

Volatile Compounds in Spanish, French, and American Oak Woods after Natural Seasoning and Toasting

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The volatile composition (volatile phenols, phenolic aldehydes, furanic compounds, lactones, phenyl ketones, and other related compounds) of Spanish oak heartwood of *Quercus robur*, *Quercus petraea*, *Quercus pyrenaica*, and *Quercus faginea* was studied by gas chromatography/mass spectrometry, in relation to the processing in barrels cooperage and in relation to the French oak of *Quercus robur* (Limousin) and *Quercus petraea* (Allier) and American oak of *Quercus alba* (Missouri), which are habitually used in cooperage. The volatile composition of seasoned oak woods varied according to individual trees, species, and origins, and the differences were more significant in Spanish species with respect to American species than with respect to French species. The toasting process influenced the volatile composition of wood. It led to high increases in the concentration of volatile phenols, furanic aldehydes, phenyl ketones, and other related structures, but the effect on w-lactones levels depended on species and origin. The volatile composition in Spanish oak species evolved during toasting like in French and American oak, but quantitative differences were found, especially important in American species with respect to European species.

KEYWORDS: Volatile compounds; seasoning; toasting; oakwood; *Quercus robur*; *Quercus petraea*; *Quercus pyrenaica*; *Quercus faginea*; *Quercus alba*

INTRODUCTION

The need for new sources of quality wood supplies for cooperage and, moreover, for new searches and profitable applications of Spanish forestry areas has led many to consider the utilization of Spanish oak as an alternative to French and American ones, habitually used in enology. We carried out several studies on the phenolic composition of Spanish oak wood (1–3) and their evolution during natural seasoning and toasting in the barrel-making process (4–6). The low molecular weight phenolic and tannic composition of the Spanish species and their evolution during seasoning and toasting were similar to those of French and American oak woods, and the quantitative differences that were found were less marked with respect to French than American species.

During barrel wine aging, physical, chemical, and physical–chemical processes take place, in which the phenolic composition of the oak wood plays an important role. It is evident that the phenolic components are involved especially in oxidation processes during aging, which are directly related to color and organoleptic properties of wine (like astringency and bitterness) (7, 8) and depend on the barrel wood quality (9–13). As a part of the study of Spanish oak wood, the evolution of color percentage intensity, phenolic compounds families, and low molecular weight phenolic compounds was studied in a Spanish red wine aged for 21 months in barrels made of Spanish, French,

and American species of woods, obtaining wines with different characteristics in relation to the kind of barrel wood. The wine aged in barrels made of Spanish oak woods showed similar or intermediate characteristics to those of the same wine aged in French and American oak woods (13).

However, in addition to phenols, other volatile compounds are extracted from the oak wood into the wine during aging that have been related with flavor properties in wine. Of course, a lot of aromas and flavors in wines come in from the grape, although not all are evident in the fruit prior to fermentation, but others are associated to conservation and the aging process. A lot of volatile compounds extracted from oak wood were identified, and their contribution to the aroma and flavor in wine has been objective in several research projects. The cis and trans isomers of β -methyl- γ -octalactone (7, 14, 15), furfural and its derivatives (16, 17), phenolic aldehydes such as vanillin and syringaldehyde, and volatile phenols such as eugenol, guaiacol, and ethyl and vinyl phenols (14) can be pointed out by their contribution to the wine aroma differences. Only some of them are originally present in wood in significant amounts, depending on the oak species and geographical origin (18–21), but many of them can be intensified during the processing of wood in cooperage, through seasoning and the toasting process (22–26). The seasoning contribution, in relation to the toasting process, appears to be limited but not negligible. During seasoning, the intensification of the oak lactones concentrations was more evident, but also, changes in the levels of volatile phenols, such as eugenol (26–28) and phenolic aldehydes

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(vanillic, syringic, coniferilic, and sinapic aldehydes) were also observed (4, 5, 27, 28).

The process of barrel toasting probably has the most influence on the chemical composition of the wood. It is carried out by applying heat and humidity in order to facilitate stave assembly and a second heating in order to help the superficial degradation of oak wood that produces new aromatic compounds (16, 18, 29, 30). During these processes, a variety of hydrothermolysis and pyrolysis reactions take place, producing the degradation of biopolymers, such as lignin, polyosides, polyphenols, and lipids. The thermodegradation of lignin mainly leads to the formation of volatile phenols and phenolic aldehydes, some phenolic alcohols, and phenyl ketones. Whereas the nontoasted oak wood had only a little quantity of volatile phenols, mainly eugenol, and traces of phenolic aldehydes, the toasted wood had a variety of mono- and dimethoxylated phenols and high levels of benzoic and cinnamic aldehydes (18, 22, 23, 29, 31–34).

The polyosides degradation leads up to furanic aldehydes, mainly furfural and 5-hydroxymethylfurfural (23, 35). Especially the hexoses, such as the glucose of cellulose, produce 5-hydroxymethylfurfural and 5-methylfurfural, whereas the pentoses, principal constituent of hemicelluloses, produce furfural (36) through reactions catalyzed by acetic acid (22). These compounds contribute to the wine aroma with a burnt almond odor (18, 35). Other volatile odorous compounds derived from sugar degradation, such as pentacyclic and hexacyclic ketones, were also identified in toasted wood but with a limited aromatic role (17, 22, 23, 37).

The degradation by heat of wood lipids leads to lactones, which are regarded as the most important of the oak volatile compounds that contribute to the flavor of barrel-aged alcoholic beverages, because of their small sensory threshold (7, 14, 16, 38, 39). The oak wood has two isomers, *cis* and *trans*, of β -methyl- γ -octalactone, responsible for the characteristic odor of oak, which is present in nontoasted wood in important quantities depending on the species and origin (14, 19, 40) and in toasted wood in quantities depending on the toasting conditions. At the beginning of toasting, the quantity of γ -lactones increases, but if the toasting is lengthy, a total destruction of these compounds can happen (22, 23).

This paper is a part of a series of extensive research about the performance of Spanish oak woods for barrel production. We have already studied the phenolic composition of Spanish species (*Quercus robur*, *Quercus petraea*, *Quercus pyrenaica*, and *Quercus faginea*), in relation to the processing of wood in cooperage (1–6), and their effect on color and phenolic compounds in a Spanish red wine aged in barrels made from these woods (13). In this work, we show the results obtained about the volatile composition of Spanish woods and their evolution with the toasting process, as compared with French (*Quercus robur* and *Quercus petraea*) and American (*Quercus alba*) oak woods.

MATERIALS AND METHODS

Collection of Wood Samples. Heartwood staves from trees grown in the Alava province (Spain), *Q. robur* (from seven trees), *Q. petraea* (from three trees), *Q. pyrenaica* (from five trees), and *Q. faginea* (from three trees), were placed in Bordeaux (France) (in Demptos Cooperage) (average annual temperature, 12.5 °C; total precipitation, 950 mm³/year; average over 50 years), where the process of natural seasoning in the open air was carried out for 3 years to make the barrels (about four barrels of each species). During the process, the staves were toasted at a medium intensity level (35 min; temperature on the wood surface,

160–170 °C), in the traditional way over a wood fire, according to the manufacturing process used at the cooperage (41). Heartwood staves of French oak of *Q. robur* (Limousin) and *Q. petraea* (Allier) and American oak of *Q. alba* (Missouri), before and after toasting, were also provided by the same cooperage.

Wood samples were taken from the nontoasted and toasted staves (a minimum of four staves of each species and each geographical origin). Three pieces of wood were cut from the center and the headboards of the staves. In the pieces obtained from toasted staves, the layer of toasted wood was cut off to a depth of 4 mm with an electric rotary saw. The wood pieces were ground and sieved, using the sawdust ranging in size from 0.80 to 0.28 mm.

Extraction. Volatile compounds were extracted using the following method, based on the method described by Chatonnet et al. (23). The sawdust samples (2 g) were soaked in 100 mL of hydro alcoholic solution (12% ethanol, 0.7 g/L tartaric acid, and 1.11 g/L potassium bitartrate) for 15 days at room temperature and darkness. After the mixture was filtered, we added the internal standard (100 μ L of γ -hexalactone down 2 mg/mL in ethanol) and 15 g of ammonium sulfate, and the solution was extracted with 45 mL of dichloromethane, distributed three times. The organic fraction was dried on anhydrous sodium sulfate and concentrated to 0.5 mL under nitrogen flux in a Kuderna-Danish apparatus, before it was submitted to gas chromatography/mass spectrometry (GC/MS) analysis.

Standards. Reference compounds numbered in **Table 1** as 3, 8, 9, 12, 13, 20, 22, 29, 30, 34, and 35 were purchased from Fluka Chimie AG (Buchs, Switzerland); 10, 19, 23, 24, 25, 36, 38, 48, and 54 from Aldrich Chimie (Neu-Ulm, Germany); 1, 5, 11, 17, 27, 31, 37, and 39 from Sigma Chemical (St. Louis, MO); 7 and 18 from Chem Service (West Chester, U.S.A.); and 42, 51, 55, and γ -hexalactone from Extrasynthèse (Genay, France) Companies.

