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Volatile Compounds in a Spanish Red Wine Aged in Barrels Made of Spanish, French, and American Oak Wood

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A red Rioja wine was aged in barrels made of Spanish oak wood (*Quercus robur*, *Quercus petraea*, *Quercus pyrenaica*, and *Quercus faginea*) during 21 months. The concentrations of some volatile compounds [syringaldehyde, vanillin, eugenol, maltol, guaiacol, 4-ethylphenol, cis and trans isomers of β-methyl-γ-octalactone, 2-furfuraldehyde, 5-methyl-2-furfuraldehyde, 5-(hydroxymethyl)-2-furfuraldehyde, and furfuryl alcohol] were studied in these wines and compared with those of the same wine aged in barrels made from French oak of *Q. robur* (Limousin, France) and *Q. petraea* (Allier, France) and American oak of *Quercus alba* (Missouri). Similar concentrations of these compounds were found in wines aged in Spanish and French oak wood barrels, and significantly different concentrations were found with respect to wines aged in barrels made of American oak wood, indicating a different behavior. Thus, wines with different characteristics were obtained, depending on the kind of wood. Also, the kind of wood had an important influence on sensory characteristics of wine during the aging process. Spanish oak wood from *Q. robur*, *Q. petraea*, and *Q. pyrenaica* can be considered to be suitable for barrel production for quality wines, because a wine aged in barrels made of these Spanish oak woods showed similar and intermediate characteristics to those of the same wine aged in French and American oak woods usually used in cooperage.

KEYWORDS: Wine; aging; volatile compounds; oak wood; *Quercus robur*; *Quercus petraea*; *Quercus pyrenaica*; *Quercus faginea*; *Quercus alba*

INTRODUCTION

Wine is a complex mixture of many organic and inorganic compounds. Its composition is very dependent on many factors. Among them, the use of oak wood (*Quercus* sp.) during its aging has a great influence on wine composition, especially on volatile and polyphenolic substances that are extracted from the wood, affecting its organoleptic properties (*1*−*3*). These depend mainly on the pool of potential extractable compounds originally present in the barrel wood and on the conditions and duration of the wine-making process. Two main groups of factors influence the chemical composition of barrel wood: on the one hand, oak species, geographical origin, and sylvocultural treatment of the tree and, on the other, processing of the wood in cooperage, that is, the method of seasoning (natural or artificial, length, and location) and method and degree of oak toasting during the barrel's manufacturing (*4*−*16*).

Among the volatile compounds susceptible to migration from oak wood to wine, cis and trans isomers of β-methyl-γ-octalactone, eugenol, vanillin, furfural, phenols, and other related compounds play a major role in the organoleptic quality of wine. They have low sensory thresholds, especially the cis isomer of methyloctalactone, vanillin, and volatile phenols (*17*). Several studies have found significant differences in the aromatic impacts of American and French oak woods. Thus, American oak contributes more to the presence of *cis*- and *trans*-β-methyl-γ-octalactone in the wine (*12*, *18*, *19*). In fact, the analysis of these two isomers has been used to distinguish between wines aged in French and American oak woods (*20*−*22*).

The need for new sources of quality wood for cooperage, with the purpose of preserving the current supplier areas and, moreover, the search for new and profitable applications for Spanish forestry areas, have led to the consideration of the utilization of Spanish oak as an alternative to French and American oaks, usually used in enology. However, the use of Spanish oak will be possible only after its enological characteristics are known. The present study is a part of an extensive research study of the use of Spanish oak woods for the aging of wines (*8*−*10*, *13*−*16*). In this study, we have concluded that the polyphenolic and volatile composition of heartwood from Spanish oak species is very similar to that of the French oak species usually used in cooperage (*Quercus robur* and *Quercus petraea*, from two different origins, Limousin and Allier), and we found quantitative differences especially important in French and Spanish species with respect to the American oak wood (*Quercus alba* L. from Missouri), which is also habitually used in cooperage.

Moreover, a typical Spanish quality red wine was aged in barrels made with the different woods cited before, to determine the changes produced by each type of wood in the color of wine,

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in its composition of phenolic and volatile compounds, and in its sensorial characteristics. In an earlier paper (*23*), we showed that the kind of wood used for the aging of wines induces important modifications in the color and polyphenolic composition of wine, because wines with different characteristics were obtained from the same wine after 21 months of aging, in relation to the kind of wood used in the barrel-making process. Moreover, the wine aged in barrels made of Spanish oak wood showed characteristics similar and intermediate to those of the same wine aged in French and American oak woods.

In this work, we present the results obtained on the concentrations of 12 volatile compounds in the red wine aged in Spanish oak barrels, and we compared those with the results for the same wine aged in French and American oak barrels. These 12 compounds [syringaldehyde, vanillin, eugenol, maltol, guaiacol, 4-ethylphenol, cis and trans isomers of β-methyl-γ-octalactone, 2-furfuraldehyde, 5-methyl-2-furfuraldehyde, 5-(hydroxymethyl)-2-furfuraldehyde (HMF), and furfuryl alcohol] are some of the most representative among all volatile compounds supplied by oak wood in the relationship of wood and wine during aging. Some organoleptic properties are also presented from sensorial analysis.

