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Study of the volatile composition of an aqueous oak smoke preparation

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Abstract

An aqueous smoke flavouring from oak (*Quercus* sp.) sawdust was obtained on the laboratory scale. Its qualitative and quantitative composition was studied by gas chromatography after previous extraction. A high number of compounds (215) was detected. In addition to the well-known smoke components, others, only recently described as smoke components, were also detected. In the first group there are aldehydes, ketones, diketones, esters, alcohols, acids, furan and pyran derivatives, syringol, guaiacol, phenol and pyrocatechol derivatives, alkyl and aryl ethers; in the second group the presence of some furan and pyran derivatives is noteworthy, as well as a significant number of lignin dimers in low proportion, a considerable number of anhydrosugars in very high proportion and some nitrogenated derivatives in low proportions. Differences between this oak aqueous liquid smoke and others previously obtained from several woods, under similar operative conditions, are due, not only to the absence or presence of some compounds, but also to the proportions of the different groups of components present in the preparation.

Keywords: Oak smoke flavouring; Production; Composition; Gas chromatography; Gas chromatography/mass spectrometry

1. Introduction

The organoleptic properties of smoked foods are decisively influenced by the composition of the smoke or of the smoke flavouring used in the smoking process (Guillén, Manzanos, Ibargoitia, Cabo, & Sopelana, 1998). In turn the composition of the smoke and smoke flavouring depends, among other factors, on the nature of the wood involved in their manufacture (Guillén & Ibargoitia, 1996; Guillén & Manzanos, 1999a, 1999b; Guillén, Manzanos, & Ibargoitia, 2001). However, there is no agreement about which wood or mixture of woods imparts the preferred sensorial properties to smoked foods (Maga, 1988; Tóth & Potthast, 1984). This fact could basically be due to the influence of the culinary habits and customs of each region on food acceptability.

The odour of oak and beech smoke has been described as excellent (Pallu, 1971) and confers much appreciated organoleptic properties to the smoked food (Tilgner, 1958). Oak also constitutes an essential element in the manufacture of casks for storage and ageing of high quality alcoholic beverages (Nykänen, Nykänen, & Maarse, 1991). It is well accepted that compounds arising from the thermal degradation of fire-charred barrel oak wood contribute to the sensory properties of the alcoholic beverages (Chatonnet, Cutzach, Pons, & Dubourdieu, 1999; Hale, McCafferty, Larmie, Newton, & Swan, 1999; Maga, 1985).

In spite of oak wood having been widely used for smoking, the composition of its smoke has hardly been studied. Pettet and Lane (1940) identified 11 components of an oak smoke condensate. Separation of oak smoke condensates in basic, carbonylic, acidic, phenolic and neutral fractions and quantification of these as a whole have also been carried out (Spanyar, Kevei, & Kiszel, 1960; Ziemba, 1957). Other authors have identified some other oak smoke components (8 in the acidic fraction, 13 in the phenolic fraction and 7 in the carbonylic fraction; Fujimaki, Kazuko, & Kurata, 1974). Finally, Maga and Chen (1985) have identified and quantified some pyrazines in oak smoke.

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In previous papers we have reported the composition of liquid smoke flavourings obtained from different vegetal sources such as vine shoots and beech wood (Guillén & Ibargoitia, 1996; Guillén et al., 2001), as well as some aromatic plants (Guillén & Manzanos, 1999a, 1999b; Guillén et al., 2001). These studies were focussed on those smoke components soluble in organic solvents. However, there are a great number of smoke components which are insoluble in organic solvents.

Taking into account the scarce information previously published about oak wood smoke composition and its wide use in Europe for food smoking, the production of an aqueous oak smoke-flavouring is reported in this paper, together with a study of its composition, to elucidate the components responsible for its well-known performance in the smoking process.

2. Materials and methods

2.1. Aqueous smoke flavouring production

The starting material was sawdust of French oak *(Quercus* sp.*)*. This was air-dried and sieved to yield a powder with a particle size $\leqslant 2$ mm. A sample of 100 g of this oak sawdust was pyrolyzed, by heating in a rheostat-controlled heating mantle in a laboratory round-bottom quartz flask. The temperature in the centre of the sawdust charge was measured with a Crison thermometer 639 K. The maximum temperature reached during the pyrolysis experiment was 557 °C. The experiment was considered finished when the sawdust was totally pyrolyzed and the smoke emission ended. The length of the process was approximately 50 min.

The resulting smoke was filtered through a glass wool filter to eliminate solid particles and collected in 150 ml of distilled water. To this aim, three successive water traps were used but only the first was considered. The amounts of smoke components collected in the second and in the third traps were negligible. The aqueous liquid smoke obtained was again filtered through a paper filter to eliminate the oily phase. The acidity of the oak liquid smoke obtained was determined by titration with 0.01 M NaOH.

