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ARTICULO INVESTIGATIVO

ANALYSIS OF VOLATILE COMPOUNDS IN DIFFERENT TYPES OF OAK BARREL USED IN THE AGING OF RUM

Análisis de los compuestos volátiles en diferentes tipos de barriles de roble usados en el añejamiento de ron.

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ABSTRACT

It is well-known that during aging, several compounds are extracted from the oak barrels that have a positive influence on the sensory characteristics of the rum. The sensory improvement is the result of many transformations that take place among the rum distillate components and those of the oak wood. These involve reactions between constituents of the spirit, reactions between substances extracted from the wood and their oxidation, and reactions between the original compounds, extracted compounds, and those formed previously. For the aging of Cuban rum in oak barrels it has been necessary to import it and there are lots of barrels with the origin known, but others unknown. This paper analyzed the profile of oak volatile compounds of three lots coming from American, former Soviet Union and Yugoslavia and three lots of unknown origin. With maceration of oak chips with ethanol 55% v/v, extraction with dichloromethane and gas chromatography-mass spectrometry analysis, 126 volatiles compounds were determined including phenol derivatives (40), esters (28), acids (17), alcohols (11), terpenes (10), aldehydes and ketones (8), acetals (4), furanic derivatives (3), lactones (3), and others with different functions (2). A total of 70 compounds showed statistical differences and the principal component and discriminant analysis classified the six lots in four groups: American, former Soviet Union and former Yugoslavia origin in different groups, two unknown origin lots in the same group with Yugoslavian lot and a remaining lot of unknown origin in a separate group.

Keywords: Rum; oak barrel; aging; volatile compounds; gas chromatography-mass spectrometry.

RESUMEN

Es bien conocido que, durante el añejamiento, se extraen numerosos compuestos de los barriles de roble que tienen una influencia positiva en las características sensoriales del ron. La mejora sensorial es el resultado de varias transformaciones que tienen lugar entre los componentes del destilado de ron y los de la madera de roble. Esto involucra reacciones entre los constituyentes de la bebida, reacciones entre las sustancias extraídas de la madera y su oxidación, así como reacciones entre los compuestos originales, compuestos extraídos y aquellos formados previamente. Para el añejamiento del ron cubano en barriles de roble se hace necesario su importación y existen lotes de barriles de procedencia conocida, pero de otros no se conoce. Este trabajo analizó el perfil de compuestos volátiles del roble de tres lotes de barriles provenientes de América del Norte, la exUnión Soviética y exYugoslavia y tres lotes de origen desconocido. Mediante maceración de las virutas de roble con etanol al 55 % v/v, extracción con diclorometano y análisis por cromatografía de gases-espectrometría de masa, 126 compuestos volátiles fueron determinados, agrupados en derivados fenólicos (40), ésteres (28), ácidos (17), alcoholes (11), terpenos (10), aldehídos y cetonas (8), acetales (4), derivados furánicos (3), lactonas (3), y otros de diferentes funciones (2). Un total de 70 compuestos mostraron diferencias estadísticas y la aplicación del análisis de componentes principales y de discriminantes clasificó los seis lotes en cuatro grupos: América del Norte, exUnión Soviética y exYugoslavia en grupos diferentes, dos lotes de origen desconocido en el mismo grupo del lote de la exYugoslavia y un lote de origen desconocido como un grupo separado.

Palabras clave: Ron; barril de roble; añejamiento; compuestos volátiles; cromatografía de gases-espectrometría de masas.

INTRODUCCIÓN

One of the more important steps in the production of Cuban rums is the aging process in oak barrel. Traditionally, Cuba has to import barrels because the only oak specie growing in the country, *Quercus oleoides*, is poor in forests and not useful for cooperage. It is well known that the major geographic areas supplying oak barrels are North America and Europe, especially France and in less extension Spain, Portugal, Russia, Bulgaria and Hungary, with mainly three species involved: *Quercus alba* at the first area and *Quercus robur* and *Quercus petraea* in the second, although Spanish ones (*Quercus pyrenaica* and *Quercus faginea*) have been tested in the last years, and some report for chesnut has been made (Caldeira *et a*l., 2002, 2006; Fernández de Simón *et al*., 2003; Díaz-Moroto *et al*., 2004).

These oak woods used in cooperage, composed mainly by cellulose, hemicelluloses and lignin, have a wide range of a low molecular weight compounds such as fatty acids, esters of fatty acids, phenols, lactones, terpenes, furanic derivatives and carotenoids, furanic derivatives and carotenoids, which can be extracted by wine and spirits during the aging process.That it can be extracted by wine and spirits during the aging process (Pérez-Coello *et al*., 1999; Nonier *et al*., 2004). The chemical composition of oak wood has high variability among trees, species and geographical locations and is influenced by silvicultural practices, the age of the wood, besides other cooperage factors such as type and time of dryness of the wood, split or saw to cut staves, the heat treatment to bend staves and toasting or charring the inner surfaces of barrels. These variations can produce differentiations in chemical composition and sensory characteristics of the wine and spirits aging in oak barrels (Cadahía *et al*., 2001; Dussot *et al*., 2002; Fernández de Simón *et al*., 2003).

At present, in Cuba there are lots of barrels with an unknown origin, American ones which are majority and others from specific countries. Taking into account these facts, the purpose of this paper was to evaluate the volatile compounds among three lots of known origin (American and former Yugoslavia and Soviet Union) and three lots of unknown origin in order to establish differences or similarities among them.

MATERIALS AND METHODS

Materials

Six lots of barrels with different time of use and origin were chosen: Lot 1 former Yugoslavia (Yu), lot 2 American (Am), lot 3 former Soviet Union (SU), and lots 4, 5 and 6 unknown (Uk 1, Uk 2 and Uk 3). A total of 30 barrels per lot were chosen in a random way.

