

## Characterization of Volatile Constituents in Commercial Oak Wood Chips

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The volatile composition of the different oak wood pieces (chips of *Quercus* spp.) that can be found on the market to be used as alternatives to barrels for aging wines, as well as of chips of *Quercus pyrenaica* which are being introduced, was studied, evaluating the contents of volatile phenols, lactones, furanic compounds, pyranones, phenolic aldehydes, phenolic ketones, and others. In regard to the overall results, the volatile composition of these products varies widely and has not been clearly laid out according to either the oak species or the wood toasting intensity. Taking into account that the different characteristics of alternatives to barrel products are reflected in the wine treated with them and that an oenological profile based on these variables (origin and toasting level) cannot be defined, only an appropriate chemical analysis would reveal the quality of alternative-to-barrel products and allow us to attempt to foresee its effects on the chemical and organoleptic characteristics of the wines treated with them. On the other hand, the *Q. pyrenaica* alternative products are very similar to those of other species, with some aromatic particularities, such as their high levels of furanic compounds, eugenol, Furanol, and *cis*-whiskylactone, and low levels of vanillin.

**KEYWORDS:** *Quercus pyrenaica*; French oak; American oak; chips; volatile compounds

### INTRODUCTION

The structural characteristics and chemical composition of the oak wood strongly influence the complex physical, chemical, and biochemical processes that take place during the oxidative aging of wine in barrels, affecting its chemical composition and organoleptic properties, and contributing to its stability. The simple extraction of volatile compounds and tannins adds wealth and complexity to the aroma and flavor of the wines, since the oak wood is able to contribute phenolic aldehydes, phenolic ketones, phenolic volatiles, lactones, furanic compounds, and pyranones, among other compounds. The aging systems alternative to barrels, such as adding wooden pieces to wine to be aged in tanks or in used barrels, have been developed to confer wood characteristics to wine faster and more simply. A great variety of oak wood pieces for this purpose can be found on the market: chips, cubes (oak beans), powder, shavings, granulates, blocks or segments, up to staves (1). The quantity of added wood, time of contact between wood and wine, piece size, way the wood is used, and many other aspects influence the sensorial and chemical characteristics of the wines produced, with the chemical composition of the wood, especially the contents of volatile compounds and tannins, the most important factors (2–5).

If the oenologist goes to the market to acquire alternatives to barrel wood products to accelerate wine aging, a large variety will be found to choose from, classified according to the terminology

accepted in cooperage for barrels (oak species, wood provenance, length of seasoning, and intensity of toasting), in addition to new specific although imprecise terminology which has been added: *original blend*, *sweet granular*, *spice*, *intense*, *high vanilla*, *high mocha*, *premium dark*, etc. On very few occasions, this terminology relies on data from chemical analyses and many times responds to special wood processing undergone during toasting, which is patented by the producing company and therefore cannot be specified in detail. In addition, the product homogeneity in different moments of production can be difficult to guarantee, because it is a natural product that responds in a variable way to the industrial process. All these factors accentuate the importance of analyzing the chemical composition of wood pieces prior to their use, in order to forecast their effect on the chemical and organoleptic characteristics of the wine.

In this context, oak alternative products produced with wood of the species *Q. pyrenaica*, known as “rebollo” or “melojo” and predominant on the Iberian Peninsula, have begun to appear in the alternative market. In recent years the oenological potential of this wood has been studied, showing balanced contents of tannins, similar to those of *Q. petraea*, and a great wealth of aromatic compounds, with similar or greater levels to those shown by American (*Q. alba*) or French (*Q. petraea*) oaks (6, 7). Wines aged in *Q. pyrenaica* barrels showed high levels of volatile phenols such as eugenol and guaiacol, levels of *cis*-whiskylactone or maltol similar to those of wines aged in American oak, and average levels between those aged in French and American oak for many other aromatic compounds. In the sensory analysis,

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they are highlighted by their wooden notes with aromas of roasting, toasting, milk coffee, spices, or wine-wood interactions, and they were highly regarded by the experts (8, 9).

We propose two objectives in our work, to know the volatile composition of alternatives to barrel oak products of oenological interest in the current market panoramic and their possible relationship to the diversity of their commercial denominations and, on the other hand, to know those manufactured with wood of *Q. pyrenaica*, as well as to define their oenological potential in relation to products of other oak species that are available in the current market.

## MATERIALS AND METHODS

**Wood Samples.** Chips of French and American oak wood, currently available from ten commercial brands, as well as of *Q. pyrenaica*, available from one commercial brand, and manufactured on an industrial scale from rejected staves or wood remains obtained from barrel-making, or from trees of small dimensions felled in silvicultural treatments, were analyzed. Except in the last case in which the wood seasoning was carried out in an accelerated way (4), for the rest of the samples, the makers specified that the wood seasoning had been carried out in natural conditions for at least 24 months. The piece sizes were quite variable: shavings, granulates, chips, cubes (1–2 cm of edge), up to small staves (5 cm × 5 cm × 1 cm). The samples specified different toasting intensities: (French oak) light toasting, 4 samples; medium, 49; medium plus, 4; and heavy, 9; (American oak) light toasting, 7 samples; medium, 44; medium plus, 4; and heavy, 9; (*Q. pyrenaica* oak) light toasting, 29 samples; medium, 35; medium plus, 8; and heavy, 30. In total, 232 samples were analyzed, of which 128 specified medium toasting intensity. For the chemical analysis, all wood samples were ground and sieved, taking the sawdust ranging in size from 0.80 to 0.28 mm.

**Chemicals.** Reference compounds of the identified volatile compounds and the internal standards were obtained from commercial sources. Those numbered in **Table 1** as 1, 4, 9, 16, 32, and 34 were purchased from Sigma Chemical (St. Louis, MO); 7, 10, 11, 12, 13, 17, 21, 22, 19, 25, 30, 33, 39, 46,  $\gamma$ -hexalactone, and *o*-vanillin from Aldrich Chimie (Neu-Ulm, Germany); 3, 5, 18, 20, 26, 28, 29, and 40 from Fluka Chimie AG (Buchs, Switzerland); 23 and 3,4-dimethylphenol from Riedel-de-Häen (Seelze, Germany); and 36, 42, and 47 from Extrasynthese (Genay, France). All reagents 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. (10) from Chatonnet et al. (11): 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 in 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. Three 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), 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 (SPELCO WAX-10) (30 m × 0.25 mm i.d., and 0.25  $\mu$ m film thickness), supplied by Supelco (Madrid, Spain), and under the working conditions described by Cadahía et al. (7): GC grade helium as carrier gas at a 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 was calculated using this column and another column with different polarity (ZB-5, 30 m × 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 shown 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 under 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**, assuming that they have the same MS response factors. The variation coefficients of duplicates were less than 3%.

**Statistical Analysis.** The obtained data were analyzed by carrying out univariate analysis using ANOVA, by applying the Student–Newman–Keuls multiple range test. Multivariate canonical discriminant analysis was also carried out using the program SAS (version 9.1; SAS Institute, Cary, NC).

