JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Volatile Compounds and Sensorial Characterization of Wines from Four Spanish Denominations of Origin, Aged in Spanish Rebollo (*Quercus pyrenaica* Willd.) Oak Wood Barrels

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The evolution of almost 40 oak-related volatile compounds and the sensorial characteristics of red wines from four Spanish denominations of origin (DOs) (Bierzo, Toro, Ribera de Duero, and Rioja) during aging in barrels made of Rebollo oak wood, *Quercus pyrenaica*, were studied and compared to the same wines aged in American and French oak barrels. Each oak wood added unique and special characteristics to the wine, and in addition, each wine showed a different ability to extract the compounds, which result in these characteristics from the oak wood. In general, wines aged in *Q. pyrenaica* wood were characterized by high levels of eugenol, guaiacol, and other volatile phenols. In regards to compounds like *cis*-whiskylactone or maltol, the behavior of this wood is very similar to that of American oaks. When considering phenolic aldehydes and ketones, the levels of these compounds are intermediate between those of French and American woods and depend greatly on the type of wine. The type of oak, on the other hand, does not affect the chromatic characteristics of the wines. In sensory analysis, the biggest differences are found in the olfactory phase. Among the four DOs studied, wine aged in *Q. pyrenaica* presented the highest notes of wood, with more aromas of roasting, toasting, milky coffee, spices, or wine−wood interactions. The wines aged in barrels made of *Q. pyrenaica* wood were highly regarded, and preference was shown for them over those same wines when they had been aged in barrels of American or French oak.

KEYWORDS: ***Quercus pyrenaica*; oak wood; wine; aging; volatile compounds**

INTRODUCTION

The need for new sources of quality wood supply for cooperage has led to looking into the possibility of utilizing Rebollo (*Quercus pyrenaica* Willd.) oak, a species native to the Iberian Peninsula, as an alternative to other European (*Quercus robur* and *Quercus petraea*) and American (*Quercus alba*) oaks in the aging wines. Besides this requirement for quality wine barrel wood, this study on the enological quality of Rebollo has been done with two other points in mind: becoming a supplier for cooperage would give an added value to the large *Q. pyrenaica*-covered regions that can be found in Castilla-León (722.773 ha) as well as in other parts of Spain (1.090.716 ha) (*1*) and the possibility of being able to give our wines their own personality, with recognizable characteristics.

The utility of this wood for enology can only be determined after knowing its behavior during wine aging. When aging in oak barrels, wine undergoes a series of processes that cause important changes in wine aroma, color, taste, and astringency. As is well-known, one of these processes is that of compound extraction from wood, since oak wood releases significant amounts of some aroma compounds, which have a great impact on the aroma profile and on the sensory characteristics of the wine. The factors that affect the pool of oak extractives are the species and geographical origin of the wood, as well as its processing, especially the method of obtaining the staves, their seasoning, and the degree of oak toasting (*2*−*7*). Also, the age of the barrel and its volume have an influence on the quantity of compounds present in the wood that pass to the wine during aging (*8*−*10*).

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10.1021/jf8014602 CCC: $40.75
Published on Web 09/09/2008

Thus, knowing the chemical composition of the oak wood in the barrel, and especially the chemical composition of the toasted layer in contact with the wine, can help us a great deal in the selection of the most appropriate casks for each wine. This wood presents structural characteristics (grain, porosity, and permeability) ideal for barrel manufacturing. Its chemical characteristics (polyphenols, tannins, and volatile compounds) are quite similar to other species that are of recognized enological quality, noting the absence of significant differences among *Q. pyrenaica* of differing origins, with regard to sensorially important chemical compounds. The evolution of these chemical characteristics during natural drying in the open air as well as toasting results in a wood whose tannic composition is well-balanced, with concentrations similar to those present in *Q. petraea* wood, and rich in aromatic compounds, with levels equal to or greater than those that can be detected in French or American oak woods (*11*−*14*). Nevertheless, we cannot forget that wine and the oak barrel in which it is aged make up an active system from physical, chemical, and biochemical points of view, and the existence of numerous concurrent phenomena other than simple extraction acting on the aroma should be considered. Among them, the oxidation of some compounds (*15, 16*), the microbiological formation of ethyl phenols (*17*), the reaction of wood aldehydes and wine flavanols (*18, 19*), and the sorption of wine aroma compounds by oak wood (*20*) should be born in mind.

There are very few data about the behavior of *Q. pyrenaica* oak wood during wine aging. In our previous work (*21, 22*), in which only one cask of this wood was used, the wine aged in *Q. pyrenaica* showed similar chemical and sensorial characteristics to those of the same wine aged in other Spanish and French oak wood barrels and was the preferred wine of some of the expert judges. More recently, Coninck et al. (*23*), using chips to simulate the process of wine aging, found a higher contribution to sensorial red wine attributes from this wood from Portugal rather than French oak wood. Similar results were described by Caldeira et al. (*24*) when using this wood, also from Portugal, on the aging of Portuguese brandies; they reported high intensities of vanilla, wood, caramel, and toasted attributes. These data outline the possibility of utilizing *Q. pyrenaica* oak as an alternative to other oak woods, but more data are necessary to better understand its behavior during wine aging. Thus, wine characteristics such as grape variety, alcoholic degree, pH, redox potential, and turbidity (*25*−*28*) have been recently studied as decisive factors that determine the final concentration of the wood-extracted compounds in wine.

The objective of our work is a better understanding of the behavior of Spanish *Q. pyrenaica* oak wood during wine aging, especially its effects on the aroma profile and on the sensory characteristics of the wine. Thus, we present in this paper the oak-related volatile chemical composition of wines from different Spanish denominations of origin (DOs) (Rioja, Ribera de Duero, Toro, and Bierzo), aged in barrels of Spanish oak (*Q. pyrenaica* from Salamanca, Gata/Peña de Francia area), and compare them with the same wine aged in French and American oak barrels. Moreover, their organoleptic properties were studied by sensory analysis.

MATERIALS AND METHODS

Wine. The wines used were red single variety wines produced on an industrial scale in 2005, in cellars of different Spanish DOs: CIDA (DOCa Rioja, cv. Tempranillo grapes), Pago de Carraovejas (DO Ribera de Duero, cv. Tempranillo grapes), Rejadorada (DO Toro, cv. Tinta de Toro grapes), and Pittacum (DO Bierzo, cv. Mencía grapes). The most important Spanish red grape variety was Tempranillo, which was given different names depending on the geographical region where it was cultivated. Thus, the variety Tinta de Toro, from the Toro region, was considered by many authors to be the same variety as Tempranillo, just named differently due to traditional and cultural factors typical of the Toro region in which it was cultivated (*29*). Mencía was a different variety, typical of the Bierzo region. The habitual chemical parameters of these wines determined at wine cellars are shown in **Table 1**. These parameters were determined before the wines were transferred to the barrels, according to the OIV methods (*30*). The main difference among wines was the alcoholic degree (13.4−15%, v/v).

