Ciência Téc. Vitiv. 32(2) 93-101. 2017

QUERCUS HUMBOLDTII (COLOMBIAN OAK): CHARACTERISATION OF WOOD PHENOLIC COMPOSITION WITH RESPECT TO TRADITIONAL OAK WOOD USED IN OENOLOGY

QUERCUS HUMBOLDTII (CARVALHO COLOMBIANO): CARACTERIZAÇÃO DA COMPOSIÇÃO FENÓLICA DA MADEIRA RELATIVAMENTE ÀS MADEIRAS DE CARVALHO TRADICIONALMENTE USADAS EM ENOLOGIA

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(Received 08.06.2017. Accepted 29.08.2017)

SUMMARY

The use of new oak barrels and the demand for oak wood in oenology is increasing. Thus, it is necessary to search for new wood sources to supply the current demand in cooperage. The aim of this work was to study the composition of ellagitannins and low molecular weight phenolic compounds (LMWP) by HPLC-DAD of green wood *Quercus humboldtii Bonpl*. (Colombian), compared to the species typically used in cooperage: *Quercus sessiliflora* Salisb. (French and Romanian) and *Quercus alba L.* (USA). In Colombian oak wood, the same LMWP and ellagitannins as in the traditional species were identified. The most abundant LMWP was ellagic acid, and its concentration was lower in *Q. humboldtii* and *Q. alba* than in *Q. sessiliflora*, so these two presented a lower content of phenolic acids. As regards phenolic aldehydes, Colombian oak wood only showed significant differences in the content of coniferyl and sinapic aldehydes in relation to French oak. Finally, the total ellagitannin content of *Q. humboldtii* was lower than that of European oaks and similar to that of American oak (*Q. alba*). None of the ellagitannins studied presented significant differences compared to *Q. alba*. Therefore, *Q. humboldtii* wood was more similar in terms of phenolic composition to *Q. alba* than to *Q. sessiliflora*.

RESUMO

O uso de novos barris de carvalho e a procura de madeira de carvalho em enologia estão aumentando. Assim, torna-se necessária a investigação de novas fontes de madeira para satisfazer a atual procura pela tanoaria. O objetivo deste trabalho foi estudar a composição de taninos elágicos e compostos fenólicos de massa molecular baixa (LMWP) por HPLC-DAD de madeiras verdes de *Quercus humboldtii Bonpl*. (colombiano), em comparação com espécies tipicamente usadas em tanoaria: *Quercus sessiliflora* Salisb. (francês e romeno) e *Quercus alba L.* (EUA). Na madeira de carvalho da Colômbia, foram identificados os mesmos LMWP e taninos elágicos do que nas espécies tradicionais. O LMWP mais abundante foi o ácido elágico, e sua concentração foi menor em *Q. humboldtii* e *Q. alba* do que em *Q. sessiliflora*, portanto estas duas madeiras apresentaram menor teor de ácidos fenólicos. Em relação aos aldeídos fenólicos, a madeira de carvalho colombiano mostrou diferenças significativas no teor de aldeídos coniferílico e sinápico em relação ao carvalho francês. Finalmente, o conteúdo total de taninos elágicos de *Q. humboldtii* foi inferior ao dos carvalhos europeus e semelhante ao do carvalho americano (*Q. alba*). Nenhum dos taninos elágicos estudados apresentou diferenças significativas relativamente a *Q. alba*. Assim, a composição fenólica da madeira de *Q. humboldtii* assemelha-se mais à da madeira de *Q. alba* do que à de *Q. sessiliflora*.

Key words: *Quercus humboldtii*, oak heartwood, ellagitannins, low molecular weight phenolic compounds.
Palavras-chave: *Quercus humboldtii*, madeira de carvalho, taninos elágicos, compostos fenólicos de massa molecular baixa.

Article available at https://www.ctv-jve-journal.org or https://doi.org/10.1051/ctv/20173202093

INTRODUCTION

Currently, the ageing trends for wines are changing towards the use of newer oak barrels, and thus the demand for oak wood in oenology is increasing. For this reason, in recent years an imbalance between the amount of oak wood available and the number of barrels produced in France has been detected (Cadahía and Fernández de Simón, 2004; Cadahía *et al.*, 2008). This need for new sources of a quality wood supply for cooperage has led to looking into the possibility of utilising new alternatives to European (*Q. sessiliflora* and *Q. robur*) and American (*Q. alba*) oak wood, which are those most commonly used in oenology. More than 800 species exist; however, very few can be used in barrel making, because of their physical, mechanical and gustatory properties (Prida, 2002). Very few oaks fully meet these conditions, and those most used belong to the white oak group. In the last few years, other white oaks have been studied for use in oenology with the aim of comparing their characteristics with those of traditional oaks (*Q. robur*, *Q. sessiliflora* and *Q. alba)*, as is the case of *Q. pyrenaica* and *Q. faginea* (Canas *et al.*, 2000; Cadahía *et al.*, 2001a,b; Fernández de Simón *et al.*, 2006; Jordão *et al.*, 2007; Gonçalves and Jordão, 2009; Cabrita *et al.*, 2011; Gallego *et al.*, 2012).

