

Phenolic and volatile compounds in *Quercus humboldtii* Bonpl wood: Effect of toasting with respect to oaks traditionally used in cooperage

Ana Martínez-Gil^{a,b,1*}, Estrella Cadahía^c, Brígida Fernández de Simón^c, Gastón Gutiérrez-Gamboa^{b,d}, Ignacio Nevares^{f,1}, María del Álamo-Sanza^{a,1}

^aDepartamento de Química Analítica, Universidad de Valladolid, Avda. Madrid, 50, 34001 Palencia, Spain *e-mail: anamaria.martinez.gil@uva.es

^bCentro Tecnológico de la Vid y el Vino, Facultad de Ciencias Agrarias, Universidad de Talca, Av. Lircay S/N, Talca, Chile

^cCentro de Investigación Forestal, CIFOR-INIA, Apdo 8111, 28080 Madrid, Spain

^dInstituto de Ciencias de la Vid y del Vino (Gobierno de La Rioja-CSIC-Universidad de La Rioja). Carretera de Burgos Km. 6 (Autovía LO-20, salida 13). Finca La Grajera. 26007 Logroño, Spain

^fDepartamento de Ingeniería Agrícola y Forestal, E.T.S. Ingenierías Agrarias, Universidad de Valladolid, Avda. Madrid, 50, 34001 Palencia, Spain

¹Grupo UVaMOX, E.T.S. Ingenierías Agrarias, Universidad de Valladolid, Avda. Madrid, 50, 34001 Palencia, Spain

Abstract

BACKGROUND: The most frequent renewal of barrels of different origins and species is a current trend but this demand does not match the current availability of wood. An alternative could be the use of *Q. humboldtii* wood. However, there is little information about its composition. Due to this, the aim was to study low molecular weight phenols (LMWP), ellagitannins and volatile compounds in untoasted and toasted *Q. humboldtii* oak, and compare these with the species traditionally used in cooperage: *Q. petraea* (French and Romanian) and *Q. alba* (American).

RESULTS: The LMWPs in *Q. humboldtii* were comparable to those in *Q. petraea* and *Q. alba*. Ellagitannin composition in *Q. humboldtii* was similar to that in *Q. alba*. The toasting process improved volatile composition, mainly in *Q. humboldtii*, presenting the highest concentration of several volatile compounds.

CONCLUSION: The results indicate that *Q. humboldtii* could be considered suitable for aging wine, although it is necessary to continue the study of this wood species to confirm its potential use in oenology.

Keywords: ellagitannins, low molecular weight phenols, *Quercus humboldtii*, seasoning, toasting, volatile compounds.

INTRODUCTION

Due to the constant search to improve wine quality, and the new trends in winemaking, the current predisposition is to use newer oak barrels of different origins and species. Therefore, demand for oak wood in oenology is constantly increasing, and in recent years an imbalance between the quantity of oak wood available and the number of oak barrels produced in cooperage has been detected. Thus, it is of interest and also necessary to study the use of different origins and species of oak wood rather than the traditional ones (French and American), as demonstrated by the number of studies focusing on this subject.

The extraction of different phenolic and volatile compounds from oak into the wine during aging depends mainly on the pool of potential extractable compounds originally present in the oak. The chemical composition of this oak is affected by two main groups of factors: on the one hand, the oak species, its geographical origin, and the silvicultural treatment of the tree,¹⁻⁴ and on the other, the processing of the wood in cooperage, that is, the method used to obtain the staves, especially the degree of oak toasting during barrel manufacture,^{1,5,6} and also the method of seasoning (natural or artificial, length, and location).^{5,7}

Low molecular weight phenols are important components of heartwood and contribute to the wood with color, smell, taste, and mechanical resistance properties. These compounds can also influence the color, astringency and bitterness of the wine.⁸ Ellagitannins are responsible for hardness and the avoidance of microbiological alterations in oak woods.⁹ These compounds can act as antioxidants in wines due to their ability to consume oxygen,^{10,11} although they degrade easily once solubilized in the wine, both in the presence and absence of oxygen,¹⁰ and may contribute to astringency and a sensation of bitterness.¹²⁻¹⁴ Volatile compounds play a key role in wine quality, especially regarding aroma, but their concentration depends on many factors, mainly the toasting process.^{15,16} This process modifies a wide range of compounds in the oak. Thus, a variety of mono- and dimethoxylated phenols, cinnamic acids, benzoic acids, and aldehydes are formed from the lignin degradation by hydrolytic and oxidative processes. This degradation would contribute to an increase in the levels of phenolic aldehydes and volatile compounds, degrading ellagitannins.¹⁷

An interesting alternative source of oak wood could be *Q. humboldtii* from Colombia, which is currently used for the aging of alcoholic drinks such as Rum or Brandy.¹⁸ Nowadays, certain cooperage companies which provide this type of oak wood for the aging of distilled beverages are trying to sell this wood to the wine industry on the basis that it is of the same quality as that traditionally used for aging wine. Moreover, the usual method of seasoning this wood in cooperage is artificial as an oven is used. However, there is little information about *Q. humboldtii* in winemaking, and it has only been found that its wood showed similar vanillin concentrations to *Q. faginea*, and a balanced syringaldehyde/vanillin relationship, a marker usually used to characterize quality oak wood, suggesting that *Q. humboldtii* has potentially good properties for wine aging.¹⁹ Moreover, the phenolic composition of green *Q. humboldtii* has been characterized as and compared to traditional oak with the most abundant phenolic acids, aldehydes and ellagitannins being the same as in traditional oak wood (*Q. alba* and *Q. petraea*), and with a phenolic composition closer to American ones.²⁰ On the other hand, to our knowledge there is no information that characterizes other low molecular weight phenolic, ellagitannins and volatile compounds in untoasted and toasted *Q. humboldtii* oak, so this study could provide more knowledge and information of interest.

As already mentioned, various authors have studied certain oak wood sources of different origin and species with the aim of providing information about other types of

oak as an alternative to French (*Q. petraea* and *Q. robur*) and American (*Q. alba*) oaks, which have traditionally been used in winemaking. Hungarian and Russian oak woods have been shown to have a lower content of oak lactones, *trans* and *cis*-isoeugenol, and higher odor intensities than the American and French ones.²¹ The unheated volatile concentration of Portuguese (*Q. pyrenaica*) oak wood was lower than that of French (*Q. petraea*) and American (*Q. alba*) ones; however, its content improved greatly after the toasting process.¹⁶ Quantitative differences were found in low molecular weight phenolic, especially in American (*Q. alba*) species compared to the Spanish (*Q. robur*, *Q. petraea*, *Q. pyrenaica*, and *Q. faginea*) and the French (*Q. robur*, and *Q. petraea*) ones.⁷ Prida and Puech³ observed that East European wood held an intermediate position between American and French oaks according to their ellagitannins and oak lactone levels, and are characterized by high values of eugenol, aromatic aldehydes and 2-phenylethanol.

For these reasons, the aim of this study was to evaluate the low molecular weight phenols, and ellagitannins by HPLC-DAD, and volatile compounds by GC-MS of untoasted and toasted oak wood of *Q. humboldtii* (Colombian oak), and to compare it to the species traditionally used in cooperage, such as *Q. petraea* (French oak) and *Q. alba* (American oak) as well as others more recently introduced (*Q. petraea* from Romania).

MATERIALS AND METHODS

Wood samples

For this study, four different oak woods (origin and/or species) were used: *Quercus petraea* (Matt.) Liebl. (called French and Romanian oak), *Quercus alba* L. (called American oak) and *Quercus humboldtii* Bonpl. (called Colombian oak). French, Romanian, American oaks were imported to Chile as green wood to the cooperage, Tonelería Nacional Chile LTDA. Therefore, the drying of these woods was carried out as usually done by this cooperage for oak wood. This process is a natural seasoning in the open air for 30 months, watering daily in summer according to the cooperage procedure. After seasoning these stave woods presented humidity between 11 and 13%. On the other hand, the Colombian oak staves were imported after a semi-accelerated seasoning process as usual in cooperage when this oak is used for brandy and rum aging. This accelerated seasoning is carried out with steam in special chambers, where the temperature gradually increases, starting with a temperature of 22 °C in the first few days of drying and ending with a temperature of 60 °C. This process is finished when the moisture content of the wood (MC) is approximately 12 to 14%, which takes approximately 3 weeks. Then the oven is turned off, and the wood is slowly adjusted to room temperature (36-48 hours).