Sample preparation

For each barrel, one stave was taken out and cut in four pieces, all sides planed down in order to eliminate dirties and, in the case of the inner surface in contact with distillates, 10 mm deep was removed. Then, each four sections per stave were ground and carefully sieved to get oak chips (20-40 mesh) and well mixed. With the 30 oak chips samples per lot of barrels, three composite samples per lot were prepared mixing equals portions by weights of 10 stave oak chips.

Preparation of oak chip macerate

Oak chips (20 g) were placed in a tight glass container and 750 mL of hydroalcoholic solution 55% v/v ethanol was added. The time of maceration was 30 days with daily stirring. At the end of maceration time, oak macerate was filtered and the oak chips were washed with the hydroalcoholic solution and, the oak extract made to 1 L with the same hydroalcoholic solution used to wash the chips.

Isolation of volatile compounds

Oak macerate (25 mL) was diluted with distillate water to 100 mL in a volumetric flask. Fifty mL of diluted macerate were placed in a 100 mL Erlenmeyer flask with cap containing 15 g of ammonium sulfate and 50 µL of γ-nonalactone (200 mg/L) in ethanol 95 % v/v) was added as internal standard. The mixture was stirred until complete solubilization. Three extractions were then carried out using 10, 5, and 3 mL of dichloromethane (Sigma-Aldrich, 99.9 %) in a separatory funnel and centrifuged at 700*g* for 3 min. The organic fractions were combined and dried over night with anhydrous sodium sulfate, and then concentrated to 100 µL under a nitrogen stream. Extractions were replicated two times.

GC-MS analysis

Analyses were performed using a HP 6890 gas chromatograph (Hewlett-Packard Co., Palo Alto, CA) equipped with a mass selective detector model HP 5973. Samples were injected in a split mode injector at 250 ºC (split ratio of 1:70) on SPB-5 (Supelco, 30 m x 0.25 mm x 0.25 µm). The column temperature program was 60 ºC for 2 min and then at 4 ºC/min until 250 ºC, isothermal for 30 min. Helium as carrier gas at 1 mL/min. The detection by the mass spectrometer was performed in the EI mode (70 eV ionization energy). The acquisition was performed in scanning mode (mass range m/z 35-400 u). Identification of the constituents was based on comparison of the retention times with those of authentic samples, comparing their linear retention indices relative and on computer matching against commercial libraries (NIST 02, Wiley 275, Palisade 600 and ADAMS 2001) and FLAVORLIB homemade library mass spectra built up from pure substances. Some of the identifications were confirmed by the injection of the chemical standards into the GC-MS system. Linear retention indices of the compounds were calculated using an *n*-alkane series. Quantitative determinations were carried out according to the internal standard method without consideration of isolation yields and calibration factors for all compounds. All analyses were replicated two times.

Statistical analysis

Chemical data were analyzed using Statistica 7.0 software (StatSoft, Inc., Tulsa, OK) for mean and standard deviation, Principal Component Analysis (PCA) and Discriminant Analysis (DA). For PCA was used an n x p matrix where p = 96 variables (volatiles compounds concentration) and n = 18 samples analyzed. The graphic of each principal component was used as exploratory criterion for graphic differentiation of samples. For DA it was started from an n x p matrix where p = 4 (the fourth first principal components) an n = 18 analyzed samples, working with four groups and a Lambda Wilkis = 0.0013; F (8, 16) = 174.3 for $p \leq 0.01$ and a tolerance value of 0.01 according to standard stepwise method (Montgomery, 2001).

RESULTS AND DISCUSSION

Table 1 shows the 126 volatile compounds found in the oak macerates, including phenol derivatives (40), esters (28), acids (17), alcohols (11), terpenes (10), aldehydes and ketones (8), acetals (4), furanic derivatives (3), lactones (3), and others with different functions (2). The major amounts of compounds were quantified in Am barrels (98), follow of Uk 3 (73), Yu (69), SU (66), Uk 1 (57) and Uk 2 (57) barrels. All lots of barrels presented more lignin derivatives than the rest of compounds type, what it is normal for seasoned and toasted oak wood (Vichi *et al*., 2007; Fernández de Simón *et al*., 2009). A major qualitative and, in some cases, quantitative profile of Am oak wood barrels in phenolics, esters, aldehydes and ketones, furanic derivatives, terpenes, and the major concentration of *cis*-β-methyl-γ-octalactone made this type of barrel different of the rest. On the contrary, SU oak wood barrels had the minor qualitative and quantitative profile in esters, alcohols and oak lactones, which made a difference from the rest of oak wood barrels. Yu, Uk 1, Uk 2 and Uk 3 barrels have a similar behavior, although Uk 3 has a greater qualitative and quantitative profile in this group.

The Am barrels gave the major amounts of vanillin and coniferaldehyde and the minor concentration of syringaldehyde and sinapaldehyde, as show Fig. 1, where vanillin/vanillic acid and syringaldehyde/siringic acid ratios are shown. The major content of vanillin in Am barrels agreed with previous reports (Cadahía *et al*., 2001).

Very important compounds like *trans*-β-methyl-γ-octalactone and *cis*-β-methyl-γ-octalactone were in very similar concentrations in Yu, Uk 1, Uk 2, and Uk 3 barrels, having the major content of total lactones. The Am barrels showed the major concentration of *cis* isomer and the minor of *trans* isomer, whereas the SU barrels have the lower level of total lactones, which is agree with some report for Russian oak (Mosedale *et al*., 1999). *Cis/trans* ratio (Fig. 2) for Yu, Uk 1, Uk 2 and Uk 3 barrels are below 2.0 which agreed for European oak wood whereas Am barrels has a value of 6.1 which is typical for American oak wood. The values found for *cis/trans* ratio agreed with those found for some authors where this value was higher in American oak wood than in European ones (Pérez-Coello *et al*., 1999; Pérez-Prieto *et al*., 2002). SU barrels show a value of 0.3, and this value is closer to European oak wood than to American *Q. alba*. In general, it is considered that the American white oak (*Q. alba*) and *Q. robur* and *Q. petraea* from France, have the major concentrations of oak lactones versus the rest of European oaks, with a major concentration of *cis* isomer in American white oak (Pérez-Coello *et al*., 1999; Díaz-Moroto *et al*., 2004).

