Variation of Extractable Compounds and Lignin Contents in Wood Fragments Used in the Aging of Wine Brandies

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Aging systems of wine brandies have been a target of investigation to reduce the costs and aging time. In this study, the extractives and Klason lignin contents of wood fragments used in the aging of wine brandies in stainless steel tanks were evaluated. Two types of wood fragments, known as staves and tablets, and two wood botanical species, Limousin oak (*Quercus robur* L. from the Limousin region of France) and Portuguese chestnut (*Castanea sativa* Mill.), with heavy toasting levels were used. The wood extractive and Klason lignin contents were analyzed before and 30 months after the aging of wine brandy. The results showed that the chestnut wood presented the highest content of extractives, while the Klason and total lignin contents were higher in the oak wood. A highly significant effect from the tablets was found on the extractives and Klason lignin contents, while the soluble lignin content was more affected by the staves. Oxygenation of the wine brandies during the aging process negatively affected the release of extractives and lignin from the wood to the brandy, and therefore will impact the overall quality of the brandy.

Keywords: Portuguese chestnut; Limousin oak; Wood extractives; Lignin content

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INTRODUCTION

During the aging process, wine brandy remains in wooden barrels for a period of time, during which its sensory properties, such as color, aroma, and flavor, are enhanced as a result of its contact with the wood (Canas *et al*. 2000a; Belchior *et al*. 2001; Caldeira *et al*. 2002; Caldeira *et al*. 2006), which increases its overall quality (Caldeira *et al*. 2006b). The chemical and sensory modifications of the brandy are mainly affected by the type of wood and the wood heat treatment (Rabier and Moutounet 1991; Canas *et al*. 1999, Belchior *et al*. 2001; Caldeira *et al*. 2006b, 2010).

Wood presents several anatomic and physicochemical characteristics that vary according to the botanical species, the geographical origin, and the cooperage operations (seasoning and heat treatment). These have a significant impact on the quality and composition of aged brandies (Belchior *et al*. 1998; Canas *et al*. 1999, 2000b; Caldeira *et al*. 2002; Canas *et al*. 2004; Caldeira *et al*., 2006a; Canas *et al*. 2006). The specific characteristics of macromolecules such as lignin, cellulose, and hemicelluloses in the wood have a great influence on the volatile and phenolic composition of the toasted wood. Indeed, the toasting process applied to the wood causes the disruption of chemical

bonds in cellulose, hemicelluloses, lignin, polysaccharides, and lipids, resulting in degradation or compositional changes, which induce an important modification of wood chemical composition (Canas *et al.*, 1999; Caldeira *et al.*, 2006a; Canas *et al.* 2007; Fernández de Simón *et al*. 2009; Van Jaarsveld *et al*. 2009).

Scientific research has been primarily focused on species of oaks from France (*Q. robur* L. and *Q. sessiliflora* Salisb.) and North America (*Q. alba* L.), while there is less knowledge concerning other types of wood and other geographical origins. A Portuguese research team (Canas *et al.* 1999; Belchior *et al.* 2001; Caldeira *et al*. 2006b, 2010) revealed the potential of Portuguese oak for the aging of wine brandies. Similarly, these studies demonstrated the suitability of other kinds of wood, including chestnut wood (*C. sativa* Mill.), for the same purpose.

The traditional aging system is a costly and time-consuming technique due to the high cost of the barrel and the long aging time of brandy. To minimize this problem, research has been conducted with different technologies, including the introduction of wood pieces (chips, staves, or other types of fragments) in brandies stored in stainless steel tanks. These techniques are permitted with oak wood and have been widely studied in the aging of wines, whereas for wine brandies, as well for the use of chestnut wood in the aging of wines and brandies this practice is still unauthorized and studies are scarce.

In the traditional system, several organic compounds of different chemical families, including furanic compounds, carboxylic acids, phenolic aldehydes, lactones, sugars, phenolic acids, coumarins, lignans, and tannins, are released from the wood to the wine brandy (Puech *et al*. 1984). The first studies of wood fragments, as an alternative system for the aging of wine brandy (Belchior *et al*. 2003; Canas *et al*. 2009; Caldeira *et al.* 2010), showed significant differences between the amounts of extractable wood compounds in the brandies aged in alternative systems and those aged using the traditional system.