MATERIALS AND METHODS

Barrels. All barrels were made in Demptos Cooperage (Bordeaux, France) following the traditional process of cooperage (*11*). During the process, the staves were toasted at a medium intensity level. The number of barrels used for each Spanish species varied depending on the proportion of usable material from each tree (five *Q. robur*, five *Q. petraea*, one *Quercus pyrenaica*, and one *Quercus faginea*). Barrels of French oak (five *Q. robur*, Limousin, and five *Q. petraea*, Allier) and American oak (five *Q. alba*, Missouri) were also provided by Demptos Cooperage.

Wine. The wine used was a quality red wine from Rioja (Spain), produced on an industrial scale by Remelluri wine cellar in 1997, from *Vitis vinifera* L. cv. Tempranillo grapes (100%), according to traditional methods. It was put into the barrels in March 1998, and samples were taken from each barrel after 12 and 21 months of aging. A sample of control wine was taken also before being put into the barrels. In the first sampling (after 12 months of aging), the analytical determinations were carried out on a proportional mixture of samples taken from all of the barrels of the same species and origin, as a single sample. However, in the second sampling (after 21 months of aging), samples from each barrel were analyzed separately (five samples of each species and origin except for *Q. pyrenaica* and *Q. faginea*).

Sensory Analysis. The sensory assessment of wines was done by two committees of specialists, at Rioja wine cellar and at the Institute of Oenologie of Bordeaux (France), and it was performed on the basis of a triangular test. Samples were presented in standard glasses in random order. An unstructured 5-unit scale, in which 0 was “attribute not perceptible” and 5 was “attribute highly perceptible”, was used. The attributes selected were related to color (intensity and limpidity), aroma (intensity, brightness, woody, fruity, and toasty), flavor (roundness, balance, bitterness, and astringency), and an arrangement for preference. Data from all judges for all samples were used, and samples were compared using the so-called “spider web diagrams”. In this diagram, the center of the figure represents the lowest average intensity, with the intensity of each attribute increasing to an intensity of five at the perimeter.

Standards. Reference compounds were purchased from Sigma-Aldrich Chimica [syringaldehyde, vanillin, eugenol, maltol, guaiacol, β-methyl-γ-octalactone, 3,4-dimethylphenol, 4-ethylphenol, 2-furaldehyde, 5-methylfurfural, 5-(hydroxymethyl)furfural, and furfuryl alcohol] and Extrasynthese (γ-hexalactone).

Extraction. Volatile compounds were analyzed using the following method based on that described by Waterhouse and Towey (*20*) and Cutzach et al. (*35*), with some modifications. Fifty microliters of a solution of γ-hexalactone (2 mg/mL in ethanol 95%) and 100 μL of a solution of 3,4-dimethylphenol (20 mg/L in ethanol) as internal standards and 15 g of ammonium sulfate were added to 100 mL of wine samples. Ammonium sulfate was used to increase the ionic strength of the wine and reduce the solubilization of the compounds in water. Three extractions were then carried out using 30, 10, and 10 mL of dichloromethane. The organic fractions were combined and dried on sodium sulfate anhydrous and then concentrated to 500 μL under a nitrogen stream in a Kuderna-Danish apparatus. In all cases, the samples were analyzed in duplicate.

GC-MS. Analyses were performed using a Hewlett-Packard 5890 gas chromatograph (Palo Alto, CA) equipped with a mass spectrometric detector model HP 5971A. Samples were injected in split mode (30:1, 0.5 min), and volatiles were separated using a fused silica capillary column (Supelcowax-10) (30 m $\times$ 0.25 mm i.d., and 0.25 μm film thickness), supplied by Supelco (Madrid, Spain) with GC grade helium as carrier gas at a flow rate of 1.1 mL/min. The working conditions were as follows: injector temperature, 230 °C; detector temperature, 290 °C; column temperature, 45 °C, heated at 3 °C/min to 230 °C, held for 25 min, and then heated at 10 °C/min to 270 °C (held for 21 min). For mass spectrometry an energy of 70 eV was used in electron impact (EI) mode. In all cases, the samples were injected two times in GC. The compounds were identified by comparing their retention times and mass spectra with those of the pure reference standards. The identities of the two isomers of β-methyl-γ-octalactone were assigned according to the work of Chatonnet (*1*), which shows that the trans isomer eluted first on a Carbowax column. Working in the SIM mode, the following ions were used: syringaldehyde, m/z 182; vanillin, m/z 151; eugenol, m/z 164; maltol, m/z 126; guaiacol, m/z 124; β-methyl-γ-octalactone, m/z 99; 3,4-dimethylphenol and 4-ethylphenol, m/z 107; 2-furaldehyde, m/z 96; 5-methyl-2-furfuraldehyde, m/z 110; HMF, m/z 97; furfuryl alcohol, m/z 98; and γ-hexalactone, m/z 85. The concentrations of each substance were measured by comparison with calibrations made with pure reference compounds analyzed under the same conditions. The corresponding calibration was made for each compound, and linear regression coefficients between 0.98 and 0.999 were obtained.

