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Influence of Geographical Origin and Botanical Species on the Content of Extractives in American, French, and East European Oak Woods

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The chemical composition of East European (Republic of Moldova, Ukraine, and Romania) oaks was investigated profoundly for the first time in the present study and compared with American and French counterparts. Taking into account the high natural variability of oak extractives contents, the wide-ranging sampling was performed for all oak origins: 276 French oaks, 102 East European oaks of both species (*Quercus robur* L. and *Quercus petraea* Liebl.), and 56 American oaks (*Quercus alba*). These oaks were compared with great attention paid to the extractives, which are most important for sensorial impact in wine or spirit maturation, such as ellagitannins and principal odorant substances (aromatic aldehydes, lactones and phenols). The substances in question were studied by application of HPLC and GC-MS techniques. The pattern of all studied extractive contents allowed adequate separation of oak samples according to their geographical origin or botanical species. The highest separation rate was for American and French oaks, whereas East European samples could be partially misclassified in two sets mentioned above. The most important variables for species discrimination were whiskey lactone related variables and ellagitannins, whereas the most important features for distinguishing the origin were eugenol, 2-phenylethanol, vanillin, and syringaldehyde. These substances allowed the distinction of French and East European woods of the same species. With regard to chemical composition, East European wood held the intermediary place between American and French oaks according to their ellagitannin and whiskey lactone levels; nevertheless, it was characterized by specific high values of eugenol, aromatic aldehydes, and 2-phenylethanol.

KEYWORDS: ***Quercus robur*; *Quercus petraea*; *Quercus alba*; origin; ellagitannins; volatiles substances; DFA; HPLC; GC-MS**

INTRODUCTION

Maturation in oak wood barrels is an important stage of high-quality wine and spirit manufacture. The oak species most often used in cooperage are *Quercus alba* and some related species, otherwise known as American white oak, and two European species, *Quercus robur* L. (pedunculate oak) and *Quercus petraea* Liebl. (sessile oak). Although they can be used practically for the same purposes, differences among these types of oak have been reported on the basis of the chemical analysis of wood extractives (*1*−*10*).

Several recent studies pointed out strong variability of the oak extractives contents as the result of different natural factors including geographical origin, species, forest practices, etc. (*8*, *11*).

The chemical studies of wood mostly provide data about oak originating from the U.S. and French forests, which is related to the high economic importance of cooperage in these countries. American oak wood is characterized by a lower total ellagitannin content when compared with wood of the European species. A high level of β-methyl-γ-octalactone (commonly called "whiskey lactone"), particularly of the *cis* isomer, is another significant feature used to differentiate American from European (French) oak (*1*, *3*−*6*, *12*, *13*).

It was suggested that several molecules could be used as chemical markers of origin. The analysis of these markers provides an efficient tool to control the provenance of raw materials in cooperage. Other authors (*6*, *7*) have observed that a high level of scopoletin is characteristic of American oak wood, although its amount was highly variable. Several nor-isoprenoid compounds have been found in American oak, but were almost absent in European oak (*9*).

However, the important research drawback in the works mentioned above is that a majority of the studied forests are monospecific or forests in which one species predominates, sometimes with insufficient sampling and identification. Thus, the effects of species and ecological conditions are often difficult to discriminate and can be mixed up; besides, insufficient sampling does not provide a reliable conclusion.

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The use of an intense experimental set of trees allows high between-tree natural variability of ellagitannin content to be taken into account (*14*, *15*). Besides, tree age effects and different ellagitannin localization in wood tissues can influence conclusions and make them unclear (*16*, *17*).

East European oak wood of the same European species (*Q. robur* L. and *Q. petraea* Liebl.) is traditionally used in local cooperage. This oak wood presents high interest for world barrel making due to its forest resources, whereas its chemical composition has been investigated only occasionally. Several results obtained by Chatonnet et al. (*18*) for Russian oaks (global indices and selected volatile compound data) and by Prida et al. (*19*) (ellagitannin data) for Moldavian oak revealed the prospective of East European oak use for wine and brandy maturation.

The aim of the current study is to analyze the chemical composition of East European (Republic of Moldova, Ukraine, and Romania) oaks in comparison with American and French oak woods. Taking into account the high natural variability of oak extractive content, observed in previous studies (*14*, *15*), the wide-ranging sampling was performed for all oak origins: 276 French oaks, 102 East European oaks of both species (*Q. robur* L. and *Q. petraea* L.), and 56 American oaks (*Q. alba*).

The oaks used in the investigation were selected to be at approximately the same age (80−110 years). Furthermore, the sample preparation was carried out identically for all samples with the aim to exclude errors related with different extractives localization in wood tissues.

During the research, we compared the oaks originating from different regions, paying attention to the extractives, which are most important for sensorial impact in wine or spirit maturation, such as ellagitannins and principal odorant substances (aromatic aldehydes, lactones, and phenols).

MATERIALS AND METHODS

Wood Sample Collection. East European oak samples of both species, *Q. robur* and *Q. petraea*, were obtained from three countries: Moldova, Ukraine, and Romania. Moldavian oak samples were taken from six different forests, situated mostly in the northern and central parts of the country (Briceni, Soroca, Calarasi, Orhei, Condrita, Cociulia; total number of samples = 45). The geographical area of sampling is characterized as typically continental with a mean rainfall of 400−560 mm per year and a mean temperature of 8 °C.

Ukrainian samples (total number = 19) were obtained from four regions (Ujgorod, Cernovtsi, Vinita, Ivano-Francovsk), situated in the western part of the country, close to the Moldavian and Romanian boundaries. Romanian woods (total number = 38) were taken from the regions of Vrancea and Iasi (eastern part, neighboring Moldova). In this case geographical representation of oak samples is rather wide, however, characterized by a dry continental climate with a cold winter and a hot dry summer.

American oak wood samples of *Q. alba* species were obtained from four states: Kentucky, Indiana, Missouri, and Pennsylvania (total number = 56).

Samples of French oak woods (118 sessile and 158 pedunculate oaks) originated from La Petite Charnie State Forest, which is located in the western part of France, characterized by a typically Atlantic climate, with a mean rainfall of 880 mm per year and a mean temperature of 11 °C. The sampled stand covers 5 ha and includes different soil types. In the northwestern part of the stand (plateau) the soil is well drained and composed of sand and slit. The southeastern part (small valley) is characterized by humid clayish soil (*20*). This confers to French woods a rather high natural variability in their extractives, even though all trees originated from the same forest site.

The species were identified using 34 foliar markers (*20*).

The overall information on sampling is given in **Table 1**.

Table 1. Overall Information on Sampling, Number of Samples

	species		
origin	*Q. robur*	*Q. petraea*	*Q. alba*
France	158	118	
Eastern Europe	64	38	
Moldova	25	20	
Romania	6	32	
Ukraine	7	12	
United States			56
Kentucky			14
Indiana			14
Missouri			14
Pennsylvania			14

Wood Processing. Each oak tree was cut at the 1.30 m height of the trunk to obtain a 10 cm width disk. A diametrical strip of 10 cm width oriented north−south was extracted from the disk by sawing. The next stage was sapwood exclusion judging by the color of the wood sample. Final sampling was carried out by shaving the 10 cm zones (approximately 35−40 rings) located at the two extremities of each diametric strip corresponding to heartwood. The wood shavings taken from the two extremities of the diametric strip were mixed to obtain one powdered sample (**Figure 1**). The shavings were ground to obtain a powder with linear dimensions equal to or smaller than 0.5 mm. Newly felled trees were used, and all of the procedures were performed identically for all trees. As an individual sample we considered the mixture of shavings as originating from an individual tree. All of the samples were analyzed separately with the aim to quantify characteristic extractives.

Analysis. Among oak wood extractives, the following substances, 10 ellagitannins (vescalin, castalin, roburins A−E, grandinin, vescalagin, castalagin) and ellagic acid and volatile substances (*trans*-whiskey lactone, 2-phenylethanol, *cis*-whiskey lactone, pantolactone, eugenol, mevalonic lactone, vanillin, syringaldehyde, coniferaldehyde), were chosen to be quantified in each oak sample using HPLC and GC-MS techniques.

HPLC. The sawdust samples (400 mg) were extracted with 20 mL of an acetone−water mixture (7:3) at room temperature for 3 h under magnetic stirring. The acetone was evaporated at 35−40 °C under vacuum, the sample volume was readjusted with water to 20 mL, and the samples were filtered on Millipore filtration membranes (0.45 μm). The quantification of ellagitannins was performed using HPLC. The HPLC process consisted of equipment from Millipore-Waters: a 490 E diode array detector, two model 510 pumps, a model 717 automatic injector, a system interface module (SIM), and Maxima 820 software (Millipore-Waters).

An RP 18 LiChrospher column (250 × 4.6 mm, 5 μm) (Merck, Darmstadt, Germany) and a precolumn from the same supplier (4 × 4 mm, 5 μm) were used to separate and determine ellagitannins.

A binary gradient was used with the following elution conditions: solvent A, 0.1% phosphoric acid in water; solvent B, water−methanol solution (50:50); flow rate, 0.8 mL/min; gradient, 0−16% B in 45 min, 16−90% B in 5 min, 90% B (constant gradient) for 5 min, 90−100% B in 15 min, 100% B (constant gradient) for 10 min, 100−0% B in 5 min.