PCA analysis showed that four principal components with eigenvalues greater than 1 explained 82.8 % of variance (F1 34.4 %, F2 22.7 %, F3 14.8 %, and F4 10.9 %). The graphical representation of three first principal components showed four groups well defined with an appreciated statistical distance among the groups (Fig. 3). Group 1 was the more represented and it was formed by samples of Yu, Uk 1 and Uk 2 barrels; to the second group corresponded samples representing Am barrels; the third group was formed by samples of SU barrels and the fourth group consisted of the samples of Uk 3 barrels.

Table 2 show loading factors for each principal component. In F1, there were among compounds with statistical significance 2-furfural, γ-terpinene, *trans*-β-methyl-γ-octalactone and vanillin; in F2, *p*-cymene, *o*-guaiacol, decanal and *cis*-β-methyl-γ-octalactone, these with great importance because of their relevant in different sensory characteristics (Caldeira *et al*., 2002; Pérez-Prieto *et al*., 2002; Fernández de Simón *et al*., 2003, 2009). On the contrary, in F3

the compounds with statistical significance are irrelevant for the aging process and their sensory impact, except for 1,1-diethoxyethane, because this type of compound has aromatic strength (Puech *et al*., 2003). As all these compounds have different sensory properties, could be possible to expect certain differences in the aroma among oak macerates belongs to each group classified by PCA.

A discriminant analysis was done with the four first principal components. Table 3 shows the discriminant functions for the four groups where in the classify functions for group 1 (Yu, Uk 1 and Uk 2 barrels) and group 2 (Am barrels), the F1 was the more contributing, especially for the group 2, whereas in the classifying functions for the group 3 (SU barrels), the major contribution belongs to F2 and; for the group 4 (Uk 3 barrels), the main contribution was for the F3. The classification matrix (Table 4) shows how the classification functions predict the membership of the observations, where all samples were correctly classified (in the diagonal matrix). The cross validation employed, the know "U Method" (Leave-one out), where each observation is classified using the classification functions (or Fisher's lineal discriminant functions), derived from the rest of the observations gave a 100% of correct classifications, having a similar result showed in Table 4. As the cross validation is a better measure of the discriminating power of the classification functions, it may considerer that the estimated classifications functions can be used to predict correctly to which group belongs a new sample of the oak woods studied.

Table 1. Volatile compounds in oak macerates[a] (µg/g of wood).

Compound	RI[f]	ID[g]	Yu[b]	Am[c]	SU[d]	Uk1[e]	Uk 2[e]	Uk 3[e]
Phenol derivatives								
2-Methoxyphenol	1086	A	tr	1.5 (0.6)	2.0 (0.8)	tr	nd	tr
4-Methyl-2-methoxyphenol	1190	A	nd	tr	tr	nd	nd	tr
(*E*)-Anethole	1285	A	nd	nd	nd	tr	tr	tr
4-Vinyl-2-methoxyphenol	1315	A	tr	3.9 (0.9)	3.0 (1.3)	tr	tr	tr
Syringol	1333	B	tr	1.4 (0.3)	tr	tr	tr	tr
Eugenol	1336	A	2.5 (0.2)	1.6 (0.1)	tr	tr	tr	tr
4-Propyl-2-methoxyphenol	1360	A	tr	tr	nd	nd	nd	tr
Vanillin	1392	A	43.4 (1.6)	58.1 (2.5)	47.0 (2.8)	46.8 (2.6)	46.6 (2.4)	50.1 (2.8)
4-Methylsyringol	1398	B	tr	1.7 (0.3)	tr	nd	nd	1.0 (0.4)
cis-Isoeugenol	1402	B	2.0 (0.4)	1.3 (0.2)	1.7 (0.4)	tr	tr	1.7 (0.4)
Homovanillin	1424	B	8.3 (0.3)	9.1 (0.2)	7.9 (0.4)	tr	tr	8.3 (0.4)
1-Guaiacylpropyne	1465	B	4.2 (0.5)	5.2 (0.3)	1.0 (0.6)	tr	3.9 (0.3)	3.9 (0.6)
Acetovanillone	1483	B	tr	4.7 (0.8)	1.4 (1.1)	0.5 (0.5)	tr	4.6 (1.1)
Guaiacylacetone	1501	B	4.4 (0.5)	7.6 (0.3)	14.7 (0.6)	tr	tr	4.3 (0.6)
4-Vinylsyringol	1532	B	13.0 (1.0)	16.8 (0.6)	tr	tr	tr	tr
Vanillic acid	1577	A	49.5 (5.5)	28.0 (1.6)	42.9 (5.1)	42.2 (2.5)	40.7 (3.5)	37.3 (5.1)
Guaiacyl vinyl ketone	1584	B	15.8 (0.7)	15.1 (2.8)	16.0 (2.5)	20.0 (1.6)	19.2 (1.3)	20.0 (2.5)
Ethyl vanillate	1590	C	35.3 (3.7)	30.3 (0.8)	38.8 (3.3)	30.9 (1.9)	29.6 (4.9)	29.2 (3.3)
4-Allyl syringol	1601	B	tr	6.2 (0.9)	tr	tr	tr	tr
Dihydroconiferyl alcohol	1632	B	56.6 (4.4)	16.6 (1.6)	37.9 (4.2)	54.8 (0.4)	44.7 (2.9)	45.3 (4.2)
Syringaldehyde	1656	A	228.3 (4.5)	225.7 (8.8)	232.7(9.5)	246.4 (1.0)	233.9 (7.4)	243.8 (9.5)

Table 1. (cont.)

