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ORIGINAL PAPER

Phenolic and furanic compounds of Portuguese chestnut and French, American and Portuguese oak wood chips

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Abstract Botanical species used on aging process must be wisely and judiciously chosen, and for this selection, a basic knowledge of the chemical composition of woods is warranted. Aiming to contribute to extend the knowledge of the chemical composition of several wood species useful for enological purposes, we have focused our studies on Portuguese chestnut and French, American and Portuguese oak chips. The profile of low molecular weight phenolic composition of these chips was achieved, using an optimized extraction method based on pressurized liquid extraction, followed by the quantification of phenolic acids, phenolic aldehydes and furanic derivatives by high-performance liquid chromatography (HPLC-DAD). The identification of those compounds was also confirmed by LC-DAD/ESI-MS. This study allowed the determination of the low molecular phenolic composition of Portuguese chestnut and French, American and Portuguese oak wood. According to our results, the influence of the botanical species seems to be more relevant than the geographic origin of the wood species.

Keywords PLE · Phenolic composition · Portuguese chestnut · Oak chips

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Introduction

Aging in wooden barrels is a traditional procedure commonly employed by winemakers in order to improve the quality. Concerning the sensorial characteristics, the maturation of wine in wood barrels modifies its smell and taste and reduces its astringency; hence, organoleptic properties of wine are improved. Wine aging, in barrels, gives to wine the structure, complexity and persistence of scents. The aging process should be carried out carefully in order to obtain elegant and well-balanced wines. During maturation, in wooden barrels, wine undergoes physical and chemical changes related to wine phenolic oxidation reactions occurring with atmospheric oxygen (which passes through wood pores). The interaction between oxygen and the wood components also promotes the release of certain wood compounds into the wine [1]. During this period, wood transfers phenolic and furanic derivatives, as well as ellagitannins, to the wine, directly contributing to aroma and flavor. The extraction of organic extractable compounds, especially those of low molecular weight, from wood barrels depends mainly on the quantity of compounds that are potentially extractable, on the contact time between wine and wood, as well as on wine composition. These organic compounds, mainly phenolics, influence the color, astringency, bitterness, oxidation level and clarity of wines. The factors affecting the pool of wood extractives are the species and geographic origin of the wood, the seasoning of the staves, the toasting level and age of the barrel [2]. Traditionally, the most used wood species for wine aging is oak, namely French and American oak, due to both their mechanical properties and their extractable compounds. Aging in oak wood allows wine to extract a series of benzoic and cinnamic compounds (vanillin, vanillic acid, syringaldehyde, syringic acid, coniferaldehyde,

sinapaldehyde), gallic and ellagic acids. These aldehydes can be oxidized to the correspondent phenolic acids (vanillic and syringic acids) [3].

In the last few years, several studies were focused on the chemical composition of French, American and Spanish oak woods as well as the influence of different factors, such as botanical species and geographic origin, the age of the wood, time and seasoning technique, and the heat treatment [2, 4–11]. The toasting level of wood plays a significant role on wine aging. In fact, during the heating treatment, large wood polymers such as lignin or cellulose and hemicelluloses [12] are fragmented by high temperature, and many compounds such as phenols, phenolic aldehydes, furanic derivatives and lactones are formed and transferred to the wine [6]. Thus, the study of the interaction between wood species and toasting levels is of great importance, in order to establish its influence on wine properties.

The financial impact on the production cost of wine aging in wood barrels is, however, enormous. Hence, the addition of wood-shaving chips, during the wine aging process, has been proposed as a less expensive alternative for producing wood-flavored wines. This practice was recently approved and legislated by the European Community (CE 2165/2005 and CE 1507/2006). Compared with the traditional barrel aging, similar aromatic results in shorter contact time are expected, but the influence of chip size on extraction kinetic should be pointed out [13]. Therefore, the knowledge of wood chemical composition is a relevant factor that influences the choice of the wood to be used on wine aging process. In general, aging studies are focused on American and French oak chips, and few articles are devoted to the use of chips from other wood species. The effect of application of oak chips has been studied in recent years, for several beverages such as vinegar [14–16], ciders [17], wines [3, 18–25] and brandies [26, 27]. As far as we known, chips or tablets of chestnut have never been used or studied in wine aging. However, there are some studies on Portuguese oak chips [4], chestnut phenolic and volatile composition [28] and on brandy aged with chestnut and oak fragments [29].

For this reason, the main goal of this work is the study and quantification of low molecular weight phenolic composition of several wood species, namely Portuguese, French and American oak and Portuguese chestnut, in order to establish which components could differentiate the wood species under study. To achieve that purpose, we have optimized an extraction method based on pressurized liquid extraction (PLE) for the extraction of phenolic aldehydes, phenolic acids and furanic derivatives from the wood species under study. The pressurized liquid extraction (PLE), also known as "Accelerated Solvent Extraction" (ASE), was introduced in 1996 [30] and is one of the most useful techniques for extraction of non-polar and medium polar solutes from solid and semi-solid samples. Among the extraction methods that use organic solvents, PLE has been proposed as an improved exhaustive extraction method; although using the same solvents as soxhlet extraction, it requires only small volumes of solvents and allows faster and systematic extractions of compounds. PLE has been used in a variety of applications, including environmental [31] and food and biological samples [32].

Within this work, we had the opportunity to evaluate the influence of the botanical specie and the geographic origin, as well as the toasting level, in the extractable amounts of several phenolic compounds and furanic derivatives from different wood species.