An alternative source could be “white oak” (*Quercus humboldtii*) from Colombia, which is currently used for the ageing of alcoholic drinks such as Rum or Brandy (González and Baleta, 2010). This white oak is a neotropical species found in the three mountain ranges, from 750 m to 3450 m above sea level, in 18 departments of Colombian Andes (Antioquia, Bolívar, Boyacá, Caldas, Caquetá, Cauca, Chocó, Cundinamarca, Huila, Quindío, Risaralda, Nariño, Norte de Santander, Santander, Tolima, Valle del Cauca, Cesar and Córdoba). It is one of the main species in Colombian forests (Avella and Cárdenas, 2010), and its wood is traditionally used for making posts, railroad ties, handles for tools, wooden rollers, charcoal, and firewood (Argoti *et al.*, 2011). Currently, some cooperage companies that provide barrels made of this wood for ageing distilled beverages are proposing this type of wood to the wine industry, ensuring the same quality as the wood traditionally used in oenology. However, there is scarce cooperage information about *Q. humboldtii*, and previous studies have found that its evaluation could be of interest since its vanillin concentration is similar to that of *Q. faginea*, and it has a balanced syringaldehyde/vanillin relationship (González *et al.*, 2008; González and Baleta, 2010), which are potentially good properties for wine ageing. Moreover, Argoti *et al.* (2011) showed that this oak wood had a good radical-scavenging activity (DPPH and superoxide assays), even higher than commercial rosemary oleoresin (reference material), proposing this species for future investigation in order to identify the compounds responsible for their activity. On the other hand, to our knowledge there is no information characterising other phenolic compounds in *Q. humboldtii* oak heartwood, so this study can provide deeper knowledge of this wood.

Low molecular weight phenolic compounds (LMWP) are important components of heartwood and contribute to colour, astringency and bitterness in wines (Garde-Cerdán and Ancín-Azpilicueta, 2006). One of the most important extractable compounds besides LMWP are ellagitannins. In oak wood, these compounds are responsible for its hardness and the avoidance of microbiological alterations (Prida, 2002). During wine ageing, they behave as antioxidants thanks to their great ability to consume oxygen (Navarro *et al.*, 2016, García-Estévez *et al.*, 2017). In addition, they accelerate anthocyanin and tannin condensation, which promotes wine flavanol polymerization (flavanoellagitannins) (Cadahía *et al.*, 2008). For this reason, they may contribute to colour stability, astringency, bitterness and wine flavour (Stark *et al.*, 2010; Michel *et al.*, 2011).

The first step to determine whether this new oak source may be of oenological interest is the study of its phenolic composition in green wood. Therefore, the aim of this work was to study the composition of ellagitannins and LMWP by HPLC-DAD of *Q. humboldtii* (Colombian) green wood, in relation to oak species traditionally used in cooperage, such as *Q. sessiliflora* (French and Romanian) and *Q. alba* (American).

MATERIAL AND METHODS

Wood samples

To carry out this study four different kinds of oak (origin and/or species) were used: *Q. sessiliflora* Salisb. (French and Romanian oak), *Q. alba L.* (American oak) and *Q. humboldtii Bonpl.* (Colombian oak). The geographical provenance of the different oaks used were: Vosges for French oak, Monte Semenic for Romanian oak, Pennsylvania for American oak, and North of the Colombian Andes for Colombian oak. French, Romanian, American and Colombian oaks were imported as green wood to the cooperage “Tonelería Nacional Chile LTDA” in Chile. The average annual growths of the wood used were: 1-2 mm in *Q. sessiliflora* oak, 1.5-2.5 mm in *Q. alba* and 3.5-4.5 mm in *Q. humboldtii*. Three lots were taken from each green wood, obtaining three repetitions per wood. Six staves of each lot were taken from the different parts of the pieces from the centre to the headboards. The selected staves were ground, sieved and mixed, taking the sawdust ranging in size from 0.80 to 0.28 mm. The samples were maintained at ambient room conditions (20°C, 55% relative humidity), so all of them had similar moisture content (MC =10%). A total of 12 sawdust samples were analysed (four kinds of wood with three repetitions).

Sample extraction

The sawdust samples (1 g) were extracted in 100 mL of methanol/water (1:1) in darkness for 24 h, following the method described by Fernández de Simón *et al.* (1996) for LMWP and by Fernández de Simón *et al.* (1998) for ellagitannins. After removal of the methanol in a rotary evaporator at a temperature below 40 °C, the aqueous solution was extracted with diethyl ether and ethyl acetate and then freeze-dried. The diethyl ether and ethyl acetate extracts were dried, dissolved in methanol/water (1:1) and used for the HPLC quantitative determination of LMWP, and the freeze-dried aqueous extract was used similarly for determining ellagitannins.