Data Analysis. Data univariate analysis was made using the BMDP-7D (ANOVA) program from BMDP Statistical Software release 7 (*25*). Student−Newman−Keuls multiple-range tests were also carried out. Canonical discriminant analysis, with all of the variables evaluated, was made using the CAND.SAS program from SAS version 8 (*26*).

RESULTS AND DISCUSSION

Volatile Compounds during Aging. The results for the volatile compounds studied on the wine at the beginning and after 12 and 21 months of aging are shown in **Tables 1** and **2**. As can be seen, only 5-methylfurfural and cis and trans isomers of β-methyl-γ-octalactone were not found in the initial wine. The remaining compounds were in the wine before the aging in oak wood barrels. However, appreciable changes in that volatile composition appeared during the aging of the wine: all components increased their concentrations but with different intensities over the time and in relation to the kind of wood used during aging. We must emphasize the high standard deviations of most of the variables in all aged wines analyzed (**Table 2**), which outline the variability among barrels made of the same type of wood and which can be responsible for the few or unremarkable significant differences among species and origins of wood, according to the variable analysis. We applied a Student−Newman−Keuls multiple-range test to determine which means are significantly different from others. The same letters in a row in **Table 2** indicate nonsignificant differences between each pair of means, and the different letters indicate significant differences at the 95% confidence level. In the case of wine aged in barrels made of Spanish *Q. pyrenaica* and *Q. faginea*, because we had only one barrel of each species, the data obtained were considered as the mean in the statistical analysis in order to know the degree of similarity or difference in the volatile composition of these wines related to the others.

Table 1. Volatile Compounds (Micrograms per Liter) in Initial Wine and in Wines Aged in Spanish, French, and American Oak Wood Barrels at 12 Months of Aging

		Spanish				French		American
	initial wine	*Q. robur*	*Q. petraea*	*Q. pyrenaica*	*Q. faginea*	*Q. robur*	*Q. petraea*	*Q. alba*
furanic derivatives[a]								
furfural	8.58	32.6	78.0	18.4	33.0	39.6	60.8	24.6
5-methylfurfural		4.96	5.81	4.87	4.42	4.57	5.40	20.2
HMF	6.25	27.1	38.7	40.1	27.3	30.5	39.9	52.1
furfuryl alcohol	128	823	1044	796	726	830	887	3057
β-methyl-γ-octalactone[b]								
trans isomer		98.0	27.6	96.7	92.1	132	133	87.7
cis isomer		336	55.1	338	242	260	251	712
cis/trans ratio		3.43	2.00	3.50	2.63	1.97	1.89	8.12
volatile phenols[c]								
4-ethylphenol	0.15	32.0	33.7	27.7	23.0	38.8	23.2	28.6
guaiacol	15.5	23.1	21.8	17.0	22.0	27.3	28.2	46.3
eugenol	15.0	40.1	23.6	48.3	33.8	47.96	38.1	80.95
other components[d]								
maltol	35.5	105	114	118	112	110	145	209
vanillin	5.37	15.5	26.1	10.5	23.1	10.5	16.3	34.5
syringaldehyde	36.5	186	167	118	125	88	167	213

[a] Furfural, 2-furancarboxaldehyde; 5-methylfurfural, 5-methyl-2-furancarboxaldehyde; HMF, 5-(hydroxymethyl)-2-furfuraldehyde; furfuryl alcohol, 2-furanmethanol. [b] β-methyl-γ-octalactone, 4-methyl-5-butyldihydro-2(3*H*)-furanone. [c] Guaiacol, 2-methoxyphenol; eugenol, 2-methoxy-4-(2-propenyl)phenol. [d] Maltol, 3-hydroxy-2-methyl-4*H*-pyran-4-one; vanillin, 4-hydroxy-3-methoxybenzaldehyde; syringaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde.