Table 1. Enological Parameters of Wines Used in This Work[a]

	Bierzo	Ribera del Duero	Toro	Rioja
alcohol level (% v/v)	14.0	15.0	15.0	13.4
dry extract (g/L)	ND	29.9	31.2	31.5
pH	3.85	3.87	3.65	3.60
total acidity[b] (g/L)	4.75	4.55	4.82	6.29
malic acid (g/L)	ND	0.20	0.10	0.15
K (mg/L)	ND	1570	1450	1184
reducing sugar (g/L)	ND	1.30	1.60	2.19
volatile acidity[c] (g/L)	0.49	0.42	0.59	0.45
free SO_2 (mg/L)	24	25	22	17
total SO_2 (mg/L)	53	65	76	22

[a] Measured according to OIV methods (*30*). [b] Expressed as tartaric acid. [c] Expressed as acetic acid. ND, not determined.

The wines were put into the barrels on January 2006, and samples were taken from each barrel after aging for 6 and 12 months. A control sample of each wine was also taken before the wine was put into the barrels and was analyzed in the same way.

Barrels. In each cellar, they used three barrels of Spanish oak (*Q. pyrenaica*, from Salamanca, Gata/Peña de Francia area), three of French oak (*Q. petraea*, from Allier, France), and three of American oak (*Q. alba*, from Missouri). In the Bierzo cellar, three barrels of Spanish oak (*Q. petraea*, from Navarra, Garaioa area) were also used. All barrels were new, with a capacity of 225 L and with a very fine grain. The seasoning of the wood was carried out in the open air for 3 years. The barrels were toasted at a medium intensity level (165 °C for 35 min). All barrels were manufactured (seasoning and toasting of wood) at the same time by the same cooperage.

Sensory Analysis. The sensory assessment of wines was done by a committee of 12 expert judges, at the Castilla-León Enological Station, located in Rueda (Valladolid). The experts were specially trained in the employment of scales and aroma descriptors used. Samples were presented in standard glasses in random order. An unstructured 7-unit scale, in which 1 was "attribute not perceptible" and 7 was "attribute highly perceptible", was used. The attributes selected by expert judges were related to visual, olfactory, and gustatory parameters, grouped in four families: descriptors of visual phase (color intensity, blue-violet, garnet-red, and red brown), descriptors of olfactive phase related to primary and secondary aromas and off-flavors (olfactive intensity, herbaceous/green, vegetal/cabbage, fruity, ripened fruit, sulfhydric, acetaldehyde, dirty/mold, oxidized, and reduced), descriptors of olfactive phase related to the wood−wine interaction (woody, vanilla, coconut, spicy, nutty, animal/leather, toasty, white coffee, chocolate, roasted, and wood−wine interaction), and finally descriptors of gustative phase (grease, acidity, astringency, green tannins, hard tannins, round tannins, dry tannins, and wine−wood interaction), and those were referred to as the overall sensory analysis (balance and global valuation). Data from all judges for all samples were used, and the average values were compared using the so-called "spider web diagrams". In this diagram, the center of the figure represented the lowest average intensity, with the intensity of each attribute increasing to an intensity of seven at the perimeter.

The expert judges also arranged the wines in order of preference for wood type for each wine cellar separately. The samples were evaluated between 1 and 3 (1, sample selected in the last place and the least preferred; 3, sample selected in the first place and the most preferred).

Extraction. Volatile compounds were analyzed using a method based on that described by Waterhouse and Towey (*31*) and Cutzach et al.

Table 2. GC Quantitative Evaluation of Furanic Compounds, Lactones, and Pyranones (Micrograms per Liter of Wine) in Wines from Different Spanish DOs, Aged in Spanish, French, and American Oak Wood Barrels, after 12 Months of Aging[a]

		Bierzo				Ribera de Duero			Toro			Rioja		
		Py	Am	Fr	Na	Py	Am	Fr	Py	Am	Fr	Py	Am	Fr
furfural	*x*	134 c	187 c	110 c	131 c	2059 bc	5256 a	1543 bc	1207 bc	1128 bc	742 c	3575 ab	1869 bc	1378 bc
5-methylfurfural	*x*	93.5 d	41.8 d	51.4 d	111 d	1029 c	1445 b	652 c	860 c	187 d	177 d	2477 a	1543 b	869 c
HMF	*x*	1704 cd	2094 c	1229 de	1233 de	3533 a	2723 b	1611 cd	757 e	713 e	1344 de	3141 ab	1193 de	986 de
furfuryl alcohol	*x*	6958 c	29740 b	6599 c	9197 c	3371 de	2554 de	2077 de	31253 a	27721 b	29836 b	1068 e	4627 de	2335 de
trans-β-methyl-γ-octalactone	*x*	222 b	236 b	245 b	735 a	192 b	178 b	291 b	184 b	141 b	125 b	231 b	150 b	305 b
cis-β-methyl-γ-octalactone	*x*	1011 bc	1313 a	611 def	1174 ab	833 cd	1216 ab	541 ef	718 de	992 bc	396 f	1096 ab	1083 ab	529 ef
cis/*trans* ratio	*x*	4.62 abcd	5.56 ab	2.7 cde	1.61 e	4.64 abcd	6.92 a	2.52 cde	3.92 bcde	6.99 a	3.16 bcde	5.07 abc	7.18 a	2.17 de
maltol	*x*	111 d	197 bc	92 d	95 d	189 bc	191 bc	156 c	201 b	159 bc	163 bc	282 a	168 bc	114 de

[a] The average (*x*) was calculated for three samples. Different letters in the same row denote a statistical difference with 95% confidence level (Student−Newman−Keuls multiple range test). Py, *Q. pyrenaica* Spanish oak from Salamanca; Am, *Q. alba* American oak from Missouri; Fr, *Q. petraea* French oak from Centro region; Na, *Q. petraea* Spanish oak from Navarra; and HMF, 5-hydroxymethylfurfural.

(*32*), with some modifications. Three internal standards were used as follows: 100 μL of a 3,4-dimethylphenol solution (20 mg/L in 95% ethanol) (for volatile phenols), 50 μL of a solution of *o*-vanillin (1 mg/mL in 95% ethanol) (for phenolic aldehydes and related compounds), and 50 μL of a solution of γ-hexalactone (2 mg/mL in 95% ethanol) (for the remaining compounds). Fifteen grams of ammonium sulfate was added to 100 mL of wine samples to increase the ionic strength of the wine and to reduce the solubilization of the compounds in water. Three liquid−liquid extractions were then carried out using 30, 10, and 10 mL of dichloromethane. The organic fractions were combined and dried on anhydrous sodium sulfate and then concentrated to 500 μL in a nitrogen stream in a Kuderna-Danish apparatus. In all cases, the samples were analyzed in duplicate.