(*Z*)-Coniferyl alcohol	1668	B	47.9 (1.0)	29.1 (1.8)	45.2 (2.0)	43.9 (1.6)	44.7 (0.4)	42.3 (2.3)
1-Syringylpropine	1677	B	17.9 (1.0)	18.8 (2.6)	25.1 (2.8)	18.9 (5.4)	24.6 (0.6)	12.6 (2.8)
(*E*)-4-Propenyl syringol	1686	B	30.2 (5.7)	30.4 (3.1)	33.5 (6.2)	25.0 (1.3)	35.7 (2.1)	28.9 (6.2)
Homosyringaldehyde	1700	B	20.9 (1.5)	30.8 (2.4)	21.4 (2.8)	21.7 (1.1)	20.3 (2.4)	18.9 (2.8)
Methyl homovanillate	1714	C	10.4 (0.3)	11.9 (0.5)	tr	tr	tr	tr
(*E*)-Coniferaldehyde	1721	A	132.7 (4.7)	148.6 (5.8)	122.1 7.5)	128.1 (2.5)	135.5 (2.1)	145.4 (7.5)
Acetosyringone	1730	B	tr	9.4 (1.0)	12.0 (1.4)	tr	tr	tr
(*E*)-Coniferyl alcohol	1735	B	59.5 (3.0)	31.3 (4.1)	56.4 (5.1)	56.6 (1.6)	69.1 (5.7)	69.3 (5.1)
Syringylacetone	1781	B	43.5 (2.1)	51.1 (2.7)	34.5 (3.4)	41.6 (3.0)	49.6 (7.5)	36.0 (3.4)
β-Hydroxypropiovanillone	1839	C	65.8 (1.5)	31.0 (1.1)	57.1 (1.8)	39.1 (1.6)	45.2 (1.4)	47.6 (1.8)
Syringil vinyl ketone	1849	B	41.6 (2.5)	33.8 (2.7)	42.1 (3.7)	40.9 (2.5)	42.1 (2.8)	44.1 (3.7)
Ethyl syringate	1856	C	194.0 (5.6)	202.2 (12.8)	200.6(13.0)	205.6 (0.6)	216.4 (1.3)	205.0 (13.0)
Syringic acid	1862	A	30.9 (1.0)	24.5 (4.0)	31.9 (6.2)	32.1 (1.0)	31.8 (0.8)	32.6 (6.2)
Ferulic acid	1924	A	nd	tr	1.5 (0.1)	nd	nd	nd
Dihydrosynapil alcohol	1938	B	30.8 (3.2)	31.3 (4.8)	35.0 (5.7)	26.8 (0.3)	23.5 (1.3)	24.5 (4.2)
(*Z*)-Sinapyl alcohol	1951	B	59.9 (3.3)	49.3 (2.7)	55.6 (4.2)	60.7 (3.9)	65.8 (0.4)	62.3 (4.2)
(*E*)-Sinapaldehyde	1981	A	408.9 (11.4)	205.3 (4.3)	316.6 (11.2)	359.5 (2.6)	365.3 (3.5)	378.3 (11.2)
(*E*)-Sinapyl alcohol	1987	B	308.9 (3.1)	305.1 (4.4)	351.5 (5.4)	320.9 (1.1)	377.6 (0.9)	315.8 (5.4)
Dihydrovanillin	2804	C	486.6 (6.3)	452.5 (24.9)	427.1 (22.1)	456.8 (0.3)	442.9 (27.3)	359.5 (22.8)
Esters								
Diethyl carbonate	780	A	tr	tr	nd	tr	tr	tr
Ethyl lactate	814	A	tr	tr	tr	tr	tr	3.5 (0.1)
Ethyl 3-hydroxybutyrate	935	A	nd	tr	tr	nd	nd	tr
Ethyl acetoacetate	948	C	nd	nd	nd	nd	nd	tr
Diethyl oxalate	994	A	nd	tr	nd	nd	nd	nd
Ethyl hexanoate	998	A	5.1 (0.4)	4.0 (0.4)	tr	nd	tr	2.8 (0.6)
Ethyl 2-furoate	1056	A	tr	0.7 (1.0)	tr	tr	tr	tr
Ethyl levulinate	1065	A	tr	0.6 (0.5)	nd	tr	tr	tr
Diethyl malonate	1073	A	tr	tr	tr	tr	tr	2.4 (0.1)
Ethyl diethoxyacetate	1094	A	tr	1.3 (1.0)	nd	tr	tr	tr
Ethyl benzoate	1170	A	nd	tr	tr	tr	tr	tr
Diethyl succinate	1181	A	14.9 (3.2)	12.4 (1.7)	tr	13.6 (0.4)	12.7 (0.6)	18.2 (3.4)
Ethyl nicotinate	1210	C	tr	0.6 (0.8)	nd	nd	nd	tr
Ethyl phenylacetate	1247	A	nd	0.7 (1.1)	nd	tr	nd	tr

Table 1. (cont.)