Table 2. Volatile Compounds (Micrograms per Liter) in Wines Aged in Spanish, French, and American Oak Wood Barrels at 21 Months of Aging[a]

	Spanish				French		American
	Q. robur	*Q. petraea*	*Q. pyrenaica*	*Q. faginea*	*Q. robur*	*Q. petraea*	*Q. alba*
furanic derivatives							
furfural	60.1 ± 19.9a	90.1 ± 26.7a	48.8a	43.9a	66.9 ± 20.2a	93.0 ± 60.3a	124 ± 55a
5-methylfurfural	12.6 ± 4.7a	26.4 ± 6.5a	14.5a	12.8a	25.7 ± 10.6a	28.0 ± 14.3a	95.7 ± 32.5b
HMF	19.7 ± 6.3a	75.4 ± 8.6d	49.3bc	26.37ab	55.6 ± 8.7c	49.1 ± 7.9bc	85.0 ± 15.3d
furfuryl alcohol	3701 ± 1198a	7681 ± 939a	6637a	3417a	3818 ± 441a	2083 ± 1033a	6998 ± 2983a
β-methyl-γ-octalactone							
trans isomer	101 ± 20.2b	28.0 ± 8.0a	67.4ab	103b	185 ± 34.0c	150 ± 13.2c	91.9 ± 19.8b
cis isomer	407 ± 75.1b	65.6 ± 20.2a	229b	352b	331 ± 47.4b	347 ± 50.2b	788 ± 100c
cis/trans ratio	4.05 ± 0.34b	2.41 ± 0.63a	3.40ab	3.41ab	1.82 ± 0.28a	2.30 ± 0.25a	8.75 ± 1.25c
volatile phenols							
4-ethylphenol	17.7 ± 3.98a	29.2 ± 5.59b	21.5ab	18.8ab	22.3 ± 7.06ab	19.4 ± 2.98ab	22.6 ± 5.01ab
guaiacol	23.2 ± 5.21a	23.9 ± 1.50a	20.2a	22.4a	27.6 ± 4.28a	27.2 ± 1.48a	42.5 ± 3.90b
eugenol	37.2 ± 11.5a	34.7 ± 3.49a	42.3ab	40.9ab	54.1 ± 5.13b	48.0 ± 4.75ab	88.6 ± 8.70c
other components							
maltol	97.54 ± 13.3a	118 ± 30.0a	78.3a	72.4a	117 ± 34.4a	135 ± 44.4a	172 ± 34.5a
vanillin	59.1 ± 24.3a	91.2 ± 6.80ab	77.5ab	74.0ab	84.0 ± 12.8ab	80.1 ± 22.3ab	145 ± 37.6b
syringaldehyde	71.9 ± 13.0a	150 ± 65.7a	74.8a	64.2a	136 ± 61.8a	135 ± 56.0a	168 ± 87.7a

[a] Average and standard deviation ($x \pm$ SD) were calculated for five samples except in *Q. pyrenaica* and *Q. faginea*. Different letters in the same row denote a statistical difference with 95% confidence level (Student–Newman–Keuls multiple-range test). See footnotes *a*–*d* of Table 1 for compound identification.

Among the studied compounds, furfuryl alcohol showed the highest concentration in all aged wines, between 700 and 12000 μg/L, followed by the cis isomer of β-methyl-γ-octalactone, except in wine aged in Spanish *Q. petraea*, with concentrations between 220 and 930 μg/L. On the contrary, volatile phenols, such as 4-ethylphenol or guaiacol, and other furanic derivatives, such as 5-methylfurfural and 5-(hydroxymethyl)furfural (HMF), presented the lowest concentration.

In relation to furanic derivatives, the initial wine contained very low quantities. Furfural and furfural derivatives, such as 5-methylfurfural and HMF, originated in the heating to which the wood is subjected during the manufacturing stage of barrels, going into the wine during the interaction of the wood and wine. An increase in its concentrations was observed at the end of the first year of aging (**Table 1**) and also during the next 9 months (**Table 2**), especially for 5-methylfurfural, which could explain why this compound was not found in wines subjected to short aging periods (*27*, *28*). At the end of aging, furfural and 5-methylfurfural reached different average concentrations in each wine, but the differences were only significant between European and American woods for 5-methylfurfural. However, the HMF concentrations during aging were somewhat different, the final wines having more significant differences in the HMF concentrations according to the kind of wood barrel. The differences in concentrations of these three components were not related to the differences in their concentrations found by us in these woods after toasting (*15*), and that led us to think that, in addition to the quantities of these compounds present in the superficial layer of toasted wood in contact with the wine, other processes are involved in their concentrations at the end of aging.

On the other hand, the concentrations of furfuryl alcohol increased dramatically in the wine during the 21 months of aging, especially in the last 9 months. This could indicate that extensive reduction of furfural had occurred in all barrels during the maturation period, because the concentrations of furfuryl alcohol in untoasted and toasted wood were negligible, and its origin in the wine is the biological reduction of furfural to the corresponding alcohol, even though alcoholic and malolactic fermentations were complete prior to the commencement of oak maturation (*28*). At the end of the aging period, furfuryl alcohol was found in different concentrations in each wine, ranging from 2000 to 12000 μg/L, in relation to the kind of wood of the barrel, although significant differences among them were not found because of the high variation coefficients, as happened with furfural concentrations. It is also well-known 5-methylfurfural reduces to 5-methylfurfuryl alcohol, and even though 5-methylfurfuryl alcohol was not studied by us, we suppose that the reduction takes place during aging, and this also could explain the low levels of this compound after 12 months of aging. However, to our knowledge the reduction of HMF has not been previously reported in wine, but biochemical transformations and chemical reactions with other wine components may also account for losses of these compounds in wine (*28*). The relative proportions of these compounds in the wines are entirely consistent with the data reported by Chatonnet et al. (*27*, *29*) and Spillman et al. (*28*).

