

# Low Molecular Weight Organic Compounds of Chestnut Wood (*Castanea sativa* L.) and Corresponding Aged Brandies

Sara Canas, M. Conceição Leandro, M. Isabel Spranger, and A. Pedro Belchior\*

Estação Vitivinícola Nacional, INIA, Quinta d'Almoinha, 2560 Dois Portos, Portugal

Oak and chestnut species have been largely used for the aging of brandies, but nowadays chestnut is rarely used. There have been no previous studies regarding the cooperage utilization of chestnut wood. This study provides, for the first time, specific information about the characterization of the northern Portuguese *Castanea sativa* wood and examines the influence of this wood and its heat treatment on the chemical composition of two-year-aged brandies, by the quantitative determination (HPLC) of low molecular weight phenolic compounds. The predominance of gallic acid among the analyzed extractable compounds both in chestnut wood and in the corresponding aged brandies was remarkable. The heat treatment has a very significant influence on the majority of extractable compounds analyzed. Thus, it could be responsible for the related sensorial properties of aged brandies and greatly affect their general balance.

**Keywords:** Chestnut wood; toasting; brandies; aging; HPLC; phenolic compounds; furanic derivatives

## INTRODUCTION

The aging of high-quality brandies requires a period of storage in wood barrels. Oak and chestnut species have been largely used for this purpose, but nowadays chestnut is rarely used.

Several studies have been made to evaluate the oak wood potential for cooperage, focusing on its physical and mechanical properties, as well as its chemical composition (Keller, 1992; Miller et al., 1992; Simon et al., 1996; Chatonnet and Dubourdieu, 1998).

These studies showed the great influence of the technological operations on the barrel-making process, namely, the heat treatment, on these wood characteristics (Sarni et al., 1990; Chatonnet et al., 1993; Singleton, 1995). This effect is essentially caused by the modifications on wood extractable phenolic compounds, namely, those of low molecular weight, that are released from wood to the distilled liquid during the aging process and contribute to the brandies' sensory properties (Artajona et al., 1990; Puech et al., 1990; Rabier and Moutounet, 1990; Viriot et al., 1993; Moutounet et al., 1995).

Some authors have reported that oak woods (*Quercus robur*, *Quercus sessiliflora*, and *Quercus alba*) are preferable to other woods for the aging of wines and spirits, but from the cooperage point of view no previous study of chestnut wood (*Castanea sativa*) or the corresponding aged brandies was found. In fact, chestnut wood has only been studied due to interest in the tannin industry (Salagoity et al., 1987; Peng et al., 1991; Krisper et al., 1992; Tang et al., 1992; Vivas et al., 1993, 1996; Viriot et al., 1994) and in the aging of wines (Clímaco et al., 1985; Clímaco and Borralho, 1995).

This work is part of a broader study of the aging process optimization of the brandies produced in Lourinhã, a Portuguese delimited region.

The results of the Lourinhã brandies' sensorial analysis, which we previously obtained, allowed us to identify a remarkable quality in the brandies aged in chestnut wood (Belchior et al., 1998).

The intent of this study is to characterize the northern Portuguese *Castanea sativa* wood and examine the influence of this wood and its heat treatment on the chemical composition of two-year-aged brandies, by the quantitative determination of low molecular weight phenolic compounds—phenolic aldehydes, phenolic acids, and coumarins—and furanic derivatives.

## EXPERIMENTAL PROCEDURES

**Materials.** Ellagic acid dihydrate, gallic acid monohydrate, vanillic acid, syringic acid, ferulic acid, vanillin, 5-(hydroxymethyl)furfural, 5-methylfurfural, furfural, scopoletin, and umbelliferone were purchased from Fluka; syringaldehyde, coniferaldehyde, sinapaldehyde, and 4-hydroxybenzaldehyde were purchased from Aldrich. All were used as standards without further purification. Solutions were prepared with ethanol/water (10:90).

**Wood.** The heartwood staves of *C. sativa* from northern Portugal were seasoned in the open air, at a cooperage industry—JMA Gonçalves. Their anatomical identification was verified (Carvalho, 1998). These staves were used to make nine barrels. Prior to heat treatment, each barrel sampling of untreated wood was carried out by gathering the wood chips, making a homogeneous group with them, and then keeping the sample. The barrels were then submitted to the heat treatment with three degrees of toasting—light (QL), medium (QM), and strong (QF)—with three replications of each degree.

