Phenolic Acids, Phenolic Aldehydes and Furanic Derivatives in Oak Chips: American vs. French Oaks

M.J. Cabrita[1,2]*, C. Barrocas Dias[3,4], A.M. Costa Freitas[1,2]

(1) Departamento de Fitotecnia, Escola de Ciências e Tecnologia, Universidade de Évora, Ap 94 7002-554 Évora, Portugal
(2) Instituto de Ciências Agrárias e Ambientais Mediterrânicas (ICAAM), Évora, Portugal
(3) Departamento de Química, Escola de Ciências e Tecnologia, Universidade de Évora, CLAV Rua Romão Ramalho 59, 7002-617 Évora, Portugal
(4) Centro de Química de Évora (CQE), Portugal

Submitted for publication: March 2011
Accepted for publication: July 2011

Key words: oak chips, phenolic compounds, HPLC-DAD

Phenolic acids (gallic, vanillic, syringic and ellagic acids), phenolic aldehydes (vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde) and furanic derivatives (furfural, 5-methylfurfural and 5-hydroxymethylfurfural) were quantified in commercial American and French oak chips. Chips with different sizes and toast degrees were used. Compounds were extracted directly from the wood samples in order to determine possible differences among woods as well as toast degree. Likewise, the compounds were extracted from a synthetic wine solution to which the chip woods had been added. The results show that French wood chips are generally richer than the American ones. The total amount of phenolic compounds increases with toasting level, with the non-toasted chips being the poorest ones. The degree of extraction from the synthetic wine solution seems to be related to the shape of the chips, rather than to the wood type or toast degree.

INTRODUCTION

Red wines are usually aged in oak barrels following traditional practices. The oak wood used in winemaking is mainly from two sources: American oak (*Q. alba*) and French oak (*Q. robur* or *Q. petraea*). Singleton (1995) studied their chemical composition and demonstrated that they are quantitatively different. Besides botanical species, geographic origin also play an important role on the content of the extractive compounds (Prida & Puech, 2006).

It is widely recognised that oak barrel ageing improves wine quality. Generally, sensorial complexity increases due to a transfer to the wine, from the wood, of significant amounts of volatile and phenolic compounds. The benefits of wood ageing are recognised, but it is also known to be very expensive. As an alternative, the use of staves or chips to provide oak characters to wines is becoming quite successful. The volatile composition of wines aged in oak barrels (Cerdán *et al*., 2002; Díaz-Plaza *et al*., 2002; Ancín *et al*., 2004) or with oak chips (Arapitsas *et al*., 2004) has been described. Furthermore, the oak wood used in winemaking has been studied by means of gas chromatographic (GC) methods coupled with mass detection (MS). Different extraction methodologies, such as simultaneous distillation-extraction (SDE), Soxhlet extraction (Pérez-Coello *et al*., 1998), liquid-liquid extraction (Caldeira *et al*., 2004), solid-phase micro-extraction (SPME) (Jordão *et al*., 2006; Bozalongo *et al*., 2007) and accelerated solvent extraction (ASE) (Vichi *et al*., 2007), have been tested to meet sample preparation requirements. The phenolic compounds of red wine aged in contact to oak chips have also been identified (Del Alamo *et al*., 2004a, 2004b; Matejícek *et al*., 2005; Del Alamo & Domínguez, 2006; Pérez-Magariño *et al*., 2009). To the best of our knowledge, the phenolic composition of oak or oak chips has not yet been studied from an oenological point of view, with the exception of several works describing oak and chestnut wood used in brandy ageing (Canas *et al*., 1999, 2007).

The ageing of wines in the presence of oak wood extracts a number of benzoic and cinnamic compounds, phenolic aldehydes and furanic derivatives that have an impact on wine characteristics, such as colour, astringency and bitterness, either directly or indirectly. The presence of ellagitannins, also arising from the wood, and the presence of oxygen are two factors of major importance to the regulation of this process. The oxidative process, which occurs naturally in the wine barrel, is sometimes substituted by micro-oxygenation in the presence of oak chips, with good results regarding wine characteristics (Sartini *et al*., 2007; Rudnitskaya *et al*., 2009).

Furthermore, it is well known that some phenolic compounds have benefits on health, namely the antioxidant

*Corresponding author: mjbc@uevora.pt
Aknowledgements: The authors thank Barbara Sistelo and Diogo Barata de Tovar from VDS Enologia, for the kind supply of the oak chips.

properties due to flavonoids and cinnamic acids (McDonald *et al*., 1998). The determination of the qualitative and quantitative composition of phenolics from oak chips might therefore contribute to enhancing the possible benefits of wine for human health.

The aim of this work was to evaluate the differences between low molecular phenolic compounds in several types of oak chips and in a model solution.

MATERIALS AND METHODS

Samples

Oak chips

The oak chips used in this work were kindly supplied by VDS Enologia and are listed in Table 1. Toasting was applied after sizing or powdering of the oak chips.