The wood extractives can be classified according to their function and location in the tree and also according to their polarity and solubility in different solvents (Sjöström and Alén 1999). In this work, the term "extractives" will be used to identify non-structural components of wood that can be extracted with solvents classified as neutral and lipophilic (water-insoluble) or hydrophilic (water-soluble) (Fengel and Wegener 1989; Sjöström and Alén 1999). The lipophilic extractives are also called “resin timber” and can be extracted using organic solvents (diethyl ether, petroleum ether, dichloromethane, acetone, ethanol, methanol, or toluene). Non-polar solvents, such as dichloromethane, extract non-polar compounds such as grease, phenolic compounds, and less polar resins. More polar solvents, such as ethanol, extract more polar compounds such as sugars and more polar phenolic compounds. Ethanol and benzene allow for the extraction of fat and some resins, such as a gum timber. Hot water is used for the extraction of tannins, gums, sugars and colorants.

The natural extractable organic compounds from oak wood belong to a large number of chemical families: phenolic compounds, including lignans, coumarins, tannins, phenolic acids, phenolic aldehydes; phenylketones; acids; carbohydrates; volatile compounds, including terpenes, noisoprenoides, lactones, and furanic aldehydes; carotenoids; and steroids (Mayer *et al*. 1967; Masuda and Nishimura 1971; Nishimura *et al*. 1983; Nomdedeu *et al*. 1988; Puech and Moutonet, 1988; Puech *et al*. 1989; Sefton *et al*. 1990; Marco *et al*. 1994; Garcia-Romero *et al*. 1998; Masson *et al*. 2000).

In spite of the fact that fewer studies have been performed on chestnut wood, several extractable compounds from different chemical families have also been identified (Mayer *et al*. 1967; Canas *et al*. 2000; Caldeira *et al*. 2006a).

The aim of this study was to evaluate the amount of extractives in dichloromethane, ethanol, and water obtained from the different types of wood fragments known as tablets and staves, which were used in the aging of brandies (Caldeira *et al.* 2010). This study also intended to evaluate the variation in lignin solubility in the same types of fragments.

MATERIAL AND METHODS

Experimental Design and Sampling

Experiment 1

To evaluate the influence of the aging system, a factorial experiment was conducted. Two different wood botanical species were used: Portuguese chestnut wood, designated "C" (*Castanea sativa* Mill.), and one French oak wood, designated "Q" (*Quercus robur* L.), from the Limousin region. Two aging systems were used for the aging of brandy: wood staves (S) and wood tablets (T) in 40-L stainless steel tanks. The wood staves with 40 cm x 10 cm x 3 cm, and the tablets with 7 cm x 3 cm x 0.8 cm were manufactured by J.M. Gonçalves cooperage (Palaçoulo, Portugal). The staves were heated over a fire of wood offcuts and the tablets were heated in an oven during 25 min, both with heavy toasting level.

The quantity of the wood staves and the tablets was determined to reproduce the surface area-to-volume ratio of a 650-L wooden barrel. The wood samples were analyzed before contact with the wine brandy (0) and after 30 months of aging (30). Four replicates from the eight wood experimental units (two woods x two aging systems x two aging times) were taken and analyzed.

The same freshly distilled Lourinhã wine brandy was aged in different ageing systems. The composition of the wine distillate was as follows: ethanol content - 78.7% v/v; total acidity - 11 g acetic acid/hL A.E. (absolute ethanol); acetaldehyde - 1.65 g/hL A.E.; ethyl acetate – 113.65 g/hL A.E.; methanol – 78.21 g/hL A.E.; higher alcohols – 395.3 g/hL A.E.

Experiment 2

To evaluate the effect of oxygenation, another experiment was performed with chestnut wood: 40-L stainless steel tanks with chestnut wood tablets subjected to oxygenation (CT30O2) were studied and compared with the same kind of tablets without oxygenation (CT30).