Standards

In the case of LMWP, standards were purchased from Fluka Chemie AG (Buchs, Switzerland) (gallic acid), Aldrich Chemie (Neu-Ulm, Germany) (vanillic acid, syringaldehyde and coniferaldehyde), Apin (ellagic acid), Chem Service (West Chester, PA) (syringic acid), Sigma Chemical (St. Louis, MO) (vanillin), Extrasynthèse (Genay, France) (sinapaldehyde). Ellagitannins, standards of vescalagin, castalagin, roburin A and E, and grandinin were kindly provided by Dr. A. Scalbert.

HPLC-DAD analyses of LMWP and ellagitannins

LMWP were analysed by the method described by Cadahía *et al.* (2001a) and the analysis of ellagitannins was performed according to the method of Cadahía *et al.* (2001b). An Agilent 1200 HPLC equipped with a diode array detector and with a C18 Hypersyl ODS (5 µm) column (20 cm × 4 mm i.d.), protected with a pre-column of the same material, were used. Elution conditions were modified as follows: flow rate, 1 mL/min; temperature, 30 °C; solvent A= H_2O/PO_4H_3 (999:1), solvent B= $MeOH/PO_4H_3$ (999:1).

LMWP and ellagitannins were detected at 325 nm (with a bandwidth of 150 nm). Chromatographic peaks were identified by comparing their retention time and the UV spectra with those of standards. Quantitative determinations were carried out by the external standard method. Roburins B-D were expressed as roburin A because they are also dimers. Each green wood were extracted in triplicate (wood samples section) and each one was analysed in duplicate (n=6).

Statistical analysis

LMWP and ellagitannins data were processed using variance analysis (ANOVA) using the SPSS Version 21.0 statistical package for Windows (SPSS, Chicago, USA). Differences between means were compared using Duncan test at 95% probability level. Principal component analysis (PCA), using Stagraphics Centurion 16.2.04, StatPoint Technologies, Inc. (Warrenton, United States), was also carried out to assess the relationship between chemical data and the different oak wood origins. Only two principal components were extracted according to the Kaiser criterion (eigenvalue>1).

RESULTS AND DISCUSSION

Low molecular weight phenolic compounds (LMWP)

Individual concentrations of LMWP are presented in Table I, which also shows the total concentration of phenolic acids and aldehydes from the different kinds of oak wood.

Table I

Low molecular weight phenolic compounds (μg/g of wood) obtained in the green wood of *Quercus sessiliflora* (French and Romanian oak), *Quercus alba* (American oak) and *Quercus humboldtii* (Colombian oak)

*Compostos fenólicos de massa molecular baixa (*μg/g *de madeira) obtidos na madeira verde de Quercus sessiliflora (carvalho francês e romeno), Quercus alba (carvalho americano) e Quercus humboldtii (carvalho colombiano)*

	Q. sessiliflora		***Q. alba***	***Q. humbolditti***
	French oak	Romanian oak	American Oak	Colombian oak
Acids				
Ellagic acid	560.73 ± 40.92 b	556.16 ± 110.26 b	352.72 ± 73.05 a	286.88 ± 80.58 a
Gallic acid	16.17 ± 6.89 a	20.79 ± 6.28 a	87.90 ± 108.18 a	77.60 ± 103.31 a
Syringic acid	8.32 ± 3.69 a	8.40 ± 3.08 a	6.09 ± 1.16 a	3.56 ± 2.70 a
Vanillic acid	6.66 ± 1.28 b	5.38 ± 1.65 a	6.18 ± 0.68 b	4.18 ± 1.40 a
Total acids	591.88 ± 41.68 a	591.17 ± 110.49 a	452.89 ± 65.43 a	372.22 ± 131.06 a
Aldehydes				
Coniferaldehyde	0.78 ± 0.56 a	3.69± 0.23 b	3.08 ± 0.56 b	2.52 ± 0.69 b
Sinapaldehyde	2.48 ± 1.00 a	4.98 ± 0.74 b	5.57 ± 1.83 b	4.90 ± 1.11 b
Syringaldehyde	8.50 ± 1.61 a	12.29 ± 2.34 a	14.40 ± 7.50 a	9.43 ± 8.68 a
Vanillin	2.79 ± 0.53 a	5.30 ± 1.29 ab	9..27 ± 3.62 b	6.33 ± 4.55 ab
Total aldehydes	14.55 ± 2.04 a	20.26 ± 2.78 ab	32.32 ±1.56 b	23.18 ±9.89 ab

Values are mean ± standard deviation (n = 6). Different letters in the same row indicate significant differences between different oaks ($p<0.05$).

