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Cyclic Polyalcohols: Fingerprints To Identify the Botanical Origin of Natural Woods Used in Wine Aging

M. Elena Alañón,*[,†] M. Consuelo Díaz-Maroto,[‡] Ignacio J. Díaz-Maroto,[§] Pablo Vila-Lameiro,[§] and M. Soledad Pérez-Coello[†]

[†]Área de Tecnología de los Alimentos, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Avenida Camilo José Cela 10, 13071 Ciudad Real, Spain

[‡]Instituto Regional de Investigación Científica Aplicada (IRICA), Universidad de Castilla La-Mancha, Campus Universitario, s/n, 13071 Ciudad Real, Spain

[§]Departamento de Ingeniería Agroforestal, Escuela Politécnica Superior, Campus Universitario s/n, Universidad de Santiago de Compostela, 27002 Lugo, Spain

ABSTRACT: Cyclic polyalcohol composition of 80 natural wood samples from different botanical species, with the majority of them used in the oenology industry for aging purposes, has been studied by gas chromatography−mass spectrometry (GC−MS) after its conversion into their trimethylsilyloxime derivatives. Each botanical species showed a different and specific cyclic polyalcohol profile. Oak wood samples were characterized by the richness in deoxyinositols, especially *proto*-quercitol. Meanwhile, other botanical species showed a very low content of cyclic polyalcohols. The qualitative and quantitative study of cyclic polyalcohols was a useful tool to characterize and differentiate woods of different botanical origin to guarantee the authenticity of chips used in the wine-aging process. Monosaccharide composition was also analyzed, showing some quantitative differences among species, but cyclic polyalcohols were the compounds that revealed the main differentiation power.

KEYWORDS: Wood, *Quercus*, botanical species, chips, cyclic polyalcohols

INTRODUCTION

Aging wines in wooden barrels is a long-used technological step at wineries. Initially, this practice was set up for the storage and transport of wines, but later, it has been used because of its positive effects on wine organoleptic characteristics and quality.

The role of wood during the aging process is crucial in several aspects. From the sensorial point of view, wood is capable of transferring aroma-responsible volatile compounds to wines. Furthermore, a reduction of astringency and changes in color are produced on aged wines as a result of the extraction of phenolic compounds from wood and the oxidation reactions produced because of the diffusion of oxygen across the pores of the wood. For these reasons, aged wines acquire distinctive sensorial characteristics that are well-appreciated by the consumer, which implies a higher price of aged wines in the marketplace.

Although several types of woods have been used in the manufacture of barrels (chestnut, cherry, etc.), oak wood is, by far, the most common wood used in making barrels for aging purposes, not only for its chemical composition but also for both its mechanical and physical properties that facilitate the conformation of barrels.

However, the aging period carried out by means of oak barrels entails a time-consuming and expensive process. On the one hand, aged wines have to be left in the barrels during a long period of time before they can be brought to market because of the slow extraction process of oak wood compounds. On the other hand, the use of barrels implies some problems, such as the cost and difficulty of their sanitization and handling.

For these reasons, the use of chips, staves, or pieces of wood as alternatives for the aging process is being widely considered in the last few years to impart a woody aroma and taste to the wine in a similar way to those provided by oak barrels. With this alternative technique, it is possible both to speed up the maturation process and cut down the costs of the production of oak wood-flavored wines.[1,2]

The International Enological Codex of the International Organization of Vine and Wine (OIV) (OENO 9/2001) first and, later, the *Official Journal of the European Union* (CE 1507/2006) approved the used of this accelerated maturation practice as an alternative wine-aging system. However, only the use of oak chips or pieces of oak wood from the genus *Quercus* is allowed by the legislation.

Nevertheless, sometimes the nature of chips or pieces of wood sold to wineries is inadequately defined. Therefore, it is necessary to identify adequately the botanical origin and the species of chips or pieces of wood to respond satisfactorily to legislation requirements and the needs of winemakers. As a consequence, from an economical and technological point of view, it is important to develop analytical methods to guarantee the authenticity of commercial oak chips or pieces of oak wood.