Four replicates from the two wood experimental units (with and without oxygenation) were taken and analyzed after 30 months of aging. Oxygenation was performed by the application of air with a specific device (consisting of a 50-mL syringe attached to a precision "Masterflex" tube with a filter for air spray at the other end) at the mid-height of the tanks: 150 mL of air after 60, 90 and 120 days, and 200 mL of air after 180 and 360 days of aging.

Chemical Analysis

The wood samples were milled, and the granulated material was screened with a vibratory seining apparatus using standard tile screens. The 40- to 60-mesh granulometric fraction was used for the chemical analysis.

Extraction with organic solvents and water was performed in a Soxtec System HT 1043 Extraction Unit apparatus, according to TAPPI T 204 cm-07 standards. The samples were extracted successively with dichloromethane, ethanol, and water. Samples were placed in thimbles (26 mm diameter x 60 mm length), and extracts were collected in aluminum extraction cups.

In this method, 2 g of each dried sample was extracted using 40 mL of dichloromethane at 110 °C for 1 h, followed successively with ethanol, then water, changing the temperature to 160 ºC and 200 ºC, respectively. All analyses were conducted on quadruplicate aliquots. The results are reported as a percentage of the original oven-dry sample mass.

The first solvent is a non-polar solvent to extract non-polar compounds such as grease, phenolic compounds, and less polar resins; the second one, a more polar solvent, extracts more polar compounds like sugars and more polar phenolic compounds; finally, the hot water extracts tannins, gums, sugars, and colorants. The total extractives content is the sum of the extraction with dichloromethane, ethanol, and water.

Klason and acid-soluble lignin contents were determined in the extracted material according to TAPPI T 222 om-11. The extractive-free wood (0.333 g) was pre-hydrolyzed with sulfuric acid (72%, 5.0 mL) at 20 ºC for 2 h, followed by dilution and autoclaving for 1 h at 120 ºC to complete the hydrolysis. Klason lignin was determined as the mass of the solid residue after drying at 103 ºC ± 2 ºC. The acid-soluble lignin was determined on the combined filtrate by measuring the absorbance at 205 nm using a UV/VIS spectrophotometer. Total lignin content was calculated as the sum of the Klason lignin and acid-soluble lignin contents.

Statistical Analysis

A two-way analysis of variance (ANOVA) was performed for Experiment 1 to analyze the effects of the wood botanical species (2 levels: chestnut wood - C and oak wood - Q), the aging system (2 levels: staves - S and tablets - T), and the aging time (2 levels: 0 months - 0 and 30 months - 30) as fixed factors.

In Experiment 2, a one-way ANOVA was performed, with a Schefée post-hoc test with 95% confidence. In the results, an equal letter (a) is attributed to mean values that are not statistically different.

The results were also subjected to a multivariate analysis (principal component analysis). All experimental data were analyzed using Statistics® from StatSoft.

RESULTS AND DISCUSSION

Extractives Content

The total extractable compounds of wood varied between 5.3 and 18.9% (Table 1). On average, this value is higher than the 10% reported by Fengel and Wegener (1989). This result could be a consequence of the wood toasting required for the aging process of wine brandy. Strong toasting increases the content of various extractable compounds (Canas *et al*. 1999). Margarido (2009) found different values for the

extractives contents of *Castanea sativa* (16.1%) and *Quercus alba* (13.3%). However, the extraction method was different, as well as the botanical origin, the stand location, and the age of the tree, all of which determine the extractives content (Canas *et al.* 2000b; Mosedale and Savill 1996).