**Brandies.** The barrels (250 L) were placed at Adegas Cooperativas da Lourinhã in similar cellar conditions and filled with the same Lourinhã brandy. Brandy sampling was made during the second year of aging, and the nine samples were identified as QL1, QL2, QL3, QM1, QM2, QM3, QF1, QF2, and QF3, according to the corresponding barrel.

**Wood Extraction.** Wood chips (50 g) were grounded in a hammer mill (Wiley) and then extracted with 1000 mL of ethanol/water (55:45 and pH 4.2, adjusted with hydrochloric acid) during 180 min at 20 °C, according to the method of Caldeira et al. (1996). The wood extracts were filtered through

\* Author to whom correspondence should be addressed [telephone 351 (2)61 712106; fax 351 (2)61 712426; e-mail inia.evn@mail.telepac.pt].

a glass microfiber filter (Whatman GF/C) on a Büchner funnel. The retention of the compounds in this filter was not significant, as proved in a previous assay.

**Wood Moisture.** The wood powder moisture was determined in a moisture analyzer (Mettler LJ 16), 12.5 min at 100 °C.

**Analysis of Low Molecular Weight Phenolic Compounds and Furanic Derivatives by High-Performance Liquid Chromatography (HPLC).** Prior to analysis, samples of wood extracts and brandies were added with an internal standard (4-hydroxybenzaldehyde, 20 mg/L) and filtered through a 0.45  $\mu$ m membrane (Titan). Low molecular weight phenolic compounds and furanic derivatives were separated by HPLC (Lachrom Merck Hitachi equipped with a quaternary pump, a UV-vis detector, a fluorescence detector, and an autosampler coupled to a data processor computer—Millennium 2010) on a Merck Lichrospher RP18 (5  $\mu$ m) column (250 mm  $\times$  4 mm i.d.). Flow rate was 1 mL/min. Injection volume was 20  $\mu$ L. Column temperature was 40 °C. Solvent A was H<sub>2</sub>O/formic acid (98:2) and solvent B, MeOH/H<sub>2</sub>O/formic acid (70:28:2). The elution program, adapted from that of Puech et al. (1988), was as follows: 0% B in 3 min, from 0 to 40% B in 22 min, from 40 to 60% B in 18 min, 60% isocratic B in 12 min, from 60 to 80% B in 5 min, and 80% isocratic B in 5 min. UV detection was at 280 and 320 nm; fluorescence detection was at 325 nm (excitation) and 454 nm (emission), as used by Puech et al. (1988).

The chromatographic method was validated on the basis of its linearity, sensitivity, and analytical limits (detection and quantification limits).

The identification of chromatographic peaks was made by comparison of their retention times and UV-vis spectra with those of external standards except for coumarins. The chromatographic purity of the peaks and the UV-vis spectra (200–400 nm) were performed using a Waters system equipped with a photodiode-array detector (Waters 996), with the same chromatographic conditions, managed by Millennium 2010 software. Quantitative determinations were carried out by calibration curves of external standards.

**Sensory Analysis of Brandies.** The brandies' sensorial analysis was made by a panel of 16 tasters, previously selected and trained (Caldeira et al., 1998).

**Statistical Analysis.** The one-way analysis of variance was performed using Statgraphics—statistical system/vs 5.0, and the multivariate analysis (clustering and principal component analysis) was performed using NTSYS—pc program/vs 1.80 (Rohlf, 1993).

## RESULTS AND DISCUSSION

The Lourinhã brandies' sensorial analysis allowed identification of a remarkable quality of the brandies aged in chestnut wood barrels. In fact, the scorings of these brandies' general balance (geq) were higher than those of other brandies aged in similar conditions in barrels of oak wood from Portugal, France, and North America (Belchior et al., 1998).

The tasting also showed that brandies stored in strong toasted barrels were the most appreciated.

Figures 1 and 2 show the HPLC chromatograms of untreated chestnut wood and two-year-aged brandies in strong toasted chestnut wood barrels. Peak identification is shown in Table 1.

**Characterization of Chestnut Wood.** The results show (Table 2) that gallic acid is the most abundant compound in chestnut wood, followed by ellagic acid.

Vivas et al. (1996) pointed out these acids as the main low molecular weight compounds in oak and chestnut woods. Delgado and Gómez-Cordovés (1987) and Martínez et al. (1996) verified that gallic acid is the most plentiful compound in oak wood.

