

Characterization of Volatiles in Extracts from Oak Chips Obtained by Accelerated Solvent Extraction (ASE)

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Sixteen commercially available oak chips, differing in origin (French or American) and toasting level, were extracted by an accelerated solvent extraction method and characterized by their volatile composition. About 80 compounds were identified and quantified, a great part of them from the thermodegradation of lignin and cellulose. One furanone (solerone) and two C-13 norisoprenoids (3-oxo- α -ionol and a 3-oxoretro- α -ionol isomer) were also tentatively identified and reported for the first time in toasted wood. Quantitative data demonstrated the oak chips to be not so different from the composition of light- or medium-toasted wood barrels, which was reported by other authors. The same data suggest that toasting level had the strongest influence on the volatile composition of chip samples. Phenyl ketones, volatile phenols, and some furanic compounds were the most influenced. On the other hand, the influence of wood origin was found to be weaker.

KEYWORDS: Oak chips; GC-MS; ASE; wine; wood aging; volatile compounds

INTRODUCTION

Alcoholic beverages (wines, vinegars, and distillates) aged in wood casks or barrels are considered to be value-added products by most consumers. The reason relies on the increased sensorial features that aged beverages demonstrate as a consequence of physical and chemical phenomena, in which both the compounds released by the casks and the oxygen diffusing through wood pores play a primary role. Traditionally, barrels are made with European (*Quercus robur* and *Quercus petrae*) or American (*Quercus alba*) oaks and sometimes with other species (*Quercus stellata* and *Quercus garryana*) or with chestnut (*Castanea sativa*) (1).

The quantitative and qualitative evolution of the processes related to the wood aging is determined by several factors such as (i) oak origin and species, (ii) length and type of wood seasoning, (iii) degree of stave charring, and (iv) technological parameters (cellar temperature and humidity, contact time between beverage and wood, and age of the barrel) (2–4).

Because of the aromatic impact of some volatiles, a number of studies have dealt with their characterization in oak-aged beverages. Accordingly, volatile phenols such as guaiacol and eugenol (5), phenolic aldehydes such as vanillin and syringaldehyde (6, 7), oak lactones (*cis* and *trans* isomers of β -methyl- γ -octalactone) (8), and furanic aldehydes (furfural and derivatives) (9) have been described as the main contributors to the sensory fingerprinting of aged alcoholic beverages.

Fresh and treated oak staves, however, possess only some of these compounds in appreciable amounts, a large part of them being formed during open-air seasoning and toasting phases (3, 10, 11).

In particular, charring was reported to deeply affect the quantity and quality of potentially extractable volatiles in wood (4, 11). For instance, degraded lipids generate *cis*- and *trans*-oak lactones with a woody and coconut character and low odor thresholds (12).

Several furanic aldehydes and ketones come from the thermodegradation of celluloses and hemicelluloses (which, as a total, represent about 60% of the dry matter of oak wood). This is the case of HMF (from cellulose-derived glucose) and furfural arising from pentoses produced by partial hydrolysis of hemicelluloses (13). These latter compounds are responsible for almond and toasty odors (13).

Finally, the thermal demolition of lignin determines the formation of methoxylated volatile phenols (i.e., guaiacyl and syringyl derivatives), phenolic ketones, and phenolic aldehydes contributing to smoked or spiced and vanilla aromas, respectively (14).

In spite of its wide acceptance, the use of wood casks is prone to some problems such as the cost and difficulty of their sanitization and handling.

In recent years, the use of oak chips as a wood alternative has been proposed (15, 16). Compared with the traditional barrel aging, similar aromatic results in shorter contact time were obtained by some authors (15) when French oak chips were used. Arapitsas et al. (17), on the other hand, when testing chips with similar surfaces but different dimensions, pointed out the influence of chip size on the extraction kinetic.

Wood alternatives are, however, growingly considered by winemakers who can take advantage of the reduced economic investment, the fast completion of the process, and the comparable results in terms of sensory impact.

In Europe, at the moment, the enological use of oak chips is not permitted, even if a great deal of attention is focused on

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this subject, especially after their authorization by the Organisation International de la Vigne et du Vin (OIV) (18), which could be a prelude to a European regulation for admission.

The main aim of the present work was to characterize the volatile compounds extractable from 15 commercially available oak chips of different origins (i.e., French or American) and toasting levels (medium or high toasting). A further nontoasted sample was also evaluated. Results from quantitative evaluation were statistically processed to gain evidence of specific effects and interactions between wood origin and toasting degree.

MATERIALS AND METHODS

Chemicals and Standards. Dichloromethane (Suprasolv) was purchased from Merck KGaA (Darmstadt, Germany). Standard compounds were supplied by Aldrich (Milano, Italy), Sigma Chemicals (St. Louis, MO), and Fluka Chimie AG (Buchs, Switzerland), as reported in **Table 1**.

Wood Chip Samples. One nontoasted and 15 toasted wood chips, commercially available, were extracted by using the accelerated solvent extraction (ASE) procedure reported in the following section.

According to information furnished by the suppliers, the chips were grouped as a function of wood origin (American, A; or French, F) and toasting degree (nontoasted, N; medium toasting, M; or high toasting, H).

As a result we had give classes, namely, AM American medium-toasted chips (one sample); AH, American highly toasted chips (four samples); FM, French medium-toasted chips (three samples); FH, French highly toasted chips (seven samples); and FN, French nontoasted chips (one sample). Specific cooperage operations and toasting procedures were not at our disposal. As a rule, however, wood chips were obtained before the toasting phase; the latter was carried out in ovens (convective charring) for 20–35 min according to the desired level of toasting.

Sample Extraction. Extraction of oak chips was performed by using the ASE 200 system (Dionex, Salt Lake City, UT). About 5 g of exactly weighed wood chips, dispersed in 2.5 g of diatomaceous earth, was placed into the sample cell, which was filled with dichloromethane and raised to 150 °C. After the selected temperature had been reached, a pressurized static extraction phase (7 min) at 20 MPa and a final purge with nitrogen followed. The obtained extracts were added to sodium sulfate, filtered, and concentrated to approximately 2 mL under nitrogen flow. 2-Octanol (100 μ L of a 500 mg/L solution) was added as internal standard before concentration.