Cis and trans isomers of β-methyl-γ-octalactone were found only in aged wine, which means they came from the oak wood. Both trans and cis isomers were extracted from the wood during the first year of aging, with only very slight variations during the next 9 months. At the end of the aging period, significant differences were found among the concentrations of these compounds in the wines, according to the kind of wood, showing the lowest concentration in the wine aged in Spanish *Q. petraea* and the highest in the wine aged in French oak (trans isomer) or American oak (cis isomer). The significantly low levels of the two isomers of β-methyl-γ-octalactone in the wine aged in barrels made of Spanish oak wood of *Q. petraea* were in relation to the low concentrations of these compounds found in both toasted and nontoasted woods (*15*). Sauvageot and Feuillat (*30*) also found similar levels of whiskey lactone in wine aged in barrels made of *Q. petraea* from the Bertranges forest and *Q. robur* from the Cîteaux forest (France), and both untoasted and toasted woods showed low concentrations of these compounds, in agreement with data from Mosedale and Savill (*31*). In the same way, the levels of these compounds in the other wines also can be related with the potentially extractable β-methyl-γ-octalactone found in untoasted and toasted woods. It can be seen especially for the wine aged in French *Q. robur*, because this wood showed very low concentrations of the two isomers in toasted wood, much lower than the levels in nontoasted wood, seeing that a destruction of these components could happen during the toasting process at cooperage (*15*). In agreement with Chatonnet et al. (*27*), these compounds could migrate from the head pieces of barrels, which were not toasted, or even from the inner layers of wood in the staves. Moreover, it is necessary to bear in mind the chemical precursors of these compounds, which could be extracted from the wood by the alcohol in the wine during aging (*20*, *32*, *33*).

The whiskey lactone isomer ratios (cis/trans) were significantly different between wines aged in European (Spanish and French) and American oak woods, during the aging. In wines aged in American oak wood the ratio varied between 7.41 and 10.20; this ratio varied between 1.40 and 4.79 in wines aged in European oak, within the limits described in the literature for wines aged in barrels made of French oak (*20*, *22*) and confirming the usefulness of this parameter for distinguishing between wines aged in American and European oak woods.

The wine also contained small quantities of volatile phenols before aging, which increased significantly during the time of contact the wood and wine, especially over the first 12 months.

Table 3. Data of Perception Thresholds, in Synthetic Solution (Micrograms per Liter) and Sensorial Descriptors Cited in the Literature for Studied Components[a]

	perception threshold	sensorial descriptors
furanic derivatives		
furfural	15000[c]	almonds
5-methylfurfural	16000[b,d]	toasted almonds
HMF		
furfuryl alcohol	15000[b,d]	
β-methyl-γ-octalactone		
trans isomer	110[b]	woody, oak-like, vanilla[c]
cis isomer	25[b]	
volatile phenols		
4-ethylphenol	440[b]	horse
guaiacol	20[b]	smoked
eugenol	15[b]	spicy
other components		
maltol	5000[d]	toasty, caramel[d]
vanillin	65[b]	vanilla;[b] coffee[c]
syringaldehyde	>50000[a,e]	

[a] See footnotes *a*–*d* of Table 1 for compound identifications. [b] Chatonnet et al. (*17*). [c] Spillman et al. (*35*). [d] Cutzach et al. (*24*). [e] In water.

At the end of the aging period, the wines aged in barrels made of Spanish or French oak woods showed concentrations of eugenol and guaiacol significantly lower than those of wines aged in barrels made of American oak wood, in line with the levels of these compounds found in the layer of toasted wood in barrels, which were significantly higher in American oak wood (*15*), and also with data in the literature (*19*, *22*, *29*). Some significant differences were also found among wines aged in European oak wood related to eugenol: in the wines aged in French *Q. robur*, eugenol concentrations found were significantly higher than those of wines aged in Spanish *Q. robur* and *petraea*.

Whereas eugenol and guaiacol came from the wood, the 4-ethylphenol content in the red wine has a microbial origin (*Brettanomyces/Dekkera* yeast), and the oak wood is able to give only very small amounts of this compound (*4*, *15*, *34*). Thus, the content of 4-ethylphenol in aged red wines could act as an indicator of the sanitary status of barrels or of yeast contamination of wood. The concentrations of this compound found by us were very low, similar to those detected by other authors in wines aged in healthy barrels (new or well sanitized). On the other hand, we detected a decrease of concentration in all wines after 12 months of aging, as was reported by Nomdedeu et al. (*35*), but without a well-known cause. Even some significant differences were found in wines according to the kind of wood used in the barrel-making process; if we bear in mind its perception threshold (**Table 3**), these differences do not have sensorial significance.