After seasoning, all the kinds of wood staves were toasted in an industrial-scale convection oven, normally used by the cooperage for alternative products. Toasting was defined by this cooperage as medium-plus toasting, which consists of a temperature ramp up to 200 °C and for a total of 140 minutes.

Three representative batches of each type of wood were prepared for the chemical analyses. Six pieces were taken from each batch of wood and ground, sawdust was obtained using a planer-thicknesser and this was sieved and mixed, taking the sawdust ranging in size from 0.80 to 0.28 mm as the representative batch sample. A total of 12 representative samples were studied for different oak woods (*Q. petraea* from France and Romania, *Q. alba*, *Q. humboldtii*) before toasting (defined as non-toasted) and another 12 representative samples after toasting (defined as toasted).

Standards

In the case of low molecular weight phenolic compounds, reference compounds were purchased from Fluka Chemie AG (Buchs, Switzerland) (gallic acid), Sigma Aldrich (Steinheim, Germany) (vanillic acid, syringic and coniferyl aldehydes), Apin (ellagic acid), Chem Service (West Chester, PA) (syringic acid), Extrasynthèse (Genay, France) (sinapaldehyde). For ellagitannins, standards of vescalagin, castalagin, roburin A and E, and grandinin were used. For volatile compounds, all standards (γ -hexalactone, 2-octanol, 4,5-dimethylfurfuraldehyde, o-vanillone, 3,4-dimethoxyphenol, furfural, 5-methylfurfural, 5-hydroxymethylfurfural, furfuryl alcohol, *trans*- β -methyl- γ -octalactone, *cis*- β -methyl- γ -octalactone, guaiacol, 4-ethylguaiacol, 4-vinylguaiacol, eugenol, *cis*-isoeugenol, *trans*-isoeugenol, syringol, vanillin, acetovanillone, benzaldehyde and 2-phenylethanol) were provided by Sigma Aldrich (Steinheim, Germany).

Low molecular weight phenols and ellagitannin extractions

The sawdust samples (1 g) were extracted with 100 mL of methanol/water (1:1) at room temperature and in darkness for 24 h, using the method described by Fernández de Simón et al.²² for low molecular weight phenols and by Fernández de Simón et al.²³ 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 taken to dryness, dissolved in methanol/water (1:1) and used for the HPLC quantitative determination of low molecular weight phenolic compounds (ellagic, gallic, syringic and vanillic acids and coniferyl, sinapic and syringic aldehydes), and the freeze-dried aqueous extract for that of ellagitannins (castalagin, vescalagin, grandinin, roburin A, B, C, D and E).

Analysis of low molecular weight phenols and ellagitannins by HPLC-DAD

Low molecular weight phenols were analyzed using the method explained by Cadahía et al.⁷ and ellagitannins according to the method of Cadahía et al.²⁴ An Agilent 1200 HPLC equipped with a diode array detector and a C18 Hypersyl ODS (5 μ m) column (20 cm \times 4 mm i.d.), protected with a precolumn of the same material, was used. Low molecular phenols: the elution conditions were modified as follows: flow rate, 1 mL/min; temperature, 30 °C; solvent A= H₂O/PO₄H₃ (999:1), solvent B= MeOH/PO₄H₃ (999:1) and a linear gradient was used, 0 to 100% B, in 70 min. Detection was at 325 nm (with a bandwidth of 150 nm) and UV spectra (240-400 nm) were also recorded. Chromatographic peaks were identified by comparing their retention time and the UV spectra with those of reference compounds and quantitative determinations were carried out by the external standard method. Ellagitannins: a gradient profile was used, 0-10% B in 0-40 min, 10-30% B in 40-70 min, 30-100% B in 70-90 min; and detection was at 325 nm (with a bandwidth of 150 nm). Quantitative determinations were carried out in accordance with the external standard method. Roburins B-D were expressed as roburin A because they are also dimers.

Volatile compound extraction

Maceration to extract the volatile compounds from sawdust was based on the method described by Chatonnet et al.²⁵ The sawdust samples (2 g) were soaked in 100 mL of hydroalcoholic (12% ethanol, 6 g L⁻¹ tartaric acid, pH 3.2) for 15 days at a room temperature of 20°C in darkness. After filtration of the mixture 300 μ L of five internal standards were added (γ -hexalactone, 2-octanol, 4,5-dimethylfurfuraldehyde, o-vanillone, and 3,4-dimethoxyphenol at a dose of 0.5 mg mL⁻¹ in ethanol). The hydroalcoholic solution with the oak aromas and the standards were then extracted using

a previously reported methodology.²⁶ For that, prepacked cartridges (total volume 3 mL) filled with 200 mg of LiChrolut EN resin (Merck, Darmstadt, Germany) were used.

Analysis of volatile compounds by GC-MS

The separation, identification and quantification of volatile compounds from the wood extract were carried out using an Agilent 7890A gas chromatograph, coupled with a 5975C mass spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA). The unit was equipped with a fused silica capillary column (60 m × 0.25 mm i.d., and 0.5 μm phase thickness, DB-Wax, J & W Scientific, Agilent). The carrier was helium applied at a flow rate of 1 mL min⁻¹. The temperature of the injector was 250 °C and 1 μL of oak or wine extract was injected. The oven temperature was initially held at 40°C for 5 min, then increased linearly at a rate of 2 °C min⁻¹ up to 130 °C and held at that for 5 min; after that, it was again increased at a rate of 2°C min⁻¹ up to 180°C and held for 2 min; finally, it was increased linearly at a rate of 4°C min⁻¹ up to 230 min. Two injections were carried out: one in split mode (50:1) for furfural and 5-methylfurfural and the other in splitless mode for the rest of the volatile compounds analyzed (5-hydroxymethylfurfural, furfuryl alcohol, *trans*-β-methyl-γ-octalactone, *cis*-β-methyl-γ-octalactone, guaiacol, 4-ethylguaiacol, 4-vinylguaiacol, eugenol, *cis*-isoeugenol, *trans*-isoeugenol, syringol, vanillin, acetovanillone, benzaldehyde and 2-phenylethanol). Ionization was by electron impact at 70eV. The operating method was a scan mode at *m/z* between 30 and 300. The NIST library was used for identification. Quantification was based on eight-point calibration curves of the respective standards (Sigma-Aldrich, Steinheim, Germany) ($R^2 > 0.95$) in a 12% (v/v) ethanol solution with 6 g L⁻¹ of tartaric acid at pH 3.2; analyzed under the same conditions.

Statistical analysis

This was carried out using the SPSS Version 21.0 statistical package for Windows (SPSS, Chicago, USA). Low molecular weight phenol, ellagitannins and volatile compounds were processed using variance analysis (ANOVA). Differences between means were compared using the Duncan test at 0.05 probability level. Principal component analysis (PCA), using Stagraphics Centurion 16.2.04, StatPoint Technologies, Inc. (Warrenton, United States), was performed individually with the low molecular weight phenol, ellagitannins and volatile compounds in the non-toasted and toasted woods.

RESULTS AND DISCUSSION

Low molecular weight phenol content in oak woods

Table 1 shows the LMWP obtained in *Q. petraea* (French and Romanian oaks), *Q. alba* (American oak) and *Q. humboldtii* (Colombian oak) woods after seasoning (non-toasted) and toasting.

The most abundant low molecular weight phenols in non-toasted wood were ellagic acid followed by gallic acid (Table 1). In toasted oak wood, the most abundant compounds were ellagic acid, sinapic aldehyde and coniferyl aldehyde. This result, both in non-toasted and toasted woods, coincides with that observed by other authors.⁷

Ellagic acid concentration in non-toasted wood showed non-significant differences among the different species or origins, and represented 68 to 90% of total LMWP (Colombian and American oaks, respectively). These results are in agreement with those described in the bibliography in *Q. petraea* and *Q. alba*.⁷ However, non-toasted Colombian oak presented the highest gallic acid concentration, with approximately twice as much as that in the other oaks. Therefore, gallic acid contribution to the total LMWP

was high in Colombian oak (29%), whilst being 10-18% (Rumanian and French, respectively) in *Q. petraea* and only 2% in American oak. The other acids studied found at lower concentrations -, syringic and vanillic acid had lower concentrations in *Q. humboldtii*, except in the case of vanillic acid in Romanian oak which presented a similar concentration (Table 1).