2.2. Extraction of the oak smoke components

A sample of 30 ml of the oak liquid smoke was exhaustively extracted with 30 ml of dichloromethane by liquid–liquid extraction, in several steps, as in previous studies (Guillén & Ibargoitia, 1996; Guillén & Manzanos, 1996b, 1999a, 1999b; Guillén et al., 2001; Guillén, Manzanos, & Zabala, 1995). Two fractions were obtained: the fraction soluble in dichloromethane or fraction 1 (F1); and the aqueous fraction which, after water elimination by evaporation, gave rise to a residue or fraction 2 (F2), soluble in methanol. Both fractions were studied by gas chromatography.

2.3. Identification and quantification of the extracted components

The separation and identification of the components was carried out by gas chromatography and mass spectrometry (GC/MS) using a Hewlett-Packard gas chromatograph, model 6890 Series II, equipped with a MSD 5973, and a Hewlett-Packard Vectra Pentium computer. A fused-silica capillary column, 30 m long, 0.25 mm internal diameter, 0.25 μm thickness, coated with a non-polar stationary phase (Hewlett-Packard-5, cross-linked 5% phenyl methyl silicone), was used. The temperature programme began at 50 °C (0.5 min) with an increase of 5 $^{\circ}\mathrm{C\ min^{-1}}$ up to 280 °C (10 min). Helium was used as the carrier gas. Injector and detector temperatures were 250 and 280 °C, respectively. Both splitless and split injection techniques were used, this latter with a split ratio 1:10. An injection volume of 1 μl was used. Mass spectra were recorded at an ionization energy of 70 eV.

Components were identified by their retention times, by their mass spectra, by comparing their mass spectra with those in a commercial library (Wiley138k, Mass Spectral Database, 1990) and with those in the literature and, in some cases, by using standards, as in previous studies (Guillén & Ibargoitia, 1996; Guillén & Manzanos, 1996b, 1999a, 1999b; Guillén et al., 1995, 2001); however, some components remained unidentified and others were only tentatively identified. All standard compounds used, available from Aldrich, Fluka and Sigma, are asterisked in Table 1. Components with higher or similar volatility to CH_2Cl_2 and CH_3OH were not analyzed by this technique.

The quantitative study of the components was accomplished with a Hewlett-Packard gas chromatograph model 5890 Series II, equipped with a flame ionization detector (FID), and a Hewlett-Packard 3395 integrator. A fused-silica capillary column (30 m long, 0.32 mm internal diameter, 0.25 μm thickness), coated with a non-polar stationary phase (Hewlett-Packard-5, cross-linked 5% phenyl methyl silicone) was used. The chromatographic conditions relative to the heating program were the same as those used in the GC/MS study. Nitrogen was used as the carrier gas. Injector and detector temperatures were 250 and 300 °C, respectively. The splitless technique injection was used and the injection volume was 1 μl. The quantification was carried out using external standards. To this aim, response factors of the large number of standard compounds, asterisked in Table 1, were determined, as mentioned previously (Guillén & Ibargoitia, 1996; Guillén & Manzanos, 1996b,

Table 1
Detected compounds in the fractions F1 and F2 of the oak liquid smoke, together with their yield expressed in mg per 100 g from oak sawdust