Gas Chromatography−Mass Spectrometry Analyses. Analyses were performed using a Hewlett-Packard 6890N gas chromatograph (Palo Alto, CA) equipped with a mass spectrophotometric detector model HP 5975B. 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 × 0.25 mm i.d. and 0.25 μm film thickness), supplied by Supelco (Madrid, Spain), and under the working conditions described in Fernández de Simón et al. (*21*). Quantitative determinations were carried out by the internal standard method, using peak areas obtained from selected ion monitoring. The selected ions for each one of the evaluated compounds were as follows: **107**/122, 3,4-dimethylphenol; 152, *o*-vanillin; 85, γ-hexalactone; 95/**96**, furfural; 109/**110**, 5-methylfurfural; **97**/126, 5-hydroxymethylfurfural (HMF); 97/**98**, furfuryl alcohol; 99, *cis*- and *trans*-β-methyl-γ-octalactone; 126, maltol; **109**/124, guaiacol; 123/**138**, 4-methylguaiacol; **137**/152, 4-ethylguaiacol; **137**/166, 4-propylguaiacol; 135/**150**, 4-vinylguaiacol; 94, phenol; **107**/122, 4-ethylphenol; **91**/120, 4-vinylphenol; **107**/108, *o*-cresol, *p*-cresol, and *m*-cresol; 164, eugenol and *t*-isoeugenol; 139/**154**, 2,6-dimethoxyphenol; 168, 4-methyl-2,6-dimethoxyphenol; 194, 4-allyl-2,6-dimethoxyphenol; **151**/152, vanillin; **137**/166, 2-(4-hydroxy-3-methoxyphenyl) acetaldehyde (HMPA); **151**/166, acetovanillone; **137**/180, 1-(4-hydroxy-3-methoxyphenyl)-2-propanone (HMPP); **151**/180, propiovanillone; **137**/194, 1-(4-hydroxy-3-methoxyphenyl)-2-butanone (HMPB); **151**/194, butyrovanillone; **137**/168, methyl vanillyl ether; **137**/182, ethyl vanillyl ether; 181/**182**, syringaldehyde; **181**/196, acetosyringone; **167**/210, 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone (HDMPP); **181**/210, propiosyringone. The *m*/*z* ion in boldface was used for quantification. 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.

Statistical Analysis. Univariate analysis was performed using analysis of variance, applying the Student−Newman−Keuls multiple range test. Multivariate canonical discriminant analysis was also carried out with all compounds evaluated, using the SAS statistical program (version 9.1; SAS Institute, Cary, NC).

RESULTS AND DISCUSSION

Volatile Compounds. A great variety of volatile compounds able to give a higher aromatic complexity to the wine has been identified in oak wood in recent years (notes of vanilla, clove, cocoa, toasty, leather, spicy, toasted bread, etc.). We analyzed the 40 compounds most representative of this contribution of wood to wine during the aging process (*9, 21, 25, 33*). They belong to very different chemical families such as the phenolic aldehydes, phenolic ketones and their isomers, volatile phenols, lactones, furanic compounds, pyranones, and others. Their concentrations cover a very wide range; all of them were in the wine before aging in oak wood barrels, except 5-methylfurfural, isobutyrovanillone, and *cis*- and *trans*-β-methyl-γ-octolactone, and all of their concentrations in the wine change during aging.

Furanic derivatives (furfural, 5-methylfurfural, and 5-hydroxymethylfurfural) were extracted from the barrel wood during the first 6 months, reaching average concentrations from 27 μg/L of 5-methylfurfural in Bierzo wine aged in American oak to 11400 μg/L of furfural in Rioja wine aged in *Q. pyrenaica*. In the following 6 months, furfural heavily decreased its concentrations, while 5-methylfurfural showed small changes, some of them statistically nonsignificant, and HMF increased from barrel wood. Similar evolutions have been previously described by others authors (*21, 26, 27, 34*).

At 12 months (**Table 2**), the concentrations of furfural and its derivatives were related as much to wood type as to wine origin, although in some cases the differences were statistically not significant, probably due to the great variability of detected concentrations in wines aged in the same kind of barrels. Regarding wood type, a uniform behavior was not detected in the four wines studied, as it was not possible to link all wines to any particular type of wood with the results of a higher or lower extraction of these compounds. The clearest differences among kinds of wood were found in the wine from Ribera de Duero, while in the wines from Bierzo and Toro, the differences among types of woods were less significant. More obvious seem the differences among kinds of wine, especially if we take into account the concentrations of wines aged in *Q. pyrenaica* barrels. As can be seen in **Table 2**, the differences were always statistically significant between Bierzo and Rioja wines, and among Bierzo, Toro, and Ribera de Duero wines for 5-methyl and 5-hydroxymethylfurfural, although these barrels were made with wood from the same forest, felled at the same time, seasoned at the same place and time, and toasted at the same cooperage, for the same length of time and with the same intensity: Not all wines studied had the same capacity to extract the furanic compounds from barrel woods. However, we cannot forget that furanic aldehydes, extracted from oak wood during aging, can participate in many reactions that take place in the wine during this process. The best-known one is the formation of furfuryl alcohol, but other reactions like the formation of 2-furanmethanethiol, having a toasty aroma (*35*), or the formation of brown adducts among the three furanic aldehydes and the (+)-catechin of wine (*19*) also contribute to the decrease of their concentrations in free forms in the wine.

Furfuryl alcohol was not extracted from oak wood, since the concentrations of this compound detected in nontoasted and toasted oak wood were only a few μg/g of wood (*6, 14*). In studied wines, its concentration increased from less than 40 μg/L in initial wines to concentrations ranging between 1000 (Rioja wine aged in *Q. pyrenaica*) and 30000 μg/L (Toro wine aged in *Q. pyrenaica*) at 12 months of aging. Its origin in the wine was the biological reduction of furfural to the corresponding alcohol, even though alcoholic and malolactic fermentation were complete prior to the commencement of oak maturation (*16*), so factors affecting enzymatic reactions, such as pH, temperature, or microbiological residual activity, will affect its formation (*36, 37*). In both Bierzo and Toro wines, independent of the wood origin, at 12 months of aging, almost all of the furfural extracted from the wood was reduced to furfuryl alcohol, highlighting the important concentrations reached in all aged wines from Toro and those from Bierzo aged in American oak. On the other hand, in Ribera de Duero and Rioja wines, although appreciable quantities were formed, high concentrations of furfural were conserved in the wine after 12 months. As conditions of pH (**Table 1**) and temperature (all cellars environments were thermostatically controlled) were very similar, we see that in these wines the microbial activity was lower than in those of Bierzo and Toro, especially if we bear in mind the mechanism proposed by Ferreira et al. (*38*), who talked about a microbiological extraction/formation of this compound, in accordance with Spillman et al. (*16*). These differences in microbial activity could be related to sulfur dioxide levels, since increased SO_2 levels would inhibit this reaction (*39*). Unfortunately, we do not have the data on sulfur dioxide levels during aging to support that statement. Thus, the kind of wood or the kind of grape variety probably had a secondary, but not negligible, influence on the presence of furanic compounds in aged wines.

These compounds have a practically null direct sensorial contribution to wine, since they do not reach its threshold levels (20 mg/L, furfural; 45 mg/L, 5-methylfurfural and furfuryl alcohol, with notes as almonds, toasted almonds, and hay, respectively) (*40*). However, it is important to consider that they may strengthen the aroma of the β-methyl-γ-octalactones (*25*).