Table 1. Extractives Contents of Analyzed Wood Samples

	Code	Dichloromethane (%)	Ethanol (%)	Water (%)	Total extractives (%)
Experiment 1	QS0	0.61 ± 0.07c	9.10 ± 0.73e	5.12 ± 0.70c,d	14.83 ± 0.81c
	QT0	0.71 ± 0.04c	9.73 ± 0.38d,e	3.78 ± 0.73b,c	14.23 ± 1.06c
	QS30	0.29 ± 0.02a	5.06 ± 0.06c	6.23 ± 1.08d	11.58 ± 1.07b
	QT30	0.33 ± 0.00a	3.33 ± 0.08a	1.65 ± 0.05a	5.31 ± 0.08a
	CS0	0.43 ± 0.05b	11.34 ± 1.39e	6.23 ± 1.28d	18.00 ± 0.16d
	CT0	0.67 ± 0.10c	15.81 ± 1.01f	2.38 ± 0.46a	18.85 ± 0.65d
	CS30	0.31 ± 0.01a	4,49 ± 0.08b	5.82 ± 0.31d	10.61 ± 0.29b
	CT30	0.28 ± 0.01a	4.03 ± 0. 07a,b	1.57 ± 0.41a	5.88 ± 0.45a
Experiment 2	CT30	0.28 ± 0.01a	4.03 ± 0. 07a	1.57 ± 0.41a	5.88 ± 0.45a
	CT30O_2	0.19 ±0.03b	5.61 ±0.07b	1.58 ±0.37a	7.38 ±0.32b

Results are represented as mean ± standard deviation.
Means with the same letter in the same columns do not differ significantly ($p<0.05$).
The analysis was made in separate for Experiment 1 and Experiment 2.

The wood samples that had not been in contact with wine brandy (aging time of 0 months) presented higher extractives contents than the wood samples that had undergone 30 months of aging (Table 1). This result was expected and confirms the extraction of compounds that occurs during the aging of wine brandy (Canas *et al.* 2002; Viriot *et al*. 1993).

Ethanol extracts more polar compounds such as phenolic compounds and sugars. The ethanol extract of chestnut wood released more extractable compounds into the wine brandy after 30 months. This explains the remarkable contribution that phenolic compounds have in the aging process of wine brandy (Viriot *et al*. 1993).

Compounds extracted with water (namely, tannin, sugars, and colorants) represented the second highest concentration. It was also observed that the tablets released more extractable compounds into the wine brandy than the staves did, probably due to a more intense toasting of the former (Table 1).

Furthermore, chestnut wood tablets used in the aging of brandies subject to oxygenation presented higher total extractives than those used in a similar system without oxygenation. This result reflects a lower extraction rate in the presence of oxygen, which is in accordance with other outcomes of aged brandies (Canas *et al*. 2009).

The results of the analysis of variance of Experiment 1 (Table 2) showed that aging time was a highly significant factor explaining the variation in the results. A total of 73% of the variability for the extract with dichloromethane and 69% of the total variability for the extract with ethanol was due to aging. This result was expected because the enrichment of wine brandy with extractable compounds during the contact with the wood is well described (Canas *et al.* 2002, 2013).

For the extracts with dichloromethane and ethanol, the differences between the botanical species were highly significant, respectively, and for both extracts, the interaction (aging system x aging time) also was highly significant. This result can be

justified by a greater release of wood compounds into the wine brandy by chestnut wood than by oak wood, which is in accordance with previous results (Canas *et al.* 2002).

The aging system was a highly significant factor (79% of the total variation) for the extractable compounds with water (*e.g.*, sugar and tannins). The tannins are easily degraded with toasting (Hale *et al*. 1999), so it is possible to conclude that the tablets are more affected by the toasting process than the staves and therefore presented lower tannin contents at the beginning of the aging process.

Finally, the results confirmed that chestnut wood was richer in extractives and allowed greater extraction during the aging process. The aging system influences the release of extractable compounds into the wine brandy. The tablets seemed to be more permeable, which may favor a more intense toasting than in the staves, originating from greater anatomical and structural changes (Boeglin *et al*. 1993; Hale *et al*. 1999) and leading to increased permeability and accessibility to solvents. However, the wine brandies that aged in contact with these tablets had lower dry extracts and a lower total polyphenol index than those aged in contact with staves (Canas *et al*. 2009), so further studies will be needed to understand this process.