GC-MS Analysis. A Thermo Finnigan Trace GC ultra gas chromatograph (San Jose, CA), equipped with a Thermo Finnigan Trace DSQ mass selective detector and a fused silica capillary column Stabilwax (Restek, Bellefonte, PA; 30 m, 0.25 mm i.d., and 0.25 μ m film thickness), was used, under the following working conditions: GC grade helium as carrier gas at a flow rate (constant flow) of 1.0 mL/min; column temperature program, 40 °C heated at 3 °C/min to 100 °C and then heated at 5 °C/min to 240 °C (held for 10 min). The injection temperature was 250 °C. Samples (1 μ L) were injected in the splitless mode. Detection was carried out by positive ion electron impact (EI) mass spectrometry in the full scan mode, using an ionization energy of 70 eV and a transfer line temperature of 280 °C. The mass acquisition range was m/z 30–400 and the scanning rate 1 scan s^{-1} . Chromatographic peaks were identified by comparing their mass spectra with those of standards and/or those reported in the literature and in commercial libraries NIST 2.0 and Wiley 7. For each compound, the linear retention index was also calculated and compared with that reported by other authors. Quantitation was carried out from total ion current peak areas according to the internal standard method; the response factor of standard volatile compounds to the internal standard was experimentally obtained and applied to correct the peak area of each analyte. For compounds lacking reference standards, the response factors of standards with similar chemical structures were used. Results were expressed as micrograms per gram of wood.

Statistical Analysis. A two-way ANOVA was carried out on data from the toasted chips (the FN sample was excluded) to obtain

information on single effects and/or interaction between factors. A further discriminant analysis was also performed on the whole set of data.

All of the statistical analyses were done using the program Statistica 6 (StatSoft Italia srl, Italy).

RESULTS AND DISCUSSION

Qualitative Characterization of Wood Chips. To gain a comprehensive chemical characterization of chip volatiles, an exhaustive extraction method was used. Perez Coello et al. (19, 20) reported that dichloromethane or methanolic Soxhlet extracts of wood contained a greater number of volatiles of wider polarity if compared with both the simultaneous distillation–extraction (SDE) procedure and liquid–liquid extraction (LLE) following water/ethanol soaking.

ASE, on the other hand, has been proposed as an improved exhaustive extraction method that, although using the same solvents as Soxhlet, permits faster and thorough extractions (21). ASE has already been used for trace analysis in environmental and food samples, where it was demonstrated to be precise and accurate, at the same time allowing the reduction of solvent volumes and extraction times, with no evidence of thermal degradation phenomena on representative thermally labile compounds extracted at 150 °C (21–23).

On the basis of previous papers, a wax GC column was preferred due to its better selectivity for polar compounds (24, 25). When used to characterize organic matter by pyrolysis–GC-MS, polar columns appeared to be more suitable for both the products derived from polysaccharides and lignin (26).

The 80 compounds identified in at least one extract are given in **Table 1**, together with their linear retention index (RI) and the method of identification.

As can be observed (**Table 1**), 39 components were identified by comparing their mass spectra and retention times with those of pure standards. The remaining 41 analytes were tentatively identified by mass fragmentation comparison with those of literature or commercial libraries (NIST 2.0 and Wiley 7), also considering their RI or chromatographic behavior already reported for similar analytical conditions (i.e., wax columns). The ion fragmentation of four further unknown compounds is also reported due to their relevant peak areas.

Several lignin-derived volatile compounds, which can be classified as guaiacyl (G) (e.g., monomethoxy phenol) or syringyl (S) (dimethoxy phenol) derivatives, constituted the wood chip extracts.

A number of these compounds have been previously reported in oak wood (4, 13, 19, 27–29) and oak chips (20, 31, 32). In particular, guaiacol and syringol together with their phenolic aldehydes (vanillin and syringaldehyde, respectively), alkenyl or alkyl phenols (4-methyl-, 4-ethyl-, 4-vinyl-, 4-allyl-, 4-propyl-, 4-propenyl- for both G and S derivatives), and phenyl ketones (aceto-, propio-, butyro- derivatives of vanillone and syringone) are reported to come from depolymerization of lignin and successive thermodegradation of monomers (coniferyl G and sinapyl S alcohols) (13, 29, 33, 34).

For these above-mentioned classes, identification of almost all of the compounds for which standards were not at our disposal was obtained according to mass fragmentation reported by other authors, as indicated in **Table 1**.

As found by Cadahia et al. (28), moreover, homosyringaldehyde, ethyl vanillyl ether, and two further phenyl 2-ketones (compounds **63** and **78**) were also identified, the thermodegradation pathway leading to phenyl ketones being also related to lignans (35).