Q. humboldtii green wood showed similar a concentration of total phenolic acids to *Q. sessiliflora* and *Q. alba* (Table I). The concentration of total phenolic aldehydes found in *Q. humboldtii* green wood was similar to that obtained in *Q. sessiliflora* and *Q. alba*. In addition, French oak presented lower total phenolic aldehydes than American oak (Table I), this result coincides with that observed by other authors (Cadahía and Fernández de Simón, 2004).

Focusing on the individual composition, *Q. humboldtii* wood presented the same compounds previously found in the oak wood traditionally used in oenology (*Q. sessiliflora*, *Q. robur* and *Q. alba*) (Miller *et al.*, 1992; Cadahía *et al.*, 2001a,b; Fernández de Simón *et al.*, 2006; Prida and Puech 2006; Zhang *et al.*, 2015), and in other oak wood studied over the last few years for their possible wine ageing potential such as *Q. pyrenaica* and *Q. faginea* of different origins (Fernández de Simón *et al.*, 1996; Cadahía *et al.*, 2001b; Caldeira *et al.*, 2006; Fernández de Simón *et al.*, 2006; Garcia *et al.*, 2012). Thus, the identified phenolic compounds in *Q. humboldtii*, as in other studied oaks, were phenolic acids, ellagic, gallic, syringic and vanillic, and phenolic aldehydes, coniferyl, sinapic, syringaldehyde and vanillin (Table I).

The most abundant phenolic acid found in *Q. humboldtii,* as in the traditional oak wood, was ellagic acid followed by gallic acid. The concentration of ellagic acid was significantly higher in *Q. sessiliflora* (French and Romanian) green wood than in *Q. alba* and *Q. humboldtii* oaks (560.73, 556.16, 352.72 and 286.88 μg/g of wood, respectively). These results are similar to those observed by different authors in green wood (Cadahía and Fernández de Simón, 2004) or in dried or toasted wood (Prida and Puech, 2006; Cabrita *et* *al.*, 2011) from *Q. sessiliflora* and *Q. alba* oaks. In addition, ellagic acid content was similar in *Q. humboldtii* and *Q. alba* green wood. However, the content of gallic acid was similar in all studied green oaks (*Q. sessiliflora*, *Q. alba* and *Q. humboldtii*) since no significant differences were observed. The concentration of syringic acid was statistically similar in all the green wood. However, the concentration of vanillic acid was significantly higher in French and American oak than in Romanian and Colombian wood.

The most abundant aldehyde found in all studied oak green wood was syringaldehyde. This result coincides with those observed in French, Romanian and American dry oak wood by Prida and Puech (2006). No significant differences were found in the syringaldehyde concentration among the species or origins of the studied oaks. Vanillin was the second most abundant phenolic aldehyde found in the samples. Its concentration in *Q. humboldtii* was statistically similar to those in *Q. sessiliflora* and *Q. alba;* however, its content was significantly higher in the American oak wood than in the French one (9.27 and 2.79 µg/g of wood respectively). Finally, coniferaldehyde and sinapic aldehyde contents were significantly lower in *Q. sessiliflora* from France, so the concentrations of these two compounds in *Q. humboldtii* were similar to those observed in Romanian and American oak wood.

As regards LMWP, the aldehyde content was higher than their respective acids. This result coincides with those observed by other authors in European oaks (Vivas *et al.*, 1998; Fernández de Simón *et al.*, 2006). As expected, the concentrations obtained showed a significant interindividual variability, since many factors have an influence on extractable composition even for the same oak wood origin. Several studies have shown great individual variability (Wilson and White 1986; Guilley *et al.*, 1999). The factors contributing to this variability are the botanical species, the individual tree, the age of the wood and the geographical origin, among others (Guilley *et al.*, 1999).

Ellagitannins

Concerning the green wood tannin composition from *Q. sessiliflora* (French and Romanian oaks), *Q. alba*, (American oak) and *Q. humboldtii*, (Colombian oak), Table II shows the total content and the detailed concentration. The main phenolic components analysed in *Q. humboldtii* were ellagitannins, with similar results to those found in other oaks traditionally used in oenology. *Q. humboldtii* green wood presented 1935.30 µg of ellagitannins versus 395.40 µg of low molecular weight phenols per gram of wood. In general, the ellagitannin concentration was lower than those recorded by Mosedale *et al.* (1996) and Fernández de Simón *et al.* (2006) but similar to those observed by Masson *et al.* (1995), Chatonnet and Dubourdieu (1998), Fernández de Simón *et al.* (1999) and Doussot *et al.* (2000). The ellagitannins analyzed were castalagin, grandinin, roburins A, B, C, D and E and vescalagin. In the case of roburins A and B, they were evaluated together since the separation of chromatographic peaks was not always possible. These eight ellagitannins were isolated and identified in the wood of *Q. sessiliflora* and *Q. Alba*, and also found in *Q. humboldtii*. The quantitative differences are clearly perceptible in Table II, where it can be observed that this oak wood (*Q. humboldtii*) presented a significantly lower concentration of total ellagitannins than the wood from *Q. sessiliflora.* However, no significant differences were found between this wood and that of *Q. Alba*. The fact that *Q. sessiliflora* contained higher amounts of the individual ellagitannins than *Q. alba* has been widely reported (Canas *et al.*, 2000; Cadahía *et al.*, 2001b). In addition, the concentration of ellagitannins is affected by a large number of interdependent factors, including the species (Canas *et al.*, 2000; Doussot *et al.*, 2002; Jordão *et al.*, 2007), forest origin (Doussot *et al.*, 2002; Jordão *et al.*, 2007), heartwood age (Matricardi and Waterhouse, 1999), grain coarseness (Jordão *et al.*, 2007) among others. Some authors (Masson *et al.*, 1995; Doussot *et al.*, 2002) reported that species discrimination and especially the species-provenance combination are the main factors determining tannin levels. Therefore, more studies about the different origin, anatomical aspect of this new oak source and ellagitannin concentration should be carried out.