## RESULTS AND DISCUSSION

A great variety of volatile compounds able to give a higher aromatic complexity to wine have been identified in toasted oak wood in recent years (notes of vanilla, clove, cocoa, toasty, leather, spicy, toasted bread, etc.). We analyzed some of the most representative of this contribution of wood to wine during the aging process. **Table 1** gives the components that were analyzed in the wood pieces studied, together with their retention indexes in two columns and their identification mode (10, 12–16). As can be observed, 47 compounds were quantified, from which 33 were identified by comparing their mass spectra and retention indexes with those of pure standards; 14 were tentatively identified by comparing their mass fragmentation with those in a commercial library and those reported in the literature, taking into account their retention indexes, structures, and molecular weights. They belong to very different chemical families, such as the volatile phenols, lactones, furanic compounds, pyranones, phenolic aldehydes, phenolic ketones, and others. Their concentrations cover a very wide range, from less than 0.1  $\mu$ g per gram of wood, up to more than 4000  $\mu$ g/g of wood. In **Tables 2** and **3**, besides the average value, the minimum and maximum values were also included in order to set out the concentration interval for each compound relating species and toasting intensity. In almost all the cases, the variability obtained was very high. However, as can be deduced from **Table 4**, which shows the *F* values from variance analysis of the quantitative evaluation in the different alternative to barrel products (ABP) analyzed, the species of *Quercus* and the toasting intensity have a great influence on the resulting volatile composition.

The concentrations of furfural, always the highest among furanic derivatives, stand out in each of the toasting intensities and in the three species. Its average concentrations were higher in *Q. pyrenaica* ABP than in those of French and American oak, for the same toasting level, and the same occurred for the other furanic derivatives, except 2,5-furandicarboxaldehyde. Taking into account data in the literature, the ABP analyzed showed a wide range of concentrations of furanic derivatives, and although most of the samples were in the lower part of the range, the maximum value was very high, especially in *Q. pyrenaica* samples.

**Table 1.** Compounds Analyzed in the Studied Alternatives to Barrel Oak Products, Retention Index, Ion and Standard Used in Quantification, and Identification Methods<sup>c</sup>

peak no.	KI DB5	KI carbowax	IUPAC name	common name	ion <sup>a</sup> m/z	ID	calibration <sup>b</sup>
1	834	1444	2-furancarboxaldehyde	furfural	96	S	
2	1081	1452	1-methoxy-2-ethoxyethyl-1-furan		97	T <sup>1</sup>	furfural
3	912	1483	1-(2-furanyl)ethanone	furyl methyl ketone	95	S	
4	965	1551	5-methyl-2-furancarboxaldehyde	5-methylfurfural	110	S	
5	913	1593	dihydro-2(3H)furanone	$\gamma$ -butyrolactone	86	S	
I.S.	987	1652	4-ethyl-dihydro-2(3H)furanone	$\gamma$ -hexalactone	85	S	
6	915	1716	2(5H)-furanone	crotonolactone	55	T <sup>1, 2</sup>	$\gamma$ -butyrolactone
7	1027	1784	2-hydroxy-2-cyclopenten-1-one	cyclotene	112	S	
8	1103	1822	2,3-dihydro-5-hydroxy-6-methyl-4H-pyran-4-one	dihydromaltol	128	T <sup>1, 4</sup>	maltol
9	1089	1833	2-methoxyphenol	guaiacol	124	S	
10	1292	1861	trans-4-methyl-5-butyl-dihydro-2(3H)-furanone	trans- $\beta$ -methyl- $\gamma$ -octalactone	99	S	
11	1325	1928	cis-4-methyl-5-butyl-dihydro-2(3H)-furanone	cis- $\beta$ -methyl- $\gamma$ -octalactone	99	S	
12	1191	1928	4-methyl-2-methoxyphenol	4-methylguaiacol	138	S	
13	1111	1938	3-hydroxy-2-methyl-4H-pyran-4-one	maltol	126	S	
14	1078	1944	2,5-furandicarboxaldehyde		124	T <sup>1, 5</sup>	furfural
15	1124	1956	1-(2-furanyl)-2-hydroxyethanone	furylhydroxymethyl ketone	95	T <sup>1, 5</sup>	furyl methyl ketone
16	983	1978	phenol		94	S	
17	1059	1980	2-methylphenol	o-cresol	107	S	
18	1009	1990	1-H-pyrrole-2-carboxaldehyde		95	S	
19	1274	2002	4-ethyl-2-methoxyphenol	4-ethylguaiacol	137	S	
20	1083	2013	4-hydroxy-2,5-dimethyl-3(2H)-furanone	Furaneol	128	S	
21	1079	2056	4-methylphenol	p-cresol	107	S	
22	1086	2064	3-methylphenol	m-cresol	107	S	
I.S.	1121	2101	2-hydroxy-3-methoxybenzaldehyde	o-vanillin	152	S	
23	1359	2139	2-methoxy-4-(2-propenyl)phenol	eugenol	164	S	
24	1314	2165	4-vinyl-2-methoxyphenol	4-vinylguaiacol	150	T <sup>1, 2</sup>	4-ethyl guaiacol
25	1309	2169	5-acetoxymethyl-2-furancarboxaldehyde	5-acetoxymethylfurfural	126	S	
I.S.	1193	2192	3,4-dimethylphenol		107	S	
26	1408	2226	cis-2-methoxy-4-(1-propenyl)phenol	cis-isoegenol	164	S	
27	1325	2230	2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	DDMP	144	T <sup>1,4</sup>	maltol
28	1353	2237	2,6-dimethoxyphenol	syringol	154	S	
29	1451	2314	trans-2-methoxy-4-(1-propenyl)phenol	trans-isoegenol	164	S	
30	1449	2322	4-methyl-2,6-dimethoxyphenol	4-methylsyringol	168	S	
31	1528	2381	4-ethyl-2,6-dimethoxyphenol	4-ethylsyringol	167	T <sup>1, 2, 6</sup>	4-methylsyringol
32	1235	2466	5-hydroxymethyl-2-furancarboxaldehyde	5-hydroxymethylfurfural (HMF)	97	S	
33	1605	2511	4-allyl-2,6-dimethoxyphenol	4-allylsyringol	194	S	
34	1399	2518	4-hydroxy-3-methoxybenzaldehyde	vanillin	151	S	
35	1461	2557	2-(4-hydroxy-3-methoxyphenyl) acetaldehyde	isoacetovanillone	137	T <sup>1, 2, 7</sup>	acetovanillone
36	1487	2595	1-(4-hydroxy-3-methoxyphenyl)ethanone	acetovanillone	151	S	
37	1534	2617	1-(4-hydroxy-3-methoxyphenyl)-2-propanone	isopropiovanillone	137	T <sup>1, 7</sup>	acetovanillone
38	1501	2661	1-(4-hydroxy-3-methoxyphenyl)propanone	propiovanillone	151	T <sup>1, 3, 7</sup>	acetovanillone
39	1534	2805	4-hydroxy-3-methoxyphenethanol	homovanillyl alcohol	137	S	
40	1643	2904	4-hydroxy-3,5-dimethoxybenzaldehyde	syringaldehyde	182	S	
41	1712	2927	2-(4-hydroxy-3,5-dimethoxyphenyl) acetaldehyde	isoacetosyringone	167	T <sup>1, 2, 7</sup>	acetosyringone
42	1651	2941	4-(ethoxymethyl)-2-methoxyphenol	ethyl vanillyl ether	137	S	
42	1744	2953	1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone	acetosyringone	181	S	
44	1785	2979	1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone	isopropiosyringone	167	T <sup>1, 2, 7</sup>	acetosyringone
45	1753	3010	1-(4-hydroxy-3,5-dimethoxyphenyl)propanone	propiosyringone	181	T <sup>1, 2, 7</sup>	acetosyringone
46	1747	3096	3-methoxy-4-hydroxycinnamaldehyde	coniferaldehyde	178	S	
47	2002	3458	3,5-dimethoxy-4-hydroxycinnamaldehyde	sinapaldehyde	208	S	

<sup>a</sup> Ion used in quantification. <sup>b</sup> Calibration used when the pure reference standard was not available. <sup>c</sup> KI = Kovats index; ID = identification mode; S = peak identified with the pure reference standard; T = peak tentatively identified with the spectrum reported in the literature; I.S. = internal standard. <sup>1</sup>Commercial libraries NIST 2.0 and Wiley 7. <sup>2</sup>Faix *et al.*, 1991. <sup>3</sup>Vichy *et al.*, 2007. <sup>4</sup>Cutzach *et al.*, 1997. <sup>5</sup>Cutzach *et al.*, 1999. <sup>6</sup>Guillen and Ibargoitia, 1998. <sup>7</sup>Cadahia *et al.*, 2003.