The ellagitannins were detected by their UV absorption at 240 nm using a diode array detector (Waters 990). Identification was achieved by cochromatography with purified reference substances and by spectral comparisons. Quantification was carried out using calibration with purified ellagitannins provided by INRA (Montpellier). Ten ellagitannins (vescalin, castalin, roburins A−E, grandinin, vescalagin, castalagin) and ellagic acid were quantified in each oak wood sample. According to definition vescalin and castalin are not ellagitannins, because they do not release ellagic acid under hydrolysis. However, in this study as well as in many others related to oak chemistry, they are classified as ellagitannins because of their presence in oak, because they have properties similar to those of other oak ellagitannins (roburins A−E, grandinin, vescalagin, and castalagin), and because they are the structural part of the latter.

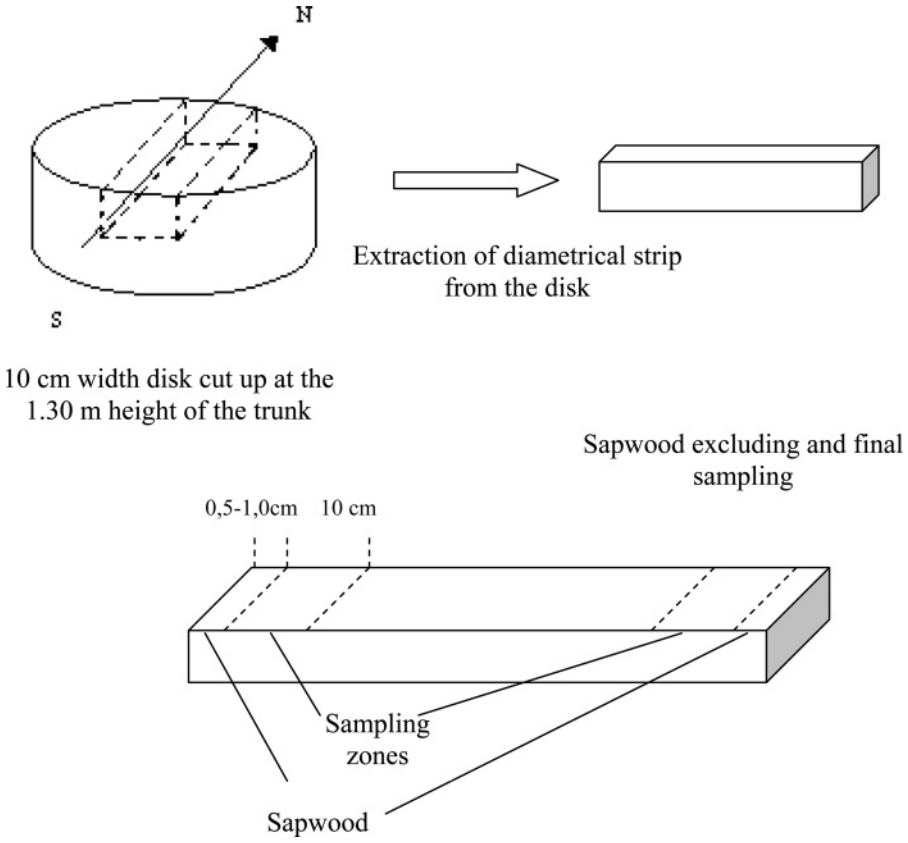

Figure 1. Wood-processing scheme.

The solvents used complied with technical quality for acetone, Milli-Q quality for water, and HPLC grade (Carlo Erba) for methanol.

GC-MS. The sawdust samples (10 g) were extracted with 100 mL of dichloromethane (for pesticide analysis quality) in bulk for 18 h at room temperature under magnetic stirring. According to the preliminary test such a procedure provided 85−100% extraction of studied compounds in liquid medium. These values are obtained by comparison of the amount of volatile substance extracted by using the current method and the sum of amounts extracted within three repeated 18-h extractions, which is considered to totally exhaust the wood, and they were regarded as satisfactory. After ∼50 times concentration of the obtained extract under vacuum (concentration from ∼100 to 1.5−2 mL of the sample volume), an internal standard (4-nonanol solution in dichloromethane, 1 mg/mL) was added to each sample with the aim to control the volume of chromatographic injection.

The GC-MS process was carried out using equipment from Hewlett-Packard: HP 6890 series GC system, HP 5973 mass selective detector, GC autosampler controller, Aglient 6890 series injector and controlled by HP ChemStation software (version A.03.00). Samples were chromatographed on a DB-Wax column (30 m × 320 μm, 0.5 μm thickness). Temperature was held at 60 °C for 3 min and then increased at 4 °C/min until it reached 238 °C. The carrier gas was helium with a constant flow of 1 mL/min. The injection volume was 1 μL. MS spectra were obtained at 70 eV, with the mass range scanned from 40 to 500 amu.

Identification was performed by mass spectrometry using the Wiley database and by cochromatography with pure reference substances. Quantification was carried out by integration of characteristic ion peaks (whiskey lactone, *m*/*z* 99; 2-phenylethanol, *m*/*z* 91; pantolactone, *m*/*z* 71; eugenol, *m*/*z* 164; mevalonic lactone, *m*/*z* 71; vanillin, *m*/*z* 151; syringaldehyde, *m*/*z* 182; coniferaldehyde, *m*/*z* 178). The method was calibrated using triplicate injections of a series of external standards for each quantified substance. Reference substances for calibration were supplied by Sigma-Aldrich.

Statistical Treatment. To achieve more reliable results in the principal statistical treatment, Moldavian, Ukrainian, and Romanian oak samples were considered as a single group, because of their relatively close geographical position.

Statistical treatments were carried out using SAS software (version 6.12 for Windows, SAS Institute Inc., Cary, NC).

Principal component analysis (PCA) and variable correlation analysis were carried out for all of the extractive variables using different sample sets, including all or several oak origins/species. The 2D variable graphs were plotted for variables, and variance was explained by each calculated axis.

Variance analysis was performed for all of the extractives. The Student−Newman−Keuls test was carried out for each variable with calculation of probabilities.

Discriminate function analysis was implemented to identify some canonical function capable of distinguishing wood origins/species. The variables contributed to distinguishing origins/species. The prediction of group membership was assumed.

RESULTS AND DISCUSSION

Correlation between Studied Parameters. Influence of Species and Geographical Origins. A 2D PCA projection of all variables observed using the overall data sets (all origins, all species) is presented in **Figure 2**.

The first principal component axis explained 37.5% of the total variation and was closely correlated with all ellagitannin variables, especially with the most abundant: vescalagin, roburin E, castalagin (correlation coefficients of 0.84, 0.87, and 0.96, respectively) as well as with the total ellagitannin content (0.98). The second axis explained 12.1% of the total variation and was related to some extent to whiskey lactone isomer compounds, as well as to their *cis*/*trans* ratio, aromatic aldehydes, and eugenol. Globally this approach allowed the complexity of oak extractive variables to be reduced to the two principal almost unrelated components: ellagitannins and a group of volatile compounds, which is commonly recognized in oak wood research (*21*−*23*). This approach allowed approximately half of total variability of oak wood data to be explained. However, each volatile compound demonstrated only slight correlation

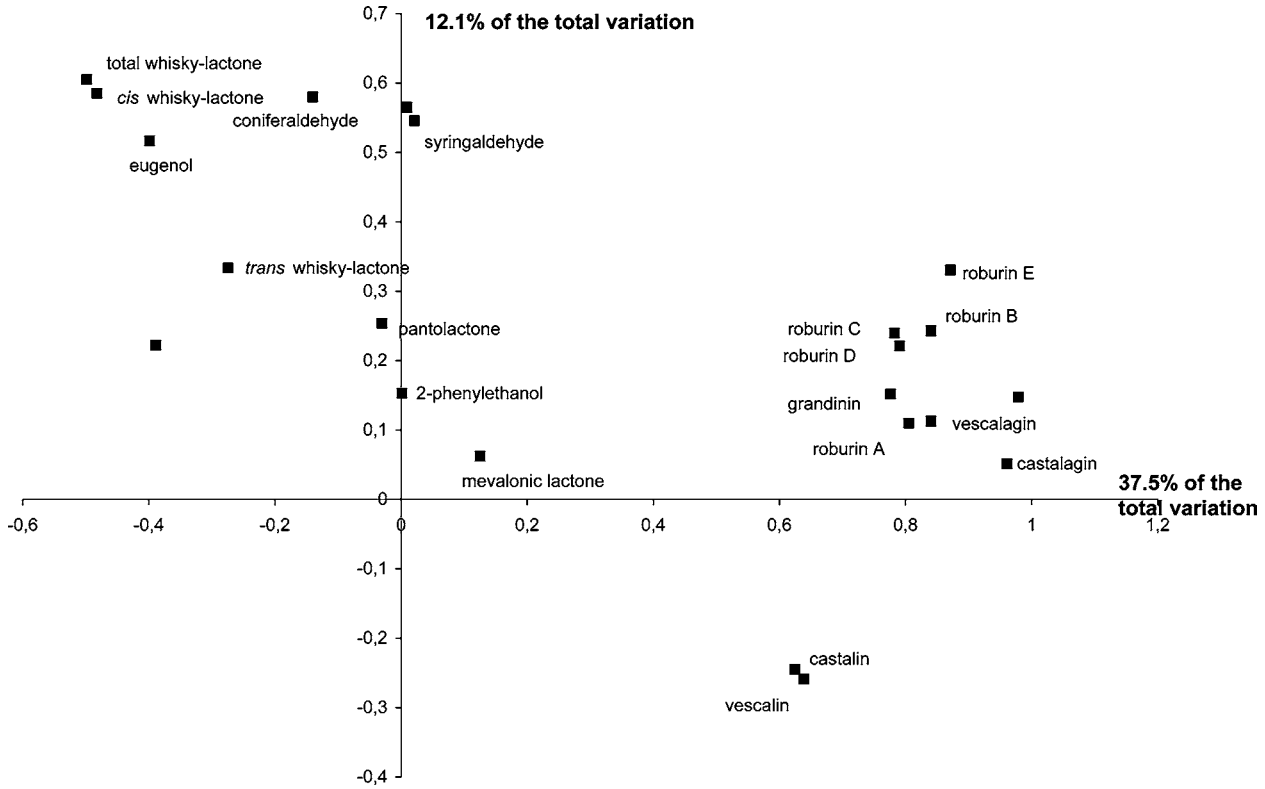

Figure 2. PCA chart for the overall sets (all origins, all species).

with the second principal component axis. Therefore, only several volatile compounds (2-phenylethanol, mevalonic lactone, pantolactone, vanillin, syringaldehyde, coniferaldehyde) could be considered as nonrelated with ellagitannins (correlations are nonsignificant). Within this group the aromatic aldehydes content was found to be closely correlated. That may be explained by the similar mechanisms of formation of these substances. Indeed, all studied aromatic aldehydes originate from lignin decomposition; thus, the amplitude of this process influences to almost the same extent each aldehyde formation (*24*).