Table 1. Volatile Compounds Detected in the ASE Wood Chips

compd	compound	common name	RI ^a	ident ^b	supplier ^c
1	hexanal	<i>n</i> -caproaldehyde	1091	S, MS	Sigma
2	2-methyl-1-propanol	isobutyl alcohol	1098	S, MS	Merck
3	ethylbenzene		1129	MS	
4	dodecane		1200	S, MS	Sigma
5	2-pentylfuran		1235	MS	
6	tridecane		1300	S, MS	Sigma
7	1-hydroxy-2-propanone	acetol	1303	MS	
8	tetradecane		1400	S, MS	Sigma
9	3-furancarboxaldehyde	3-furaldehyde	1437	MS	
10	ethanoic acid	acetic acid	1463	S, MS	Aldrich
11	2-furancarboxaldehyde	furfural	1470	S, MS	Sigma
12	1-(2-furanyl)ethanone	2-furylmethyl ketone	1507	MS	
13	benzaldehyde		1521	S, MS	Fluka
14	methanoic acid	formic acid	1528	S, MS	Sigma
15	propanoic acid		1547	S, MS	Sigma
16	5-methyl-2-furancarboxaldehyde	5-methylfurfural	1567	S, MS	Sigma
17	methyl-3-furoate		1573	MS	
18	5-methyl-1 <i>H</i> -pyrrole-2-carboxaldehyde		1604	MS	
19	dihydro-2(3 <i>H</i>)-furanone	γ -butyrolactone	1611	S, MS	Fluka
20	butanoic acid	butyric acid	1627	S, MS	Fluka
21	benzeneacetaldehyde	phenylacetaldehyde	1633	MS	
22	1-phenyl-1-ethanone	acetophenone	1639	S, MS	Sigma
23	2-furanmethanol	furfuryl alcohol	1661	S, MS	Fluka
24	3-methyl-2(5 <i>H</i>)-furanone	α -methylcrotonolactone	1718	MS	
25	5-ethoxydihydro-2(3 <i>H</i>)-furanone	τ -ethoxybutyrolactone	1728	MS	
26	2(3 <i>H</i>)-furanone	crotonolactone	1760	MS	
27	2-hydroxy-3-methyl-2-cyclopenten-1-one	cyclotene	1839	MS ¹	
28	hexanoic acid	caproic acid	1865	S, MS	Fluka
29	2,3-dihydro-5-hydroxy-6-methyl-4 <i>H</i> -pyran-4-one	dihydromaltol	1870	MS ²	
30	2-methoxyphenol	guaiacol	1875	S, MS	Sigma
31	unknown ^d 114 (100), 58 (31), 57 (14), 85 (6)		1883		
32	<i>trans</i> -4-methyl-5-butylidihydro-2(3 <i>H</i>)-furanone	<i>trans</i> -oak lactone	1898	S, MS	Aldrich
33	2-phenylethanol	phenylethyl alcohol	1925	S, MS	Fluka
34	benzothiazole		1965	S, MS	Fluka
35	<i>cis</i> -4-methyl-5-butylidihydro-2(3 <i>H</i>)-furanone	<i>cis</i> -oak lactone	1967	S, MS	Fluka
36	4-methyl-2-methoxyphenol	4-methylguaiacol	1969	MS ¹	
37	3-hydroxy-2-methyl-4 <i>H</i> -pyran-4-one	maltol	1975	S, MS	Aldrich
38	2,5-furandicarboxaldehyde		1996	MS ³	
39	1-(2-furanyl)-2-hydroxyethanone	furylhydroxymethyl ketone	2022	MS ³	
40	phenol		2026	S, MS	Sigma
41	1 <i>H</i> -pyrrole-2-carboxaldehyde		2044	MS	
42	4-ethyl-2-methoxyphenol	4-ethylguaiacol	2047	S, MS	Sigma
43	5-ethoxydihydro-2(3 <i>H</i>)-furanone	solerone	2082	MS ^{4,5}	
44	unknown ^b 197 (100), 155 (44), 212 (37), 198 (16), 153 (15)		2101		
45	2-methoxy-4-(2-propenyl)phenol	eugenol	2185	S, MS	Sigma
46	4-vinyl-2-methoxyphenol	4-vinylguaiacol	2211	S, MS	Sigma
47	<i>cis</i> -2-methoxy-4-(1-propenyl)phenol	<i>cis</i> -isoeugenol	2264	S, MS	
48	2,6-dimethoxyphenol	syringol	2273	S, MS	Fluka
49	2,3-dihydro-3,5-dihydroxy-6-methyl-4 <i>H</i> -pyran-4-one	DDMP	2275	MS ²	
50	3,5-dihydroxy-2-methyl-4 <i>H</i> -pyran-4-one	5-hydroxymaltol	2295	MS ³	
51	<i>trans</i> -2-methoxy-4-(1-propenyl)phenol	<i>trans</i> -isoeugenol	2347	S, MS	Fluka
52	4-methyl-2,6-dimethoxyphenol	4-methylsyringol	2350	MS ⁶	
53	1,4:3,6-dianhydro- α -D-glucopyranose		2394	MS ⁷	
54	2-furancarboxylic acid	2-furoic acid	2467	S, MS	Sigma
55	5-hydroxymethyl-2-furancarboxaldehyde	HMF	2509	S, MS	Sigma
56	syringyl derivative		2542	MS	
57	4-hydroxy-3-methoxybenzaldehyde	vanillin	2567	S, MS	Sigma
58	4-vinyl-2,6-dimethoxyphenol	4-vinylsyringol	2573	MS ⁶	
59	4-propyl-2-methoxyphenol	4-propylguaiacol	2603	MS ¹	
60	9-hydroxymegastigma-4,7-dien-3-one	3-oxo- α -ionol	2658	MS ^{8,9}	
61	1-(4-hydroxy-3-methoxyphenyl)ethanone	acetovanillone	2667	S, MS	Aldrich
62	(2 <i>E</i>)-3-(4-hydroxy-2-methoxyphenyl)-2-propenal	4-hydroxy-2-methoxycinnamaldehyde	2681	MS	
63	1-(4-hydroxy-3-methoxyphenyl)-2-propanone	guaiacylacetone	2700	MS ¹⁰	
64	1-(4-hydroxy-3-methoxyphenyl)propanone	propiovanillone	2719	S, MS	Aldrich
65	4-allyl-2,6-dimethoxyphenol	4-allylsyringol	2733	MS ¹	
66	2,6-dimethoxy-4-(1-propenyl)phenol	methoxyeugenol isomer	2758	MS ¹	
67	1-(4-hydroxy-3-methoxyphenyl)butanone	butyrovannillone	2771	MS ¹⁰	
68	unknown 208 (100), 131 (77), 119 (69), 91 (55), 147 (44), 190 (42)		2776		
69	unknown 170 (100), 155 (50), 127 (46), 112 (16), 69 (14), 168 (10)		2783		
70	9-hydroxymegastigma-4,6-dien-3-one (<i>E</i> or <i>Z</i> isomer)	3-oxoretro- α -ionol	2797	MS ^{8,11}	
71	hexadecanoic acid		2820	S, MS	Sigma
72	4-(1 <i>E</i>)-3-hydroxy-1-propenyl-2-methoxyphenol	<i>cis</i> -coniferyl alcohol	2832	MS ¹²	
73	4-hydroxy-3,5-dimethoxybenzaldehyde	syringaldehyde	2854	S, MS	Aldrich
74	2-(4-hydroxy-3,5-dimethoxyphenyl)acetaldehyde	homosyringaldehyde	2878	MS ^{10,12}	
75	1 <i>H</i> -indole-3-ethanol	tryptophol	2882	MS	

