *** | ns | *** | ns | *** | ns |
| 4-Vinylguaiacol | ns | ns | *** | ns | ns | ns |
| Guaiacols | | | | | | |
| Guaiacol | ** | *** | *** | ns | ns | *** |
| 4-Propylguaiacol | ns | ** | *** | ns | * | ns |
| 4-Methylguaiacol | ns | *** | *** | ns | ns | * |
| Vanillins | | | | | | |
| Vanillin | ns | *** | *** | ns | ns | ns |
| Methyl vanillate | *** | ns | *** | ns | ns | ns |
| Ethyl vanillate | ns | ns | *** | ns | ns | ns |
| Acetovanillone | * | *** | ns | ns | ns | ns |
| Syringaldehyde | * | *** | *** | ns | ns | *** |
| Others | | | | | | |
| 2,6-Dimethoxyphenol | ns | *** | *** | ns | ns | *** |

ns: not significative.
*** $p < 0.001$.
** $p < 0.01$.
* $p < 0.05$.

for three (eugenol, 4-vinylphenol and 4-propylguaiacol) and seven (furfural, 5-methylfurfural, furfuryl alcohol, guaiacol, 4-methylguaiacol. Syringaldehyde and 2,6-dimethoxyphenol) compounds, respectively (Table 6). Concerning compounds showing toasting × time interactions, they did not show significant differences with aging time for barrels with light toasting TL2, except for the case of syringaldehyde. Differently, for the rest of toasting levels, significant changes in their concentration levels were observed during aging. Thus, concentration levels at the end of alcoholic fermentation were the most different for any of the toasting levels. Light toasting level type 1 (TL1) was similar to medium toasting type 1 (TM1) for those compounds.

Regarding the interaction variety × aging time, three compounds showed significant interaction, as can be seen in Table 6. In all cases eugenol and 4-propylguaiacol increased after 12 months, while 4-vinylphenol decreased (Table 2). Interestingly, Sauvignon blanc wines presented higher concentrations of eugenol while the Chardonnay wines had higher concentrations of 4-vinylphenol and 4-propylguaiacol.

**Table 5**
Average odor activity values for individual compounds or family in wines aged in barrels with different toasting. One-way ANOVA (toasting).

| | TL1 | TL2 | TL3 | TM1 |
|---|---|---|---|---|
| Guaiacols | 0.89[a] | 0.78[a] | 1.1[a] | 1.8[b] |
| 2,6-Dimethoxyphenol | 0.016[a] | 0.014[a] | 0.017[a] | 0.041[b] |
| Vanillins | 0.16 | 0.11 | 0.20 | 0.33 |
| (Z)-Whiskylactone | 2.1 | 2.6 | 2.4 | 2.1 |
| Furfurals | 3.4 | 2.3 | 4.1 | 6.0 |

TL1: light toasting type 1. TL2: light toasting type 2. TL3: light toasting type 3. TM1: medium toasting type 1. Different letters mean different groups after Student-Newman-Keuls ($p < 0.05$) post hoc test.

### *3.2. Sensory analysis*

In both sets of samples (Chardonnay and Sauvignon blanc), the duplicate sample was used to test panel repeatability through a two-way ANOVA (replicate and wine as fix factors). No significant effects of replicates and replicate × wine interactions were observed. Thus, quality scores of duplicate samples were averaged.

#### *3.2.1. Chardonnay*

Judges' loadings were spread out over the PCA, suggesting disagreement among judges. Further cluster analysis calculated on individual scores allowed the identification of two groups of judges (Fig. 1) using similar quality criteria for Chardonnay wines aged for 12-months in French oak barrels with different toasting levels. The most numerous group was cluster 1, which was composed of nineteen judges (76% of the panel) sharing the same quality criteria. Cluster 2 was formed by exclusively six judges (24% of the panel), which differed in quality scores from cluster 1. These results show that there is a heterogeneous quality concept among this panel of experts. This result is in apparent contradiction with other works that have shown that experts from similar production regions have similar quality concepts. This statement is based in the fact that when tasting a wine, experts compare the sensory properties of wines with idiotypic recollections generated during previous experience to perform their quality judgement. This would induce them to build shared memory representations of wine quality through exposure, especially for experts belonging to the same wine region (Ballester, Patris, Symoneaux, & Valentin, 2008; Langlois, Ballester, Campo, Dacremont, & Peyron, 2010; Sáenz-Navajas et al., 2016), even if groups of experts from different regions (Rioja in Spain vs Côtes du Rhône in France) have also been reported to present such commonalities (Sáenz-Navajas, Ballester, Pêcher, Peyron, & Valentin, 2013). Interestingly, in the present work the varieties studied have recently been