Another group of substances (eugenol, whiskey lactone isomers, and total content of whiskey lactone isomers), as well as the whiskey lactone *cis*/*trans* ratio, were found to be anticorrelated with ellagitannins (**Table 2**).

These anticorrelations demonstrated the opposite character of metabolism of these two groups of substances in wood tissues. On the other hand, the botanical (species) or geographical (origin) factors could influence the specific distribution of these compounds, to achieve the anticorrelations mentioned above. With the aim to test the last hypothesis, the same PCA and correlation analysis were applied to sample subsets (origins, species).

The 2D PCA projection of all variables observed using the American oak data set was performed. Similar to the overall sets, the first principal component was closely related with ellagitannin variables. Correlation coefficients were 0.97 for total ellagitannin content and 0.88 for castalagin. However, contrary to the overall set case, there was a good correlation of whiskey lactone variables with the second principal component axis (0.90 for total whiskey lactone, 0.82 for the *trans*-isomer, and 0.84 for the *cis* isomer). Hence, in the case of the American variable set, contrary to the overall sets, the two groups of substances (ellagitannins and whiskey lactone isomers) were really unrelated. The binary correlations between each ellagitannin content and each whiskey lactone isomer were insignificant.

Table 2. Principal Correlations[a] between Variables

	total ellagitanin content	vescalagin	castalagin
	Overall Set (All Origins, All Species)		
eugenol	–0.317**	–0.304**	–0.349**
trans-WL[b]	–0.227**	–0.204**	–0.244**
cis-WL	–0.370**	–0.338**	–0.408**
total WL	–0.388**	–0.353**	–0.425**
cis/trans	–0.324**	–0.321**	–0.351**
	French Oak Set		
trans-WL	–0.187**	–0.173**	–0.202**
cis-WL	–0.181**	–0.222**	–0.214**
total WL	–0.227**	–0.248**	–0.259**
cis/trans	ns	–0.151*	ns
	East European Oak Set		
eugenol	–0.249*	ns	–0.223*
trans-WL	–0.409**	–0.312**	–0.447**
cis-WL	–0.275**	ns	–0.300**
total WL	–0.391**	ns	–0.427**
	FreNch and East European Oak Set (French Set/east European Set); Particular Case of Aromatic Aldehydes		
vanillin	0.227**/0.289**	0.275**/0.409**	0.155**/0.239*
syringaldehyde	ns/ns	0.166**/ns	ns/–0.221*
coniferaldehyde	0.161**/–0.321**	0.212**/ns	ns/–0.380**
	French Pedunculate Oak Set; Correlation with Vanillin and Eugenol		
vanillin	0.279**	0.295**	0.190*
eugenol	0.315**	0.276**	0.295**

[a] Correlations significant at the 0.01 level (two-tailed) (**) and at the 0.05 level (two-tailed) (*); ns, nonsignificant. [b] WL, whiskey lactone; *cis*/*trans*, ratio of *cis*- and *trans*-whisey lactone.

Also contrary to the previous study, it seems that the eugenol content could not be considered in the same group with whiskey lactone isomers. Its content was correlated neither with ellagitannins nor with whiskey lactone isomers.

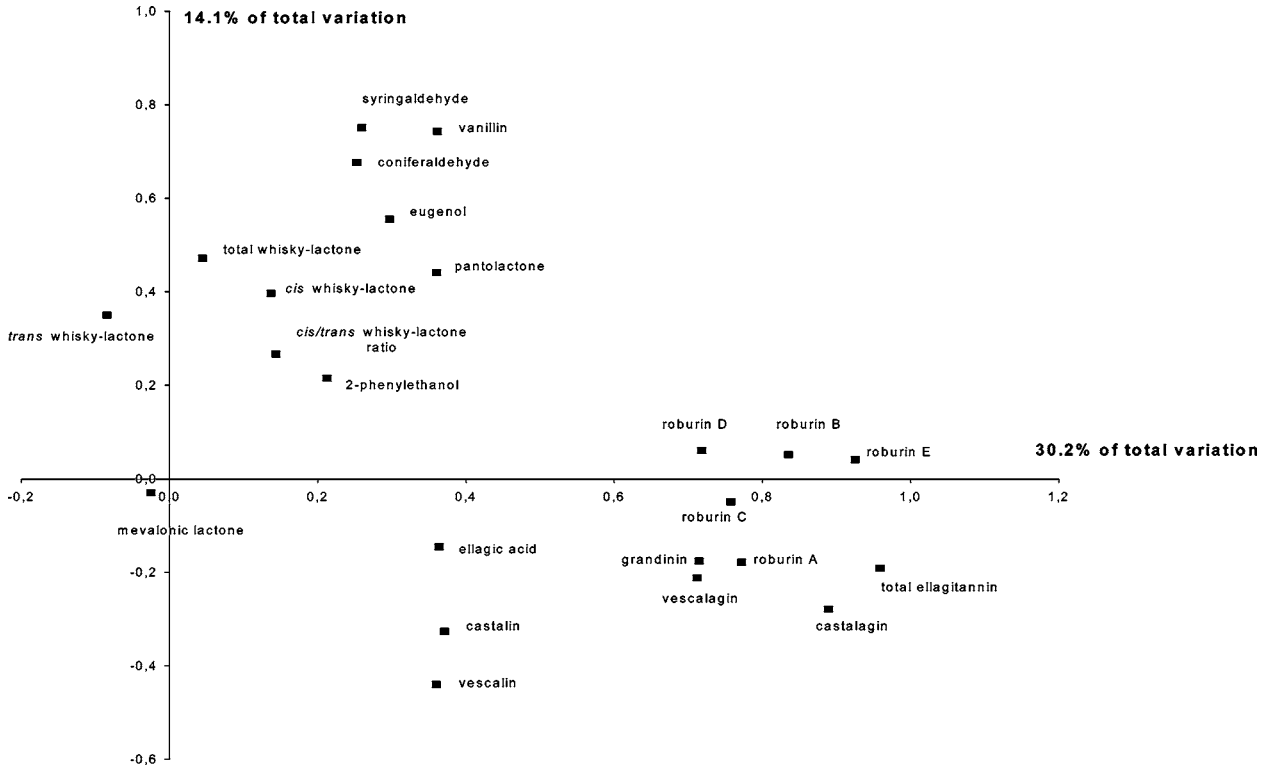

Figure 3. PCA chart for the pedunculate oak sets.

The same procedure was applied to French and East European sets.

In the case of the French sets as well as in the previous studies, two unrelated groups of substances were elucidated: volatile compounds and ellagitannins. Thus, in the current case, the volatile substance group was composed of 2-phenylethanol, eugenol, vanillin, syringaldehyde, and coniferaldehyde. Their correlation coefficients with the second principal component axis were relatively high: 0.66, 0.67, 0.78, 0.79, and 0.74, respectively. Likewise, in the global set, whiskey lactone isomer contents were anticorrelated with ellagitannin indices (**Table 2**).

Contrary to the global sets, eugenol was independent (total ellagitannin × eugenol correlation coefficient is 0.087 at $p = 0.151$).

Similarly to the French oak sets, the East European set showed anticorrelation between ellagitannins and whiskey lactone indices. However, in this case the *cis*/*trans*-oak lactone ratio seemed to be independent from these variables (ellagitannins and whiskey lactone isomer contents). The eugenol content was rather directly anticorrelated with ellagitannin content; nevertheless, the correlation value was less than for the overall oak sample sets (**Table 2**).

It should be mentioned that in the case of East European and French oak sets, contrary to the overall and American oak sets, there was a certain correlation between aromatic aldehydes and ellagitannins, which in some cases was positive and in some others negative (**Table 2**).

In the case of the total *Q. robur* set, there were two groups of substances contributing to the total variability: ellagitannins and aromatic aldehydes (**Figure 3**). The whiskey lactone isomer variables did not contribute much to this variability. This observation could be explained by the small accumulation of whiskey lactone in the *Q. robur* species and probably by random distribution of their isomers related with it.

The overall set of *Q. robur* was divided into two subsets of European and French oaks. Each subset demonstrated similar relationships between variables, excluding the appearance of the slight correlation of vanillin and eugenol with ellagitannin variables for the French sets (**Table 2**).

In the *Q. petraea* case, the *cis* isomer and total whiskey lactone were essentially substances correlated with the axis of the second principal component (correlation coefficients of 0.69 and 0.68, respectively), but the other volatile compounds also demonstrated ellagitannin-independent behavior (**Figure 4**).