Table 1. (Continued)

compd	compound	common name	RI ^a	ident ^b	supplier ^c
76	4-(ethoxymethyl)-2-methoxyphenol	ethyl vanillyl ether	2888	MS ¹⁰	
77	1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone	acetosyringone	2900	S, MS	Aldrich
78	1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone	syringol propan-2-one	2916	MS ¹⁰	
79	3,4,5-trimethoxyphenol	antiarol	2960	MS	
80	1-(4-hydroxy-3,5-dimethoxyphenyl)propanone	propiosyringone	2990	MS ¹⁰	
81	3-(4-hydroxy-3-methoxyphenyl)-2-propen-1-ol	coniferyl alcohol	2999	S, MS	Sigma
82	1-(4-hydroxy-3,5-dimethoxyphenyl)butanone	butyrosyringone	3019	MS	
83	sinapyl derivative		3034	MS	
84	4-hydroxy-3-methoxycinnamaldehyde	coniferyl aldehyde	3038	S, MS	Aldrich

^a Linear retention index. ^b Method of identification: S, by comparison of mass spectrum and retention time with those of standard compounds; MS, by comparison of mass spectrum with those included in the NIST 2.0 and Wiley 7 libraries or with mass spectra reported in the following references: ¹ Nonier et al. (27), ² Cutzach et al. (9), ³ Cutzach et al. (36), ⁴ Martin et al. (41), ⁵ Augustyn et al. (38), ⁶ Steinbiss et al. (34), ⁷ Guillen and Manzano (42), ⁸ Winterhalter et al. (45), ⁹ Nonier et al. (46), ¹⁰ Cadahia et al. (28), ¹¹ Sefton et al. (44), ¹² Ralph and Hatfield (33). ^c For compounds identified by comparison of standard compounds, the supplier is given. ^d For unidentified compounds, principal fragment ions are given (in parentheses are given the relative percentages).

Compound **72**, tentatively identified as *cis*-coniferyl alcohol, was found in only one AM sample.

The chip extracts were also demonstrated to possess a wide number of molecules derived from degradation of sugars. Apart from furfural, HMF, and methylfurfural, a series of compounds with pyranone, pyrrole, or furan structures were found (compounds **18**, **29**, **37**, **38**, **39**, **41**, **49**, and **50**). Such compounds have already been reported in wood extracts and in heated glucose/proline mixtures (9, 13, 36, 37).

Cutzach et al. (9), in particular, reported the identification of maltol, dihydromaltol, 1*H*-pyrrole-2-carboxaldehyde, 5-hydroxymaltol, and DDMP in cooperage woods, contextually confirming that their genesis is related to Maillard reactions, the same origin they reported for cyclotene (compound **26**). In another study, the same authors (36) identified 2,5-furandicarboxaldehyde (compound **38**) and furylhydroxymethyl ketone (compound **39**) in dichloromethane extracts of oak wood and in heated glucose/proline mixtures. Moreover, Kim et al. (37) highlighted the primary role of DDMP as a pyranone precursor and stable degradation compound of hexoses.

All of the above-mentioned compounds have been described as being responsible for "toasted" (compounds **29**, **37**, and **49**) or "honeyed" (compounds **38**, **39**, and **50**) notes and may well contribute to the organoleptic characteristics of wood-aged alcoholic beverages.

The presence of solerone (compound **43**) in wood chips could be somewhat surprising because this furanone, to date, was reported only as a wine aroma formed during the course of sherry fermentation under oxidative conditions (38, 39). As discussed by Pollnitz et al. (40) referring to some volatiles extracted from oak wood, its artifactual formation due to GC-MS analysis (high injector temperature) or ASE (high temperature and relatively polar solvent) could not be excluded. However, this compound, the aromatic contribution of which in oxidized wines is actually controversially debated (41), has already been identified in small portions after the heating of a DDMP acid solution (37).

Compound **53** was reported in an aqueous oak smoke preparation arising from both wood and cellulose or carbohydrate pyrolysis (42).

In Figures 1 and 2 are reported the mass spectra of compounds **60** and **70**, which were tentatively identified as the C-13 norisoprenoids 3-oxo- α -ionol and a 3-oxoretro- α -ionol isomer, respectively.

Norisoprenoids have already been reported in oak wood as a consequence of the degradation of carotenoids (43) and also occur as glycoconjugates in grapes and wines (44, 45). The mass

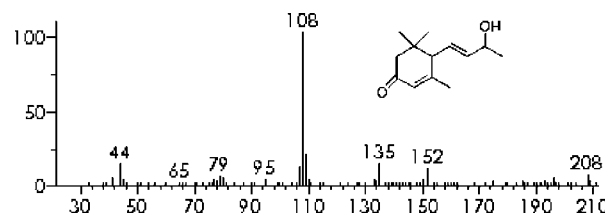


Figure 1. EI-MS mass spectrum of peak 60 (see Table 1), tentatively identified as 9-hydroxymegastigma-4,7-dien-3-one (3-oxo- α -ionol).