The *cis* and *trans* isomers of β-methyl-γ-octalactone (whiskey lactone) were not detected in initial wines, without contact with oak wood, for which reason they were considered as markers of oak wood-aged wines. The two isomers were extracted from the wood during all aging periods, showing statistically significant differences between the concentrations found at 6 and at 12 months of aging, in all wines (data not shown), as described in the literature (*34*). At the end of aging, there were clear differences among the wines related to the kind of wood (**Table 2**). In general, wines aged in American oak stand out because of their high levels of *cis* isomer, while those aged in *Q. petraea* stand out because of their high levels of *trans* isomer, especially the wines aged in barrels made with *Q. petraea* Spanish oak from Navarra. These last wines showed high concentrations of both isomers, which is one of the more important characteristics of wines aged in this wood, independent of grape variety (*41, 42*). The wines aged in Spanish *Q. pyrenaica* showed concentrations of two isomers similar to those of wines aged in American oak, with wine from Rioja having the highest level of all. These high concentrations of whiskey lactones are related to the high concentrations detected in *Q. pyrenaica* wood from Salamanca, especially before toasting (4.04 μg/g *trans* and 87.7 μg/g *cis*, before toasting, and 1.10 μg/g *trans* and 10.51 μg/g *cis*, after toasting) (*14*), confirming the results obtained in other papers (*7, 21*) that describe a closer relationship between the levels of whiskey lactones in wine and in seasoned wood than in wine and in toasted wood. In other wines aged in Spanish *Q. pyrenaica* but from Basque Country, the levels of whiskey lactones detected were similar to those of wines aged in French oak (*21*).

In addition, differences among wines related to the kind of wine were detected if we take into account the four wines aged in *Q. pyrenaica*, but only for the *cis* isomer. The wine with the highest capacity to extract this compound from wood was Rioja wine, and the lowest was Toro wine, but differences were not significant among all of the wines. Similar results for the *cis* isomer were obtained by Ortega-Heras et al. (*27*) when aging 12 red single variety wines in American oak barrels.

The ratio between the two isomers (*cis*/*trans*) has been used by many authors as a marker for distinguishing wines aged in barrels of American or French oak (*25, 31*), since it is usually around 2 in the wines aged in French oak and higher than 5 in the wines aged in American oak. The wines aged in Spanish *Q. robur* and *Q. petraea* oaks present a *cis*/*trans* ratio similar to that of the wines aged in French oak, since they are the same species, and significantly different to that of the wines aged in American oak (*21, 41*). In wines aged in Spanish *Q. pyrenaica* oak wood barrels, this ratio is around 4, superior to that of the wines aged in French oak and inferior to the ones aged in American oak, independently of the kind of wine.

These compounds correspond to toasted, wood, coconut, or vanilla notes, and they can exercise a synergistic effect on the aromatic implications of phenolic aldehydes like syringaldehyde and especially vanillin (*43*). In all of the wines, the concentration of the *cis* isomer was above 54 μg/L, the threshold level in red wines, but that of the *trans* isomer was below its threshold level (370 μg/L), except in wines aged in Spanish *Q. petraea* from Navarra (*44*).

The wine, before aging, contains small quantities of maltol. This compound is extracted throughout the whole process of aging and communicates aromas such as caramel and toast. The concentrations detected were similar in all wines (**Table 2**), with few statistically significant differences, although the highest levels were reached in wines aged in American oak wood (Bierzo and Ribera de Duero) or in those aged in *Q. pyrenaica* (Toro and Rioja), according to data in the literature referring to wines aged in American and French oak (*21*). In any case, superior concentrations than detection threshold (5000 μg/L in synthetic solution) (*32*) were reached, for which reason its aromatic implication in these wines is minimal.

The levels in the wines of oak-related volatile phenols (guaiacol; 4-methylguaiacol; phenol; *o*-, *p*-, and *m*-cresol; eugenol, *t*-isoeugenol; and 2,6-dimethoxyphenol and derivatives) (**Table 3**) were also related to the wood and wine types. Looking at eugenol and guaiacol, the most important for their sensorial properties, the wines aged in *Q. pyrenaica* wood showed the highest concentrations, although the differences observed for guaiacol were not always statistically significant. These results are in accordance with their levels in the toasted wood layer, especially for eugenol, which was higher in Spanish *Q. pyrenaica* (1−22 μg/g) than in American (1−8 μg/g) or French

Table 3. GC Quantitative Evaluation of Volatile Phenols (Micrograms per Liter of Wine) in Wines from Different Spanish DOs, Aged in Spanish, French, and American Oak Wood Barrels, after 12 Months of Aging[a]

		Bierzo				Ribera de Duero			Toro			Rioja		
		Py	Am	Fr	Na	Py	Am	Fr	Py	Am	Fr	Py	Am	Fr
guaiacol	*x*	42.1 bc	40.9 bc	27.2 c	31.2 bc	33.9 bc	54.6 b	40.2 bc	31.2 bc	27.1 c	25.3 c	76.1 a	41.5 bc	36.3 bc
4-methylguaiacol	*x*	36.9 c	32.5 c	24.1 de	22.8 de	37.2 c	65.7 a	47.6 b	16.5 de	15.6 e	17.2 de	35.9 c	21.9 de	25.6 d
phenol	*x*	19.1 c	17.5 c	12.1 cde	14.9 cd	6.64 de	15.1 cd	9.32 de	8.54 de	7.59 de	5.95 e	36.7 b	36.8 b	45.1 a
o-cresol	*x*	1.51 b	1.94 b	1.08 b	1.31 b	1.23 b	1.57 b	1.16 b	2.16 b	1.72 b	1.89 b	3.17 a	2.12 b	2.24 b
p-cresol	*x*	3.68 a	3.66 a	2.25 bc	2.08 bc	1.68 c	2.87 ab	1.62 c	1.57 c	1.24 c	1.21 c	3.64 a	1.93 c	1.87 c
m-cresol	*x*	1.39 bcd	1.56 bc	0.98 cd	1.04 cd	0.91 cd	0.95 cd	0.85 cd	0.73 cd	0.64 d	0.66 d	3.25 a	1.91 b	1.93 b
eugenol	*x*	84.2 bc	51.9 de	22.7 f	43.7 def	81.1 bc	60.6 cd	29.7 ef	96.2 b	50.4 def	36.2 def	116 a	63.3 cd	35.7 def
t-isoeugenol	*x*	41.9 de	41.4 de	26.8 e	29.9 e	93.7 bc	82.2 c	99.9 bc	57.5 d	30.3 e	28.2 e	111 ab	81.4 c	120 a
2,6-dimethoxyphenol	*x*	367 bc	327 bc	290 bc	255 bc	373 bc	724 a	511 ab	241 bc	185 c	194 c	736 a	302 bc	631 a
4-methyl-2,6-dimethoxyphenol	*x*	131 cde	144 cd	102 defg	115 def	185 c	347 a	242 b	42.4 fg	25.7 g	40.7 fg	100 defg	40.7 fg	65.2 efg
4-allyl-2,6-dimethoxyphenol	*x*	65.2 efg	80.6 efg	46.2 g	51.4 fg	125 bcd	176 a	135 bc	131 bc	97.3 cde	87.9 def	154 ab	105 cde	104 def
4-ethylguaiacol	*x*	43.7 c	24.9 cd	31.5 cd	45.9 c	8.07 f	20.7 ef	14.6 ef	45.3 c	77.1 b	105 a	5.26 f	4.98 f	5.59 f
4-propylguaiacol[b]	*x*	15.1 c	21.1 b	8.59 d	9.65 d	1.75 e	2.88 e	3.14 e	19.6 b	33.5 a	24.3 b	2.19 e	3.59 e	3.25 e
4-vinylguaiacol[b]	*x*	93.1 ef	109 def	73.5 f	68.3 f	178 cdef	269 bc	204 bcde	271 bc	229 bcd	221 bcd	315 b	242 bc	409 a
4-ethylphenol	*x*	161 c	205 bc	155 c	226 ab	10.1 d	31.6 d	16.1 d	220 ab	170 c	251 a	8.06 d	15.4 d	14.5 d
4-vinylphenol	*x*	2247 bc	3028 a	1910 cde	1941 cde	2241 bcd	2521 b	2364 bc	1954 cde	1922 cde	2016 cde	1455 e	1406 e	1569 de