Synthetic wine

A synthetic wine (13,8% ethanol, 3,2 g/L tartaric acid) was bottled with 6 g/L of ten different oak chips (Table 1) and kept in a dark room at 20ºC for a month before analysis. These assays were done in triplicate.

Reagents and standards

The water used was previously purified in a Mili-Q system (Millipore, Bedford, MA, USA). HPLC-grade methanol, ethyl acetate and diatomaceous earth (powder) were purchased from Merck (Darmstadt, Germany). Phenolic compounds, gallic acid, gentisic acid, protocatechuic acid, protocatechuic aldehyde, (+)-catechin, syringic acid, vanillic acid and ferulic acid were supplied by Extrasynthese (Genay, France). The caffeic acid, *p*-coumaric acid, coniferaldehyde and sinapaldehyde were from Sigma-Aldrich (St Louis, MO). The furfural was from Merck (Darmstadt, Germany), while 5-methyl-furfural, 5-hydroxymethylfurfural, syringaldehyde and ellagic acid dihydrate were purchased from Acrós Organics (New Jersey, USA).

Sample preparation

Oak chips

Oak chips were ground in a coffee mill in order to avoid a size effect. A total of 1.5 g of each sample was extracted with 10 mL of methanol for three hours. The extract was filtered through a nylon filter (Whatman, Schleicher & Schuell, England) before injection. Extraction was done in triplicate and the results were expressed as the mean value.

Synthetic wine

Samples were prepared using a solid-supported liquid-liquid extraction (SS-LLE) methodology, with diatomaceous earth as the solid support (Nave *et al*., 2007). Manual cartridges were made with 4 g of diatomaceous earth. Six mL of synthetic wine were adsorbed and the phenolic compounds were extracted under vacuum, using 10 mL of ethyl acetate. The organic phase, dried over anhydrous sodium sulphate, was evaporated to dryness in a rotary evaporator (T = 30ºC), and the residue was recovered with 1 mL of methanol/water (1:1 v/v) and filtered through a nylon filter (Whatman, Schleicher & Schuell, England) into a vial. All samples were done in triplicate and the results are expressed as the mean value. Concentration was taken into account for the results, presented in Tables 5 and 6.

Instrumentation and conditions

The equipment used for the analytical HPLC was a Hewlett Packard series 1050 equipped with a quaternary pump and a Hewlett Packard Diode Array detector series 1100 (Agilent Technologies, Waldbronn, Germany). The column was a reversed phase Superspher® 100, C18 (5 µm packing, 250 mm x 4,6 mm i.d.) (Merck, Germany) protected with a guard column of the same packing material.

Chromatographic conditions were based on Canas *et al*. (2003): flow rate 1 mL/min; mobile phase, solvent A – water:acetic acid (98:2 v/v); solvent B – water:methanol:acetic acid (68:30:2 v/v/v) programmed as follows: from 5% to 30% B in 12 min, from 30% to 55% B in 13 min, from 55% to 70% B in 5 min, from 70% to 100% B in 18 min, 100% isocratic B in 22 min. A chromatogram from a standard solution is shown in Fig. 1.

The monitored wavelengths were 280 nm, 254 nm and 320 nm, and the UV-Vis spectra (scanning from 190 to 400 nm) were recorded for all peaks. Phenolic compounds were identified by comparison of the retention times with those of standard solutions, and quantified by an external standard method using calibration curves.

Calibration curves

Calibration curves were made for all phenolic compounds, except for 5-hydroxymethylfurfural, which, due to its high hygroscopic nature, was used only for identification purposes. Gallic acid, furfural, 5-methylfurfural, syringic acid and vanillin were monitored at 280 nm; 254 nm was used to detect vanillic and ellagic acids; syringaldehyde, coniferaldehyde and sinapaldehyde were monitored at 320 nm. Stock solutions were prepared in methanol/water (1:1 v/v), except for ellagic acid, which was prepared in absolute ethanol. Solutions were prepared using the following range of concentrations: gallic acid from 280 to 0.27 mg/L; furfural and 5-methylfurfural from 200 to 0.39 mg/L; vanillic acid from 180 to 0.35 mg/L;

TABLE 1
Code for American and French oaks chips

American Oak	French Oak
Classic oak chips, untoasted – **A1**	Classic oak chips, untoasted – **F1**
Toasted oak powder – **A2**	Toasted oak powder – **F2**
Classic oak chips, large size, medium toast – **A3**	Classic oak chips, large size, medium toast – **F3**
Premium oak chips, dark roasted – **A4**	Premium oak chips, high vanilla – **F4**
Classic oak chips, large size, heavy toast – **A5**	Classic oak chips, large size, heavy toast – **F5**

syringic acid and coniferaldehyde from 390 to 0.38 mg/L; vanillin, coniferaldehyde and sinapaldehyde from 190 to 0.37 mg/L. The highest concentration was considered as a stock solution and all the concentrations below were made by successive dilutions until no measurable area was perceived. The lowest concentration was the lowest detectable signal. Each calibration curve was plotted with seven data points, and three replicates were done for each point. Peak areas were related to the concentration of the phenolic compound stock solution, resulting in linear correlation with r^2 values higher than 0,998 for all compounds. The calibration results are shown in Table 2.