To the best of our knowledge, this is the first report concerning the phenolic composition of chips from different wood species, namely Portuguese oak and Portuguese chestnut, using PLE as extraction method.

Materials and methods

Chemicals

5-hydroxymetylfurfural, 5-methylfurfural and syringaldehyde were purchased from Acros Organics (Geel, Belgium). Sinapaldehyde and coniferaldehyde were purchased from Aldrich (Steinheim, Germany). Gallic acid, vanillic acid, syringic acid, ferulic acid and 4-hydroxybenzaldehyde (IS) were purchased from ExtraSynthèse (Genay, France). Furfural and vanillin were purchased from Merck (Darmstadt, Germany). All of them were used as standards (purity >97 %) without further purification.

All solutions were prepared with methanol/water (50:50 (v/v)), except the ellagic acid solution which was prepared in ethanol, and were freshly prepared prior to use.

All solvents used in the chromatographic analysis were HPLC grade and purchased from Aldrich (Steinheim, Germany) and VWR (Leuven, Belgium).

Woods

The wood chips of Portuguese oak (*Quercus pyrenaica* Will—*Gerês forest*), French oak (*Quercus petraea*—French forest, Allier region), American oak (*Quercus alba*) and Portuguese chestnut (*Castanea sativa* L.) were provided, with four different toasting levels: untoasted, light toast (2 h at 160 °C), medium toast (2 h at 200 °C) and heavy toast (2 h at 240 °C), by JM Gonçalves Cooperage industry. Woods were seasoned in the open air during 22 months for chestnut and 32 months for oak. Wood seasoning in cooperage is usually performed under natural conditions in open air during a variable period of time

(18–36 months depending on wood characteristics). Natural seasoning has a more positive effect on the phenolic profile of wood, thus is preferentially used instead of artificial seasoning. Wood chips were produced from ten staves of each botanical species and mixed before grounded in order to reduce the variability among them. This is a common procedure with this kind of samples because our objective was to assess the phenolic profile of these woods.

Sample preparation: wood extraction

Extraction from wood chips, previously grounded in a coffee mill into powder, was carried out using an Accelerated Solvent Extractor ASE 100 (Dionex, ASE 100). Five hundred milligrams (mg) of chips was weighted and homogenized with diatomaceous earth and placed in the 10-mL inox extraction cell in the instrument oven. Extraction was carried out at a temperature of 150 °C using methanol as extraction solvent. After injection of the solvent into the cell, a pressurized static extraction phase lasting 5 min was carried out (12 MPa), followed by a flow of fresh methanol. After removal of the solvent from the extracts (approx. 35 mL) using a rotator evaporator, the brown residue was dissolved in 1,990 μL of a methanol/water (50:50 (v/v)), and 10 μL of a 4.08 gL^{-1} solution was added as internal standard (4-hydroxybenzaldehyde). Prior to the analysis, on RP-HPLC, the wood extracts samples were filtered through a 0.45-μm membrane (Sartolon Polyamid, Sartorius Stedim Biotech GmbH, Goettingen, Germany) and analyzed by direct injection. The chromatographic conditions used in RP-HPLC are described below. Samples were prepared in duplicate and injected twice.

HPLC analysis

The chromatographic analysis were performed with a HPLC system UltiMate 3000 (Dionex Corp., Sunnyvale, C.A.) consisted of a quaternary pump, a column oven, a DAD-RS detector, an autosampler and a Chromeleon 7.0 software for management, acquisition and treatment of data. A 250 mm × 4 mm ID Lichrospher RP18 (5 μm) column (Merck, Darmstadt, Germany) was chosen as the stationary phase.

The following chromatographic conditions were selected: column temperature 40 °C, flow rate 1.0 $mLmin^{-1}$, injection volume of 25 μL, binary gradient consisting of solvent A, water-formic acid (98:2 (v/v)) and solvent B, methanol/water/formic acid (70:28:2 (v/v/v)) as follows: linear gradient from 0 to 40 % B in 45 min, from 40 to 60 % B in 25 min.

The identification of each compound was established by comparing the retention time and UV-Vis spectra of the peaks with those obtained by injection of standards. Simultaneous detection was done at 254, 280 and 320 nm for all peaks. Quantification was carried out at 280 nm by means of the internal standard method.

LC-DAD/ESI-MS analysis

Chromatographic analysis was performed on a Surveyor Thermo Finnigan HPLC system with autosampler and PDA detector. MS analysis was carried out in an LCQ Fleet mass spectrometer (Thermo Finnigan—San Jose, CA, USA) equipped with an electrospray ionization (ESI) source and using an ion trap mass analyzer. The analytical column used was Grace Smart RP18, 150 mm × 2.1 mm ID, 3.0 μm. The binary mobile phase consisted of solvents A (water- formic acid (99.9:0.1 (v/v)) and B (methanol) as follows: 5–45 % B from 0 to 35 min; then 70 % B from 35 to 40 min and 70 % B from 40 to 50 min. The flow rate was fixed at 0.2 $mLmin^{-1}$ during the entire chromatographic process. The column oven was kept at 30 °C, and the sample tray was set at a temperature of 24 °C. The injection volume was 10 μL, and PDA detection was set between 200 and 600 nm to monitor the UV-Vis absorption. The conditions of MS analysis were as follows: capillary temperature of 300 °C, source voltage of 5.0 kV, source current of 100.0 μA and capillary voltage of −20.0 V in negative ion mode.

Analytes were detected in full MS mode (m/z 100–1,200). The source fragmentation was set at 30 V whenever additional fragmentation was needed for compound identification.