The overall *Q. petraea* set as well was represented by two subsets: European and French oaks. Likewise, each subset illustrated similar relationships between variables, excluding the appearance of a slight correlation of vanillin with ellagitannin variables for the East European set. Correlation coefficients were 0.533 for vescalagin, 0.483 for castalagin, and 0.520 for the total ellagitannin content (all correlations were significant at the 0.01 level).

One can observe for both the *Q. petraea* and *Q. robur* sets very characteristic features of the three variables grouping (vescalin, castalin, and ellagic acid), with high correlation within the group and with a rather weak one with other ellagitannins. That could be explained by participation of all three substances in the hydrolysis reaction of other ellagitannins, which equally affects each of these substances (*25*, *26*). On the other hand, vescalin, castalin, and ellagic acid metabolism in plant tissues differs considerably from that of other ellagitannins.

In conclusion to this portion of the study, it should be stated that within the limits of a single species set the two categories of variables were perfectly unrelated, but closely correlated within groups: ellagitannins and the group formed by whiskey lactone isomers and a variable of the *cis*/*trans* whiskey lactone ratio. The contribution of variability explained by whiskey lactone variables to the total variability decreased gradually from American oak (*Q. alba*) through sessile oak to pedunculate oak. Other volatile compounds contributed slightly to total variability; nevertheless, in certain cases the vanillin and eugenol contents correlated positively or negatively with ellagitannin variables.

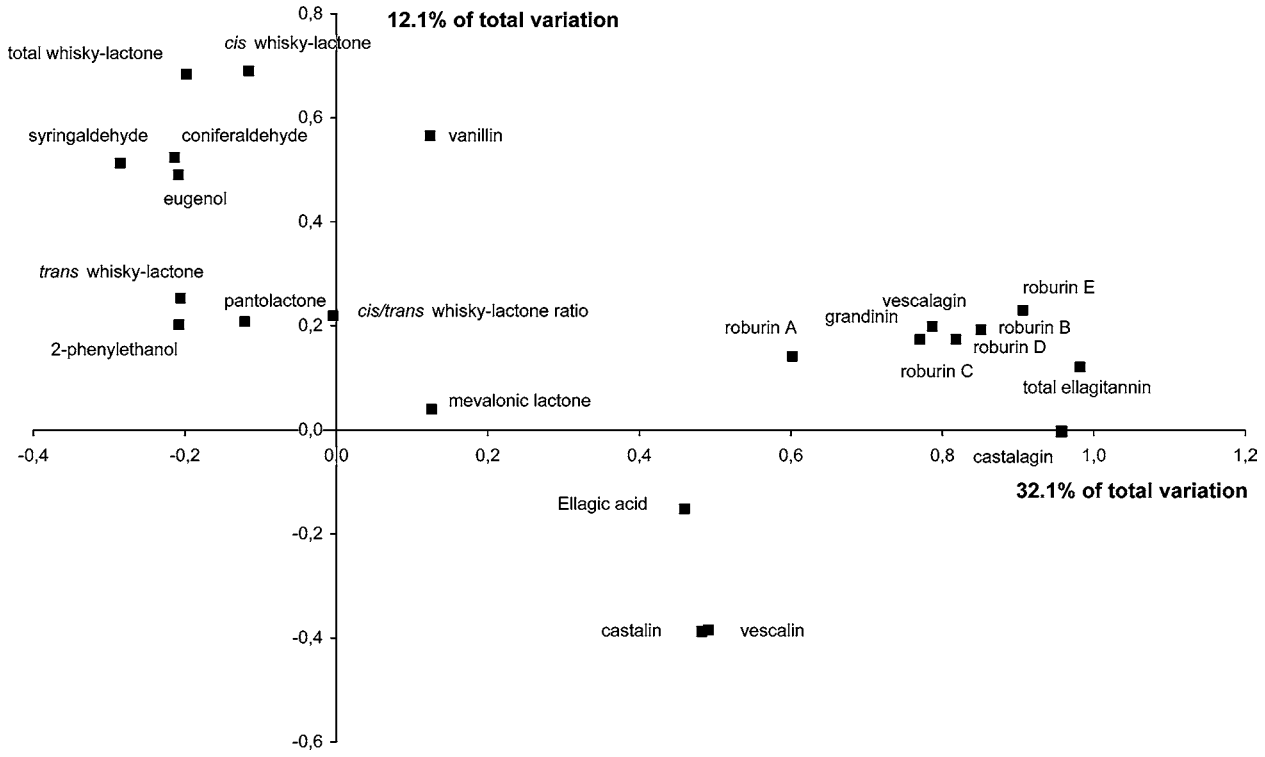

Figure 4. PCA chart for the sessile oak sets.

Table 3. Means and Standard Deviations of Extractive Compounds in Oak Wood of Different Origins (Volatile Substance Content, Micrograms per Gram of Dry Wood; Ellagitanin Content, Milligrams per Gram of Dry Wood)

	Moldova		Ukraine		Romania		France		U.S.
compound[a]	*Q. robur*	*Q. petraea*	*Q. robur*	*Q. petraea*	*Q. robur*	*Q. petraea*	*Q. robur*	*Q. petraea*	*Q. alba*
trans-WL	0.040 ± 0.025	9.001 ± 10.585	0.072 ± 0.052	7.568 ± 9.339	0.113 ± 0.062	3.319 ± 3.332	0.2796 ± 0.924	3.878 ± 6.412	2.183 ± 2.130
2-phenylethanol	1.421 ± 1.810	0.881 ± 0.701	1.9335 ± 2.970	0.375 ± 0.289	0.190 ± 0.040	0.234 ± 0.110	0.162 ± 0.129	0.140 ± 0.084	0.470 ± 0.179
cis-WL	0.129 ± 0.106	11.996 ± 14.398	0.170 ± 0.151	17.472 ± 12.824	0.552 ± 0.307	16.114 ± 14.389	0.326 ± 1.092	6.899 ± 7.532	14.209 ± 6.818
pantolactone	0.346 ± 0.159	0.332 ± 0.115	0.327 ± 0.138	0.291 ± 0.144	0.330 ± 0.054	0.585 ± 1.755	0.251 ± 0.160	0.223 ± 0.133	0.211 ± 0.097
eugenol	1.084 ± 0.842	2.532 ± 2.151	0.979 ± 0.363	2.398 ± 1.889	0.387 ± 0.095	2.393 ± 1.991	0.299 ± 0.300	0.584 ± 0.694	2.242 ± 1.259
mevalonic lactone	0.596 ± 0.669	0.521 ± 0.565	0.472 ± 0.321	0.529 ± 1.138	0.000 ± 0.000	1.197 ± 4.565	0.883 ± 0.538	1.022 ± 0.747	0.162 ± 0.259
vanillin	5.829 ± 2.270	5.213 ± 3.015	4.601 ± 1.476	17.821 ± 28.731	7.157 ± 0.672	9.171 ± 13.004	3.795 ± 1.991	3.168 ± 1.604	4.556 ± 1.389
syringaldehyde	5.291 ± 3.678	5.051 ± 3.609	8.318 ± 2.024	10.306 ± 5.689	10.476 ± 1.129	13.874 ± 8.369	6.623 ± 1.489	5.685 ± 2.778	6.968 ± 2.040
coniferaldehyde	1.856 ± 0.871	2.084 ± 1.036	2.549 ± 0.691	3.722 ± 1.722	3.958 ± 0.786	4.228 ± 1.474	3.440 ± 2.626	2.799 ± 2.013	2.335 ± 0.653
total WL	0.168 ± 0.108	20.997 ± 18.859	0.242 ± 0.189	25.041 ± 13.528	0.666 ± 0.343	19.434 ± 16.089	0.605 ± 1.604	10.778 ± 10.376	16.392 ± 8.275
cis/trans	3.2398 ± 2.092	2.3642 ± 1.499	2.849 ± 2.629	5.142 ± 4.418	5.0043 ± 2.152	6.974 ± 5.202	1.949 ± 1.649	4.587 ± 4.554	10.274 ± 6.764
vescalin	0.7295 ± 0.414	0.497 ± 0.410	0.802 ± 0.310	0.343 ± 0.131	0.9053 ± 0.265	0.396 ± 0.216	1.087 ± 0.728	0.730 ± 0.613	0.113 ± 0.067
castalin	0.5620 ± 0.264	0.481 ± 0.414	0.633 ± 0.285	0.277 ± 0.244	0.632 ± 0.181	0.189 ± 0.120	0.652 ± 0.391	0.487 ± 0.349	0.102 ± 0.060
roburin A	2.2604 ± 0.778	1.369 ± 1.079	2.525 ± 0.919	2.050 ± 2.202	3.259 ± 0.430	1.147 ± 1.145	3.257 ± 2.096	1.672 ± 0.889	0.400 ± 0.280
roburin B	4.063 ± 1.419	2.074 ± 1.655	4.473 ± 1.352	2.129 ± 2.252	4.670 ± 1.027	1.409 ± 1.244	3.103 ± 1.703	2.412 ± 1.434	0.826 ± 0.511
roburin C	2.789 ± 1.018	1.498 ± 1.052	2.929 ± 0.773	1.564 ± 1.470	3.238 ± 1.815	1.405 ± 1.572	2.541 ± 1.728	2.083 ± 1.656	0.541 ± 0.326
grandinin	3.591 ± 1.064	2.822 ± 1.331	3.359 ± 5.344	1.948 ± 0.815	4.435 ± 2.314	1.674 ± 0.858	3.204 ± 2.174	2.734 ± 1.618	0.633 ± 0.380
roburin D	5.178 ± 1.056	3.184 ± 1.978	5.3444 ± 1.537	2.263 ± 2.160	3.451 ± 3.203	2.424 ± 2.015	4.285 ± 2.829	3.193 ± 2.241	0.625 ± 0.440
vescalagin	5.812 ± 2.381	4.674 ± 3.472	5.435 ± 1.592	4.038 ± 3.987	6.657 ± 2.674	4.268 ± 3.018	11.048 ± 5.622	6.358 ± 3.372	1.344 ± 1.001
roburin E	3.918 ± 0.841	2.651 ± 1.144	3.880 ± 0.958	2.142 ± 1.404	4.111 ± 0.295	2.044 ± 1.301	3.398 ± 1.914	2.983 ± 1.597	0.974 ± 0.503
castalagin	13.817 ± 2.985	9.104 ± 4.799	14.117 ± 3.369	7.370 ± 4.564	10.251 ± 0.416	7.044 ± 2.987	15.784 ± 6.070	11.756 ± 4.869	2.807 ± 1.376
ellagic acid	2.762 ± 1.131	2.104 ± 1.027	2.893 ± 1.346	1.861 ± 0.641	1.834 ± 0.349	1.500 ± 0.462	1.843 ± 0.889	1.200 ± 1.156	*b*
total ellagitanin	42.711 ± 9.134	28.354 ± 16.005	43.498 ± 11.272	24.122 ± 16.198	41.608 ± 2.433	22.000 ± 11.635	48.359 ± 20.950	34.407 ± 15.619	8.363 ± 4.197