In fact, we expected lower values for these compounds than those found in traditional barrel roasting, in accordance with the data from Chatonnet (17) and earlier data obtained by us (4, 18), since few conditions of industrial roasting of oak wood pieces cause the simultaneous production of both carbohydrate and lignin derivatives in relative concentrations close to those obtained by the traditional heating of barrel-making, resulting in low levels of furanic aldehydes in the small pieces of ABP. However, it is possible that different methods of roasting adopted for chips are able to generate high quantities of furanic aldehydes. In **Table 4** we can see that furanic aldehydes showed higher *F*-values with regard to oak species than roasting intensity, but only furfural and

5-methylfurfural allowed differentiation among the samples of the three species. These compounds have been described as being responsible for “almond” and “toasted almond” notes (19), but their participation in many reactions that take place during wine aging, such as the formation of furfuryl alcohol (20) or of brown adducts with (+)-catechin from wine (21), makes it difficult that the detection thresholds are reached, since they are quite high (20–45 mg/L). However, some authors described a synergistic effect with the sensorial incidence of whisky-lactones (22, 23).

Besides furanic aldehydes, other derivatives from carbohydrate degradation by heat, with their genesis being related to Maillard reactions (13, 14), were found. Thus, a series of compounds with

**Table 2.** Average Concentrations of Volatile Compounds ( $\mu\text{g/g}$  of Wood) in Alternatives to Barrel Oak Wood Products<sup>a</sup>

origin:	Spanish <i>Q. pyrenaica</i>				French oak				American oak			
	toasting intensity:	L	M	M+	H	L	M	M+	H	L	M	M+
furfural	368ab	919ab	1140a	1126a	78.0b	357ab	301ab	170b	41.0b	681ab	825ab	61.0b
5-methylfurfural	43.4bc	135ab	169a	130ab	16.5bc	42.3bc	37.8bc	25.1bc	6.73c	95.2abc	70.8abc	10.8c
HMF	198bcd	322b	494a	214bc	37.2de	58.3cde	54.3cde	44.2cde	14.6e	74.5cde	65.5cde	30.2de
5-acetoxymethylfurfural	3.34c	29.2bc	107a	46.7b	2.76c	5.78c	10.2c	10.3c	1.00c	11.3c	10.9c	9.94c
1-methoxy-2-ethoxyethyl-1-furan	158b	435b	1075a	342b	10.4b	51.7b	219b	78.5b	3.24b	116b	215b	28.4b
2,5-furandicarbaldehyde	2.80ab	8.91ab	5.08ab	4.81ab	11.9ab	9.56ab	7.94ab	9.81ab	1.57b	13.3a	8.49ab	6.12ab
2-furylmethyl ketone	3.75a	6.45a	6.55a	4.70a	0.11a	1.95a	4.22a	2.89a	0.18a	4.96a	2.92a	0.86a
furylhydroxymethyl ketone	12.4a	13.3a	6.71b	5.48b	1.43b	1.77b	1.61b	0.98b	2.05b	1.93b	1.22b	0.52b
1-H-pyrrolicarboxaldehyde	3.75abc	4.71ab	5.77a	3.28bcd	0.99cd	1.34cd	1.10cd	0.85cd	0.66d	2.88bcd	1.49cd	0.89cd
maltol	5.20cd	17.8b	28.2a	31.2a	5.20cd	16.2b	15.7bc	15.6bc	1.97d	14.1bc	18.0b	12.0bc
dihydromaltol	0.35ab	0.84ab	0.47ab	1.58a	0.01b	0.96ab	0.14b	0.05b	0.11b	0.66ab	0.08b	0.04b
DDMP	1.59a	1.35a	0.23a	1.30a	0.62a	0.29a	0.17a	0.11a	0.28a	0.41a	0.09a	0.14a
cyclotene	0.62cd	2.01abcd	3.64a	3.23ab	0.20d	1.08cd	1.07cd	0.82cd	0.14d	1.78abc	2.28bcd	0.86cd
Furaneol	1.00bc	1.47b	2.70a	1.53b	n.d. d	0.35cd	0.31cd	0.18cd	0.12cd	0.50cd	0.60cd	0.34cd
$\gamma$ -butyrolactone	1.35de	2.54cde	3.82bcd	3.46bcd	1.20de	2.94cde	5.02bc	8.24a	0.48e	4.76bc	5.39bc	5.83b
crotonolactone	32.9bc	50.6a	59.8a	38.4b	13.3d	30.7bcd	25.9bcd	26.4bcd	13.7d	26.7bcd	25.6bcd	17.7cd
w-lactone <i>trans</i>	8.18b	11.2ab	19.6a	8.65b	11.5ab	9.65b	6.11b	4.43b	3.35b	6.63b	6.58b	2.78b
w-lactone <i>cis</i>	46.8abc	46.5abc	75.7a	52.2ab	11.4bc	12.1bc	6.12c	7.59c	24.9bc	31.1bc	17.3bc	14.6bc
phenol	0.19b	0.43ab	0.62ab	0.97a	0.59ab	0.52ab	0.69ab	0.69ab	0.57ab	0.62ab	0.72ab	0.62ab
<i>o</i> -cresol	0.02c	0.07bc	0.13abc	0.14ab	0.08abc	0.09abc	0.12abc	0.10abc	0.10abc	0.15ab	0.19a	0.18a
<i>p</i> -cresol	0.06b	0.10ab	0.15ab	0.16ab	0.13ab	0.10ab	0.11ab	0.15ab	0.12a	0.15ab	0.15ab	0.11ab
<i>m</i> -cresol	0.04b	0.05ab	0.10ab	0.10ab	0.12ab	0.08ab	0.07ab	0.10ab	0.15a	0.08ab	0.12ab	0.12ab
guaiacol	0.44b	1.28b	2.64ab	3.05ab	0.34b	1.67ab	2.26ab	1.65ab	0.42b	2.69ab	4.13a	2.09ab
4-methylguaiacol	0.47d	1.58bcd	2.57abcd	3.01abcd	1.00cd	4.37a	3.59ab	3.45abc	0.70d	2.98abcd	4.55a	1.62bcd
4-ethylguaiacol	0.03a	0.11a	0.27a	0.36a	0.05a	0.29a	0.35a	0.42a	0.05a	0.37a	0.59a	0.43a
4-vinylguaiacol	0.60a	0.62a	1.44a	0.84a	0.33a	1.24a	0.55a	0.66a	0.17a	1.64a	0.98a	0.40a
eugenol	5.10ab	5.00ab	6.05a	4.43ab	1.17c	1.37c	1.69c	0.90c	1.63c	2.48bc	2.69bc	0.95c
<i>trans</i> -isoeugenol	0.13bc	0.31bc	1.11a	0.56b	0.07c	0.31bc	0.28bc	0.10c	0.09c	0.37bc	0.50bc	0.07c
<i>cis</i> -isoeugenol	2.29b	3.02b	8.85a	3.67b	2.03b	2.66b	2.28b	1.18b	2.19b	3.70b	4.02b	0.91b
syringol	1.32c	3.36bc	10.9abc	9.83abc	1.37c	7.29abc	8.11abc	11.1abc	1.30c	8.36abc	12.3ab	16.3a
4-methylsyringol	0.94c	3.10bc	8.89abc	7.76abc	1.86c	11.9ab	14.4a	13.8a	0.72c	7.02abc	13.5a	8.61abc
4-ethylsyringol	0.10c	0.32c	1.59bc	0.67bc	0.19c	1.57bc	1.71bc	2.73abc	0.15c	1.13bc	3.10ab	4.32a
4-allylsyringol	2.64bc	4.13bc	11.3a	6.74b	1.28c	4.73bc	4.72bc	5.18bc	0.86c	4.41bc	11.2a	5.63bc
vanillin	28.3d	54.4 cd	80.3cd	73.2 cd	120bcd	172b	145bc	262a	27.4d	120bcd	143bc	244a
acetovanillone	1.50c	3.44bc	8.88abc	8.20abc	3.34bc	12.2a	9.28abc	14.7a	0.91c	7.22abc	10.3ab	13.7a
isoacetovanillone	7.91cde	12.6bcd	32.9a	19.0b	6.27de	16.5bc	12.9bcd	16.6bc	2.02e	11.7bcd	19.5b	5.92de
propiovanillone	3.93bc	4.63bc	7.85a	6.55ab	3.67bc	4.52bc	3.74bc	4.67bc	3.32c	4.89bc	5.89abc	4.45bc
isopropiovanillone	9.93de	27.9cde	104a	57.2bc	8.46de	25.9cde	37.2 cd	56.8bc	1.37e	28.3cde	73.4b	47.9bc
homovanillyl alcohol	1.94b	2.47b	6.59a	2.52b	2.71b	3.85ab	3.61ab	4.44ab	2.61b	3.28ab	3.55ab	3.91ab
ethyl vanillyl ether	28.3cde	36.8bcd	92.0a	51.3bc	19.2de	31.0bcde	34.3bcde	44.4bcd	8.82e	26.9cde	57.1b	41.3bcd
syringaldehyde	82.7d	135 cd	206cd	241cd	196cd	443bc	731ab	721ab	57.4d	343cd	632ab	768a
acetosyringone	2.68b	6.12b	18.2ab	23.6ab	5.71b	37.6ab	39.2ab	48.2a	1.43b	23.8ab	48.6a	50.5a
isoacetosyringone	10.36cde	14.5cde	43.5b	26.1bcde	8.88de	31.2bcd	33.9bcd	36.2bc	3.01e	23.0bcde	62.9a	20.3bcd
propiosyringone	7.14cd	8.11bcd	14.5abc	13.7abc	5.53cd	12.6abc	13.6abc	16.0ab	2.22d	8.48bcd	18.7a	12.3abc
isopropiosyringone	21.7e	58.3de	213ab	146abcd	15.3e	77.6cde	131bcd	185ab	2.33e	77.6cde	247a	168abc
coniferaldehyde	148bc	245ab	368a	350a	179abc	293ab	272ab	283ab	37.1c	324ab	366a	192abc
sinapaldehyde	231cd	509bcd	646bcd	1011ab	385bcd	781abc	833abc	803abc	49.1d	902abc	1327a	490bcd