GC/MS Analysis. GC/MS analysis of extracts was carried out according to Chatonnet et al. (23). A HP 5890 gas chromatograph (Palo Alto, CA), equipped with an HP 5971A selective mass detector and a fused silica capillary column (SUPELCOWAX-10, 30 m \times 0.25 mm i.d. and 0.25 μ m film thickness), was used, under the following working conditions: GC grade helium as carrier gas at flow rate of 1.15 mL/min, 9.00 psi; column temperature program, 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). The injection temperature was 230 °C. Detection was carried out by electron impact mass (EI) in the full scan mode, using an ionization energy of 70 eV and interphase detection temperature of 290 °C. Chromatographic peaks were identified by comparing their retention times and mass spectra with those of standards and/or those reported in the literature. The identities of the two isomers (*cis* and *trans*) of β -methyl- γ -octalactone were assigned according to the work of Chatonnet (7), which shows that the *trans* isomer eluted first on a Carbowax column. Quantitative determinations were carried out from total ion current peak areas, by the internal standard method, using calibration made with standard or with the closest chemical structure, analyzed under the same conditions.

Statistical Analysis. Univariate analysis was done using the BMDP-7D (ANOVA) program (42). Student Newman–Keuls multiple range test was also carried out considering together seasoned and toasted oak woods. Multivariate canonical discriminant analysis was also carried out with all of the compounds evaluated, using the CAND.SAS program (43).

RESULTS AND DISCUSSION

Identifying Compounds Present in Extract from Seasoned and Toasted Spanish Oak Woods. The GC/MS analysis of the hydro alcoholic wood extracts revealed the presence in Spanish oak wood of the majority of the molecules previously identified by other authors in French (7, 17, 22, 44) or American (45, 46) oak woods. Moreover, other volatile compounds not mentioned before in oak wood were found. **Table 1** shows 55 peaks characterized in seasoned and/or toasted wood in at least one of the species studied, with their retention times and their identification methods. Most of the peaks were identified by

Table 1. Volatile Compounds Found by GC/MS in Nontosted or Tosted Spanish, French, and American Oak Woods^a

	compound (IUPAC name)	common name	RT (min)	
1	1-hexanal		5.4	L B S
2	2-pentyl furan		9.3	L B
3	1-hexanol		13.9	L B S
4	1-nonenal		15.5	L B
5	2-furancarboxaldehyde	furfural	18.3	L B S
6	acetic acid		18.3	L B
7	2-ethyl-1-hexanol		19.4	L B S
8	1-(2-furanyl)ethanone	furanyl-1-ethanone	19.9	L B S
9	benzaldehyde		20.5	L B S
10	<i>trans</i> -2-nonenal		21.1	L B S
11	5-methyl-2-furancarboxaldehyde	5-methylfurfural	22.7	L B S
12	dihydro-2(3 <i>H</i>)-furanone	butyrolactone	24.7	L B S
13	2-furanmethanol	furfuryl alcohol	26.3	L B S
14	hydroxybenzaldehyde		26.7	L B
15	2(3 <i>H</i>)-furanone		29.4	L B
16	2-hydroxy-2-cyclopenten-1-one	cyclotene	33.4	L B
17	2-methoxyphenol	guaiacol	33.6	L B S
18	phenylmethanol/benzenemethanol		34.2	L B S
19	<i>trans</i> -4-methyl-5-butylidihydro-2(3 <i>H</i>)-furanone	<i>trans</i> - β -methyl- γ -octolactone	34.6	L B S
20	2-phenylethanol		35.4	L B S
21	unknown compound		35.8	
22	benzothiazole		36.7	L B S
23	<i>cis</i> -4-methyl-5-butylidihydro-2(3 <i>H</i>)-furanone	<i>cis</i> - β -methyl- γ -octolactone	37.2	L B S
24	4-methyl-2-methoxyphenol	4-methylguaiacol	37.2	L B S
25	3-hydroxy-2-methyl-4 <i>H</i> -pyran-4-one	maltol	37.5	L B S
26	2,5-furandicarboxaldehyde		38.1	B
27	phenol		38.8	L B S
28	4-ethyl-2-methoxyphenol	4-ethylguaiacol	39.4	L B
29	1 <i>H</i> -pyrrole-2-carboxaldehyde		39.4	L B S
30	2-phenoxyethanol		43.3	L S
31	2-methoxy-4-(2-propenyl)phenol	eugenol	44.1	L B S
32	4-vinyl-2-methoxyphenol	4-vinylguaiacol	45.0	L B
33	3-hydroxyfuran-2-yl-methyl ketone	isomaltol	45.2	L B
34	2,6-dimethoxyphenol	syringol	47.2	L B S
35	2-methoxy-4-(1-propenyl)phenol	isoeugenol	49.7	L B S
36	4-methyl-2,6-dimethoxyphenol	4-methylsyringol	49.8	L B S
37	5-hydroxymethyl-2-furancarboxaldehyde	5-hydroxymethylfurfural	54.4	L B S
38	4-allyl-2,6-dimethoxyphenol	4-allylsyringol	55.5	L B S
39	4-hydroxy-3-methoxybenzaldehyde	vanillin	56.2	L B S
40	2-(4-hydroxy-3-methoxyphenyl) acetaldehyde		56.9	L
41	4-hydroxy-3-methoxybenzoic acid, ethyl ester	ethyl vanillate	57.3	L B
42	1-(4-hydroxy-3-methoxyphenyl)ethanone	acetovanillone	58.0	L B S
43	1-(4-hydroxy-3-methoxyphenyl)-2-propanone		58.4	L
44	1-(4-hydroxy-3-methoxyphenyl)propanone	propiovanillone	59.7	B
45	1-(4-hydroxy-3-methoxyphenyl)-2-butanone		62.0	L
46	1-(4-hydroxy-3-methoxyphenyl)butanone	butyrovanillone	63.0	B
47	methyl vanillyl ether		63.4	L
48	4-hydroxy-3,5-dimethoxybenzaldehyde	syringaldehyde	67.2	L B S
49	2-(4-hydroxy-3,5-dimethoxyphenyl) acetaldehyde		67.6	L
50	ethyl vanillyl ether		68.0	L
51	1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone	acetosyringone	68.7	L B S
52	1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone		69.3	L
53	1-(4-hydroxy-3,5-dimethoxyphenyl)propanone	propiosyringone	70.9	B
54	3-methoxy-4-hydroxycinnamaldehyde	coniferilic aldehyde	75.9	L B S
55	3,5-dimethoxy-4-hydroxycinnamaldehyde	sinapic aldehyde	93.8	L B S

^a L, compound was identified by comparison of mass spectra with published mass spectra. B, compound was identified before in wood by other authors. S, compound was identified by comparison of mass spectra and retention time with that of standard compound.

comparison of mass spectra and retention times with those obtained from standard compounds when they were available or with those described in the literature data, but others were only tentatively identified using mass spectra library data (Willey). The chromatographic peaks (**Table 1**) indicate individual compounds; the most relevant from a sensory standpoint are volatile phenols, phenolic aldehydes, furanic compounds, lactones, and others. Also, a few molecules that have been identified as causes of disagreeable oak wood aromas (47) were considered (**Table 1**).

Several new molecules in oak wood were detected as follows. 2-Phenoxyethanol: RT (min) 43.3. MS (EI) m/z (%): 94 (100), 77 (35), 138 (30), 66 (20), 51 (20), 95 (15), 65 (12), 45 (12).

Methyl vanillyl ether: RT (min) 63.4. MS (EI) m/z (%): 137 (100), 168 (70), 122 (15), 94 (10), 65 (8), 107 (5). Ethyl vanillyl ether: RT (min) 68.0. MS (EI) m/z (%): 137 (100), 182 (75), 138 (50), 123 (18), 93 (18), 122 (12), 94 (12), 106 (8). Unknown compound: RT (min) 35.8. MS (EI) m/z (%): 99 (100), 155 (15), 57 (15), 41 (12), 139 (10), with a fragmentation that could correspond to a lactone structure. On the other hand, in addition to acetovanillone [RT (min) 58.0; MS (EI) m/z (%): 151 (100), 166 (50), 123 (20), 108 (10)], propiovanillone [RT (min) 59.7; MS (EI) m/z (%): 151 (100), 180 (20), 123 (16), 108 (10)], and butyrovanillone [RT (min) 63.0; MS (EI) m/z (%): 151 (100), 123 (20), 108 (15), 194 (5) (22)], their respective acetaldehyde and 2-one isomers were detected as follows. 2-(4-

Table 2. Volatile Phenols ($\mu\text{g/g}$) of Spanish, French, and American Oak Wood after Natural Seasoning and Toasting