The concentration of ellagitannins showed a strong interindividual variability, as occurred with the content of LMWP. This has also been described by other authors (Masson *et al.*, 2000) and explained by the same influential factors mentioned above. The most abundant ellagitannins in all the studied wood were castalagin, followed by vescalagin, and roburin D. Grandinin was the only one of all the studied ellagitannins without any significant differences among the different species and/or geographical origins. Regarding the other ellagitannins (Cast, Vesc, Rob A+ B, Rob C, Rob D and Rob E), *Q. humboldtii* wood presented the lowest concentration of all of them. Moreover, *Q. alba wood* did not present significant differences with respect to the Colombian oak in any of the identified ellagitannins (Table II).

Table II

Ellagitannin concentration (μg/g of wood) obtained in the green wood of *Quercus sessiliflora* (French and Romanian oak), *Quercus alba* (American oak) and *Quercus humboldtii* (Colombian oak)

*Concentração de taninos elágicos (*μg/g *de madeira) obtida na madeira verde de Quercus sessiliflora (carvalho francês e romeno), Quercus alba (carvalho americano) e Quercus humboldtii (carvalho colombiano)*

	Q. sessiliflora		***Q. alba***	***Q. humbolditti***
	French oak	Romanian oak	North American Oak	Colombian oak
Monomers				
Castalagin	3892.85 ± 951.02 b	4059.92 ± 1662.94 b	1189.63 ± 826.49 a	636.37 ± 657.11 a
Vescalagin	3604.30 ± 2701.25 b	2975.84 ± 1315.84 ab	695.49 ± 556.33 ab	317.28 ± 390.81 a
Pentosylated monomers				
Roburin E	780.03 ± 692.98 a	1724.02 ± 547.04 b	291.95 ± 236.50 a	165.86 ± 213.63 a
Grandinin	763.17 ± 576.92 a	1019.13 ± 549.43 a	378.03 ± 172.48 a	257.17 ± 168.60 a
Dimers				
Roburin A+B	820.53 ± 660.42 b	546.89 ± 322.46 ab	125.51 ± 13.53 ab	62.90 ± 88.83 a
Pentosylated dimers				
Roburin C	296.80 ± 84.49 b	205.14 ± 84.70 ab	127.89 ± 101.49 ab	68.70 ± 97.96 a
Roburin D	1716.00 ± 939.25 ab	2454.13 ± 815.70 b	674.43 ± 510.85 a	427.03 ± 488.21 a
Total ellagitannins	11873.68 ± 3378.67 b	12985.06 ± 2423.73 b	3482.87 ± 2577.45 a	1935.30 ± 395.40 a

Values are mean ± standard deviation (n = 6). Different letters in the same row indicate significant differences between different oaks ($p<0.05$).

Castalagin concentration was significantly higher in *Q. sessiliflora* green wood (French and Romanian oak) than in *Q. alba* and *Q. humboldtii* wood (3892.85, 4059.9, 1189.63 and 636.37 μg/g of wood, respectively, Table II). However, *Q. humboldtii* had a significantly lower vescalagin concentration than French green wood and its content was similar to that of Romanian and American oak. French oak wood showed a higher concentration of roburins A, B and C than the new wood (Colombian oak), without any significant difference to the rest of the studied wood. In addition, the contents of roburins D and E were higher in Romanian oak wood than in *Q. humboldtii* and *Q. alba*.