<sup>a</sup> Averages were calculated with a different number of samples in each group (see wood samples in M&M). n.d. = not detected; L = light toasting; M = medium toasting; M+ = medium plus toasting; H = heavy toasting. HMF = 5-hydroxymethylfurfural; DDMP = 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one. Different letters in the same row denote a statistical difference with 95% confidence level (Student–Newman–Keuls multiple range test).

pyranone, pyrrole, or furanone structures, such as maltol, dihydromaltol, DDMP, 2,5-furandicarbaldehyde, and furylhydroxymethyl ketone, responsible for “toasty caramel” and “honey” odors, in addition to 1-H-pyrrolicarboxaldehyde, cyclotene, and Furaneol, related to caramel-like notes, and crotonolactone and  $\gamma$ -butyrolactone, were evaluated. Among them, maltol was the pyranone that showed the highest concentrations, with average values significantly higher in *Q. pyrenaica* ABP, than in French and American, at medium plus and heavy toasting. In **Table 3** we can see that almost all carbohydrate derivatives showed concentrations significantly higher in *Q. pyrenaica* than in French and American oak. On the other hand, few carbohydrate derivatives showed statistically significant differences between French and

American ABP, and their *F*-values were not very high. If we only take into account the toasting level, and not the origin of oak, for none of the carbohydrate derivatives was it possible to differentiate the four intensities of toasting.

Referring to the most characteristic compounds provided to wine by oak wood—the *cis*- and *trans*-isomers of  $\beta$ -methyl- $\gamma$ -octalactone (24)—their average concentrations were as expected in French and American ABP (10, 18, 25) and higher than expected in *Q. pyrenaica* ABP, especially for the *cis* isomer, since values similar to these average values were only found in big pieces, as staves, resulting in low average levels in the small pieces (4). However, less than 25% of *Q. pyrenaica* samples showed concentrations higher than the average value at each

Table 3. Minimum and Maximum Concentrations of Volatile Compounds ( $\mu\text{g/g}$  of Wood) in Alternatives to Barrel Oak Wood Products<sup>a</sup>