RT (min)		Compound[a] (mass spectral data, *m*/*z*)	F1	F2
Aldehydes			65.7	–
1.59		Ethanal (acetaldehyde) *	1.4	–
2.20		3-Methylbutanal (isovaleraldehyde) *	15.0	–
2.50		Pentanal (valeraldehyde) *	4.3	–
3.16		2-Ethylbutanal *	45.0	–
Ketones			305	–
1.70		2-Propanone *	nq[b]	–
1.92		2-Butanone *	nq	–
2.25		3-Methyl-2-butanone *	1.2	–
2.87		4-Methyl-2-pentanone *	6.2	–
2.95		2-Methyl-3-pentanone *	4.0	–
3.02		3-Methyl-2-pentanone *	tr[c]	–
3.34		3-Hexanone *	2.2	–
3.42		2-Hexanone *	15.5	–
3.49		Cyclopentanone *	9.1	–
4.30		4-Hydroxy-4-methyl-2-pentanone *	3.0	–
4.37		3-Methylcyclopentanone	1.3	–
4.52	ϕ	3,4-Dimethyl-2-hexanone (or isomer)	35.0	–
4.76		1-Acetoxy-propan-2-one	40.7	–
5.13		2-Heptanone *	6.7	–
5.34		Cyclohexanone *	2.4	–
5.58		2-Methyl-2-cyclopenten-1-one *	23.8	–
6.22		2-Cyclohexen-1-one	3.8	–
6.88		1-Acetoxy-butan-2-one	nq	–
7.00		3-Methyl-2-cyclopenten-1-one *	98.1	–
7.89		2,3-Dimethyl-2-cyclopenten-1-one	5.1	–
8.54		Dimethyl-2-cyclopenten-1-one (or isomer)	5.9	–
8.95		3,4,5-Trimethyl-2-cyclopenten-1-one	4.3	–
9.02		3-Ethyl-2-cyclopenten-1-one	10.1	–
9.72		1-Phenylethanone (acetophenone) *	nq	–
12.55		1-(2-Hydroxyphenyl)-ethanone	1.4	–
13.09	ϕ	Ethyl-dimethyl-2-cyclopenten-1-one (or isomer)	5.3	–
13.29		2-Ethyl-2,5-dimethylcyclopenten-1-one (or isomer)	15.8	–
15.84		1-(2,4-Dihydroxyphenyl)-ethanone	4.2	–
16.03		2,3-Dihydro-1H-inden-1-one	nq	–
Diketones			53.9	–
1.85		2,3-Butanedione (diacetyl) *	nq	–
6.10		2,5-Hexanedione	7.4	–
8.66		3-Methyl-1,2-cyclopentanedione (cyclotene) *	41.0	–
9.45		3,5-Dimethyl-1,2-cyclopentanedione	1.9	–
11.33		3-Ethyl-1,2-cyclopentanedione (3-ethylcyclopentenolone) *	3.6	–
Furan and pyran derivatives			1748	60.6
4.14		2-Furancarboxaldehyde (furfural) *	1036	nq
4.50		2-Furanmethanol (furfuryl alcohol) *	nq	nq
4.76		5-Methyl-2(3*H*)-furanone (α-angelicalactone) *	tr	–
4.87		2,5-Dimethoxytetrahydrofuran	–	nq
4.93		2-Ethylfuran	tr	–
5.01	ϕ	Dihydro-2*H*-pyran-3(4*H*)-one (or isomer)	3.5	–
5.26		Dimethoxytetrahydrofuran	–	nq
5.69		1-(2-Furanyl)-ethanone (2-acetylfuran) *	19.6	–
5.73		2(5*H*)-Furanone (γ-crotonolactone) *	373	–
5.73		2-Dihydrofuranone	nq	–
5.95	ϕ	Dihydro-5-methyl-2-furanone (or isomer)	36.2	nq
6.34	ϕ	Dihydro-methylfuranone (isomer)	19.7	nq
6.80		3-Methyl-2,5-furandione	–	14.1
6.95		5-Methyl-2-furancarboxaldehyde (5-methylfurfural) *	141	–
7.10		Hydroxy-dihydro-pyranone	–	20.8
7.29		3-Methyl-2(5*H*)-furanone *	45.7	–
7.85	ϕ	3,4-Dihydro-5-methyl-2*H*-pyran-2-one (or isomer)	nq	–
8.12		1-(2-Furanyl)-propanone	nq	–
9.41		Ethyl furoate *	9.0	–
10.18		Tetrahydro-2-furanmethanol	–	tr

(continued on next page)

Table 1 (*continued*)

RT (min)		Compound[a] (mass spectral data, *m/z*)	F1	F2