Statistical analyses

Means and standard deviations were calculated and a two-factors ANOVA was performed. The mean comparison was done by the Tukey multiple comparison tests at the 95% confidence level, using SPSS 13.0. Comparisons were done between different chips of French or American oak, and between oaks for the same kind of chip.

RESULTS AND DISCUSSION

Tables 3 and 4 show the results obtained for the phenolic compounds extracted from the oak chips. Vanillin and syringic acid are presented together due to the poor resolution obtained under these chromatographic conditions.

The total amount of phenolic compounds shows that chips from French oak are richer than chips from American oak, and in both cases chips that have not been toasted are poorer than the others. This result would be expected, as the toasting process that the wood undergoes is the main reason for the presence of phenolic compounds. When comparing samples 1, 3 and 5 of either A or F, an increase in the total amount of compounds can be observed with an increase in toasting level.

The phenolic acids, gallic and ellagic, are the most abundant compounds, even in untoasted chips. Ellagic acid could derive from ellagitannin degradation during heat treatment, but also from ellagitannin hydrolysis during the ageing process of woods, while vanillic and syringic acids come from lignin degradation (Puech *et al*., 1989). Gallic

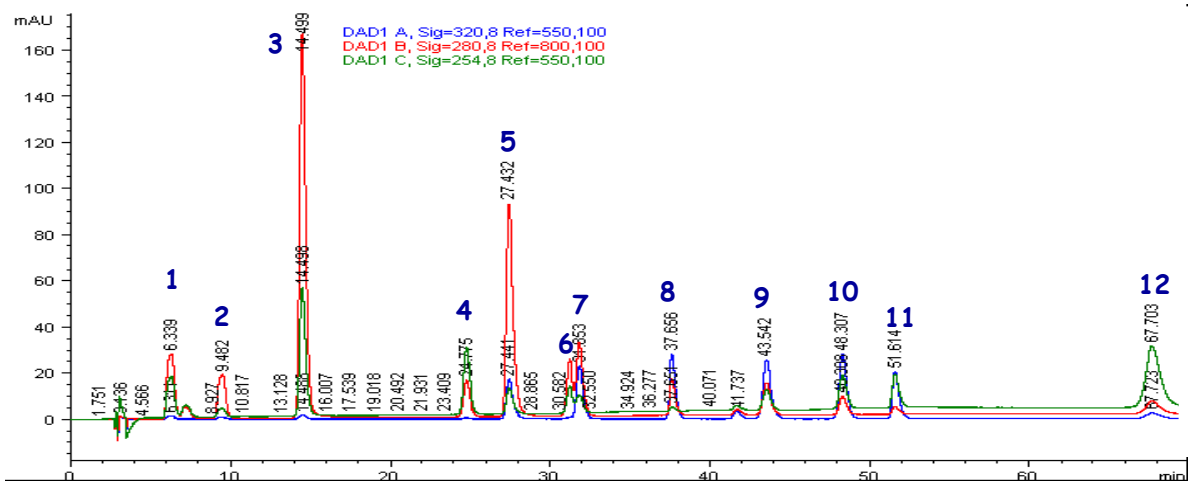

FIGURE 1

Chromatogram from a standard solution (conditions as under experimental).

1 – gallic acid (280 nm); 2 – 5-hidroxi-methyl furfural (280 nm); 3 – furfural (280nm); 4 – vanillic acid (254 nm); 5 – 5-methylfurfural (280 nm); 6 – syringic acid (280 nm); 7 – vanillin (280 nm); 8 – syringaldehyde (320 nm); 9 – ferulic acid (320 nm); 10 – coniferaldehyde (320 nm); 11 – sinapaldehyde (320 nm); 12 – ellagic acid (254 nm).

TABLE 2

Parameters for the calibration of low molecular weight phenolic compounds

Compound	RT ± SD (min)	λ (nm)	equation	r^2
Gallic acid	6.34 ± 0.01	280	y = 20.914x-19.951	0.999
Furfural	14.50 ± 0.27	280	y = 151.19x-27.452	0.999
Vanillic acid	24.80 ± 0.21	254	y = 28.333x-1.493	0.999
5-methyl-furfural	27.40 ± 1.31	280	y = 61.76x-7.0062	1
Syringic acid + vanillin	31.05 ± 1.51	280	y = 32.313x-3.5718	0.999
Syringaldehyde	37.70 ± 0.21	320	y = 29.108x-0.8375	0.999
Coniferaldehyde	48.30 ± 0.39	320	y = 49.119x-2.9552	0.999
Sinapaldehyde	51.60 ± 0.39	320	y = 35.772x-4.9892	0.999
Ellagic acid	67.71 ± 1.81	254	y = 175.54x-251.73	0.998