Thus, total concentration of phenolic acids in non-toasted woods was higher in *Q. humboldtii* than in *Q. alba*; however, no significant differences were found when comparing *Q. humboldtii* to *Q. petraea* (Table 1). The phenolic acids in *Q. petraea* and *Q. alba* after the toasting process presented higher or similar concentrations to those found before toasting (non-toasted), these results being similar to those observed by Cadahía et al.⁷ Therefore, the toasting process increased the total phenolic acids in these oak species (*Q. petraea* and *Q. alba*,) by between 45 and 69%. Table 1 shows that syringic and vanillic acids increased in all oak woods due to the toasting process, while ellagic acid only did so in *Q. petraea* from France and *Q. alba*, since the concentration in *Q. petraea* from Romania and *Q. humboldtii* remained constant. However, gallic acid concentration in *Q. alba* and in *Q. petraea* from Rumania increased, remained constant in French oak wood and even decreased in the case of Colombian oak: after toasting this was approximately 68% in *Q. humboldtii*, which showed a decrease of 16% of total phenolic acids (Table 1). The concentration of some compounds, like gallic acid, has been seen to increase in Acacia heartwood after light and medium toasting, but to decrease at a higher toasting intensity (185 °C for 45 min).²⁷ In this study, the toasting intensity is the same for all oaks, with all of them being toasted at the same time in the same oven. The differences could thus be because this oak may have a different composition in compounds not studied in this work, possibly lignin.

After toasting ellagic acid had the highest content but its contribution to the total LMWP decreased with toasting, representing around 22 to 35% of the total (Colombian and French oaks, respectively). This was due to the increase of other compounds by toasting being higher (coniferyl and sinapic aldehydes). Ellagic acid was higher in French oak than in American wood, an already known fact; moreover, its concentration in Colombian oak was similar to that in the American one. Although after seasoning the Colombian oak had the highest gallic acid, after the toasting process this and the American were those with the lowest concentration of this compound. Though *Q. humboldtii* oak before seasoning had low syringic and vanillic acid concentrations, after toasting it had the highest content, but syringic acid showed no differences in comparison with French oak. Consequently, Colombian toasted wood presented a similar total concentration of phenolic acids to American oak, and lower than *Q. petraea* but only significantly as regards French wood (Table 1).

With respect to the aldehydes, the non-toasted Colombian oak together with the Romanian were those with the lowest concentrations of coniferyl and syringic aldehydes. However, *Q. humboldtii* had the highest sinapic aldehyde content.

Table 1 shows that *Q. alba* was the oak with the highest concentration of total aldehydes in non-toasted woods. Aldehydes showed a significant increase in their concentration after toasting. This result coincides with that observed by Cadahía et al.⁷ The highest increase of LMWP from seasoning to toasting was observed in the total aldehyde content, increasing from 1263 to 1799 $\mu\text{g g}^{-1}$ of wood (Romanian and Colombian oaks, respectively). The total phenolic aldehyde content did not show any significant differences among species or origins after toasting (Table 11).

Thus, after the toasting process, coniferyl and sinapic aldehydes did not show any significant differences among the different species or origins. These two compounds were those that increased most during toasting, so sinapic aldehyde contributed a great deal to

the total LMWP representing around 38 to 47% (Romanian and Colombian oaks, respectively) and coniferyl aldehyde was around 15 to 22% of total LMWP (*Q. petraea* and *Q. alba*, respectively). However, although the syringic aldehyde concentration was low in *Q. humboldtii* before toasting, this oak showed the highest concentration after this process, but without any significant differences with respect to *Q. alba* (Table 1).

Thus, syringic aldehyde and vanillin are considered as markers for the aging of distilled beverages since they are useful for evaluating the quality of aged ones.^{28,29} In addition, during the aging of wines in oak barrels, lignin is degraded into syringic aldehyde and vanillin, the latter contributing to the vanilla flavors typical of all wines aged in oak barrels.³⁰ Puech and Jouret³¹ reported that a syringic aldehyde/vanillin ratio between 1.4 and 2.5 indicates a balance between the products of lignin degradation. In our samples, this ratio ranged from 1.51 to 4.74 in the *Q. alba* and *Q. humboldtii* oak woods (Table 1 and 3); however, this ratio was 3.49 in *Q. petraea* of French origin, and 3.06 in *Q. petraea* from Romania, being higher in all oak woods except *Q. alba* than that reported by Puech and Jouret³¹ in different species of toasted oak woods, and higher than that obtained by González et al.¹⁹ in *Q. humboldtii* toasted oak wood.

The principal component analysis (PCA), shown in Figure 1, was carried out to evaluate the discriminant power of LMWP for the four kinds of oak wood studied before (a) and after (b) the toasting process.

Before toasting, the percentage of variance was 77.01% with two components (principal components 1 and 2 explaining 58.72% and 19.00% of the variance, respectively). Component 1 shows a wide distance between *Q. humboldtii* with respect to *Q. petraea* and *Q. alba* (Figure 1a). It has been noted that the most significant parameters to differentiate *Q. humboldtii* oak from the traditional ones were gallic acid, sinapic aldehyde and ellagic acid. The second component was principally correlated positively to syringic, gallic and vanillic acids, with the French oak being located more on the positive side of the second component axis.

The percentage of variance in Figure 1b (PCA of toasted woods) was 87.79%, component 1 explained 57.04% of the variance and component 2 26.74%. Component 1 has a closer negative correlation with syringic acid, vanillic acid, coniferyl aldehyde, sinapic aldehyde and syringic aldehyde with *Q. humboldtii*, the oak situated furthest to the left of the negative side of the first principal component axis. The second component did not differentiate either species or origin.

Considering this, it can be observed that the Colombian wood differentiated very clearly from the rest of the species before toasting, which may be due to a different composition of the fresh wood or to the different seasoning method used. However, after the toasting treatment there is a greater similarity in its composition to the species traditionally used in cooperage, especially since ellagic acid decreased its contribution to total LMWP and increased the contribution of coniferyl and sinapic aldehydes with the last two compounds having similar concentrations in all the species studied.

Ellagitannins

Table 2 shows ellagitannin compounds obtained from *Q. petraea* (French and Romanian oaks), *Q. alba* (American oak) and *Q. humboldtii* (Colombian oak) after seasoning and toasting.

The most abundant ellagitannin compounds in non-toasted woods were castalagin and vescalagin as reported by Glabasia and Hofman.¹² Castalagin represented 29 to 34% of total ellagitannins in non-toasted oak woods (French and Colombian oaks, respectively). Vescalagin represented 17 to 35% of total ellagitannins in non-toasted oak woods (Colombian and French oaks, respectively). The compound with the next highest

concentration was roburin D, 14 to 20% of total ellagitannins (French and American oaks, respectively). Therefore, it could be stated that the relationship between the different ellagitannins in *Q. humboldtii* is of the same order as in traditional oak woods. As in non-toasted wood, the major ellagitannins in traditional toasted oaks were castalagin and vescalagin, these results being consistent with those observed by other authors^{3,32}. Castalagin presented 63 to 54% of total ellagitannins in traditional toasted oak woods (American and Rumanian oaks, respectively) and vescalagin 25% to 15% (French and American oaks, respectively). However, after toasting the Colombian oak did not present the same relationship with respect to traditional ones among ellagitannins, since castalagin and vescalagin represented 15 to 11% of total ellagitannins, respectively. The major compounds in this oak were roburin D and grandinin with 38 to 22% of the total. Roburin C was the lowest quantified ellagitannin in non-toasted and toasted oak wood, as reported by Cadahía et al.,²⁴ this compound also being the lowest in *Q. humboldtii* oak (Table 2). This concentration represented 0.9 to 4.9% of total ellagitannin compounds in non-toasted oak woods (French and American oaks, respectively), and 0.5 to 1.8% in toasted ones (French and American oaks, respectively).

Regarding the quantitative contents in the composition of non-toasted oak woods, *Q. humboldtii* and *Q. alba* presented a lower concentration of monomers (castalagin and vescalagin), pentosylated monomers (grandinin and roburin E), dimers (roburin A+B) and roburin D than *Q. petraea*. Also, *Q. humboldtii* showed the lowest roburin C content after *Q. alba*. In addition, differences due to geographical origin were found, since French oak showed higher castalagin, vescalagin, roburin E and roburin A+B concentrations than Rumanian wood, though they are the same species (*Q. petraea*) (Table 2).