**Table 6**
One-way ANOVA (time) for those compounds for which interactions were found after three-way ANOVA (toasting × time, variety × time). Average concentration values (μg $L^{-1}$).

| | TL1 | | | TL2 | | | TL3 | | | TM1 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | FFA | 5M | 12M | FFA | 5M | 12M | FFA | 5M | 12M | FFA | 5M | 12M |
| Furfural | 343[a] | 4432[b] | 4907[b] | 278 | 1796 | 1429 | 458[a] | 3587[ab] | 7131[b] | 504[a] | 10775[b] | 11416[b] |
| 5-Mthylfurfural | 11[a] | 281[b] | 290[b] | 7.1 | 105 | 72 | 23 | 340 | 525 | 17[a] | 1210[b] | 998[b] |
| Furfuryl alcohol | 3632[a] | 4899[a] | 18774[b] | 3796 | 4589 | 5539 | 6252[a] | 4506[a] | 22245[b] | 5197[a] | 6555[a] | 41927[b] |
| Guaiacol | 2.7[a] | 6.8[b] | 11[c] | 2.8 | 6.1 | 6.9 | 3.5[a] | 7.3[a] | 14[b] | 3.8[a] | 14[b] | 22[c] |
| 4-Methylguaiacol | 3.2[a] | 7.0[b] | 8.1[b] | 3.4 | 5.6 | 6.1 | 4.2[a] | 7.0[ab] | 9.8[b] | 6.3[a] | 15[b] | 19[b] |
| Syringaldehyde | 34[a] | 975[b] | 2109[c] | 24[a] | 557[b] | 820[c] | 39[a] | 876[a] | 2673[b] | 43[a] | 2396[b] | 4822[c] |
| 2,6-Dimethoxyphenol | 3.8[a] | 12[b] | 17[b] | 4.2 | 9.9 | 12 | 2.8[a] | 12[b] | 22[c] | 6.6[a] | 35[b] | 40[b] |
| | CH | | | SB | | | | | | | | |
| | FFA | 5M | 12M | FFA | 5M | 12M | | | | | | |
| Eugenol | 5.8[a] | 16[b] | 19[c] | 7.7[a] | 20[b] | 31[c] | | | | | | |
| 4-Vinylphenol | 694[c] | 285[b] | 138[a] | 371[c] | 210[b] | 101[a] | | | | | | |
| 4-Propylguaiacol | 0.01[a] | 0.21[b] | 0.17[b] | 0.01[a] | 0.06[a] | 0.25[b] | | | | | | |

TL1: light toasting type 1. TL2: light toasting type 2. TL3: light toasting type 3. TM1: medium toasting type 1. FFA: end of alcoholic fermentation. 5 M: 5 months of barrel aging. 12 M: 12 months of barrel aging Different letters mean different groups after Student-Newman-Keuls ($p < 0.05$) post hoc test.

authorized in the D.O.Ca Rioja region and thus the panel of experts was not familiar with them. This fact could explain why there is not still a homogeneous aroma quality concept for aged Chardonnay white wines in the region, even if there is a relatively big group of experts (cluster 1) sharing quality concept.

Fig. 2a shows that the sample with the highest quality score for cluster 1 (TM1), 6.55 points, was the sample with the lowest score for cluster 2, with just 2.22 points. Moreover, the sample with the highest score for cluster 2 (TL3), 7.82 points, was the sample with the lowest score for cluster 1, just 2.5. No significant differences were found for samples TL1, TL2 and TM1 in cluster 1 while in cluster 2 no differences were found for samples TL1 and TM1, which were the lowest rated among all the samples, or between TL2 and TL3, which were the highest rated among all the samples. According to these results TL2 was the most highly valued sample overall for both clusters of judges. The highest valued samples for cluster 1 were described as intense, balanced and complex and the lowest rated samples as flavorless, less expressive and less genuine.

Fig. 3a shows the PCA plot calculated with chemical variables as active variables and quality scores as illustrative variable. The first principal component (PC1), which explains 67.58% of the original variance, is positively correlated to aroma quality scores and to most of the analyzed compounds, while it is negatively correlated to *(Z)*-whiskylactone and 4-vinylphenol (Fig. 3a). This is in accordance with the fact that the wine with the highest quality score for cluster 1 (TM1) had the highest concentration of most of the quantified compounds (furfural, furfuryl alcohol, *(E)*-isoeugenol, 4-vinylguaiacol, guaiacol, 4-methylguaiacol