TABLE 3
Phenolic compounds (mg/100 g) from American oak chips

Compound	A1	A3	A5	A2	A4
Gallic acid	35.91^{a*}± 4.16	107.04^{c}± 6.27	54.10^{b*}± 3.34	48.83^{b} ± 2.05	32.56^{a*}± 2.08
Vanillic acid	2.51^{a}± 0.83	7.61^{b}± 0.33	11.03^{c}± 1.59	10.01^{c}± 1.89	10.79^{c}± 0.55
Syringic acid + vanillin	6.96^{a*}± 3.08	47.82^{b}± 11.21	62.84^{c}± 3.41	52.28^{b}± 2.04	42.28^{b}± 2.04
Ellagic acid	90.66^{b}± 15.94	172.38^{d}±12.85	126.83^{c*}± 3.90	17.51^{a*}± 2.98	92.12^{b*}± 2.77
5-OH-methyl-furfural$^{(*)}$	0.53^{a}± 0.18	13.16^{d}± 2.55	6.09^{c}± 0.25	6.20^{c}± 1.34	4.88^{b*}± 0.92
5-methyl-furfural	1.13^{a}± 0.36	2.60^{b*}± 0.43	7.35^{c}± 0.42	1.84^{a*}± 0.10	1.12^{a*}± 0.16
Furfural	1.13^{a}± 0.08	12.23^{c}± 4.12	25.58^{d}± 1.07	7.87^{bc}± 0.77	5.53^{b*}± 0.60
Syringaldehyde	4.21^{a}± 0.36	18.97^{b}± 0.97	65.79^{c*}± 3.67	65.61^{c}± 2.33	89.94^{d}± 2.85
Coniferaldehyde	1.31^{a}± 0.27	29.77^{b*}± 1.15	95.32^{d}± 5.39	69.87^{c}± 1.94	70.87^{c}± 6.90
Sinapaldehyde	3.26^{a}± 1.01	35.26^{b*}± 1.14	194.54^{c}± 10.95	188.84^{c}± 5.50	209.09^{c}± 7.13
Total	**147.62**	**446.84**	**647.46**	**568.85**	**562.18**

Different letters in a row denote significant difference at the 95% confidence level in the Tukey multiple comparison test.
* denotes a significant difference at the 95% confidence level in the Tukey multiple comparison test when comparing American (Table 3) and French oak (Table 4) for the same compound$^{(*)}$ expressed as 5-methyl-furfural.

TABLE 4
Phenolic compounds (mg/100 g) from French oak chips

Compound	F1	F3	F5	F2	F4
Gallic acid	69.68^{b*}± 2.19	195.96^{d}± 2.48	19.16^{a*}± 1.50	62.02^{b}± 13.06	81.30^{c*}± 2.86
Vanillic acid	4.97^{a}± 0.60	6.72^{a}± 2.06	15.24^{c}± 1.02	10.62^{b}± 1.91	7.39^{ab}± 1.04
Syringic acid + vanillin	12.64^{a*}± 0.85	69.98^{b}± 3.31	76.26^{c}± 3.14	68.02^{bc}± 11.65	66.69^{b}± 2.24
Ellagic acid	126.16^{a}± 10.06	212.52^{c}± 4.85	319.67^{d*}±20.67	145.83^{a*}± 19.90	189.42^{b*}± 9.44
5-OH-methyl-furfural$^{(*)}$	4.79^{a}± 0.51	23.10^{d}± 1.10	8.41^{b}± 0.71	7.75^{b}± 2.01	18.19^{c*}± 0.69
5-methyl-furfural	1.95^{a}± 0.23	16.06^{c*}± 1.01	10.39^{b}± 2.21	8.30^{b*}± 2.20	9.65^{b*}± 0.08
Furfural	3.82^{a}± 0.40	25.95^{c}± 1.55	32.30^{d}± 0.49	8.69^{b}± 1.04	36.35^{d*}± 0.63
Syringaldehyde	4.77^{a}± 0.43	36.30^{b}± 0.46	209.96^{e*}± 4.14	81.85^{d}± 15.79	60.82^{c}± 0.97
Coniferaldehyde	0.93^{a}± 0.11	85.03^{c*}± 2.04	42.19^{b}± 4.03	80.27^{c}± 10.69	97.31^{c}± 0.50
Sinapaldehyde	2.03^{a}± 0.18	148.19^{b*}± 3.22	179.48^{c}± 5.40	222.03^{d}±27.74	216.04^{d}± 2.28
Total	**231.75**	**819.77**	**913.06**	**695.37**	**783.16**

Different letters in a row denote significant difference at the 95% confidence level in the Tukey multiple comparison test.
* denotes a significant difference at the 95% confidence level in the Tukey multiple comparison test when comparing American (Table 3) and French oak (Table 4) for the same compound $^{(*)}$ expressed as 5-methyl-furfural