In relation to the ellagitannin composition in toasted oak woods, the differences were similar in comparison with that found in non-toasted oak woods. *Q. humboldtii* and *Q. alba* were those with the lowest content of each ellagitannin, although in this case without any significant differences with respect to Romanian oak as regards some (roburin E and roburin D), or in grandinin when compared to French oak. Thus, comparing toasted *Q. petraea* of both origins, French oak presented a higher content of castalagin, vescalagin, and roburin A+B, while exhibiting lower amounts of grandinin than Romanian oak wood; these differences due to geographical origin were also observed by Prida and Puech.³

Therefore, total ellagitannin concentration in non-toasted and toasted oak wood was lower in *Q. humboldtii* and *Q. alba* than in *Q. petraea* (Table 2). Total ellagitannin content decreased during toasting in all oak wood species. During the toasting process, a variety of hydrothermolysis and pyrolysis reactions take place degrading wood constituents, including ellagitannins.³³ In addition, it has been shown that roburins A-E, grandinin, vescalagin, and castalagin decreased during toasting²⁴ with this decrease usually being higher when the toasting temperature increases.³² It ranged from 83 to 87% in wood traditionally used in cooperage, and decreased by 92% in *Q. humboldtii* oak wood in our samples at 200°C. Thus, the toasting process affects the ellagitannin composition of *Q. humboldtii* more than the rest of the oak woods studied. These results concerning ellagitannin content in toasted *Q. alba* and *Q. petraea* oaks have also been reported by several authors.^{3,24,32}

Another principal component analysis (PCA) was carried out to evaluate the discriminant power of ellagitannins for the four kinds of oak wood studied, before (Figure 2a) and after (Figure 2b) toasting. PCA was defined mainly by one component, since component 1 was 93.48 % and 82.73% of variance, respectively (non-toasted and toasted woods), and the second component was 4.50% and 14.71%, respectively. The main component (PC 1) differentiated the European oaks from the *Q. humboldtii* and *Q. alba*

woods and has a closer positive correlation with all ellagitannins in both non-toasted and toasted woods. However, component 2 in the non-toasted wood principally differentiated the American from the Colombian oak. This component is especially correlated positively with vescalagin, castalagin, A, B and E roburins. Once toasted, the composition of the Colombian wood resembled American oak even more; thus neither component could separate these two oaks. Moreover, after the toasting process, component 2 separated the French oaks from the Romanian ones. This was positively correlated with grandinin and roburin C, thus defining Romanian oak. In addition, a high variability in *Q. petraea* (French and Romanian oaks) was observed, which has been reported by several authors.²⁴ However, *Q. alba* and *Q. humboldtii* presented similar compound concentrations.

Volatile compounds

Table 3 shows the volatile compounds in *Q. petraea* (French and Romanian oaks), *Q. alba* (American oak) and *Q. humboldtii* (Colombian oak) in non-toasted and toasted woods.

The most abundant volatile compounds in non-toasted wood were 5-hydroxymethylfurfural, vanillin, *trans*- β -methyl- γ -octalactone, and *cis*- β -methyl- γ -octalactone, which represented 85 to 88% in the oak woods traditionally used in cooperage but 18% in *Q. humboldtii*. These compounds also presented high concentrations in non-toasted French and American oaks in the study by Fernández de Simón et al.⁴ Table 3 shows that furfural was not detected in these non-toasted oak wood samples. Also 5-hydroxymethylfurfural or *trans*- β -methyl- γ -octalactone were not detected in the Colombian non-toasted wood nor was guaiacol in *Q. petraea*. Furfuryl alcohol, 4-ethylguaiacol, 4-vinylguaiacol, and *cis*-isoeugenol did not show any statistical differences among the studied non-toasted oak woods. Cadahía et al.⁵ found similar concentrations of these compounds in non-toasted oaks and also no significant differences between *Q. petraea* from France and *Q. alba*. Non-toasted *Q. humboldtii* wood presented the lowest concentration of vanillin after *Q. petraea*, with the highest one in *Q. alba* oak (Table 3). Moreover, *Q. alba* showed the highest content of *cis*- β -methyl- γ -octalactone, acetovanillone, benzaldehyde, and 2-phenylethanol, and these compounds did not show any significant differences between *Q. petraea* and *Q. humboldtii*. However, *Q. petraea* non-toasted oak wood presented the highest concentration of 5-hydroxymethylfurfural while French wood had the lowest one and Romanian oak showed the highest concentration of *trans*- β -methyl- γ -octalactone. Finally, *Q. humboldtii* wood evidenced the highest content of guaiacol, and *trans*-isoeugenol.

However, in toasted oak wood the most abundant compounds were furfural, 5-methylfurfural, 5-hydroxymethylfurfural, *cis*- β -methyl- γ -octalactone and vanillin. These represented 96 to 99% of total volatile compounds (Colombian and French oak, respectively). In contrast, 4-ethylguaiacol, benzaldehyde and 2-phenylethanol showed the lowest abundance in toasted oak woods, and represented 0.03 to 0.10% of total volatile compounds (*Q. petraea* of Romanian origin and *Q. humboldtii*, respectively).

Regarding toasted oak woods, 2-phenylethanol was the only compound that did not show any significant differences in concentration among the different origins and species. In toasted wood, *Q. humboldtii* exhibited higher amounts of several volatile compounds with respect to the other oak woods studied. These compounds were 5-methylfurfural, furfuryl alcohol, guaiacol, 4-ethylguaiacol, 4-vinylguaiacol, *cis*-isoeugenol, *trans*-isoeugenol and syringol. In addition, this oak also presented the highest concentrations of eugenol together with the Romanian one. Prida and Puech³ also observed a higher eugenol content in *Q. petraea* from Romania than that from France and *Q. alba*. The odor descriptors usually used to characterize the aromatic contribution

of these compounds in wines are almond, caramel, moldy hay, burnt sugar, honey, smoke, phenolic, spice, flower, pink pepper and clove.^{34,35} However, *Q. humboldtii* showed the lowest furfural, 5-hydroxymethylfurfural and *cis*- β -methyl- γ -octalactone concentrations, compounds with bread, almond, sweet, oaky, coconut and vanilla aroma notes.³⁴ On the other hand, *Q. alba* toasted oak wood presented the highest concentration of furfural, *cis*- β -methyl- γ -octalactone, vanillin, acetovanillone and benzaldehyde. The fact that furfural and/or *cis*-octalactone are found in high concentrations in American oak has been observed by other authors^{3-5,36-38}; however, as regards vanillin and benzaldehyde this is not clear since some of these authors found a higher concentration in *Q. alba* and others in *Q. petraea*. Romanian oak wood evidenced the highest content of 5-hydroxymethylfurfural, and *trans*- β -methyl- γ -octalactone.

Therefore, total volatile composition in non-toasted woods was lower in *Q. humboldtii* than traditional oaks, with significant differences with respect to *Q. alba* and *Q. petraea* from Romania; however, none were found when compared to French *Q. petraea* (Table 3). The toasting process increased the volatile composition of oak wood, as has been reported by various authors.^{4,5} A perceptible increase due to the toasting treatment was higher in the *Q. humboldtii* oak wood, since its initial concentration increased 103 times, followed by *Q. petraea* of both origins (France and Romania), which showed a 49-fold increase, and finally *Q. alba* with a 29-fold increase. In spite of the high increase due to toasting, total volatile composition in the Colombian wood remained significantly lower than in *Q. petraea* from Romania and *Q. alba*, but statistically similar to *Q. petraea* from France (Table 3). This was due to the compounds whose concentration increased most after toasting which were furfural and 5-hydroxymethylfurfural, representing 90-96% of the total volatile composition after toasting, while *Q. humboldtii* and *Q. petraea* from France had lower concentrations of these. Other authors, Cadahía and Fernández de Simón,³⁹ also reported that these two compounds were the most abundant in toasted oak woods.