[a] The average (*x*) was calculated for three samples. Different letters in the same row denote a statistical difference with 95% confidence level (Student−Newman−Keuls multiple range test). Py, *Q. pyrenaica* Spanish oak from Salamanca; Am, *Q. alba* American oak from Missouri; Fr, *Q. petraea* French oak from Centro region; and Na, *Q. petraea* Spanish oak from Navarra. [b] Expressed as 4-ethylguaiacol equivalent.

(0−4 μg/g) (*6, 14, 45*) toasted oak. These phenols did not reach their sensory thresholds (500 μg/L for eugenol and 75 μg/L for guaiacol) in the wines (*46*), but in a complex medium like wine, addition and synergistic effects can take place and show sensory influences even with concentrations lower than threshold.

Rioja wine aged in *Q. pyrenaica* wood revealed a higher capacity to extract these compounds from wood, with statistically significant differences in relation to other wines aged in *Q. pyrenaica*. It also showed this same high capacity to extract other volatile phenols from oak wood, such as phenol, *o*-, *p*-, and *m*-cresol, *t*-isoeugenol, 2,6-dimethoxyphenol, and 4-allyl-2,6-dimethoxyphenol, with statistically significant differences in relation to other wines aged in *Q. pyrenaica*. Again, different wines aged in barrels made with basically the same oak wood showed different characteristics. This wine also showed higher concentrations, with statistically significant differences, for most of these compounds in relation to the same wine aged in American or French oak wood. However, it was not possible to correlate a wood type to a higher or lower extraction of these compounds in all wines, since if in one case Rioja the wine aged in *Q. pyrenaica* was the one that had higher concentrations; in another case, it was Ribera de Duero aged in American oak. The wines from Toro and Bierzo did not show statistically significant differences among kinds of wood, except for eugenol and *t*-isoeugenol in Toro wine and 4-methylguaiacol, phenol, *p*-cresol, eugenol, and *t*-isoeugenol in Bierzo wine.

These compounds were extracted from wood during the whole period of aging in oak barrels, showing significant increases in their levels between 6 and 12 months of aging. Generally, the extraction was slower in the first 6 months, except in Ribera de Duero wines that were extracted at a constant rate during the entire 12 months. Similar results were obtained by Garde et al. (*26*) and Ortega-Heras et al. (*27*), when aging different varietal wines in new American oaks barrels: The kinetics of extraction of these compounds is related to the characteristics of the wine.

The rest of the volatile phenols reflected in **Table 3** are also provided by the wood but in very small quantities. They are formed during wine aging by microbiological transformation of hydroxycinnamic acids of wines (*17*), whose levels show important variability among grape varieties, origin, and cultural practices (*47*). However, we think that the differences found among wines cannot be explained only by varietal characteristics, especially for 4-ethyl derivatives and 4-propylguaiacol, considering the levels of these compounds correlated to those of 4-ethylguaiacol, as was recently proposed (*37, 38*). The significantly higher levels of these three compounds in Bierzo and Toro wines might have been due to an increase in microbial activity, probably related with the aforementioned low sulfur dioxide levels in these two wines. The SO_2 inhibits microbial growth and prevents the conditions that favor the formation of 4-ethyl derivatives from 4-vinyl (*17*), although it is hard to keep the concentration stable over prolonged aging periods in barrels where the environment is lightly oxidizing. Almost certainly the decrease of its level at any point in the aging process gave rise to a higher microbial activity and a higher formation of 4-ethyl and 4-propyl derivatives. Bierzo and especially Toro wines showed statistically significant differences depending on wood type, but at this point, we do not have a possible explanation for that. Elevated concentrations of 4-ethylphenol in red wine are associated with disagreeable aromas described as phenolic, animal, or stable. The sensorial threshold of this compound is 620 μg/L in red wine (*48*). 4-Ethylguaiacol affects wine aroma to a lesser extent, but it is also related to disagreeable aromas, as phenolic, bacon, or smoked. The sensorial threshold of this compound is 140 μg/L in red wine (*49*). However, its sensory impact is additive, and the sensorial threshold of a mixture of the two compounds is 420 μg/L. In any case, concentrations superior to detection threshold were reached for all where its aromatic implication in these wines is low.

In relation to 4-vinyl derivatives, their concentrations were similar in all wines studied, except 4-vinylguaiacol in Bierzo wine, significantly lower than in Toro and Rioja wines, and 4-vinylphenol in Rioja wine, significantly lower than in Ribera de Duero and some Bierzo wines. Similar levels of these compounds were described in other wines, with important varietal differences, highlighting the high levels in Tempranillo wines as compared to those of Merlot or Cabernet Sauvignon wines (*50*). Significant differences due to wood type were not detected among the wines. The sensory thresholds for these compounds in red wine are 380 μg/L for 4-vinylguaiacol and 1500 μg/L for 4-vinylphenol, contributing with notes as pink pepper, clove, or dature, respectively (*46*).