	$\bar{x} \pm \text{SD}$						
	Spanish				French		American
	<i>Q. robur</i>	<i>Q. petraea</i>	<i>Q. pyrenaica</i>	<i>Q. faginea</i>	<i>Q. robur</i>	<i>Q. petraea</i>	<i>Q. alba</i>
	seasoned wood						
guaiacol	0.11 \pm 0.02 a	0.11 \pm 0.03 a	0.08 \pm 0.02 a	0.29 \pm 0.18 a	0.08 \pm 0.01 a	0.12 \pm 0.03 a	0.11 \pm 0.07 a
4-methylguaiacol	0.65 \pm 0.38 ab	0.10 \pm 0.02 a	0.54 \pm 0.32 ab	0.53 \pm 0.33 ab	0.17 \pm 0.08 a	0.37 \pm 0.48 ab	0.76 \pm 0.14 ab
4-ethylguaiacol ^a	0.05 \pm 0.01 ab	0.05 \pm 0.01 ab	0.04 \pm 0.01 ab	0.15 \pm 0.09 ab	0.05 \pm 0.002 ab	0.05 \pm 0.01 ab	0.01 \pm 0.03 a
4-vinylguaiacol ^a	1.03 \pm 0.73 a	0.99 \pm 0.57 a	1.96 \pm 0.46 a	1.07 \pm 0.69 a	1.27 \pm 0.46 a	1.14 \pm 0.41 a	0.51 \pm 0.52 a
phenol	0.29 \pm 0.10 a	0.29 \pm 0.04 a	0.50 \pm 0.08 ab	0.73 \pm 0.27 ab	0.41 \pm 0.07 ab	0.25 \pm 0.04 a	0.39 \pm 0.07 ab
eugenol	1.58 \pm 0.47 ab	0.57 \pm 0.27 a	2.31 \pm 0.94 ab	1.98 \pm 1.46 ab	1.05 \pm 0.93 a	3.23 \pm 2.76 abc	5.74 \pm 3.61 c
isoeugenol	0.32 \pm 0.11 a	0.21 \pm 0.03 a	0.40 \pm 0.04 a	0.36 \pm 0.10 a	0.32 \pm 0.02 a	0.33 \pm 0.14 a	0.34 \pm 0.17 a
syringol	0.23 \pm 0.16 a	0.15 \pm 0.05 a	0.32 \pm 0.12 a	1.63 \pm 0.97 a	0.24 \pm 0.05 a	0.28 \pm 0.12 a	0.19 \pm 0.09 a
4-methylsyringol	0.38 \pm 0.08 a	0.17 \pm 0.07 a	ND a	0.54 \pm 0.14 a	0.64 \pm 0.14 a	0.41 \pm 0.21 a	0.36 \pm 0.58 a
4-allylsyringol	0.84 \pm 0.43 a	0.80 \pm 0.40 a	1.42 \pm 0.26 a	1.54 \pm 0.93 a	0.53 \pm 0.24 a	0.78 \pm 0.84 a	1.70 \pm 1.51 a
	toasted wood						
guaiacol	0.17 \pm 0.02 a	0.17 \pm 0.03 a	0.35 \pm 0.12 a	0.36 \pm 0.09 a	0.53 \pm 0.06 a	0.41 \pm 0.20 a	1.22 \pm 0.84 b
4-methylguaiacol	1.03 \pm 0.17 bc	0.78 \pm 0.12 abc	1.48 \pm 0.26 c	1.46 \pm 0.69 c	0.90 \pm 0.26 abc	2.12 \pm 0.20 d	1.52 \pm 0.48 c
4-ethylguaiacol ^a	0.17 \pm 0.04 ab	0.15 \pm 0.03 ab	0.25 \pm 0.08 ab	0.28 \pm 0.13 b	0.23 \pm 0.05 ab	0.57 \pm 0.26 c	0.48 \pm 0.29 c
4-vinylguaiacol ^a	1.48 \pm 0.57 a	1.13 \pm 0.66 a	1.92 \pm 0.85 a	2.53 \pm 1.48 a	1.86 \pm 0.52 a	7.42 \pm 3.88 b	0.53 \pm 0.19 a
phenol	0.23 \pm 0.02 a	0.22 \pm 0.01 a	0.43 \pm 0.14 ab	0.45 \pm 0.16 ab	0.86 \pm 0.32 b	0.70 \pm 0.61 ab	0.39 \pm 0.15 ab
eugenol	1.01 \pm 0.33 a	0.85 \pm 0.15 a	1.86 \pm 0.52 ab	2.35 \pm 0.89 ab	1.37 \pm 0.31 a	3.27 \pm 1.53 abc	5.29 \pm 2.52 bc
isoeugenol	0.33 \pm 0.10 a	0.39 \pm 0.06 a	1.31 \pm 0.56 a	0.99 \pm 0.65 a	1.76 \pm 1.99 a	4.21 \pm 3.02 b	3.83 \pm 1.17 b
syringol	1.22 \pm 0.78 ab	1.25 \pm 0.19 ab	2.63 \pm 0.62 ab	2.58 \pm 0.25 ab	2.95 \pm 0.73 b	3.28 \pm 1.31 b	2.39 \pm 2.26 ab
4-methylsyringol	2.59 \pm 1.24 ab	2.06 \pm 0.7 ab	8.44 \pm 1.67 c	7.13 \pm 6.58 bc	6.41 \pm 3.16 abc	5.70 \pm 3.49 abc	5.72 \pm 3.14 abc
4-allylsyringol	3.21 \pm 1.43 ab	3.33 \pm 0.85 ab	4.64 \pm 1.16 ab	3.22 \pm 0.83 ab	5.13 \pm 1.13 ab	7.26 \pm 2.71 b	17.05 \pm 6.15 c

^a Expressed as 4-methylguaiacol. Average and SD ($\bar{x} \pm \text{SD}$) were calculated for four samples. The Student Newman–Keuls multiple range test was carried out together for seasoned and toasted oak woods. The same letters indicate, for each compound in both seasoned and toasted woods, no significant differences between each pair of means, and the different letters indicate significant differences at the 95.0% confidence level. ND, not detected.

Hydroxy-3-methoxyphenyl) acetaldehyde: RT (min) 56.9. MS (EI) m/z (%): 137 (100), 166 (30), 122 (20), 94 (16). 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone: RT (min): 58.4. MS (EI) m/z (%): 137 (100), 180 (20), 122 (16), 94 (12). 1-(4-Hydroxy-3-methoxyphenyl)-2-butanone: RT (min) 62.0. MS (EI) m/z (%): 137 (100), 194 (40), 119 (20), 91 (20), 151 (15). The same was observed for acetosyringone [RT (min) 68.7; MS (EI) m/z (%): 181 (100), 196 (45), 153 (15), 65 (15)] and propiosyringone [RT (min) 70.9; MS (EI) m/z (%): 18 (100), 210 (30), 153 (10), 65 (10)], whose respective isomers 2-(4-hydroxy-3,5-dimethoxyphenyl) acetaldehyde [RT (min) 67.6; MS (EI) m/z (%): 167 (100), 196 (50), 123 (10), 106 (10)] and 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone [RT (min) 69.3; MS (EI) m/z (%): 167 (100), 210 (20), 123 (10), 106 (5)] were also identified.

Volatile Compounds in Seasoned Wood. The GC/MS quantitative evaluations of the volatile compounds that were extracted from Spanish, French, and American seasoned woods are included in **Tables 2–4**, arranged by family compounds. In relation to the volatile phenols (**Table 2**), the most abundant components in seasoned wood were eugenol, 4-vinylguaiacol, and 4-allylsyringol, contending for the first place depending on wood species and origin. The eugenol concentration was the only one that showed significant differences among species and provenances, and its concentration was higher in American woods with respect to Spanish and French woods. Considering European species, Spanish *Q. pyrenaica* and French *Q. petraea* showed eugenol concentrations higher than the others, even though no significant differences were observed because of the high standard deviations (SD) shown by these variables. Just a few or unremarkable significant differences among species and origins were observed for other studied volatile phenols, according to the Newman–Keuls multiple range test, possibly because of the high variability shown by their values.

The majority of studies reported in the literature about volatile phenols is only relative to eugenol, because of their aromatic

potential (threshold value of 0.015 mg/L in synthetic solution; 48). The high variability in the contents of this compound, among individual trees, species, and origins, was already reported in green and seasoned French oak wood by other authors (18, 21), who found concentrations of 0–10 $\mu\text{g/g}$ for the same French species that we studied; the mean concentration in French *Q. petraea* (8 $\mu\text{g/g}$) is normally higher than in *Q. robur* (2 $\mu\text{g/g}$) (18, 21, 46). In relation to the high eugenol content shown by American oak wood (*Q. alba* from Missouri) (**Table 2**), the few studies published do not always agree with our results. However, it is very difficult to compare the results because only a few studies have clearly identified the origin of American wood studied, there are not comparative studies among different species and origins of American white oak, and, in addition, the methodology used for its evaluation is very different. Chatonnet and Dubourdiou (46) reported eugenol levels of 5.29 $\mu\text{g/g}$ for seasoned American oak wood similar to ours (4 \pm 1.5 $\mu\text{g/g}$) also coming from Missouri, but this value was smaller than French *Q. petraea* (8 $\mu\text{g/g}$). Sefton et al. (27) issued a eugenol mean concentration for seasoned French wood (from Vosgos and Tronçais) of 3.4 $\mu\text{g/g}$, and for French (Limousin) and American (Ohio) wood, the concentration was 1.4 $\mu\text{g/g}$. Also, its concentration has been related to the time and method of seasoning, but the results of different studies were not always in agreement. Whereas Sefton et al. (27) observed a regular and constant decrease of eugenol content during natural seasoning and Masson et al. (26) observed the same during kiln drying, Chatonnet (28) found the opposite effect: a little increase in relation to the seasoning duration.