10.42	ϕ	2,3-Dihydro-5-hydroxy-6-methyl-4*H*-pyran-4-one (dihydromaltol) (or isomer)	nq	–
10.91		Methyl 2-furancarboxylate	–	nq
11.14		3-Hydroxy-2-methyl-4*H*-pyran-4-one (maltol) *	43.5	–
13.27	ϕ	Dihydroxy-2-methyl-4*H*-pyran-4-one (or isomer)	nq	nq
13.71		3,5-Dihydroxy-2-methyl-4*H*-pyran-4-one (hydroxymaltol) (or isomer)	4.1	–
14.60		5-Hydroxymethyl-2-furancarboxaldehyde *	16.8	25.7
16.75		1,3-Isobenzofurandione	–	nq
19.23		4-Methyl-1,3-isobenzofurandione	–	nq
20.97	ϕ	3-Acetyl-6-methyl-2*H*-pyran-2,4(3*H*)-dione (or isomer)	nq	–
Alcohols, esters and acids			68.0	24.0
1.65		Ethyl alcohol *	0.4	–
1.95		Acetic acid *	nq	–
2.07		Ethyl acetate *	2.7	–
2.10		Methyl propionate *	7.0	–
2.56		2-Pentanol *	tr	–
2.79		3-Methyl-3-buten-1-ol *	tr	–
2.82		3-Methyl-1-butanol *	tr	–
3.62	ϕ	2-Hexanol *	2.0	–
3.62		Ethyl butyrate *	13.5	–
3.73		Butyric acid *	4.9	–
3.81		Butyl acetate *	1.8	–
3.92		Methyl 2-butenoate	–	nq
4.37		Hexanol	–	tr
4.40		Ethyleneglycol monoacetate *	0.8	–
5.32	ϕ	2,4-Pentanediol *	11.4	–
5.38		Ethyl pentanoate *	1.0	–
5.58		Pentanoic acid *	12.9	–
5.83		Methyl hexanoate *	4.1	–
7.07	ϕ	1-Heptanol *	1.3	–
7.41		4-Oxo-pentanoic acid methyl ester (methyl levulinate) *	nq	–
7.88	ϕ	Oxo-pentanoic acid methyl ester (or isomer)	–	nq
8.08		Hexanoic acid *	2.7	–
8.51		Methyl heptanoate *	1.5	–
9.60		4-Oxo-pentanoic acid (levulinic acid) *	–	24.0
14.23		Methyl nonanoate *	tr	–
18.04	ϕ	3-Phenyl-2-propenoic acid (cinnamic acid) (or isomer)	nq	–
Phenol and derivatives			157	–
7.41		Phenol *	55.6	–
9.45		2-Methylphenol *	19.2	–
10.05		3-Methylphenol *	52.9	–
10.97		2,6-Dimethylphenol *	2.7	–
11.89		2-Ethylphenol *	3.3	–
12.20		2,5-Dimethylphenol *	7.3	–
12.83		3-Ethylphenol *	12.9	–
12.99		3,5-Dimethylphenol *	tr	–
13.09		2,3-Dimethylphenol *	nq	–
13.81		2,4,6-Trimethylphenol *	1.0	–
14.51		2,4,5-Trimethylphenol	tr	–
15.84		2,3,5-Trimethylphenol *	1.0	–
16.31		2-Isopropyl-5-methylphenol (thymol) *	0.6	–
17.14		4-Propenylphenol	nq	–
Guaiacol and derivatives			239	nq
10.47		2-Methoxyphenol (guaiacol) *	84.9	–
13.52		4-Methyl-2-methoxyphenol (4-methylguaiacol) *	54.7	–
16.03		4-Ethyl-2-methoxyphenol (4-ethylguaiacol) *	27.6	–
17.02		4-Vinyl-2-methoxyphenol (4-vinylguaiacol) *	17.7	–
17.14		1-(3-Hydroxy-2-methoxyphenyl)-ethanone	2.7	–
18.25		4-(2-Propenyl)-2-methoxyphenol (eugenol) *	2.3	–
18.21		4-Ethyl-6-methyl-2-methoxyphenol (or isomer)	tr	–
18.52		4-Propyl-2-methoxyphenol (4-propylguaiacol) *	3.5	nq
19.38		4-Hydroxy-3-methoxybenzaldehyde (vanillin) *	11.8	–
19.63		4-(1-Propenyl)-2-methoxyphenol (*trans*-isoeugenol) *	2.5	–
20.74		4-(1-Propenyl)-2-methoxyphenol (*cis*-isoeugenol) *	5.0	–