The extraction of vanillin, syringaldehyde, and other phenolic compounds displayed in **Table 4** was also related to wine and wood kind. Looking at the two phenolic aldehydes, wines aged

Table 4. GC Quantitative Evaluation of Phenolic Aldehydes and Related Compounds (Micrograms per Liter of Wine) in Wines from Different Spanish DOs, Aged in Spanish, French, and American Oak Wood Barrels, after 12 Months of Aging[a]

		Bierzo				Ribera de Duero			Toro			Rioja		
		Py	Am	Fr	Na	Py	Am	Fr	Py	Am	Fr	Py	Am	Fr
vanillin	*x*	342 d	540 b	389 cd	357 d	512 bc	806 a	854 a	347 d	437 bcd	490 bcd	574 b	482 bcd	466 bcd
HMPA[b]	*x*	46.1 bc	36.1 bc	41.9 bc	29.4 c	104 abc	85.6 abc	100 abc	67.8 abc	84 abc	60.7 abc	127 a	74 abc	115 ab
acetovanillone	*x*	121 cde	153 bcde	102 e	112 de	223 b	286 a	309 a	138 cde	128 cde	146 bcde	203 bc	174 bcde	192 bcd
HMPP[b]	*x*	200 e	512 b	175 e	160 e	423 cd	522 b	620 b	583 b	385 cd	334 d	904 a	571 b	389 cd
propiovanillone[b]	*x*	171 bc	226 a	145 c	153 bc	159 bc	147 c	219 a	140 c	166 bc	95.3 d	154 bc	193 ab	145 c
HMPB[b]	*x*	19.1 ab	17.5 ab	19 ab	20.6 ab	16.1 ab	22.7 ab	26.1 ab	17.5 ab	14.5 b	14.9 b	28.6 a	25.3 ab	22.3 ab
butyrovanillone[b]	*x*	977 ab	995 ab	981 ab	952 ab	1034 ab	937 ab	981 ab	897 ab	488 c	417 c	1164 a	752 b	769 b
methyl vanillyl ether[c]	*x*	523 b	592 b	561 b	551 b	794 a	888 a	816 a	498 b	563 b	449 b	494 b	516 b	509 b
ethyl vanillyl ether[c]	*x*	1600 a	1764 a	1607 a	1559 a	1353 a	1496 a	1656 a	1582 a	1644 a	1572 a	1530 a	1535 a	1510 a
syringaldehyde	*x*	553 d	1378 c	743 d	735 d	1306 c	2274 a	2244 a	1318 c	1687 b	1727 b	1748 b	1715 b	1495 bc
acetosyringone	*x*	178 b	232 b	159 b	142 b	321 a	485 a	593 a	167 b	174 b	195 b	249 b	197 b	218 b
HDMPP[d]	*x*	444 e	972 cd	253 e	233 e	940 cd	1362 bc	1294 b	1426 b	1128 bcd	812 d	1980 a	1221 bc	895 cd
propiosyringone[d]	*x*	223 a	187 ab	194 ab	190 ab	198 ab	187 ab	176 ab	202 ab	119 c	12 c	228 a	157 bc	196 ab

[a] The average (*x*) was calculated for three samples. Different letters in the same row denote a statistical difference with 95% confidence level (Student−Newman−Keuls multiple range test). Py, *Q. pyrenaica* Spanish oak from Salamanca; Am, *Q. alba* American Oak from Missouri; Fr, *Q. petraea* French Oak from Centro region; and Na, *Q. petraea* Spanish oak from Navarra. [b] Expressed as acetovanillone equivalent. [c] Expressed as vanillin equivalent. [d] Expressed as acetosyringone equivalent; HMPA, 2-(4-hydroxy-3-methoxyphenyl) acetaldehyde; HMPP, 1-(4-hydroxy-3-methoxyphenyl)-2-propanone; HMPB, 1-(4-hydroxy-3-methoxyphenyl)-2-butanone; and HDMPP, 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone.

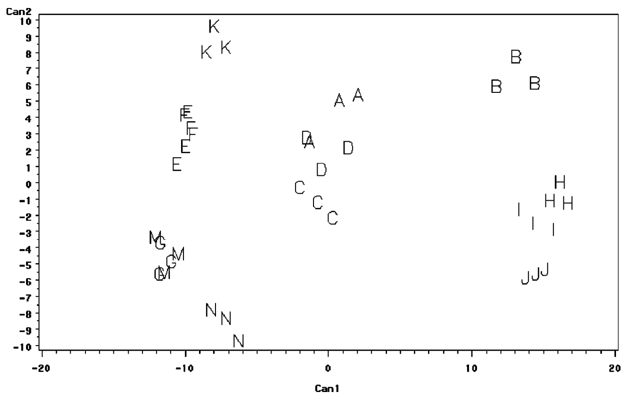

Figure 1. Canonical discriminant analysis of lactones, furanic compounds, and pyranones in wines from different Spanish DOs, aged in Spanish, French,and American oak wood barrels, after 12 months of aging. A, Bierzo *Q. pyrenaica*; B, Bierzo *Q. alba*; C, Bierzo *Q. petraea* French oak; D, Bierzo *Q. petraea* Spanish oak from Navarra; E, Ribera del Duero *Q. pyrenaica*; F, Ribera del Duero *Q. alba*; G, Ribera del Duero *Q. petraea* French oak; H, Toro *Q. pyrenaica*; I, Toro *Q. alba*; J, Toro *Q. petraea* French oak; K, Rioja *Q. pyrenaica*; M, Rioja *Q. alba*; and N, Rioja *Q. petraea* French oak (76.57% of dispersion. Canonical correlations of 0.99 and 0.98 and eigenvalues of 163.9 and 36.2 for Can 1 and Can 2, respectively. The total canonical structure coefficients of functions 1 and 2 were, respectively, as follows: furfural, −0.44 and 0.20; 5-methylfurfural, −0.55 and 0.22; furfuryl alcohol, 0.95 and −0.05; HMF, −0.47 and 0.65; *trans*-β-methyl-γ-octalactone, −0.13 and 0.08; *cis*-β-methyl-γ-octalactone, 0.06 and 0.71; *cis*/*trans* ratio 0.01 and 0.29; and maltol; −0.01 and 0.47.

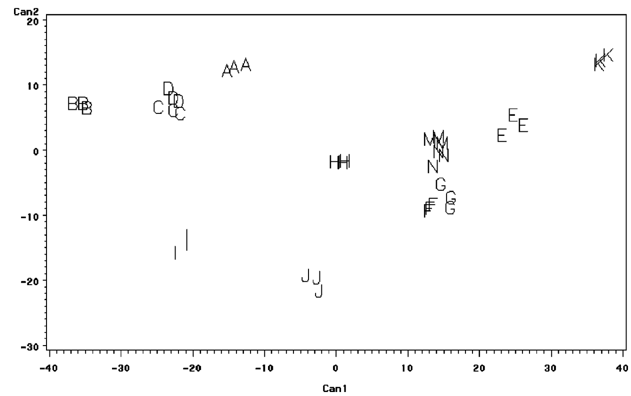

Figure 2. Canonical discriminant analysis of volatile phenols in wines from different Spanish DOs, aged in Spanish, French, and American oak wood barrels, after 12 months of aging. Letters A−N are the same as in **Figure 1**; 79.87% of dispersion. Canonical correlations of 0.99 and 0.99 and eigenvalues of 666.7 and 147.0 for Can 1 and Can 2, respectively. The total canonical structure coefficients of functions 1 and 2 were, respectively, as follows: guaiacol, 0.51 and 0.38; 4-methylguaiacol, 0.36 and 0.08; 4-ethylguaiacol, −0.40 and −0.66; 4-propylguaiacol −0.66 and −0.41; 4-vinylguaiacol, 0.63 and −0.30; phenol, 0.38 and 0.40; 4-ethylphenol, −0.85 and −0.10; 4-vinylphenol, −0.39 and −0.08; *o*-cresol, 0.35 and 0.12; *p*-cresol, −0.06 and 0.65; *m*-cresol, 0.42 and 0.55; eugenol, 0.42 and 0.42; isoeugenol, 0.85 and 0.13; 2,6-dimethoxyphenol, 0.60 and 0.19; 4-methyl-2,6-dimethoxyphenol, 0.21 and 0.02; and 4-allyl-2,6-dimethoxyphenol, 0.72 and −0.22.