However, if the presence of ellagic acid is easily explained by its wood free content (Chen, 1970; Seikel

**Table 1. Retention Times, Spectral Characteristics (Maximum Absorption Wavelength), and Identification of the Chromatographic Peaks**

peak	retention time <sup>a</sup> (min)	$\lambda_{\text{max}}$ (nm)	identification
1	7.19 $\pm$ 0.15	271	gallic acid (gall)
2	12.50 $\pm$ 0.24	285	5-(hydroxymethyl)furfural (HMF)
3	15.66 $\pm$ 0.38	233, 276	furfural (furf)
4	20.81 $\pm$ 0.37	221, 285	4-hydroxybenzaldehyde
5	22.09 $\pm$ 0.67	262, 295	vanillic acid (van)
6	23.18 $\pm$ 0.71	295	5-methylfurfural (5mfurf)
7	24.99 $\pm$ 1.05	276	syringic acid (syrg)
8	25.08 $\pm$ 0.57	238, 280–309	vanillin (vanil)
9	27.73 $\pm$ 0.61	238, 309	syringaldehyde (syrd)
10	30.68 $\pm$ 1.04	236, 296–323	ferulic acid (ferul)
11	32.50 $\pm$ 0.58	243, 306–342	coniferaldehyde (cofde)
12	33.33 $\pm$ 0.85	246, 347	sinapaldehyde (snpde)
13	39.06 $\pm$ 1.49	252, 365	ellagic acid (ellag)
14	28.19 $\pm$ 0.50		umbelliferone (umb)
15	30.19 $\pm$ 0.64		scopoletin (scop)

<sup>a</sup>  $x \pm$  SD (mean  $\pm$  standard deviation).

et al., 1971; Puech et al., 1988) and by the hydrolysis of numerous wood ellagitannins (Quinn and Singleton, 1985; Scalbert et al., 1986; Peng et al., 1991; Klumpers et al., 1994; Viriot et al., 1994), the origin of gallic acid is more questionable. The increasing content of gallic acid during the aging of trees (Viriot et al., 1994) suggests it has derived from the hydrolysis of some galloyl esters probably associated with the parietal composites of the cells. We cannot exclude the occurrence of gallotannins in wood (Seikel et al., 1971; Vivas et al., 1993), but it has never been confirmed. It is possible that part of the gallic acid results from its hydrolysis (Vivas et al., 1996), considering the identification of digallic acid in tannin extracts of chestnut wood made by Salagoity et al. (1987).

The higher diffusion rate of gallic acid than of other extractable compounds in oak wood extracts, as stated by Moutounet et al. (1989), may also occur in these chestnut wood extracts and partially contribute to its predominance.

Minor compounds, such as vanillic, syringic, and ferulic acids, were also identified in chestnut wood, similarly to the compounds found in oak wood by Monties (1992) and Simon et al. (1996). Among them, syringic acid has a major proportion.