The quantitative evaluation of the β -methyl- γ -octalactone (**Table 3**) showed a high variability of concentration of two isomers, cis and trans, in all seasoned oak woods. Spanish *Q. petraea* was especially poor in cis-methyl octalactone, but the other Spanish species *Q. robur*, *Q. pyrenaica*, and *Q. faginea* showed concentrations halfway between French *Q. petraea* and American *Q. alba*. We must emphasize the high variability

Table 3. Lactones, Furanic Compounds, Pyranones, and Other Volatile Compounds ($\mu\text{g/g}$) of Spanish, French, and American Oak Wood after Natural Seasoning and Toasting

	$\bar{x} \pm \text{SD}$							
	Spanish				French		American	
	<i>Q. robur</i>	<i>Q. petraea</i>	<i>Q. pyrenaica</i>	<i>Q. faginea</i>	<i>Q. robur</i>	<i>Q. petraea</i>	<i>Q. alba</i>	
	seasoned wood							
2-furanyl-1-ethanone	0.13 \pm 0.09 a	0.14 \pm 0.08 a	0.22 \pm 0.03 a	0.03 \pm 0.002 a	0.15 \pm 0.03 a	0.19 \pm 0.06 a	0.07 \pm 0.05 a	
butyrolactone	0.50 \pm 0.13 ab	0.52 \pm 0.09 ab	0.46 \pm 0.08 ab	ND a	0.33 \pm 0.03 ab	0.42 \pm 0.06 ab	0.31 \pm 0.16 ab	
benzaldehyde	0.32 \pm 0.10 abc	0.33 \pm 0.06 bc	0.28 \pm 0.08 abc	0.65 \pm 0.11 d	0.19 \pm 0.02 ab	0.27 \pm 0.03 abc	0.17 \pm 0.07 a	
hydroxybenzaldehyde ^a	ND a	0.01 \pm 0.03 a	0.03 \pm 0.00 a	ND a	0.03 \pm 0.01 a	0.03 \pm 0.003 a	0.01 \pm 0.03 a	
benzothiazole	0.17 \pm 0.04 a	0.20 \pm 0.07 a	0.18 \pm 0.03 a	0.21 \pm 0.05 a	0.27 \pm 0.02 a	0.21 \pm 0.01 a	0.12 \pm 0.08 a	
1H-pyrrole-2-carboxaldehyde	0.78 \pm 0.55 a	0.67 \pm 0.35 a	0.76 \pm 0.52 a	ND a	0.59 \pm 0.15 a	0.48 \pm 0.09 a	ND a	
phenylmethanol	1.07 \pm 0.35 ab	0.63 \pm 0.27 ab	1.81 \pm 0.46 c	1.41 \pm 0.87 bc	0.74 \pm 0.13 ab	0.57 \pm 0.18 ab	0.96 \pm 0.58 ab	
2-phenylethanol	0.22 \pm 0.05 ab	0.17 \pm 0.11 a	0.25 \pm 0.17 ab	0.35 \pm 0.14 ab	0.33 \pm 0.10 ab	0.17 \pm 0.05 ab	0.83 \pm 0.29 c	
2-phenoxyethanol	1.12 \pm 0.69 abc	1.35 \pm 0.44 abc	1.74 \pm 0.60 bc	1.34 \pm 0.14 abc	1.40 \pm 0.21 abc	0.98 \pm 0.10 abc	1.01 \pm 1.13 abc	
maltol	0.37 \pm 0.12 a	0.35 \pm 0.09 a	0.28 \pm 0.06 a	0.36 \pm 0.04 a	0.25 \pm 0.04 a	0.23 \pm 0.03 a	0.24 \pm 0.04 a	
isomaltol ^b	0.16 \pm 0.02 a	0.16 \pm 0.04 a	0.13 \pm 0.03 a	0.14 \pm 0.02 a	0.13 \pm 0.001 a	0.10 \pm 0.06 a	0.13 \pm 0.01 a	
furfural	10.8 \pm 5.11 a	10.3 \pm 3.68 a	19.7 \pm 8.54 a	17.6 \pm 7.23 a	8.90 \pm 3.04 a	19.9 \pm 6.88 a	4.04 \pm 2.07 a	
5-methylfurfural	1.97 \pm 0.80 a	1.53 \pm 0.45 a	1.54 \pm 0.71 a	1.81 \pm 0.64 a	1.11 \pm 0.14 a	1.73 \pm 0.59 a	0.30 \pm 0.11 a	
furfuryl alcohol	0.13 \pm 0.03 ab	0.15 \pm 0.03 ab	0.48 \pm 0.08 cd	0.12 \pm 0.02 ab	0.36 \pm 0.11 bc	0.14 \pm 0.03 ab	0.06 \pm 0.12 a	
5-hydroxymethylfurfural	2.70 \pm 1.90 a	2.64 \pm 1.99 a	3.85 \pm 2.14 a	1.54 \pm 0.80 a	0.83 \pm 0.30 a	0.53 \pm 0.12 a	1.77 \pm 0.74 a	
trans- β -methyl- γ -octalactone	3.98 \pm 4.32 a	0.09 \pm 0.07 a	4.57 \pm 3.4 a	1.74 \pm 1.61 a	3.41 \pm 5.43 a	7.84 \pm 13.7 a	3.46 \pm 3.22 a	
cis- β -methyl- γ -octalactone	22.9 \pm 15.5 abc	0.42 \pm 0.42 a	17.5 \pm 12.5 ab	15.5 \pm 11.8 ab	2.83 \pm 3.10 a	12.0 \pm 21.5 ab	32.5 \pm 10.9 bc	
cis/trans ratio	6.97 \pm 4.27 ab	3.48 \pm 1.57 ab	3.68 \pm 1.00 ab	10.6 \pm 7.45 abc	4.02 \pm 5.60 ab	4.94 \pm 7.92 ab	15.7 \pm 10.0 bc	
NI (<i>m/z</i> = 99)	2.88 \pm 1.77 d	2.71 \pm 0.8 cd	3.45 \pm 1.62 d	2.48 \pm 0.3 bcd	3.22 \pm 0.30 d	3.03 \pm 0.4 d	1.03 \pm 1.4 ab	
	toasted wood							
2-furanyl-1-ethanone	0.65 \pm 0.27 ab	0.82 \pm 0.90 ab	1.02 \pm 0.48 bc	1.13 \pm 0.22 bc	1.56 \pm 0.58 c	0.76 \pm 0.08 ab	2.77 \pm 1.21 d	
butyrolactone	0.80 \pm 0.20 abc	0.68 \pm 0.09 abc	1.60 \pm 0.40 cd	1.76 \pm 0.35 d	1.32 \pm 0.29 bcd	0.80 \pm 0.20 abc	2.81 \pm 1.68 e	
benzaldehyde	0.22 \pm 0.04 abc	0.21 \pm 0.01 abc	0.19 \pm 0.02 abc	0.34 \pm 0.08 abc	0.21 \pm 0.01 abc	0.27 \pm 0.10 c	0.25 \pm 0.07 abc	
hydroxybenzaldehyde ^a	0.21 \pm 0.06 b	0.22 \pm 0.01 b	0.26 \pm 0.12 b	0.18 \pm 0.06 b	0.47 \pm 0.15 c	0.39 \pm 0.20 c	0.78 \pm 0.16 d	
benzothiazole	0.24 \pm 0.03 a	0.20 \pm 0.03 a	0.27 \pm 0.05 a	0.25 \pm 0.09 a	0.09 \pm 0.03 a	0.19 \pm 0.22 a	0.19 \pm 0.11 a	
1H-pyrrole-2-carboxaldehyde	1.81 \pm 0.40 ab	1.84 \pm 0.17 ab	2.84 \pm 0.84 b	1.8 \pm 0.49 ab	4.03 \pm 2.15 c	1.93 \pm 1.29 ab	6.40 \pm 1.41 c	
phenylmethanol	0.61 \pm 0.10 ab	0.49 \pm 0.02 a	0.53 \pm 0.07 ab	1.01 \pm 0.19 ab	0.76 \pm 0.20 ab	0.60 \pm 0.29 ab	0.94 \pm 0.28 ab	
2-phenylethanol	0.21 \pm 0.07 ab	0.31 \pm 0.08 ab	0.13 \pm 0.08 a	0.20 \pm 0.11 a	0.24 \pm 0.10 ab	0.22 \pm 0.12 ab	0.53 \pm 0.12 b	
2-phenoxyethanol	1.08 \pm 0.12 abc	1.10 \pm 0.05 abc	1.85 \pm 0.56 bc	2.11 \pm 0.59 c	0.55 \pm 0.11 a	1.06 \pm 0.71 abc	0.18 \pm 0.08 a	
maltol	1.37 \pm 0.37 b	1.15 \pm 0.06 b	1.63 \pm 0.22 b	1.51 \pm 0.47 b	1.57 \pm 0.53 b	1.49 \pm 0.43 b	3.38 \pm 0.89 c	
isomaltol ^b	0.80 \pm 0.32 a	1.08 \pm 0.10 a	1.05 \pm 0.99 a	0.82 \pm 0.19 a	2.50 \pm 0.86 a	1.13 \pm 0.30 a	7.40 \pm 8.17 b	
furfural	103 \pm 71.9 ab	186 \pm 43.5 b	170 \pm 158 b	96.0 \pm 38.1 ab	340 \pm 77.0 c	58.9 \pm 14.6 ab	346 \pm 170 c	
5-methylfurfural	18.5 \pm 6.09 a	26.3 \pm 5.06 a	30.1 \pm 20.7 a	30.1 \pm 23.7 a	80.9 \pm 72.6 b	30.2 \pm 6.35 a	85.0 \pm 35.7 b	
furfuryl alcohol	0.22 \pm 0.04 abc	0.40 \pm 0.08 bcd	0.48 \pm 0.12 cd	0.41 \pm 0.08 bcd	0.51 \pm 0.07 cd	0.68 \pm 0.13 d	1.87 \pm 0.45 e	
5-hydroxymethylfurfural	40.9 \pm 26.5 ab	51.7 \pm 8.25 b	55.7 \pm 44.7 b	57.5 \pm 13.0 b	112 \pm 46.5 c	43.8 \pm 9.33 ab	103 \pm 32.9 c	
trans- β -methyl- γ -octalactone	4.11 \pm 6.59 a	0.10 \pm 0.09 a	3.35 \pm 2.40 a	1.08 \pm 1.67 a	0.25 \pm 0.23 a	14.9 \pm 1.41 b	4.36 \pm 5.01 a	
cis- β -methyl- γ -octalactone	4.98 \pm 8.11 a	0.30 \pm 0.44 a	13.8 \pm 9.18 ab	3.25 \pm 4.98 a	0.25 \pm 0.06 a	19.8 \pm 9.38 ab	44.1 \pm 32.1 c	
cis/trans ratio	4.46 \pm 3.81 ab	2.87 \pm 1.99 ab	4.35 \pm 0.78 ab	3.62 \pm 2.62 ab	1.56 \pm 1.12 a	1.34 \pm 0.63 a	18.5 \pm 11.3 c	
NI (<i>m/z</i> = 99)	2.64 \pm 0.38 cd	2.38 \pm 0.23 bcd	1.65 \pm 0.12 abc	1.20 \pm 0.19 abc	0.26 \pm 0.23 a	0.65 \pm 0.43 a	ND a	