TABLE 5
Phenolic compounds (mg/L) in model wine with American oak chips

Compound	A1	A3	A5	A2	A4
Gallic acid	1.68^{a}± 0.76	1.53^{a}± 0.93	1.18^{a}± 0.24	1.10^{a}± 0.11	0.88^{a}± 0.18
Vanillic acid	0.12^{a}± 0.08	0.20^{a}± 0.09	0.33^{a}± 0.49	0.33^{a}± 0.03	0.33^{a}± 0.49
Syringic acid + vanillin	0.36^{a}± 0.04	0.67^{a}± 0.06	1.57^{b}± 0.16	1.64^{b}± 0.27	1.57^{b}± 0.25
Ellagic acid	nd**	nd**	0.32^{a}± 0.11	0.37^{a}± 0.06	0.42^{a}± 0.11
5-OH-methyl-furfural$^{(*)}$	0.05^{a}± 0.01	0.16^{b}± 0.04	0.22^{b}± 0.01	0.25^{b}± 0.02	4.21^{b}± 0.28
Syringaldehyde	0.19^{a}± 0.08	0.65^{a}± 0.19	2.23^{b}± 0.15	2.69^{b}± 0.43	2.83^{b}± 0.51
Coniferaldehyde	0.09^{a}± 0.02	0.61^{a}± 0.23	2.06^{b}± 0.16	2.10^{b}± 0.35	1.89^{b}± 0.39
Sinapaldehyde	0.19^{a}± 0.08	0.74^{a}± 0.37	4.14^{b}± 0.87	5.24^{b}± 0.96	5.86^{b}± 1.36
Total	**2.68**	**4.56**	**12.05**	**13.72**	**17.99**

Different letters in a row denote significant difference at the 95% confidence level in the Tukey multiple comparison test.
Extracts from model wine obtained by SSLLE (chromatographic conditions described above)
$^{(*)}$ expressed as 5-methyl-furfural
** means below the LOD and LOQ values

TABLE 6
Phenolic compounds (mg/L) in model wine with French oak chips

Compound	F1	F3	F5	F2	F4
Gallic acid	$1.49^{a}\pm 0.35$	$3.63^{b}\pm 0.26$	$0.50^{a}\pm 0.87$	$1.57^{a}\pm 0.35$	$1.98^{a}\pm 0.22$
Vanillic acid	$0.19^{a}\pm 0.08$	$0.29^{ab}\pm 0.02$	$0.38^{abc}\pm 0.04$	$0.58^{c}\pm 0.05$	$0.44^{bc}\pm 0.01$
Syringic acid+ vanillin	$0.41^{a}\pm 0.08$	$0.99^{a}\pm 0.18$	$2.32^{b}\pm 0.13$	$1.84^{b}\pm 0.13$	$1.78^{b}\pm 0.17$
Ellagic acid	nd**	nd**	$0.72^{b}\pm 0.08$	$0.36^{a}\pm 0.01$	$0.53^{ab}\pm 0.01$
5-OH-methyl-furfural(*)	$0.05^{a}\pm 0.00$	$0.44^{c}\pm 0.04$	$0.31^{b}\pm 0.01$	$0.23^{b}\pm 0.01$	$0.48^{c}\pm 0.01$
Syringaldehyde	$0.18^{a}\pm 0.01$	$1.19^{a}\pm 0.13$	$5.77^{c}\pm 0.67$	$3.19^{b}\pm 0.06$	$2.35^{ab}\pm 0.02$
Coniferaldehyde	$0.08^{a}\pm 0.01$	$2.62^{bc}\pm 0.18$	$1.17^{d}\pm 0.21$	$2.76^{b}\pm 0.06$	$3.58^{c}\pm 0.23$
Sinapaldehyde	$0.16^{a}\pm 0.06$	$4.04^{c}\pm 0.22$	$4.49^{bc}\pm 0.76$	$7.06^{bd}\pm 0.29$	$7.59^{d}\pm 0.67$
Total	**2.56**	**13.20**	**15.66**	**17.77**	**18.73**

Different letters in a row denote significant difference at the 95% confidence level in the Tukey multiple comparison test.
Extracts from model wine obtained by SSLLE (chromatographic conditions described above)
(*) expressed as 5-methyl-furfural
** means below the LOD and LOQ values

acid presents its higher value in medium toasted chips, which means that gallic acid is degraded at high temperatures and might even present values that are smaller than those in untoasted wood. The same results have been described by other authors (Gimenez-Martinez *et al*., 1996; Canas, 2003).