Volatile composition of oak wood species most often used in oenology has been widely studied, showing some quantitative

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differences among them.[3−7] More recently, the volatile profile of other botanical species has been compared to oak wood.[8] Also, in this case, the qualitative profile seems to be quite similar among different types of wood studied, while quantitatively, some differences have been observed. However, differentiation of botanical wood species based on their volatile composition cannot be a good tool because of the great variability of these compounds in wood samples as a result of the interaction between different natural factors, geographical provenance, etc.[3,7,9]

Cyclic polyalcohols, cyclitols, are widely distributed in plants and have been employed as good markers of quality or origin of some products, in concentrated rectified grape must and in juices to detect adulteration.[10,11] *proto*-Quercitol, also known as quercitol, is a deoxyinositol very abundant in all *Quercus* species[12] and has been proposed as an authentic aging marker of wines in oak barrels[13] and as a marker to differentiate oak honeydew honeys from honeys of different origins.[14] However, the presence of *proto*-quercitol has also been detected in some species of *Eucalyptus*.[15] Therefore, their use as a single marker is not recommendable.

Sugar composition also seems to be a good indicator of several parameters, to guarantee the caramel authenticity,[16] as a quality marker of honey and coffee,[17] to classify Brandy from Jerez according to its aging,[18] to monitor and determine the intensity of the toasting process of oak wood used in the aging practice,[19] and to identify the nature of oenological tannins.[20]

In previous studies, the cyclitol profile of different *Quercus* species has been examined and it seems that the *Quercus* genus shares a characteristic cyclitol profile, which represents a good data set for *Quercus* wood characterization.[21,22] However, the sample size studied was very small. Therefore, the aim of this work was to study the carbohydrate composition of several woods from different genera and species to find out the feasibility of these compounds as chemical markers to differentiate the botanical origin of woods.

For that purposes, a rigorous sampling procedure was applied to a set of 10 samples from 8 different wood species carefully selected to guarantee the identification of the wood pieces according to their botanical origin. Furthermore, all samples were stabilized to the same water content, and their preparation was carried out identically for all samples, with the aim to exclude errors and provide reliable conclusions.

MATERIALS AND METHODS

Wood Sample Collection. Woods of deciduous species were collected to carry out this study. Four species of oak wood, belonging to genus *Quercus*, were selected. The sample set included woods from three species of Spanish oaks, *Quercus robur* L. ($n = 10$), *Quercus petraea* Matts Liebl. ($n = 10$), and *Quercus pyrenaica* Wild. ($n = 10$), from several forests located in the northwest of the Iberian peninsula. The climate of the geographical sampling area is typically oceanic, with mild temperatures and high precipitations. The other species considered was *Quercus alba* L., and the samples were obtained from the Appalachian region located in Nashville, TN. The number of *Quercus alba* samples was the same, 10.

Other woods, also managed in the aging process, that were carried out this study were chestnut (*Castanea sativa* Mill.) and cherry (*Prunus avium* L.), both obtained from the forest of Lugo (northwest Spain). The sample size was in all cases 10 samples.

Other botanical species were also analyzed to complete this research, common alder [*Alnus glutinose* (L.) Gaertn.], wood used for smoking foods, and birch (*Betula alba* L.). A total of 10 samples of each species, grown in the northwest of Spain, were analyzed.

All wood samples were collected following the pattern provided by the Spanish Association for Standardisation and Certification (UNE 56-528-78). From each tree, disks of wood were obtained at a height of 1.3 m from the base of the trunk. From each disk, test tubes (heartwood) measuring 20 × 20 × 40 mm were taken.

The wooden blocks were dried as follows: test tubes were saturated with water, to the saturated state, and then stabilized to 12% of internal humidity at 20 ± 2 °C and 65% relative moisture. Finally, these were heated to dryness (0% internal humidity) in an oven at 103 ± 2 °C. For its analysis, the wooden blocks were ground with a mechanical mill and sieved (size <1 mm) to obtain homogeneous sawdust.

Reagents and Standards. Methanol, chromatographic purity, was supplied by Scharlau Chemie, S.A. (Barcelona, Spain). Derivatization reagents, hydroxylamine chloride, pyridine, hexamethyldisilazane, and trifluoroacetic acid, were purchased from Sigma-Aldrich (Madrid, Spain). Meanwhile, all reference standard compounds were also supplied by Sigma-Aldrich (Madrid, Spain), except for *proto*-quercitol, which was obtained from TCI (Zwijndrecht, Netherlands).