toasting intensity:	Spanish <i>Q. pyrenaica</i>				French oak				American oak			
	L	M	M+	H	L	M	M+	H	L	M	M+	H
furfural	24.2–1738	103–2674	768–1679	155–4082	18.2–237	29.6–1480	133–578	44.6–385	21.2–110	26.7–3053	198–1688	35.5–112
5-methylfurfural	2.57–213	19.1–405	121–226	27.2–374	3.24–43.5	8.06–309	17.3–69.6	10.2–54.5	3.56–15.5	6.24–385	17.6–135	5.70–253
HMF	22.6–592	28.8–657	326–593	41.3–756	5.13–87.3	15.8–188	28.0–81.9	24.7–71.5	2.77–58.3	20.2–194	34.9–91.3	19.1–46.2
5-acetoxymethylfurfural	0.43–9.67	0.39–128	73.5–146	10.5–135	0.44–8.01	0.20–32.8	0.20–17.8	2.23–24.3	0.34–3.39	0.27–101	0.51–17.4	3.18–17.2
1-methoxy-2-ethoxyethyl-1-furan	2.12–613	16.3–1623	246–1433	10.5–1704	0.27–37.7	2.28–439	4.34–816	6.02–453	0.59–9.29	1.78–1728	14.9–326	4.30–68.1
2,5-furandicarboxaldehyde	0.58–8.78	1.24–42.5	3.71–8.16	1.10–9.42	2.31–33.8	2.02–47.9	2.35–13.4	2.68–20.6	0.47–5.18	3.76–41.8	5.01–11.53	3.28–11.3
2-furylmethyl ketone	0.06–13.7	0.48–13.8	4.43–8.62	0.47–10.9	0.02–0.25	0.12–8.91	0.26–6.13	0.40–6.61	0.11–0.20	0.22–26.8	0.19–6.32	0.28–1.85
furylhydroxymethyl ketone	0.40–40.2	1.48–45.9	3.80–10.4	0.60–27.8	0.13–4.43	0.24–6.63	0.50–4.27	0.42–1.81	0.04–6.37	0.28–5.23	0.77–1.42	0.23–1.65
1-H-pyrrolicarboxaldehyde	1.03–7.58	0.61–8.31	3.66–7.50	0.66–8.20	0.44–1.80	0.35–6.60	0.44–2.08	0.38–2.11	0.38–1.15	0.42–7.68	0.73–2.13	0.38–1.18
maltol	0.70–13.9	2.09–38.3	2.60–36.9	10.7–44.5	1.50–11.8	3.44–40.1	1.08–30.2	6.60–22.8	1.16–4.05	1.42–25.2	2.89–27.8	10.1–15.1
dihydromaltol	0.01–2.39	nd–3.92	0.14–2.06	0.04–4.14	nd–0.03	0.03–3.93	0.02–0.38	0.02–0.11	nd–0.45	nd–2.77	nd–0.29	0.02–0.07
DDMP	nd–8.40	0.03–5.77	0.13–0.78	0.04–8.07	nd–0.62	0.03–1.32	0.09–0.19	0.02–0.21	nd–0.47	0.02–3.42	0.03–0.19	0.04–0.19
cyclotene	0.14–2.51	0.42–4.38	2.42–4.78	0.74–8.15	0.02–0.46	0.09–6.17	0.03–2.57	0.20–1.79	0.10–0.18	0.13–9.63	0.22–2.98	0.47–1.19
Furaneol	0.23–2.50	0.10–4.27	1.73–8.30	0.37–4.59	nd	0.05–0.99	0.05–0.54	0.12–0.27	nd–0.63	0.05–1.67	0.46–0.74	0.09–0.45
$\gamma$ -butyrolactone	0.52–8.61	1.06–5.23	0.73–8.30	1.75–5.56	0.76–1.39	0.81–9.21	3.30–7.26	3.60–11.8	nd–1.73	1.06–12.2	3.15–7.57	4.87–7.29
crotonalactone	0.55–84.3	26.3–79.9	48.6–89.6	22.1–71.7	6.45–20.0	11.3–73.0	5.72–34.5	18.9–36.7	10.6–16.9	13.4–51.6	9.55–33.9	14.3–24.2
w-lactone <i>trans</i>	0.06–53.2	0.07–50.5	2.37–58.6	0.09–14.9	3.53–24.5	0.01–29.2	1.23–9.29	0.47–9.57	2.11–6.57	1.05–18.3	2.17–10.4	1.09–6.00
w-lactone <i>cis</i>	0.34–117	0.10–116	27.5–122	0.65–21.2	6.71–14.9	0.03–32.3	1.26–14.8	1.50–20.3	16.7–38.4	5.99–74.5	11.2–34.2	5.97–37.7
phenol	0.05–0.38	0.10–1.19	0.40–1.01	0.31–1.98	0.46–0.90	0.16–1.33	0.13–1.51	0.31–1.57	0.12–0.86	0.17–1.44	0.22–1.00	0.40–1.02
<i>o</i> -cresol	nd–0.09	0.01–0.24	0.09–0.18	0.04–0.41	0.06–0.11	0.01–0.25	0.01–0.23	0.04–0.18	0.04–0.16	0.02–0.43	0.04–0.28	0.07–0.35
<i>p</i> -cresol	nd–0.11	0.01–0.19	0.10–0.20	0.04–0.28	0.10–0.26	0.01–0.25	0.04–0.18	0.07–0.34	0.07–0.34	0.03–0.19	0.09–0.19	0.06–0.18
<i>m</i> -cresol	nd–0.07	0.01–0.10	0.06–0.16	0.02–0.28	0.06–0.19	0.01–0.50	0.02–0.14	0.03–0.18	0.03–0.25	0.01–0.23	0.04–0.17	0.04–0.16
guaiacol	0.13–1.23	0.11–4.33	1.39–4.30	0.64–8.91	0.22–0.48	0.10–5.94	0.09–6.94	0.29–2.74	0.31–0.62	0.32–10.8	0.50–5.63	1.05–4.30
4-methylguaiacol	0.12–1.43	0.29–7.17	2.15–3.45	0.29–5.19	0.38–1.75	0.37–12.7	0.18–9.22	1.63–4.90	0.59–1.05	0.16–6.72	0.87–7.21	1.08–2.14
4-ethylguaiacol	0.01–0.07	0.02–0.41	0.01–0.50	0.04–1.77	0.03–0.10	0.03–1.01	0.02–0.86	0.07–0.83	0.04–0.07	0.03–3.79	0.10–0.82	0.12–1.01
4-vinylguaiacol	0.04–1.44	0.14–1.96	1.18–1.84	0.24–2.72	0.14–0.56	0.12–6.74	0.15–0.89	0.18–1.07	0.10–0.21	0.09–8.68	0.19–1.40	0.15–0.66
eugenol	1.17–14.6	0.71–11.3	3.50–7.96	1.79–11.6	0.83–1.50	0.31–3.18	0.80–2.40	0.45–1.33	1.08–3.59	0.85–5.61	2.21–3.26	0.44–2.11
<i>trans</i> -isoeugenol	0.03–0.39	0.04–1.10	0.80–1.64	0.15–1.52	0.05–0.11	0.03–1.17	0.09–0.50	0.03–0.21	0.07–0.12	0.03–2.65	0.12–1.04	0.05–0.13
<i>cis</i> -isoeugenol	0.15–8.64	0.69–9.89	6.76–13.9	0.79–9.77	1.42–3.13	0.28–6.07	1.26–3.29	0.46–3.00	1.09–3.19	0.40–7.12	1.30–8.33	0.60–1.21
syringol	0.38–2.91	0.90–13.3	7.25–19.6	1.72–32.7	0.86–2.53	0.45–29.9	0.36–24.2	1.67–20.8	0.59–1.82	0.72–49.9	0.84–21.0	3.08–27.0
4-methylsyringol	0.22–4.16	0.07–11.4	5.66–15.5	0.89–20.5	0.47–4.11	0.60–38.5	0.37–42.0	2.65–21.7	0.48–0.93	0.82–34.2	0.71–20.0	2.52–12.1
4-ethylsyringol	0.02–0.34	0.05–1.69	0.98–3.74	nd–6.68	0.07–0.38	0.05–8.32	0.04–4.78	0.18–7.87	0.04–0.21	0.06–14.9	0.07–5.11	0.24–9.95
4-allylsyringol	0.69–5.23	1.25–14.0	7.76–18.3	2.19–22.5	0.12–2.53	0.48–26.9	0.93–8.97	1.33–8.49	0.67–1.01	0.77–13.1	1.28–18.9	1.62–8.25
vanillin	8.69–54.0	25.5–114	69.2–95.0	23.8–235	21.6–233	40.3–456	21.6–260	122–325	20.7–38.1	38.4–273	57.9–188	116–331
acetovanillone	0.48–4.01	1.55–9.54	6.79–11.0	2.18–17.8	0.89–8.08	0.96–46.4	0.76–21.3	6.17–19.3	0.65–1.17	0.08–22.2	1.45–16.9	6.13–20.3
isoacetovanillone	1.87–28.5	4.92–25.5	26.9–43.0	4.40–45.6	1.04–12.9	2.08–29.9	1.38–22.7	9.55–23.1	0.65–6.51	3.01–27.7	4.60–29.0	1.39–8.79
propiovanillone	1.23–8.41	1.81–10.0	4.18–9.86	3.41–11.3	2.43–5.25	1.39–8.38	2.73–5.07	3.99–5.65	2.24–6.65	2.26–9.24	5.35–6.82	2.77–6.74
isopropiovanillone	1.81–51.4	6.56–79.2	66.7–153	7.05–148	1.06–22.0	1.36–113	1.05–79.2	7.94–102	0.86–2.76	2.38–86.5	2.96–117	1.80–79.4
homovanillyl alcohol	0.55–62.4	0.84–7.23	4.86–9.13	1.36–7.44	1.83–3.57	0.79–20.8	2.00–5.03	3.08–5.83	1.61–4.90	1.02–11.5	2.23–5.83	1.80–53.5
ethyl vanillyl ether	8.39–78.6	2.99–76.5	70.7–122	22.9–99.1	7.54–30.3	8.36–95.1	9.13–52.8	4.29–65.5	6.87–15.0	8.43–70.6	11.3–87.1	18.4–67.3
syringaldehyde	16.4–193	52.8–263	168–278	128–507	54.5–389	66.5–1447	57.3–1760	276–1095	53.7–63.2	81.5–1113	105–851	225–1347
acetosyringone	0.70–9.18	1.87–20.7	13.0–30.9	5.28–75.2	1.13–13.8	1.61–188	1.45–115	13.4–82.4	0.62–2.03	2.79–140	2.20–83.2	4.86–106
isoacetosyringone	2.80–32.7	4.66–44.8	31.3–63.4	3.25–91.8	2.62–15.8	3.22–78.9	2.89–78.2	13.8–63.5	1.58–6.58	3.61–94.2	6.50–86.7	12.0–34.9
propiosyringone	2.71–15.4	1.86–16.5	8.94–20.7	6.98–26.8	2.83–8.68	1.79–44.5	3.95–30.2	6.82–25.2	1.92–2.69	1.61–35.7	3.48–26.7	1.11–23.9
isopropiosyringone	3.39–121	7.69–238	146–315	14.4–330	2.04–38.5	2.00–330	2.78–317	16.4–296	1.94–2.98	2.93–315	5.03–335	14.3–311
coniferaldehyde	22.8–390	103–501	318–402	199–499	17.0–362	73.5–612	27.6–513	123–494	16.8–108	85.0–620	128–550	160–300
sinapaldehyde	5.85–1394	164–1401	549–868	682–1421	37.6–796	64.7–2221	51.3–1678	328–1284	25.2–100	114–2058	180–2108	375–620