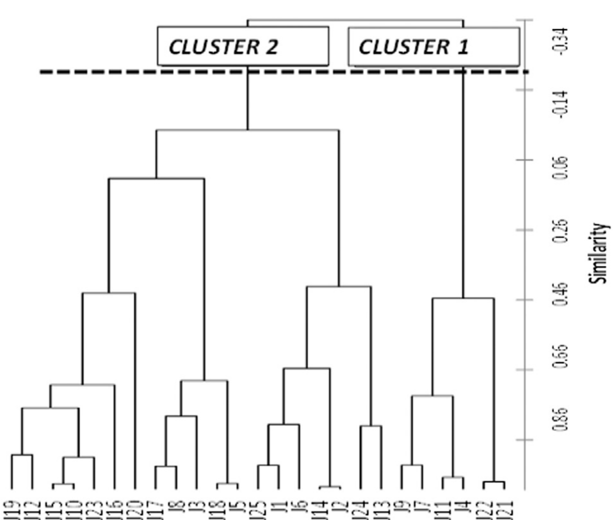


**Fig. 1.** Dendogram obtained through cluster analysis for the scores given by the judges in the orthonasal aroma quality evaluation of Chardonnay wines with 12 months of aging.

and vanillin), while the lowest concentration of *(Z)*-whiskylactone and 4-vinylphenol (Table 2). In contrast, the sample with the lowest quality score (TL3) had the highest concentration of *(Z)*-whiskylactone and 4-vinylphenol. As shown in Fig. 3a, aroma quality scores presented the highest positive correlations with 4-vinylguaiacol and *(E)*-isoeugenol and negative with *(Z)*-whiskylactone and 4-vinylphenol. Thus, these compounds are suggested to be main drivers of aroma quality for Chardonnay wines aged in French oak barrels for 12 months. Interestingly, medium toasting level increases whiskylactone degradation, which may explain why the sample with medium toasting level (TM1) obtained the highest quality score for most experts (cluster 1). This result would also suggest that French oak may be more appropriate according to experts from D.O.Ca. Rioja (Spain) for aging

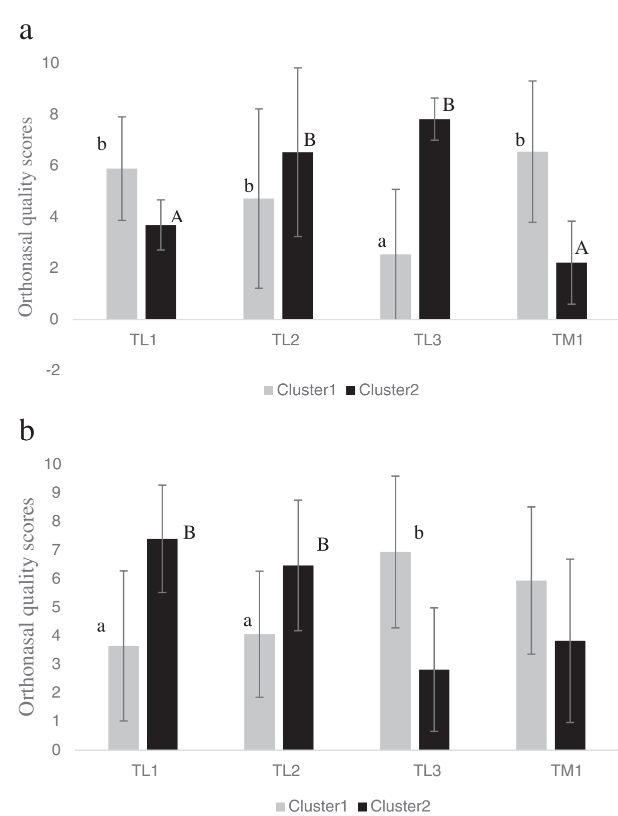


**Fig. 2a.** Orthonasal quality scores for Chardonnay samples. Different letters in same color columns mean significative differences among wines (Student-Newman-Keules test ($p < 0.05$)) b. Orthonasal aroma quality scores for Sauvignon blanc samples. Different letters in same color columns mean significative differences among wines (Student-Newman-Keuls test ($p < 0.05$)).

Please cite this article as: Herrero, P., et al., Study of Chardonnay and Sauvignon blanc wines from D.O.Ca Rioja (Spain) aged in different French oak wood barrels: Chemical and ar..., *Food Research International* (2016), http://dx.doi.org/10.1016/j.foodres.2016.08.002