^a Expressed as benzaldehyde. ^b Expressed as maltol. Average and SD ($\bar{x} \pm \text{SD}$) were calculated for four samples. The Student Newman-Keuls multiple range test was carried out together for seasoned and toasted oak woods. The same letters indicate, for each compound in both seasoned and toasted woods, no significant differences between each pair of means, and the different letters indicate significant differences at the 95.0% confidence level. ND, not detected; NI, not identified.

among wood samples (high values of SDs) that is responsible for little or unremarkable significant differences observed, according to the variance analysis (Table 3). The only significant difference was shown by American *Q. alba* with respect to Spanish *Q. petraea* and French *Q. robur*. On the other hand, the mean values of the cis/trans oak octalactone ratio (Table 3) varied among species and origins, from 3.48 to 10.6 for European oaks studied, showing that American *Q. alba* had the highest value (15.7). However, this proportion also varied among wood samples from the same species and origin, especially for French *Q. robur* and *Q. petraea*, in which some wood samples contained higher proportions of trans-methyl octalactone than cis-methyl octalactone.

These results reinforce those obtained by Masson et al. (19), which showed high variability of levels and ratios of cis/trans-methyl octalactone in French and American oaks, among trees, forests, and species. These also revealed important differences in the proportion of cis oak lactone for American with respect to Pedunculata and Sessile oaks (French *Q. robur* and *Q. petraea*) and higher proportions of trans isomer in some French woods from different forests. American oak was characterized

by higher levels of methyl octalactones, particularly of cis isomers, than French oaks in other published studies (45, 49). The cis isomer has a threshold value in synthetic solution (0.025 mg/L; 48) smaller than the trans isomer (0.11 mg/L; 48) that leads to a high aromatic potential in wine.

Concerning the other volatile compounds evaluated in seasoned oak woods, like furanic compounds and others (Table 3), phenolic aldehydes, phenyl ketones, and others (Table 4), no remarkable variations were observed if we compare the results obtained from Spanish seasoned woods to French or American oak woods, except the Spanish *Q. faginea*, which showed higher concentrations for 2-(4-hydroxy-3-methoxyphenyl)acetaldehyde (HMPA) and 2-(4-hydroxy-3,5-dimethoxyphenyl)acetaldehyde (HDMPA) phenyl ketones.

To compare the aromatic potential of seasoned Spanish woods with respect to French and American woods, we carried out two canonical discriminant analyses, considering volatile family compounds involved in wine flavor. The first one, in which we considered volatile phenols (Table 2), leads to a mathematical model that explained 100% of the total dispersion, distributed among six canonical functions. Figure 1 shows the graphical

Table 4. Phenolic Aldehydes and Related Compounds ($\mu\text{g/g}$) of Spanish, French, and American Oak Wood after Natural Seasoning and Toasting