<sup>a</sup> nd = not detected; L = light toasting; M = medium toasting; M+ = medium plus toasting; H = heavy toasting; DMF = 5-hydroxymethylfurfural; DDMP = 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one.

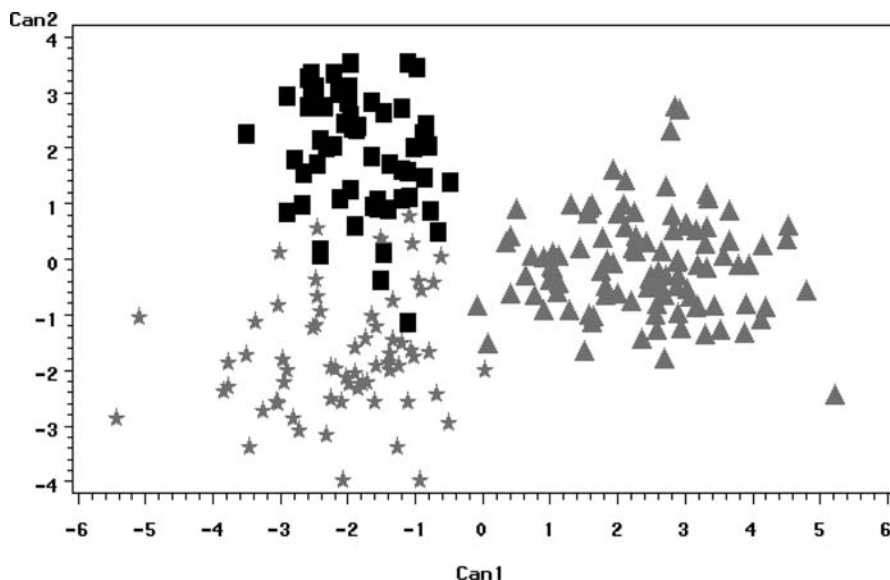
**Table 4.** *F*-Values from the Analysis of Variance (ANOVA) of Quantitative Evaluation of Volatile Compounds as Alternatives to Barrel Oak Wood Products<sup>a</sup>

compound	origin	toasting level	origin x toasting
furfural	15.2*** (a c b)	4.37* (b a b b b)	5.91***
5-methylfurfural	17.6*** (a c b)	4.47* (b a a a)	7.18***
HMF	83.5*** (a b b)	3.61	21.8***
5-acetoxymethylfurfural	26.8*** (a b b)	24.6*** (c c a b)	24.7***
1-methoxy-2-ethoxyethyl-1-furan	24.3*** (a b b)	9.74*** (b b a b)	10.5***
2,5-furandicarbaldehyde	11.5*** (b a a)	7.88*** (b a b b)	4.62***
2-furylmethyl ketone	12.0*** (a c b)	1.14	3.74***
furylhydroxymethyl ketone	60.4*** (a b b)	5.57* (a b b b)	16.5***
1- <i>H</i> -pyrrolcarboxaldehyde	48.7*** (a c b)	1.03	10.8***
maltol	9.17*** (a b b)	44.8*** (c b a a)	21.4***
dihydromaltol	3.49	5.97** (b a b b a)	4.61***
DDMP	18.8*** (a b b)	3.70	4.19***
cyclotene	12.8*** (a c b)	14.9*** (c b a a)	10.1***
Furaneol	76.9*** (a b b)	6.81** (b b a b)	19.3***
$\gamma$ -butyrolactone	10.2*** (c b a)	19.3*** (b a a a)	14.8***
crotonolactone	44.9*** (a b b)	3.99* (b b a b)	15.2***
w-lactone <i>trans</i>	6.10* (a a b)	2.55	3.29**
w-lactone <i>cis</i>	47.8*** (a c b)	2.80	9.68***
phenol	0.59	14.4*** (c b b a)	5.64***
<i>o</i> -cresol	13.9*** (b b a)	13.8*** (b a a a)	8.12***
<i>p</i> -cresol	4.76	4.03* (b a a a)	5.37***
<i>m</i> -cresol	4.96	4.09* (b a b a a)	3.62**
guaiaicol	3.95	12.9*** (b a a a)	5.95***
4-methylguaiaicol	22.7*** (c a b)	19.7*** (b a a a)	12.8***
4-ethylguaiaicol	4.49	7.45*** (b a a a)	3.22**
4-vinylguaiaicol	3.17	3.37	2.26
eugenol	79.4*** (a c b)	4.81* (a b b a b a b)	14.2***
<i>cis</i> -isoeugenol	3.82	14.9*** (c b a b)	9.79***
<i>trans</i> -isoeugenol	5.50* (a b a)	11.4*** (b b a b)	9.76***
syringol	3.52	15.8*** (c b a a)	6.18***
4-methylsyringol	19.9*** (c a b)	14.1*** (b a a a)	9.04***
4-ethylsyringol	9.72*** (b a a)	6.20** (b a a a)	5.81***
4-allylsyringol	0.84	20.0*** (d c a b)	6.93***
vanillin	52.1*** (c a b)	12.2*** (b a a a)	20.7***
acetovanillone	22.9*** (c a b)	15.7*** (b a a a)	11.2***
isoacetovanillone	7.18** (a a b)	23.7*** (c b a b)	13.5***
propiovanillone	4.49	11.1*** (b b a a)	5.95***
isopropiovanillone	2.43	46.4*** (d c a b)	15.5***
homovanillyl alcohol	4.39	6.50** (b b a b)	3.71**
ethyl vanillyl ether	12.1*** (a b b)	28.6*** (c c a b)	12.9***
syringaldehyde	30.1*** (c a b)	11.6*** (b a a a)	13.9***
acetosyringone	16.7*** (c a b)	9.17*** (b a a a)	6.93***
isoacetosyringone	5.65* (b a b)	16.5*** (c b a b)	7.62***
propiosyringone	5.07* (b a b)	13.5*** (c b a a)	5.74***
isopropiosyringone	0.01	37.9*** (d c a b)	11.1***
coniferaldehyde	0.26	14.8*** (b a a a)	5.67***
sinapaldehyde	2.67	15.2*** (b a a a)	7.12***