[a] WL, whiskey lactone; *cis*/*trans*, ratio of *cis*- and *trans*-whiskey lactone. [b] Not quantified.

The influence of geographical factors (case of the overall set) changed essentially the representations mentioned above. Whiskey lactone variables were no more ellagitannin-unrelated, but demonstrated in these conditions, as well as eugenol did, a high anticorrelation with ellagitannin contents. Thus, the hypothesis of specific distribution of several volatile substances affected by geographical origin was confirmed. Special attention should be paid to these molecules to distinguish geographical origins of oak growing.

Distribution of Extractive Compounds in Relation to Botanical Species and Geographical Origin of Oak Growing. The major results (averages with standard deviations) for the different species/origins are presented in **Table 3**.

American oak wood could be characterized by the considerably lower level of ellagitannins in comparison with European oaks, whatever their origin is. At the same time, American oak possessed a high level of whiskey lactone; however, there was no substantial difference between Romanian and Ukrainian oaks.

Table 4. One-Way ANOVA for Different Botanical Species

compound[a]	values: μg/g for volatile substances; mg/g for ellagitannins; absolute units for *cis/trans* ratio			$F_{species}$/ $F_{species\ except\ Q.\ alba}$[b]
	Q. robur	*Q. petraea*	*Q. alba*	
trans-WL	0.236[a]	4.587[b]	2.183[c]	41.69***/74.73***
2-phenylethanol	0.3876[a]	0.2535[a]	0.4699[a]	ns/ns
cis-WL	0.3019[a]	9.7767[b]	14.2085[c]	111.42***/144.36***
pantolactone	0.2682[a]	0.3028[a]	0.2107[a]	ns/ns
eugenol	0.4262[a]	1.2355[b]	2.2424[c]	59.44***/46.79***
mevalonic lactone	0.9652[a]	0.8045[a]	0.1617[b]	7.39***/ns
vanillin	4.1860[a]	5.4145[a]	4.5560[a]	ns/ns
syringaldehyde	6.6315[a]	7.3595[a]	6.9688[a]	ns/ns
coniferaldehyde	3.2222[a]	3.0323[a]	2.3352[b]	3.96*/ns
total WL	0.5385[a]	14.3634[b]	16.3917[b]	125.16***/197.20***
cis/trans	2.2433[a]	4.8124[b]	10.2738[c]	82.34***/47.48***
vescalin	1.0260[a]	0.6200[b]	0.1130[c]	60.49***/40.45***
castalin	0.6394[a]	0.4202[b]	0.1015[c]	61.39***/35.74***
roburin A	3.1034[a]	1.5710[b]	0.3996[c]	92.27***/87.39***
roburin B	3.3224[a]	2.1801[b]	0.8256[c]	66.57***/47.12***
roburin C	2.6070[a]	1.8651[b]	0.5408[c]	42.73***/20.04***
grandinin	3.2968[a]	2.5052[b]	0.6328[c]	55.10***/18.26***
roburin D	4.4114[a]	2.9953[b]	0.6245[c]	63.24***/31.81***
vescalagin	10.0450[a]	5.6526[b]	1.3438[c]	102.43***/83.22***
roburin E	3.5031[a]	2.7259[b]	0.9742[c]	58.40***/20.77***
castalagin	15.3038[a]	10.3466[b]	2.8067[c]	144.90***/81.04***
total ellagitanin	47.2587[a]	30.8823[b]	8.3629[c]	130.97***/80.75***

[a] WL, whiskey lactone; *cis*/*trans*, ratio of *cis*- and *trans*-whiskey lactone. [b] Probabilities: ns, >0.05 (nonsignificant); *, <0.05 (significant); **, <0.01 (very significant); ***, <0.001 (extremely significant).

Table 5. One-Way ANOVA for Different Geographical Origins

compound	values: μg/g for volatile substances; mg/g for ellagitannins; absolute units for *cis/trans* ratio			F_{origin}/ $F_{origin\ except\ U.S.}$
	Eastern Europe	France	U.S.	
trans-WL	3.7181[a]	1.8184[b]	2.1832[b]	5.40**/9.62**
2-phenylethanol	0.7839[a]	0.1527[b]	0.4699[c]	36.57***/62.24***
cis-WL	9.5388[a]	3.1361[b]	14.2085[c]	52.45***/41.77***
pantolactone	0.4093[a]	0.2389[b]	0.2107[b]	4.99**/7.79**
eugenol	1.8850[a]	0.4208[b]	2.2424[c]	114.81***/150.54***
mevalonic lactone	0.7183[a]	0.9423[a]	0.1617[b]	7.75***/ns
vanillin	8.1615[a]	3.5269[b]	4.5560[b]	20.01***/35.09***
syringaldehyde	9.0392[a]	6.2218[b]	6.9688[b]	16.57***/29.81***
coniferaldehyde	3.0355[a]	3.1660[a]	2.3352[b]	3.71**/ns
total WL	13.2570[a]	4.9545[b]	16.3917[c]	39.07***/40.82***
cis/trans	4.6163[a]	3.1465[b]	10.2738[c]	65.30***/11.19**
vescalin	0.5489[a]	0.9346[b]	0.1130[c]	52.21***/27.93***
castalin	0.4045[a]	0.5816[b]	0.1015[c]	49.24***/17.59***
roburin A	1.7884[a]	2.5789[b]	0.3996[c]	44.71***/15.51***
roburin B	2.6767[a]	2.8078[a]	0.8256[b]	35.85***/ns
roburin C	1.9919[a]	2.3451[a]	0.5408[b]	31.96***/ns
grandinin	2.6792[a]	3.0030[a]	0.6328[b]	44.22***/ns
roburin D	3.4898[a]	3.8182[a]	0.6245[b]	42.44***/ns
vescalagin	4.9198[a]	9.0427[b]	1.3438[c]	82.47***/54.21***
roburin E	2.8804[a]	3.2207[a]	0.9742[b]	46.29***/ns
castalagin	9.8204[a]	14.0614[b]	2.8067[c]	115.09***/42.91***
total ellagitanin	31.2004[a]	42.3943[b]	8.3629[c]	89.90***/26.22***

[a] WL, whiskey lactone; *cis*/*trans*, ratio of *cis*- and *trans*-whiskey lactone. [b] Probabilities: ns, >0.05 (nonsignificant); *, <0.05 (significant); **, <0.01 (very significant); ***, <0.001 (extremely significant).

The high *cis*/*trans* whiskey lactone ratio was a very typical feature of American oak wood (10.2 against 1.9−6.7 for European woods). This observation complies with the previous research concerning determination of whiskey lactone isomers in wines aged in American and European oak barrels (*5*, *10*).

Table 6. Two-Way ANOVA

compound	species	origin	interaction	model estimation
trans-WL	74.21***	ns	4.16*	23.14***
2-phenylethanol	36.24***	102.19***	32.75***	31.86***
cis-WL	159.28***	22.48***	23.87***	76.15***
pantolactone	ns	7.24**	ns	2.85*
eugenol	55.13***	111.18***	25.33***	79.36***
mevalonic lactone	ns	ns	ns	4.51**
vanillin	4.35*	31.63***	8.55**	12.46***
syringaldehyde	8.38**	23.98***	23.11***	14.59***
coniferaldehyde	ns	ns	13.40***	5.42***
total WL	213.12***	21.67***	24.82***	83.92***
cis/trans	19.00***	4.61**	ns	42.66***
vescalin	27.72***	21.74***	ns	37.21***
castalin	33.75***	10.74***	ns	35.43***
roburin A	57.45***	9.35**	ns	49.60***
roburin B	80.99***	ns	25.81***	41.68***
roburin C	27.69***	ns	7.24**	23.87***
grandinin	26.93***	ns	8.00**	30.17***
roburin D	39.28***	ns	5.00*	33.10***
vescalagin	40.01***	53.38***	10.38**	72.37***
roburin E	32.92***	ns	12.04***	33.24***
castalagin	69.43***	31.72***	ns	87.41***
total ellagitanin	69.18***	16.39***	ns	73.00***

[a] WL, whiskey lactone; *cis*/*trans*, ratio of *cis*- and *trans*-whiskey lactone. [b] Probabilities: ns, >0.05 (nonsignificant); *, <0.05 (significant); **, <0.01 (very significant); ***, <0.001 (extremely significant).