The last principal component analysis (PCA) was performed with the aim of identifying and evaluating the volatile compounds as this could differentiate oak according to species and origin, *Q. petraea* (French and Romanian oak), *Q. alba* (American oak) and *Q. humboldtii* (Colombian oak) before and after toasting (Figures 3a and b, respectively). These figures provide a graphical representation of the oak sample projections for each group on a plane defined by two main components (1 and 2). Before toasting, the percentage of variance was 68.71% with two components (component 1 explained 36.65% of the variance and 2 explained 32.06%). After toasting, the percentage of variance was 73.87% with two components (component 1 explained 51.05% of the variance with component 2 explaining 22.82%). It shows a wide distance between *Q. humboldtii* with respect to *Q. petraea* and *Q. alba* samples, both before and after toasting, since component 1 had the most weight of variance. This component could only separate *Q. humboldtii* from the traditional ones. *Q. humboldtii* in figure 3a (non-toasted PCA) was located on the negative side of the first principal component axis defined by guaiacol, 4-ethylguaiacol, eugenol, *trans*-isoeugenol, *cis*-isoeugenol, vanillin and 5-methylfurfural; however, in figure 3b (toasted PCA) *Q. humboldtii* samples were located on the positive side of first principal component axis defined, like the other PCA, by guaiacol, 4-ethylguaiacol, *trans*-isoeugenol, *cis*-isoeugenol and 5-methylfurfural and also by 5-methylfurfural, 4-vinylguaiacol, and syringol. In this figure, component 1 again shows what is described above about the different behavior of the Colombian wood after toasting when compared to the woods traditionally used in cooperage for wine.

In both cases (non-toasted and toasted) *Q. alba* oaks and *Q. petraea* ones (French and Romanian) were separated in component 2, while *Q. humboldtii* wood was situated

between the two, being closer to *Q. petraea*, especially after toasting (Figure 3). As regards this component, non-toasted and toasted *Q. petraea* woods were defined by furfural, trans- β -methyl- γ -octalactone and 5-hydroxymethylfurfural. Before toasting they were also defined by syringol and after toasting by eugenol, *cis*-isoeugenol and 5-methylfurfural.

According to the information provided by the variables related to PCA 1, and PCA 2 it has been concluded that *Q. humboldtii* wood volatile composition differed from that of *Q. petraea* and *Q. alba* oak woods while being more similar to European woods than American ones.

CONCLUSION

Q. humboldtii (Colombian oak) showed interesting attributes of quality in relation to its low molecular weight phenolic, ellagitannins and volatile composition, points to be considered for cooperage. Non-toasted *Q. humboldtii* oak wood evidenced the same concentration of total phenolic acids and aldehydes as *Q. petraea*. The total low molecular weight phenols concentration in the toasted Colombian oak was statistically similar to the other oak woods. Total ellagitannin concentration in non-toasted and toasted *Q. humboldtii* and *Q. alba* oak woods was much lower than in *Q. petraea* from France and Romania, being similar to that in *Q. alba*. The significant concentration of volatile compounds quantified in toasted oak wood from *Q. humboldtii* with respect to the others suggests that this oak wood may be considered an important source of some volatile compounds. Ellagitannins and volatile composition of the oak woods more than the total low molecular weight phenols concentration allowed the differentiation of *Q. humboldtii* oaks compared to those traditionally used. Toasted *Q. humboldtii* oak wood presented the highest concentration of 5-methyl furfural, furfuryl alcohol, guaiacol, 4-ethylguaiacol, 4-vinylguaiacol, *cis* and *trans*-isoeugenol, and syringol. Moreover, Colombian oak showed the lowest furfural, 5-hydroxymethylfurfural and *cis*- β -methyl- γ -octalactone concentrations. Thus, *Q. humboldtii* wood volatile composition differed from that of *Q. petraea* and *Q. alba*.

Considering the results obtained, Colombian *Q. humboldtii* wood can be considered suitable for aging wine, although further study is needed to adapt its treatments in cooperage and to evaluate its potential for oenology.

ACKNOWLEDGEMENTS

This work was funded by CONICYT, Fondecyt de Iniciación Grant N° 11150462, Chile, and with the collaboration of Tonelería Nacional LTDA, Santiago de Chile. G.G.-G. would like to thank the financial support given by CONICYT through BCH/Doctorado - 72170532. This work was financed by the European Regional Development Fund FEDER, Interreg Spain-Portugal Programme, under the framework of the project Iberphenol. We would like to thank Ann Holliday for her services in revising the English.

REFERENCES

1. Canas SM, Conceição L, Spranger MI and Belchior, AP, Influence of botanical species and geographical origin on the content of low molecular weight phenolic compounds of woods used in Portuguese cooperage. *Holzforshung* **54**:255–261 (2000).
2. Doussot F, De Jéso B, Quideau S and Pardon P, 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 (2002).
3. Prida A and Puech JL, 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 (2006).
 4. Fernández de Simón B, Esteruelas E, Muñoz AM, Cadahía E and Sanz M, Volatile compounds in acacia, chestnut, cherry, ash, and oak woods, with a view to their use in cooperage. *J Agric Food Chem* **57**:3217–3227 (2009).
 5. Cadahía E, Fernández de Simón B and Jalocha J, Volatile compounds in Spanish, French and American oak woods after natural seasoning and toasting. *J Agric Food Chem* **51**:5923–5932 (2003).
 6. Bozalongo R, Carrillo JD, Fernández-Torroba MA and Tena MT, Analysis of French and American oak chips with different toasting degrees by headspace solid-phase microextraction-gas chromatography–mass spectrometry. *J Chromatogr A* **1173**:10–17 (2007).
 7. Cadahía E, Muñoz L, Fernández de Simón B and Garcia-Vallejo MC, 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 (2001).
 8. Garde-Cerdán T and Ancín-Azpilicueta C, Review of quality factors on wine ageing in oak barrels. *Trends Food Sci Technol* **17**:438–447 (2006).
 9. Prida A, Use of oak wood in manufacture of barrels for preparing and aging wines. In *Oak; ecology, types and management*. ed by Cláudio Aleixo Chuteira and Abraham Bispo Grão. Nova publishers, New York, United States, pp. 173–193 (2002).
 10. Navarro M, Kontoudakis N, Giordanengo T, Gómez-Alonso S, García-Romero E, Fort F and Zamora F, 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 (2016).
 11. Alcalde-Eon C, Martínez-Gil AM, Rivas-Gonzalo JC, Escribano-Bailón MT, Nevares I and Del Álamo-Sanza M, An approach to the study of the interactions between ellagitannins and oxygen during oak wood aging. *J Agric Food Chem* **65**:6369–6378 (2017).
 12. Glabasnia A and Hofman T, Sensory-directed identification of taste-active ellagitannins in American (*Quercus alba* L.) and European oak wood (*Quercus robur* L.) and quantitative analysis in bourbon whiskey and oak-matured red wines. *J Agric Food Chem* **54**:3380–3390 (2006).
 13. Stark T, Wollmann N, Wenker K, Lösch S, Glabasnia A and Hofmann T, 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 (2010).
 14. Sáenz-Navajas MP, Fernández-Zurbano P and Ferreira, V, Contribution of nonvolatile composition to wine flavor. *Food Rev Int* **28**:389–411 (2012).
 15. Garde-Cerdán T, Rodríguez-Mozaz S and Ancín-Azpilicueta C, Volatile composition of aged wine in used barrels of French oak and of American oak. *Food Res Int* **35**:603–610 (2002).
 16. Jordão AM, Ricardo-Da Silva JM and Laureano O, Comparison of volatile composition of cooperage oak wood of different origins (*Quercus pyrenaica* vs. *Quercus alba* and *Quercus petraea*). *Mitt. Klosterneuburg* **55**:22–31 (2005).

