

## Volatile Compounds in Acacia, Chestnut, Cherry, Ash, and Oak Woods, with a View to Their Use in Cooperage

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Extracts of wood from acacia, European ash, American ash, chestnut, cherry, and three oak species (*Quercus pyrenaica*, *Quercus alba* and *Quercus petraea*) before and after toasting in cooperage were studied by GC–MS. 110 compounds were detected, and 97 of them were identified. In general, all studied woods showed more lignin derivatives than lipid and carbohydrate derivatives, with a higher variety of compounds detected and abundance of them. The toasting led to an increase in the concentrations of most of these compounds, and this increase is especially important in acacia, chestnut and ash woods. The *cis* and *trans* isomers of  $\beta$ -methyl- $\gamma$ -octalactone and isobutyrovanillone were only detected in oak wood, 3,4-dimethoxyphenol and 2,4-dihydroxybenzaldehyde only in acacia wood, and *p*-anisaldehyde and benzylsalicylate only in cherry wood, before and after toasting, and these compounds could be considered chemical markers for each one of these woods. Moreover, each wood has a characteristic volatile composition, from a quantitative point of view, and therefore we can expect a characteristic sensorial profile. The oak wood turned out to be the most balanced, since although it provides a lot of volatile compounds to the aroma and flavor of aged wine, it can do so without masking their primary and secondary aroma. On the whole, toasted acacia and chestnut woods showed a very high richness of studied compounds, as lignin as lipid and carbohydrate derivatives, while cherry and ash were much richer than toasted oak wood in lignin derivatives, but much poorer in lipid and carbohydrate derivatives.

**KEYWORDS:** *Quercus pyrenaica*; *Quercus alba*; *Quercus petraea*; acacia; chestnut; cherry; ash; toasting; volatile compounds

### INTRODUCTION

The use of wood during the processes of fermentation and/or aging of wines is a common practice in most of the world's wine-producing regions. In this process, wine undergoes important changes in its aroma, color, taste and astringency. The complexity of the aroma is increased because of the extraction of certain compounds present in the wood, which are transferred to wine during the aging process. The factors that affect the pool of wood 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 (1–6). In addition, 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 (7–9).

Oak is the main material used in making containers in the cooperages. Many volatile compounds have been identified in oak wood, and their contribution to the aroma and flavor of wine has been the objective of several research projects. The *cis* and *trans* isomers of  $\beta$ -methyl- $\gamma$ -octalactone, furfural and its derivatives, phenolic aldehydes such as vanillin and syringaldehyde, and volatile phenols such as eugenol, guaiacol and 4-methylguaiacol are notable due to their contribution to the wine aroma differences. Only some of them are originally present in wood in significant amounts (3, 4, 10–13), and many of them are intensified during the processing of wood in cooperage, especially in the toasting process. During toasting, a variety of hydrothermolysis and pyrolysis reactions take place, resulting in a degradation of biopolymers, such as lignin, polysaccharides, polyphenols and lipids. This thermodegradation leads to the formation of volatile phenols, phenolic aldehydes,

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phenolic alcohols, phenyl ketones, furanic aldehydes, furan and pyran derivatives, lactones, etc., which can be transferred to the wine during the aging process (1, 4, 5, 10, 14, 15).

In a wine cellar, the wood takes part in the manufacturing of wine in many ways: from large vats to barrels, as containers, and, in recent years, pieces of many sizes (powder, shavings, chips, cubes, staves) used as a cheaper alternative. We should keep in mind that barrels are expensive, and as their lifetime is short, it is necessary to renew them with certain frequency. In addition, the barrels take up a lot of space in the winery, and for these reasons some alternatives have been developed to make the aging process less expensive while ensuring that the wood extractives are released into the wine. One of these techniques involves putting new pieces of wood (toasted or untoasted) into inert containers (stainless steel tanks or used barrels) (16–18).

Usually, they are oak pieces, but other woods could also be used, in order to give a special personality to the wine. Although oak is the main material used in making containers in cooperages, other species like chestnut, cherry and, more rarely, acacia and mulberry have been considered as possible sources of wood, for production of both wines and their derived products like vinegar, cider, or spirits like brandies (19–24). Many producers even prefer using local woods in order to reduce cost (25), and recently some wine cellars have ordered barrels with some nonoak staves included from cooperages.

There are very little available data about the chemical composition of these woods. During wine aging, in all cases significant differences were found in the characteristics of wines or spirits, depending on the kind of wood used. The objective of this work is to study the volatile composition of some woods that could be used in cooperage, before and after the toasting process, as a first step of the enological characterization of these woods in order to find out what effects they may have on the aroma profile and sensory characteristics of the wine.

## MATERIAL AND METHODS

**Wood Samples.** The oak heartwood used in this work comes from staves of *Quercus petraea* trees grown in Allier (France), from *Quercus alba* grown in Missouri (EEUU), and from *Quercus pyrenaica* grown in Salamanca (Spain), provided by Tonelería Intona. Acacia, chestnut, cherry, European ash and American ash were also provided as staves for making barrels by Tonelería Intona, SL (Navarra, Spain). Woods were naturally seasoned for 24 months, and toasted at the same time, with a medium intensity (185 °C for 45 min). Samples were taken before and after toasting. Several wood pieces were cut out of each stave, from five staves of each wood. The pieces of each wood were ground, sieved, and mixed, taking the sawdust ranging from 0.80 to 0.28 mm. The samples of each wood were mixed because our objective was to know the volatile profile of these woods, before and after toasting, without going deeply into their natural variation.

**Chemicals.** Reference compounds of the volatile identified and the internal standards were obtained from commercial sources: those numbered in **Table 1** as 1, 5, 14, 31, 42, 67, and 72 were purchased from Sigma Chemical (St. Louis, MO); 3, 4, 13, 28, 29, 35, 38, 39, 40, 43, 46, 49, 50, 53, 56, 63, 68, 74, 88, 93, 99, 103, 107,  $\gamma$ -hexalactone, 2-octanol and *o*-vanillin from Aldrich Chemie (Neu-Ulm, Germany); 8 and 34 from Chem Service (West Chester, PA); 9, 10, 17, 19, 36, 37, 45, 47, 58, 59, 62, 84, 90, 96, and 101 from Fluka Chimie AG (Buchs, Switzerland); 54, 57 and 3,4-dimethylphenol from Riedel-de-Häen (Seelze, Germany); 75, 86, 95, and 110 from Extrasynthese (Genay, France); and 104 from ABCR GmbH & Co. (Karlsruhe, Germany). All reactives used (ethanol, dichloromethane, tartaric acid, potassium bitartrate, and anhydrous sodium sulfate) were purchased from Panreac (Barcelona, Spain).

**Extraction of Volatile Compounds.** Volatile compounds were extracted from wood following the method modified by Cadahía et al. (5) from Chatonnet et al. (15): the sawdust samples (2 g) were soaked

in 100 mL of a hydro-alcoholic solution (12% ethanol, 0.7 g/L tartaric acid, 1.11 g/L potassium bitartrate), for 15 days at room temperature and darkness, in order to simulate the migration of compounds during wine aging. After the mixture was filtered, we added the internal standards 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. Four internal standards were used: 100  $\mu$ L of a solution of 3,4-dimethylphenol (20 mg/L in 95% ethanol) (for volatile phenols), 100  $\mu$ L of a solution of *o*-vanillin (1 mg/mL in 95% ethanol) (for phenolic aldehydes and related compounds), 50  $\mu$ L of a solution of 2-octanol (1 mg/mL in 95% ethanol) (for aldehydes and alcohols with a linear chain), and 100  $\mu$ L of a solution of  $\gamma$ -hexalactone (2 mg/mL in 95% ethanol) (for the remaining compounds). In all cases, the samples were analyzed in duplicate.