The existence of furanic aldehydes is linked to sugar thermodegradation. In 1967, Hodge proposed a mechanism explaining that 5-hydroxymethylfurfural and 5-methylfurfural came from hexoses existing in cellulose, and how furfural comes from pentoses, the principal constituents of hemicelluloses. Our results show that French oak chips are richer in furanic aldehydes than American oak chips. According to several authors, untoasted wood presents small amounts of furfural, 5-methylfurfural (Nabeta, *et al*., 1986; Marsal & Sarre, 1987; Chatonnet *et al*., 1989; Marco *et al*., 1994; Gétaz *et al*., 1996; Garcia-Romero *et al*., 1998; Perez-Coello *et al*., 1999; Masson *et al*., 2000) and 5-hydroxymethylfurfural (Artajona, 1991; Masson *et al*., 2000). Both Chatonnet *et al*. (1989) and Artajona (1991) suggest that furfural is the most abundant in toasted wood, due to hemicelluloses being highly instable at increasing temperature (Bourgois & Guyonnet, 1988). Significant differences observed between samples 1, 3 and 5 (A and F) seem to indicate that toasting intensity affects the levels of furanic aldehydes in wood. Furfural levels increased with toast level and 5-OH methyl furfural presents its higher value in medium toasted wood, in both the American and French wood chips. As previously found (Nomdedeu *et al*., 1988; Artajona, 1991; Canas, 2003), 5-methyl furfural levels increase with toast level in American chips, but in French chips the levels increase from untoasted to medium toast and then decrease with heavy toast, which is in accordance with the findings of Chatonnet *et al*. (1989). In medium toasted chips, the contents of furfural and 5-hydroxymethyl furfural are very similar, but furfural is the major compound in heavily toasted chips.

According to several authors (Nomdedeu *et al*., 1988; Chatonnet *et al*., 1989; Artajona, 1991; Marco *et al*., 1994; Canas, 2003), untoasted wood has low contents of phenolic aldehydes (vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde), arising from lignin degradation (Puech *et al*., 1989, 1990), with wood toasting being responsible for the increased amounts found (Nishimura *et al*., 1983; Nomdedeu *et al*., 1988, Chatonnet *et al*., 1989; Dubois, 1989; Sarni *et al*., 1990; Artajona, 1991; Mosedale & Ford, 1996; Canas, 2003). Phenolic aldehydes, however, are thermodegradable into phenolic acids or volatile phenols (Chatonnet, 1995). The toasting effect has not yet been explained fully; Chatonnet *et al*. (1989) claim that phenolic aldehydes reach higher levels at medium toast, decreasing afterwards with toast intensity, but Artajona (1991) states that they continue to increase with increasing toasting level.

With the temperature used for medium toast levels, decarboxylation followed by cleavage of the aryl-alkyl-ether bonds of the terminal units of lignin might occur, with the consequent formation of cinnamic aldehydes like coniferaldehyde and sinapaldehyde. In contrast, with the use of higher temperatures to obtain heavily toasted chips, oxidative cleavage of the C-C skeleton of these aldehydes might occur, leading to the corresponding benzoic aldehydes, vanillin and syringaldehyde (Sarni *et al*., 1990; Chatonnet, 1995). These reactions might explain why, in French chips with heavy toast (F5), a lower value was found for coniferaldehyde, while a higher value was observed for syringaldehyde. The same effect is not observed as clearly in the results for American oak, since the values obtained for coniferaldehyde and sinapaldehyde during medium toast are not as high as the ones obtained for French oak (Tables 3 and 4).

Regarding the results obtained for samples 2 and 4, significant differences were found for gallic and ellagic acids, syringaldehyde and 5-OH methylfurfural, both in French and American wood. These chips were presented as powder (sample 2). Differences might also be due to extraction conditions as a result of the size effect.

Tables 5 and 6 show the results obtained for phenolic compounds in a model solution containing the oak chips. The results are perfectly in accordance with those obtained for wood chips. Model wines containing French oak chips are richer in the total number of phenolic compounds than

model wines containing American oak chips, and the total number of phenolic compounds extracted from the wine model solution increased with the toast level of the wood, in accordance with the results described above. The American chip medium toast sample is again the poorest if untoasted chips are not considered. The higher amounts obtained with chips 2 and 4 are probably related to size, as these chips are presented as powder (2) or very small pieces (4).

CONCLUSIONS

This study provides information on the phenolic composition of several commercial wood chips and their extractability into a synthetic wine. The chips being studied came from American and French oak and were used in a large size, as powder and in small pieces, and with different levels of toasting. All of these factors affect the extractability of phenolic compounds from the wood chips into a synthetic wine. There are significant differences in phenolic composition of the chips when comparing French with American oak (Tables 3 and 4). Increasing the toasting level leads to a change in chemical composition of the wood extracts, but a higher temperature during the toasting process may also promote some degradation of compounds.

LITERATURE CITED

Ancín, C., Garde, T., Torrea, D. & Jimenez, N., 2004. Extraction of volatile compounds in model wine from different oak woods: effect of SO_2. Food Res. Int. 37, 375-383.

Arapitsas, P., Antonopoulos, A., Stefanou, E. & Dourtoglou, V.G., 2004. Artificial aging of wines using oak chips. Food Chem. 86, 563-570.

Artajona, J., 1991. Caracterisation del roble según su origen y grado de tostado, mediante la utilizacion de GC y HPLC. Viticultura/Enologia Profesional 14, 61-72.