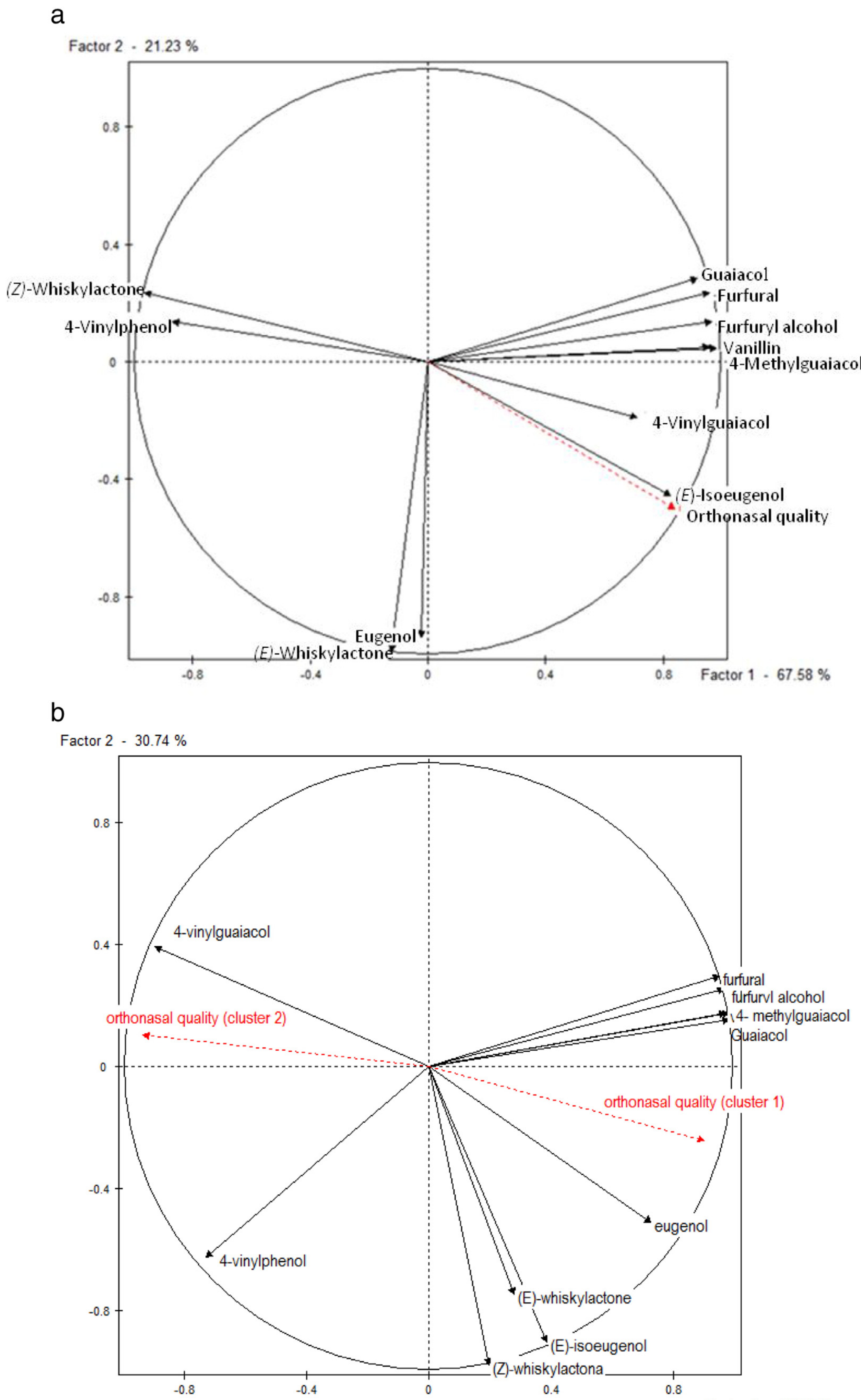


**Fig. 3.** Correlation circle of PCA. The dotted arrow (illustrative variable) shows orthonasal aroma quality for Cluster 1 in Chardonnay samples b. Correlation circle of PCA. The dotted arrow (illustrative variable) shows orthonasal aroma quality for Cluster 1 and Cluster 2 in Sauvignon blanc samples

Please cite this article as: Herrero, P., et al., Study of Chardonnay and Sauvignon blanc wines from D.O.Ca Rioja (Spain) aged in different French oak wood barrels: Chemical and ar..., *Food Research International* (2016), http://dx.doi.org/10.1016/j.foodres.2016.08.002

Chardonnay wine due to its lower whiskylactone content in comparison with American oak.

*3.2.2. Sauvignon blanc*

No consensus among the judges was reached in the evaluation of the orthonasal aroma quality of Sauvignon blanc wines, as observed by the dispersion of judges in the PCA plot (data not shown). As reported above, this lack of agreement among wine experts in aroma quality of Sauvignon blanc wines could be mostly attributed to the fact that this variety has been recently introduced in the region and there is still an absence of a common quality concept. According to cluster analysis (Fig. 4), judges could be classified in two main groups, one made up of 14 judges (56%, cluster 1) and the second one with 11 judges (44%, cluster 2).