Statistical analysis

Differences in the phenolic composition of several wood chips were assessed by one-way analysis of variance (ANOVA); mean comparisons were performed using Tukey–Kramer multiple-comparison test at the 95 % confidence level. Analyses were accomplished using NCSS 6.0 software.

Results and discussion

PLE of low molecular weight compounds from several wood species

In this work, we have optimized a pressurized liquid extraction (PLE) method for the extraction of some compounds from several wood chips (data not shown). During the optimization process, several variables like temperature (100, 120 and 150 °C), solvent polarity (methanol, acetonitrile), number of extraction cycles (2 and 3) and sample

amount (0.5 and 1.0 g) were evaluated. After optimization, methanol, a temperature of 150 °C and 3 cycles of extraction were used to extract the wood chips. The extraction conditions were chosen in order to maximize the extraction of phenolic compounds, aiming to obtain a profile of the sample preparation as complete as possible (Fig. 1). The temperature applied during the extraction process increases the ability of the solvent to solubilize the compounds and decreases the viscosity of the solvent, allowing better penetration of the liquid into the matrix.

Since extractions are done at elevated temperatures, thermal degradation is a potential concern. Pollnitz et al. [12] have reported, for some volatiles compounds extracted from oak wood, artifacts formation due to the high injector temperature used for GC-MS analysis or the high temperature and relatively polar solvent used on PLE. We did not observe any artifacts, and most of the compounds identified have already been detected, in similar samples, using others extraction techniques [3, 7, 33, 34]. However, to discard the possibility of thermal degradation, during PLE extraction, a mixture of standards compounds **1–12** (Table 3) spiked on diatomaceous earth has been extracted and analyzed in the same conditions as real samples. The results obtained showed no evidence of thermal degradation, for the compounds under study, using the experimental conditions described in this work (data not shown).

Screening of phenolic composition of wood extracts by HPLC-DAD/ESI-MS

Aiming to perform a screening of the phenolic composition of Portuguese chestnut and French, American and Portuguese oak wood chips, we have analyzed the methanolic extracts by HPLC-DAD/ESI-MS. Within this study, we are able to confirm the phenolic composition of different wood species. Low molecular weight compounds were identified by comparing their retention times and UV and mass spectra with those of the standards. Additionally, 17 peaks corresponding to compounds with related structures were tentatively identified on the basis of their retention time, UV spectra and MS patterns, as well as taking into account data in related literature [35–37]. Most of those compounds tentatively assigned were hydrolysable tannins, which comprise gallotannins and ellagitannins. Gallotannins are composed by a glucose molecule in which hydroxyl groups are partly or completely substituted with galloyl groups while ellagitannins are esters of the hexahydroxydiphenoyl (HHDP) group consisting of a polyol core (glucose) [35]. Relevant information concerning the identified compounds obtained from DAD and ESI-MS data is shown in Tables 1 and 2: λ_{max} as well as shoulders if they exist from UV spectra, fragment ions observed in negative ionization mode, their percentage in the MS spectra, and the structure attribution of ions. The low molecular weight phenolic compounds were identified by HPLC-DAD/ESI-MS, and the results are summarized in Table 1 for the Portuguese Chestnut.

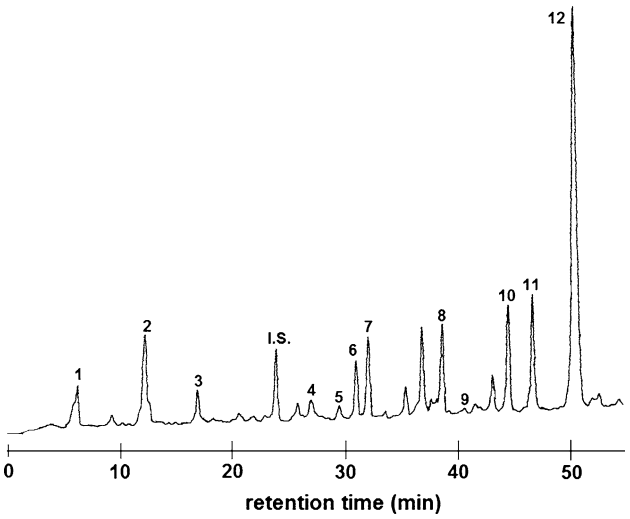

Fig. 1 RP-HPLC Chromatogram of American oak wood chips extract ($\lambda = 280$ nm). For peak identification, see Table 3

In all the wood samples under study, we have found the gallic and ellagic acids and the aldehydes vanillin, syringaldehyde, coniferaldehyde, sinapaldehyde, as well as the furanic derivatives 5-hydroxymethylfurfural and furfural. The furanic derivatives were identified only by their UV-Vis spectra and compared with commercial standards on the basis of the retention times. Except in the furanic derivatives, the respective $[M–H]^-$ deprotonated molecule was the base peak in the MS pattern. Gallic acid also gave $[M–H-44]^-$ fragment ion via loss of a CO_2 group from the carboxylic acid moiety. For methoxylated aldehydes (vanillin, syringaldehyde and coniferaldehyde), the mass spectrum shows the respective deprotonated molecules at m/z 151, 181 and 177, respectively. The mass spectrum of the more retained hydroxycinnamic aldehyde, the sinapaldehyde, also gave the deprotonated molecule $[M–H]^-$ at *m/z* 207, although the main fragment present is due to the loss of a methyl group. All these attributions were confirmed with the authentic standards.