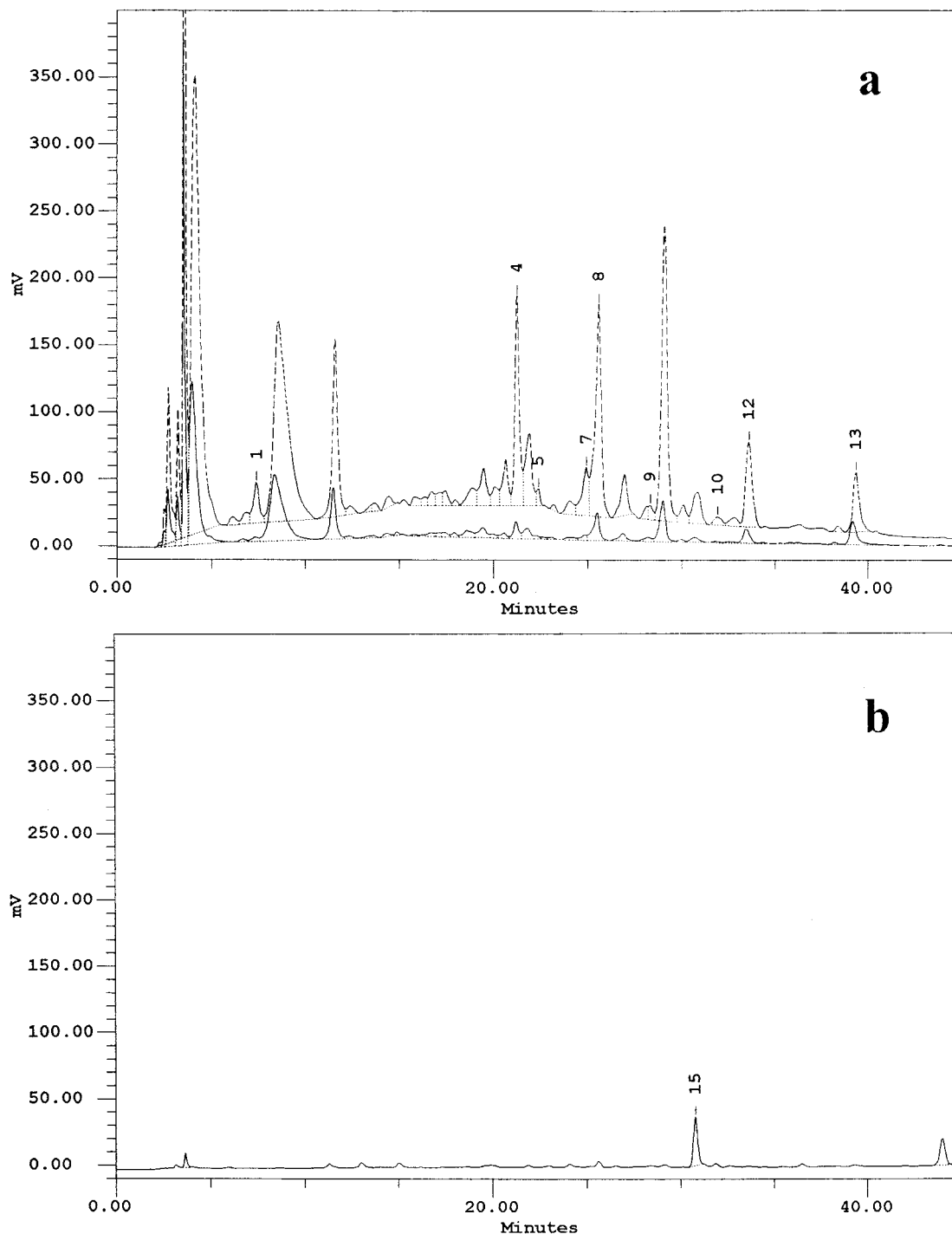
The phenolic aldehydes, vanillin, syringaldehyde, and sinapaldehyde, were present in chestnut wood, but coniferaldehyde was not detected. Vanillin has a higher concentration, followed by sinapaldehyde. The syringaldehyde content was very low.

Martinez et al. (1996) did not detect those compounds in oak wood. Many authors reported their presence in it, but in small amounts (Seikel et al., 1971; Delgado and Gómez-Cordovés, 1987; Nabeta et al., 1987; Chatonnet, 1995). Guymon and Crowell (1968) and Monties (1992) related that phenolic aldehydes are on the free form or linked to parietal constituents in oak wood.

The furanic derivatives were not detected in untreated chestnut wood.

Among the coumarins, only the scopoletin was identified in chestnut wood. This compound was found in chestnut wood by Salagoity (1992), being  $\sim$ 5-fold less than in oak wood.

**Characterization of Brandies.** The results of variance analysis (Table 2) show that heat treatment has a very significant influence on the total content of low