Principal component analysis (PCA)

Principal component analysis (PCA) was carried out to evaluate the discriminant power of these 16 compounds for the four kinds of oak wood studied. Table III reports the information concerning the first two main components of PCA. It shows the variables that presented the greatest correlations with each principal component, as well as the corresponding calculated component loadings. The first two components accounted for 56.05% to 18.11% of the total explained variance among samples from different origins. Figure 1 shows the distribution of samples into four groups of oak wood origin. It was found that the most significant parameters to differentiate between European oak wood and American oak wood were defined by function 1. Function 1 of PCA had a closer positive correlation with tannins, vanillic acid, syringic acid and ellagic acid, which defined the *Q. sessiliflora* (French and Romanian oak wood). On the contrary, *Q. alba* and *Q. humboldtii* (American and Colombian oak wood, respectively) were located in the negative side of the first principal component axis, defined by gallic acid and sinapaldehyde, syringaldehyde, vanillin and coniferaldehyde. The aldehydes differentiated the European wood, since the component 2 separated them, being Romanian oak wood closer to American oak, having more vanillin, syringaldehyde, sinapaldehyde and coniferaldehyde content than the French one. On the other hand, gallic acid principally defined *Q.alba* and *Q. humboldtii* since these oak were in the left side of the component 2.

Table III

Principal Component analysis results carried out with low molecular weight phenolic compounds and ellagitannins oak samples composition of different origin

Resultados da análise em Componentes Principais realizada com compostos fenólicos de massa molecular baixa e taninos elágicos das amostras de carvalho de diferentes origens

	Component 1	Component 2
Roburin A+B (Rob A+B)	0.3083	-0.1197
Roburin C (Rob C)	0.3199	-0.0197
Grandinin (Gran)	0.3117	0.0478
Roburin D (Rob D)	0.3273	0.0778
Vescalagin (Vesc)	0.3201	-0.0896
Roburin E (Rob E)	0.2942	0.1218
Castalagin (Cast)	0.3362	-0.0557
Gallic acid (Gal Ac)	-0.1862	-0.1245
Vanillic acid (Vani Ac)	0.2317	0.1545
Vainillin (Vani Al)	-0.0542	0.5373
Syringic acid (Sir Ac)	0.2937	0.1276
Syringaldehyde (Sir Al)	0.1007	0.5050
Coniferaldehyde (Con Al)	-0.0480	0.4663
Sinapaldehyde (Sin Al)	-0.1477	0.3522
Ellagic acid (Ela Ac)	0.2907	-0.1009
Cum Variance	**56.06**	**74.17**

CONCLUSIONS

If the results obtained so far are considered, it can be concluded that the phenolic composition in green wood from *Q. humboldtii* is qualitatively similar to that of *Q. sessiliflora* and *Q. alba*, only showing quantitative differences in some compounds. *Q. humboldtii* green wood presented statistically similar concentrations of total phenolic acids and aldehydes as *Q. sessiliflora* and *Q. alba*. In addition, this oak had a statistically similar concentration of total ellagitannins to *Q. alba*, although a significantly lower one than that of *Q. sessiliflora*. Colombian oak showed that the most abundant phenolic acids, aldehydes and ellagitannins were the same as in traditional oak wood (ellagic acid, gallic acid, syringaldehyde and castalagin), and without any significant differences in any of them with respect to American oak. Therefore, its wood phenolic composition was closer to that of American oak than to that of French oak. Finally, this wood seems to have an adequate composition as a new oak wood source for wine ageing, although it is necessary to continue the study of this wood species to confirm its potentialities for oenology.

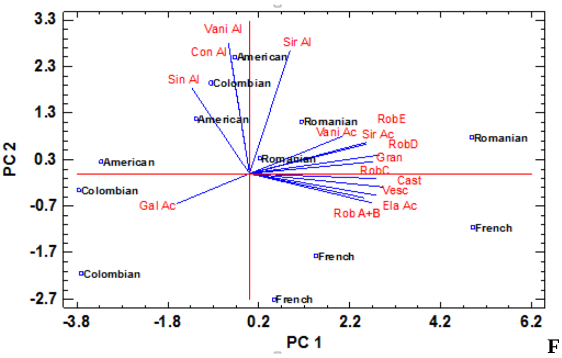

Figure 1. Principal Component analysis results carried out with low molecular weight phenolic compounds and ellagitannins oak samples composition from green wood of *Quercus sessiliflora* (French and Romanian oak), *Quercus alba* (American oak) and *Quercus humboldtii* (Colombian oak). The percentage of variance explained was 74.17% by component 1 and 2 (function 1 explaining 56.06% of the variance and function 2 explaining 18.11% of the variance). Roburin A+B (Rob A+B), Roburin C (Rob C), Grandinin (Gran), Roburin D (Rob D), Vescalagin (Vesc), Roburin E (Rob E), Castalagin (Cast), Gallic acid (Gal Ac), Vanillic acid (Vani Ac), Vanillin (Vani Al), Syringic acid (Sir Ac), Syringaldehyde (Sir Al), Coniferaldehyde (Con Al), Sinapaldehyde (Sin Al), Ellagic acid (Ela Ac).