For Portuguese Chestnut wood, we have also identified some hydrolysable tannins, which are summarized in Table 2. Some of these compounds are hydrolysable tannins since they can be hydrolyzed leading to the formation of gallic acid and/or ellagic acid. Those compounds were identified by their HPLC-DAD/ESI-MS and also by comparing these data with the literature [35–37]. Concerning the UV spectrum, the identified compounds belong to two main groups. One group of compounds exhibit a characteristic UV spectrum of ellagic acid ($\lambda_{máx} = 254$ nm and $\lambda_{máx} = 360$ nm) and the other group shows a UV spectra pattern mainly with gallic acid-like spectra ($\lambda_{máx} = 272$ nm). In

Table 1 Spectroscopic and spectrometric data of low molecular weight phenolic compounds in Portuguese chestnut chips

Sample (ID)[a]	R_t (min)	LC-DAD data (nm)	LC-MS data (*m/z*) ESI^-(% in MS) [attribution]	Identification
	6.64	264	**169** (25) $[M–H]^-$, 125 (80)$[M–H-44]^-$	Gallic acid
	7.31	238	–	5-Hydroxymethylfurfural
	8.33	237, 283	–	Furfural
S1	18.56	265	–	5-Methylfurfural
	21.60	242	**167** (100) $[M–H]^-$	Vanillic acid
	25.85	238, 278	**151** (100) $[M–H]^-$	Vanillin
	26.50	240, 271	**197** (100) $[M–H]^-$	Syringic acid
	29.65	239, 304	**181** (100) $[M–H]^-$	Syringaldehyde
	33.25	241, 270	**193** (100) $[M–H]^-$	Ferulic acid
	35.02	280, 339	**177** (100) $[M–H]^-$	Coniferaldehyde
	36.71	250, 345	**207** (30) $[M–H]^-$, 192 (100) $[M–H-15]^-$	Sinapaldehyde
	44.63	253, 366	**301** (100) $[M–H]^-$	Ellagic acid

m/z mass fragmentation pattern, molecular ion in bold

[a] Sample ID notation: S1- Portuguese Chestnut

Table 2 Spectroscopic and spectrometric data of hydrolyzable tannins with UV spectrum like gallic and ellagic acids in portuguese chestnut wood chips

Sample (ID)[a]	R_t (min)	LC-DAD data (nm)	LC-MS data (*m/z*) ESI^-(% in MS) [attribution]	Identification
Galloyl and Hexahydroxydiphenoyl derivatives				
	18.90	270	**183** (100) $[M–H]^-$	Methyl gallate
	17.06	263	**483** (100) $[M–H]^-$, 313 (10) [M–H-gallic acid]$^-$, 211 (15)	Digalloyl glucose
	27.00	270	**785** (40) $[M–H]^-$, 301 (60) [M–H-digalloylglucose]$^-$	Digalloyl-HHDP-glucose
	24.03	271	**635** (40) $[M–H]^-$, 483 (100) [M–H-galloyl]$^-$	Trigalloyl glucose
	25.18	277	**635** (25), 483(100)	Trigalloyl glucose
	29.23	273	**635** (100) $[M–H]^-$	Trigalloyl glucose
	30.19	270	**635** (100) $[M–H]^-$, 465 (40) [M–H-gallic acid]$^-$	Trigalloyl glucose
	24.09	270	977 (30), 635 (98), 483 (100), 301 (20), 193 (15)	Unknown
	25.24	277	**785** (100) $[M–H]^-$, 483 (20) [digalloylglucose-H]$^-$, 301 (30) [M–H-digalloylglucose]$^-$	Digalloyl-HHDP-glucose
	29.47	273	**787** (20) $[M–H]^-$, 635 (100) [M–H-galloyl]$^-$, 465 (15) [M–H-gallic acid-galloyl]$^-$, 301 (10) [ellagic acid-H]$^-$	Tetragalloyl glucose
S1	34.06	271	**787** (100) $[M–H]^-$, 617 (10) [M–H-gallic acid]$^-$	Tetragalloyl glucose
	35.59	270	**787** (100) $[M–H]^-$, 635 (50) [M–H-galloyl]$^-$, 465 (25) [M–H-gallic acid-galloyl]$^-$, 313 (15) [M–H-gallic acid-digalloyl]$^-$, 169 (25) [gallic acid-H]$^-$	Tetragalloyl glucose
	36.00	270	**787** (100) $[M–H]^-$, 617 (40) [M–H-gallic acid]$^-$, 169 (10) [gallic acid-H]$^-$	Tetragalloyl glucose
	38.51	276	**939** (100) $[M–H]^-$, 769 (15) [M–H-gallic acid]$^-$, 617 (10) [M–H-galloyl-gallic acid]$^-$, 169 (10) [gallic acid-H]$^-$	Pentagalloyl glucose
Ellagic derivatives				
	36.96	252, 365	**469** (30) $[M–H]^-$, 301 (100) [ellagic acid-H]$^-$	Valoneic acid dilactone
	47.28	254, 360	**585** (100) $[M–H]^-$, 301 (25) [ellagic acid- H]$^-$	Ellagic acid dimer dehydrated
	10.64	243, 280 (sh)	**933** (100) $[M–H]^-$, 631 (25) [M–H-ellagic acid]$^-$, 301 (20) [ellagic acid-H]$^-$	Vescalagin