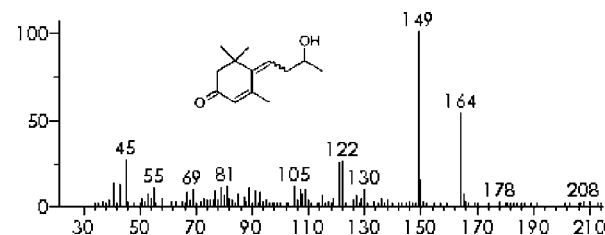


Figure 2. EI-MS mass spectrum of peak 70 (see Table 1), tentatively identified as 9-hydroxymegastigma-4,6-dien-3-one (3-oxo-retro- α -ionol).

spectrum shown in Figure 1 is in agreement with the spectra reported by the NIST library and by Winterhalter et al. (45) and Nonier et al. (46) for 3-oxo- α -ionol. These latter authors identified this compound, together with other C-13 norisoprenoids, as a major component in a dichloromethane extract of hydroalcoholic soaked seasoned wood. In the same work, GC analysis with polar columns was found to be the most suitable for separating these molecules. Similarly, the spectrum depicted in Figure 2 was assigned to a 3-oxo-retro- α -ionol isomer due to the close accordance with spectra published by Sefton et al. (43) and Winterhalter et al. (45). This compound has already been found in wines (44, 45) and oak wood (43), and its accumulation in vegetal tissues is thought to be interdependent on that of 3-oxo- α -ionol (44). Both compounds **60** and **70** are regarded as probable precursors of components associated with tobacco-like aroma.

To the best of our knowledge, this is the first report of the presence of such norisoprenoids in toasted wood chips. The hypothesis of their artifactual formation during extraction and/or GC analysis, however, should be further investigated even if the small amounts of carotenoids in wood, the sensitivity of norisoprenoids to the heating (46) and the short ASE extraction time make that hypothesis somewhat unlikely.

Quantitative Characterization of Oak Chips. In Tables 2–5, the quantified compounds in wood chips are reported according to their chemical family. In these tables, wood chip extracts are grouped as a function of their origin and toasting

Table 2. Two-Way ANOVA and Mean Content in Guaiacol and Derivatives of Wood Chips Grouped as a Function of Origin and Toasting Degree (A, American; F, French; M, Medium Toasting; H, High Toasting; N, Nontosted)

	$\mu\text{g/g} \pm \text{SD}$					effects ^a		
	AM (1) ^b	AH (4)	FM (3)	FH (7)	FN (1) ^c	O	T	O × T
guaiacol	0.19	1.21 ± 0.74	0.18 ± 0.02	0.75 ± 0.34	0.17		*	
4-methylguaiacol ^d	0.03	0.39 ± 0.16	0.06 ± 0.03	0.29 ± 0.18	ND ^e		*	
4-ethylguaiacol	0.01	0.07 ± 0.04	0.03 ± 0.04	0.15 ± 0.18	ND			
eugenol	0.64	2.32 ± 1.24	1.40 ± 0.06	1.86 ± 0.57	1.70		*	
4-vinylguaiacol	0.50	7.76 ± 5.98	2.52 ± 0.85	6.53 ± 3.08	1.59		*	
cis-isoegenol	ND	0.19 ± 0.10	0.10 ± 0.00	0.14 ± 0.04	ND		*	
trans-isoegenol	1.70	23.6 ± 5.38	22.1 ± 11.9	19.3 ± 5.60	7.59			*
vanillin	15.3	137 ± 10.0	51.5 ± 16.2	119 ± 44.0	12.0		*	
propylguaiacol ^d	6.48	46.4 ± 9.70	27.7 ± 7.44	38.1 ± 9.26	5.52		*	*
acetovanillone	0.22	7.61 ± 0.33	2.63 ± 0.64	6.74 ± 2.64	0.17		*	
guaiacylacetone ^f	0.12	13.7 ± 7.89	2.93 ± 0.80	9.01 ± 3.58	0.86		*	
propiovanillone	2.55	1.23 ± 1.01	0.72 ± 0.13	1.73 ± 1.42	1.16			
butirovanillone ^f	1.41	13.3 ± 4.46	10.9 ± 4.21	10.9 ± 4.38	7.26			
ethylvanillyl ether ^g	2.44	11.2 ± 5.26	5.75 ± 1.06	9.11 ± 2.00	2.48		*	
coniferyl alcohol	3.29	0.79 ± 0.12	2.29 ± 1.09	2.27 ± 2.17	2.34			
coniferyl aldehyde	17.2	118 ± 41.6	94.5 ± 44.4	126 ± 46.7	22.6		*	
sum	52.1	385 ± 91.2	225 ± 59.0	352 ± 102	65.1		*	

^a Main effects and interactions: O, origin; T, toasting; O × T, interaction. Effects flagged with an asterisk are significant for $p < 0.05$. ^b The number of chip samples for each group is given in parentheses. ^c This sample was not included in the statistical analysis. ^d Expressed as guaiacol. ^e Not detected. ^f Expressed as propiovanillone. ^g Expressed as vanillin.

Table 3. Two-Way ANOVA and Mean Content in Syringol and Derivatives of Wood Chips Grouped as a Function of Origin and Toasting Degree (A, American; F, French; M, Medium Toasting; H, High Toasting; N, Nontosted)

	$\mu\text{g/g} \pm \text{SD}$					effects ^a		
	AM (1) ^b	AH (4)	FM (3)	FH (7)	FN (1) ^c	O	T	O × T
syringol	0.54	6.08 ± 2.27	4.06 ± 2.69	4.17 ± 2.02	0.10			
4-methylsyringol ^d	ND ^e	4.09 ± 0.47	2.25 ± 1.76	3.35 ± 1.50	ND			
4-vinylsyringol ^d	0.35	8.56 ± 2.31	7.29 ± 4.08	6.84 ± 3.18	0.61			
4-allylsyringol ^d	1.92	28.0 ± 8.06	20.8 ± 11.0	29.3 ± 13.9	6.72			
metoxyeugenol ^d	3.05	1.87 ± 1.09	6.57 ± 0.38	2.38 ± 1.89	6.49			
syringaldehyde	28.5	386 ± 18.8	75.5 ± 20.6	320 ± 143	46.8		*	
homosyringaldehyde ^d	6.94	67.9 ± 8.27	24.6 ± 1.94	50.7 ± 16.5	2.43		*	
acetosyringone	0.69	22.1 ± 1.31	6.39 ± 3.42	17.3 ± 8.58	0.29		*	
syringyl propan-2-one ^d	0.54	35.0 ± 12.0	4.60 ± 1.46	23.1 ± 10.8	0.62		*	
propiosyringone ^d	ND	3.35 ± 0.68	1.01 ± 0.46	3.00 ± 1.20	ND		*	
butyrosyringone ^d	2.14	53.2 ± 11.0	14.5 ± 4.64	39.6 ± 17.9	21.8		*	
sinapyl derivative ^d	0.01	54.6 ± 41.0	144 ± 33.2	99.0 ± 69.4	ND	*		
sum	44.8	671 ± 50.2	312 ± 22.9	600 ± 229	85.9		*	