Compound	**RI[f]**	**ID[g]**	**Yu[b]**	**Am[c]**	**SU[d]**	**Uk1[e]**	**Uk 2[e]**	**Uk 3[e]**
Diethyl malate	1274	C	6.7 (0.5)	5.5 (0.5)	nd	6.5 (0.6)	7.5 (0.5)	7.6 (0.7)
Ethyl decanoate	1395	A	tr	tr	tr	nd	nd	tr
Ethyl undecanoate	1495	A	tr	tr	tr	tr	tr	tr
Ethyl dodecanoate	1595	A	28.9 (0.9)	15.7 (2.5)	tr	tr	29.1 (0.8)	29.0 (2.3)
Ethyl citrate	1661	C	nd	tr	nd	tr	tr	tr
Ethyl tetradecanoate	1792	A	20.2 (5.3)	9.1 (4.4)	tr	tr	tr	3.5 (1.3)
Ethyl hexadecanoate	1993	A	136.0 (6.9)	146.9 (4.1)	38.4 (7.8)	123.4 (1.7)	129.6 (1.7)	137.0 (7.8)
Ethyl linoleate	2152	A	43.9 (2.4)	16.0 (2.5)	28.1 (7.1)	tr	tr	23.5 (7.1)
Ethyl oleate	2172	A	193.0 (8.7)	134.4 (20.0)	164.3 (20.2)	168.2 (1.2)	187.2 (0.6)	199.9 (20.2)
Dibutyl sebacate	2186	C	nd	tr	tr	tr	nd	nd

Ethyl octadecanoate	2197	A	43.7 (3.9)	25.0 (1.1)	40.1 (10.0)	47.7 (1.4)	40.2 (1.3)	43.7 (10.0)
Ethyl eicosanoate	2397	C	19.9 (0.8)	22.5 (1.5)	nd	tr	21.2 (1.2)	tr
Ethyl docosanoate	2596	C	52.9 (3.2)	46.4 (0.8)	nd	38.7 (3.4)	56.2 (4.9)	52.0 (4.7)
Ethyl tetracosanoate	2794	C	58.7 (0.6)	56.6 (0.8)	tr	53.2 (0.6)	54.4 (1.8)	TR
Acids								
Acetic	600	A	tr	tr	tr	nd	tr	tr
Butanoic	790	A	tr	nd	tr	nd	tr	2.5 (0.1)
3-Methylbutanoic	835	A	nd	tr	tr	tr	tr	1.0 (0.1)
Pentanoic	886	C	nd	nd	tr	tr	nd	nd
Hexanoic	981	A	nd	tr	tr	tr	nd	4.4 (0.1)
Heptanoic	1078	C	nd	nd	tr	tr	nd	tr
2-Ethylhexanoic	1122	A	tr	-	-	-	-	tr
Octanoic	1179	A	5.4 (0.4)	1.5 (0.2)	8.8 (0.4)	tr	tr	1.7 (0.4)
Nonanoic	1282	A	tr	2.4 (2.0)	4.8 (0.7)	tr	tr	tr
Decanoic	1382	A	6.3 (0.4)	6.9 (0.9)	7.9 (1.0)	7.0 (0.5)	6.6 (0.5)	6.1 (1.0)
Dodecanoic	1568	A	tr	0.7 (1.0)	1.9 (0.1)	1.3 (0.2)	1.3 (0.3)	2.6 (0.1)
Tetradecanoic	1770	A	56.9 (1.9)	38.4 (5.7)	48.2 (5.2)	50.0 (1.2)	46.7 (3.3)	42.9 (5.2)
Pentadecanoic	1873	A	0.5 (0.8)	nd	1.3 (0.1)	0.7 (0.8)	nd	nd
(*Z*)-9-Hexadecenoic	1962	C	33.2 (4.8)	24.8 (1.7)	32.8 (4.7)	35.2 (9.3)	28.7 (0.8)	19.6 (4.7)
Hexadecanoic	1973	A	239.8 (34.4)	145.3 815.6)	242.5 (35.4)	275.4 (2.5)	211.6 (6.5)	260.5 (35.4)
(*Z*)-9-Octadecenoic	2137	A	125.2 (1.2)	187.4 (4.6)	126.7 (4.1)	124.1 (2.8)	131.0 (1.1)	127.8 (4.1)
Octadecanoic	2175	A	nd	tr	tr	tr	nd	nd
Alcohols								
2-Methylpropanol	622	A	tr	tr	nd	tr	tr	tr
3-Methyl-1-butanol	734	A	20.3 (0.6)	17.9 (0.4)	19.0 (0.7)	20.9 (0.1)	25.0 (1.1)	24.3 (0.7)
2-Methyl-1-butanol	737	A	12.7 (2.3)	16.4 (0.8)	13.3 (2.3)	15.9 (0.4)	12.5 (0.6)	12.0 (2.3)
3-Methyl-2-buten-1-ol	778	C	8.1 (0.7)	8.0 (0.8)	nd	7.4 (0.6)	8.7 (0.3)	8.9 (1.0)
2,2-Diethoxyethanol	928	C	6.6 (0.5)	6.1 (0.6)	tr	6.4 (0.4)	8.7 (1.0)	7.1 (0.7)
2-Ethyl-1-hexanol	1031	C	4.1 (1.3)	4.7 (1.0)	4.8 (1.7)	tr	tr	4.9 (1.7)
Benzyl alcohol	1034	A	tr	tr	tr	tr	tr	tr
1-Octanol	1070	A	nd	nd	tr	tr	tr	tr
2-Phenylethyl alcohol	1110	A	tr	1.8 (1.4)	3.0 (0.1)	tr	tr	4.4 (0.1) b
2-Phenoxyethanol	1217	C	nd	nd	tr	nd	nd	nd
1-Dodecanol	1471	C	nd	tr	1.5 (0.1)	tr	tr	tr
Terpenes								
β-Pinene	979	A	nd	tr	nd	nd	nd	nd
Myrcene	991	C	nd	tr	nd	nd	nd	nd
1,4-Cineole	1015	C	nd	0.7 (1.2)	nd	nd	nd	nd
p-Cymene	1025	A	tr	0.7 (1.2)	nd	tr	tr	tr
Limonene	1028	A	tr	6.3 (2.4)	2.4 (1.7)	tr	tr	3.8 (3.4)
1,8-Cineole	1030	A	nd	0.6 (1.0)	nd	nd	nd	nd
γ-Terpinene	1060	A	nd	1.9 (2.4)	nd	nd	nd	tr
Camphor	1146	A	nd	tr	nd	nd	nd	nd
Borneol	1169	A	nd	0.6 (1.0)	nd	tr	nd	nd
α-Terpineol	1189	A	nd	0.4 (0.6)	nd	nd	nd	nd

Table 1. (cont.)