Isolation of Target Compounds. Extraction of target compounds from wood samples were carried out using a accelerated solvent extractor ASE 200 (Dionex Corporation, Sunnyvale, CA) equipped with a solvent controller. Extractions were performed using the optimized method developed in a previous study by our group.[21] A total of 300 mg of sawdust mixed with 2 g of diatomaceous earth as a dispersant agent were placed in inox extraction cells of 11 mL. Extractions were carried out using methanol at 90 °C. After the injection of solvent into the cell, a pressurized static extraction phase lasting 15 min was carried out under pressure, at 1500 psi. Between extractions, a rinse of the complete system was performed to avoid any carryover.

Derivatization Procedure. A derivatization step must be conducted before gas chromatography−mass spectrometry (GC−MS) analysis of carbohydrates to improve their chromatographic responses. A two-step derivatization procedure (oxidation and trimethylsilylation) was used.[23] Wood extracts were evaporated under vacuum at 40 °C. Then, the residue was derivatized by adding 350 μL of hydroxylamine chloride (2.5%) in pyridine and heated to 70 °C for 30 min. The oximes obtained in this step were silylated with 350 μL of hexamethyldisilazane and 35 μL of trifluoroacetic acid at 45 °C for 30 min.[24] The reaction mixture was centrifuged at 3600*g* for 5 min at 5 °C.[25] Supernatants containing the carbohydrate oximes were injected onto the GC column or stored at 4 °C prior their analysis.

GC−MS Analysis. GC−MS analyses were performed with an Agilent Technologies HP-G 1800B, GCD system coupled to a mass detector (Agilent Technologies, Palo Alto, CA), with helium as the carrier gas and a linear velocity of 28 cm s^{-1}. Capillary column and operation parameters were those described in a previous paper.[21] A HP-5 capillary column (5% phenylmethylpolysiloxane) stationary phase (30 m, 0.25 mm inner diameter, and 0.25 μm film thickness) was used. The oven temperature was held at 80 °C for 3 min, increased to 250 °C at 3 °C min^{-1}, then increased at 8 °C min^{-1} to 290 °C, and held for 30 min. The injector temperature was 300 °C. The solvent delay was set at 15 min, and 1 μL was injected in split mode with a ratio of 1:18.

The temperatures of the ion source and transfer line were 170 and 280 °C, respectively. Positive-ion electron impact spectra were recorded at 70 eV ionization energy in SCAN mode with a 35−450 amu mass acquisition range.

Chromatographic peaks were identified by comparing their linear retention index (I^T) and mass spectra to those of pure standards. For compounds in which it was not possible to obtain standards, the identification was carried out by a comparison of their mass spectra and retention index to those reported in the literature. The linear retention index was calculated using *n*-alkanes as external references. Quantitative assessment of compounds was carried out by means of response factors of standard compounds.

Table 1. Linear Retention Index of Trimethylsilylated Oxime Derivatives of Monosaccharides and Cyclic Polyalcohols Found in Wood Samples Studied

I^T	compound	type	identification[a]	quantification[b]
1758	arabitol	sugar polyalcohol	S	
1793/1801	xylose	monosaccharide	S	
1801/1802	arabinose	monosaccharide	S	
1830	*proto*-quercitol	deoxyinositol	S	
1897	*epi*-quercitol	deoxyinositol	T	*proto*-quercitol
1913	*vibo*-quercitol	deoxyinositol	T	*proto*-quercitol
1946	*muco*-inositol	inositol	S	
1969	mannitol	sugar polyalcohol	S	
1986/1994	fructose	monosaccharide	S	
1991	*chiro*-inositol	inositol	T	*muco*-inositol
2003	*scyllo*-quercitol	deoxyinositol	T	*proto*-quercitol
2032/2058	galactose	monosaccharide	S	
2045/2058	glucose	monosaccharide	S	
2069	*scyllo*-inositol	inositol	S	
2124	*myo*-inositol	inositol	S	

[a] Identification mode: S, peak identified with the pure reference standard; T, peak tentatively identified with the spectrum and linear retention index found in the literature. [b] Response factor used when a pure reference standard was not available.

Statistical Analysis. Chemical data were analyzed using the Student−Newman−Keuls test for the comparison of means. Principal component analysis (PCA) and variable correlation analysis were also carried out for the concentrations of monosaccharides and polyalcohols found in all extracts analyzed. A linear discriminate analysis was applied as well. All statistical treatments were carried out using the SPSS 17.0 for Windows statistical package.