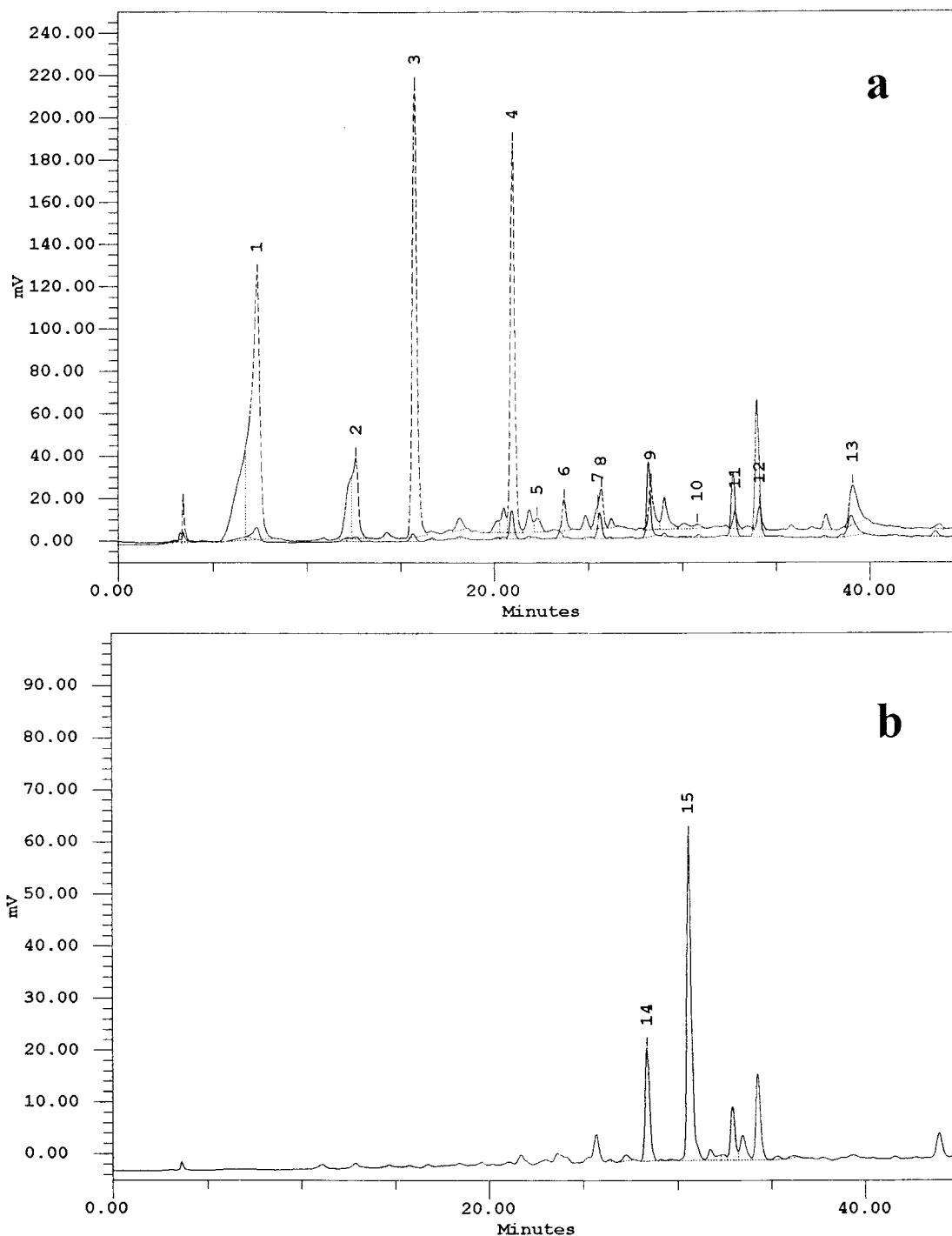
**Figure 1.** HPLC chromatograms of untreated chestnut wood: (a) UV, top tracing from 280 nm and bottom tracing from 320 nm; (b) fluorescence.

molecular weight extractable compounds analyzed in two-year-aged brandies in chestnut barrels. It possibly derives from the action of three major factors, under toasting effect (Sarni et al., 1990):

- the increase in wood permeability and the better access of brandy to wood extraction sites caused by the fragmentation of cell structures and reorganization of lignocellulose network;
- the availability increase of some soluble compounds proceeding from the wood constituents' degradation (tannins, lignins, hemicelluloses, cellulose, ...), which could be released to the brandy; and
- the formation of heat treatment specific compounds, such as HMF and 5-methylfurfural, that could be released to the brandy, too.

The heat treatment has a very significant effect on HMF content and a significant effect on 5-methylfurfural content of brandies aged in chestnut barrels. However, the furfural content was not affected. The predominance of HMF and the lesser importance of 5-methylfurfural in any toasting degree are evident.

Their evolution profiles are similar: as toasting temperature increases (from QL to QM) their concentrations rise, reaching the highest values in the corre-



**Figure 2.** HPLC chromatograms of two-year-aged brandies in strong toasted chestnut wood barrels: (a) UV, top tracing from 280 nm and bottom tracing from 320 nm; (b) fluorescence.

sponding brandies. At QF their contents decreased but remain higher than in QL.