Análise em Componentes Principais realizada compostos fenólicos de massa molecular baixa e taninos elágicos da madeira verde de Quercus sessiliflora (carvalho francês e romeno), Quercus alba (carvalho americano) e Quercus humboldtii (carvalho colombiano). A percentagem de variância explicada pelas componentes 1 e 2 foi de 74,17% (função 1 explicando 56,06% da variância e função 2 explicando 18,11% da variância

ACKNOWLEDGMENTS

This work was funded by Grant Nº 11150462 from Fondecyt, Chile. Thanks to the collaboration of Tonelería Nacional LTDA, Santiago de Chile. This paper has received funding from FEDER, Interreg España-Portugal Programme, under the framework of the project Iberphenol. We wish to thank the financial support given by CONICYT through BCH/Doctorado - 72170532.

REFERENCES

Argoti J.C., Salido S., Linares-Palomino P.J., Ramírez B., Insuastya B., Altarejos J., 2011. Antioxidant activity and free radical scavenging capacity of a selection of wild-growing Colombian plants. *J. Sci. Food Agric*., **91**, 2399– 2406.

Avella A., Cárdenas L.M., 2010. Conservación y uso sostenible de los bosques de roble en el corredor de conservación guantiva -

la Rusia - Iguaque, departamentos de santander y Boyacá, Colombia. *Colombia Forestal*, **1**, 5-25.

Cabrita M.J., Barrocas Dias C., Costa Freitas A.M., 2011. Phenolic acids, phenolic aldehydes and furanic derivatives in oak chips: American vs. French oaks. *S. Afr. J. Enol. Vitic*., **32**, 204–210.

Cadahía E., Fernández de Simón B., 2004. Utilización de roble español en el envejecimiento de vino. Comparación con roble francés y americano. 136 p. Ed: Instituto Nacional de Investigación Agraria y Alimentaria. Ministerio de Educación y Ciencia, Madrid.

Cadahía E., Fernández de Simón B., Poveda P., Sanz M., 2008. Utilización de *Quercus pyrenaica Willd.* de Castilla y León en el envejecimiento de vinos. Comparación con roble francés y americano. Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria. 175 p. Monografías INIA (ed), Serie Forestal, Madrid.

Cadahía E., Muñoz L., Fernández de Simón B., García-Vallejo M.C., 2001a. Changes in low molecular weight phenolic compounds in Spanish, French, and American oak woods during natural seasoning and toasting. *J. Agric. Food Chem*., **49**, 1790–1798.

Cadahía E., Varea S., Muñoz L., Fernández de Simón B., García-Vallejo M.C., 2001b. Evolution of ellagitannins in Spanish, French, and American oak woods during natural seasoning and toasting. *J. Agric. Food Chem*., **49**, 3677–3684.

Caldeira I., Clímaco M.C., Bruno de Sousa R., Belchior A.P., 2006. Volatile composition of oak and chestnut woods used in brandy ageing: modification induced by heat treatment. *J. Food Eng.*, **76**, 202-211.

Canas S., Leandro M.C., Spranger M.I., Belchior A.P., 2000. Influence of botanical species and geographical origin on the content of low molecular weight phenolic compounds of woods used in Portuguese cooperage. *Holzforschung*, **54**, 255-261.

Chatonnet P., Dubourdieu D., 1998. Comparative study of the characteristics of American white oak (*Quercus alba*) and European oak (*Quercus petraea and Q. robur*) for production of barrels used in barrel ageing of wines. *Am. J. Enol. Vitic*., **49**, 79–85.

Doussot, F., de Jéso B., Quideau S., Pardon P., 2002. Extractives content in cooperage oak wood during natural seasoning and toasting; influence of tree species, geographic location, and single-tree effects. *J. Agric. Food Chem.*, **50**, 5955–5961.

Doussot F., Pardon P., Dedier J., De Jeso B., 2000. Individual, species and geographic origin influence on cooperage oak extractible content (*Quercus robur* L. and *Quercus petraea* Liebl.). *Analysis*, **28**, 960–965.

Fernández de Simón B., Cadahía E., Conde E., García-Vallejo M.C., 1996. Low molecular weight phenolic compounds in Spanish oak woods. *J. Agric. Food Chem*., **44**, 1507–1511.

Fernández de Simón B., Cadahía E., Conde E., García-Vallejo M.C., 1998. Ellagitannins in woods of Spanish oaks. *J. Sci. Tech. Tonnellerie*, **4**, 91–98.

Fernández de Simón B., Cadahía E., Conde E., García-Vallejo M.C., 1999. Ellagitannins in wood of Spanish, French and American oaks. *Holzforschung*, **53**, 147–150.

Fernández de Simón B., Sanz M., Cadahía E., Poveda P., Broto M., 2006. Chemical characterization of oak heartwood from Spanish forests of *Quercus pyrenaica (Wild.)* ellagitannins, low molecular weight phenolic, and volatile compounds. *J. Agric. Food Chem*., **54**, 8314–8321.

Gallego L., Del Alamo M., Nevares I., Fernández J., Fernández de Simon B., Cadahía E., 2012. Phenolic compounds and sensorial characterization of wines aged with alternative to barrel products made of Spanish oak wood (*Quercus pyrenaica Willd*.). *Food Sci. Technol. Int*., **18**, 151–165.