<sup>a</sup> \*\*, \*, and \*\*\* indicate significance at  $p < 0.01$ ,  $p < 0.001$ , and  $p < 0.0001$ , respectively. In the column "origin", letters between parentheses show the significance among origins, in the order *Q. pyrenaica*, French oak, and American oak. In the column "toasting level", letters between parentheses show the significance among them, in the order light, medium, medium plus, and heavy.

toasting level, although these were really high, as can be deduced by the wide concentration range. The ANOVA results in **Table 3** showed that the levels of the *trans* isomer were similar in French and *Q. pyrenaica* ABP samples and higher than those in American samples without taking the toasting intensity into account; the *cis* isomer, with high *F*-value, allowed the differentiation of the samples of the three origins, with the lowest concentrations being those showed by French oak, confirming the results in the literature (10, 18, 25, 26). However, the toasting levels did not show significant differences among them, which is probably related to the great variability of concentrations detected, verifying previous results (4). These compounds correspond to toasted, wood, coconut, or vanilla notes, and they can exercise a synergistic effect on the aromatic implications of phenolic aldehydes such as syringaldehyde and especially vanillin (27).

Several lignin-derived volatile phenols were found, which can be classified as simple, monomethoxy, and dimethoxy phenols. The lowest levels were those of simple phenols, since they are the final products of the thermodegradation of lignin, and their formation is higher at heavy toasting. Their average concentrations were similar to those detected in other ABP or in barrels manufactured with all three species of oak wood (4, 9–11, 25, 18). However, in **Table 3** we can see that the concentrations detected in some samples were very high, up to 1.98  $\mu\text{g/g}$  and 0.5  $\mu\text{g/g}$  for phenol and cresol, respectively, and these levels were only found in faulty (28) or burned oak woods, being responsible for ink, bitumen, or pharmacy notes in aged wines. Phenol and *o*-cresol were the most correlated with toasting level (**Table 4**), showing also significantly higher *o*-cresol concentrations in American ABP than in woods of other origins. Dimethoxy phenols were



**Figure 1.** Canonical discriminant analysis of volatile compounds in alternative to barrel oak products related to origin: triangles = *Q. pyrenaica* ( $n = 102$ ); boxes = American oak ( $n = 64$ ); stars = French oak ( $n = 66$ ). 100% of dispersion (71.75% Can1 and 28.25% Can2). Canonical correlation of 0.91 and 0.81 is for Can1 and Can2, respectively.

the volatile phenols that showed the highest concentrations, at all toasting intensities, in the three origins, except eugenol at light and medium toast, and also *cis*-isoeugenol in French and American light toast. If we take into account the easier thermodepolymerization of dimethoxyphenyl units compared to monomethoxyphenyl (29), this explains the high concentrations of these compounds in toasted wood, as has already been described (4, 10, 30). The average concentrations detected were similar or slightly higher than those in the literature, but also a wide range of concentrations were found, with some of the detected levels being very high, more suitable for very heavy toasting than for medium or medium plus, as happened in the studied samples. However, dimethoxy phenols were well correlated with toasting intensity, and 4-methylsyringol allowed the differentiation among the samples of the three origins. It is considered that these compounds are responsible for smoky notes in wines, but their detection thresholds in wines are quite high (2 mg/L) (31).

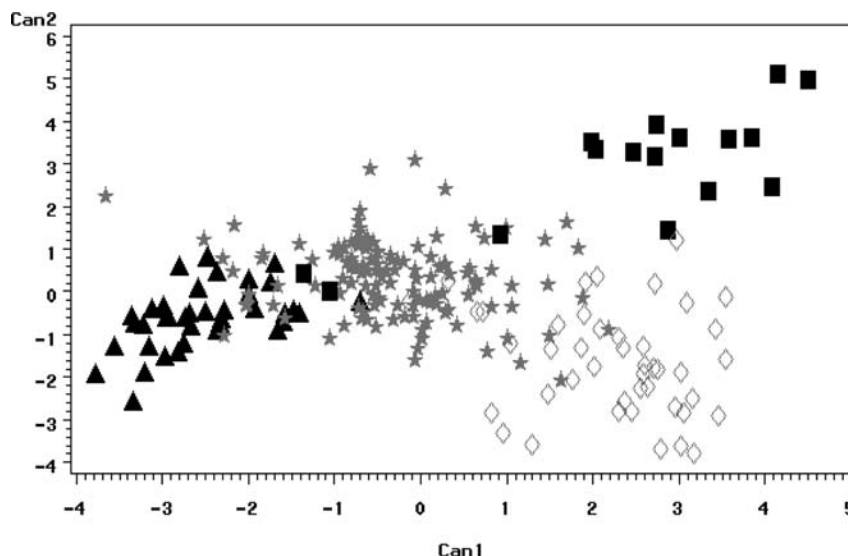
High levels of eugenol in toasted *Q. pyrenaica* wood are a characteristic of this wood (4, 9, 18), and in fact, the volatile phenol with the highest *F*-value related to the origin of ABP was eugenol, followed by 4-methylguaiaicol, but its *F* was much lower. Thus, the concentrations of eugenol in *Q. pyrenaica* ABP were the highest, followed by American and French samples, in that order, with the opposite being true for 4-methylguaiaicol.

The degradation of lignin by heat also produces the formation of mono- and dimethoxy hydroxyphenyl aldehydes and ketones, with the average concentrations of aldehydes, especially hydroxycinnamic aldehydes, always being higher. In all analyzed ABP, the average concentrations of sinapaldehyde were the highest among lignin derivatives, in accordance with the easier thermodepolymerization of dimethoxyphenyl units compared to monomethoxyphenyl (29). Moreover, the average concentrations of vanillin were the lowest among the aldehydes, and these two features have already been described in oak (4, 9, 18, 30) and other woods (24). Regarding the other two aldehydes, syringaldehyde showed higher average concentrations than coniferaldehyde in French and American ABP, while in *Q. pyrenaica* ABP the average concentrations of coniferaldehyde were higher, at all four toasting levels. Data in the literature do not allow confirming these results because both syringaldehyde and coniferaldehyde

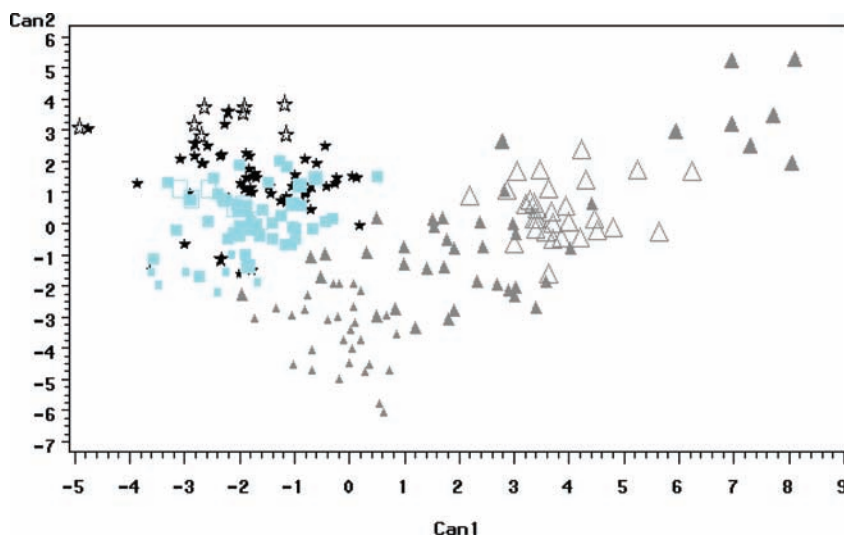
showed concentrations alternatively higher, related to neither origin nor toasting level (4, 9, 18, 25, 30).