RESULTS AND DISCUSSION

To determine sugars present in wood samples, a previous derivatization procedure that involves successive derivatizations was employed prior to GC−MS analysis. Reducing sugars, such as monosaccharides, could provide up to six peaks corresponding to their trimethylsilyl derivatives upon direct silylation (α and β pyranose and furanose forms and the acyclic hydrate and carbonyl forms), which implies difficulties in both identification and quantification processes. After sequential oxidation and silylation reactions, each reducing sugar gives rise to only two peaks, corresponding to their *syn*- (*Z*) and *anti*- (*E*) trimethylsilyloxime isomers, respectively. In contrast, non-reducing sugars, such as polyalcohols, give only one peak corresponding to their trimethylsiyloxime derivatives. In this way, this protocol allowed for a rapid discrimination between peaks arising from reducing or non-reducing carbohydrates. Table 1 displays the compounds studied and the linear retention index of their trimethylsilylated oxime derivatives. Among them, it was possible to detect various monosaccharides, sugar polyalcohols, and several cyclic polyalcohols, also known as cyclitols or inositols, with some of them being deoxyinositols.

Table 2 shows the mean values of monosaccharide composition of studied wood samples comprised of xylose, arabinose, fructose, glucose, and galactose, as well as some sugar alcohols, such as arabitol and mannitol. Xylose and arabinose could not be quantified individually because of overlapping of the second xylose peak with the first arabinose chromatographic signal. On the other hand, galactose and glucose were also quantified together, because one of the glucose chromatographic signals appeared to overlap a galactose peak.

All woods are mainly composed of larger polymers, such as cellulose, which is a linear polymer made up of long chains of glucose monomers, and hemicellulose, which is a mixture of polysaccharides derived from glucose, mannose, galactose, xylose, and arabinose, among others. Therefore, it is reasonable not to have found qualitative differences between diverse botanical origins with respect to these compounds.

Despite the variability of cyclic polyalcohol and monosaccharide content among samples belonging to the same species, it was possible to draw some conclusions. For instance, all natural oak wood samples showed the highest values of xylose and arabinose compared to the rest of the woods studied. With regard to the fructose content, it is worth noting the high concentration found in the species *A. glutinose*, while no significant differences were detected among the rest of the samples. On the other hand, the low content in galactose and glucose in *P. avium* samples and the high concentrations of them found in *Q. robur*, *A. glutinose*, and *Q. alba* must be remarkable. Concerning sugar polyalcohols, arabitol and mannitol, there was not great difference among species.

The study of cyclic polyalcohols, also known as cyclitols or inositols, has been carried out in this research as well. Up to eight cyclitols, four of them deoxyinositoles (*proto*-, *epi*-, *vibo*-, and *scyllo*-quercitols), were identified.

On the basis of the results, the inositol profile seems to be more specific to differentiate botanical origins than the monosaccharide content. In Table 3, it is possible to observe both qualitative and quantitative differences regarding the inositol content. It must be taken into account that, because of the overlapping of *epi*-quercitol with quinic acid, the values of *epi*-quercitol were not quantified, only its presence or absence were considered.

As seen in Table 3, all oak wood samples belonging to genus *Quercus* show the same cyclic polyalcohol profile. In these samples, up to eight different inositols, four of them inositols (*muco*-, *chiro*-, *scyllo*-, and *myo*-inositols) and four of them deoxyinositols (*proto*-, *epi*-, *vibo*-, and *scyllo*-quercitols), were detected. This fact was in a good agreement with those found in previous studies.[21,22] The joint presence of all cyclic polyalcohols identified was not found in the rest of the samples. Furthermore, the occurrence of deoxyinositols in samples different from the *Quercus* genus was not detected, except for small amounts of *vibo*-quercitol identified in *A. glutinose* samples.

The most abundant cyclitol of oak wood samples was *proto*-quercitol, a deoxyinositol, that is regarded as a good marker of the genus *Quercus* in various applications.[13,14,20] The high value of *proto*-quercitol detected in some oak wood samples (more than 11.00 mg g^{-1}) is remarkable, with all of them belonging to *Q. robur* species. *scyllo*-Quercitol was also abundant, and again, the samples with the highest values of this deoxyinositol were *Q. robur* samples. Among inositols detected, *scyllo*- and *myo*-inositols were the two inositols found in higher quantities, while the amounts of *chiro*-inositol were low in all oak wood samples.