m/z mass fragmentation pattern, molecular ion in bold

[a] Sample ID notation: S1- Portuguese Chestnut

accordance with mass data for Portuguese chestnut summarized in Table 2, it was possible to identify the series of galloyl glucose esters which comprises different isomers of galloyl glucose, digalloyl glucose, trigalloyl glucose, tetragalloyl glucose and pentagalloyl glucose. As described in the literature, the major characteristic of the mass spectrum of these compounds is the presence of a fragment correspondent to the deprotonated molecule $[M–H]^-$ (m/z 483, 635, 787, 939, respectively) and fragments related to the loss of one or more galloyl groups and/or gallic acid. For digalloyl glucose (as depicted in Scheme 1), the MS spectrum exhibit a $[M–H]^-$ ion at m/z 483 and other peaks at m/z 313 and 211 attributed to the loss of gallic acid and galloyl glucose fragmentation, respectively. Trigalloyl glucose structure afforded $[M–H]^-$ ions at m/z 635 and peaks of m/z 483 and 465 caused by the loss of galloyl residue and gallic acid, respectively. Hence, in tetragalloyl glucose the breakdown of the molecular ion $[M–H]^-$ at m/z 787 produced a first loss of a galloyl residue [M–H-152] to give a fragment at m/z 635, and in addition the sequential loss of gallic acid and another galloyl residue to give a fragment at m/z 313. The same behavior was also observed for pentagalloyl glucose. In this case, the MS spectrum shows the molecular ion $[M–H]^-$ at m/z 939 and fragments related to a first loss of a gallic acid (m/z 769) and a galloyl and gallic acid residue (m/z 617). As shown in Table 2, another isomeric combination of gallic acid and hexahydroxydiphenic (HHDP) acid with glucose was also detected as digalloyl-HHDP- glucose (Scheme 1). Its MS spectrum gave the $[M–H]^-$ ion at m/z 785, and the sequential losses of galloyl and hexahydroxydiphenoyl were also observed (Scheme 1). As illustrated in Table 2, the presence of a compound with the same molecular weight at different retention times is due to isomeric forms of that compound. Several isomeric forms of hydrolysable tannins were also reported by other authors [35, 37]. Additionally, compounds with ellagic acid–like UV-spectra were detected, namely valoneic acid dilactone (Scheme 1), ellagic acid dimer and vescalagin. The presence of those compounds in Portuguese chestnut extracts is in agreement with other authors [37].

Quantification of low molecular weight phenolic (LMWP) compounds and furanic derivatives by HPLC

Calibration curves

Aiming the quantification of phenolic composition of the wood species under study, we have prepared standard

Scheme 1 Fragmentation patterns of some galloyl derivatives and valoneic acid dilactone

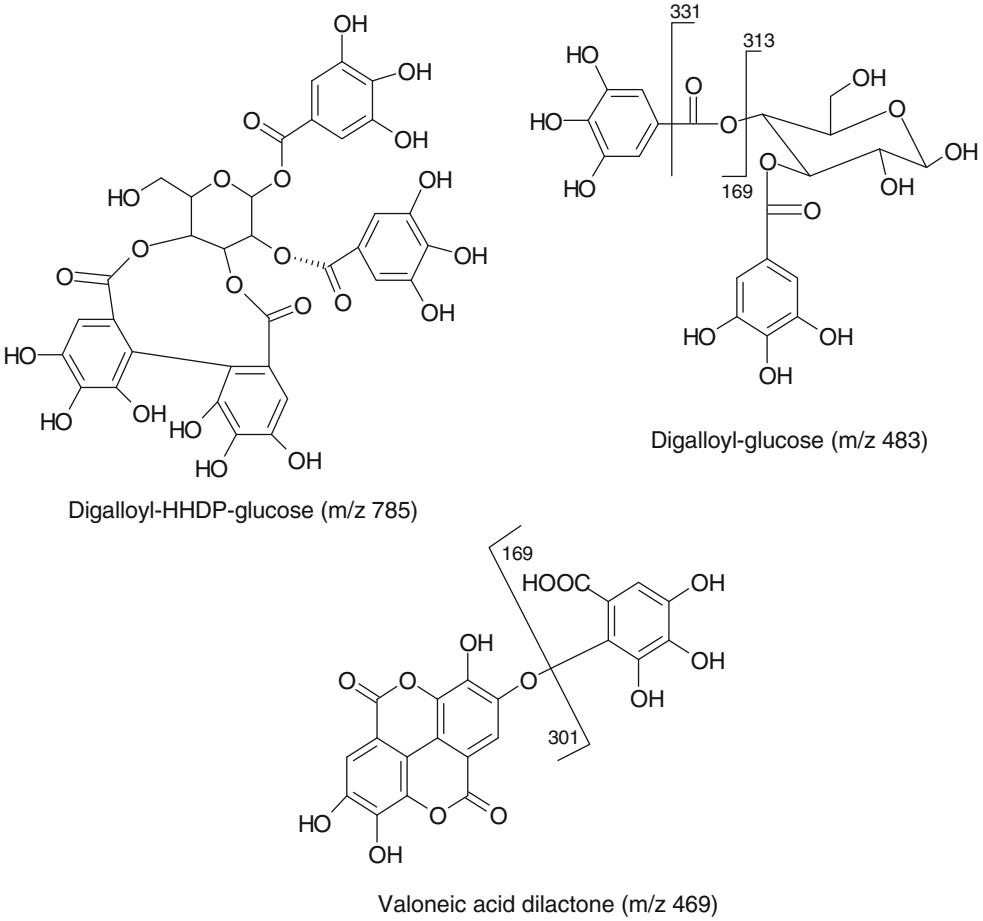

Table 3 Retention times and parameters for the calibration of low molecular weight compounds