(continued on next page)

Table 1 (*continued*)

RT (min)		Compound[a] (mass spectral data, *m*/*z*)	F1	F2
20.97	ϕ	1-(4-Hydroxy-3-methoxyphenyl)-ethanal (homovanillin) (or isomer)	5.7	–
21.70		1-(4-Hydroxy-3-methoxyphenyl)-ethanone (acetovanillone) *	4.6	–
22.42		4-Hydroxy-3-methoxybenzoic acid methyl ester (methyl vanillate) *	2.3	nq
22.86		1-(4-Hydroxy-3-methoxyphenyl)-2-propanone (guaiacylacetone)	11.5	–
23.92	ϕ	1-(4-Hydroxy-3-methoxyphenyl)-2-propenyl alcohol (*cis*-coniferyl alcohol) (or isomer)	1.0	–
24.15		1-(4-Hydroxy-3-methoxyphenyl)-1-propanone (propiovanillone)	1.4	–
25.83		4-Hydroxy-3-methoxybenzoic acid (vanillic acid) *	nq	–
27.87		1-(4-Hydroxy-3-methoxyphenyl)-2-propen-1-al (coniferyl aldehyde) *	nq	–
Syringol and derivatives			276	nq
17.41		Dimethoxyphenol (isomer)	tr	–
17.83		Dimethoxyphenol (isomer)	4.2	–
18.06		2,6-Dimethoxyphenol (syringol) *	82.0	–
18.40		3,4-Dimethoxyphenol (or isomer)	8.4	–
18.95		Dimethoxyphenol (isomer)	0.9	–
20.66		4-Methyl-2,6-dimethoxyphenol (4-methylsyringol) *	56.2	–
21.38		2,6-Dimethoxyphenyl acetate	3.7	–
22.03		3-Ethyl-2,6-dimethoxyphenol (3-ethylsyringol) (or isomer)	tr	–
22.73		4-Ethyl-2,6-dimethoxyphenol (4-ethylsyringol)	19.6	–
23.70		4-Vinyl-2,6-dimethoxyphenol (4-vinylsyringol)	1.4	–
24.65		4-(2-Propenyl)-2,6-dimethoxyphenol (4-allylsyringol) *	5.3	–
24.82		4-Propyl-2,6-dimethoxyphenol (4-propylsyringol)	3.0	–
25.83		4-(1-Propenyl)-2,6-dimethoxyphenol (*trans*-propenylsyringol)	2.2	–
26.01		4-Hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde) *	12.9	–
26.18		4-(1-Propenyl)-2,6-dimethoxyphenol (or isomer)	0.6	–
26.98		4-(1-Propenyl)-2,6-dimethoxyphenol (*cis*-propenylsyringol)	1.1	–
27.03	ϕ	1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanal (homosyringaldehyde) (or isomer)	0.9	–
27.73		1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone (acetosyringone) *	19.7	nq
28.60		1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone (syringylacetone)	43.0	–
28.89		1-(4-Hydroxy-3,5-dimethoxyphenyl)-butanone (butyrosyringone)	tr	–
29.78		1-(4-Hydroxy-3,5-dimethoxyphenyl)-1-propanone (propiosyringone)	7.9	–
31.11	ϕ	1-(4-Hydroxy-3,5-dimethoxyphenyl)-1-propanol (dihydrosinapyl alcohol) (or isomer)	tr	–
32.87		1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propen-1-al (sinapaldehyde) *	3.2	–
Lignin dimers			4.4	–
33.48		Unidentified 254(82), 194(43), 179(14), 167(100), 163(26)	0.4	–
36.89		3,3′-Dimethoxy-4,4′-dihydroxy-1,1′-biphenyl (1,1′-diguaiacol) (or isomer) 246(100), 199(16), 171(17)	tr	–
38.84		1,2-bis(Methoxyhydroxyphenyl)-ethane (or isomer) 274(20), 167(11), 151(6), 137(100), 122(9), 94(12)	tr	–
41.06		Unidentified 302(71), 194(100)	0.4	–
42.03		Unidentified 316(57), 194(100), 149(22)	tr	–
42.15		Unidentified 316(60), 194(100)	0.3	–
42.46		4,4′-Dihydroxy-3,3′,5-trimethoxybibenzyl (moscatilin) (or isomer) 304(13), 179(7), 167(100), 151(8), 137(39)	tr	–
42.71		Unidentified 316(54), 194(100), 179(9), 149(13)	tr	–
43.17		Unidentified 330(38), 194(100), 163(35)	tr	–
43.78		Unidentified 330(48), 208(14), 194(100), 180(16), 163(31), 149(18)	0.3	–
43.86		Unidentified 330(42), 195(15), 194(100), 179(8), 163(23)	0.5	–
44.51		Unidentified 332(49), 194(100)	tr	–
44.79		4,4′-bis(2,6-Dimethoxyphenol)-methylene (4,4′-disyringylmethylene) (or isomer) 320(100), 289(24), 167(14)	1.1	–
45.14		Unidentified 348(28), 181(100)	0.5	–
45.80		1,2-bis-(Dimethoxyhydroxyphenyl)-ethane (or isomer) 334(20), 167(100)	0.4	–
46.08		Unidentified 346(35), 194(100)	0.5	–
49.54		Unidentified 360(28), 194(100)	tr	–
Pyrocatechol derivatives and related			77.1	138
13.97		1,2-Benzenediol (pyrocatechol) *	2.5	82.6
15.17		1,4-Benzenediol (hydroquinone)	–	19.8
15.50		3-Methoxy-1,2-benzenediol (3-methoxypyrocatechol) *	65.9	nq
15.65		3-Methyl-1,2-benzenediol (3-methylpyrocatechol) *	1.5	tr
16.34		4-Methyl-1,2-benzenediol (4-methylpyrocatechol) *	6.0	28.1
17.17		2-Methyl-1,4-benzenediol (2-methylhydroquinone) (or isomer)	–	7.1
18.95		4-Ethylbenzenediol (or isomer)	1.2	–

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Table 1 (*continued*)