Table 7. Classification Results for Overall Sets

original	predicted				
	East European *Q. robur*	East European *Q. petraea*	U.S. *Q. alba*	French *Q. robur*	French *Q. petraea*
East European *Q. robur*	**91.18**	2.94	0	2.94	2.94
East European *Q. petraea*	6.35	**66.67**	15.87	0	11.11
U.S. *Q. alba*	0	7.14	**92.86**	0	0
French *Q. robur*	2.11	0	0	**85.92**	11.97
French *Q. petraea*	3.39	2.54	5.08	11.02	**77.97**

Table 3 demonstrates as well the high level of French oak (single forest) extractive variability comparable with variability of East European and American oak (multiple forests). This fact shows that intraforest variability has an approximately similar level with interforest variability.

One can also observe a high level of aromatic aldehydes and eugenol in East European woods in comparison with French oaks.

To develop and examine in detail these observations, the one-step ANOVA was performed both for oak origin and for oak species. The most valuable results are given in **Tables 4** and **5**.

One can observe very evident differences for practically all of the variables among species and origins. Thus, the whiskey lactone isomer proportion, as well as that of eugenol, increased from *Q. robur* to *Q. petraea* to *Q. alba*, whereas the ellagitannin (total or individual ellagitannin) proportion decreased. Other volatile substances (2-phenylethanol, pantolactone, mevalonic lactone, aromatic aldehydes) did not contribute or contributed only slightly to distinguishing the various species. The high values of the *F* factor were probably related to the presence of American oak (*Q. alba*), which has quite a different composition compared with European species. Therefore, *F* factors were also calculated for samples aside from American oaks. As one can see, high *F* values were found for the majority of compounds, comparable with *F* values for the overall set. This fact

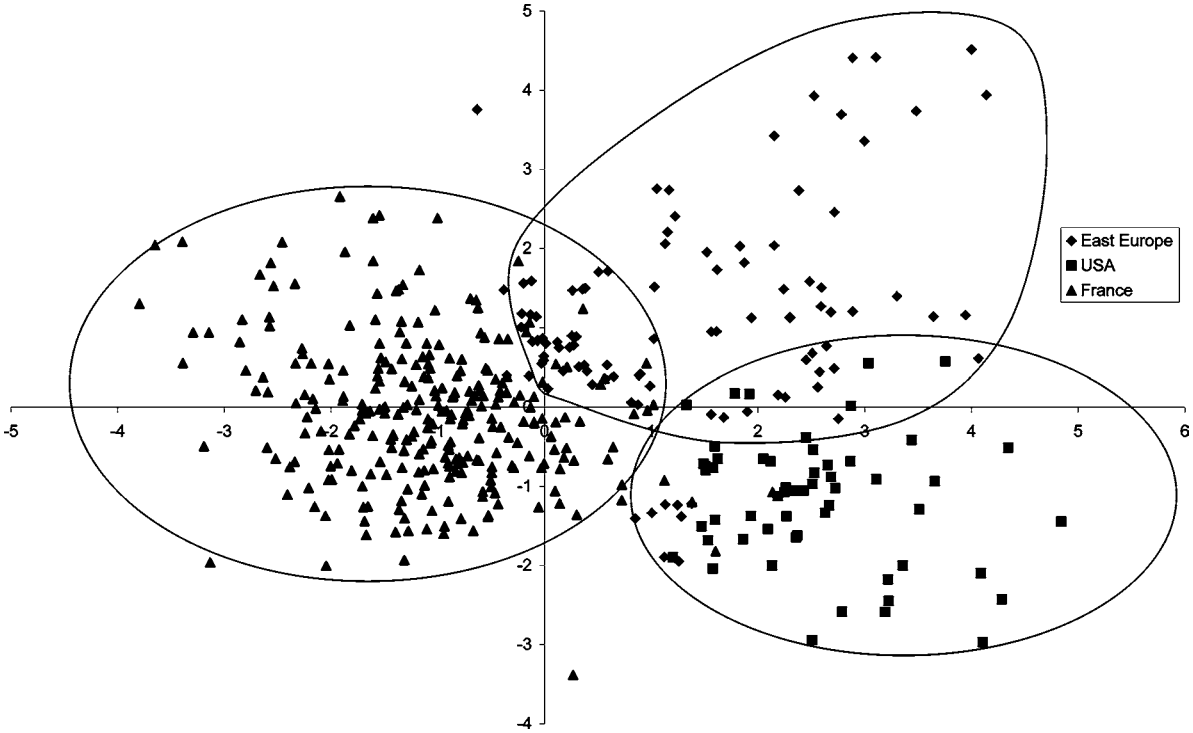

Figure 5. DFA reduced chart for the overall sets (origin differentiation).

emphasized the strong difference between *Q. robur* and *Q. petraea*.

With regard to wood origins, the proportion of eugenol and whiskey lactone isomer compounds grew from French oaks to East European to American oak, whereas the ellagitannin (total or individual ellagitannin) proportion decreased. Furthermore, the aromatic aldehyde contents (vanillin, syringaldehyde, coniferaldehyde) were slightly higher for East European oaks in comparison with American and French woods. By analogy with the previous case *F* factors were calculated additionally for samples aside from American oaks. However, the obtained values did not substantially change the aforementioned statements about statistical difference in the chemical composition of wood of different origins.

To distinguish the species or origin effect, for the sets in which species−origin interaction could take place, the two-way ANOVA was carried out (**Table 6**).

One can conclude that the species factor is the most important for whiskey lactone related variables and ellagitannins, whereas the most important feature for origin distinguishing is the eugenol level (in this case, origin effect predominated that of species). The other substances, which could allow origin discrimination, were aromatic aldehydes, mostly vanillin and syringaldehyde.

Discrimination between Origins and Species. Using all of the above-mentioned observations concerning compounds, which could be specific markers of origin or species, the discrimination models were constructed to assume reliability of each marker.

Rather clear distinction of the French pedunculate oak and American white oak, on the one hand, and East European pedunculate oak, on the other, was observed. This conclusion was confirmed by the percentage of predicted origin membership by DFA model recalculation (**Table 7**).

Therefore, one can see that principal variables, which allow American oak samples to be distinguished from French pedunculate oak, along with the first canonical function are the total oak lactone and its *cis* isomer, eugenol (positive coefficients for correlations with first canonical function: 0.426, 0.426, and 0.458, respectively), and the total ellagitannin content, castalagin, vescalagin, vescalin, and castalin (negative coefficients for correlations with first canonical function: −0.427, −0.478, −0.423, −0.326, and − 0.307, respectively). Along the first canonical function, three zones could be separated: the negative zone (French pedunculate oak), the positive zone (American oak and East European sessile oak that could not be distinguished by using this function), and the intermediary negative zone (French sessile and East European pedunculate oak that could not be distinguished by using this function either). The second canonical function was correlated negatively especially with 2-phenylethanol and roburin B (correlation coefficients of −0.489 and − 0.456, respectively) and with whiskey lactone (*cis* and total) positively (correlation coefficients of 0.284 and 0.301, respectively). This allows us to make a clear distinction between East European oaks of *Q. petraea* species and all remaining species. These remaining samples could not be separated by means of only this second function because of their important superposition along it.

Table 8. Classification Results for Reduced Overall Sets (Origin Differentiation)

	predicted		
original	Eastern Europe	France	U.S.
Eastern Europe	**76.29**	12.37	11.34
France	4.62	**92.69**	2.69
U.S.	7.14	0	**92.86**

To simplify sample distribution, the new DFA analysis was performed by regrouping woods according to their origin (United States, France, Eastern Europe) and species (*Q. robur*, *Q. petraea*, and *Q. alba*).

The graph of origin discrimination is shown in **Figure 5**, and misclassification estimation is represented in **Table 8**.

Estimating misclassification was rather good for all origins, but more optimistic, however, for France and the United States.

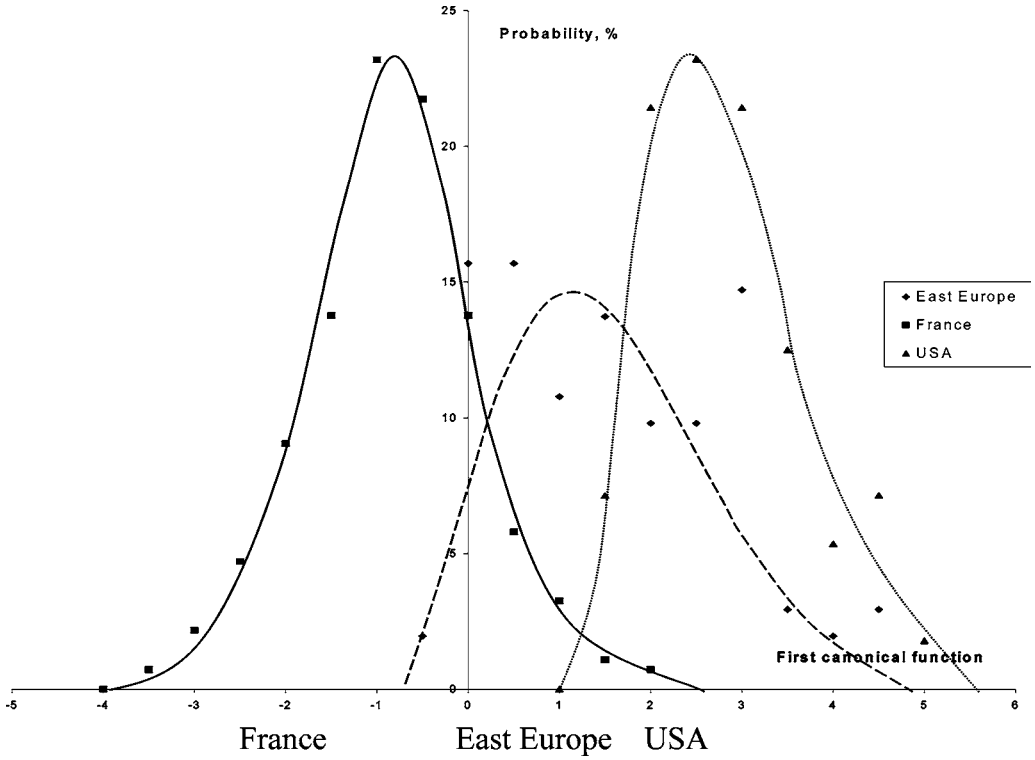

Figure 6. Distribution along the first canonical function (overall reduced sets – origin differentiation).