Compound	RI[f]	ID[g]	Yu[b]	Am[c]	SU[d]	Uk1[e]	Uk 2[e]	Uk 3[e]
Aldehydes and ketones								
Hexanal	800	A	tr	tr	tr	tr	tr	tr
2-Heptanone	892	A	nd	nd	nd	nd	nd	1.1 (0.1)
2(5*H*)-Furanone	921	C	nd	tr	tr	nd	nd	tr
Benzaldehyde	961	A	tr	1.3 (0.4)	tr	tr	tr	1.5 (0.6)
Nonanal	1102	A	tr	0.7 (1.0)	2.4 (0.3)	tr	tr	tr
Decanal	1204	A	0.5 (0.4)	0.4 (0.6)	2.2 (0.3)	tr	tr	tr
2,6-Dimethoxy-1,4-benzoquinone	1556	C	18.1 (1.2)	56.2 (3.4)	22.2 (3.3)	16.4 (2.5)	18.5 (2.4)	17.8 (3.3)
Benzophenone	1628	A	nd	3.0 (2.7)	tr	nd	nd	nd
Acetals								
1,1-Diethoxyethane	731	C	7.9 (0.7)	7.0 (0.5)	11.2 (0.8)	7.5 (0.5)	10.5 (0.4)	14.0 (0.8)
1,1-Diethoxybutane	923	C	1.5 (0.3)	2.0 (0.6)	tr	nd	nd	tr
2-Furfural diethyl acetal	1075	C	tr	2.1 (0.3)	tr	tr	tr	tr
1,1-Diethoxy-2-methylpropane	1106	C	tr	0.5 (0.6)	tr	tr	tr	tr
Furanic derivatives								
2-Furfural	830	A	5.4 (0.1)	8.6 (0.4)	6.2 (1.0)	4.1 (0.3)	5.3 (0.4)	5.8 (1.0)
5-Methyl-2-furfural	964	A	tr	tr	tr	tr	tr	tr
5-Hydroxymethyl-2-furfural	1240	C	tr	tr	tr	tr	43.4 (61.2)	tr
Lactones								
γ-Butyrolactone	916	A	nd	nd	tr	nd	nd	tr
trans-β-Methyl-γ-octalactone	1301	A	21.2 (0.7)	5.8 (0.3)	9.6 (0.7)	21.3 (0.4)	22.3 (0.3)	24.4 (0.7)
cis-β-Methyl-γ-octalactone	1323	A	28.9 (0.5)	35.6 (0.6)	3.2 (0.8)	24.5 (1.0)	27.9 (1.1)	29.3 (0.8)
Others compounds								
Dibutyl phthalate	1969	C	29.7 (6.0)	36.2 (2.0)	209.9 (2.8)	39.6 (1.3)	58.7 (2.9)	39.3 (2.8)
bis (2-Ethylhexyl) phthalate	2548	C	395.7 (9.9)	244.8 (20.4)	350.7 (21.5)	386.6 (4.4)	424.8 (1.8)	404.8 (21.5)

[a] Mean (standard deviation); tr: ≤ 0,1 µg/g of wood; nd : none detected. [b]former Yugoslavia barrels. [c]American barrels. [d]former Soviet Union barrels. [e]unknown origin barrels. [f]Retention index on HP-5MS. [g]ID: the reliability of the identification proposal is indicated by the following: A, mass spectrum and retention index agreed with standards; B, mass spectrum and retention index agreed with literature data; C, mass spectrum agreed with mass spectral database.

Table 2. Loading factors.

Compound	F1	F2	F3	F4
1,1-Diethoxyethane	-0.5029	-0.0701	0.7335*	0.2482
3-Methyl-2-buten-1-ol	0.1153	0.9734*	-0.0667	-0.0173
Butanoic acid	-0.2574	0.3472	0.8007*	0.4081
Ethyl lactate	-0.2257	0.3594	0.8142*	0.3868
2-Furfural	0.8626*	-0.1256	0.1501	0.1890
3-Methylbutanoic acid	-0.1919	0.3194	0.8769*	0.2845
2-Heptanone	-0.2243	0.3591	0.8136*	0.3833
1,1-Diethoxybutane	0.7744*	0.1625	-0.4187	0.3631
2,2-Diethoxyethanol	-0.0312	0.9517*	-0.1059	-0.1691
Hexanoic acid	-0.2121	0.3447	0.8271*	0.3779
Ethyl hexanoate	0.4734	0.3917	-0.2969	0.7262*
p-Cymene	-0.2179	0.8033*	-0.1701	0.0211
2-Ethyl-1-hexanol	0.4050	-0.2577	0.2116	0.7948*
γ-Terpinene	0.7270*	0.0708	0.0540	0.0118
Ethyl levulinate	0.7818*	0.1399	0.0952	-0.1870
Diethyl malonate	-0.2254	0.3594	0.8141*	0.3861
2-Furfural diethyl acetal	0.9813*	0.0559	0.0327	-0.0946
2-Methoxyethanol	0.5390	-0.7398*	0.1316	0.0576
Ethyl diethoxyacetate	0.7925*	0.0928	0.0198	-0.0960
Nonanal	0.1344	-0.8768*	0.1692	0.0108
1,1-Diethoxy-2-methylpropane	0.2771	-0.2403	0.8601*	0.3444
Octanoic acid	-0.1329	-0.7519*	-0.2049	0.5991
Diethyl succinate	-0.0358	0.9299*	0.0361	0.1753
Decanal	-0.0392	-0.9467*	0.0107	0.2022
Diethyl malate	-0.1131	0.9766*	-0.0593	-0.0240
Nonanoic acid	0.3781	-0.8218*	0.1453	0.0199
trans-β-Methyl-γ-octalactone	-0.8239*	0.5536	0.0063	0.0737
4-Vinylguaiacol	0.7916*	-0.5204	0.1045	-0.0088
cis-β-Methyl-γ-octalactone	0.4606	0.8749*	-0.0917	0.0100
Syringol	0.9687*	0.0554	0.0275	-0.0845
Vanillin	0.8365*	0.0043	0.3857	-0.0456
4-Methylsyringol	0.8269*	0.1959	0.4279	0.1332