in American or French oak showed the highest concentrations, except Rioja wine, but in this case, the differences were not significant. Similar results were obtained in an earlier work and were partly in accordance with its levels in the toasted wood layer (*21*). Vanillin is associated with a vanilla aroma but also with coffee, black chocolate, or smoked (*15*). The quantities given by the barrels top the sensory threshold for red wine (320 μg/L). Syringaldehyde has a higher sensory threshold (50000 μg/L) that was not reached in any wine. The rest of the compounds in **Table 4** showed few significant differences among wood types, but when they existed, they followed the same pattern as aldehydes: Wines aged in American or French oak showed the highest concentrations, except in the case of Rioja wine. Wines aged in *Q. pyrenaica* oak wood barrels only showed higher concentrations of HMPP, butyrovanillone, HDMPP, and propiosyringone in Toro and Rioja wines, with respect to the same wines aged in American or French oak. Bierzo wine aged in *Q. pyrenaica* does not present any difference with respect to the same wine aged in *Q. petraea* (French or Spanish). Ribera de Duero wine aged in *Q. pyrenaica* showed low concentrations of these compounds with respect to the same wine aged in American or French oak. As we can see from aforementioned compounds, it was not possible to relate a wood type with a higher or lower extraction of all of these compounds in all wines.

If we take into account only the wines aged in *Q. pyrenaica*, Rioja (in the cases of vanillin, HMPA, HMPP, syringaldehyde, and HDMPP) and Ribera de Duero (in the cases of vanillin,

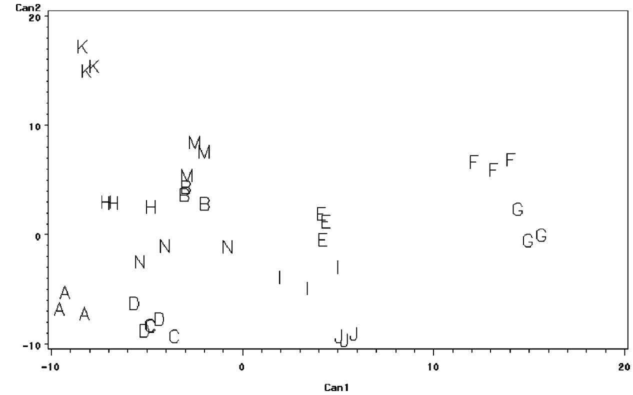

Figure 3. Canonical discriminant analysis of phenolic aldehydes and other lignin-derived compounds in wines from different Spanish DOs, aged in Spanish, French, and American oak wood barrels, after 12 months of aging. Letters A−N are the same as in **Figure 1**; 70.38% of dispersion. Canonical correlations of 0.99 and 0.99 and eigenvalues of 81.9 and 74.3 for Can 1 and Can 2, respectively. The total canonical structure coefficients of functions 1 and 2 were, respectively, as follows: vanillin, 0.77 and 0.45; HMPA, 0.22 and 0.49; acetovainillone 0.68 and 0.51; HMPP, 0.12 and 0.93; propiovanillone, 0.06 and 0.43; HMPB, −0.002 and 0.53; butirovanillone, −0.22 and 0.43; methyl vanillyl ether, 0.73 and 0.15; ethyl vanillyl ether, −0.06 and −0.03; syringaldehyde, 0.73 and 0.52; acetosyringone, 0.75 and 0.36; HDMPP, 0.21 and 0.83; and propiosyringone, −0.42 and 0.29.

acetovanillone, acetosyringone, and methyl vanillyl ether) wines showed the highest capacity to extract these compounds from wood, with statistically significant differences in relation to other wines aged in *Q. pyrenaica*.

To establish the overall characteristics of these wines after 12 months of aging, with regard to oak-related volatile compounds, three canonical discriminant analyses were carried out taking into account the compounds listed in **Tables 2−4**. The graphic representation on the plane determined by the two main canonical axes (**Figures 1**, **2**, and **3**, respectively) shows groups of points related to oak type and wine, particularly in the first two figures. In **Figure 1**, wines from Rioja (K−N) and Ribera de Duero (E−G) appear separated from those of Bierzo (A−D), and especially from those of Toro (H−J), considering canonical function 1, which accounted for 62.7% of total variance, and was related, according to the coefficients of total canonical structure, mainly to levels of furfuryl alcohol, with a positive coefficient, and in smaller proportion furfural, 5-methylfurfural, and HMF, with negative coefficients. Considering canonical function 2, which was related mainly to levels of *cis*-β-methyl-γ-octalactone, HMF, and maltol, all with positive coefficients, we can see that among wines from the same wine cellar, there were statistical distances with regard to the kind of wood. The largest distances appear in Rioja (K, M, and N) and Ribera de Duero (E, F, and G) wines.

A higher discrimination among wine and oak kinds was obtained when we took into account the volatile phenols (**Figure 2**). Also in this case, wines from Rioja (K−N) and Ribera de Duero (E−G) appear separated from those of Bierzo (A−D) and Toro (H−J), considering the canonical function 1, which accounted for 65.44% of total variance, and was related mainly to levels of 4-ethylphenol, with a negative coefficient, and isoeugenol and 4-allyl-2,6-dimethoxyphenol, with positive coefficients. In this figure, we can also see that the distances between the wines from the first two wine cellars (Rioja and Ribera de Duero) were small, considering both canonical functions 1 and 2, particularly for wines aged in French and American oaks (M, N, F, and G). Canonical function 2 showed negative coefficients for the 4-ethyl, 4-vinyl, and 4-propyl derivatives of guaiacol and phenol and positive for the other compounds, except 4-allyl-2,6-dimethoxyphenol, and it allows discrimination between Bierzo and Toro wines. The statistical distances among the 13 wines obtained at the end of barrel aging were small regarding phenolic aldehydes and other lignin derivatives (**Figure 3**), with it being possible to distinguish only Ribera de