The decrease of furanic derivatives at QF may be a consequence of its degradation and the volatilization of produced compounds at high temperatures, as observed in oak wood by Sarni et al. (1990) and Chatonnet (1995).

HMF and 5-methylfurfural proceeding from the hexoses of cellulose and furfural derived from the pentoses, the main constituents of hemicelluloses (Hodge, 1967). As the hemicelluloses are the most thermosensitive polymers in wood (Fengel and Wegener, 1989), they are preferentially degraded during heat treatment, contributing to making furfural the main furanic derivative in

toasted oak wood (Biermann et al., 1987; Chatonnet, 1995) and in the corresponding aged brandies. However, furfural already exists in the distilled liquid.

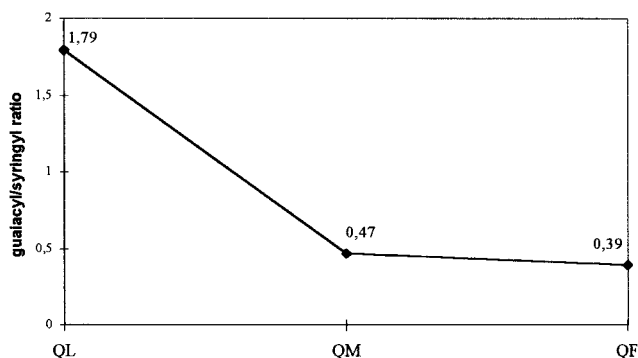
It is reliable that the abundance of HMF in the analyzed brandies is probably related to a larger amount of cellulose in chestnut wood than in oak wood [47.3 versus 41.1%, according to Fengel and Wegener (1989)].

Concentrations of phenolic aldehydes in brandies are dependent on chestnut wood toasting degree and present similar behaviors; that is, the increase in wood treatment temperature produces a significant increase in vanillin, syringaldehyde, sinapaldehyde, and coniferaldehyde contents in brandies. Except for syringaldehyde, the main difference is found between QL and QM.

**Table 2. Content of Phenolic Compounds and Furanic Derivatives in Chestnut Wood Extracts and in Two-Year-Aged Brandies in Chestnut Barrels (Concentrations in Milligrams per Liter of Absolute Ethanol Except for Coumarins, Which Are in Micrograms per Liter of Absolute Ethanol)**

	HMF	furf	5mfurf	ellag	gall	van	syrg	ferul	vanil	syrd	cofde	sipde	umb	scop	total	
	Untreated Wood <sup>a</sup>															
<i>x</i>	0.00	0.00	0.00	97.76	163.16	17.42	60.79	42.29	0.26	0.08	0.00	0.14	0.000	80.42	381.99	
SD	0.000	0.000	0.000	22.210	180.164	11.094	30.969	18.707	0.151	0.043	0.000	0.076	0.000	35.863	223.479	
	Brandies <sup>b</sup>															
toasting effect	**	ns	*	**	*	*	ns	ns	**	**	**	*	**	ns	**	
light	<i>x</i>	2.33a	0.00	0.00 <sub>a</sub>	16.53a	167.12a	9.97a	22.64	5.07	1.91a	0.82a	0.37a	0.45a	0.14a	42.95	227.47a
(QL)	SD	0.177	0.000	0.000	1.346	25.519	0.903	2.040	2.337	0.175	0.150	0.034	0.060	0.003	5.542	32.057
medium	<i>x</i>	10.02b	2.28	(1.36)b	39.93b	217.63b	13.12ab	22.43	3.00	5.22b	11.49b	5.30b	10.89b	0.68b	65.07	342.75b
(QM)	SD	3.291	0.988	(0.629)	8.858	22.339	1.220	7.877	0.672	0.474	2.204	1.315	4.021	0.113	16.888	38.539
strong	<i>x</i>	8.34b	2.16	(0.97)b	61.14c	207.84ab	15.13b	23.74	3.31	6.03b	16.23c	5.64b	13.68b	0.94c	47.20	364.26b
(QF)	SD	3.701	1.747	(0.500)	10.405	13.626	2.317	4.137	0.610	0.732	2.777	1.359	5.232	0.153	11.910	33.670

<sup>a</sup> Wood: *x* = mean of nine values; SD = standard deviation. <sup>b</sup> Brandies: *x* = mean of three values; means followed by the same letter in a column are not significantly different at the 0.05\* or 0.01\*\* level of significance; ns = without significant difference; 0.00 indicates value < detection limit; parentheses indicate value < quantification limit.