**GC–MS analyses.** Analyses were performed using an Agilent 6890N GC system gas chromatograph (Palo Alto, CA) equipped with a quadrupole mass spectrometer Agilent 5975B. Samples were injected in split mode (30:1), and volatiles were separated using a fused silica capillary column (SUPELCO WAX-10) (30 m  $\times$  0.25 mm i.d., and 0.25  $\mu$ m film thickness), supplied by Supelco (Madrid, Spain), and under the working conditions described in Cadahía et al. (26): 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 290 °C (MS source at 230 °C, and MS quad at 150 °C). The Kovats Index values were calculated in this column, and in another column with different polarity (ZB-5, 30 m  $\times$  0.25 mm i.d., and 0.25  $\mu$ m film thickness), supplied by Phenomenex (Madrid, Spain). Quantitative determinations were carried out by the internal standard method, using peak areas obtained from selected ion monitoring (SIM). The selected ions for each of the evaluated compounds are showed in **Table 1**. 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 0.973 and 0.9996 were obtained. In general, more than one linear regression was made for each compound, at different concentration levels. The detection limits for these compounds in these analytical conditions were between 0.001 and 0.01  $\mu$ g/g of wood, except for vanillyl and homovanillyl alcohol (0.05  $\mu$ g/g) and  $\gamma$ -butyrolactone (0.03  $\mu$ g/g). Calibration of a similar compound was used when the pure reference standard was not available, as listed in **Table 1**. The variation coefficients of duplicates were minor than 3%.

## RESULTS AND DISCUSSION

**Identification of Volatile Compounds.** The GC–MS analysis of the hydro-alcoholic wood extracts revealed the presence in these woods of the majority of the molecules previously identified in oak woods (4–6, 15, 26–31). Moreover other volatile compounds not mentioned before in oak wood were found. **Table 1** gives the components that were detected in at least one of the studied woods, together with their retention index in two columns, and their identification mode (5, 28, 30–35). As can be observed, 110 compounds were detected from which 54 compounds were identified by comparing their mass spectra and retention index with those of pure standards; 42 were tentatively identified by comparing their mass fragmentation with those in a commercial library and with those reported in the literature, also taking into account their retention index, structure and molecular weight. Finally, 13 compounds remained unidentified.

**Table 1.** Compounds Detected in at Least One of the Studied Woods, Retention Times, Ion and Standard Used in Quantification, and Identification Methods

peak no.	K1 <sup>a</sup>		name		ion <sup>b</sup> m/z	ID <sup>c</sup>	calibration <sup>d</sup>
	DB5	carbowax	IUPAC	common			
1	801	1084	1-hexanal		56	S	
2	866	1358	1-hydroxy-2-butanone		57	T <sup>g</sup>	2-ethyl-1-hexanol
3	1109	1384	1-nonanal		57	S	
4	901	1416	2-octenal		70	S	
5	834	1444	2-furancarboxaldehyde	furfural	96	S	
6	1081	1452	1-methoxy-2-ethoxyethyl-1-furan		97	T <sup>f</sup>	furfural
7	870	1454	1-(acetyloxy)-2-propanone	acetol acetate	43	T <sup>g</sup>	2-ethyl-1-hexanol
8	912	1483	1-(2-furanyl)-ethanone		95	S	
9	1032	1489	2-ethyl-1-hexanol		57	S	
10	962	1493	benzaldehyde		106	S	
11	1172	1520	n.i. <sup>e</sup>		111		2-ethyl-1-hexanol
12	1159	1521	<i>trans</i> -2-nonenal		70	S	
13	969	1521	1-acetyloxy-2-butanone		57	T <sup>f</sup>	2-ethyl-1-hexanol
14	965	1551	5-methyl-2-furancarboxaldehyde	5-methylfurfural	110	S	
15	978	1558	methyl-2-furoate		95	T <sup>g</sup>	furfural
16	913	1593	dihydro-2(3 <i>H</i> )furanone	$\gamma$ -butyrolactone	86	S	
17	1094	1595	benzoic acid, methyl ester	methyl benzoate	105	T <sup>f</sup>	benzaldehyde
18	1094	1620	1-phenyl ethanone	acetophenone	105	T <sup>h</sup>	1-(2-furanyl)-ethanone
19	1368	1644	hydroxybenzaldehyde		122	T <sup>h</sup>	benzaldehyde
20	857	1647	2-furanmethanol	furfuryl alcohol	98	S	
21	1091	1658	3-ethyl-2-hydroxy-2-ciclopenten-1-one	3-ethylcyclohexenone	126	T <sup>f</sup>	cyclohexenone
22	979	1683	3-methyl-2(5 <i>H</i> )-furanone	$\alpha$ -methylcrotonolactone	98	T <sup>h</sup>	$\gamma$ -butyrolactone
23	1094	1696	n.i.		97		$\gamma$ -butyrolactone
24	1067	1696	5-ethoxydihydro-2(3 <i>H</i> )-furanone	$\gamma$ -ethoxybutyrolactone	85	T <sup>i</sup>	$\gamma$ -butyrolactone
25	1016	1698	4,5-dimethyl-2-ciclohexen-1-one		82	T <sup>f</sup>	cyclohexenone
26	915	1716	2(5 <i>H</i> )-furanone	crotonolactone	55	T <sup>h</sup>	$\gamma$ -butyrolactone
27	1057	1777	3,5-dimethyl-2-hydroxy-2-ciclopenten-1-one	3,5-dimethylcyclohexenone	126	T <sup>f</sup>	cyclohexenone
28	1252	1781	ethanol-2-(2-butoxyethoxy)		57	S	
29	1027	1784	2-hydroxy-2-cyclopenten-1-one	cyclohexenone	112	S	
30	1178	1820	n.i.		85		$\gamma$ -butyrolactone
31	1103	1822	2,3-dihydro-5-hydroxy-6-methyl-4 <i>H</i> -pyran-4-one	dihydromaltol	128	T <sup>j</sup>	maltol
32	1089	1833	2-methoxyphenol	guaiacol	124	S	
33	998	1842	4-hydroxy-5,6-dihydro-(2 <i>H</i> )-pyran-2-one		114	T <sup>g</sup>	maltol
34	1036	1854	phenylmethanol		79	S	
35	1292	1861	<i>trans</i> -4-methyl-5-butylidihydro-2(3 <i>H</i> )-furanone	<i>trans</i> - $\beta$ -methyl- $\gamma$ -octalactone	99	S	
36	1113	1888	2-phenylethanol		91	S	
37	1231	1915	benzothiazole		135	S	
38	1325	1928	<i>cis</i> -4-methyl-5-butylidihydro-2(3 <i>H</i> )-furanone	<i>cis</i> - $\beta$ -methyl- $\gamma$ -octalactone	99	S	
39	1191	1928	4-methyl-2-methoxyphenol	4-methylguaiacol	138	S	
40	1111	1938	3-hydroxy-2-methyl-4 <i>H</i> -pyran-4-one	maltol	126	S	
41	1078	1944	2,5-furandicarboxaldehyde		124	T <sup>k</sup>	furfural
42	983	1978	phenol		94	S	
43	1059	1980	2-methylphenol	<i>o</i> -cresol	107	S	
44	1255	1986	4-methoxybenzaldehyde	<i>p</i> -anisaldehyde	135	T <sup>f</sup>	benzaldehyde
45	1009	1990	1- <i>H</i> -pyrrole-2-carboxaldehyde		95	S	
46	1274	2002	4-ethyl-2-methoxyphenol	4-ethylguaiacol	137	S	
47	1083	2013	4-hydroxy-2,5-dimethyl-3(2 <i>H</i> )-furanone	Furaneol	128	S	
48	1129	2026	5-acetyldihydro-2(3 <i>H</i> )-furanone	solerone	85	T <sup>f</sup>	$\gamma$ -butyrolactone
49	1079	2056	4-methylphenol	<i>p</i> -cresol	107	S	
50	1086	2064	3-methylphenol	<i>m</i> -cresol	107	S	
51	1153	2066	n.i.		128		$\gamma$ -butyrolactone
52	1461	2083	4-propyl-2-methoxyphenol	4-propylguaiacol	137	T <sup>h</sup>	4-ethyl guaiacol
53	1220	2115	2-phenoxyethanol		94	S	
54	1359	2139	2-methoxy-4-(2-propenyl) phenol	eugenol	164	S	
55	1314	2165	4-vinyl-2-methoxyphenol	4-vinylguaiacol	150	T <sup>h</sup>	4-ethyl guaiacol
56	1309	2169	5-acetoxymethyl-2-furancarboxaldehyde		126	S	
57	1193	2192	3,4-dimethylphenol		107	S	
58	1408	2226	<i>cis</i> -2-methoxy-4-(1-propenyl) phenol	<i>cis</i> -isoeugenol	164	S	
59	1353	2237	2,6-dimethoxyphenol	syringol	154	S	
60	1431	2250	n.i.		43		2-ethyl-1-hexanol
61	1406	2307	n.i.		155		vanillin
62	1451	2314	<i>trans</i> -2-methoxy-4-(1-propenyl) phenol	<i>trans</i> -isoeugenol	164	S	
63	1449	2322	4-methyl-2,6-dimethoxyphenol	4-methylsyringol	168	S	
64	1250	2338	n.i.		43		2-ethyl-1-hexanol
65	1528	2381	4-ethyl-2,6-dimethoxyphenol	4-ethylsyringol	167	T <sup>h,l</sup>	4-methylsyringol
66	1164	2389	benzenecarboxylic acid	benzoic acid	105	T <sup>f</sup>	benzaldehyde
67	1301	2415	n.i.		43		2-ethyl-1-hexanol
68	1612	2452	4-propyl-2,6-dimethoxyphenol	4-propylsyringol	167	T <sup>h,l</sup>	4-methylsyringol
69	1235	2466	5-hydroxymethyl-2-furancarboxaldehyde	5-hydroxymethylfurfural	97	S	
70	1605	2511	4-allyl-2,6-dimethoxyphenol	4-allylsyringol	194	S	
71	1648	2518	9-hydroxymegastigma-4,7-dien-3-one	3-oxo- $\alpha$ -ionol	108	T <sup>m</sup>	
72	1399	2518	4-hydroxy-3-methoxybenzaldehyde	vanillin	151	S	
73	1461	2557	2-(4-hydroxy-3-methoxyphenyl) acetaldehyde	isoacetovanillone	137	T <sup>h,n</sup>	acetovanillone
74	1518	2565	4-hydroxy-3-methoxy benzoic acid, methyl ester	methyl vanillate	151	S	
75	1487	2595	1-(4-hydroxy-3-methoxyphenyl) ethanone	acetovanillone	151	S	
76	1534	2617	1-(4-hydroxy-3-methoxyphenyl)-2-propanone	isopropiovanillone	137	T <sup>n</sup>	acetovanillone
77	1263	2627	3-methyl-1,2-benzenediol	3-methylcatechol	124	T <sup>f</sup>	phenol