Regarding orthonasal aroma quality, sample TL3 followed by TM1 were the most appreciated by cluster 1 (56% of the panelists) with scores of 6.94 and 5.94, respectively. A different scenario was found for cluster 2 (44% of the panelists) whose highest rated samples were TL2 and TL1 with scores of 6.47 and 7.40, respectively (Fig. 2b). The highest rated samples for cluster 1 were described as intense, well-integrated and complex and the samples with low scores as flavorless and lacking a fruity note. In contrast, the best quality samples for cluster 2 were described as fruity and well assembled, and the ones with least quality were reported to have an excess of woody aroma.

Fig. 3b shows the projection of the variables onto the first two principal components of the PCA calculated on chemical variables and considering average aroma quality scores of clusters 1 and 2 as illustrative variables. As can be seen in the plot, the first principal component (PC1), explaining 62.33% of the total variance, is positively correlated to aroma quality scores of cluster 1, while negatively to quality scores of cluster 2. Thus, PC1 can be interpreted as the quality perceived by experts of cluster 1. Chemical compounds projected on the right side of the plot (eugenol, guaiacol, 4-methylguaiacol, vanillin, furfuryl alcohol and furfural) are positively related to aroma quality perceived by experts of cluster 1, while those plotted on the left side (4-vinylguaiacol and 4-vinylphenol) are negatively linked to aroma quality. Just the opposite is observed for experts in cluster 2. The most and least appreciated sample according to cluster 1 and cluster 2, respectively, TL3, has the highest contents of eugenol and *(E)*-isoeugenol (Table 3), while the least appreciated has the lowest concentration of these two compounds as well as whiskylactone and the maximum concentration of 4-vinylguaiacol.

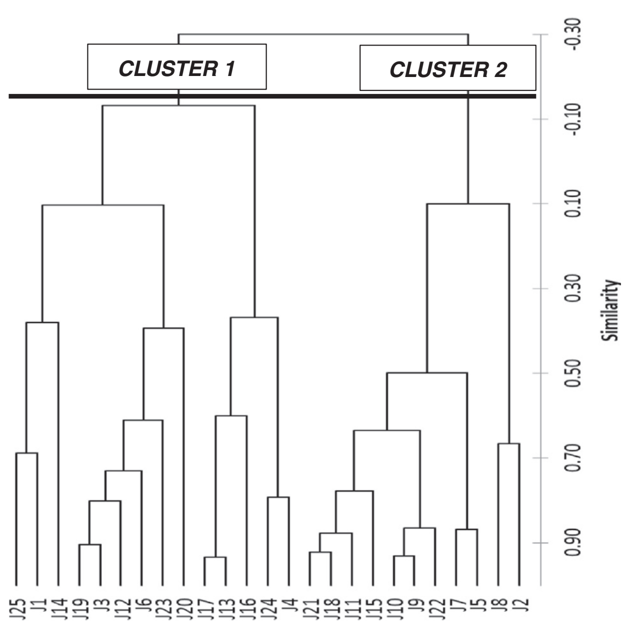


**Fig. 4.** Dendrogram obtained through cluster analysis for the scores given by the judges in the orthonasal aroma quality evaluation of Sauvignon blanc wines with 12 months of aging.

## 4. Conclusions

Sensory and chemical strategies have been employed to study the perceived aroma quality of barrel-aged wines and to explore the correlations between perceived quality and chemical composition.

The analysis of the wood–related compounds revealed that the factor with the greatest effect on the compounds, in 19 cases out of 21, was the time wines aged in the barrels. The concentrations of all the quantified compounds (vanillins, furfurals, guaiacols, eugenols and lactones) increased over time. Only vinylphenols and ethyl vanillate decreased over time. The toasting level affected 13 out of the 21 compounds. The maximum concentrations of furfurals, guaiacols and vanillins were found in medium toasting level barrels. Interactions between the toasting level and time were found as well as between the variety and time.

A heterogeneous aroma quality concept for aged Chardonnay and especially for Sauvignon blanc aged white wines among experts in the DOCa Rioja area was observed. For Sauvignon blanc wines, average quality scores of cluster 1 (56%) were just the contrary of cluster 2 (44%). Aroma quality scores according to the main cluster of experts formed by 76% of experts and cluster 1 for Chardonnay and Sauvignon blanc samples, respectively, were negatively correlated to 4-vinylphenol and positively to *(E)*-isoeugenol whiskylactone was negatively correlated to aroma quality, while 4-vinylphenol positively for aged Chardonnay wines, while just the contrary was observed for Sauvignon blanc wines.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.foodres.2016.08.002.