	$\bar{x} \pm \text{SD}$							
	Spanish				French		American	
	<i>Q. robur</i>	<i>Q. petraea</i>	<i>Q. pyrenaica</i>	<i>Q. faginea</i>	<i>Q. robur</i>	<i>Q. petraea</i>	<i>Q. alba</i>	
	seasoned wood							
vanillin	15.9 \pm 2.82 a	18.8 \pm 3.51 a	10.6 \pm 2.2 a	10.6 \pm 5.24 a	9.34 \pm 3.12 a	14.1 \pm 4.13 a	7.90 \pm 2.29 a	
HMPA ^a	0.51 \pm 0.16 a	0.54 \pm 0.06 a	0.42 \pm 0.08 a	10.2 \pm 2.89 c	0.50 \pm 0.09 a	0.29 \pm 0.13 a	0.11 \pm 0.07 a	
acetovanillone	0.98 \pm 0.22 a	1.19 \pm 0.26 a	0.69 \pm 0.10 a	1.48 \pm 0.42 a	0.69 \pm 0.14 a	0.93 \pm 0.33 a	0.51 \pm 0.20 a	
HMP ^a	0.60 \pm 0.17 a	0.49 \pm 0.16 a	0.40 \pm 0.12 a	5.37 \pm 1.16 ab	0.40 \pm 0.14 a	0.30 \pm 0.06 a	0.24 \pm 0.10 a	
propiovanillone ^a	4.29 \pm 0.89 ab	2.51 \pm 1.13 a	3.22 \pm 2.07 ab	3.69 \pm 0.78 ab	3.33 \pm 1.70 ab	5.75 \pm 4.35 ab	7.42 \pm 2.59 b	
HMPB ^a	0.05 \pm 0.03 a	0.17 \pm 0.12 a	0.04 \pm 0.02 a	0.07 \pm 0.06 a	0.10 \pm 0.11 a	0.60 \pm 0.57 a	0.43 \pm 0.42 a	
butirovanillone ^a	2.49 \pm 0.83 a	2.26 \pm 0.39 a	2.39 \pm 0.44 a	6.59 \pm 2.72 a	1.68 \pm 0.50 a	1.89 \pm 0.16 a	1.55 \pm 0.33 a	
methyl vanillyl ether ^b	1.10 \pm 0.19 ab	0.93 \pm 0.15 ab	0.84 \pm 0.20 ab	0.43 \pm 0.23 a	0.73 \pm 0.58 ab	1.49 \pm 0.96 ab	0.98 \pm 1.33 ab	
syringic aldehyde	17.5 \pm 3.11 a	19.3 \pm 3.18 a	15.1 \pm 2.80 a	10.1 \pm 5.70 a	13.8 \pm 3.35 a	16.7 \pm 3.14 a	15.5 \pm 1.50 a	
HDMPA ^c	0.24 \pm 0.12 a	0.16 \pm 0.09 a	0.29 \pm 0.06 a	4.59 \pm 1.45 bc	0.35 \pm 0.10 a	0.06 \pm 0.03 a	0.16 \pm 0.08 a	
ethyl vanillyl ether ^b	2.58 \pm 0.78 ab	2.33 \pm 0.56 ab	3.23 \pm 0.89 ab	3.95 \pm 1.80 ab	2.65 \pm 1.21 ab	2.62 \pm 0.44 ab	2.25 \pm 1.01 a	
acetosyringone	0.95 \pm 0.15 ab	1.18 \pm 0.33ab	0.64 \pm 0.04 ab	1.55 \pm 0.57 ab	0.61 \pm 0.06 ab	0.82 \pm 0.12 ab	0.51 \pm 0.21 a	
HDMPP ^c	0.93 \pm 0.16 ab	0.87 \pm 0.36 ab	0.56 \pm 0.13 ab	8.12 \pm 2.13 ab	0.59 \pm 0.06 ab	0.32 \pm 0.07 ab	0.31 \pm 0.13 a	
propiosyringone ^c	2.98 \pm 1.38 a	1.91 \pm 0.37 a	3.46 \pm 1.32 ab	5.15 \pm 1.48 abc	4.00 \pm 2.34 ab	3.64 \pm 0.50 ab	2.75 \pm 1.50 a	
coniferilic aldehyde	5.21 \pm 2.35 a	5.91 \pm 0.60 a	4.06 \pm 0.33 a	1.53 \pm 1.00 a	3.97 \pm 0.98 a	2.12 \pm 0.62 a	3.07 \pm 0.44 a	
sinapic aldehyde	3.78 \pm 0.53 a	3.89 \pm 1.00 a	4.15 \pm 0.45 a	1.46 \pm 1.19 a	3.52 \pm 0.916 a	4.39 \pm 1.21 a	3.24 \pm 0.35 a	
	toasted wood							
vanillin	130 \pm 25.8 b	119 \pm 16.3 b	210 \pm 63.0 cd	258 \pm 60.1 d	172 \pm 69.8 bc	370 \pm 116 e	39.7 \pm 6.68 a	
HMPA ^a	5.15 \pm 0.80 b	5.49 \pm 0.32 b	8.83 \pm 3.63 c	8.04 \pm 2.51 bc	5.22 \pm 1.92 b	9.36 \pm 0.95 c	8.30 \pm 2.03 bc	
acetovanillone	3.90 \pm 0.52 bcd	2.67 \pm 0.28 b	4.61 \pm 1.02 de	5.27 \pm 1.60 e	3.02 \pm 0.84 bc	7.88 \pm 1.03 f	4.17 \pm 1.19 cde	
HMP ^a	7.76 \pm 1.43 ab	8.01 \pm 1.17 ab	10.7 \pm 4.59 b	9.12 \pm 2.72 b	12.3 \pm 2.23 b	13.8 \pm 3.20 b	25.1 \pm 14.4 c	
propiovanillone ^a	4.82 \pm 1.05 ab	4.37 \pm 2.14 ab	5.53 \pm 0.73 ab	5.06 \pm 1.64 ab	5.49 \pm 0.98 ab	5.87 \pm 1.40 ab	6.15 \pm 0.71 ab	
HMPB ^a	0.17 \pm 0.25 a	0.21 \pm 0.03 a	0.19 \pm 0.20 a	0.10 \pm 0.04 a	0.21 \pm 0.07 a	0.35 \pm 0.17 a	0.28 \pm 0.11 a	
butirovanillone ^a	13.13 \pm 2.43 b	16.1 \pm 0.73 bc	16.3 \pm 5.58 bc	15.7 \pm 4.13 bc	17.6 \pm 3.96 bc	24.6 \pm 3.65 d	21.5 \pm 7.20 cd	
methyl vanillyl ether ^b	1.43 \pm 0.32 ab	1.33 \pm 0.29 ab	1.33 \pm 0.52 ab	1.23 \pm 0.48 ab	1.47 \pm 0.45 ab	2.08 \pm 0.54 b	1.07 \pm 0.40 ab	
syringic aldehyde	162 \pm 70.5 bc	160 \pm 46.5 bc	280 \pm 82.9 d	243 \pm 100 cd	216 \pm 67.2 cd	452 \pm 139 e	102 \pm 28.3 ab	
HDMPA ^b	2.78 \pm 0.84 ab	3.16 \pm 0.76 ab	7.23 \pm 4.02 c	4.88 \pm 0.89 bc	4.27 \pm 2.41 bc	10.2 \pm 4.41 d	6.94 \pm 2.00 c	
ethyl vanillyl ether ^b	7.28 \pm 1.87 abc	7.39 \pm 1.87 abc	14.6 \pm 5.70 c	23.9 \pm 5.92 d	20.7 \pm 11.8 d	11.9 \pm 3.08 bc	10.3 \pm 2.58 abc	
acetosyringone	5.12 \pm 1.44 bc	3.69 \pm 1.00 abc	7.52 \pm 3.45 c	7.65 \pm 2.77 c	6.02 \pm 2.58 c	15.3 \pm 4.28 d	7.82 \pm 3.13 c	
HDMPP ^c	9.06 \pm 2.78 ab	10.0 \pm 3.59 ab	16.1 \pm 7.52 ab	12.0 \pm 2.32 ab	18.4 \pm 5.09 ab	24.1 \pm 9.06 b	47.2 \pm 37.4 d	
propiosyringone ^c	4.12 \pm 1.96 ab	3.00 \pm 1.73 a	8.17 \pm 1.92 c	5.32 \pm 1.54 abc	6.69 \pm 2.31 bc	6.44 \pm 1.13 bc	7.34 \pm 2.62 bc	
coniferilic aldehyde	177 \pm 82.1 ab	115 \pm 18.0 ab	307 \pm 144 bc	215 \pm 99.9 ab	127 \pm 40.2 ab	418 \pm 334 bc	169 \pm 77.8 ab	
sinapic aldehyde	116 \pm 36.0 a	123 \pm 33.4 a	349 \pm 173 b	147 \pm 99.7 a	233 \pm 141 ab	704 \pm 276 c	200 \pm 63.0 ab	

^a Expressed as acetovanillone. ^b Expressed as vanillin. ^c Expressed as acetosyringone. Average and SD ($\bar{x} \pm \text{SD}$) were calculated for four samples. The Student Newman-Keuls multiple range test was carried out together for seasoned and toasted oak woods. The same letters indicate, for each compound in both seasoned and toasted woods, no significant differences between each pair of means, and the different letters indicate significant differences at the 95.0% confidence level. ND, not detected; NI, not identified; HMPA, 2-(4-hydroxy-3-methoxyphenyl) acetaldehyde; HMPP, 1-(4-hydroxy-3-methoxyphenyl)-2-propanone; HMPB, 1-(4-hydroxy-3-methoxyphenyl)-2-butanone; and HDMPA, 2-(4-hydroxy-3,5-dimethoxyphenyl) acetaldehyde; HDMPP, 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone.

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 represented a cumulative proportion of 89% of the total dispersion, canonical correlations of 0.983 and 0.928, and eigenvalues of 29.73 and 6.19, respectively. Discriminant function 1 was related mainly to levels of eugenol, ethylguaiaicol, vinylguaiaicol, syringol, phenol, and methylguaiaicol, according to importance, whereas function 2 was related to those of phenol, allylsyringol, eugenol, methylguaiaicol, syringol, and isoeugenol. The coefficients of the total canonical structure for each variable in functions 1 and 2, with their positive or negative sign, are included in the **Figure 1** caption. The sets of points showed a pattern of distribution in which three well-defined groups can be distinguished, related more to species than origin of woods. Especially function 1 distinguished American *Q. alba* with respect to all other woods, and function 2 distinguished Spanish and French *Q. robur* and *Q. petraea* with respect to Spanish *Q. pyrenaica* and *Q. faginea* and American *Q. alba*. The set of points of Spanish and French *Q. robur* and *Q. petraea* was overlapped. Although eugenol was the only volatile phenol that showed concentrations with significant differences in American wood with respect to European woods (**Table 2**), it was the variable that showed the highest contribution to canonical function 1 (**Figure 1**), and in addition, it has a high aromatic potential (perception threshold in synthetic solution = 0.015

mg/L; 48); others volatile phenols that also contribute to discriminant functions can carry out to differences in organoleptic properties of the woods studied, because of their little perception thresholds, like ethylguaiaicol (0.047 mg/L; 48) and methylguaiaicol (0.03 mg/L; 48).