Compound	RT ± SD (min)	Equation	r^2	Linear range (mg L^{-1})
Gallic acid (**1**)	6.39 ± 0.30	$y = 0.019x$	0.9997	8.53–1,279.50
5-Hydroxymethylfurfural (**2**)	12.36 ± 0.16	$y = 0.0504x$	0.9998	1.19–119.00
Furfural (**3**)	17.07 ± 0.32	$y = 0.0632x$	1.0000	1.13–112.80
Vanillic acid (**4**)	26.07 ± 0.01	$y = 0.0118x$	0.9997	8.51–170.20
5- Methylfurfural (**5**)	29.46 ± 0.93	$y = 0.0455x$	1.0000	5.93–118.60
Syringic acid (**6**)	30.81 ± 0.18	$y = 0.0209x$	1.0000	9.95–199.00
Vanillin (**7**)	31.84 ± 0.16	$y = 0.0315x$	0.9961	7.70–154.00
Syringaldehyde (**8**)	37.56 ± 0.26	$y = 0.0122x$	1.0000	9.19–294.08
Ferulic acid (**9**)	41.17 ± 0.24	$y = 0.0174x$	0.9978	9.77–195.40
Coniferaldehyde (**10**)	46.40 ± 0.39	$y = 0.0103x$	0.9989	8.98–359.20
Sinapaldehyde (**11**)	46.97 ± 0.51	$y = 0.005x$	0.9978	10.57–845.60
Ellagic acid (**12**)	50.01 ± 0.52	$y = 0.0145x$	0.9995	200.80–3,222.40

RT ± *SD* retention time ± estimated standard deviation ($n = 3$), r^2 determination coefficient

solutions of several compounds (see Table 3). Determinations were made using the internal standard method, with commercial standards. Calibrations were carried out for each substance from a stock solution with the low molecular weight compounds, by dilution in a solution of methanol/H_2O (1:1(v/v)) to different concentrations (see Table 1). Table 3 summarizes the parameters for the calibration of low molecular weight phenolic compounds and furanic derivatives. Data in Table 3 clearly show that linearity is satisfactory in almost all cases, with the correlation coefficient (r^2) ranging from 0.9961 (vanillin) to 1.0000 (furfural, 5-methylfurfural, syringic acid, syringaldehyde).

Quantification of LMWP compounds and furanic derivatives

The quantification of low molecular weight phenolic compounds and furanic derivatives of several wood species was achieved by HPLC using the internal standard method. This study allowed the evaluation of botanical species and geographic origin influence on the contents of low molecular weight phenolic compounds (see Table 4). The toasting effect was also studied in this work for French oak wood chips. Results are summarized in Table 5.

Influence of the botanical species

The concentration of phenolic compounds found in oak and chestnut woods is influenced by several factors, namely the wood species. According to several authors, the botanical species is a relevant factor that explains the difference in wood composition [38]. The results of variance analysis (Table 4) show that Portuguese oak and Portuguese chestnut have the highest content of total low molecular weight phenolic compounds. Particularly, in the case of Portuguese oak it is possible to distinguish this wood from the others botanical species based on phenolic acids content. As described in our previous work, the total amount of phenolic compounds also shows that chips from French oak are richer than chips from American oak [39]. Gallic and ellagic acids are the most abundant compounds within the phenolic acids group. These data are consistent with Vivas et al. [40] that indicated these acids as the main low molecular weight compounds in oak and chestnut woods. In this discussion, the readers should become aware that our data were obtained using PLE as extraction method and we will compare our results with others available in the literature that used different extraction methods. As shown in Table 4, it is also noticed that ellagic acid predominates in Portuguese oak. According to our results, there are very significant differences on ellagic acid content between the four woods under study. American oak possesses the poorest ellagic acid content. According to our results, gallic acid also shows higher contents in Portuguese oak and Portuguese chestnut when compared with French and American oak. Concerning ellagic acid content in oak wood, our results are in agreement with Canas et al. [7]. However, ellagic acid contents in chestnut wood are higher than those found by these authors. Other authors reported ellagic acid as the most abundant phenolic acid in oak wood [5, 40, 41]; however, these results are not in accordance with the studies of Delgado and Gomez-Cordovés [42], Rabier and Moutounet [43] and Gimenez- Martinez et al. [8]. The presence of ellagic acid could be explained by wood free content and by the hydrolysis of numerous wood ellagitannins. The increasing amount of gallic acid during the trees growth is due to the hydrolysis of some galloyl esters probably associated with the parietal composites of the cells [33].

Table 4 Phenolic compounds in medium toast level chips from French, American and Portuguese oaks and Portuguese chestnut