**Figure 3.** Effect of heat treatment on the guaiacyl/syringyl ratio of two-year-aged brandies in chestnut barrels

Several studies (Reazin, 1981; Nishimura et al., 1983; Puech et al., 1984, 1985; Rabier and Moutounet, 1990; Sarni et al., 1990; Monties, 1992) ask us to accept unquestioningly that one of the most characteristic aspects of aging in oak barrels is the diffusion from the wood of phenolic compounds derived from lignin degradation.

Under temperature effect there are decarboxylation and breaking of lignin aryl ether bonds, which cause the formation of cinnamic aldehydes with guaiacylpropane (coniferaldehyde) and syringylpropane (sinapaldehyde) structures. At higher temperatures an oxidative cleavage of the double C–C bond of these aldehydes could happen, leading to the formation of corresponding benzoic aldehydes, with guaiacylpropane (vanillin) and syringylpropane (syringaldehyde) structures. These compounds are then released to the brandy (Monties, 1992). This explains the higher increase of cinnamic aldehydes from QL to QM and the larger increase of benzoic aldehydes from QM to QF in brandies aged in chestnut wood barrels.

In addition, according to Nishimura et al. (1983), Puech et al. (1984), and Viriot et al. (1993), during the aging process the cinnamic aldehydes are further oxidized to yield the benzoic aldehydes.

The results also show (Figure 3) that the increased amounts of syringyl-type compound ratios (sinapaldehyde and syringaldehyde) are much higher than the ones of guaiacyl-type compounds (coniferaldehyde and vanillin), as observed by Nishimura et al. (1983) in whiskies aged in oak wood barrels and by Sarni et al. (1990) and Chatonnet (1995) in oak wood. This fact may be associated with the higher thermal stability of syringyl compounds. Assuming that syringyl units have a higher sensitivity toward oxidation (Viriot et al., 1993),

it can mean that in this initial stage of the aging process, also in chestnut barrels, the extractive phenomenon exceeds the oxidative phenomenon, although the extraction process already involves some oxidation (Belchior and San Romão, 1982).

The heat treatment of chestnut barrels has a very significant effect on the ellagic acid content of the corresponding aged brandies and a significant effect on gallic and vanillic acids contents, as well. However, their evolution patterns are distinct.

The ellagic acid content increases significantly from QL to QF, becoming the second most important extractable compound of brandies aged in QM and QF barrels. The increase probably results from ellagitannin degradation (Rabier and Moutounet, 1990; Viriot et al., 1993; Chatonnet, 1995), and the accumulation may also be a consequence of its high fusion point (>450 °C).

Gallic acid is the most abundant extractable compound of brandies aged in chestnut wood barrels with any toasting degree. In a previous study (Canas et al., 1998) we noticed that the brandy aged in chestnut barrels was richer in gallic acid than brandies aged in barrels of oak wood from Portugal, France, and North America.

We observed a significant increase of gallic acid content from QL to QM and a slight decrease at QF. Artajona et al. (1990), Lavergne et al. (1990), and Rabier and Moutounet (1990) revealed a similar behavior in brandies aged in oak barrels.

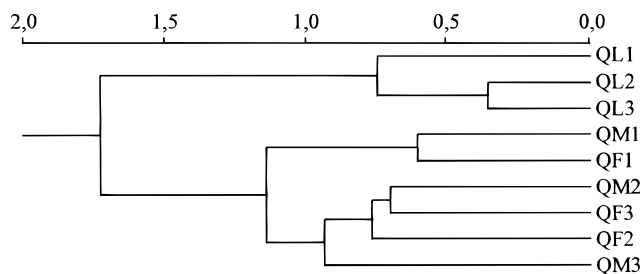
The low amounts of gallic acid found in untreated chestnut wood seem to be insufficient to explain its content in the aged brandies. Therefore, the gallic acid present in brandies and the increase of its content with toasting intensity possibly result from the hydrolysis of wood digallic acid (Vivas et al., 1996).

The vanillic acid content increases with toasting intensity, but only the difference between QL and QF is significant. According to Puech et al. (1984), vanillic acid present in brandies is produced by the oxidation of both vanillin and guaiacylpropane units.