The initial wine also contained maltol (3-hydroxy-2-methyl-4*H*-pyran-4-one), but at a low level. This compound increased in concentration during the first 12 months of aging, in similar quantities in all wines aged in Spanish and French oak woods and rather higher in wines aged in American oak woods. These data are sufficiently in line with the levels of this compound found in the layer of toasted wood into barrels, which were significantly higher in American oak wood (*15*), and also with literature data about French red wines aged in French and American oak wood barrels during 12 months (*29*). However, during the next 9 months, the concentrations did not vary or decreased slightly in all wines, showing no significant differences related to the kind of wood at the end of the aging period. Reduction of maltol levels during oxidative aging was reported

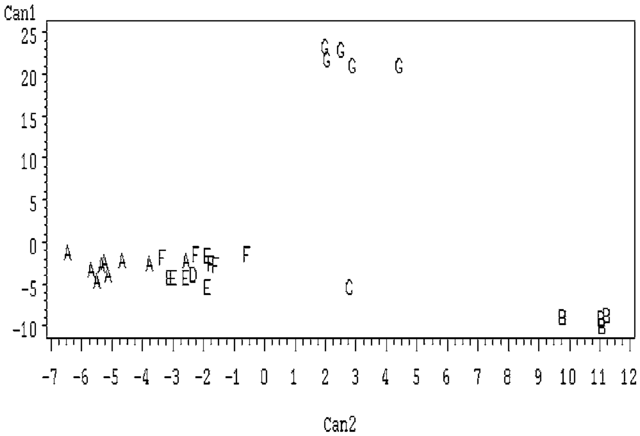

Figure 1. Canonical discriminant analysis of volatile compounds in wines aged on Spanish, French, and American oak wood barrels at 21 months of aging. Projections of the points of each species and provenance are given on the two principal canonical axes. A = *Q. robur*, B = *Q. petraea*, C = *Q. pyrenaica*, and D = *Q. faginea*, from Spain; E = *Q. robur* and F = *Q. petraea*, from France; G = *Q. alba* from America. Standarized coefficients of discriminant functions 1 and 2 were as follows for each variable: furfural, 0.40 and 0.30; 5-methylfurfural, 0.83 and 0.31; HMF, 0.44 and 0.76; furfuryl alcohol, 0.20 and 0.71; *trans*-whiskey lactone, 0.05 and –0.65; *cis*-whiskey lactone, 0.91 and –0.32; cis/trans ratio, 0.90 and 0.06; 4-ethylphenol, –0.33 and 0.44; guaiacol, 0.85 and 0.16; eugenol, 0.89 and 0.09; maltol, 0.37 and 0.28; vanillin, 0.67 and 0.42; syringaldehyde, 0.26 and 0.40.

only by Cutzach et al. (*24*) in red sweet natural nonmuscat wines from Rivesaltes.

Last, two phenol aldehydes were studied: vanillin and syringaldehyde. Both aldehydes increased in concentration during aging, but with some differences. Vanillin is extracted from the wood, especially after the first 12 months of aging, whereas syringaldehyde passes into the wine during the first year, with decreases or no variation of concentration during the next 9 months. The low levels of vanillin at 12 months can also be explained by the reduction to vanillyl alcohol (*17*, *28*). Comparing the oak origin, the levels of these compounds at the end of aging showed significant differences only between the concentrations of vanillin in the wine aged in Spanish *Q. robur* and in the wine aged in American *Q. alba*. Therefore, the differences in the concentrations of these compounds found in toasted wood (*13*) were not closely reflected in the aged wine.

In the interaction of wood and wine during aging, each volatile compound has a characteristic extraction profile that is a function of not only the barrel but also the compound itself and its particular relationship with the barrel: quantity of compound in the superficial layer of toasted wood in contact with wine, and also in untoasted wood (heads pieces of barrels or even inner layers in the staves); susceptibility to biological and chemical degradation reactions, such as the transformation of aldehydes to alcohols; presence in the wood of its chemical precursors; duration of contact time between wood and wine, etc.