Table 2. Component Variance Analysis for the Total Extractives Content of Wood Samples (Experiment 1)

Variables	Source	DF	Sig	Var (%)
Dichloromethane (%)	Species (S)	1	0.003 **	3.1
	Aging system (AS)	1	0.000 ***	5.6
	Aging time (AT)	1	0.000 ***	73.3
	SxAS	1	0.412 n.s.	0.0
	SxAT	1	0.028 *	2.9
	ASxAT	1	0.000 ***	9.8
	Residual	25		5.2
Ethanol (%)	Species (S)	1	0.000 ***	5.7
	Aging system (AS)	1	0.012 *	0.6
	Aging time (AT)	1	0.000 ***	68.9
	SxAS	1	0.000 ***	4.1
	SxAT	1	0.000 ***	10.8
	ASxAT	1	0.000 ***	8.5
	Residual	25		1.5
Water (%)	Species (S)	1	0.442 n.s.	0.0
	Aging system (AS)	1	0.000 ***	78.7
	Aging time (AT)	1	0.035 *	1.6
	SxAS	1	0.040 *	3.0
	SxAT	1	0.853 n.s.	0.0
	ASxAT	1	0.001 **	10.0
	Residual	25		6.6
DF – degrees of freedom; Sig. – significance level; Var – Variance percentage; n.s. – not significant, p > 0,05; * Significant, 0.01 < p <0.05; ** very significant, 0.001 < p < 0.01; *** highly significant, p < 0.001				

Lignin Content

Table 3 summarizes the results of the lignin content obtained in the samples under study.

Table 3. Lignin Content of Analyzed Wood Samples.

	Code	Klason lignin (%)	Soluble lignin (%)	Total lignin (%)
Experiment 1	QS0	44.2 ± 3.1b	3.5 ± 0.1e	47.7 ± 3.1b
	QT0	59.0 ± 3.4c	2.1 ± 0.0c	61.1 ± 3.4c
	QS30	30.4 ± 2.2a	3.2 ± 0.1d	33.6 ± 2.2a
	QT30	59.9 ± 5.2c	1.1 ± 0.0a	61.0 ± 5.2c
	CS0	39.9 ± 7.3b	3.5 ± 0.1e	43.4 ± 7.3b
	CT0	49.2 ± 5.7b	2.0 ± 0.0c	51.2 ± 5.7b
	CS30	33.2 ± 3.5a	3.1 ± 0.1d	36.3 ± 3.5a
	CT30	44.6 ± 1.6b	1.5 ± 0.0b	46.1 ± 1.6b
Experiment 2	CT30	44.6 ± 1.6a	1.5 ± 0.0a	46.1 ± 1.6a
	$CT30O_2$	50.7 ± 4.2b	1.4 ± 0.0b	52.1 ± 4.2b

Results are represented as mean ± standard deviation.
Means with the same letter in the same columns do not differ significantly ($p<0.05$).
The analysis was made in separate for Experiment 1 and Experiment 2.

The oak wood presented higher lignin content than the chestnut wood. The Klason lignin content in all toasted samples was generally higher (higher than 30%) than that reported in the literature for untoasted wood (Fengel and Wegener 1989).

During the aging process, there was a decrease in the lignin content in the wood. The observed reductions correspond to the values reported by Puech *et al.* (1984) for the decrease occurring in oak wood barrels (3 to 5.8%) during 10 years of wine brandy aging. Furthermore, the oak staves released more compounds into the wine brandy than the chestnut staves did.

Table 4 summarizes the results of the ANOVA for the soluble lignin and Klason lignin of the analyzed wood.

Table 4. Component Variance Analysis for the Total Extractives Content of Wood Samples (Experiment 1)

Parameters	Source	DF	Sig	Var (%)
Klason lignin (%)	Species (S)	1	0.000 ***	7.8
	Aging system (AS)	1	0.000 ***	52.7
	Aging time (AT)	1	0.000 ***	8.5
	SxAS	1	0.000 ***	16.3
	SxAT	1	0.957 n.s.	0.0
	ASxAT	1	0.002 **	8.3
	Residual	25		6.4
Soluble lignin (%)	Species (S)	1	0.059 n.s.	0.0
	Aging system (AS)	1	0.000 ***	85.8
	Aging time (AT)	1	0.000 ***	10.4
	SxAS	1	0.034 *	0.4
	SxAT	1	0.008 **	0.7
	ASxAT	1	0.000 ***	2.0
	Residual	25		0.7

DF – degrees of freedom; Sig. – significance level; Var – Variance percentage; n.s. – not significant, $p > 0.05$; * Significant, $0.01 < p < 0.05$; ** very significant, $0.001 < p < 0.01$; *** highly significant, $p < 0.001$

The tablets had significantly higher concentrations of lignin than the staves did. The aging system is a highly significant factor that explained 53% and 86% of the total

variance for Klason lignin and soluble lignin, respectively. The aging time was also highly significant, but only explained a low percentage of the total variance.