The second discriminant analysis carried out considering w-lactones, furanic compounds, pyranones, and other compounds evaluated in **Table 3** provided a mathematical model, which a representation of on the plane determined by two principal canonical axes is shown in **Figure 2**. We can also distinguish groups of points related to the species and origins of woods, overlapping only, in this case, the set of points of French *Q. petraea* and American *Q. alba*. The variables with higher participation in discriminant functions 1 and 2 were the following volatile compounds, some of them with recognized influence in wine flavor but with a higher sensory threshold than volatile phenols considered before: benzaldehyde, maltol (5 mg/L; 50), hydroxybenzaldehyde, and furfuryl alcohol (15 mg/L; 48) for function 1 and butyrolactone, hydroxymethylfurfural, 1-pyrrolicarboxaldehyde (5 mg/L; 50), and isomaltol for function 2. Hydroxybenzaldehyde and furfuryl alcohol are the only ones that presented negative canonical coefficients, as can be observed in **Figure 2**. In addition, compounds with a high aromatic potential, especially *cis*-methyl octalactone (0.025 mg/L; 48) and *trans*-methyl octalactone (0.11 mg/L; 48), which

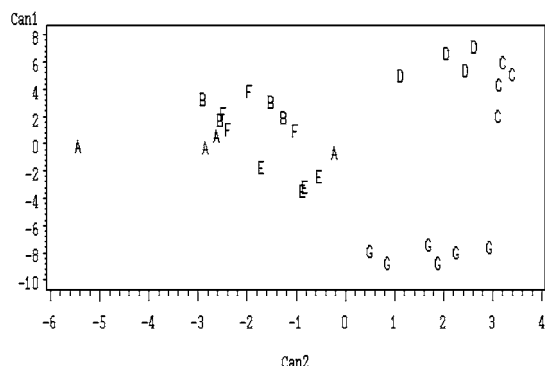


Figure 1. Canonical discriminant analysis of volatile phenols of seasoned woods (Table 2). Mathematical model: 100% of total dispersion in six canonical functions, with cumulative proportion of 89% in functions 1 and 2. Projections of the points of each species and provenance on plane defined by the two principal canonical axes 1 and 2. (A) *Q. robur*, (B) *Q. petraea*, (C) *Q. pyrenaica*, and (D) *Q. faginea*, Spanish oak woods; (E) *Q. robur* and (F) *Q. petraea*, French oak woods; and (G) *Q. alba*, American oak wood. Eigenvalues for functions 1 and 2 were 29.73 and 6.19, and canonical correlations were 0.983 and 0.928, respectively. The total canonical structure coefficients of functions 1 and 2 were, respectively, as follows: guaiacol, 0.26 and 0.25; 4-methylguaiacol, -0.35 and 0.39 ; 4-ethylguaiacol, 0.56 and 0.12; 4-vinylguaiacol, 0.48 and 0.13; phenol, 0.4 and 0.60; eugenol, -0.59 and 0.39 ; isoeugenol, 0.01 and 0.36; syringol, 0.44 and 0.37; 4-methylsyringol, -0.04 and -0.22 ; and 4-allylsyringol, -0.14 and 0.47 .

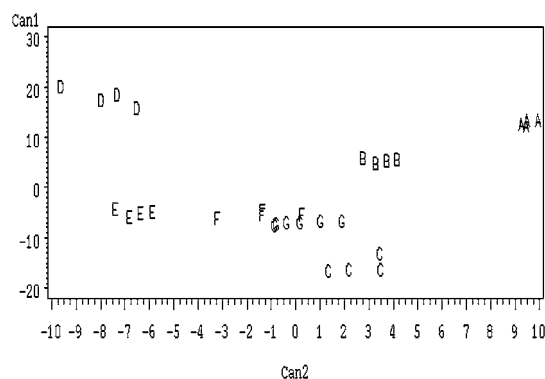


Figure 2. Canonical discriminant analysis of methyl-octalactones, furanic compounds, pyranones, and other compounds of seasoned woods (Table 4). Mathematical model: 100% of total dispersion in six canonical functions with a cumulative proportion of 85% in functions 1 and 2. Projections of the points of each species and provenance on plane defined by the two principal canonical axes 1 and 2. (A) *Q. robur*, (B) *Q. petraea*, (C) *Q. pyrenaica*, and (D) *Q. faginea*, Spanish oak woods; (E) *Q. robur* and (F) *Q. petraea*, French oak woods; and (G) *Q. alba*, American oak wood. Eigenvalues for functions 1 and 2 were 154.67 and 37.81, and canonical correlations were 0.997 and 0.987, respectively. The total canonical structure coefficients of the discriminant functions 1 and 2 were, respectively, as follows: furanyl-1-ethanone, -0.44 and 0.22 ; butyrolactone, -0.33 and 0.63 ; benzaldehyde, 0.69 and -0.34 ; hydroxybenzaldehyde, -0.52 and -0.18 ; benzothiazole, 0.10 and -0.22 ; 1*H*-pyrrole-2-carboxaldehyde, -0.10 and 0.46 ; phenylmethanol, -0.05 and 0.06 ; 2-phenylethanol, -0.22 and -0.07 ; 2-phenoxyethanol, -0.08 and 0.05 ; maltol, 0.59 and 0.27; isomaltol, 0.36 and 0.40; furfural, 0.03 and -0.30 ; 5-methylfurfural, 0.41 and 0.03; furfuryl alcohol, -0.48 and 0.09 ; 5-hydroxymethylfurfural, 0.07 and 0.46 ; *trans*- β -methyl- γ -octalactone, -0.18 and -0.08 ; and *cis*- β -methyl- γ -octalactone, -0.08 and 0.11 .

contributed to the total canonical structure with small coefficients, must be considered in the discrimination among different groups of studied wood.

Volatile Compounds in Toasted Woods. Tables 2–4 show the results of GC/MS analysis of the different families of volatile compounds and the Student Newman–Keuls multiple range test carried out together for seasoned and toasted oak woods. In relation to volatile phenols, if we compare the levels obtained from Spanish, French, and American toasted woods to those obtained from the same seasoned woods (Table 2), it can be pointed out that the average contents of most of the compounds, especially isoeugenol, syringol, 4-methylsyringol, and 4-allylsyringol, increased during toasting process. The exceptions were phenol in Spanish and American woods and 4-vinylguaiacol in Spanish *Q. pyrenaica* and American woods. The effect of toasting on eugenol was different according to species and origin of wood, but in general, no drastic changes were observed. Whereas its concentration increased in Spanish *Q. petraea* and *Q. faginea* and French *Q. robur*, in French *Q. petraea* and American *Q. alba*, it remained constant, and in Spanish *Q. robur* and *Q. pyrenaica*, it showed a decreasing tendency (Table 2). Accordingly, the main components in all toasted woods were 4-allylsyringol, 4-methylsyringol, eugenol, isoeugenol, syringol, 4-methylguaiacol, and 4-vinylguaiacol with a different abundance order according to species and origin. The high concentration of 4-allylsyringol shown by American wood with respect to the Spanish and French woods was exceptional. Both guaiacol and its 4-ethyl derivative and phenol showed low concentrations. The exception was 4-vinylguaiacol in French *Q. petraea*, whose concentration was significantly higher than that found in other woods.

It is well-known that the volatile phenols are products of lignin thermodegradation (51, 52), and the high increases of monomethoxyphenols (series guaiacyl) and, especially, dimethoxyphenols (series syringyl) with regard to simple phenols have been explained by the predominance of groups guaiacyl and syringyl in relation to phenyl, in the lignin general structure of angiosperms. Our results are in accordance with those described early for other French woods [*Q. petraea* from Allier (23) and from Centre (22)]. The mean levels, yielded in the conditions of medium toasting used at the cooperage, could correspond to those obtained by others in French wood after light or medium toasting (syringol, 0.94 and 3.66 $\mu\text{g/g}$; 4-methylsyringol, 0.94 and 4.07 $\mu\text{g/g}$; 4-allylsyringol, 1.13 and 3.88 $\mu\text{g/g}$; eugenol, 1.87 and 1.27 $\mu\text{g/g}$, respectively) (23). Although small concentrations of phenol and only traces of 2-phenylmethanol and 2-phenylethanol were presented in the toasted wood, other simple phenols such as cresols were not detected, which are characteristic of burned woods (22) and transmit an undesirable aroma to wine like ink, bitumen, pharmaceuticals, etc. (16, 48).

Referring to the compounds that derive from sugar thermodegradation (36), like furanic compounds, cyclic ketones (furanones and pyranones), and pyrrole structures, whose evaluation is shown in Table 3, the furanic aldehydes furfural, 5-methylfurfural, and 5-hydroxymethylfurfural showed, with a difference, the highest increments during toasting. The mean values obtained in toasted wood were higher in French *Q. robur* and American woods than in the other studied woods, in agreement with those obtained in French oak wood by Chatonnet et al. (23), when they used light toasting (115–125 $^{\circ}\text{C}$). The increase during toasting of 2-furanyl-1-ethanone, butyrolactone, hydroxybenzaldehyde, 1-pyrrole-2-carboxaldehyde, maltol, and isomaltol was also higher in American wood than in French and Spanish woods, according to the variance analysis (Table 3). This indicates an effect of toasting more drastic in the American species, in agreement with Mosedale and Ford (53) that showed a dependence on properties and origin of the wood.

The effect of toasting on methyl octalactone levels also depended on species and origin of studied wood (Table 3). French *Q. petraea* and American *Q. alba* woods showed an increase of both *cis*- and *trans*-lactones, while Spanish species and French *Q. robur* showed a decrease of *cis*-methyl octalactone, which was the isomer more abundant in seasoned woods. These variations were especially evident for Spanish *Q. robur*, in which *cis*-methyl octalactone concentration decreased from 22.9 $\mu\text{g/g}$ in seasoned wood to 4.98 $\mu\text{g/g}$ in toasted wood. Both contradictory effects were described previously in different cooperage conditions (22, 35, 53) and sometimes attributed to variations in toasting intensity and method. At the first toasting in laboratory or cooperage conditions, an increase of methyl octalactone contents in superficial wood layer was observed, but when the toasting was prolonged, a total destruction of these compounds took place (22, 23). However, sometimes, methyl octalactone concentration varied more among trees, species, and origins than among different heat treatments in cooperage (53). Our results corroborated that the chemical and structural characteristics of wood and toasting conditions may influence the reaction to heating, and this process is complicated by the possible loss of notable compounds, like ω -lactones. It is evident that our toasting conditions (usually in the Demptos cooperage) were more suitable for French *Q. petraea* and American *Q. alba* species usually used in this cooperage.