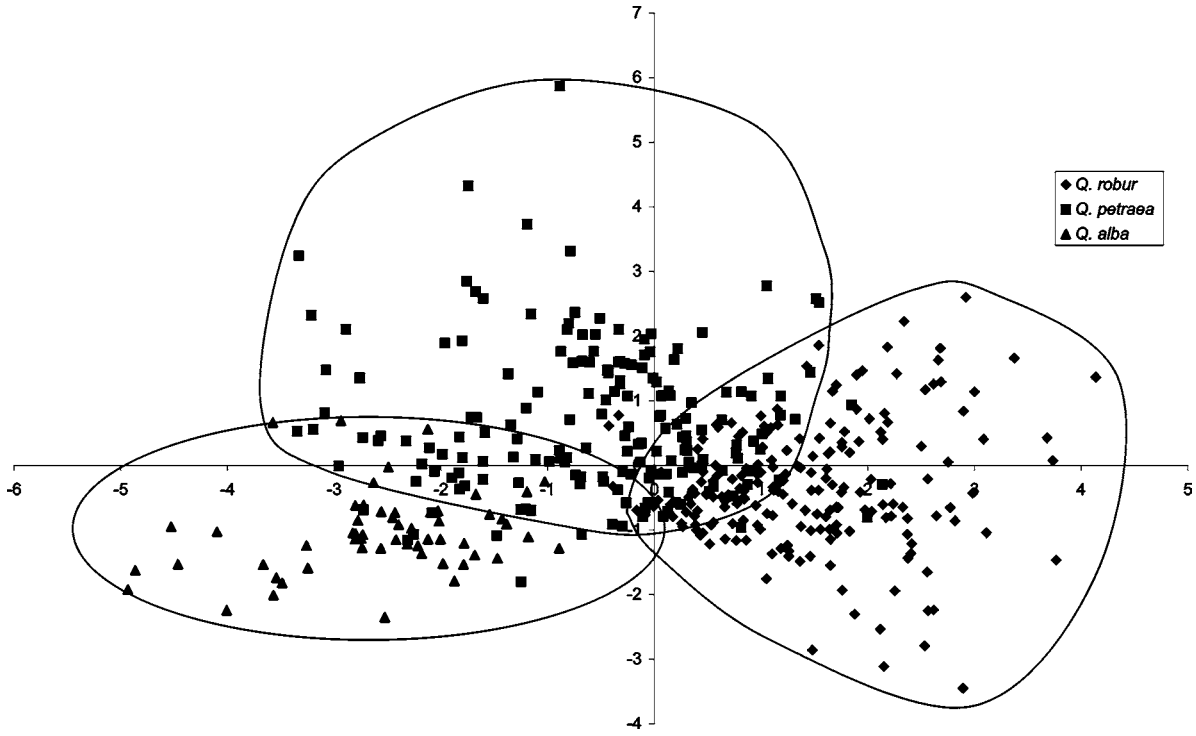

Figure 7. DFA reduced chart for the overall sets (species differentiation).

For these two origins the boundary is clearly established, so mutual misclassification is poor: absent for American samples if classified as French, and just 2.69% of French samples if classified as American ones. Furthermore, the first canonical function was sufficient for differentiation between these two origins. In contrast, the first canonical function could not differentiate clearly East European wood from American and French oaks (**Figure 6**).

With regard to variables correlating with each function, the most important variables for distinguishing French/American origin were *cis*-shiskey lactone and eugenol (coefficients of correlation with first canonical function were 0.352 and 0.524, respectively), as well as most representative ellagitannins: castalagin, vescalagin (coefficients of correlation with first canonical function were −0.504 and −0.435, respectively) and obviously their summary content (−0.437). This fact complies with research results of other authors (*2*−*4*).

However, the principal variables for distinguishing East European/American origins, which occurs along the second canonical function, were less representative of ellagitannins, such

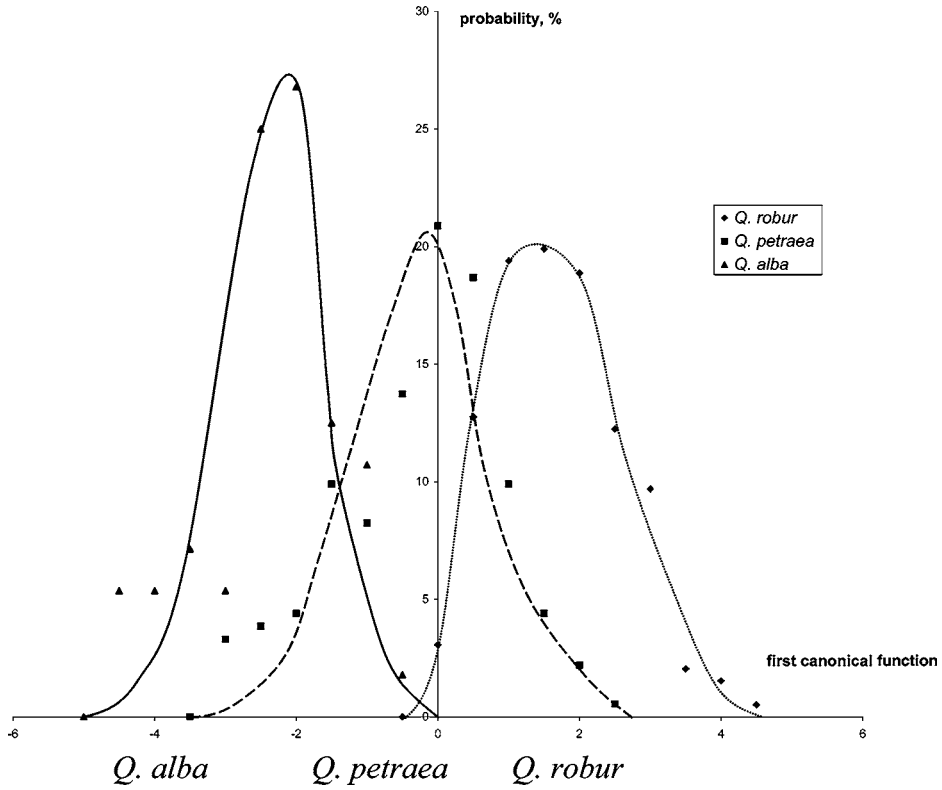

Figure 8. Distribution along the first canonical function (overall reduced sets – species differentiation).

Table 9. Classification Results for Reduced Overall Sets (Species Differentiation)

	predicted		
original	*Q. robur*	*Q. petraea*	*Q. alba*
Q. robur	**93.18**	6.82	0.00
Q. petrea	17.13	**67.40**	15.47
Q. alba	0.00	5.36	**94.64**

as roburins D, B, and E and grandinin, as well as the *cis*/*trans* oak lactone ratio (coefficients of correlations with second canonical function were 0.422, 0.390, 0.388, 0.368, and −0.412, respectively). This observation means that in spite of a general difference between the ellagitannin proportion in European and American woods reported previously, the mentioned individual ellagitannins are more significant indices for differentiation.

In **Figure 7** the DFA species diagram is plotted.

There is a rather good visualization of the three groups, which correspond to three oak species; however, some sessile samples were misclassified as pedunculate ones and vice versa. By analogy, several sessile oaks and *Q. alba* woods were mutually misclassified (**Table 9**).

The first canonical function allows sufficiently good differentiation between European oak species and the American one (**Figure 8**), and it was correlated positively with principal ellagitannins: vescalagin, castalagin, total content (correlation coefficients were 0.507, 0.601, and 0.569, respectively) as well as negatively with the *cis*/*trans*-oak lactone ratio, total oak lactone, and the *cis* isomer proportion (correlation coefficients were −0.456, −0.501, and −0.503, respectively).

The second canonical function also contributed to differentiation, mainly for the distinguishing of sessile and American oak samples. The principal significant variable for this case was *trans*-oak lactone level (correlation coefficient was 0.476), which was rather high for sessile wood as mentioned previously (**Table 4**).