Table 1. Continued

peak no.	DB5	carbowax	IUPAC	common	ion <sup>b</sup> <i>m/z</i>	ID <sup>c</sup>	calibration <sup>d</sup>
78	1606	2646	n.i.		121		vanillin
79	1201	2657	1,2-benzenediol	catechol	110	T <sup>f</sup>	phenol
80	1501	2661	1-(4-hydroxy-3-methoxyphenyl) propanone	propiovanillone	151	T <sup>fi,n</sup>	acetovanillone
81	1703	2696	<i>cis</i> or <i>trans</i> 2,6-dimethoxy-4-(1-propenyl) phenol		194	T <sup>fh,i</sup>	4-allyl syringol
82	1293	2727	4-methyl-1,2-benzenediol	4-methylcatechol	124	T <sup>fh</sup>	phenol
83	1448	2732	3,4-dimethoxyphenol		154	T <sup>f</sup>	syringol
84	1872	2737	2-hydroxybenzoic acid, phenyl methyl ester	benzylsalicylate	91	S	
85	1655	2754	1-(4-hydroxy-3-methoxyphenyl)-2-butanone	isobutyrovanillone	137	T <sup>f</sup>	acetovanillone
86	1423	2764	4-hydroxy-3-methoxybenzyl alcohol	vanillyl alcohol	154	S	
87	1590	2770	1-(4-hydroxy-3-methoxyphenyl) butanone	butyrovanillone	151	T <sup>fi,n</sup>	acetovanillone
88	1534	2805	4-hydroxy-3-methoxyphenethanol	homovanillyl alcohol	137	S	
89	1778	2832	n.i.		137		vanillin
90	1643	2904	4-hydroxy-3,5-dimethoxybenzaldehyde	syringaldehyde	182	S	
91	1473	2918	2-methoxy-1,4-benzenediol	2-methoxy hydroquinone	140	T <sup>f</sup>	phenol
92	1712	2927	2-(4-hydroxy-3,5-dimethoxyphenyl) acetaldehyde	isoacetosyringone	167	T <sup>fh,n</sup>	acetosyringone
93	1780	2933	4-hydroxy-3,5-dimethoxy benzoic acid, methyl ester	methyl syringate	181	S	
94	1651	2941	4-(ethoxymethyl)-2-methoxyphenol	ethyl vanillyl ether	137	S	
95	1744	2953	1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone	acetosyringone	181	S	
96	1442	2965	4-(2-hydroxyethyl)phenol	tyrosol	107	S	
97	1785	2979	1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone	isopropiosyringone	167	T <sup>fh,n</sup>	acetosyringone
98	1753	3010	1-(4-hydroxy-3,5-dimethoxyphenyl) propanone	propiosyringone	181	T <sup>fh,n</sup>	acetosyringone
99	1614	3026	3,4,5-trimethoxyphenol		169	S	
100	1827	3056	n.i.		167		vanillin
101	1450	3074	2,4-dihydroxybenzaldehyde		137	S	
102	1835	3085	1-(4-hydroxy-3,5-dimethoxyphenyl) butanone	butyrosyringone	181	T <sup>fi</sup>	acetosyringone
103	1747	3096	3-methoxy-4-hydroxycinnamaldehyde	coniferaldehyde	178	S	
104	2339	3122	2-ethyl hexyl-2(E)-3-(4-methoxyphenyl)-2-propenoate	2-ethyl hexyl <i>trans</i> -4-methoxycinnamate	178	S	
105	1731	3174	n.i.		167		vanillin
106	2019	3183	n.i.		167		vanillin
107	1745	3213	4-((1E)-3-hydroxy-1-propenyl)-2-methoxyphenol	coniferyl alcohol	137	S	
108	1741	3215	2-(4-hydroxy-3-methoxyphenyl) acetic acid, methyl ester	methyl homovanillate	137	T <sup>fi</sup>	homovanillic acid
109	1898	3304	3,5-dimethoxy-4-hydroxy-dihydro cinnamyl alcohol	dihydrocinapyl alcohol	168	T <sup>fh</sup>	coniferyl alcohol
110	2002	3458	3,5-dimethoxy-4-hydroxycinnamaldehyde	sinapaldehyde	208	S	

<sup>a</sup> KI = Kovats Index. <sup>b</sup> Ion used in quantification. <sup>c</sup> ID = identification mode. S = peak identified with the pure reference standard. T = peak tentatively identified with the spectrum reported in the literature. <sup>d</sup> Calibration used when the pure reference standard was not available. <sup>e</sup> Not identified. <sup>f</sup> Commercial libraries NIST 2.0 and Wiley 7. <sup>g</sup> Faix et al., 1990 (37). <sup>h</sup> Faix et al., 1991 (33). <sup>i</sup> Vichi et al., 2007 (31). <sup>j</sup> Cutzach et al., 1997 (28). <sup>k</sup> Cutzach et al., 1999. <sup>l</sup> Guillen and Ibargoitia, 1998 (34). <sup>m</sup> Natali et al., 2006 (30). <sup>n</sup> Cadahia et al., 2003 (5).