In relation to other volatile compounds evaluated (Table 4), excluding the phenolic aldehydes, because they have been the object of discussion in our previous studies about polyphenols in Spanish oak woods (5), the concentration of all phenyl ketones increased in toasted wood with respect to the seasoned wood. This increase was more evident, in general, for the acetaldehyde and 2-one isomers than for the own vanillones. Ethyl vanillyl ether also increased considerably during the toasting process. The origin of phenyl ketones during toasting of wood is not well-known, but it is accepted that they come in from degradation of polyphenolic structures of wood, more related with lignans presented in oak wood (54) than lignin (22). These compounds were linearly increased with heat intensity (22), and although their aromatic potential is relatively small (acetovanillone, 15 mg/L in synthetic solution) (48), their contribution to the organoleptic complexity of wine (wood and vanilla flavor) can be considerable, because of their high concentration in toasted wood and also the presence of a variety of molecules with similar chemical structures in the toasted wood that can give up similar aromatic properties.

The discriminant analysis carried out considering the volatile phenols evaluated for toasted woods (Table 2), whose graphical representation is shown in Figure 3, yielded a pattern of point distribution in which it can distinguish two groups, corresponding to American and European woods. Moreover, European woods presented chemical variability with a continuous distribution through canonical axis 2 and overlapping of Spanish *Q. pyrenaica* and *Q. faginea* and French *Q. petraea* (Allier), on one hand, and Spanish *Q. robur* and *Q. petraea* and French *Q. robur* (Limousin), on the other. However, the statistical distance among the groups was more marked by American *Q. alba* with regard to all of the other oak woods. The principal discriminant variables of function 1 were 4-allylsyringol, eugenol, guaiacol, isoeugenol, and 4-ethylguaiacol, in this contribution order, whereas those of function 2 were 4-vinylguaiacol and 4-methylsyringol, with positive canonical coefficients for all of these variables except for the last one (Figure 3).

Considering the discriminant analysis carried out with methyl octalactones, furanic compounds, pyranones, and other com-

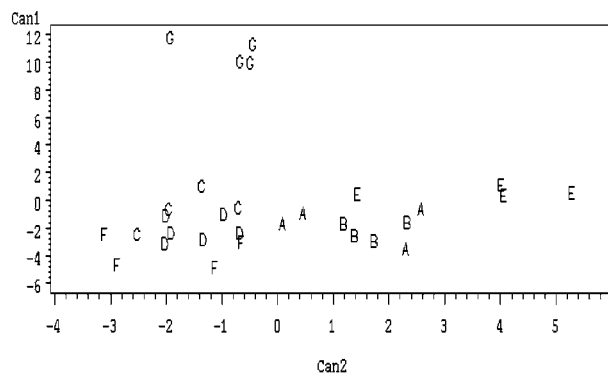


Figure 3. Canonical discriminant analysis of volatile phenols of toasted woods (Table 2). Mathematical model: 100% of total dispersion in six canonical functions, with a cumulative proportion of 84% in functions 1 and 2. Projections of the points of each species and provenance on plane defined by the two principal canonical axes 1 and 2. (A) *Q. robur*, (B) *Q. petraea*, (C) *Q. pyrenaica*, and (D) *Q. faginea*, Spanish oak woods; (E) *Q. robur* and (F) *Q. petraea*, French oak woods; and (G) *Q. alba*, American oak wood. Eigenvalues for functions 1 and 2 were 25.34 and 5.02, and canonical correlations were 0.981 and 0.913, respectively. The total canonical structure coefficients of functions 1 and 2 were, respectively, as follows: guaiacol, 0.68 and -0.26 ; 4-methylguaiacol, 0.29 and 0.22; 4-ethylguaiacol, 0.47 and 0.25; 4-vinylguaiacol, -0.13 and 0.55; phenol, -0.11 and -0.13 ; eugenol, 0.74 and -0.03 ; isoeugenol, 0.52 and 0.21; syringol, 0.04 and -0.11 ; 4-methylsyringol, -0.03 and -0.37 ; and 4-allylsyringol, 0.87 and -0.05 .

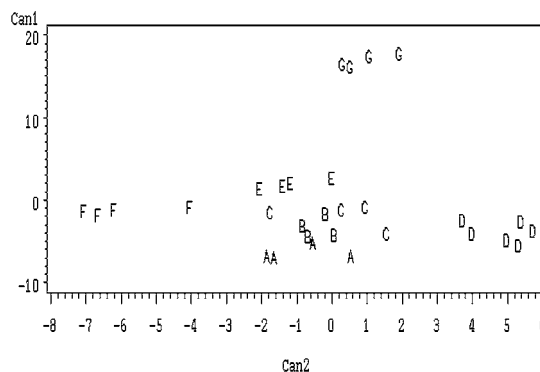


Figure 4. Canonical discriminant analysis of methyl octalactones, furanic compounds, pyranones, and other compounds of toasted woods (Table 4). Mathematical model: 100% of total dispersion in six canonical functions with a cumulative proportion of 82% in functions 1 and 2. Projections of the points of each species and provenance on plane defined by the two principal canonical axes 1 and 2. (A) *Q. robur*, (B) *Q. petraea*, (C) *Q. pyrenaica*, and (D) *Q. faginea*, Spanish oak woods; (E) *Q. robur* and (F) *Q. petraea*, French oak woods; and (G) *Q. alba*, American oak wood. Eigenvalues for functions 1 and 2 were 64.47 and 12.97, and canonical correlations were 0.992 and 0.963, respectively. The total canonical structure coefficients of the discriminant functions 1 and 2 were, respectively, as follows: furanyl-1-ethanone, 0.73 and -0.01 ; butyrolactone, 0.57 and 0.29; benzaldehyde, 0.02 and 0.54; hydroxybenzaldehyde, 0.83 and -0.29 ; benzothiazole, -0.14 and 0.43; 1*H*-pyrrole-2-carboxaldehyde, 0.75 and -0.21 ; phenylmethanol, 0.27 and 0.39; 2-phenylethanol, 0.68 and -0.01 ; 2-phenoxyethanol, -0.56 and 0.58; maltol, 0.81 and 0.10; isomaltol, 0.61 and -0.05 ; furfural, 0.47 and -0.39 ; 5-methylfurfural, 0.48 and -0.28 ; furfuryl alcohol, 0.95 and 0.05; 5-hydroxymethylfurfural, 0.42 and -0.30 ; *trans*- β -methyl- γ -octalactone, 0.22 and -0.08 ; and *cis*- β -methyl- γ -octalactone, 0.74 and 0.09.

pounds evaluated in Table 4 (Figure 4), four groups of woods, French *Q. petraea*, American *Q. alba*, Spanish *Q. faginea*, and all other studied woods, can be distinguished. However, the

statistical distance among the groups was marked only by American *Q. alba* with regard to all European species, and it was accounted for canonical function 1 with furfuryl alcohol, hydroxybenzaldehyde, maltol, *cis*-methyl octalactone, and 2-furanyl-1-ethanone as principal discriminant variables, according to the coefficients of total canonical structure that resulted in positives (Figure 4). French *Q. petraea* and Spanish *Q. faginea* are separated from other European species according to canonical function 2 that showed as principal discriminant variables 2-phenoxyethanol, benzaldehyde, benzothiazole, phenylmethanol, furfural, and hydroxymethylfurfural, all of them with positive coefficients except the last two, but the statistical distance in this case was smaller. This explains the different aromatic potential relating to volatile compounds, imputed to American wood with respect to French wood, proven in different wines (45, 55, 56) and with regard to Spanish woods (57) and, moreover, indicates more similarity among Spanish and French species.

In view of the joint results, the volatile composition of Spanish seasoned oak wood (*Q. petraea*, *Q. robur*, *Q. pyrenaica*, and *Q. faginea*) and its evolution during the toasting process were similar to those of French (*Q. petraea* and *Q. robur*) and American (*Q. alba*) oak woods, habitually used in aging wine. The chemical differences shown by Spanish species were only quantitative and were less marked by Spanish *Q. petraea*, *Q. robur*, and *Q. pyrenaica* with regard to French *Q. petraea* and *Q. robur*. If we consider these results and the studies carried out to date on the low molecular polyphenolic composition and tannic composition of the same Spanish oak woods in relation to French and American ones and in relation to the cooperage processing (1–6), Spanish *Q. petraea*, *Q. robur*, and *Q. pyrenaica* wood can be considered suitable for aging wine.

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