## Acknowledgements

The authors thank Tonelería Murua, S. A. for funding and Bodegas Tobía, S.L. for participating in the project. M.P.S.N. acknowledges the Spanish Ministry of Economy and Competitiveness (MINECO) for her postdoctoral fellowship (Formación Posdoctoral 2013). LAAE acknowledges the continuous support of Diputación General Aragón (T53) and Fondo Europeo.

## References

Aiken, J. W., & Noble, A. C. (1984). Comparison of the aromas of oak- and glass-aged wines. *American Journal of Enology and Viticulture*, *35*(4), 196–199.

Ballester, J., Patris, B., Symoneaux, R., & Valentin, D. (2008). Conceptual vs. perceptual wine spaces: Does expertise matter? *Food Quality and Preference*, *19*(3), 267–276.

Blanchard, L., Tominaga, T., & Dubourdieu, D. (2001). Formation of furfurylthiol exhibiting a strong coffee aroma during oak barrel fermentation from furfural released by toasted staves. *Journal of Agricultural and Food Chemistry*, *49*(10), 4833–4835.

Boidron, J. N., Chatonnet, P., & Pons, M. (1988). Effects of wood on aroma compounds of wine. *Connaissance de la Vigne et du Vin*, *22*, 275–294.

Bozalongo, R., David Carrillo, J., Fernández Torroba, M. A., & Tena, M. T. (2007). Analysis of French and American oak chips with different toasting degrees by headspace solid-phase microextraction-gas chromatography–mass spectrometry. *Journal of Chromatography A*, *1173*(1–2), 10–17.

Cadahía, E., Muñoz, L., Fernández de Simón, B., & García-Vallejo, M. C. (2001). Changes in low molecular weight phenolic compounds in Spanish, French, and American oak woods during natural seasoning and toasting. *Journal of Agricultural and Food Chemistry*, *49*(4), 1790–1798.

Cadahía, E., Fernández de Simón, B., & Jalocha, J. (2003). Volatile compounds in Spanish, French, and American oak woods after natural seasoning and toasting. *Journal of Agricultural and Food Chemistry*, *51*(20), 5923–5932.

Campbell, J. J., Polnitz, A. P., Sefton, M. A., Herderich, M. J., & Pretorius, I. P. (2006). Factors affecting the influence of oak chips on wine flavour. *Wine Industry Journal*, *21*(4), 38–42.

Cerdán, T. G., Rodríguez Mozaz, S., & Ancín Azpilicueta, C. (2002). Volatile composition of aged wine in used barrels of French oak and of American oak. *Food Research International*, *35*(7), 603–610.

Cerdán, T. G., Goñi, D. T., & Azpilicueta, C. A. (2004). Accumulation of volatile compounds during ageing of two red wines with different composition. *Journal of Food Engineering*, *65*(3), 349–356.

Chatonnet, P. (1998). Volatile and odoriferous compounds in barrel-aged wines: Impact of cooperage techniques and aging conditions. *Chemistry of wine flavor*. *714*. (pp. 180–207). American Chemical Society.

Chatonnet, P., & Dubourdieu, D. (1998). Comparative study of the characteristics of American white oak (*Quercus alba*) and European oak (*Quercus petraea* and *Q. robur*) for production of barrels used in barrel aging of wines. *American Journal of Enology and Viticulture*, *49*(1), 79–85.

Chatonnet, P., Boidron, J. N., & Pons, M. (1989). Effect on heat on oak wood and its chemical composition. Part 2. Variations of certain compounds in relation to toasting intensity. *Connaissance de la Vigne et du Vin*, *23*, 223–250.

Chatonnet, P., Dubourdie, D., Boidron, J. -N., & Pons, M. (1992). The origin of ethylphenols in wines. *Journal of the Science of Food and Agriculture*, *60*(2), 165–178.

Chatonnet, P., Boidron, J. N., Dubourdieu, D., & Pons, M. (1994). Évolution de certains composés volatils du bois de chêne au cours de son séchage. Premiers résultats. *Journal International des Sciences de la Vigne et du Vin*, *28*(4), 359–380.

Chatonnet, P., Dubourdieu, D., & Boidron, J. N. (1995). The influence of Brettanomyces/Dekkera sp. yeasts and lactic acid bacteria on the ethylphenol content of red wines. *American Journal of Enology and Viticulture*, *46*(4), 463–468.

Culleré, L., Fernández de Simón, B., Cadahía, E., Ferreira, V., Hernández-Orte, P., & Cacho, J. (2013). Characterization by gas chromatography–olfactometry of the most odor-active compounds in extracts prepared from acacia, chestnut, cherry, ash and oak woods. *LWT - Food Science and Technology*, *53*(1), 240–248.