RT (min)	Compound[a] (mass spectral data, *m/z*)	F1	F2
Alkyl aryl ethers		10.6	–
12.04	1,2-Dimethoxybenzene (veratrole) *	1.7	–
13.31	1,4-Dimethoxybenzene *	2.7	–
14.86	2,6-Dimethoxytoluene	2.6	–
17.61	Trimethoxybenzene (isomer)	1.7	–
18.68	1,3,5-Trimethoxybenzene *	1.9	–
19.52	5-Methyl-1,2,3-trimethoxybenzene	nq	–
27.98	Propenyl-trimethoxybenzene (isomer)	tr	–
28.18	Propenyl-trimethoxybenzene (isomer)	tr	–
Carbohydrate derivatives and related		9.3	927
3.58	Unidentified 98, 69, 54(100), 43	–	4.9
5.13	Unidentified 72, 60(100), 42	–	7.6
7.56	Unidentified 57(100), 44, 43	–	12.7
7.93	1,5-Anhydro-4-deoxypent-1-en-3-ulose 114(100), 58	9.3	23.6
8.40	Unidentified 70, 42(100), 41	–	10.3
8.70	Unidentified 115, 99, 86, 71, 56, 43(100)	–	9.6
9.41	Unidentified 128, 98(100), 71, 54, 43	–	25.2
9.80	Unidentified 104, 101, 74, 55(100), 43	–	5.6
10.24	Unidentified 71, 57, 44(100)	–	29.1
10.83	Unidentified 98(100), 96, 81, 68, 53, 42	–	18.2
11.28	Unidentified 147, 131, 115, 99, 87, 71, 57, 43(100)	–	4.0
11.59	Unidentified 130, 129, 98, 71, 58, 43(100)	–	4.5
11.94	Unidentified 130, 129, 85, 71, 58, 43(100)	–	12.0
13.68	1,4:3,6-Dianhydro-α-D-glucopyranose 144, 114, 98, 86, 69(100), 60, 57, 41	–	58.6
14.62	Unidentified 126, 116, 98, 70, 69, 57, 55, 43, 42(100), 41	–	25.7
16.41	Unidentified 73, 57, 45(100)	–	17.7
16.82	Unidentified 102, 82, 73, 57(100), 43	–	9.9
18.00 ϕ	Levoglucosan isomer 144, 98, 73, 60(100), 57, 43	–	22.6
18.35	1,6-Anhydro-α-D-galactopyranose 144, 126, 98, 73, 60(100), 57, 43	–	10.1
18.70	Unidentified 115, 98, 87, 74(100), 59, 57	–	7.6
20.06	1,6-Anhydro-β-D-mannopyranose 144, 116, 98, 73, 60(100), 57, 43	–	29.6
21.77	1,6-Anhydro-β-D-glucopyranose (levoglucosan) * 144, 115, 98, 85, 73, 60(100), 57, 43	–	494
22.03	Unidentified 164, 136, 122(100), 107, 94, 79, 66, 51	–	5.9
22.45	Unidentified 186, 115, 98, 85, 73, 60, 43(100)	–	20.4
23.28	1,6-Anhydro-β-D-glucofuranose 115, 103, 98, 85, 73(100), 69, 61, 60, 57, 44, 43	–	30.1
23.63	Unidentified 144, 115, 99, 73, 60, 43(100)	–	20.0
23.67	Unidentified 117, 103, 73, 71(100), 43	–	7.6
23.83	1,6-Anhydro-α-D-galactofuranose 115, 98, 85, 73(100), 69, 61, 57, 44	–	nq
Nitrogenated compounds and others		1.2	nq
3.23	Methylbenzene (toluene) *	1.2	–
3.29	2-Methylpyridine *	–	tr
4.52	3-Methylpyridine *	–	nq
6.55	2,3-Dimethylpyridine *	–	nq
8.41	3-Methoxypyridine *	–	nq
37.28	Docosane *	tr	–
Yield of quantified components in fractions F1 and F2			4154
% and yield of total carbonylic, carboxylic and alcoholic derivatives (~56%)			2325
% and yield of total carbohydrate derivatives and related (~22%)			927
% and yield of total phenolic derivatives and alkyl aryl ethers (~22%)			902
% and yield of nitrogenated compounds and others (~0.03%)			1.2

[a] Asterisked compounds were used as standards for identification and quantification, compounds indicated with the symbol ϕ were detected for the first time in smoke or smoke flavourings.

[b] nq, Compound not quantified because its separation was not adequate.

[c] tr, Compounds in very small proportion.

1999a, 1999b; Guillén et al., 1995, 2001). Response factors of compounds of a similar nature were used for the quantification of compounds not available commercially. In addition, the tentative identification of those compounds, having a higher or similar volatility to CH_2Cl_2 or to CH_3OH, was based on retention times of standards.

Each experimental step, namely the smoke generation, the acidity determination, the smoke flavouring extraction and the chromatographic studies, was carried out several times to obtain accurate results.

3. Results and discussion

At the temperature reached during the pyrolytic process the thermal degradation of the three main components of the oak wood (cellulose, hemicellulose and lignin) can be considered complete (Maga, 1988). The smoke components produced were collected in 150 ml of water, obtaining 178 ml of the liquid smoke preparation. The acidity of this aqueous flavouring preparation was 390 meq acid l^{-1}. This preparation is brown in colour, and its odour has been described as strong smoky. The yields, in smoke components volume and acidity value are, in general terms, similar to those of other smoke-flavourings obtained in the laboratory under similar conditions, from *Fagus sylvatica* L. (181 ml, 394 meq acid l^{-1}) and *Vitis vinifera* L. shoots (184 ml, 358 meq acid l^{-1}) (Guillén & Ibargoitia, 1996).

Table 1 gives the detected components, identified and unidentified, of the two fractions, grouped in families by their nature, together with their yields from 100 g of oak powder. This Table also shows the yields of the groups of compounds as well as their proportions in the sample. As can be observed, 215 compounds were detected from which 99 compounds, asterisked in Table 1, were identified using standards; 84 were tentatively identified by comparing their mass spectra with those in a commercial library and with those in the literature and also taking into account their retention time, structure, molecular weight and other properties related to chromatographic retention (Bermejo & Guillén, 1987) finally, 32 compounds remained unidentified whose mass spectra base peaks, together with the main mass fragments, are also given. The nature of some of these has been tentatively deduced from their mass spectra; however, their assignation to specific compounds is very difficult with the available data. The compounds, whose separation, because of peak overlapping, was not good enough, were not quantified (nq in Table 1).