Bourgois, J. & Guyonnet, R., 1988. Characterization and analysis of torrefied wood. Wood Sci. Technol. 22, 143-155.

Bozalongo, R., Carrillo, J.D., Torroba, M.A.F. & Tena, M.T., 2007. Analysis of French and American oak chips with different toasting degrees by head space solid-phase microextraction-gas chromatography-mass spectrometry. J. Chromatogr. A 1173, 10-17.

Canas, S., 2003. Estudo dos compostos extraíveis de madeira (Carvalho e Castanheiro) e dos processos de extracção na perspectiva do envelhecimento em Enologia. Tese de Doutouramento em Engenharia Agro-Industrial, UTL-ISA, Lisboa.

Canas, S., Belchior, A.P., Spranger, M.I. & Bruno-de-Sousa, R., 2003. High performance liquid chromatography method for analysis of phenolic acids, phenolic aldehydes and furanic derivatives in brandies. Development and validation. J. Sep. Sci. 26, 496-502.

Canas, S., Falcão, A., Gonçalves, J.A., Spranger, M.I. & Bruno-de-Sousa, INITIALS, 2007. Effect of heat treatment on the thermal and chemical modifications of oak and chestnut wood used in brandy ageing. Ciência Téc. Vitic. 22(1), 5-14.

Canas, S., Leandro, M.C., Spranger, M.I. & Belchior, A.P., 1999. Low molecular weight organic compounds of chestnut wood (*Castanea sativa* L.) and corresponding aged brandies. J. Agric. Food Chem. 47, 5023-5030.

Caldeira, I., Pereira, R., Clímaco, M.C., Belchior, A.P. & Bruno de Sousa, R., 2004. Improved method for extraction of aroma compounds in aged brandies and aqueous alcoholic wood extracts using ultrasounds. Anal. Chim. Acta 513, 125-134.

Cerdán, T.G., Mozaz, S.R. & Azpilicueta, C.A., 2002. Volatile composition of aged wine in used barrels of French oak and of American oak. Food Research International 35, 603-610.

Chatonnet, P., 1995. Influence des procédés de tonnellerie et des conditions d´élevage sur la composition et la qualité des vins élévés en fût de chêne. Thèse Doctorat. UFR Institut d´Oenologie, Université de Bordeaux II, Bordéus.

Chatonnet, P., Boidron, J.N. & Pons, M., 1989. Incidence du traitement thermique du bois de chêne sur sa composition chimique. 2. partie: Évolution de certains composés en fonction de l´intensité de brûlage. Conn. Vigne Vin 23, 223-250.

Del Alamo, M. & Domínguez, I.N., 2006. Wine aging in bottle from artificial systems (staves and chips) and oak woods. Anthocyanin composition. Analytica Chemica Acta, 563, 255-263.

Del Alamo, M., Domínguez, I.N., Cárcel, L.M.C. & Gracia, L.N., 2004a. Analysis for low molecular weight phenolic compounds in a red wine aged in oak chips. Analytica Chemica Acta, 513, 229-237.

Del Alamo, M., Escudero, J.A.F. & Torío, R.C., 2004b. Changes in phenolic compounds and color parameters of red wine aged with oak chips and in oak barrels. Food Sci. Tech. Int. 10, 233-241.

Díaz-Plaza, E.M., Reyero, J.R., Pardo, F. & Salinas, M.R., 2002. Comparison of wine aroma with different tannic content aged in French oak barrels. Analytica Chimica Acta 458, 139-145.

Dubois, P., 1989. Apport du fût de chêne neuf à l'arôme des vins. R. F. Oenol. 120, 19-24.

Garcia-Romero, E., Pérez-Coello, M.S., Sanz, J. & Cabezudo, M.S., 1998. Quantitative analysis of the principal volatile compounds in oak wood by direct thermal desorption (DTD) and GC/MS. Analusis 26, 33-35.

Gétaz, J., Canetti, J., Lebedeff, J. & Horisberger, D., 1996. Utilisation de chênes indigènes pour la construction de barriques: une solution d´avenir. Rev. Suisse Vitic. Arboric. Hortic. 28, 183-194.

Gimenez-Martinez, R., Garcia de la Serrana, H.L., Villalon Mir, M., Granados, J.Q. & Martinez, M.C.L., 1996. Influence of wood heat treatment, temperature and maceration time on vanillin, syringaldehyde, and gallic acid contents in oak wood and wine spirit mixtures. Am. J. Enol. Vitic. 47, 441-446.

Hodge, J.E., 1967. Non-enzymatic browning reaction. In: Schultz, H.W., Day, E.A. & Libbey, L.M. (eds.). Symposium on foods. Chemistry and physiology of flavors. AVI Publishing, Westport. pp. 465-491.

Jordão, A.M., Ricardo-da-Silva, J., Laureano, O., Adams, A., Demyttenaere, J., Verhé, R. & De Kimpe, N., 2006. Volatile composition analysis by solid-phase microextraction applied to oak wood used in cooperage (*Quercus pyrenaica* and *Quercus petrea*): effect of botanical species and toasting process. J. Wood Sci. 52, 514-521.