Among detected compounds, many of them were low-molecular-weight phenolic compounds, arising from wood lignin degradation. The most simple structures identified were phenol and its 2-, 3-, and 4-methyl derivatives, as well as catechol and its 3- and 4-methyl derivatives, of which these last had not been mentioned before in oak wood chips or barrels, like 2-methoxy-1,4-benzenediol. Moreover, a wide number of guaiacol (2-methoxyphenol) and syringol (2,6-dimethoxyphenol) derivatives were detected and identified, due to the structure of angiosperm lignin (36). The mass fragments of the two series of compounds were distinguished by a *m/z* 30, due to the presence of an additional methoxy group, as also occurs with 3,4-dimethoxy and 3,4,5-trimethoxyphenol that were also identified. Among these derivatives we found 4-alkyl, alcohol, ether, aldehyde, keto, acid and ester for both guaiacyl and syringyl, in structures such as C<sub>6</sub>-C<sub>1</sub> (benzyl) and C<sub>6</sub>-C<sub>3</sub> (cinnamyl), with the cinnamyl structure occurring more frequently.

In addition, other simpler lignin derivatives identified were benzaldehyde and their hydroxy, 2,4-dihydroxy and 4-methoxy derivatives, and compounds like phenylmethanol, 2-phenylethanol, tyrosol, 2-phenoxyethanol and acetophenone.

Some of the unidentified compounds have been considered as lignin derivatives, as in the cases of peaks 89 [MS (EI) *m/z* (%): 137 (100), 164 (60), 224 (50), 149 (35)]; 100 [MS (EI) *m/z* (%): 167 (100), 210 (42), 182 (38), 154 (25)]; 105 [MS (EI) *m/z* (%): 167 (100), 198 (30)]; and 106 [MS (EI) *m/z* (%): 167 (100), 254 (70), 194 (45), 168 (38)], which have base peaks *m/z* = 137 or 167, characteristics of compounds derived from guaiacol and syringol, respectively. In fact, the mass spectrum of peak 100 is very similar to that of peak 97 [MS (EI) *m/z* (%): 167 (100), 210 (20), 123 (10), 106 (5)], tentatively

identified as 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone (5,32). Peaks 61 [MS (EI) *m/z* (%): 155 (100), 109 (65), 127 (40)] and 78 [MS (EI) *m/z* (%): 121 (100), 119 (62), 137 (30), 138 (30), 161 (28)] were also considered lignin derivatives. However, this needs an additional confirmation.

In addition to lignin derivatives, we can also find in **Table 1** some compounds arising from wood carbohydrate and lipid degradation, such as aldehydes, ketones, alcohols, lactones, furan and pyran derivatives and some others. Regarding the compounds deriving from the degradation of sugars, nine furan derivatives were detected in the analyzed extracts, including 1-methoxy-2-ethoxyethyl-1-furan, methyl-2-furoate and 5-acetoxymethyl furfural, besides the furan derivatives usually detected in oak wood (4, 5). Furthermore, in addition to maltol, two compounds tentatively identified as dihydromaltol and 4-hydroxy-5,6-dihydro-(2*H*)-pyran-2-one were detected. The furanic and pyranic derivatives are the products of multiple dehydrations and rearrangements of carbohydrates under heating, along with cyclopentanone or cyclohexanone structures, included nitrogen compound specific from Maillard reaction.

Among unidentified compounds, peaks 60 [MS (EI) *m/z* (%): 43 (100), 69 (15), 128 (13)]; 64 [MS (EI) *m/z* (%): 43 (100), 57 (30), 85 (15)]; and 67 [MS (EI) *m/z* (%): 43 (100), 69 (38), 73 (25), 86 (20)] could be considered carbohydrate derivatives because they have as base peak *m/z* = 43, and peak with *m/z* = 57 or 69, characteristics of unidentified compounds generated during cellulose thermodegradation (37). Peaks 11 [MS (EI) *m/z* (%): 111 (100), 139 (85), 184 (15)]; 23 [MS (EI) *m/z* (%): 97 (100), 69 (65), 41 (50), 126 (42)]; 30 [MS (EI) *m/z* (%): 85 (100), 102 (28), 75 (28), 131 (20)]; and 51 [MS (EI) *m/z* (%): 128 (100), 99 (80), 57 (40), 98 (35)] remain unidentified, and

they were included in lipid and carbohydrate derivatives in **Tables 2** and **3**.

We also found four low-molecular weight lactones, tentatively identified, which had only been mentioned before in oak wood chips extracted by accelerated solvent extraction (30):  $\gamma$ -crotonolactone,  $\alpha$ -methyl- $\gamma$ -crotonolactone, 5-ethoxy- $\gamma$ -butyrolactone, and solerone. The origin of lactones could be the dehydration of  $\alpha$ -hydroxyacids and a later cyclation. On the other hand, the enzymatic or chemical degradation by autoxidation of polyunsaturated fatty acids leads to the formation of volatile alkyl aldehydes or ketones (38, 39), some of them identified in these woods (**Table 1**).

Lastly, a C-13 norisoprenoid was tentatively identified, 3-oxo- $\alpha$ -ionol (peak 69), a compound that has previously been reported in oak wood as a consequence of the degradation of carotenoids (40, 41), and which is considered a probable precursor of components associated with tobacco-like aroma (30).

**Volatile Composition of Studied Woods.** The GC-MS quantitative evaluations of the volatile compounds that were extracted from acacia, chestnut, cherry, European and American ash, and Spanish, American and French oak woods, seasoned and toasted, in our analytical conditions, are included in **Tables 2** and **3**, respectively, arranged depending on whether or not they are lignin derivatives or lipid and carbohydrate derivatives. A characteristic profile was observed for each wood extract, and some compounds were only detected in one type of wood, seasoned and toasted. Thus, 3,4-dimethoxyphenol and 2,4-dihydroxybenzaldehyde in acacia wood, *p*-anisaldehyde and benzylsalicylate in cherry wood, peak 78 in ash wood, and the *cis* and *trans* isomers of  $\beta$ -methyl- $\gamma$ -octalactone and isobutyrovanillone in oak wood could be considered to be chemical markers of each one of these woods. However, it is necessary to keep in mind that the presence (although in a very small quantity) of the *cis* and *trans* isomers of  $\beta$ -methyl- $\gamma$ -octalactone was mentioned in ethanolic extracts (55%, pH = 4.2) used to simulate brandy aging in chestnut wood barrels (23), but not in the simulation of red wine aging (ethanol 12%, pH = 3.5) (42), under more similar conditions to those in this study.

From a quantitative point of view, the characteristic profile of each wood should include more compounds. In general, all seasoned wood studied showed more lignin derivatives than lipid and carbohydrate derivatives, with a higher variety of compounds detected and abundance of them (**Table 2**). Taken as a whole, the seasoned acacia wood was the one poorest in these compounds, as much in lignin derivatives as in lipid and carbohydrate derivatives, with sinapaldehyde being the most abundant (21  $\mu\text{g/g}$ ), followed by coniferyl alcohol, 2,4-dihydroxybenzaldehyde, coniferaldehyde, syringaldehyde, peak 105, and 3,4,5-trimethoxyphenol, with concentrations higher than 5  $\mu\text{g/g}$ . On the contrary, the seasoned chestnut wood was the richest one, especially with regard to lignin derivatives, highlighting the concentrations of coniferyl alcohol (56.5  $\mu\text{g/g}$ ), and syringaldehyde (52.6  $\mu\text{g/g}$ ), together with sinapaldehyde, coniferaldehyde, ethyl vanillyl ether, vanillic and dihydrocinapic alcohol, with all of them showing concentrations higher than 20  $\mu\text{g/g}$ . A higher concentration of low-molecular-weight phenolic compounds in chestnut wood when compared to oak wood has been mentioned by Canas et al. (43). In seasoned cherry wood, three compounds were the most abundant: methylsyringate (69.7  $\mu\text{g/g}$ ), 3,4,5-trimethoxyphenol (60.3  $\mu\text{g/g}$ ), and benzoic acid (43.7  $\mu\text{g/g}$ ), with an abundance of benzylsalicylate and methylvanillate, as well as propiosyringone and peak 30 also being characteristic of this wood. This wood showed very low concentrations of phenyl aldehydes and phenyl

ketones, all of them lower than 1  $\mu\text{g/g}$ , except vanillin (1.14  $\mu\text{g/g}$ ) and syringaldehyde (2.62  $\mu\text{g/g}$ ). Flamini et al. (44) also detected a high concentration of 3,4,5-trimethoxyphenol in seasoned cherry wood.