Garcia R., Soares B., Barrocas Dias C., Costa Freitas A.M., Cabrita M.J., 2012. Phenolic and furanic compounds of Portuguese chestnut and French, American and Portuguese oak wood chips. *Eur. Food Res. Technol*., **235**, 457–467.

García-Estévez I., Alcalde-Eon C., Martínez-Gil AM., Rivas-Gonzalo J.C., Escribano-Bailón M.T., Nevares I., del Alamo-Sanza M., 2017. An approach to the study of the interactions between ellagitannins and oxygen during oak wood aging. *J. Agric. Food Chem*., doi: 10.1021/acs.jafc.7b02080.

Garde-Cerdán T., Ancín-Azpilicueta C., 2006. Review of quality factors on wine ageing in oak barrels. *Trends Food Sci. Tech*., **17**, 438–447.

Gonçalves F.J., Jordão A.M., 2009. Changes in antioxidant activity and the proanthocyanidin fraction of red wine aged in contact with Portuguese (*Quercus Pyrenaica Willd.*) and American (*Quercus Alba L.*) oak wood chips. *Ital. J. Food Sci.*, **21**, 51-64.

González R.E., Baleta L.C., 2010. Quantification and comparison of ageing markers substances of accelerated aging rums and in oak (*Quercus humboldtii*) barrels. *Rev. Venez. Cienc. Tecnol. Aliment*., **1**, 170–183.

González R.E., Calderón L., Cabeza R., 2008. Quantification of ageing markers substances in *Quercus humboldtii* throught high efficiency liquid cromatography. *Temas Agrarios*, **13**, 56–63.

Guilley E., Hervé J.C., Huber F., Nepveu G., 1999. Modelling variability of within-ring density components in *Quercus petraea* Liebl. with mixed-effect models and simulating the influence of contrasting silvicultures on wood density. *Ann. For. Sci*., **56**, 449–458.

Jordão A.M., Ricardo-da-Silva J.M., Laureano O., 2007. Ellagitannins from Portuguese oak wood (*Quercus pyrenaica* Willd.) used in cooperage: Influence of geographical origin, coarseness of the grain and toasting level. *Holzforschung*, **61**, 155–160.

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

Masson G., Moutounet M., Puech J.-L., 1995. Ellagitannins content of oak wood as a function of species and of sampling position in the three. *Am. J. Enol. Vitic*., **46**, 262–268.

Matricardi L., Waterhouse A.L., 1999. Influence of toasting technique on color and ellagitannins of oak wood in barrel making. *Am. J. Enol. Vitic*. **50**, 519–525.

Michel J., Jourdes M., Silva M.A., Giordanengo T., Mourey N., Teissedre P.-L., 2011. Impact of concentration of ellagitannins in oak wood on their levels and organoleptic influence in red wine. *J. Agric. Food Chem*., **59**, 5677–5683.

Miller D.P., Howell G.S., Michaelis C.S., Dickmann D.I., 1992. The content of phenolic acid and aldehyde flavor components of white oak as affected by site and species. *Am. J. Enol. Vitic*., **43**, 333–338.

Mosedale J., Charrier B., Crouch N., Janin G., Savill P., 1996. Variation in the composition and content of ellagitannins in the heartwood of European oaks (*Quercus robur* and *Q. petraea*). A comparison of two French forests and variation with heartwood age. *Ann. For. Sci*., **53**, 1005–1018.

Navarro M., Kontoudakis N., Giordanengo T., Gómez-Alonso S., García-Romero E., Fort, F., Zamora F., 2016. Oxygen consumption by oak chips in a model wine solution; influence of the botanical origin, toast level and ellagitannin content. *Food Chem*., **199**, 822–827.

Prida A., 2002. Use of oak wood in manufacture of barrels for preparing and aging wines. *In: Oak; ecology, types and management*. 173–193. Aleixo Chuteira C., Bispo Grão A. (eds.), Nova publishers, New York.

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

Stark T., Wollmann N., Wenker K., Lösch S., Glabasnia A., Hofmann T., 2010. Matrix calibrated LC-MS/MS quantitation and sensory evaluation of oak ellagitannins and their transformation products in red wines. *J. Agric. Food Chem*., **58**, 6360–6369.

Vivas N., Pianet I., Bourgeois G., Vitry C., Servens C., Glories Y., 1998. Characterization of heartwood lignin fractions from *Quercus robur* L. and *Quercus petraea* (Matt) Liebl., the main oak species used for barrel making. *Am. J. Enol. Vitic*., **49**, 49–55.

Wilson K., White D.J.B., 1986. The anatomy of wood: its diversity and variability. 1–309. Stobart and Son, London.

Zhang B.O., Cai J., Duan C., Reeves M.J., He F., 2015. A review of polyphenolics in oak woods. *Int. J. Mol. Sci*., **16**, 6978–7014.