To compare the wines aged in Spanish, French, and American oak wood barrels, we carried out a canonical discriminant analysis considering the data in **Table 2**. The resulting mathematical model explained 100% of the total dispersion, which was distributed among six canonical functions. **Figure 1** shows the graphical representation of the projections of the points of each group on the plane defined by the two principal canonical axes (functions 1 and 2), which explained 87.80% of the total variance, with canonical correlations of 0.9961 and 0.9863 and eigenvalues of 127.68 and 35.89, respectively. Discriminant function 1 depended mainly on the content of *cis*-whiskey lactone, the cis/trans isomer ratio, and the content of eugenol, in this sequence, whereas discriminant function 2 depended mainly on the contents of HMF, furfuryl alcohol, and *trans*-whiskey lactone, as can be deduced from the correlation to total canonical structure coefficients of discriminant functions 1 and 2, gathered in the legend of **Figure 1**. The important differences of wines aged in barrels made of Spanish and French oak woods when compared with those aged in American oak wood were accounted for especially in canonical function 1, which showed as principal discriminant variables the content of *cis*-whiskey lactone and the cis/trans isomer ratio. This confirms again the usefulness of this parameter to distinguish between wines aged in American and European oak woods and especially influence of the content of *cis*-whiskey lactone in the differentiation of wines aged in American oak wood. On the contrary, the sets of points of wines aged in Spanish and French oak woods were very close according to canonical function 1, showing only appreciable statistical distance, according to canonical function 2, the wine aged in barrels made of Spanish *Q. petraea* with respect to the rest of the wines aged in European oak wood. These results reaffirm the incidence of the species and geographical origin of oak wood in the wine aging, because wines with different characteristics were obtained from the same wine, after 21 months of aging, in relation to the kind of wood used in the barrel-making process.

Sensorial Analysis. Data found in the literature about the perception thresholds in a synthetic solution and the sensorial descriptors for studied components are shown in **Table 3**. The extrapolation of these data on the sensory impact to wine should be treated with caution, because it may vary with the properties of the wine, such as the degree of alcohol, astringency, and level and composition of phenolic compounds (*30*), and it is also necessary to bear in mind that it may also depend on the presence of other wine components which could modify, mask, or enhance its aroma and taste properties, because, for example, furfural has been reported to have an important modifying effect on the perception of the aroma of oak lactones in wine (*37*).

As can be seen from a comparison of **Table 3** with **Tables 1** and **2**, all aged wines analyzed by us showed concentrations of furfural and furanic derivatives, 4-ethylphenol, maltol, and syringaldehyde very much lower than perception thresholds in a synthetic solution, so the role of these molecules in the aroma of these wines will be quite limited with regard to their perception thresholds. On the contrary, cis and trans isomers of whiskey lactone, guaiacol, and eugenol in wines aged in French oak and in some wines aged in Spanish *Q. robur* and vanillin in almost all wines after 21 months of aging showed concentrations higher than perception thresholds. We must emphasize that the high concentrations of the cis isomer of whiskey lactone found in the wines aged in American oak wood were ≥10-fold higher than perception thresholds in red wine (74 μg/L) (*17*), and this can lead to an excessive woody character in these wines or a resinous smell that can mask the fruity character of wine and to the depreciation in global wine aroma (*27*, *30*).

The results of sensorial analysis of all aged wines (**Figures 2** and **3**) showed a clear evolution of characteristics of wines. The visual perception (intensity and limpidity of color, **Figure 2**) changed from the uniformity at 12 months of aging to values between 1 and 4 for limpidity and between 2 and 4 for intensity,

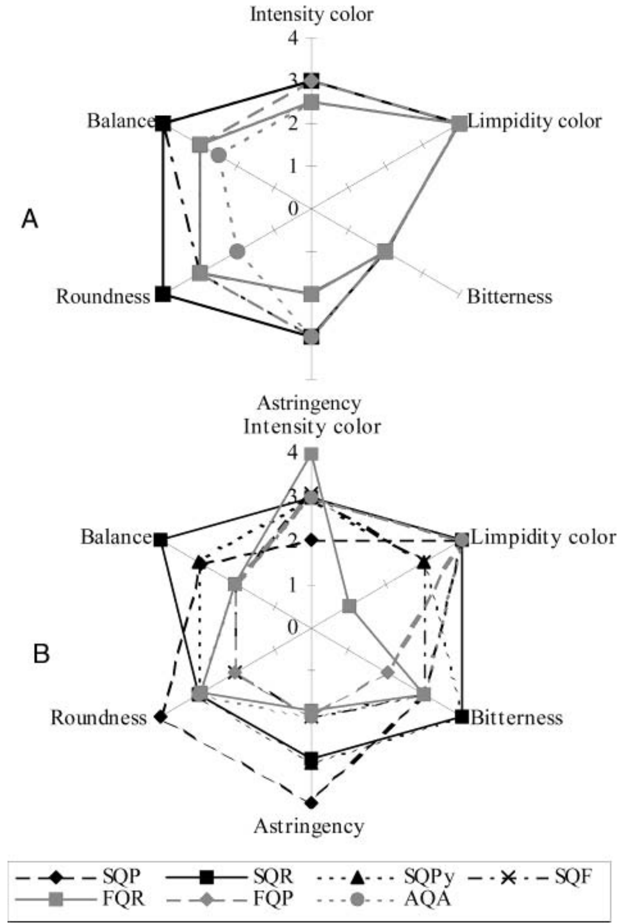

Figure 2. Spider web diagram of average scores obtained by sensorial analysis of aged wines, in visual and taste appreciation. A = 12 months of aging; B = 21 months of aging; SQP = Spanish *Q. petraea*; SQR = Spanish *Q. robur*; SQPy = Spanish *Q. pyrenaica*; SQF = Spanish *Q. faginea*; FQR = French *Q. robur*; FQP = French *Q. petraea*; AQA = American *Q. alba*.