^a Main effects and interactions: O, origin; T, toasting; O × T, interaction. Effects flagged with an asterisk are significant for $p < 0.05$. ^b The number of chip samples is given in parentheses. ^c This sample was not included in the statistical analysis. ^d Expressed as syringol. ^e Not detected.

degree, leading to four distinct classes as a consequence of two origins and two toasting degrees.

A two-way ANOVA was conducted on this set of data to outline single effects and interactions for each variable and level. Quantitative data for the unique seasoned sample (nontosted) are also separately given as a reference, which was not included in the statistical elaboration.

The huge variations around the mean value of many quantified compounds (**Tables 2–5**) account for differences among single trees, position in the tree of the obtained staves (3), or, even, cooperage differences, and must be somewhat considered in the interpretation of the results.

As far as compounds originating from lignin degradation are concerned (**Tables 2 and 3**), coniferyl aldehyde, the sinapyl derivative (both deriving directly from the constitutive alcohols), and the phenolic aldehydes vanillin and syringaldehyde were largely the most abundant compounds in wood chips. This is in accordance with the postulated thermodegradation pathway of lignins that generate propenyl aldehydes at the very first step and phenyl aldehydes, via radical rupture of an α - β linkage, in a successive step (13).

Quantitatively relevant is the presence of phenyl ketones. Even if their direct derivation from lignin is still debated, their accumulation in oak wood has been reported to be directly related to the toasting intensity. This fact is confirmed by our findings based on ANOVA (**Tables 2 and 3**).

Volatile phenols such as guaiacol, syringol, and their alkyl and alkenyl derivatives were found in relatively lower amounts. However, their sensory contribution to wood-aged beverages would probably be given because of the very low perception threshold (between 50 and 100 $\mu\text{g/L}$ in wines for 4-methylguaiacol, guaiacol, and syringol, respectively) (47).

Almost all of the guaiacyl and syringyl derivatives were found to increase with the duration and temperature of toasting. As a sum, syringyl derivatives were present at higher amounts than guaiacyl derivatives at both toasting levels (with S/G ratio increasing from 1.32 to 1.70), probably due to the easier thermodepolymerization of S lignins compared to G lignins (13).

No influence of the origin of wood was recorded except for the sinapyl derivative that was higher in French woods.

Altogether, their content in oak wood agreed with findings of Cadahía et al. (28) and Chatonnet et al. (35) for barrels from

Table 4. Two-Way ANOVA and Mean Content in Furanic Compounds, Furanones, Pyranones, and Lactones of Wood Chips Grouped as a Function of Origin and Toasting Degree (A, American; F, French; M, Medium Toasting; H, High Toasting; N, Nontasted)

	$\mu\text{g/g} \pm \text{SD}$					effects ^a		
	AM (1) ^b	AH (4)	FM (3)	FH (7)	FN (1) ^c	O	T	O × T
2-pentylfuran ^d	0.14	0.08 ± 0.05	0.18 ± 0.02	0.09 ± 0.05	0.32		*	
3-furfural ^e	0.06	0.71 ± 0.12	0.16 ± 0.00	0.64 ± 0.27	0.30		*	
2-furfural	114	261 ± 194	226 ± 86.9	240 ± 130	90.7			
2-furylmethyl ketone ^e	0.66	1.41 ± 1.31	1.19 ± 0.40	1.43 ± 0.86	1.02			
5-methylfurfural	13.4	37.5 ± 39.0	31.9 ± 14.5	32.6 ± 23.8	16.5			
methyl-3-furoate	0.39	0.24 ± 0.19	0.11 ± 0.06	0.23 ± 0.15	0.37			
5-methyl-1 <i>H</i> -pyrrole-2-carbaldehyde ^e	0.32	0.35 ± 0.26	0.41 ± 0.16	0.29 ± 0.16	0.28			
γ -butyrolactone	0.88	3.54 ± 1.52	1.13 ± 0.37	2.64 ± 1.81	1.21			
furfuryl alcohol	1.11	1.22 ± 0.23	0.82 ± 0.18	1.14 ± 0.47	1.42			
3-methyl-2(5 <i>H</i>)-furanone ^g	0.07	0.63 ± 0.55	0.23 ± 0.14	0.45 ± 0.38	0.09			
5-ethoxydihydro-2(3 <i>H</i>)-furanone ^g	1.17	5.23 ± 1.76	2.23 ± 0.59	4.30 ± 1.30	2.29		*	
cyclotene ^h	0.06	0.21 ± 0.14	0.02 ± 0.01	0.14 ± 0.05	0.01		*	
2-(3 <i>H</i>)-furanone ^g	3.74	9.73 ± 3.24	7.84 ± 2.33	8.22 ± 2.00	4.15			
maltol	0.21	3.32 ± 1.77	0.58 ± 0.21	2.14 ± 1.04	0.07		*	
2,5-furandicarboxaldehyde ^e	1.44	4.42 ± 4.02	6.60 ± 4.13	3.55 ± 2.26	0.12			
furylhydroxymethyl ketone	0.98	0.32 ± 0.08	1.18 ± 0.47	0.58 ± 0.57	0.85			
1 <i>H</i> -pyrrole-2-carboxaldehyde ^f	1.83	1.25 ± 0.34	1.37 ± 0.63	2.20 ± 1.90	2.23			
solerone ^h	0.11	0.75 ± 0.46	0.14 ± 0.07	0.56 ± 0.36	0.61		*	
5-hydroxymaltol ^h	0.17	0.19 ± 0.04	0.19 ± 0.04	0.18 ± 0.06	0.03			
2-furoic acid	0.03	0.56 ± 0.65	0.04 ± 0.06	0.63 ± 0.62	ND ⁱ			
DDMP ^h	0.20	0.04 ± 0.02	0.34 ± 0.26	0.12 ± 0.08	0.33		*	
HMF	43.7	53.1 ± 28.9	87.2 ± 29.2	56.1 ± 22.8	98.6			
<i>trans</i> - β -methyl- γ -octolactone	4.05	5.16 ± 3.12	8.84 ± 3.57	5.30 ± 2.87	3.76			
<i>cis</i> - β -methyl- γ -octolactone	37.1	33.3 ± 15.5	16.1 ± 9.69	20.5 ± 11.0	14.7			
<i>cis/trans</i> -oak lactones	9.16	6.55 ± 1.56	2.51 ± 2.40	4.11 ± 2.36	3.92	*		