17. Zhang B, Cai J, Duan CQ, Reeves MJ and He F. A review of polyphenolics in oak woods. *Int J Mol Sci* **16**:6978–7014 (2015).
18. González RE and Baleta LC, Quantification and comparison of ageing markers substances of accelerated aging rums and in oak (*Quercus humboldtii*) barrels. *RVCTA* **1**:170–183 (2010).
19. González RE, Calderón LS and Cabeza RA, Quantification of aging markers substances in *Quercus humboldtii* through high efficiency liquid chromatography. *Temas Agrarios* **13**:56–63 (2008).
20. Martínez-Gil AM, Cadahía E, Fernández de Simón B, Gutiérrez-Gamboa G, Nevares I and Del Álamo Sanza M, *Quercus humboldtii* (Colombian oak): characterization of oak wood phenolic composition with respect to traditional oak woods in oenology. *Ciência Téc Vitiv* **32**:93-101 (2017).
21. Díaz-Maroto MC, Guchu E, Castro-Vázquez L, de Torres C and Pérez-Coello MS, Aroma active compounds of American, French, Hungarian and Russian oak woods studied by Gas Chromatography-Mass Spectrometry and Gas Chromatography-Olfactometry. *Flavour Frag J* **23**:93–98 (2008).
22. Fernández de Simón B, Cadahía E, Conde E and García-Vallejo MC, Low molecular weight phenolic compounds in Spanish oak woods. *J Agric Food Chem* **44**:1507–1511(1996).
23. Fernández de Simón B, Cadahía E, Conde E and García-Vallejo MC, Ellagitannins in woods of Spanish oaks. *J Coop Sci Technol* **4**:91–98 (1998).
24. Cadahía E, Varea S, Muñoz L, Fernández de Simón B and García-Vallejo MC, Evolution of ellagitannins in Spanish, French, and American oak woods during natural seasoning and toasting. *J Agric Food Chem* **49**:3677–3684 (2001).
25. Chatonnet P, Pons M and Dubourdiou D, Monitoring toasting intensity of barrels by chromatographic analysis of volatile compounds from toasted oak wood. *J Agric Food Chem* **47**:4310–4318 (1999).
26. López R, Aznar M, Cacho J and Ferreira V, Determination of minor and trace volatile compounds in wine by solid-phase extraction and gas chromatography with mass spectrometric detection. *J Chromatogr A* **966**:167–177 (2002).
27. Sanz M, Fernández de Simón B, Esteruelas E, Muñoz AM, Cadahía E, Hernández, T, Estrella I and Pinto E, Effect of toasting intensity at cooperage on phenolic compounds in acacia (*Robinia pseudoacacia*) heartwood. *J Agric Food Chem* **59**:3135–3145 (2001).
28. Martínez R.G, Mir MV, Serrana HLG, Martínez, MCL and Herrera O Simultaneous determination of vanillin and syringaldehyde using high performance liquid chromatography. Application to the static and soleras aged brandies. *J Liq Chromatogr* **16**:4079–4094 (1993).
29. De Aquino FWB, Rodrigues S, Do Nascimento RF and Casimiro ARS, Simultaneous determination of aging markers in sugarcane spirits. *Food Chem* **98**:569–574 (2006).
30. Puech JL, Extraction of phenolic compounds from oak wood in model solutions and evolution of aromatic aldehydes in wines aged in oak barrels. *Am J Enol Vitic* **38**:236–238 (1987).
31. Puech JL and Jouret C, Dosage des aldéhydes aromatiques des eaux-de-vie conservées en futs de chene: Detection d'adulteration. *Ann Fals Expert Chim* **75**:81–90 (1982).
32. Jordão AM, Ricardo-Da Silva JM and Laureano O, 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 (2007).
33. Matricardi L and Waterhouse AL, Influence of toasting technique on color and ellagitannins of oak wood in barrel making. *Am J Enol Vitic* **50**:519–526 (1999).
 34. Rodríguez-Bencomo JJ, Ortega-Heras M, Pérez-Magariño S and González-Huerta C, Volatile compounds of red wines macerated with Spanish, American, and French oak chips. *J Agric Food Chem* **57**:6383–6391(2009).
 35. Spillman PJ, Sefton MA and Gawel R, The effect of oak wood source, location of seasoning and coopering on the composition of volatile compounds in oak-matured wines. *Aust J Grape Wine Res* **10**:216–226 (2004).
 36. Pérez-Coello MS, Sanz J and Cabezudo MD, Determination of volatile compounds in hydroalcoholic extracts of French and American Oak Wood. *Am J Enol Vitic* **50**:162–165 (1999).
 37. Chatonnet P and Dubourdieu D, 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 aging of wines. *Am J Enol Vitic* **49**:79–85 (1998).
 38. Natali N, Chinnici F and Riponi C, Characterization of volatiles in extracts from oak chips obtained by Accelerated Solvent Extraction (ASE). *J Agric Food Chem* **54**:8190–8198 (2006).
 39. Cadahía E and Fernández de Simón B. In *Utilización de roble español en el envejecimiento de vino. Comparación con roble francés y americano*, ed by Instituto Nacional de Investigación Agraria y Alimentaria. Ministerio de Educación y Ciencia, Madrid, España, Vol. 10, pp. 136 (2004).

Table 1. Low molecular weight phenolic compounds concentration ($\mu\text{g g}^{-1}$ of wood) obtained in wood of *Quercus petraea* (French and Romanian oak), *Quercus alba* (American oak) and *Quercus humboldtii* (Colombian oak) after seasoning (non-toasted) and already toasted

	<i>Q. petraea</i>		<i>Q. alba</i>	<i>Q. humboldtii</i>
	French oak	Romanian oak	American Oak	Colombian oak
Non-toasted				
Acids				
Ellagic acid	613.19 ± 44.88 a	597.74 ± 58.13 a	419.94 ± 90.05 a	562.05 ± 193.61 a
Gallic acid	139.28 ± 43.12 c	70.90 ± 30.01 b	8.51 ± 1.24 a	244.05 ± 26.39 d
Syringic acid	8.15 ± 0.73 c	6.33 ± 0.88 b	6.54 ± 0.80 b	3.49 ± 0.52 a
Vanillic acid	7.95 ± 0.53 c	4.07 ± 0.66 a	6.59 ± 0.75 b	4.05 ± 0.08 a
Total acids	768.57 ± 62.24 b	679.04 ± 9.64 b	441.58 ± 20.40 a	813.64 ± 195.40 b
Aldehydes				
Coniferyl aldehyde	3.74 ± 0.40 b	2.91 ± 0.34 a	3.99 ± 0.33 b	2.47 ± 0.05 a
Sinapic aldehyde	6.41 ± 0.66 c	3.42 ± 0.38 a	5.28 ± 0.51 b	10.18 ± 0.29 d
Syringic aldehyde	12.13 ± 0.41 b	8.90 ± 1.19 ab	18.15 ± 4.27 c	5.51 ± 0.39 a
Total aldehydes	22.27 ± 1.10 b	15.23 ± 1.56 a	27.42 ± 4.36 c	18.16 ± 0.60 ab
Toasted				
Acids				
Ellagic acid	1012.05 ± 233.90 b	786.61 ± 199.45 ab	641.69 ± 45.72 a	552.53 ± 99.36 a
Gallic acid	157.27 ± 34.74 b	160.98 ± 31.01 b	69.87 ± 12.97 a	78.27 ± 13.85 a
Syringic acid	26.11 ± 5.18 ab	24.59 ± 5.39 a	19.82 ± 2.13 a	33.84 ± 3.18 b
Vanillic acid	10.79 ± 1.14 a	13.07 ± 2.44 a	13.86 ± 1.94 a	21.06 ± 1.10 b
Total acids	1206.22 ± 261.78 b	985.24 ± 237.16 ab	745.24 ± 51.28 a	685.71 ± 116.50 a
Aldehydes				
Coniferyl aldehyde	428.41 ± 98.88 a	339.54 ± 72.42 a	513.97 ± 122.29 a	485.45 ± 60.62 a
Sinapic aldehyde	1162.04 ± 234.30 a	867.44 ± 151.86 a	1007.98 ± 207.35 a	1181.60 ± 104.50 a
Syringic aldehyde	78.68 ± 12.20 a	70.86 ± 14.42 a	86.23 ± 16.60 ab	110.93 ± 8.64 b
Total aldehydes	1669.14 ± 343.77 a	1277.83 ± 233.92 a	1608.18 ± 346.20 a	1817.15 ± 166.25 a

All parameters are given with their standard deviation (n = 3). Different letters in the same column indicate significant differences (p<0.05) between the different oak woods.