When the results obtained for oak wood species are taken in consideration, it is worth pointing out that *Q. robur* was statically different from the rest of the oak samples because of its high *proto*-quercitol, *scyllo*-quercitol, and *scyllo*-inositol concentrations. While, the low amount of *vibo*-quercitol seemed to be characteristic of *Q. alba* samples. On the other hand, no statistical differences were found between *Q. petraea* and *Q. pyrenaica* samples with regard to the cyclic polyalcohols, except for *myo*-inositol.

Table 2. Mean Values of Monosaccharide and Sugar Alcohol Compositions (mg g^{-1}) of Woods Analyzed by GC−MS[a]

	samples (each species n = 10)							
compounds	*Q. alba*	*Q. petraea*	*Q. pyrenaica*	*Q. robur*	*C. sativa*	*P. avium*	*A. glutinose*	*B. alba*
arabitol	0.009 a,b,c (0.002−0.017)	0.011 b,c (0.005−0.022)	0.015 c (0.007−0.031)	0.017 c (0.008−0.028)	0.011 a,b,c (0.002−0.027)	0.010 a,b,c (0.005−0.025)	0.003 a (0.000−0.005)	0.004 a,b (0.003−0.007)
xylose and arabinose	1.144 c (0.800−1.764)	0.601 b (0.136−1.184)	0.943 c (0.135−1.750)	0.970 c (0.269−1.473)	0.254 a (0.178−0.405)	0.070 a (0.056−0.089)	0.246 a (0.200−0.342)	0.119 a (0.087−0.237)
mannitol	0.018 a,b,c (0.005−0.028)	0.020 a,b,c (0.005−0.038)	0.034 c (0.016−0.055)	0.025 b,c (0.012−0.035)	0.014 a,b (0.006−0.022)	0.006 a (0.003−0.012)	0.046 d (0.016−0.091)	0.030 b,c (0.000−0.055)
fructose	0.822 a (0.172−2.344)	0.322 a (0.063−0.853)	0.928 a (0.174−1.699)	0.659 a (0.292−1.187)	0.220 a (0.062−0.561)	0.160 a (0.044−0.365)	3.780 b (0.969−9.271)	1.478 a (1.075−2.567)
galactose and glucose	1.834 c,d (1.212−2.281)	1.137 b,c (0.360−2.010)	1.375 b,c (0.221−3.133)	2.235 d (0.684−3.959)	0.695 a,b (0.468−1.377)	0.260 a (0.115−0.548)	2.195 d (0.632−4.142)	1.015 a,b,c (0.600−1.361)

[a] Different letters in the same row indicate statistical differences at the 0.05 level according to the Student−Newman−Keuls test. Minimum and maximum values found in samples are given in parentheses.

Table 3. Mean Values of Cyclic Polyalcohol Composition (mg g^{-1}) of Woods Analyzed by GC−MS[a]

	samples (each species n = 10)							
compounds	*Q. alba*	*Q. petraea*	*Q. pyrenaica*	*Q. robur*	*C. sativa*	*P. avium*	*A. glutinose*	*B. alba*
proto-quercitol	3.647 a (2.039−5.174)	3.506 a (1.609−6.384)	4.229 a (2.189−6.285)	6.643 b (1.883−11.314)	nd	nd	nd	nd
epi-quercitol[b]	dt	dt	dt	dt	nd	nd	nd	nd
vibo-quercitol	0.067 b (0.027−0.102)	0.176 d (0.085−0.272)	0.157 d (0.087−0.254)	0.117 c (0.051−0.230)	nd	nd	0.042 a,b (0.012−0.070)	nd
muco-inositol	0.107 d (0.096−0.123)	0.046 b (0.015−0.072)	0.053 b (0.024−0.088)	0.111 d (0.075−0.149)	0.071 c (0.032−0.125)	0.001 a (0.000−0.004)	nd	nd
chiro-inositol	0.032 a (0.021−0.051)	0.016 a (0.002−0.029)	0.013 a (0.006−0.022)	0.025 a (0.017−0.034)	0.198 b (0.053−0.395)	0.033 a (0.025−0.056)	nd	nd
scyllo-quercitol	0.139 a (0.087−0.213)	0.343 a (0.187−0.567)	0.333 a (0.144−0.683)	0.620 b (0.155−1.367)	nd	nd	nd	nd
scyllo-inositol	1.422 b (1.248−1.840)	1.144 b (0.259−2.149)	0.987 b (0.442−1.824)	1.997 c (0.312−4.188)	0.082 a (0.013−0.159)	nd	nd	nd
myo-inositol	0.367 c (0.227−0.502)	0.216 b (0.024−0.362)	0.141 a (0.020−0.200)	0.368 c (0.246−0.486)	0.383 c (0.107−0.828)	0.031 a (0.021−0.039)	0.046 a (0.024−0.065)	0.046 a (0.014−0.112)

[a] Different letters in the same row indicate statistical differences at the 0.05 level according to the Student−Newman−Keuls test. Minimum and maximum values found in samples are given in parentheses. dt, detected; nd, not detected. [b] Values are not quantified because of its overlapping with quinic acid.