De Rosso, M., Panighel, A., Dalla Vedova, A., Stella, L., & Flamini, R. (2009). Changes in chemical composition of a red wine aged in acacia, cherry, chestnut, mulberry, and oak wood barrels. *Journal of Agricultural and Food Chemistry*, *57*(5), 1915–1920.

Díaz-Maroto, M. C., Sánchez-Palomo, E., & Pérez-Coello, M. S. (2004). Fast screening method for volatile compounds of oak wood used for aging wines by headspace SPME-GC–MS (SIM). *Journal of Agricultural and Food Chemistry*, *52*(23), 6857–6861.

Díaz-Maroto, M. C., Guchu, E., Castro-Vázquez, L., de Torres, C., & Pérez-Coello, M. S. (2008). Aroma-active compounds of American, French, Hungarian and Russian oak woods, studied by GC–MS and GC–O. *Flavour and Fragance Journal*, *23*(2), 93–98.

Dubois, P. (1983). Volatile phenols in wine. In R. (Ed.), *Flavour of distilled beverages, origin and developments* (pp. 110–119). Chichester UK: Ellis Horwood.

Faix, O., Meier, D., & Fortmann, I. (1990). Thermal degradation products of wood. *Holz als Roh- und Werkstoff*, *48*(7–8), 281–285.

Fernández de Simón, B., Cadahía, E., & Jalocha, J. (2003). Volatile compounds in a Spanish red wine aged in barrels made of Spanish, French, and American oak wood. *Journal of Agricultural and Food Chemistry*, *51*(26), 7671–7678.

Fernández de Simón, B., Cadahía, E., Hernández, T., & Estrella, I. (2006). Evolution of oak-related volatile compounds in a Spanish red wine during 2 years bottled, after aging in barrels made of Spanish, French and American oak wood. *Analytica Chimica Acta*, *563*(1–2), 198–203.

Fernández de Simón, B., Esteruelas, E., Muñoz, Á. M., Cadahía, E., & Sanz, M. (2009). Volatile compounds in acacia, chestnut, cherry, ash, and oak woods, with a view to their use in cooperage. *Journal of Agricultural and Food Chemistry*, *57*(8), 3217–3227.

Fernández de Simón, B., Muiño, I., & Cadahía, E. (2010). Characterization of volatile constituents in commercial oak wood chips. *Journal of Agricultural and Food Chemistry*, *58*(17), 9587–9596.

Fernández de Simón, B., Martínez, J., Sanz, M., Cadahía, E., Esteruelas, E., & Muñoz, A. M. (2014). Volatile compounds and sensorial characterisation of red wine aged in cherry, chestnut, false acacia, ash and oak wood barrels. *Food Chemistry*, *147*(0), 346–356.

Flamini, R., Vedova, A. D., Cancian, D., Panighel, A., & De Rosso, M. (2007). GC/MS-positive ion chemical ionization and MS/MS study of volatile benzene compounds in five different woods used in barrel making. *Journal of Mass Spectrometry*, *42*(5), 641–646.

Gómez García-Carpintero, E., Gómez Gallego, M. A., Sánchez-Palomo, E., & González Viñas, M. A. (2012). Impact of alternative technique to ageing using oak chips in alcoholic or in malolactic fermentation on volatile and sensory composition of red wines. *Food Chemistry*, *134*(2), 851–863.

Guchu, E., Díaz-Maroto, M. C., Pérez-Coello, M. S., González-Viñas, M. A., & Ibáñez, M. D. C. (2006). Volatile composition and sensory characteristics of Chardonnay wines treated with American and Hungarian oak chips. *Food Chemistry*, *99*(2), 350–359.

Gutiérrez Alfonso, V. L. (2002). Sensory descriptive analysis between white wines fermented with oak chips and in barrels. *Journal of Food Science*, *67*(6), 2415–2419.

Hale, M. D., Mccafferty, K., Larmie, E., Newton, J., & Swan, J. S. (1999). The influence of oak seasoning and toasting parameters on the composition and quality of wine. *American Journal of Enology and Viticulture*, *50*(4), 495–502.

Herjavec, S., Jeromel, A., Da Silva, A., Orlic, S., & Redzepovic, S. (2007). The quality of white wines fermented in Croatian oak barrels. *Food Chemistry*, *100*(1), 124–128.

Ibern-Gómez, M., Andrés-Lacueva, C., Lamuela-Raventós, R. M., Lao-Luque, C., Buxaderas, S., & De la Torre-Boronat, M. C. (2001). Differences in phenolic profile between oak wood and stainless steel fermentation in white wines. *American Journal of Enology and Viticulture*, *52*(2), 159–164.