Regarding seasoned ash wood, we can see quantitative differences between European and American, with American being the richer (**Table 2**), except in five compounds: vanillyl and homovanillyl alcohol, ethyl vanillyl ether, isoacetosyringone, and isopropiosyringone, although the differences in the three last are insignificant. These woods are characterized by their high concentrations of syringaldehyde and coniferaldehyde (American ash), as well as of tyrosol. Peak 78, only detected in ash wood, shows very different concentrations between European (0.13  $\mu\text{g/g}$ ) and American (11.4  $\mu\text{g/g}$ ) ash.

Lastly, the seasoned oak wood, besides the qualitative differences already mentioned, shows quantitative differences when compared to the other woods. Regarding lipid and carbohydrate derivatives, we have detected higher concentrations of 1-hexanal, ethanol-2-(2-butoxyethoxy), crotonolactone, furfural, 5-hydroxymethylfurfural, and maltol, in addition to the presence of the *cis* and *trans* isomers of  $\beta$ -methyl- $\gamma$ -octalactone, the most characteristic compounds of this wood. With regard to lignin derivatives, the seasoned oak wood is characterized by the significant presence of phenyl aldehydes (especially syringaldehyde), alcohols (except vanillyl), and ketones, and the absence of catechol and their derivatives, and phenyl methyl esters, although methyl syringate was detected in small quantities. The presence of eugenol is also significant, especially in *Q. pyrenaica*. However, as a whole, the total content of lignin derivatives is higher in seasoned chestnut, cherry or American ash woods.

Comparing the results shown in **Tables 2** and **3**, we can see that toasting leads to an increase in the concentration of most of these compounds, and this increase is especially important in acacia, chestnut, cherry and ash woods, regarding lignin derivatives, and even more important regarding the other compounds, in such a way that the characteristic profile of each toasted wood is different from that of untoasted wood.

Among lignin derivatives, sinapaldehyde shows the highest concentrations in all toasted woods, with concentrations from 240  $\mu\text{g/g}$  (oak) to 965  $\mu\text{g/g}$  (European ash). It is well-known that the angiosperm lignin is a three-dimensional heteropolymer formed by copolymerization of two phenylpropenoic alcohols: coniferylic and sinapylic. During wood toasting, a depolymerization of the lignin takes place that produces phenolic aldehydes, since as a first step the alcohol is depolymerized and thermooxidated into corresponding aldehydes. If we take into account the easier thermodepolymerization of dimethoxyphenyl units compared to monomethoxyphenyl (45), this explains the high concentrations of this compound in toasted wood, as has already been described in oak wood (5, 14). However, the highest concentration of sinapaldehyde is the only common feature in the studied toasted woods, since the toasting also produces the cleavage of  $\alpha$ - $\beta$  bonds of cinnamic aldehydes and their thermo-oxidation and thermodecarboxylation, which leads to the formation of a great variety of molecules, and the concentration of each one of these molecules is related to the lignin structure of each wood.

Toasted acacia wood showed high levels of sinapaldehyde, isopropiosyringone, coniferaldehyde and syringaldehyde, all of them higher than 200  $\mu\text{g/g}$  of wood. On the other hand, compounds such as 4-propyl and 4-allylsyringol (with a smoky aroma) and *cis*- or *trans*-2,6-dimethoxy-4-(1-propenyl)phenol showed the highest concentrations than the other toasted woods,

**Table 2.** GC Quantitative Evaluation of Volatile Compounds (Micrograms per Gram of Dried Wood) (Average of Duplicate) in Extracts of Different Seasoned Woods

peak	compound	acacia	chestnut	cherry	European ash	American ash	Spanish oak ( <i>Q. pyrenaica</i> )	American oak ( <i>Q. alba</i> )	French oak ( <i>Q. petraea</i> )
Lignin Derivatives									
42	phenol	0.13	0.10	0.42	0.12	0.15	0.09	0.06	0.07
43	<i>o</i> -cresol		0.02	0.02	0.04				
49	<i>p</i> -cresol		0.03	0.09	0.03	0.06			
79	catechol	0.13	0.04	0.35					
77	3-methylcatechol	0.08		0.03					
91	2-methoxy hydroquinone	0.19	0.34	3.26	0.10	0.42	0.34	0.32	0.42
32	guaiacol	0.43	0.05	0.18	0.08	0.11	0.38	0.04	0.05
39	4-methylguaiacol	0.04	0.07	0.01	0.13	0.75	0.42	0.07	0.56
46	4-ethylguaiacol	0.09	0.02	0.01		0.02	0.01		
52	4-propylguaiacol					0.04	0.02		
55	4-vinylguaiacol	0.40	0.32	0.27	0.40	0.60	0.88	0.18	0.18
54	eugenol	0.10	1.97	0.06	0.19	0.44	5.52	1.38	1.41
58	<i>cis</i> -isoeugenol	0.03	0.05			0.07	0.05	0.04	0.07
62	<i>trans</i> -isoeugenol	1.00	2.17	0.04	1.28	2.35	1.39	1.81	2.24
83	3,4-dimethoxyphenol	1.24							
59	syringol	0.83	0.12	0.38	0.16	0.16	1.06	0.12	0.14
63	4-methylsyringol	0.34	0.16	0.03	0.19	0.31	0.33	0.23	0.17
65	4-ethylsyringol	0.06	0.02	0.04	0.03	0.02	0.04	0.16	0.02
68	4-propylsyringol	0.07	0.05			0.06			
70	4-allylsyringol	0.45	2.35	0.36	0.40	0.47	2.85	0.91	0.34
81	<i>cis</i> - or <i>trans</i> -2,6-dimethoxy-4-(1-propenyl)-phenol	2.36	0.36	0.22	1.40	1.97	2.19	5.05	4.08
99	3,4,5-trimethoxyphenol	5.31	1.56	60.30	0.01	0.28	2.11	1.42	7.05
86	vanillyl alcohol				3.89	0.71			
88	homovanillyl alcohol	1.19	0.42	0.64	8.17	1.46	1.44	1.60	0.65
107	coniferyl alcohol	19.60	56.50		1.09	1.50	2.21	4.39	19.10
109	dihydrosinapyl alcohol	2.10	20.80	2.05	0.24	2.35	18.10	8.83	7.13
94	ethyl vanillyl ether	0.55	28.00	0.93	1.24	0.77	22.90	13.70	12.00
10	benzaldehyde	0.11	0.08	0.39	0.06	0.29	0.06	0.05	0.04
19	hydroxybenzaldehyde					0.06			
101	2,4-dihydroxybenzaldehyde	14.90							
44	<i>p</i> -anisaldehyde			0.33					
72	vanillin	1.68	24.40	1.14	7.25	14.70	11.70	7.16	12.10
90	syringaldehyde	6.03	52.60	2.62	44.70	50.80	48.20	18.90	47.30
103	coniferaldehyde	9.30	28.40	0.84	9.51	59.00	8.72	14.60	19.70
110	sinapaldehyde	21.00	43.40	0.79	1.82	9.63	1.31	14.90	23.10
75	acetovanillone	0.22	0.45	0.22	0.23	0.44	0.61	0.42	0.38
80	propiovanillone	0.15	0.87	0.99	0.23	0.42	4.71	7.55	1.42
87	butyrovannillone	0.65	1.99	0.42	0.59	1.96	3.10	1.45	1.39
95	acetosyringone	0.54	0.57	0.76	0.44	0.40	0.96	1.14	0.56
98	propiosyringone	0.51	3.02	6.92	0.15	0.38	9.49	1.83	2.39
102	butyrosyringone	1.43	1.42	0.66			6.34	3.63	3.22
73	isoacetovanillone	2.07	3.41	0.07	2.54	5.29	8.28	2.78	3.01
76	isopropiovanillone	0.93	1.19	0.07	0.91	1.84	3.65	1.29	1.30
85	isobutyrovannillone						0.06	0.09	0.07
92	isoacetosyringone	1.96	2.94	0.79	2.91	2.18	3.57	3.65	4.44
97	isopropiosyringone	1.47	1.47	0.25	1.75	1.31	6.79	2.39	1.79
66	benzoic acid	1.20	0.12	43.70	0.45	1.24			
17	methyl benzoate			0.05					
108	methyl homovanillate			1.31	5.41	7.22			
74	methyl vanillate		0.05	8.83		0.15			
93	methyl syringate		0.18	69.70	0.38	0.39	0.13	0.44	0.28
84	benzyl salicylate			7.67					
104	2-ethyl hexyl <i>trans</i> -4-methoxycinnamate		0.27	0.16	0.18	0.43	0.07	0.19	0.21
34	phenylmethanol	2.73	2.65	2.68	2.77	2.85	3.39	3.68	3.96
36	2-phenylethanol	0.14	0.20	0.45	0.28	1.08	0.34	0.18	0.10
96	tyrosol				15.20	20.90	1.37	4.16	0.11
53	2-phenoxyethanol	0.34	0.48	0.46	0.98	6.11	0.82	1.21	0.33
18	acetophenone	0.01	0.02	0.01	0.01	0.02			0.01
	peak 61		0.05			0.02			
	peak 78				0.13	11.40			
	peak 89		0.74		0.84	0.13			
	peak 100		0.03						
	peak 105	5.78	0.93	4.26	3.43	1.16	6.43	3.24	1.63
	peak 106		0.60						
	<i>total</i>	110.08	288.11	226.36	123.59	216.96	193.36	138.93	184.60
Lipid and Carbohydrate Derivatives									
1	1-hexanal	0.27	0.87	0.41	0.05		3.73	2.78	1.94
3	1-nonanal	0.22			0.04	0.25			
12	2-nonenal		0.34	0.25			1.00	0.29	0.38
4	2-octenal			0.15		0.05	0.17	0.05	0.24
9	2-ethyl-1-hexanal	0.15	0.16	0.16	0.01	0.17	0.23	0.11	0.15
28	ethanol-2-(2-butoxyethoxy)	0.25	0.45	0.44	0.08	0.28	0.47	1.91	4.92
13	1-acetyloxy-2-butanone		0.05	0.05					
26	crotonolactone		1.43		0.94	2.04	2.94	2.16	10.5
22	$\alpha$ -methylcrotonolactone				0.06	0.16			