Table 2. Ellagitannin concentration ($\mu\text{g g}^{-1}$ of wood) obtained in wood of *Quercus petraea* (French and Romanian oak), *Quercus alba* (American oak) and *Quercus humboldtii* (Colombian oak) after seasoning and after toasting

	<i>Q. petraea</i>		<i>Q. alba</i>	<i>Q. humboldtii</i>
	French oak	Romanian oak	American Oak	Colombian oak
<i>Non-toasted</i>				
Monomers				
Castalagin	9941.73 \pm 1200.14 c	7455.44 \pm 2215.01 b	1357.86 \pm 86.68 a	541.81 \pm 75.28 a
Vescalagin	11763.17 \pm 2645.92 c	6643.83 \pm 2051.53 b	895.62 \pm 52.50 a	272.03 \pm 36.94 a
pentosylated monomers				
Grandinin	1878.33 \pm 155.54 b	1976.19 \pm 505.07 b	357.39 \pm 45.16 a	224.65 \pm 20.72 a
Roburin E	3294.31 \pm 501.52 c	23211.44 \pm 680.49 b	299.72 \pm 24.89 a	165.51 \pm 23.46 a
Dimers				
Roburin A+B	1997.08 \pm 325.30 c	1355.27 \pm 298.30 b	176.82 \pm 25.4 a	35.59 \pm 5.64 a
pentosylated dimers				
Roburin C	303.55 \pm 27.89 c	279.78 \pm 20.57 c	202.36 \pm 6.76 b	45.12 \pm 2.67 a
Roburin D	4679.15 \pm 614.07 b	3862.19 \pm 1036.34 b	843.73 \pm 48.83 a	320.44 \pm 33.38 a
<i>Total ellagitanins</i>	33857.31 \pm 3033.26 c	23894.14 \pm 3316.12 b	4133.49 \pm 126.51 a	1605.16 \pm 95.62 a
<i>Toasted</i>				
Monomers				
Castalagin	3344.38 \pm 1314.90 c	1975.80 \pm 152.21 b	346.57 \pm 154.81 a	17.05 \pm 19.90 a
Vescalagin	1455.92 \pm 600.01 c	869.99 \pm 71.06 b	82.10 \pm 40.65 a	12.78 \pm 9.11 a
pentosylated monomers				
Grandinin	85.73 \pm 45.03 a	305.47 \pm 66.63 b	41.14 \pm 9.95 a	25.33 \pm 6.97 a
Roburin E	302.41 \pm 210.58 b	163.51 \pm 40.17 ab	17.48 \pm 16.48 a	11.12 \pm 4.91 a
Dimers				
Roburin A+B	238.97 \pm 96.06 c	140.49 \pm 10.24 b	18.62 \pm 2.50 a	3.82 \pm 0.53 a
pentosylated dimers				
Roburin C	29.80 \pm 18.05 bc	41.02 \pm 11.48 c	9.65 \pm 2.95 ab	1.08 \pm 0.89 a
Roburin D	377.39 \pm 283.48 b	183.71 \pm 76.11 ab	36.76 \pm 9.86 a	43.97 \pm 8.12 a
<i>Total ellagitanins</i>	5834.59 \pm 1491.72 b	3679.98 \pm 200.75 b	552.33 \pm 161.55 a	115.15 \pm 24.87 a

All parameters are given with their standard deviation (n = 3). Different letters in the same column indicate significant differences (p<0.05) between the different oak woods.

Table 3. Volatile composition ($\mu\text{g g}^{-1}$ of wood) obtained in wood of *Quercus petraea* (French and Romanian oak), *Quercus alba* (American oak) and *Quercus humboldtii* (Colombian oak) after seasoning and toasting

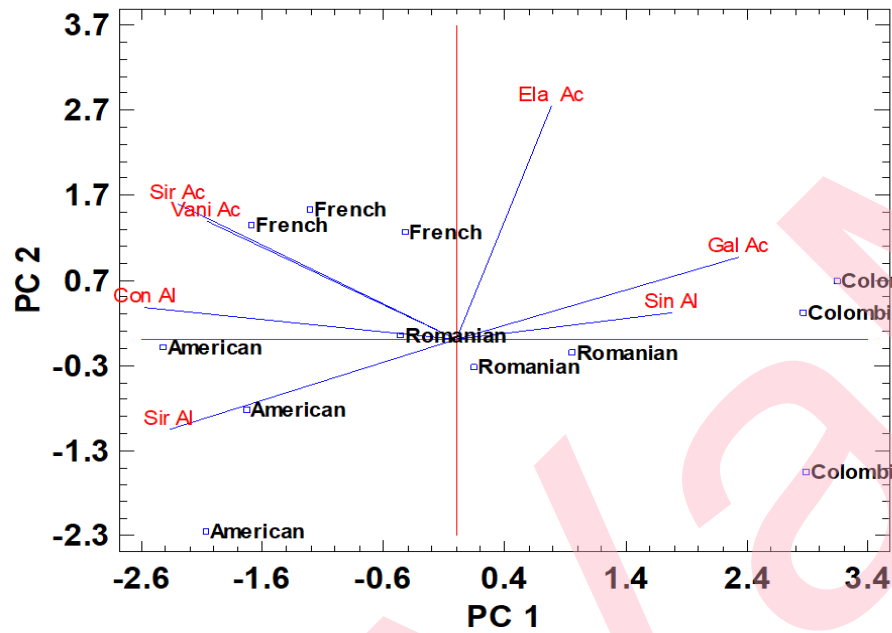
	<i>Q. petraea</i>		<i>Q. alba</i>	<i>Q. humboldtii</i>
	French oak	Romanian oak	American oak	Colombian oak
<i>Non-toasted</i>				
furfural	nd	nd	nd	nd
5-methylfurfural	0.34 ± 0.51 a	2.09 ± 0.58 b	2.25 ± 0.19 b	2.76 ± 0.29 b
5-hydroxymethylfurfural	13.99 ± 3.45 b	15.23 ± 3.63b	3.83 ± 1.05 a	nd
furfuryl alcohol	1.07 ± 0.09 a	1.01 ± 0.04 a	0.97 ± 0.04 a	0.97 ± 0.02 a
<i>trans</i> - β -methyl- γ -octalactone	1.82 ± 0.10 a	13.24 ± 6.47 b	4.99 ± 0.36 a	nd
<i>cis</i> - β -methyl- γ -octalactone	5.93 ± 6.08 a	7.67 ± 4.30 a	50.15 ± 20.96 b	0.02 ± 0.00 a
guaiacol	nd	nd	0.05 ± 0.01 b	0.10 ± 0.01 c
4-ethylguaiacol	0.03 ± 0.00 a	0.03 ± 0.01 a	0.03 ± 0.00 a	0.04 ± 0.01 a
4-vinylguaiacol	0.50 ± 0.01 a	0.50 ± 0.04 a	0.51 ± 0.06 a	0.49 ± 0.07 a
eugenol	0.46 ± 0.22 a	2.04 ± 1.55 b	1.85 ± 0.03 ab	2.65 ± 0.08 b
<i>cis</i> -isoeugenol	0.21 ± 0.03 a	0.20 ± 0.04a	0.22 ± 0.09 a	0.22 ± 0.01 a
<i>trans</i> -isoeugenol	0.69 ± 0.01 a	0.69 ± 0.01 a	0.73 ± 0.02 a	0.95 ± 0.06 b
syringol	0.08 ± 0.00 a	0.10 ± 0.01 b	0.09 ± 0.01 ab	0.09 ± 0.00 ab
vanillin	6.06 ± 0.66 b	5.81 ± 0.80 b	10.58 ± 2.18 c	1.97 ± 0.19 a
acetovanillone	0.29 ± 0.04 a	0.31 ± 0.02 a	0.42 ± 0.07 b	0.26 ± 0.01 a
benzaldehyde	0.07 ± 0.02 a	0.05 ± 0.02 a	1.06 ± 0.15 b	0.05 ± 0.01 a
2-phenylethanol	0.73 ± 0.28 a	0.40 ± 0.03 a	1.79 ± 0.91 b	0.25 ± 0.09 a
<i>Total volatile</i>	32.28 ± 3.55 ab	49.38 ± 4.79 bc	79.50 ± 12.01 c	10.81 ± 0.95 a
<i>Toasted</i>				
furfural	924.15 ± 129.00 b	1149.63 ± 162.83 c	1363.16 ± 41.56 d	533.53 ± 26.20 a
5-methylfurfural	27.74 ± 4.55 b	23.41 ± 5.05 ab	16.92 ± 2.00 a	45.40 ± 1.32 c
5-hydroxymethylfurfural	579.01 ± 76.76 ab	1191.90 ± 285.05c	804.27 ± 59.41 b	463.42 ± 38.03 a
furfuryl alcohol	1.20 ± 0.04 a	1.56 ± 0.06 a	1.50 ± 0.09 a	12.32 ± 0.45 b
<i>trans</i> - β -methyl- γ -octalactone	2.05 ± 0.21 a	19.51 ± 9.75 b	3.47 ± 0.42 a	0.06 ± 0.01 a