Table 2. (cont.)

Compound	PC 1	PC 2	PC 3	PC 4
cis-Isoeugenol	0.1552	-0.2160	0.0314	0.8967*
Homovanillin	0.5164	-0.1918	0.1302	0.8175*
1-Dodecanol	-0.1595	-0.9530*	0.2022	0.0263
Guaiacylacetone	0.3438	-0.8307*	0.1712	0.3922
4-Vinylsyringol	0.7815*	0.1938	-0.4623	0.3445
2,6-Dimethoxy-1,4-benzoquinone	0.9811*	-0.0379	0.0563	-0.0833
Dodecanoic acid	-0.5749	-0.1713	0.7845*	-0.0686
Vanillic acid	-0.7416*	-0.1026	-0.4677	0.2899
Ethyl vanillate	-0.1937	-0.6565	-0.3467	0.4239
Ethyl dodecanoate	-0.0741	0.7096*	-0.0543	0.4407
4-Allyl syringol	0.9861*	0.0560	0.0426	-0.1122
Benzophenone	0.7593*	0.0282	0.0687	-0.1359
Dihydroconiferyl alcohol	-0.8814*	0.1940	-0.3062	0.1659
(*Z*)-Coniferyl alcohol	-0.9228*	-0.0898	-0.2704	0.2208
Homosyringaldehyde	0.8965*	-0.0582	-0.0779	-0.1485
Methyl homovanillate	0.7331*	0.2026	-0.5058	0.3914
Acetosyringone	0.6217	-0.7587*	0.1460	0.0006
(*E*)-Coniferyl alcohol	-0.9236*	0.1668	0.1427	0.1070
Syringyl vinyl ketone	-0.8392*	-0.0185	0.1309	0.2336
Ethyl syringate	-0.7579*	-0.0621	0.0890	0.0913
Pentadecanoic acid	-0.2750	-0.7885*	0.0570	-0.1728
Ferulic acid	-0.0716	-0.9713*	0.1510	0.0745
(*Z*)-Sinapyl alcohol	-0.8240*	0.3219	0.0163	-0.0731
Dibutyl phtalate	-0.1927	-0.9413*	0.1758	-0.0064
Hexadecanoic acid	-0.8447*	-0.0531	0.0750	0.1440
(*E*)-Sinapaldehyde	-0.9052*	0.2400	-0.1909	0.2800
Ethyl hexadecanoate	0.3234	0.9239*	-0.1151	0.0243
Oleic acid	0.9768*	0.0666	0.0721	-0.1247
Ethyl linoleate	-0.0139	-0.1685	-0.2738	0.9355*
Ethyl oleate	-0.7631*	0.2988	-0.0014	0.3935
Ethyl octadecanoate	-0.8606*	0.0450	-0.0567	0.0939
bis (2-Ethylhexyl) phthalate	-0.9443*	0.2272	-0.0384	0.0487
Ethyl docosanoate	0.0730	0.9611*	-0.1473	0.0528
Ethyl tetracosanoate	0.3108	0.4684	0.7657*	-0.3034
Dihydrovanillin	0.1670	-0.0310	0.9100*	-0.0831

**Significant value for $p \leq 0.05$.*

Table 3. Clasification function coefficients.

	G 1:1	G 2:2	G 3:3	G 4:4
	p=0.500	p=0.212	p=0.142	p=0.142
CP 1	-103.744	199.318	23.772	40.355
CP 2	41.802	-28.891	-109.587	6.616
CP 3	-211.279	95.793	121.359	474.428
CP 4	-80.806	17.696	51.040	205.238
constant	-116.789	-183.461	-148.414	-543.841

Table 4. Classification matrix of discriminant analysis.

	G 1:1	G 2:2	G 3:3	G 4:4	Correct assignment (%)
G 1:1	7	0	0	0	100
G 2:2	0	3	0	0	100
G 3:3	0	0	2	0	100
G 4:4	0	0	0	2	100