Table 2. Continued

peak	compound	acacia	chestnut	cherry	European ash	American ash	Spanish oak ( <i>Q. pyrenaica</i> )	American oak ( <i>Q. alba</i> )	French oak ( <i>Q. petraea</i> )
16	$\gamma$ -butyrolactone		0.19		0.28	1.20	0.31	0.18	
24	$\gamma$ -ethoxybutyrolactone					1.73			
35	<i>trans</i> - $\beta$ -methyl- $\gamma$ -octalactone						33.8	2.52	13.7
38	<i>cis</i> - $\beta$ -methyl- $\gamma$ -octalactone						31.5	26.2	23.3
29	cyclotene	0.02			0.03	0.03			
25	4,5-dimethyl-2-ciclohexen-1-one					0.05			
20	2-furanmethanol		0.05	0.09	0.26	0.38	0.22	0.16	0.09
41	2,5-furandicarboxaldehyde		0.74				0.19	0.28	0.31
56	5-acetoxymethyl-2-furfural		0.11						
5	furfural	0.45	5.46	0.49	0.80	1.21	10.90	4.68	4.81
14	5-methylfurfural	0.02	0.12	0.03	0.04	0.03	0.24	0.15	0.08
69	5-hydroxymethylfurfural	0.18	13.93	0.22	0.89	1.56	12.80	6.34	4.04
6	1-methoxy-2-ethoxyethyl-1-furan		0.28			0.07	0.27	0.1	0.36
8	1-(2-furanyl)- ethanone		0.06	0.01	0.01	0.01	0.08	0.04	0.02
40	maltol	0.85	1.14	0.36	0.18	0.79	1.36	0.48	0.82
37	benzothiazole	0.05	0.07	0.08	0.07	0.08	0.04		
	peak 23					0.08			
	peak 30	7.26	7.62	7.87	7.05	7.41	1.71	1.67	1.15
	peak 60					0.11			
	total	9.66	33.01	10.54	10.72	18.13	117.40	50.09	66.86

besides 2,4-dihydroxybenzaldehyde and 3,4-dimethoxyphenol, were only detected in this wood. As a whole we can consider acacia quite rich in lignin derivatives, especially with regard to toasted oak woods. However, the same as in seasoned woods, chestnut was the richest one, especially when considering lignin derivatives, highlighting the concentrations of sinapaldehyde, isopropiosyringone, and syringaldehyde (higher than 300  $\mu\text{g/g}$ ), together with isopropiovanillone, butyrosyringone, conifer-aldehyde, butyrovannillone and vanillin (higher than 100  $\mu\text{g/g}$ ). In comparison with the other woods studied, chestnut showed the highest concentrations of all phenyl ketones, dihydrosinapic alcohol, ethyl vanillyl ether, homovanillic acid methyl ester, and 4-methyl and 4-ethylsyringol. Although the organoleptic role of phenylketones is relatively limited, vanillones have vanilla and heliotrope notes which could increase the high odor of vanilla. In spirits, a transformation from vanillone into vanillin has been demonstrated, but this reaction probably does not exist in wines due to the lower alcohol content (45).

In toasted cherry wood, sinapaldehyde (804  $\mu\text{g/g}$ ), syringaldehyde (455  $\mu\text{g/g}$ ), and coniferaldehyde (145  $\mu\text{g/g}$ ) were the most abundant. As it happened in seasoned woods, the concentration of vanillin was the lowest in relation to other woods, followed by the acacia wood. On the contrary, toasted cherry wood showed the highest concentrations of methyl syringate, vanillate and benzoate, benzoic acid, 3,4,5-trimethoxyphenol, 4-methylcatechol and 4-methylphenol. This last compound could confer undesirable ink or bitumen taints.

Regarding toasted ash wood, we can also see quantitative differences between European and American varieties, with the American being the richest in general (Table 3). These woods are characterized by their high concentrations of sinapaldehyde, coniferaldehyde, syringaldehyde, vanillin, isopropiosyringone and isopropiovanillone. In comparison with the other woods, besides its richness in aldehydes, toasted ash wood is especially rich in tyrosol (only detected in ash wood), syringol, eugenol and *cis*- and *trans*-isoeugenol, guaiacol, catechol, 3-methylcatechol, and benzaldehyde, many of which could contribute to the wine aroma with taints such as spicy, smoky, etc. As in seasoned wood, peak 78, only detected in ash wood, shows very different concentrations between European (0.66  $\mu\text{g/g}$ ) and American (13.9  $\mu\text{g/g}$ ) ash.

Toasted oak wood, as a whole, is the poorest in lignin derivative compounds, at these toasting conditions. In the

literature, we can find data of other toasted oak wood that showed a higher richness (1, 10, 46, 47), since the level of formation of these compounds is related to oak species and toasting conditions, and with a higher intensity of toasting (time and/or temperature), we can get a higher degradation of lignin. Also in lipid and carbohydrate derivatives, the toasted oak woods show low concentrations of the studied compounds, in relation to the other woods, and probably, this difference in the richness of volatile compounds when comparing oak woods and the others, at this toasting intensity, is one of the reasons for the historical preference for oak in wine aging, since although many volatile compounds are contributed to the aroma and flavor of aged wine, it is done without masking their primary and secondary aroma.