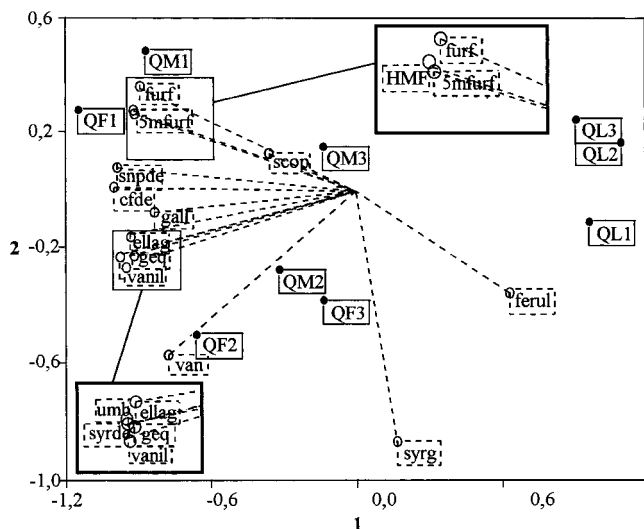
The content of syringic acid shows a slight increase at QF, along with the increase of syringaldehyde, which is its main precursor (Puech et al., 1984).

The ferulic acid content tends to decrease, as a consequence of its decarboxylation and degradation under toasting effect (Chatonnet, 1995).

It is possible to distinguish the brandies aged in chestnut barrels with different toasting degrees by their content of umbelliferone. The results show a regular



**Figure 4.** Phenogram of UPGMA clustering of two-year-aged brandies aged in chestnut barrels according to low molecular weight phenolic compounds and furanic derivative contents and general equilibrium.



**Figure 5.** Projection of two-year-aged brandies aged in chestnut barrels and low molecular weight phenolic compounds and furanic derivative contents and general equilibrium in the space defined by the first and second principal components: (●) brandies; (○) compounds.

increase of this compound, with significant differences between any toasting degrees. The scopoletin content increases at QM and decreases at QF, although the QF content is higher than the QL content.

The effect of heat treatment on coumarins has never been studied. Thus, further experiments are required to understand the mechanisms involved in their formation and degradation.

In a global analysis of the results it is possible to verify that the difference between brandies aged in QM and QF chestnut barrels is not so evident. This could be due to the characteristic empiricism of heat treatment (Lavergne et al., 1990; Sarni et al., 1990; Cantagrel et al., 1992; Chatonnet et al., 1993), the many parameters of which remained uncontrolled, increased by the use of chestnut wood.

This is confirmed by the phenogram of UPGMA clustering (Figure 4), which illustrates the existence of two clusters: one contains the three brandies corresponding to QL barrels and the other includes the brandies aged in QM and QF barrels, which are not so perfectly separated.

The first and second components of the principal component analysis (Figure 5), which accounted for 72.7 and 11.3%, respectively, of the total variance, make the splitting of those two main clusters QL and QM–QF. Phenolic aldehydes, umbelliferone, ellagic acid, and ferulic acid are the most important extractable com-

pounds that distinguish the two-year-aged brandies in chestnut barrels belonging to those clusters.

## CONCLUSIONS

This study, for the first time, provides specific information about the chemical characterization of chestnut wood and the brandies aged in chestnut wood barrels.

The predominance of gallic acid among the analyzed extractable compounds both in chestnut wood and in corresponding aged brandies is remarkable.

The heat treatment has a very significant influence on the majority of low molecular weight extractable compounds analyzed (HMF, 5-methylfurfural, phenolic aldehydes, ellagic acid, gallic acid, vanillic acid, and umbelliferone) in two-year-aged brandies in chestnut barrels. Thus, it could be responsible for the related sensorial properties of aged brandies and greatly affect their general balance.

As the temperature increases, the increment of syringyl-type compounds (sinapaldehyde and syringaldehyde) is much higher than those of guaiacyl-type compounds (coniferaldehyde and vanillin) in these aged brandies.

However, assuming that syringyl units have a higher sensitivity toward oxidation, it can mean that in this initial stage of the aging process, also in chestnut barrels, the extractive phenomenon supplants the oxidative phenomenon, although the extraction process already involves some oxidation.

In a global analysis of the results it is possible to verify that the difference between brandies aged in medium and strong toasted chestnut barrels is not clear. This could be due to the characteristic empiricism of heat treatment, which must be suitably studied.

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