Compound (mg/100 g wood)	French oak	American oak	Portuguese oak	Portuguese chestnut	*p* value
Gallic acid	$39.56^{a} \pm 5.43$	$18.19^{a} \pm 0.57$	$558.82^{b} \pm 55.11$	$410.28^{c} \pm 21.63$	0.000000
Vanillic acid	$5.82^{a} \pm 2.68$	$11.11^{b} \pm 1.45$	$23.88^{c} \pm 3.79$	$10.84^{b} \pm 2.03$	0.000001
Syringic acid	$17.04^{b} \pm 0.87$	$15.04^{ab} \pm 0.77$	$9.51^{a} \pm 0.75$	$34.00^{c} \pm 5.09$	0.000015
Ferulic acid	$15.65^{b} \pm 1.78$	$1.74^{a} \pm 0.07$	$22.79^{c} \pm 3.52$	$4.00^{a} \pm 1.02$	0.000000
Ellagic acid	$582.84^{b} \pm 25.87$	$257.31^{a} \pm 5.74$	$1{,}156.06^{c} \pm 214.07$	$600.33^{b} \pm 27.84$	0.000008
5-Hydroxymethylfurfural	$6.13^{ab} \pm 0.29$	$10.79^{b} \pm 3.08$	$27.70^{c} \pm 3.35$	$5.13^{a} \pm 1.63$	0.000001
5-Methylfurfural	$1.91^{a} \pm 0.24$	$1.79^{a} \pm 0.28$	$3.70^{a} \pm 0.97$	$4.93^{b} \pm 1.19$	0.001223
Furfural	$4.16^{ab} \pm 1.25$	$2.61^{a} \pm 0.19$	$11.83^{b} \pm 6.27$	$5.15^{ab} \pm 1.03$	0.035274
Vanillin	$16.77^{b} \pm 1.20$	$14.59^{b} \pm 0.66$	$11.28^{a} \pm 5.74$	$29.12^{c} \pm 2.41$	0.000004
Syringaldehyde	$63.47^{d} \pm 4.00$	$40.09^{b} \pm 3.67$	$24.84^{a} \pm 6.44$	$48.86^{c} \pm 4.67$	0.000006
Coniferaldehyde	$48.26^{b} \pm 6.54$	$59.20^{c} \pm 2.10$	$41.36^{a} \pm 9.05$	$38.92^{a} \pm 2.62$	0.000056
Sinapaldehyde	$106.39^{b} \pm 13.88$	$136.10^{b} \pm 6.02$	$48.71^{a} \pm 16.54$	$234.19^{c} \pm 14.41$	0.000000
Total	908.00	568.56	1,940.48	1,425.75	

Different letters in a row denote significant difference with 95 % confidence level in the Tukey–Kramer multiple-comparison test

Table 5 Phenolic compounds in French oak chips submitted to different toasting levels

Compound (mg/100 g wood)	Untoasted	Light toast	Medium toast	Heavy toast	*p* value
Gallic acid	$20.06^{a} \pm 4.56$	$43.92^{b} \pm 4.29$	$39.56^{b} \pm 5.43$	$39.26^{b} \pm 5.28$	0.000047
Vanillic acid	$30.76^{b} \pm 6.95$	$4.94^{a} \pm 2.57$	$5.82^{a} \pm 2.68$	$9.55^{a} \pm 2.12$	0.000009
Syringic acid	nd	$10.02^{a} \pm 2.00$	$17.04^{a} \pm 0.87$	$46.83^{b} \pm 9.73$	0.000305
Ferulic acid	$1.94^{a} \pm 1.39$	$5.59^{b} \pm 1.12$	$15.65^{c} \pm 1.78$	$5.47^{b} \pm 0.56$	0.000000
Ellagic acid	$472.89^{a} \pm 66.29$	$617.50^{a} \pm 48.86$	$582.84^{a} \pm 25.87$	$602.72^{a} \pm 113.94$	0.050835
5-Hydroxymethylfurfural	$5.73^{a} \pm 3.01$	$7.99^{ab} \pm 1.29$	$6.13^{a} \pm 0.29$	$12.66^{b} \pm 3.36$	0.027014
5-Methylfurfural	$0.61^{a} \pm 0.04$	$2.83^{d} \pm 0.77$	$1.91^{c} \pm 0.24$	$1.20^{b} \pm 0.23$	0.000000
Furfural	$7.18^{a} \pm 1.31$	$14.36^{b} \pm 2.40$	$4.16^{a} \pm 1.25$	$28.62^{c} \pm 4.80$	0.000003
Vanillin	nd	$12.86^{a} \pm 1.21$	$16.77^{b} \pm 1.20$	$24.76^{c} \pm 2.46$	0.000017
Syringaldehyde	$50.53^{a} \pm 4.36$	$72.21^{b} \pm 12.42$	$63.47^{a} \pm 4.00$	$75.28^{b} \pm 8.71$	0.000297
Coniferaldehyde	$1.18^{a} \pm 0.12$	$27.07^{b} \pm 2.28$	$48.26^{c} \pm 6.54$	$82.25^{d} \pm 5.97$	0.000000
Sinapaldehyde	$5.90^{a} \pm 1.16$	$50.41^{b} \pm 3.99$	$106.39^{c} \pm 13.88$	$287.91^{d} \pm 15.46$	0.000000
Total	596.78	869.70	908.00	1,216.51	

Different letters in a row denote significant difference with 95 % confidence level in the Tukey–Kramer multiple-comparison test

Minor compounds, such as 5-methylfurfural, furfural and ferulic acid were identified in all the wood species studied. The results of furanic aldehydes contents in oak wood chips indicated that the amounts of these compounds increase in the order 5-methylfurfural < furfural < 5-hydroxymethylfurfural, while chestnut wood chips have identical levels of these compounds. According to our results, Portuguese oak wood have the highest levels of those furanic aldehydes, being 5-hydroxymethylfurfural the most abundant. It is known that the abundance of 5-hydroxymethylfurfural is related to the cellulose contents and, consequently, dependent of the botanical species [33].

Regarding the phenolic aldehyde contents, Portuguese chestnut wood possess a high value when compared with the others botanical species under study. In this class of compounds, sinapaldehyde shows high concentrations in all wood species studied while vanillin is present in low amount. It is also interesting to note that the highest level of sinapaldehyde was found in chestnut wood, which is in agreement with other work [29]. Some authors have stated that the syringaldehyde/vanillin ratio must be in the range 1.4–2.5, which means that the products of lignin decomposition are balanced [44]. For the wood chips studied, the syringaldehyde/vanillin proportion is greater than 1.4, ranging from 1.68 to 3.78. According to this criterion, Portuguese oak and Portuguese chestnut chips with medium toast level are within the range considered with an adequate decomposition of lignin.