As we can see in Table 3, furfural is the most abundant volatile compound in toasted acacia, chestnut, and oak wood, with very important increases of its concentration, especially in acacia (from 0.45 to 804  $\mu\text{g/g}$ ) and chestnut (from 5.46 to 1505  $\mu\text{g/g}$ ). In cherry and ash the increases of furfural were much slighter, probably due to a different structure of their polysaccharides, resulting in a higher resistance to thermodegradation. Also important increases in other carbohydrate derivatives, such as furanic and pyranic, were detected in all studied woods, as well as the formation of compounds not detected in seasoned woods: 3-ethylcyclotene, 3,5-dimethylcyclotene, methyl-2-furoate, Furaneol, dihydromaltol, and 4-hydroxy-5,6-dihydro-2(2H)-pyranone. The furanic and pyranic derivatives are the products of multiple dehydrations and rearrangements of carbohydrates under heating, along with cyclopentanone or cyclohexanone structures, included nitrogen compound specific from Maillard reaction. It is evident that during toasting, the thermodegradation of macromolecules is very easy in the case of polyosides. When wood is heated, pentoses, the main constituents of hemicelluloses, produce furfural, while from the hexose units of cellulose are formed 5-hydroxymethyl and 5-methylfurfural. Although cellulose is more abundant in wood than hemicellulose, its crystalline structure provides a higher resistance to degradation (48), which could explain the differences in the concentrations of these compounds. The derivatives with enolone structure, like maltol or cyclotene for example, come from sugar thermal degradation in the presence of nitrogenous substances via Maillard reactions (28, 35).

**Table 3.** GC Quantitative Evaluation of Volatile Compounds (Micrograms per Gram of Dried Wood) (Average of Duplicate) in Extracts of Different Toasted Woods

peak	compound	acacia	chestnut	cherry	European ash	American ash	Spanish oak ( <i>Q. pyrenaica</i> )	American oak ( <i>Q. alba</i> )	French oak ( <i>Q. petraea</i> )
Lignin Derivatives									
42	phenol	0.46	1.21	0.90	0.81	1.25	0.95	0.75	0.68
43	<i>o</i> -cresol	0.14	0.09	0.10	1.08	1.24	0.24	0.27	0.18
49	<i>p</i> -cresol	0.10	0.12	2.36	0.21	0.22	0.15	0.11	0.10
50	<i>m</i> -cresol	0.08	0.07	0.06	0.26	0.32	0.10	0.11	0.07
79	catechol	4.86	2.51	6.19	12.7	22.7			
77	3-methylcatechol	1.19		0.36	3.82	5.15			
82	4-methylcatechol	0.56		6.28	0.68	1.23			
91	2-methoxy hydroquinone	2.74	2.96	4.08	3.68	4.12	0.57	0.57	0.77
32	guaiacol	5.36	5.13	1.71	5.97	14.07	3.98	4.89	2.41
39	4-methylguaiacol	1.51	6.88	1.92	2.31	2.63	7.17	5.87	7.23
46	4-ethylguaiacol	0.55	0.78	0.43	0.29	0.43	0.40	0.37	0.35
52	4-propylguaiacol	0.24	0.18	0.06	0.1	0.17	0.10	0.09	0.06
55	4-vinylguaiacol	0.57	0.57	0.19	0.5	1.23	0.35	0.17	0.16
54	eugenol	2.36	2.13	1.50	2.18	3.21	2.12	1.29	1.83
58	<i>cis</i> -isoeugenol	1.22	0.40	0.11	1.03	1.61	0.24	0.25	0.17
62	<i>trans</i> -isoeugenol	11.5	1.96	0.59	10.5	16.6	0.75	1.26	0.76
83	3,4-dimethoxyphenol	0.79							
59	syringol	20.6	12.9	4.96	19.8	21.3	6.90	9.65	5.76
63	4-methylsyringol	7.82	19.1	10.1	10.4	7.59	11.2	15.1	15.3
65	4-ethylsyringol	3.78	3.92	2.81	1.32	1.21	0.87	1.23	1.06
68	4-propylsyringol	4.00	1	0.68	0.48	0.7	0.30	0.36	0.24
70	4-allylsyringol	16.7	8.35	10.0	6.52	7.51	2.37	2.86	2.24
81	<i>cis</i> - or <i>trans</i> -2,6-dimethoxy-4-(1-propenyl)-phenol	33.0	5.05	2.85	12.8	17.7	2.10	1.77	1.45
99	3,4,5-trimethoxyphenol	1.06	1.29	11.0	0.09	0.17	0.87	0.33	0.42
86	vanillyl alcohol	0.24	0.68	0.12	0.26	7.82			
88	homovanillyl alcohol	1.95	3.36	1.32	11.3	4.37	0.81	0.59	0.54
109	dihydrosinapyl alcohol	8.59	351	15.8	4.93	11.9	20.3	9.46	10.5
94	ethyl vanillyl ether	1.94	130	15.3	3.64	7.06	16.3	8.43	8.69
10	benzaldehyde	0.25	0.26	0.91	2.21	2.5	0.96	0.74	0.8
19	hydroxybenzaldehyde	0.81	0.59	0.75	0.81	0.86	1.99	1.83	2.02
101	2,4-dihydroxybenzaldehyde	90.9							
44	<i>p</i> -anisaldehyde			4.41					
72	vanillin	77.1	142	68.3	119	162	114	102	117
90	syringaldehyde	272	311	455	334	311	250	226	221
103	coniferaldehyde	227	175	145	415	703	174	96.2	106
110	sinapaldehyde	912	491	804	965	719	439	239	263
75	acetovanillone	10.8	17.8	9.44	13.2	18.8	9.54	8.98	9.05
80	propiovanillone	1.64	5.32	1.60	2.83	4.63	2.89	2.38	1.59
87	butyrovannillone	44.7	159	18.9	13.8	30.9	17.4	113.4	14.8
95	acetosyringone	28.8	37.9	34.5	32.6	28.4	20.7	20.6	16.2
98	propiosyringone	7.18	129	12.7	6.91	8.52	5.96	3.85	3.79
102	butyrosyringone	79.2	192	56.4			36.1	29.9	26.5
73	isoacetovanillone	27.3	83.5	10.6	6.00	8.04	6.62	6.04	9.36
76	isopropiovanillone	111	217	21.0	70.5	172	17.1	15.4	13.1
85	isobutyrovannillone						0.09	0.10	0.05
92	isoacetosyringone	42.1	77.7	33.6	12.1	8.08	8.19	7.03	9.25
97	isopropiosyringone	324	339	103	132	173	40.7	35.1	26
66	benzoic acid	1.40	1.24	103	1.07	1.76	1.48	0.84	0.65
17	methyl benzoate			2.01			0.12	0.08	0.2
108	methyl homovanillate		50.5	24.2	13.8	32.4	8.39	2.84	4.25
74	methyl vanillate		0.61	8.1	2.18	6.22	0.58	0.81	0.47
93	methyl syringate		1.92	61.8	7.10	9.03	2.63	2.99	0.64
84	benzyl salicylate			0.68					
104	2-ethyl hexyl <i>trans</i> -4-methoxycinnamate		0.31	0.27	0.63	1.15	0.14		
34	phenylmethanol	3.12	2.82	2.71	3.69	3.21	2.43	2.48	2.52
36	2-phenylethanol	0.16	0.19	1.79	0.30	0.4	0.23	0.20	0.24
96	tyrosol				24.6	26.4			
53	2-phenoxyethanol	0.31	0.40	0.39	1.19	2.47	0.24	0.24	0.12
18	acetophenone	0.02	0.02	0.03	0.03	0.03	0.04	0.03	0.03
	peak 61	2.00	5.63	1.22	0.59	2.04	0.15	0.14	0.46
	peak 78				0.66	13.9			
	peak 89	0.24	14.5	0.37	1.00	0.77	1.72	0.56	0.41
	peak 100	16.9	16.9	17.1	13.9	9.29	5.14	3.46	3.73
	peak 105	9.89	7.29	11.9	18.7	6.57	3.88	1.80	2.08
	peak 106		19.0			1.18	0.93	0.67	0.46
	<i>total</i>	2424	2926	2117	2355	2654	1251	891	917
Lipid and Carbohydrate Derivatives									
1	1-hexanal	0.12	0.12	0.37	0.11	0.16			
3	1-nonanal								
12	2-nonenal		0.10	0.16					
4	2-octenal			0.08					
9	2-ethyl-1-hexanol	0.18	0.28	0.16	0.16	0.21	0.33	0.23	0.23
28	ethanol-2-(2-butoxyethoxy)	0.39	0.44	0.35	0.37	0.31	0.15	0.22	0.19
7	1-acetyloxy-2-propanone	28.2	53.4	21.1	11.2	12.4	4.75	4.51	2.54
2	1-hydroxy-2-butanone	2.19	0.85	1.19	6.30	9.84	0.72	0.96	0.35