Table 1 shows that fraction F1 contains a high number of components arising, basically, from wood carbohydrate thermal degradation (Fengel & Wegener, 1983; Shafizadeh, 1984), such as aldehydes, ketones, diketones, esters, alcohols, acids, furan and pyran derivatives and some others. In addition, it also contains a significant number of components arising from lignin thermal degradation (Fengel & Wegener, 1983; Shafizadeh, 1984), such as phenol, guaiacol, syringol, pyrocatechol and their derivatives, methyl-alkyl-ethers and some others.

Many of the compounds found in fraction F1 have been detected previously in smoke and smoke-flavourings and have been considered responsible for organoleptic, antioxidant and antimicrobial properties in the smoking process (Maga, 1988; Tóth & Potthast, 1984). However, some other components, identified tentatively in fraction F1, have been detected in this oak smoke for the first time as smoke components. These include some dihydro-methylfuranones, in high yields, together with dihydromaltol or isomers, in very low proportions; this latter compound, showing toasty caramel notes, has also been described as a component of toasted oak wood extracts (Chatonnet et al., 1999; Cutzach, Chatonnet, Henry, & Dubourdieu, 1997). As well, there are some compounds derived from lignin degradation, such as homovanillin and *cis*-coniferyl alcohol or isomers. Noteworthy is the presence, in this fraction F1, of a considerable number of compounds tentatively identified as lignin dimers, which have also recently been detected in commercial smoke-flavourings (Guillén & Ibargoitia, 1998, 1999; Guillén & Manzanos, 1996a). Fig. 1 shows the structures of some of them; these compounds are characterized by a high antioxidant activity (even higher than that of compounds such as guaiacol or syringol and their derivatives) (Barclay, Xi, & Norris, 1997) and some have shown antimutagenic activity, antiviral and therapeutic properties (Ayres & Loike, 1990; Cushman, Nagarathnam, Gopal, Chakraborti, Lin, & Hamel, 1991; MacRae, Hudson, & Towers, 1989). Although the presence of such compounds

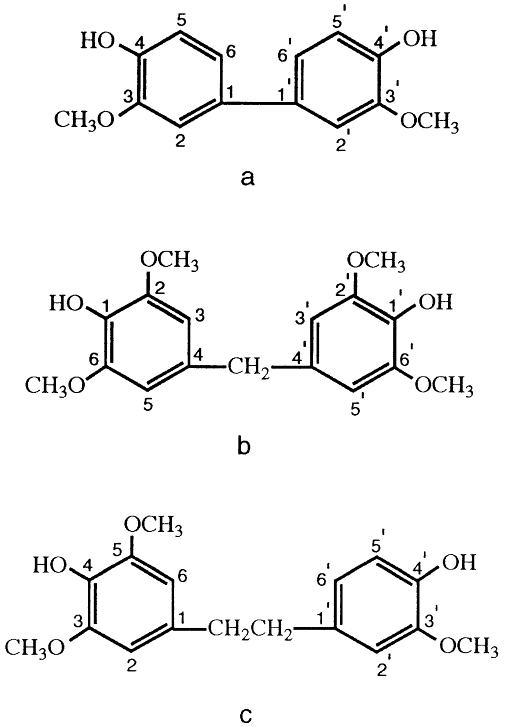

Fig. 1. Structures of (a) 3,3′-dimethoxy-4,4′-dihydroxy-1,1′-biphenyl or 1,1′-diguaiacol, (b) 4,4′-bis(2,6-dimethoxyphenol)-methylene or 4,4′-disyringylmethylene and (c) 4,4′-dihydroxy-3,3′,5-trimethoxybibenzyl (moscatilin).

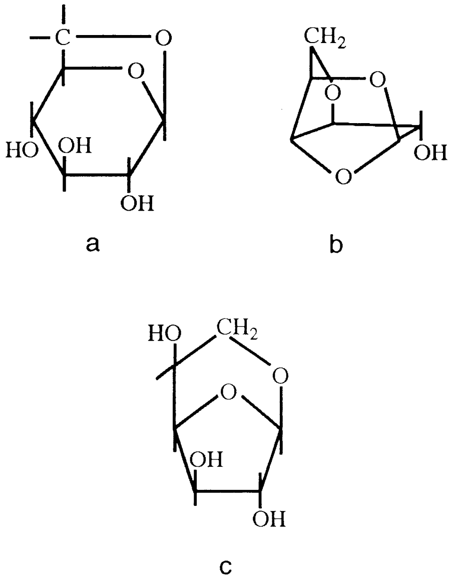

Fig. 2. Structures of (a) 1,6-anhydro-β-D-glucopyranose or levoglucosan, (b) 1,4:3,6-dianhydro-α-D-glucopyranose and (c) 1,6-anhydro-β-D-glucofuranose.

has not been detected in alcoholic beverages until now, some authors have pointed out that lignin oligomers are the main polyphenols in aged beverages (Nabeta, Yonekubo, & Miyake, 1987; Puech, 1992).