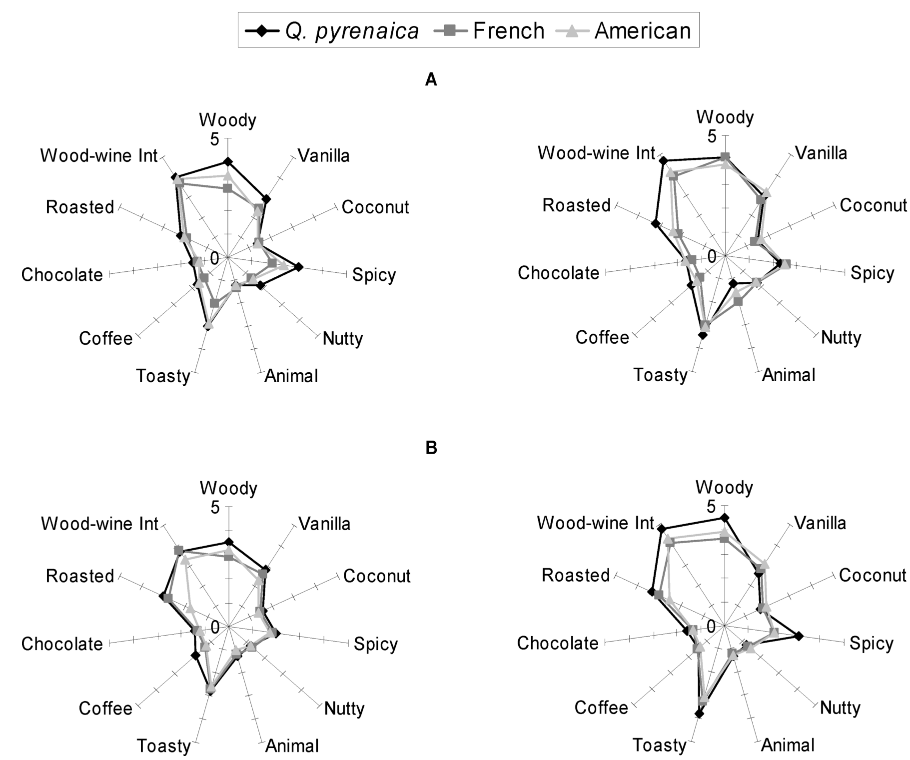

Figure 4. Sensory profile of the olfactive phase (aromas related to the wood−wine interaction) of wines from the four DOs studied after 12 months of aging in barrels. (**A**) Bierzo, (**B**) Ribera del Duero, (**C**) Toro, and (**D**) Rioja.

Duero wines from those of Bierzo and Rioja, considering canonical function 1 (36.9% of total dispersion), which was related mainly to levels of vanillin, acetosyringone, and syringaldehyde (positive coefficients). All wines aged in *Q. pyrenaica* barrels (A, E, H, and K) broke away from their homologues aged in other oaks, as well as it happens in **Figure 2** and for Rioja wine in **Figure 1**. Thus, we can deduce that Spanish *Q. pyrenaica* barrels could provide wines with different characteristics to those supplied by oak woods traditionally used in cooperage (French *Q. petraea* and American *Q. alba*).

On the other hand, the varietal characteristics of each wine were very important in the wood–wine interaction, since the four wines aged in *Q. pyrenaica* barrels (A, E, H, and K) showed statistical distances among them big enough to show a clear discrimination, in **Figures 1–3**, although these barrels were made with wood from the same forest, felled at the same time, seasoned at the same place and time, and toasted for the same cooperage, at the same time and intensity: The wines showed different extraction capacities for wood compounds, and so, with the same wood (*Q. pyrenaica*), we have obtained different wines depending on the grape variety.

Although it is not the objective of this work, we find it interesting to highlight that, as we can see in three figures derived from discriminant analysis (**Figures 1–3**), the Bierzo wines aged in *Q. petraea* from both French (C) and Spanish (D) origin, were overlapping. This confirms the results obtained in other studies, in which barrels of oak wood of *Q. petraea* from Navarra (Spain) were compared to barrels of *Q. petraea* from Centre Region (France), made by five different cooperages, showing a great similarity between the woods from these two origins (*40, 50*).

Sensory Analysis. According to results obtained in sensory analysis of wines before aging, it was considered that the four studied wines were capable of being aged in barrels, since they were wines with high color intensity, rich in fruity aromas, balanced and structured in mouth, and with an appropriate tannic and phenolic level for their stay in barrel. After 12 months in the barrel, in none of the four studied wines were appreciable differences in the visual phase descriptors or attributes found among the three oak wood types, for which reason we suggest that the oak type did not affect the chromatic characteristics of the wines. In the olfactive phase, there were no differences in the primary and secondary aromas, which are the fruity, herbaceous/green, and vegetable/cabbage aromas, nor in unwanted aromas like dirty, sulfhydric, etc. Only the wines aged in American oak presented higher ripened fruit aromas than the wines aged in *Q. pyrenaica* and in French oak.

The main differences were found in the olfactive phase, in the attributes related to aging in barrels, which is to say with the wood (**Figure 4**). This way, in general, the wines aged in *Q. pyrenaica* presented higher values of the attributes woody and wood–wine interaction, as well as toasty, roasty, and white coffee. Besides, the wines of Bierzo and Rioja aged in *Q. pyrenaica* were noted for their high spicy notes. This fact was not observed in the other two wines.

In the gustative phase, at 12 months of aging, there were few differences, and these were not very important in most of the parameters. We would only like to highlight that the wines of Ribera de Duero aged in American oak presented smaller valuations of grease, balance, and global valuation and that, in general, the wines aged in *Q. pyrenaica* presented a higher global valuation.

In the arrangement for preference, the wines aged in *Q. pyrenaica* were consistently the favorites, although in Bierzo and Rioja wines, there were no significant differences among oak kinds, since wines aged in *Q. pyrenaica* or American oak wood took turns in the first place together with wines aged in French oak wood, according to the personal preference of each judge. The Ribera de Duero and Toro wines aged in *Q. pyrenaica* were the favorites for 70 and 55% of expert judges, respectively.

Taking into account the joint overall results, we can conclude that each oak wood added unique and special characteristics to the wine, and in addition, each wine showed a different ability to extract these compounds from the oak wood. In general, wines aged in *Q. pyrenaica* wood were characterized by high levels of eugenol, guaiacol, and other volatile phenols. With regard to compounds like *cis*-whiskylactone or maltol, the behavior of this wood is very similar to that of American oaks. When considering phenolic aldehydes and ketones, the levels of these compounds are intermediate between those of French and American woods and depend greatly on the type of wine. In sensory analysis, the biggest differences are found in the olfactory phase. Among the four DOs studied, wine aged in *Q. pyrenaica* presented the highest notes of wood, with more aromas of roasting, toasting, milky coffee, spices, or wine–wood interactions. The wines aged in barrels made of *Q. pyrenaica* wood were highly regarded, and preference was shown for them over those same wines when they had been aged in barrels of American or French oak.

ACKNOWLEDGMENT

We thank Antonio Sánchez for his help throughout the chemical analysis; Tonelería Intona S.A. for his collaboration; and CIDA, Pago de Carraovejas, Rejadorada, and Pittacum wine cellars for supplying the wine for this study and manipulating it during aging.

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Received for review May 9, 2008. Revised manuscript received August 4, 2008. Accepted August 7, 2008. This study was financed by the Spanish Government (Project RTA-05-022). M.S. received a grant from the INIA FPI program.

JF8014602