<i>cis</i> - β -methyl- γ -octalactone	12.65 \pm 1.41 b	13.27 \pm 7.28 b	27.10 \pm 3.84 c	0.30 \pm 0.09 a
guaiacol	0.40 \pm 0.03 a	0.55 \pm 0.12 a	0.93 \pm 0.20 b	3.74 \pm 0.26 c
4-ethylguaiacol	0.14 \pm 0.01 a	0.11 \pm 0.01 a	0.26 \pm 0.08 b	0.61 \pm 0.02 c
4-vinylguaiacol	0.49 \pm 0.01 a	0.51 \pm 0.02 ab	0.54 \pm 0.04 b	0.67 \pm 0.03 c
eugenol	1.60 \pm 0.21 a	5.59 \pm 0.50 b	2.07 \pm 0.26 a	3.34 \pm 0.19 b
<i>cis</i> -isoeugenol	1.74 \pm 0.11 a	2.11 \pm 0.62 a	1.52 \pm 0.44 a	7.23 \pm 0.49 b
<i>trans</i> -isoeugenol	1.96 \pm 0.05 a	2.24 \pm 0.39 a	2.90 \pm 0.24 b	5.39 \pm 0.30 c
syringol	1.43 \pm 0.08 a	1.92 \pm 0.52 a	3.39 \pm 0.66 b	10.14 \pm 0.87 c
vanillin	22.54 \pm 3.89 a	23.18 \pm 0.80 a	57.00 \pm 12.79 b	22.36 \pm 1.21 a
acetovanillone	1.44 \pm 0.19 a	1.34 \pm 0.10 a	4.33 \pm 1.29 b	2.29 \pm 0.20 a
benzaldehyde	0.16 \pm 0.01 a	0.15 \pm 0.01 a	0.27 \pm 0.04 b	0.17 \pm 0.01 a
2-phenylethanol	0.27 \pm 0.09 a	0.43 \pm 0.13 a	0.40 \pm 0.23 a	0.38 \pm 0.02 a
<i>Total volatile</i>	1578.96 \pm 255.45 a	2437.42 \pm 386.85 b	2290.02 \pm 370.89 b	1111.37 \pm 163.88 a

All parameters are given with their standard deviation (n = 3). Different letters in the same column indicate significant differences (p<0.05) between the different oak woods. nd=not detected.

Figure 1. Principal Component analysis results carried out with all low molecular weight phenolic compounds found in *Quercus petraea*, (French and Romanian) *Q. alba*, (American), and *Q. humboldtii* (Colombian) oak woods. PCA of non-toasted wood (figure 1a) and PCA of toasted wood (figure 1b).

a)



b)

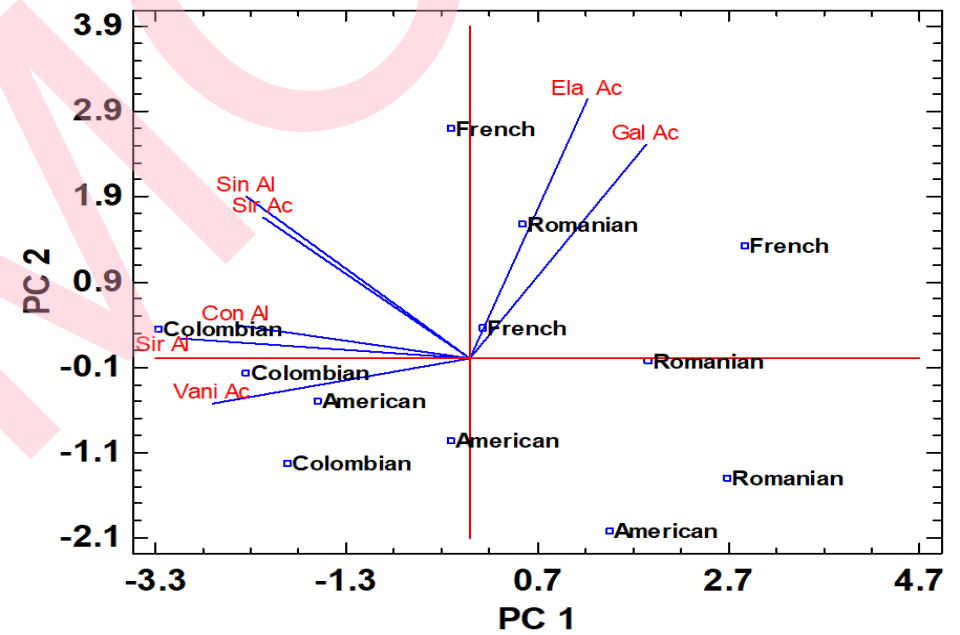


Figure 2. Principal Component analysis results carried out with all ellagitannins found in *Quercus petraea*, (French and Romanian) *Q. alba*, (American), and *Q. humboldtii* (Colombian) oak woods. PCA of non-toasted wood (figure 2a) and PCA of toasted wood (figure 2b).

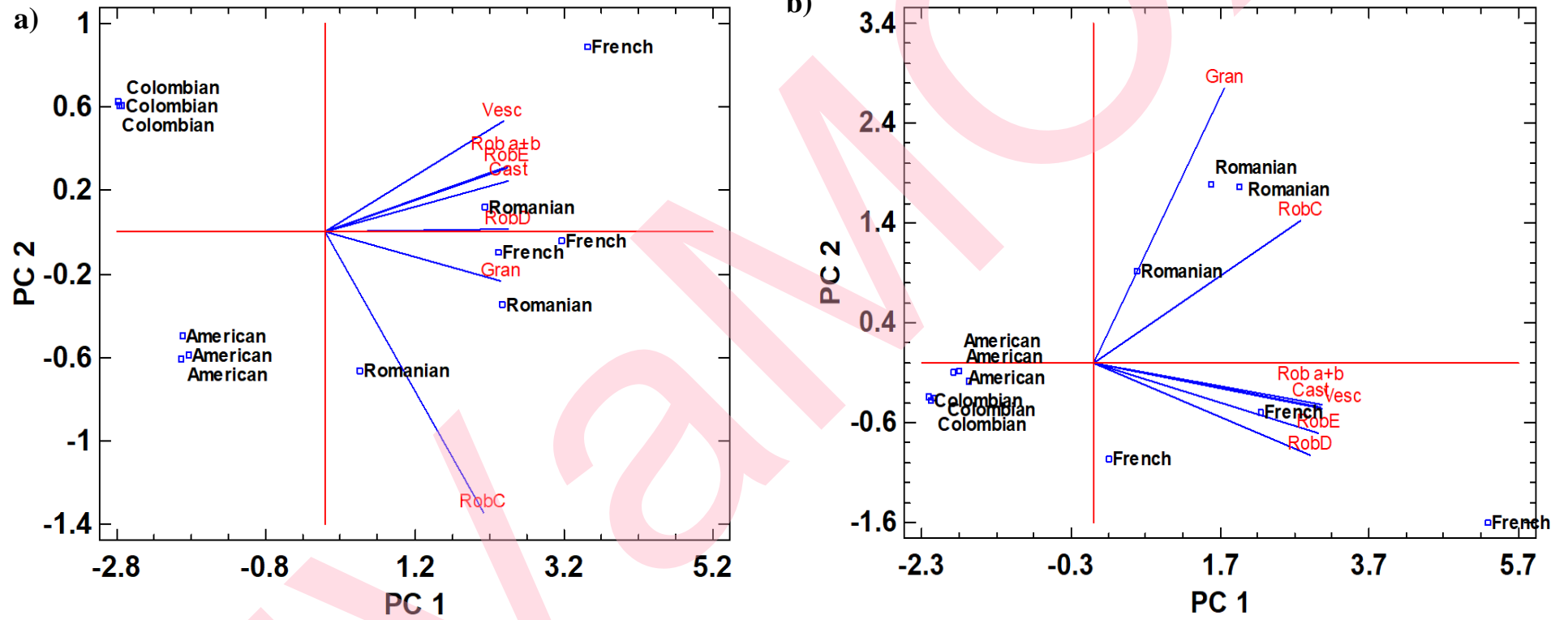


Figure 3. Principal Component analysis results carried out with all volatile compounds found in *Quercus petraea*, (French and Romanian) *Q. alba*, (American), and *Q. humboldtii* (Colombian) oak woods. PCA of non-toasted wood (figure 3a) and PCA of toasted wood (figure 3b).