Table 3. Continued

peak	compound	acacia	chestnut	cherry	European ash	American ash	Spanish oak ( <i>Q. pyrenaica</i> )	American oak ( <i>Q. alba</i> )	French oak ( <i>Q. petraea</i> )
13	1-acetyloxy-2-butanone	1.84	1.07	1.08	2.28	3.29			
26	crotonolactone	34.1	57.0	31.6	26.0	24.5			
22	$\alpha$ -methylcrotonolactone	2.58	2.43	2.59	8.00	7.57	4.95	3.50	3.29
16	$\gamma$ -butyrolactone	3.72	3.14	2.10	12.2	16.8	3.18	2.89	2.16
24	$\gamma$ -ethoxybutyrolactone	16.6	18.9	8.52	13.9	9.78	13.7	17.0	16.9
48	solerone	7.91	5.03	7.80	35.3	42	2.78	3.52	1.76
35	<i>trans</i> - $\beta$ -methyl- $\gamma$ -octalactone						9.77	3.36	14.6
38	<i>cis</i> - $\beta$ -methyl- $\gamma$ -octalactone						30.0	31.8	21.1
29	cyclotene	3.35	4.99	2.31	5.41	6.47	1.55	1.55	1.02
21	3-ethylcyclotene	0.74	0.45	0.51	5.17	6.21	0.44	0.83	0.33
27	3,5-dimethylcyclotene	0.14	0.09	0.08	0.78	0.83	0.11	0.14	0.07
25	4,5-dimethyl-2-ciclohexen-1-one	0.40	0.17	0.15	2.00	2.58			
15	methyl-2-furoate	3.07	1.45	4.87	1.67	1.94	3.49	3.27	2.19
20	2-furanmethanol	3.25	1.60	1.08	30.9	40.9	1.36	1.98	1.17
41	2,5-furandicarboxaldehyde	2.35	2.45	1.25	2.32	2.63	4.67	3.92	4.96
56	5-acetoxymethyl-2-furfural	15.80	21.1	2.27	8.16	13.3	5.94	4.63	3.69
5	furfural	804	1505	23.3	58.5	82.3	494	395	430
14	5-methylfurfural	94.2	75.9	31.3	10.5	20.1	56.3	38.3	35.1
69	5-hydroxymethylfurfural	113	103	47.6	59.9	90.3	28.9	21.1	22.9
6	1-methoxy-2-ethoxyethyl-1-furan	98.7	896	29.7	5.95	11.6	29.1	34.1	51.3
8	1-(2-furanyl)- ethanone	2.74	1.12	0.80	0.38	0.69	3.54	1.73	1.51
47	Furaneol	2.59	0.91	0.59	1.12	1.77	0.25	0.18	0.13
40	maltol	20.2	17.6	13.5	30.8	30.6	36.9	20.6	18.1
31	dihydromaltol	2.01	1.65	0.51	0.91	1.38	0.75	0.45	0.57
33	4-hydroxy-5,6-dihydro-(2 <i>H</i> )-pyran-2-one	13.3	20.9	3.78	3.38	3.9	1.07	2.50	2.21
45	1 <i>H</i> -pyrrole-2-carboxaldehyde	17.4	1.67	1.35	2.45	3.57	0.61	0.46	0.35
37	benzothiazole	0.07	0.06	0.07	0.08	0.07	0.13	0.04	0.04
	peak 11	13.4	13.7	3.53	0.90	2.38	2.88	2.68	3.20
	peak 23	1.41	0.38	0.52	22.1	27.1			
	peak 30	7.97	8.72	7.65	8.29	8.2	10.7	10.7	10.9
	peak 51	8.43	16.6	5.92	5.10	4.67	1.22	1.34	0.81
	peak 60	13.1	196	3.86	0.89	2.87	0.70	1.60	1.20
	peak 64	31.2	195	15.4	3.70	6.23	3.77	6.28	5.90
	peak 67	24.4	108	14.1	5.05	6.18	2.70	4.33	3.95
	total	1395	3339	295	392	506	791	643	693

Besides the highest concentration of furfural, toasted chestnut wood also shows the highest concentrations of 1-methoxy-2-ethoxyethyl-1-furan (896  $\mu\text{g/g}$ ), 5-acetoxymethyl-2-furfural (21.1  $\mu\text{g/g}$ ), and 4-hydroxy-5,6-dihydro-(2*H*)-pyran-2-one (20.9  $\mu\text{g/g}$ ), as well as four unidentified peaks: peak 51 (16.6  $\mu\text{g/g}$ ), peak 60 (196  $\mu\text{g/g}$ ), peak 64 (195  $\mu\text{g/g}$ ) and peak 67 (108  $\mu\text{g/g}$ ). In addition, toasted acacia wood shows high concentrations of furfural derivatives, this wood being that which shows the highest increase in the presence of these compounds. On the other hand, ash and cherry were the poorest in furfural derivatives, and cherry stands out because of the low concentration of carbohydrate and lipid derivatives altogether. In toasted ash woods, the most significant findings are the concentrations of cyclotene, 3-ethyl and 3,5-dimethylcyclotene (related to the licorice aroma in aged wines), as well as 4,5-dimethyl-2-ciclohexen-1-one,  $\alpha$ -methylcrotonolactone,  $\gamma$ -butyrolactone, solerone, 2-furanmethanol, and peak 23, and this means that, together with the low concentration of furfural and their derivatives, this wood shows a very different profile of carbohydrate derivatives, from a quantitative point of view. These quantitative differences, besides being related to characteristics of polyosides, could be considered as different sensitivity to toasting, or a different capacity for thermodegradation, since it is known that the intensity of formation of these compounds is directly related to the intensity of toasting, as is well described in oak wood (1, 5, 10, 30, 47).

Only a few compounds were found in significantly lower concentrations in toasted wood than in seasoned wood. Coniferyl alcohol, for example, was not detected in any toasted wood, as well as 3,4-dimethoxyphenol and 3,4,5-trimethoxyphenol among lignin derivatives, which is possibly due to oxidation reactions. As reported by Campbell et al. (49), and Vichi et al. (31), the

outcome of heating oak is a combined process of volatile formation and possible losses due to volatilization and/or decomposition, including oxidation, and the same thing we could expect in the other woods. In fact, the evolution of concentrations of other phenyl alcohols was not the same in all woods, which in general increased in acacia, chestnut, cherry, and ash woods, while in oak wood they either decreased or did not vary, which is the case with vanillyl, homovanillyl, and dihydrosinapyl alcohols, methyl vanillate and tyrosol. Among lipid derivatives, only alkyl aldehydes decrease during toasting, as described by Chatonnet and Dubourdiu (39), and the isomers *cis* and *trans* of  $\beta$ -methyl- $\gamma$ -octalactone in some oak woods, as has already been broadly described (1, 4, 5, 15).

As we can see, the particular characteristics of macromolecules, lignin, cellulose, hemicelluloses, and lipids in each wood have a great influence on the volatile composition of seasoned and especially on toasted wood that can be used in cooperage. In general, all the woods studied showed more lignin derivatives than lipid and carbohydrate derivatives, with a higher variety of compounds detected and abundance of them. The toasting led to an increase in the concentration of most of these compounds, and these increases are especially significant in acacia, chestnut and ash woods, most notably in toasted chestnut wood as it is the richest as a whole, with regard to lignin as well as lipid and carbohydrate derivatives. Moreover, each wood has a characteristic volatile composition, from a quantitative point of view, and therefore we could also expect a characteristic sensorial profile. The oak wood turned out to be the most balanced, since although it provides many volatile compounds to the aroma and flavor of aged wine, it does so without masking their primary and secondary aromas. On the whole, toasted acacia and chestnut woods showed a very high richness of

studied compounds, lignin, lipid and carbohydrate derivatives, while cherry and ash were much richer than toasted oak wood in lignin derivatives, but much poorer in lipid and carbohydrate derivatives, and with a quantitatively different profile. In order to establishing the consequences of these chemical differences on organoleptic quality of wine, a new study of interaction wood-wine will be carried out as continuation of this work.

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