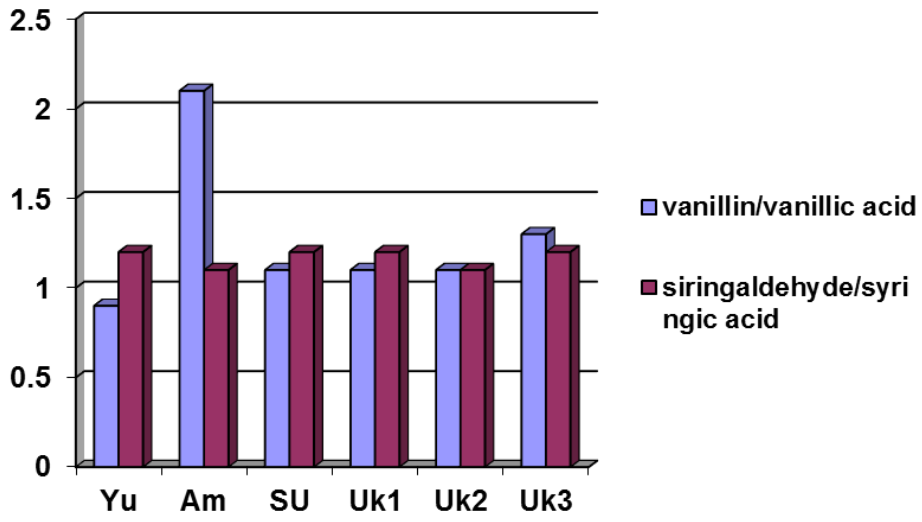

Fig. 1. Vanillin/vanillin acid and syringaldehyde/syringic acid ratio in barrels. Yu: former Yugoslavian, Am: American, SU: former Soviet Union; Uk1, Uk2 and Uk3: Unknowns 1, 2 and 3.

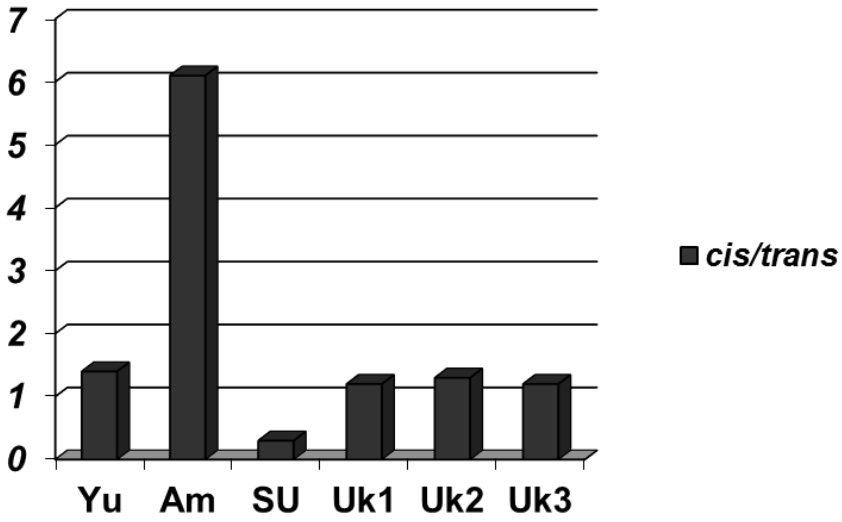

Fig. 2. Cis/trans relationships for oak lactones isomers in barrels. Yu: former Yugoslavian, Am: American, SU: former Soviet Union; UK1, Uk2 and Uk3: unknowns 1, 2 and 3.

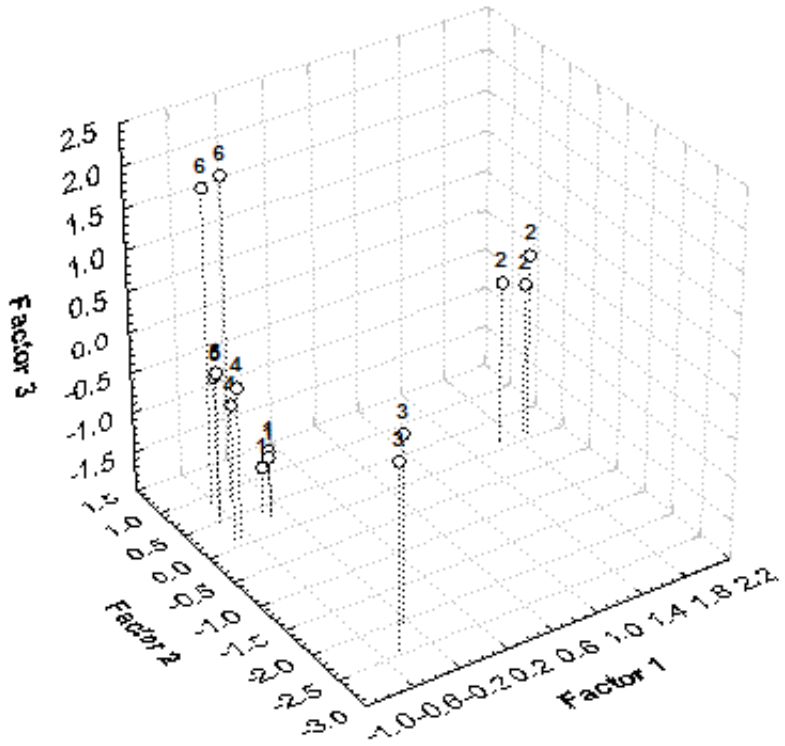

Fig. 3. Three-dimensional representation of PCA analysis. (1) Yu: former Yugoslavian, (2) Am: American, (3) SU: former Soviet Union; (4) UK1, (5) Uk2 and (6) Uk3: unknowns 1, 2 and 3.

CONCLUSIONS

It was established that the three lots of barrels with known origin (American, former Yugoslavian and former Soviet Union) gave a different compounds profile according to its origin and belongs to different types of wood, as it was confirmed by PCA and DA. Two lots with unknown origin (Unknown 1 and 2) gave a compound profile like former Yugoslavian barrels and belongs to the same group defined by multivariate analysis and, for that reason, we assume that these barrels coming from Europe. The Unknown 3 barrels, although belongs to a different group in PCA to the rest, is closer to come from Europe than from other origin because their quantitative compound profile is closer to former Yugoslavian than American or former Soviet Union origin, mainly if we are bearing in mind the *cis*/*trans* ratio of β-methyl-γ-octalactone.

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