Thus, the results obtained for extractives and lignin in Experiment 1 suggest that the extraction that occurred in each aging system (staves or tablets) was quite different. Accordingly, the contents of volatile phenols, phenolic aldehydes, phenyl ketones, and some phenyl alcohols, which are mainly formed from lignin thermodegradation and identified in toasted wood (Canas *et al.* 1999; Caldeira *et al.* 2006a), presented significant differences in the corresponding brandies aged with staves or with tablets (Canas *et al.* 2009; Caldeira *et al.* 2010). These compounds resulting from the thermal degradation of lignin contribute to smoke or spiced (methoxylated volatile phenols) and vanilla (phenolic aldehydes) aromas (Caldeira *et al.* 2008) and could explain some sensory differences verified in the brandies aged in the different systems (Caldeira *et al.* 2010).

Concerning the oxygenation effect (Experiment 2), a high level of lignin in the chestnut tablets used in the aging of brandies subject to oxygenation in comparison with those used in a similar system without oxygenation was verified. Similar to the results for total extractives, this result demonstrated a lower extraction rate in the presence of oxygen, which is also in accordance with the results obtained in the corresponding brandies (Canas *et al*. 2009).

Principal Component Analysis

Results of principal component analysis using data from wood without contact with the wine brandy are shown in Fig. 1. Only the wood samples on the plane of the two main factors were projected, which explains 80.8% of the total variation. There was a clear separation of samples by aging system and wood species.

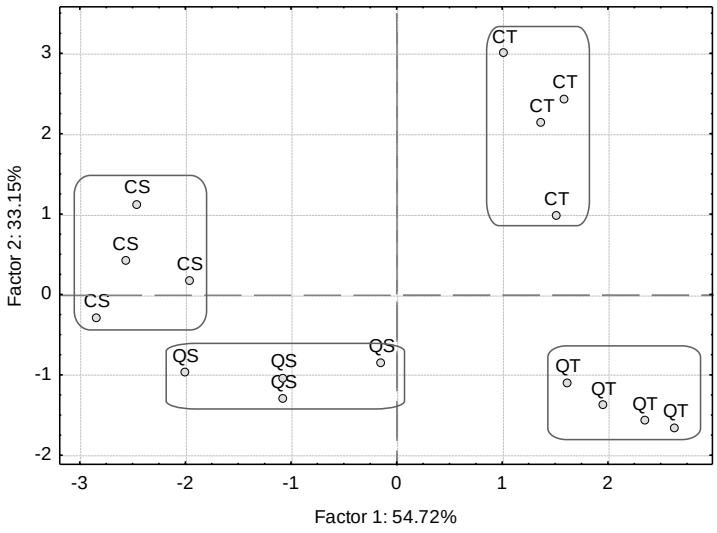

Fig. 1. Projection of the wood samples on the plane of the two main factors resulting from the principal component analysis for all measured chemical parameters of the wood samples without contact with the wine brandy. C – Chestnut; Q – Oak; S – Staves; T – Tablets

As observed previously, the highest difference found considering the overall chemical composition for the aging system (tablets *versus* staves) was related to a higher toasting in the tablets caused by their smaller size and thickness, even though the toasting conditions were similar. Another important outcome was the observed difference

between the wood species, with higher performance of the chestnut wood, as reported in other studies (Canas *et al*. 1999; Canas *et al*. 2000; Caldeira *et al*. 2002, 2010).

Figure 2 shows the projection of the samples resulting from the principal component analysis using data from the wood samples from two species, two aging systems, and the effect of aging time, which explain 88.7% of the total variation. The separation by the botanical species is again obvious, as is the different behavior of both species in relation to the performance of the extractable and lignin content migration during the aging process.