C. sativa was characterized by the absence of deoxyinositols. Statistically, its values of *chiro*-, *muco*-, and *scyllo*-inositols were different from the rest of the samples. However, *myo*-inositol was the most abundant cyclic polyalcohol found in all chestnut samples.

On the other hand, the lack of deoxyinosiols in *P. avium* is also noticeable. This species showed low inositol content, just presenting small quantities of *chiro*- and *myo*-inositols and traces of *muco*-inositol. No quantities of *scyllo*-inositol were detected among samples belonging to this species.

Concerning *A. glutinose* samples, only *myo*-inostol and *vibo*-quercitol, a deoxyinositol, were found, while *myo*-inositol was the only inositol detected in *B. alba* samples.

To highlight differences between wood samples of different origins, experimental data were subjected to PCA. All data were considered in the analysis, except the values of *epi*-quercitol. The three principal components accounted for 79.3% of the total variance. The variables that displayed the best correlations with each principal component are exposed in Table 4, with their correlation coefficients.

Sample distributions in the plane formed by PC1 and PC3 are shown in Figure 1. The main principal component, PC1, separated *Quercus* samples from the rest of the woods because of higher concentrations of *proto*-quercitol, *scyllo*-inositol, *scyllo*-quercitol, *vibo*-quercitol, xylose, and arabinose. Principal component 3 separated *C. sativa*, *Q. robur*, and *Q. alba* samples from the rest of the samples considered because of their higher concentrations of *myo*-, *chiro*-, and *muco*-inositols. *Q. alba* and *Q. robur* presented slight differences from *Q. petrae* and *Q. pyrenaica* with regard to the monosaccharide content (Table 2). However, these differences were more accentuated when they were compared to *C. sativa* and *P. avium* because of the low monosaccharide content of these woods. This aspect was considered by PC1 and PC2,

which were exclusively correlated with monosaccharide compounds.

Table 4. Correlation Coefficient for Monosaccharide and Cyclic Polyalcohol Compounds against Principal Components 1, 2, and 3 (PC1, PC2, and PC3)

principal component	compound[a]	correlation coefficient
PC1	*proto*-quercitol	0.96
	scyllo-inositol	0.91
	scyllo-quercitol	0.89
	vibo-quercitol	0.81
	xylose and arabinose	0.79
PC2	fructose	0.92
	mannitol	0.88
	galactose and glucose	0.81
PC3	*myo*-inositol	0.88
	chiro-inositol	0.81
	muco-inositol	0.70

[a] Only compounds with absolute correlation coefficients greater than 0.70 have been included.

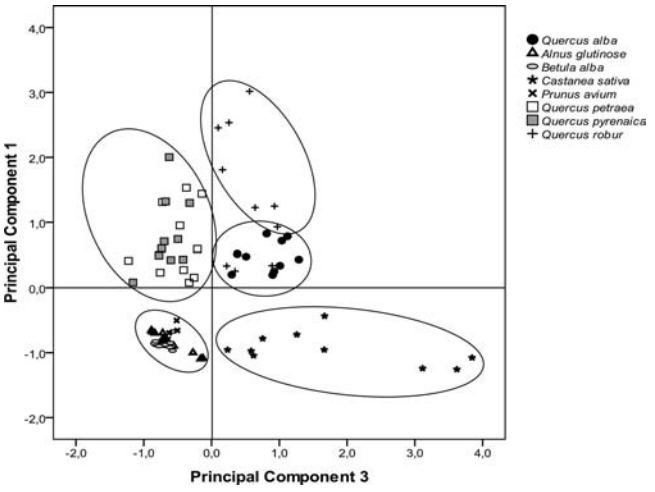

Figure 1. Plot of wood samples of different species on the plane defined by two principal components (PC1 and PC3).