^a Main effects and interactions: O, origin; T, toasting; O × T, interaction. Effects flagged with an asterisk are significant for $p < 0.05$. ^b The number of chip samples is given in parentheses. ^c This sample was not included in the statistical analysis. ^d Quantified assuming a response factor = 1. ^e Expressed as furfural. ^f Expressed as 5-methylfurfural. ^g Expressed as γ -butyrolactone. ^h Expressed as maltol. ⁱ Not detected.

Table 5. Two-Way ANOVA and Mean Content in Hydrocarbons, Acids, Phenols, Norisoprenoids, and Other Compounds of Wood Chips Grouped as a Function of Origin and Toasting Degree (A, American; F, French; M, Medium Toasting; H, High Toasting; N, Nontasted)

	$\mu\text{g/g} \pm \text{SD}$					effects ^a		
	AM (1) ^b	AH (4)	FM (3)	FH (7)	FN (1) ^c	O	T	O × T
hydrocarbons								
dodecane	0.83	0.70 ± 0.07	0.63 ± 0.08	0.72 ± 0.10	1.05			
tridecane	0.69	0.65 ± 0.13	0.62 ± 0.05	0.63 ± 0.06	0.86			
tetradecane	0.65	0.48 ± 0.02	0.41 ± 0.05	0.49 ± 0.04	0.86			
acids								
acetic	437	502 ± 248	446 ± 154	488 ± 222	1559			
formic	ND ^d	4.73 ± 5.29	0.91 ± 1.16	5.63 ± 5.91	0.16			
propanoic	3.02	21.9 ± 10.2	4.29 ± 1.09	10.2 ± 4.33	0.83		*	
butanoic	2.92	1.85 ± 1.14	1.20 ± 1.14	1.24 ± 0.81	0.29	*		*
hexanoic	0.99	1.19 ± 0.48	0.59 ± 0.39	0.72 ± 0.63	0.33	*		
hexadecanoic	12.0	7.51 ± 3.57	16.0 ± 5.18	9.34 ± 5.16	31.0			
phenols								
ethylbenzene ^e	2.63	2.20 ± 0.20	2.29 ± 0.15	2.29 ± 0.31	2.61			
benzaldehyde	0.16	0.15 ± 0.18	0.22 ± 0.02	0.12 ± 0.11	0.19			
benzeneacetaldehyde ^e	0.03	0.02 ± 0.01	0.04 ± 0.01	0.07 ± 0.09	0.06			
acetophenone	0.60	0.91 ± 0.11	0.79 ± 0.12	0.88 ± 0.26	0.85			
2-phenylethanol	0.30	0.20 ± 0.12	0.19 ± 0.03	0.13 ± 0.08	0.53			
phenol	0.11	0.23 ± 0.10	0.08 ± 0.02	0.20 ± 0.07	0.09		*	
antiarol ^e	0.30	2.06 ± 0.38	2.74 ± 1.27	2.08 ± 0.63	1.99	*		*
norisoprenoids								
3-oxo- α -ionol ^f	0.18	0.00 ± 0.01	0.34 ± 0.09	0.04 ± 0.04	0.58		*	
3-oxo-retro- α -ionol ^f	0.30	0.16 ± 0.09	0.06 ± 0.10	0.07 ± 0.06	ND	*		
others								
benzothiazole	ND	0.01 ± 0.01	0.00 ± 0.01	0.02 ± 0.03	ND			
hexanal	1.38	0.84 ± 0.37	2.33 ± 0.63	1.08 ± 0.51	2.60		*	
1-hydroxy-2-propanone ^f	1.72	1.14 ± 0.37	1.54 ± 0.24	1.15 ± 0.33	1.33		*	

^a Main effects and interactions: O, origin; T, toasting; O × T, interaction. Effects flagged with an asterisk are significant for $p < 0.05$. ^b The number of chip samples is given in parentheses. ^c This sample was not included in the statistical analysis. ^d Not detected. ^e Expressed as benzaldehyde. ^f Quantified assuming a response factor = 1.

American and/or French origin at medium toasting level except for 4-allylsyringol, isoeugenol, and homosyringaldehyde, the contents of which in wood chips were up to 5-, 10-, and 20-fold higher, respectively.

Comparison with other works dealing with the characterization of oak chips is difficult due to the scarcity of papers and the diversity of either the method of extraction or the target compounds of those research papers. Anyway, in water/ethanol-

extracted wood chips, Perez Coello et al. (20) found comparable values of eugenol but substantially lower amounts of vanillin and syringaldehyde.

Table 4 reports the quantification of furans, pyranones, lactones, and related compounds. Furanic aldehydes (e.g., furfural, HMF, and 5-methylfurfural) were the most abundant in this class of compounds. Their amount was similar to that found in light- and medium-toasted woods by Cadahía et al. (28) and Chatonnet et al. (35).