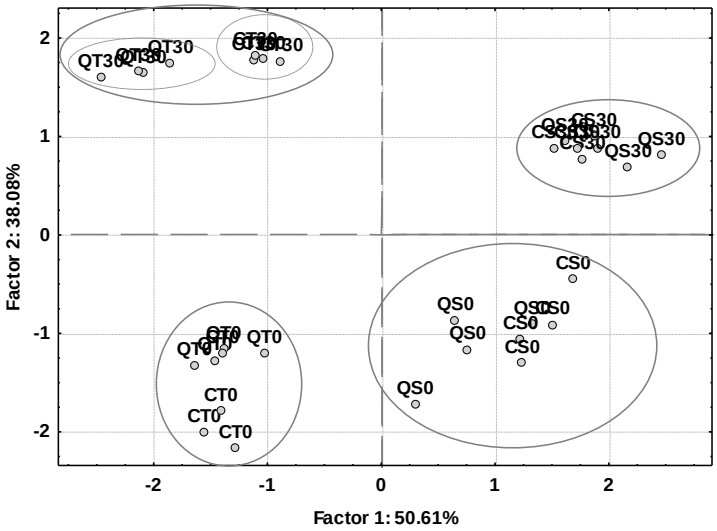

Fig. 2. Projection of the wood samples on the plane of the two main factors resulting from the principal component analysis for all measured parameters for the aging system and aging time. C – Chestnut; Q – Oak; S – Staves; T – Tablets; 0 - before contact with the wine brandy; 30 - after 30 months of aging

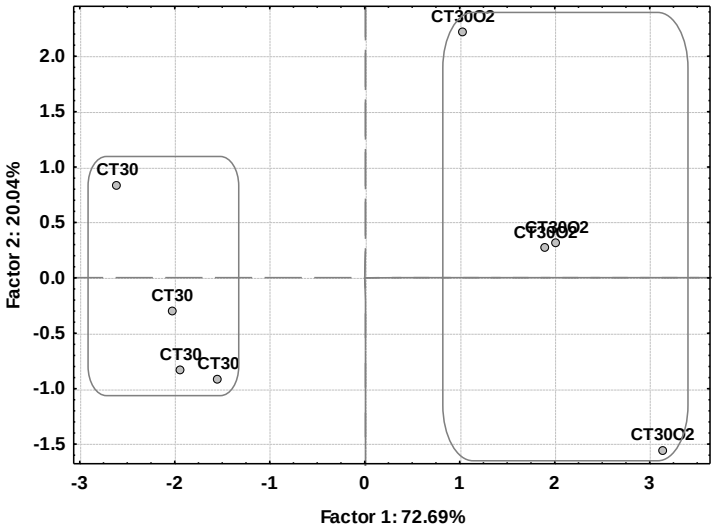

Fig. 3. Projection of the wood samples on the plane of the two main factors resulting from the principal component analysis for all measured parameters comparing the effect of the oxygen. C – Chestnut; T – Tablets; 30 - after 30 months of aging; O – with oxygen

The global effect of oxygenation on the wood chemical composition is shown in Fig. 3. The two main factors explained 92.7% of the total variation and created a separation between the samples of chestnut wood tablets used in the aging of brandies with oxygenation and those used in a similar system without oxygenation. The most important characteristics to distinguish the two kinds of samples were the total extractives content and the total lignin content, which were both higher in the chestnut wood tablets subject to oxygenation.

CONCLUSIONS

1. The characteristic profile of extractives and lignin of toasted wood was completely different according to the wood species (chestnut or oak) and the aging system (staves or tablets).

2. The extraction pattern of the compounds during the aging of the brandies was also quite different for the two aging systems.

3. The chestnut wood presented the highest content of extractives and favored their release during aging, while the Klason and total lignin contents were higher in the oak wood.

4. The tablets had a highly significant content of extractives and Klason lignin, but the staves had a higher impact on the release of lignin.

5. The oxygenation of the wine brandies during the aging process negatively affected the release of extractives and lignin from the wood to the brandy and therefore will impact on the overall quality of the brandy.

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