Comparing the total phenolic composition of the different wood species under study (Table 2), we can

conclude that American oak possess small contents of low molecular weight phenolic compounds. However, attending to the distribution of these compounds by different classes (phenolic acids, phenolic aldehydes and furanic aldehydes), the total amounts observed for American and French oak are rather similar.

Influence of toasting process

Toasting treatment, during oak barrel manufacture, induces modifications on the macromolecular structure of the wood, leading to the degradation of polysaccharides and polyphenols, the appearance of new compounds and an increase in odoriferous volatile substances, like furans and phenols [45]. The effect of toasting level on phenolic composition of French oak wood is shown in Table 5. The results show that, in general, the total amount of compounds present in the wood increases significantly after the heat treatment. Some furanic derivatives such as furfural and the phenolic aldehydes are significantly influenced by the toasting process. However, vanillic acid concentrations decrease with the increment of the toasting level while syringic acid contents increase. This is probably due to the occurrence of a degradation process in some molecules that are thermosensitive leading to the formation of syringic acid. During heat treatment, phenolic aldehydes can be oxidized to the correspondent phenolic acids [3], which can explain our results. However, at high temperatures degradation of phenolic acids can occur. In particular, during the heat treatment ferulic acid can suffer degradation leading to some volatile compounds, namely guaiacol [46], which might explain the decrease on ferulic acid contents observed on heavy toasted French oak chips. Usually, ellagic acid levels increases with toasting level, but in our study ellagic content showed no significant differences among the four toasting levels. Among the extractable substances, hydrolysable tannins present in wood comprise gallotannins and ellagitannins and are oenologically important. In particular, ellagitannins play an important role in wine oxidation processes [47] and could also affect the condensation rate of proanthocyanidin [48]. Heating treatment can cause decomposition of gallotannins and ellagitannins giving rise to gallic and ellagic acids, respectively [46, 49–51]. According to our results, the effect of heating in gallic tannins and consequently the increase in gallic acid is more evident than the raise of ellagic acid.

Furanic aldehydes, furfural, 5-methylfurfural and 5-hydroxymethylfurfural have been identified in all the degree of toasting (Table 5). The increase in furanic aldehydes, namely furfural and 5-hydroxymethylfurfural in toasted French oak wood chips, is notices as opposed to the untoasted chips. Hydroxymethylfurfural and 5-methylfurfural proceed from the hexoses of cellulose and furfural derives from the pentoses, which are the main constituents of hemicelluloses. In general, during the toasting process some oak wood components such as hemicelluloses, which are the most thermosensitive polymers in wood, are preferentially degraded thus leading to the formation of furfural. This degradation process contributes significantly to make furfural the main furanic derivative in toasted oak wood [4]. As expected, the contents of furanic aldehydes, furfural, 5-hydroxymethylfurfural and 5-methylfurfural, increases in the toasted chips, being furfural the main compound in heavy toasted French oak chips. Thus, heat treatment has a very significant effect on furfural content and a considerable effect on 5-hydroxymethylfurfural and 5-methylfurfural in French oak wood chips. The results clearly demonstrate the predominance of furfural over 5-methylfurfural and 5-hydroxymethylfurfural, on French oak chips, when toasting degree increases.

As far as phenolic aldehydes are concerned, the effect of the toasting degree is observed since French oak chips, with heavy toast, showed higher concentrations, of these compounds, than the untoasted chips. Results are in accordance with the fact that these phenolic derivatives are formed by thermodegradation of lignin in the wood's toasting process [52]. However, at higher temperatures an oxidative cleavage of the double C–C bond of cinnamic aldehydes (coniferaldehyde and sinapaldehyde) could occur, leading to the formation of the corresponding benzoic aldehydes (vanillin and syringaldehyde). Our results show a higher increase in cinnamic aldehydes from untoasted chips to heavy toasted and the raise of benzoic aldehydes from light toasted to heavy toasted chips in French oak wood. Sinapaldehyde is the major phenolic aldehyde present in toasted French oak (approximately 61 % of total aromatic aldehydes in heavy toasted French oak chips), followed by syringaldehyde and coniferaldehyde (16 and 17.5 %, respectively). In the case of syringaldehyde, toasting effect was more significant for the heavy toasted chips than in medium toasted chips. The overall results obtained for French oak wood seem to indicate that phenolic composition of this botanical wood specie is closely related to toasting intensity, but the particular characteristics of the species can also determine the rate of modification during the toasting process.

Conclusions

This comparative study provides data that suggest the suitability of the PLE extraction method, coupled with the HPLC-DAD/ESI-MS analysis, for the qualitative and quantitative chemical characterization of Portuguese chestnut and French, American and Portuguese oak chips,

particularly the low molecular weight phenolic composition. Results showed that the influence of the botanical species (oak and chestnut) seems to be more significant than the geographic origin (American, French, Portuguese) of the wood species. Within this study, it became also evident that, in the case of French oak chips, the toasting process has a significant influence on phenolic composition of that botanical specie. The results indicated that the use of chestnut chips could induce specific and distinctive attributes to the wines, improving the sensorial complexity, leading to a differentiation of the final product. Then, it became evident that the extension of this study into wine is crucial to evaluate the impact on the phenolic composition as well as on the organoleptic characteristics of the final product. Further work will be also done in order to evaluate the effect of toasting level of different wood species on the hydrolysable tannins content and their relevance to enological purposes.

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