Vanillin is the most important from an organoleptic point of view, in relation to aging of wines, since it is an impact molecule with a vanilla smell. In fact, some ABP-makers modify their production system with the objective of obtaining the biggest possible quantity of this compound; in the market the ABP are described as *high vanilla* or something similar. The quantity of this compound in the analyzed samples was strongly correlated to their origin, as well as syringaldehyde, with the highest levels in French oak, intermediate levels in American oak, and the lowest in *Q. pyrenaica* oak, with statistically significant differences among the three, which is in accordance with data in the literature. As happened with most of the compounds, a very wide range of concentrations was detected at each toast level. However, these ranges were especially wide in medium toast French-ABP, with a difference of 415  $\mu\text{g/g}$  between the two ends of the interval, because of the very high detected levels, given that the low values were similar to those found in American ABP. According to Chatonnet (17), when small pieces of oak are toasted, convection heating spreads to favor the production of phenolic aldehydes in relation to toasting of barrels by fire, although, working finely, it is possible to obtain similar profiles. However, since more quantity of heat is able to generate more vanillin, but at very intense toasting aldehydes are degraded and other compounds, as volatile phenols, are generated, it is to be expected that the highest concentrations of vanillin are found at medium plus or heavy levels, as was detected in other papers (4, 17, 25). Looking at the results in Table 3, we can observe that any vanillin level is possible in the different toasting intensities, especially in medium toast French-ABP, and that the variability detected by us in the analyzed samples was much higher than that found when a smaller number of samples is studied, so that it is not possible to relate a toast intensity with a level of vanillin. In the same way, the concentrations of the other three phenolic aldehydes were very high in some samples, showing very wide concentration ranges, highlighting those of sinapaldehyde.

In relation to phenolic ketones, iso-propiosyringone and iso-propiovanillone showed the highest average concentrations and



**Figure 2.** Canonical discriminant analysis of volatile compounds in alternatives to barrel oak products related to toasting level: triangles = light ( $n = 40$ ); stars = medium ( $n = 128$ ); boxes = medium plus ( $n = 16$ ); diamonds = heavy ( $n = 48$ ). 80.70% of dispersion (54.77% Can1 and 25.93% Can2). Canonical correlation of 0.85 and 0.74 is for Can1 and Can2, respectively.



**Figure 3.** Canonical discriminant analysis of volatile compounds in alternatives to barrel oak products related to origin and toasting level: small gray triangles = light ( $n = 29$ ), larger gray triangles = medium ( $n = 35$ ), largest gray triangles = medium plus ( $n = 8$ ), white triangles = heavy ( $n = 30$ ) *Q. pyrenaica*; small blue boxes = light ( $n = 7$ ), larger blue boxes = medium ( $n = 44$ ), largest blue boxes = medium plus ( $n = 4$ ), white boxes = heavy ( $n = 9$ ) American oak; small black stars = light ( $n = 4$ ), larger black stars = medium ( $n = 49$ ), largest black stars = medium plus ( $n = 4$ ), white stars = heavy ( $n = 9$ ) French oak. 54.08% of dispersion (35.15% Can1 and 18.94% Can2). Canonical correlation of 0.93 and 0.88 is for Can1 and Can2, respectively.

a good correlation with toasting intensity (Table 4). In fact, they are, besides 4-allylsyringol, the only compounds that allow the four levels of toasting to be distinguished, being, in decreasing order, medium plus, heavy, medium, and light. The other phenolic ketones were also more correlated to toasting intensity than to sample origins, but they showed lower  $F$ -values except in the cases of acetovanillone and acetosyringone.

With the purpose of having an overall view of the influence that origin and toasting level have on the volatile composition of ABP, we carried out three multivariate analyses of data, grouping the samples in accordance with these two factors, together and separately. The graphic representation of the samples in the space defined by the two main canonical functions obtained in each case shows a distribution of samples that does not allow clear distinctions among all the groups of samples, but some of them. In Figure 1, with samples grouped only considering origin, we can see

that the canonical function 1 (Can 1) almost allows us to distinguish *Q. pyrenaica* ABP from the other two origins, although the statistical distances among samples of the three origins vary widely. This function explain 71.75% of variance, and the more correlated variables were HMF, eugenol, Furaneol, furylhydroxymethyl ketone, and *cis*-whiskylactone, with positive coefficients, and vanillin and syringaldehyde, with negative ones, according to total canonical structure. We can also see some distribution of French and American samples throughout Can2, but this function overlaps *Q. pyrenaica* ABP with French and American. Acetovanillone, iso-acetovanillone, 4-methylsyringol, and 4-methylguaiaicol, with negative coefficients, and *o*-cresol, *cis*-whiskylactone, and guaiacol, with positive, were the more correlated variables. Therefore, the three origins of analyzed ABP showed similar volatile composition with some particularities, but these particularities do not allow a clear distinction of the origin of the ABP.



When samples were grouped only taking into account the toasting level (Figure 2), we obtain a clear separation among light toasting and medium plus and heavy, according to Can 1, except for two medium plus samples included in the light group. Moreover, these medium plus and heavy groups are almost separated throughout Can 2. However, the medium toasted ABP overlap all the others, showing a wide dispersion, so it is not possible to classify the samples as a function of toasting intensity specified by the manufacturer. According to total canonical structure, maltol, iso-propiovanillone, and iso-propiosyringone were the variables most correlated to Can 1, all with positive coefficients, as well as *cis*- and *trans*-isoeugenol, which are the most correlated to Can 2.

Lastly, the two principal canonical functions obtained when taking into account both ABP origin and toasting level explain only 54% of the total variance. In Figure 3 we can see that *Q. pyrenaica* ABP with medium plus and heavy toasting appear separated from French and American ones, although, at light and medium level, it is not so clear. Moreover, the distances between French and American samples were much smaller, although a certain distribution throughout Can 2 can be appreciated. The more correlated variables to Can 1 were carbohydrate derivatives, all with positive coefficients, while the more correlated variables to Can 2, also with positive coefficients, were lignin constituents.

In regard to the overall results, we can deduce that the volatile composition of alternatives to barrel oak products available on the current market varies greatly and has not been clearly related either to oak species or to wood toasting levels. Taking into account that the different characteristics of ABP were reflected in the wine treated with them (4, 18) and that an oenological profile based on these variables (origin and toasting level) cannot be defined, only an appropriate chemical analysis would tell us the quality of alternatives to barrel products, and to foresee their effect on the chemical and organoleptic characteristics of the wines treated with them. On the other hand, the ABP of *Q. pyrenaica* are very similar to those of other species, with some aromatic particularities, such as their high levels of furanic compounds, eugenol, furaneol, and *cis*-whiskylactone, and low levels of vanillin.

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