Table 10. Classification Results for Distinguishing Sessile/Pedunculate Sample Sets

	predicted			
	sessile		pedunculate	
original	Eastern Europe	France	Eastern Europe	France
Eastern Europe	**88.89**	11.11	**94.12**	5.88
France	1.74	**98.26**	1.41	**98.59**

Table 11. Most Potent Variables for Distinguishing Origin (France/Eastern Europe) for Sessile and Pedunculate Oaks; Coefficients of Correlations with Most Distinguishing Function

sessile		pedunculate	
eugenol	0.459	eugenol	–0.378
2-phenylethanol	0.360	2-phenylethanol	–0.270
syringaldehyde	0.302	vanillin	–0.233
castalagin	–0.293	vescalagin	0.219
total whiskey lactone	0.260	*cis*/*trans*-whiskey lactone ratio	–0.198
cis-whiskey lactone	0.257	roburin B	–0.191

Of particular interest was distinguishing between French and East European samples because the same biological species were studied in each case. The DFA was carried out for each species set.

The misclassification rate is given in **Table 10**.

Thus, we can summarize that the most obvious difference between East European and French woods was observed in case of the *Q. robur* species. Moreover, the principal misclassifications originated from the East European samples and not from the French sets. Perhaps it was related with a wide sampling of these woods, contrary to the French sets representing a single forest site.

The most significant variables allowing origin separation are given in **Table 11**. In all cases the principal substances were

eugenol, 2-phenylethanol, aromatic aldehydes (vanillin or syringaldehyde), and less significant variables: the most representative ellagitannins (vescalagin or castalagin) and whiskey lactone indices.

Conclusion. For the first time, the current study investigated and compared the chemical compositions of East European (Republic of Moldova, Ukraine, and Romania) oaks and compared with American and French counterparts. The research was performed on a wide sample set of more than 400 samples.

In the limits of the single species set, there were singled out two categories of variables perfectly unrelated, but closely correlated within categories: ellagitannins and the group formed by whiskey lactone isomers and variable of *cis*/*trans*-whiskey lactone ratios. The contribution of variability explained by whiskey lactone variables to the total variability decreased gradually from American oak (*Q. alba*) to sessile oak to pedunculate oak. Other volatile compounds contributed slightly to total variability; nevertheless, in certain cases vanillin and eugenol proportions correlated positively or negatively with ellagitannin variables.

The influence of geographical factors (case of overall sets) changed essential representations mentioned above, because of the specific impact of these factors on the extractives content. Whiskey lactone variables were no more ellagitannin-unrelated but demonstrated in these conditions high anticorrelation with ellagitannin contents as well as eugenol.

The pattern of all studied extractives contents allowed good separation of oak samples according to their geographical origin or botanical species. The highest separation rate was for American and French oaks, whereas East European samples could be partially misclassified into the two sets mentioned above.

The most important variables for species distinction were whiskey lactone related variables and ellagitannins, whereas the most important features for distinguishing origin were eugenol, 2-phenylethanol, and aromatic aldehydes, mostly vanillin and syringaldehyde. These substances allowed the distinction of French and East European woods of the same species.

With regard to chemical composition, East European wood held the intermediary place between American and French oaks according to their ellagitannin and whiskey lactone levels; meanwhile, it was characterized by specific high values of eugenol, aromatic aldehydes, and 2-phenylethanol.

ABBREVIATIONS USED

HPLC, high-performance liquid chromatography; UV, ultraviolet; GC-MS, gas chromatography−mass spectrometry; PCA, principal component analysis; ANOVA, analysis of variance; 2D, two-dimensional; DFA, discriminant function analysis; WL, whiskey lactone; *cis/trans*, ratio of *cis*- and *trans*-whiskey lactone.

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LITERATURE CITED

(1) Fernandez de Simon, B.; Cadahia, E.; Conde, E.; Garcia-Vallejo, M. C. Ellagitannins in woods of Spanish, French and American oaks. *Holzforschung* **1999**, *53* (2), 147−150.

(2) Guichard, E.; Fournier, N.; Masson, G.; Puech, J. L. Stereoisomers of β-methyl-γ-octalactone. I. Quantification in brandies as a function of wood origin and treatment of the barrels. *Am. J. Enol. Vitic.* **1995**, *46* (*4*), 419−423.

(3) Masson, G.; Guichard, E.; Fournier, N.; Puech, J. L. Stereoisomers of β-methyl-γ-octalactone. 2. Contents in the wood of French (*Quercus robur* and *Quercus petraea*) and American (*Quercus alba*) oaks. *Am. J. Enol. Vitic.* **1995**, *46* (*4*), 424−428.

(4) Perez-Coello, M. S.; Sanz, J.; Cabezudo, D. Determination of volatile compounds in hydroalcoholic extracts of French and American oak wood. *Am. J. Enol. Vitic.* **1999**, *50* (*2*), 162−165.

(5) Waterhouse, A.; Towey, J. Oak lactone isomer ratio distinguishes between wines fermented in American and French oak barrels. *J. Agric. Food Chem.* **1994**, *42*, 1971−1974.

(6) Masson, G.; Puech, J.-L.; Moutounet, M. The chemical composition of barrel oak wood. *Bull. O.I.V.* **1996**, *785*−*786*, 635−657.

(7) Puech, J. L.; Moutounet, M. Liquid chromatographic determination of scopoletin in hydroalcoholic extract of oak wood and in matured distilled alcoholic beverages. *J. Assoc. Off. Anal. Chem.* **1988**, *71* (*3*), 512−514.

(8) Snakkers, G.; Nepveu, G.; Guilley, E.; Cantagrel, R. Variabilités géographique, sylvicole et individuelle de la teneur en extractibles de chênes sessiles français (Q*uercus petraea* Liebl): polyphénols, octalactones et phénols volatils. *Ann. Sci. For.* **2000**, *57*, 251−260.

(9) Sefton, M.; Francis, I.; Williams, P. Volatile norisoprenoid compounds as constituents of oak woods used in wine and spirit maturation. *J. Agric. Food Chem.* **1990**, *38*, 2045−2049.

(10) Fernandez de Simon, B.; Cadahia, E.; Jalocha, J. Volatile compounds in a Spanish red wine aged in barrels made of Spanish, French, and American oak wood. *J. Agric. Food Chem.* **2003**, *51*, 7671−7678.

(11) Mosedale, J.; Savill, P. Variation of heartwood phenolics and oak lactones between the species and phenological types of *Quercus petraea* and *Q. robur*. *Forestry* **1996**, *69* (1), 47−55.

(12) Chatonnet, P.; 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.* **1998**, *49* (*1*), 79−85.

(13) Masson, G.; Guichard, E.; Fournier, N.; Puech, J. L. The β-methyl-γ-octalactone stereoisomer contents of European and American oak. Applicable to wines and spirits. *J. Sci. Tech. Tonnellerie* **1997**, *3*, 9−15.

(14) Doussot, F.; Pardon, P.; Dedier, J.; De Jeso, B. Individual, species and geographical origin influence on cooperage oak extractible content (*Quercus robur*, L., and *Quercus petraea* Liebl.). *Analusis* **2000**, *98*, 960−965.

(15) Doussot, F. *Variabilité des teneurs en extractibles des chênes sessile (Quercus petraea Liebl.) et pédonculé (Quercus robur L.). Influence sur l'élevage des vins en barrique*; Université Bordeaux 1: Bordeaux, France, 2000; 360 pp.

(16) Masson, G.; Puech, J.-L.; Moutounet, M. Localization of the ellagitannins in the tissues of *Quercus robur* and *Quercus petraea* woods. *Phytochemistry* **1994**, *37* (5), 1245−1249.

(17) Masson, G.; Moutounet, M.; Puech J. L. Ellagitannin content of oak wood as a function of species and of sampling position in the tree. *Am. J. Enol. Vitic.* **1995**, *46*, 2 262−268.

(18) Chatonnet, P.; Sarishivilli, N. G.; Oganessyants, L. A.; Dubourdieu, D.; Codier, B. Caractéristiques et intérêts du bois de chêne de Russie pour l'élevage des vins fins. *Rev. Fr. Oenol.* **1997**, *167*, 46−51.

(19) Prida, A.; Puech, J. L. Ellagitannins in differents oak species. *Vinodel. Vinograd.* **2002**, *5*, 24−25.

(20) Bacilieri, R.; Ducousso, A.; Kremer, A. Genetic, morphological, ecological and phenological differentiation between *Quercus petreae* (Matt) Liebl. and *Quercus robur* L. in a mixed stand of Northwest of France. *Silvae Genetica.* **1995**, *44*, 1−10.

(21) Feuillat, F.; Moio, L.; Guichard, E.; Marinov, M.; Fournier, N.; Puech, J. L. Variation in the concentration of ellagitannins and *cis*- and *trans*-β-methyl-γ-octalactone extracted from oak wood (*Quercus robur* L., *Quercus petraea* L.) under model wine cask conditions. *Am. J. Enol. Vitic.* **1997**, *48* (4), 509−515.

(22) Mosedale, J. R.; Ford, A. Variation of the flavor and extractives of European oak wood from two French forests. *J. Sci. Food Agric.* **1996**, *70*, 273−287.

(23) Mosedale, J. R.; Feuillat, F.; Baumes, R.; Dupouey, J. L.; Puech, J. L. Variability of wood extractives among *Quercus robur* and *Quercus petraea* trees from mixed stands and their relation to wood anatomy and leaf morphology. *Can. J. For. Res.* **1998**, *28*, 1−13.

(24) Puech, J. L. 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.* **1987**, *38* (3), 236−238.

(25) Klumpers, J.; Scalbert, A.; Janin G. Ellagitannins in European oak wood: polymerization during wood aging. *Phytochemistry* **1994**, *36* (5), 1249−1252.

(26) Viriot, C.; Scalbert, A.; Hervé du Penhoat, C.; Moutounet, M. Ellagitannins in woods of sessile oak and sweet chestnut: dimerization and hydrolysis during wood ageing. *Phytochemistry* **1994**, *36* (5), 1253−1260.

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