Marco, J., Artajona, J., Larrechi, M.S. & Rius, F.X., 1994. Relationship between geographical origin and chemical composition of wood for oak barrels. Am. J. Enol. Vitic. 45, 192-200.

Marsal, F. & Sarre, C., 1987. Étude par chromatographie en phase gaseuse de substances volatiles issues du bois de chêne. Conn. Vigne Vin 21, 71-80.

Masson, E., Baumes, R., Moutounet, M. & Puech, J.-L., 2000. The effect of kiln-drying on the levels of ellagitannins and volatile compounds of European oak (*Quercus petraea* Liebl.) stave wood. Am. J. Enol. Vitic. 51, 201-214.

Matejícek, D., Mikes, O., Klejdus, B., Sterbová, D. & Kubán, V., 2005. Changes in contents of phenolic compounds during maturation of barrique red wine. Food Chemistry 90, 791-800.

McDonald, M.S., Hughes, M., Burns, J., Lean, M.E.J., Matthews, D. & Crozier, A., 1998. Variations in the free and conjugated myricetin and quercetin content of sixty-five red wines of different geographical origins. J. Agric. Food Chem. 46, 368-375.

Mosedale, J.R. & Ford, A., 1996. Variation of the flavour and extractives of European oak wood from two French forests. J. Sci. Food Agric. 70, 273-287.

Nabeta, K., Yonekubo, J. & Miyake, M., 1986. Analysis of volatile constituents of European and Japanese oaks. Mokuzai Gakkaishi 32, 921-927.

Nave, F., Cabrita, M.J. & Costa, C., 2007. The use of solid-supported liquid-liquid extraction in the analysis of polyphenols in wine. Journal of Chromatography A 1169, 23-30.

Nishimura, K., Ohnishi, M., Masuda, M., Koga, K. & Matsuyama, R., 1983. Reactions of wood components during maturation. In: Piggott, J.R. (ed.). Flavour of distilled beverages: origin and development. Ellis Horwood Limited, Chichester, England, pp. 241-255.

Nomdedeu, L., Leaute, R., GrandChamp, B., Bonnichon, C., Laurichesse, D. & Trichet, P., 1988. Brûlage des barriques de chêne et qualité des vins de Médoc. Progrés Agricole et Viticole 105, 505-556.

Pérez-Coello, M.S., Sanz, J. & Cabezudo, M.D., 1998. Gas chromatographic-mass spectrometric analysis of volatile compounds in oak wood used for ageing of wines and spirits. Chromatographia 47(7/8), 427-432.

Pérez-Coello, M.S., Sanz J. & Cabezudo, M.D., 1999. Determination of volatile compounds in hydroalcoholic extracts of French and American oak wood. Am. J. Enol. Vitic. 50, 162-165.

Pérez-Magariño, S., Ortega-Heras, M., Cano-Mozo, E. & González-Sanjosé, Mª.L., 2009. The influence of oak wood chips, micro-oxygenation treatment, and grape variety on colour, and anthocyanin and phenolic composition of red wines. Journal of Food Composition and Analysis 22, 204-211.

Prida, A. & Puech, J.-L., 2006. Influence of geographical origin and botanical species on the content of extractives in American, French, and East European oak woods. J. Agric. Food Chem. 54, 8115-8126.

Puech, J.-L., Robert, A. & Mouttet, B., 1989. Evolution of oak wood lignin subjected to flash hydrolysis. Holzforschung 43, 235-238.

Puech, J.-L., Sarni, F., Labidi, A., Mouttet, B. & Robert, A., 1990. Delignification of oak wood with an ethanol-water solution in a flow-through reactor. Holzforschung 44, 367-371.

Rudnitskaya, A., Schmidtkec, L.M., Delgadillo, I., Legin, A. & Scollaryd, G., 2009. Study of the influence of micro-oxygenation and oak chip maceration on wine composition using an electronic tongue and chemical analysis Analytica Chimica Acta 642, 235-245.

Sarni, F., Moutounet, M., Puech, J.-L. & Rabier, Ph., 1990. Effect of heat treatment of oak wood extractable compounds. Holzforschung 44, 461-466.

Sartini, E., Arfelli, G., Fabiani, A. & Piva, A., 2007. Influence of chips, lees and micro-oxygenation during aging on the phenolic composition of a red Sangiovese wine. Food Chemistry 104, 1599-1604.

Singleton, V.L., 1995. Maturation of wines and spirits: comparisons, facts and hypotheses. Am. J. Enol. Vitic. 46, 98-115.

Vichi, S., Santini, C., Natali, N., Riponi, C., López-Tamames, E. & Buxaders, S., 2007. Volatile and semi-volatile components of oak wood chips analysed be accelerated solvent extraction (ASE) coupled to gas chromatography-mass spectrometry (GC-MS). Food Chemistry, 102, 1260-1269.