Moreover, small differences between medium- and high-toasted wood were found. According to Chatonnet et al. (35), in fact, the largest variations are expected to be mainly recorded immediately after the beginning of the process, between seasoned and light-toasted samples.

If compared with other published studies on the volatile composition of oak woods, our extracts proved to be qualitatively richer in compounds deriving from the Maillard reaction.

This result could be the consequence of the different methods of toasting adopted for chips compared to barrels (convective vs direct fire) but also could result from the combination of exhaustive ASE extraction and suitable chromatographic conditions.

Quantitatively speaking, however, the contents of maltol, 1*H*-pyrrole-2-carboxaldehyde, cycлотene, and furfuryl alcohol were in accordance with the findings of Cadahía et al. (28) and Chatonnet et al. (35).

Solerone, cycлотene, and maltol proved to be significantly and directly influenced by the degree of toasting, whereas, for DDMP, an inverse correlation was verified.

As for lignin-derived compounds, the origin of wood had no influence on Maillard products, probably as a consequence of the high variability within each group of samples.

Oak lactones, the mean content of which is in accordance with that reported in wood barrels by Cadahía et al. (28) or in chips by Pérez Coello et al. (20), were slightly influenced by the heat treatment. Their ratio, which is a characteristic indicator of oak species (48), was statistically higher in American chips (**Table 4**).

The remaining quantified compound concentrations are shown in **Table 5**. Among carboxylic acids, acetic acid was largely predominant. Its formation has been reported to derive from both lignin and cellulose (13). On the other hand, propionic acid could probably derive from alkyl chain breakdown of depolymerized lignin, and its amount increased with toasting degree.

Phenols, such as ethylbenzene, benzaldehyde, phenol, and antiarol, were found in wood chips in relatively small amounts. Other phenols, which could confer undesirable ink or bitumen taints (e.g., cresols) were absent.

In **Table 5**, the content of the two identified norisoprenoids is also reported. Both compounds appeared to be reduced as the degree of toasting increased, the 3-oxo- α -ionol reduction being statistically significant. Moreover, the 3-oxo-retro- α -ionol isomer was found in the highest concentration in American wood chips. This finding, which is in accordance with Sefton et al. (43), who found a higher amount of 3-oxo-retro- α -ionol isomers (about 80-fold) in seasoned American woods compared to French oak, could represent a distinctive characteristic of wood from *Quercus alba*.

Sefton et al. (43) reported the 3-oxo-retro- α -ionol isomers to be the main C-13 norisoprenoids in nontoasted American wood with concentrations up to 2.9 $\mu\text{g/g}$ of wood. They also reported that 3-oxo- α -ionol was the principal carotenoid-derived compound in French oak with amounts that were of the same

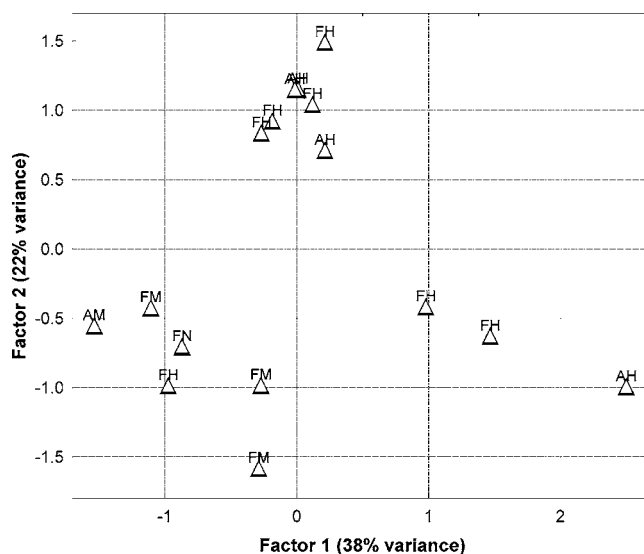


Figure 3. Plot of factor analysis on the first two factors, carried out on the whole set of data. For variables ranking, see the text.

order of magnitude as our nontoasted French sample (0.90 and 0.58 $\mu\text{g/g}$, respectively).

To obtain a comprehensive representation of the main parameters that could differentiate the chip samples, a factor analysis was carried out on all of the quantified volatiles.

In **Figure 3**, the positions of the 16 samples in the space formed by the first two factors (60% of the variance, as a sum) are shown.

On factor 1, which accounted for the highest variance (38%), only two FH and one AH sample were clearly discriminated from each other, hence confirming that differences between single samples (independent of origin or toasting degree) are the main cause of variability in wood chips. On this factor, the principal parameters were guaiacylacetone, α -methylcrotonolactone, 4-vinylguaiacol, and ethyl vanillyl ether.

Factor 2 (22% of total variance) discriminated two groups of samples: a group composed of seven highly toasted French or American chips and a second group with all of the remaining samples, where four medium-toasted, one nontoasted, and four highly toasted wood samples are indistinguishable.

Parameters that mainly accounted for this variance were acetophenone, acetol, HMF, and hexanal.

A further factor (factor 3) discriminated the FN sample from all other wood chips. It explained 12% of variance, and the main contributors were dodecane, 2-phenylethanol, and benzaldehyde.

On the whole, the overall data we obtained suggest the suitability of the ASE coupled with the GC-MS analysis for the qualitative chemical characterization of wood chips. Detailed studies on method performance and validation are, however, requested and will be carried out in our laboratories. In spite of the wide variability among the single samples, the effects of increased toasting temperature and duration were established to involve a number of lignin-derived (phenyl ketones particularly) and Maillard intermediate products. On the other hand, the influence of wood origin was found to be weaker.

Wood chip composition was not too different from the composition of wood from barrels, as reported by other authors.

Solerone, 3-oxo- α -ionol, and a 3-oxo-retro- α -ionol isomer were identified for the first time in toasted woods. This latter compound appeared to be significantly higher in American

woods, and further studies may be needed to exclude any artifactual formation during analysis and to confirm its use as an indicator of wood species.

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