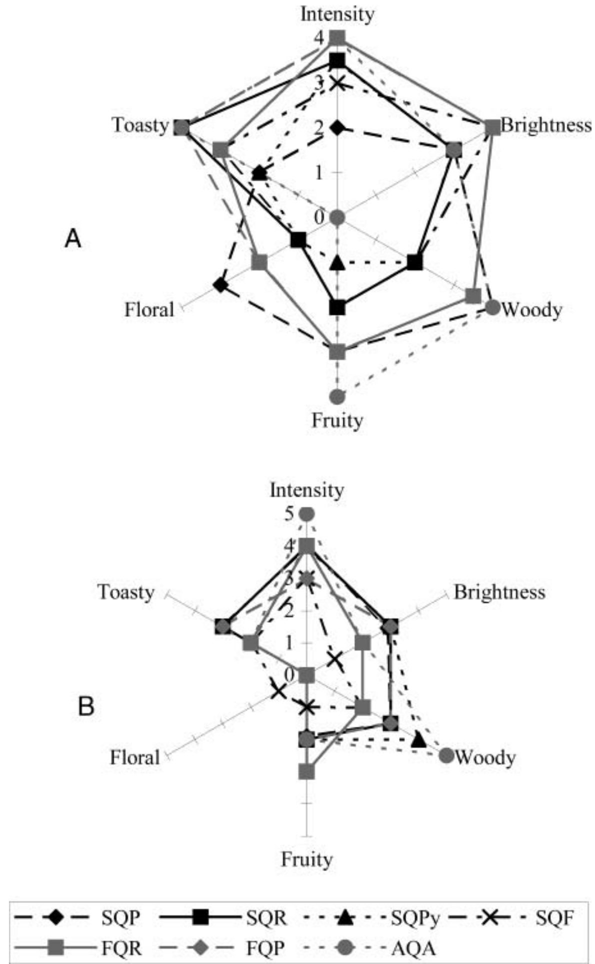

Figure 3. Spider web diagram of average scores obtained by sensorial analysis of aged wines, in olfactory appreciation. A = 12 months of aging; B = 21 months of aging; SQP = Spanish *Q. petraea*; SQR = Spanish *Q. robur*; SQPy = Spanish *Q. pyrenaica*; SQF = Spanish *Q. faginea*; FQR = French *Q. robur*; FQP = French *Q. petraea*; AQA = American *Q. alba*.

pointing out the evolution of wine aged in French *Q. robur*: decrease in limpidity from 4 to 1 and increase in intensity from 2.5 to 4, the values of both characteristics probably being related. At 12 months of aging, we can see that, in the taste perception, the wines aged in Spanish oak wood showed the same average scores in all attributes, except roundness in Spanish *Q. faginea*. The wines aged in French and American oak woods showed the same or lower average values as those of Spanish oak wood, American *Q. alba* showing the lowest values of roundness and balance (harmony among the rest of the attributes). At 21 months of aging, we can see a higher variability among the different wines, showing increases, decreases, or no variation of scores in relation to the kind of wood barrel.

In olfactory perception (**Figure 3**), there is a lower uniformity of average scores of wines aged during 12 and 21 months related to the kind of wood. Floral, fruity, brightness, and toasty (except in Spanish *Q. petraea*) attributes decreased and intensity of aroma (except in French *Q. petraea*) and woody character in some wines (especially in American *Q. alba*) increased from 12 to 21 months of aging.

In the arrangement for preference from two committees of specialists (data not shown), there was no clearly favorite wine, because wines aged in Spanish or French oak woods alternated in first place together with wines aged in American oak wood, according to the personal preference of each judge. There was only one agreement: the wine aged in Spanish *Q. faginea*, at 21 months of aging, was always the last in the arrangement for preference and also obtained the lowest scores in almost all characteristics (**Figures 2** and **3**). These data, together with the studies carried out to date on the low molecular polyphenolic, tannic, and volatile composition of Spanish oak wood, in relation to French and American ones (*13*−*15*), and on the polyphenolic composition and color of wines aged in barrels made of these woods (*23*), and the particular physical structure of this wood (irregular fiber, gross grain, full of knots) (*38*), which produces a very low proportion of usable material, lead us to think that the wood of this species of *Quercus* cannot be considered suitable for cooperage.

All of the data obtained reveal that the kind of wood used for the aging of wines induces important modifications, because wines with different characteristics were obtained from the same wine, after 21 months of aging, in relation to the kind of wood used in the barrel-making process. Moreover, Spanish oak wood from *Q. robur*, *Q. petraea*, and *Q. pyrenaica* can be considered suitable for barrel production for quality wines; wines aged in barrels made of these Spanish oak woods showed characteristics similar and intermediate to those of the same wines aged in French and American oak woods.

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