From the relative position of samples with respect to PC1, it could be possible to differentiate woods of *Q. robur* from those of *Q. alba*, because of the higher quantities of quercitols, *scyllo*-inositol, xylose, and arabinose of the *Q. robur* samples. However, the differentiation between *Q. petraea* and *Q. pyrenaica* on the basis of their polyalcohol and monosaccharide compositions was not possible. Samples from *A. glutinose*, *B. alba*, and *P. avium* were concentrated in the region defined by the negative side of two component axes, because of their poor concentrations of cyclic polyalcohols.

After PCA, a linear discriminant analysis (LDA) was applied to the quantitative data to classify samples according to their botanical origins. Table 5 shows the coefficients of classification functions obtained for each studied compound. The correct percentage of classification was 100% for *Q. alba* and *P. avium*, 90% for *Q. petraea*, *Q. pyrenaica*, and *C. sativa*, 80% for *Q. robur* and *B. alba*, and 60% for *A. glutinose*. Therefore, 86.3% of all studied samples were classified correctly on the basis of studied compounds.

On the basis of the results, it was possible to conclude that cyclic polyalcohols were the main responsible compounds of differentiation among natural woods of several species. They allowed for not only the distinction of natural wood samples of diverse botanical origins but also the differentiation between oak wood samples from different species. For that reasons, cyclic polyalcohols could be used in the oenological industry to determine wood botanical origin and control and guarantee the authenticity of natural oak wood samples.

The toasting process, a common practice used in cooperage, affects the chemical composition of these compounds.[19] This fact could compromise the utility of cyclic polyalcohols to identify wood chips used in enology. However, it was demonstrated that, inclusive at 250 °C (high temperature rarely used in cooperage), the presence of quercitol, mainly, and other inositols was still detected.[19] As a consequence, the occurrence of these deoxyinositols in toasted wood samples will continue to be a marker of *Quercus* species. In preliminary results performed by our research group with medium-toasted and non-toasted oak wood samples, the differentiation between botanical origins was also possible. Cyclic polyalcohols were less sensible to thermal degradation than monosaccharides, and they decreased in linear tendency, especially in the case of quercitol, one of the main compounds in term of discriminating power to identify the botanical origin of woods. Therefore, *Q. alba* and *Q. robur* toasted and non-toasted

Table 5. Coefficients of Classification Functions Given by the LDA

compound	*Q. alba*	*Q. petraea*	*Q. pyrenaica*	*Q. robur*	*C. sativa*	*P. avium*	*A. glutinose*	*B. alba*
arabitol	−6.852	64.104	159.752	12.120	−134.197	323.147	72.570	124.953
xylose and arabinose	13.943	2.983	14.387	4.270	−3.496	0.702	0.330	−0.113
proto-quercitol (quercitol)	1.034	−1.191	−0.162	0.446	−1.204	−0.330	−0.835	−0.112
vibo-quercitol	1.554	134.210	111.771	39.915	14.593	−2.110	33.468	−1.879
muco-inositol	391.473	145.766	243.308	378.667	209.885	−20.419	−1.376	−5.499
mannitol	138.038	222.276	383.182	204.126	223.558	53.420	165.175	212.375
fructose	−0.765	−2.414	−1.938	−3.026	−3.949	−0.504	0.341	−1.538
chiro-inositol	−45.442	−0.058	4.175	−20.314	172.823	13.636	5.715	−4.295
scyllo-quercitol	−24.410	5.157	1.161	−1.352	5.277	−0.106	−0.518	−3.548
galactose and glucose	−0.646	0.344	−3.138	2.704	5.051	0.433	2.572	1.819
scyllo-inositol	2.229	−0.526	−3.979	0.829	−1.223	−1.143	−1.251	−1.175
myo-inositol	−5.586	−7.332	−28.895	−13.009	−20.357	0.204	−2.853	0.961
constant	−31.425	−18.181	−25.382	−31.440	−24.545	−4.187	−10.149	−5.346

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samples were differentiated from *Q. petraea* toasted and non-toasted samples by their content of cyclic polyalcohols. These findings were in a good agreement with those exposed in our paper. However, further studies about this issue will be performed in future studies with a higher number of samples to obtain more reliable conclusions.

AUTHOR INFORMATION

Corresponding Author

*Telephone: (34)-926295300, ext. 3425. Fax: (34)-926295318. E-mail: mariaelena.alanon@uclm.es.

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