Table 1 shows the components detected in fraction F2. This fraction was studied after water evaporation; for this reason compounds with similar volatility to water may also have been eliminated. In spite of this, several components, most arising from wood carbohydrate thermal degradation, were also detected. Among them are furan and pyran derivatives, not detected in fraction F1, such as 3-methyl-2,5-furandione and hydroxy-dihydro-pyranone, and others also present in fraction F1, such as 5-hydroxy-5-methyl-2-furancarboxaldehyde which were partitioned between the organic and water phases in the extraction step in function of their partition coefficient. Some esters and acids, such as 4-oxo-pentanoic acid, are also present.

In addition, fraction F2 contains a large number of compounds considered as carbohydrate derivatives because of their mass spectra. They have been included in this group because most of their base peaks and mass fragments coincide with those of the mass spectra of the mixture of products arising from glucose pyrolysis at 540 °C (Evans, Wang, Agblevor, Chum, & Baldwin, 1996) or of anhydrosugars originating from wood pyrolysis or from mycrocrystalline cellulose pyrolysis (Faix, Fortmann, Bremer, & Meier, 1991a, 1991b; Pouwels, Eijkel, & Boon, 1989); furthermore, many of them have as base peaks $m/z=43$ and 57, characteristic of unidentified compounds generated in cellulose pyrolysis (Jakab, Liu, & Meuzelaar, 1997).

Noteworthy, within this latter group is the presence of some anhydro sugars such as 1,6-anhydro-β-D-glucopyranose (or levoglucosan), 1,4:3,6-dianhydro-α-D-glucopyranose, 1,6-anhydro-β-D-glucofuranose, 1,6-anhydro-β-D-mannopyranose and 1,5-anhydro-4-deoxypent-1-en-3-ulose, recently reported as important smoke components (Guillén et al., 2001). Fig. 2 shows the structure of some of them. Some of these compounds had previously been detected in carbohydrate wood pyrolysis (Alén, Kuoppala, & Oesch, 1996; Hirata, 1995; Jakab et al., 1997; McKenzie, Hao, Richards, & Ward, 1994; Simoneit et al., 1999), and in the heating of glucose syrup at 100 °C (Belitz & Grosch, 1999); likewise levoglucosan has been found in human urine where its presence has been associated with diet (Dorland, Wadman, Fabery de Jonge, & Ketting, 1986). The property of levoglucosan to form complexes with metals (Ahlrichs, Ballauff, Eichkorn, Hanemann, Kettenbach, & Klufers, 1998; Gack & Klufers, 1996) could be considered of interest for eliminating toxic metals from the human body.

In fraction F2 there are also compounds, in significant proportions, arising, basically, from lignin thermal degradation, such as some dihydroxybenzene derivatives; these compounds are important due to their high antioxidant ability.

Finally, in fraction F2, some alkylpyridine derivatives have been detected which could be generated from the thermal degradation of wood nitrogen derivatives such as proteins, aminoacids or alkaloids (Maga, 1988; Viani & Horman, 1974); some nitrogenated derivatives have also been found in the basic fraction of charred white oak wood for cask manufacturing (Maga, 1985).

Taking into account the compounds here quantified in both fractions, it can be said that those arising from wood carbohydrate degradation constitute approxi-

Table 2
Ratio between yields of some components of vine shoots, beech and oak smoke

Ratio	Vine shoots	Beech	Oak	Ratio	Vine shoots	Beech	Oak
Ap/Cyclotene	2.2	0.7	1.0	Phenol/Guaiacol	0.5	0.3	0.6
Ap/Croto	0.5	0.3	0.1	Guaiacol/Syringol	1.3	0.8	1.0
Furfural/Croto	1.1	1.5	2.8	Guaiacol/4Mg	3.7	1.8	1.5
Furfural/5Mfurf	15.0	7.9	7.3	Syringol/4Ms	5.0	2.5	1.5

Ap, 1-acetoxy-propan-2-one; Croto, 2(5*H*)-furanone; 5Mfurf, 5-methylfurfural; 4Mg, 4-methyl-2-methoxyphenol; 4Ms, 4-methyl-2,6-dimethoxyphenol.

mately 78% and are the main oak smoke components, and those arising from lignin degradation constitute approximately 22%, as can be expected from the wood composition. Among the first, the main ones are furan and pyran derivatives, which have caramel, sweet, butterscotch, brandy, burnt, sweet-spicy and sugar notes (Maga, 1988), followed by those compounds included in the "carbohydrate derivatives" group whose functionality in the smoking process needs to be studied in the future. Among the second, the main ones are syringol, guaiacol and pyrocatechol derivatives, which have pungent, cresolic, heavy, burnt and smoky notes (Maga, 1988), together with antioxidant and antimicrobial activity.

Differences between the oak smoke studied here and those obtained from different wood sources under similar pyrolytic conditions are due, not only to the presence or absence of some components, but also to the proportions of the common components as the ratios between proportions of significant components show. Table 2 gives some of these ratios in vine shoots, beech and oak smoke.

In conclusion, besides the classical smoke components, until now considered as responsible for the changes to food in the smoking process, other components have also been detected, such as lignans, nitrogen derivatives and anhydro carbohydrates and related compounds, whose effects in the smoking should also be studied and taken into account in the future, for a better understanding of this process.

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