Jackson, R. S. (1994). Oak and cooperage. In S. L. (Ed.), *Wine science, principles and applications* (pp. 299–311). New York: Academic Press.

Jarauta, I. (2004). *Estudio analítico de fenómenos concurrentes en la generación del aroma durante la crianza del vino en barricas de roble con diferentes grados de uso*. Nuevos métodos de análisis de importantes aromas y caracterización de su papel sensorial: Universidad de Zaragoza.

Jarauta, I., Cacho, J., & Ferreira, V. (2005). Concurrent phenomena contributing to the formation of the aroma of wine during aging in oak wood: An analytical study. *Journal of Agricultural and Food Chemistry*, *53*(10), 4166–4177.

Kozlovic, G., Jeromel, A., Maslov, L., Pollnitz, A., & Orlić, S. (2010). Use of acacia barrique barrels — Influence on the quality of Malvazija from Istria wines. *Food Chemistry*, *120*(3), 698–702.

Langlois, J., Ballester, J., Campo, E., Dacremont, C., & Peyron, D. (2010). Combining olfactory and gustatory clues in the judgement of aging potential of red wine of wine professionals. *American Journal of Enology and Viticulture*, *61*(1), 15–22.

Liberatore, M. T., Pati, S., Nobile, M. A. D., & Notte, E. L. (2010). Aroma quality improvement of Chardonnay white wine by fermentation and ageing in barrique on lees. *Food Research International*, *43*(4), 996–1002.

Pérez-Coello, M. S., Sanz, J., & Cabezudo, M. D. (1999). Determination of volatile compounds in hydroalcoholic extracts of French and American oak wood. *American Journal of Enology and Viticulture*, *50*(2), 162–165.

Prida, A., & Chatonnet, P. (2010). Impact of oak-derived compounds on the olfactory perception of barrel-aged wines. *American Journal of Enology and Viticulture*, *61*(3), 408–413.

Puech, J. -L., Feuillat, F., & Mosedale, J. R. (1999). The tannins of oak heartwood: Structure, properties, and their influence on wine flavor. *American Journal of Enology and Viticulture*, *50*(4), 469–478.

Reazin, G. H. (1981). Chemical mechanisms of whiskey maturation. *American Journal of Enology and Viticulture*, *32*(4), 283–289.

Rodríguez-Bencomo, J. J., Ortega-Heras, M., Pérez-Magariño, S., & González-Huerta, C. (2009). Volatile compounds of red wines macerated with Spanish, American, and French oak chips. *Journal of Agricultural and Food Chemistry*, *57*(14), 6383–6391.

Rodríguez-Nogales, J. M., Fernández-Fernández, E., & Vila-Crespo, J. (2009). Characterisation and classification of Spanish Verdejo young white wines by volatile and sensory analysis with chemometric tools. *Journal of the Science of Food and Agriculture*, *89*(11), 1927–1935.

Sáenz-Navajas, M. P., Ballester, J., Pêcher, C., Peyron, D., & Valentin, D. (2013). Sensory drivers of intrinsic quality of red wines. Effect of culture and level of expertise. *Food Research International*, *54*(2), 1506–1518.

Sáenz-Navajas, M. P., Avizcurri, J. M., Echevarri, J. F., Ferreira, V., Fernández-Zurbano, P., & Valentin, D. (2016). Understanding quality judgements of red wines by experts: Effect of evaluation condition. *Food Quality and Preference*, *48*, 216–227.

San Juan, F., Cacho, J., Ferreira, V., & Escudero, A. (2012). Aroma chemical composition of red wines from different price categories and its relationship to quality. *Journal of Agricultural and Food Chemistry*, *60*, 5045–5056.

Spillman, P. J., Sefton, M. A., & Gawel, R. (2004). The contribution of volatile compounds derived during oak barrel maturation to the aroma of a Chardonnay and Cabernet Sauvignon wine. *Australian Journal of Grape and Wine Research*, *10*(3), 227–235.

Towey, J. P., & Waterhouse, A. L. (1996). The extraction of volatile compounds from French and American oak barrels in Chardonnay during three successive vintages. *American Journal of Enology and Viticulture*, *47*(2), 163–172.

Vichi, S., Santini, C., Natali, N., Riponi, C., López-Tamames, E., & Buxaderas, S. (2007). Volatile and semi-volatile components of oak wood chips analysed by accelerated solvent extraction (ASE) coupled to gas chromatography–mass spectrometry (GC–MS). *Food Chemistry*, *102*(4), 1260–1269.

Waterhouse, A. L., & Towey, J. P. (1994). Oak lactone isomer ratio distinguishes between wine fermented in American and French oak barrels. *Journal of Agricultural and Food Chemistry*, *42*(9), 1971–1974.