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CHEMICAL CHARACTERIZATION OF DIFFERENT WOOD FRAGMENTS AND THEIR VOLATILE COMPOSITION IN MODEL SPIRIT SOLUTIONS

Article Highlights

- Volatile profiles of wood staves used to hasten brandies' aging were obtained
- Among wood samples, the lowest lignin content is detected in the wild cherry wood (23.58%)
- Volatile profiles of alternative woods and oaks significantly differ
- Sakuranin is a potential marker for wild cherry wood identification
- GC-MS is a suitable tool for distinguishing brandies aged with the alternatives

Abstract

This study characterizes oak (sessile and pedunculate oak) and alternative wood (black locust, Myrobalan plum, wild cherry, and mulberry) species as important sources of volatile compounds of aged spirits. Nowadays, their fragments are used to hasten the brandies' aging process. The ATR-FTIR spectra of analyzed wood samples are similar, only the mulberry FTIR spectrum contains unique peaks primarily due to its highest lignin content (40.93%). Using the untargeted GC-MS approach, a total of forty-one volatile compounds were identified in the wood extracts in a model spirit solution. The volatile profiles of alternative wood extracts in a model spirit solution were significantly different, both quantitatively and qualitatively, compared to those of oak. Coniferyl (23.14 μg/g–26.6 μg/g) and sinapyl (23.56 μg/g–25.82 μg/g) alcohols were the most abundant volatile compounds in investigated oak extracts. Resorcinol and coniferyl alcohol were the most abundant volatile compounds in black locust, sakuranin in wild cherry, while resorcinol and β-resorcinaldehyde in mulberry wood. To the best of our knowledge, sakuranin has not been detected in wild cherry wood until now. Besides wood chemical characteristics, the technology used during the aging process strongly influences on volatile profiles of aged brandies, thus, these compounds are potential chemical markers for discrimination between wood species as well as aging technologies.

Keywords: oak, alternative wood, volatile compounds, model spirit solutions.

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Wood barrels have been used for centuries in the process of aging brandies, which contribute to significantly better sensorial features (such as appearance and aroma), as well as the quality of brandy [1–4]. Among wood species, oak wood is distinguished as the most convenient and reputable material due to its unique mechanical, physical, and chemical properties [5]. Despite disadvantages, such as expense and length, aging has been established as a notable and irreplaceable process in the production of high-quality brandies [6].

During the process of aging, the contact between brandy and wood surface provokes a wide variety of

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physical and chemical interactions, resulting in a release of extractable compounds as well as hydrolysis of the wood's constituents (e.g. hemicelluloses and lignin) [3,4,7]. Namely, the hardwoods, exclusively utilized for barrel production, have a highly heterogeneous chemical composition, including three main components: cellulose (40–44%), hemicelluloses (15–35%), and lignin (18–25%), as well as extractives (up to 2%) [8]. In addition, the porosity and density of different wood species affect the composition of the final extract [9]. While wild cherry is highly porous, black locust and mulberry wood possess low and medium porosities, respectively [2]. During the process of aging, the linkages between the main lignin constituents (guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl (H) units [10] are broken and the compounds are released from the wooden cask by alcoholysis in the initial alcohol-water mixture [11].

Since the importance of aging is unquestioned and even more fundamental for the quality of a large number of wines and spirits, the investigation of this process has been subjected to current studies to accelerate the traditional process without any quality impairment [5,8]. The International Organization of Vine and Wine (OIV) approved the use of wood fragments (wood staves or sticks) to accelerate the aging process of wines and spirits, which usage is regulated by the Oenological Codex (resolution OENO 3/2005, Oeno 430/2010) [12]. In addition, oak chips are approved for the aging of spirits according to ECFR regulation [13]. According to EEC regulation No. 1507/2006, 11 October 2006, it is possible to use oak and chestnut pieces for hastening the process of aging wine [12].

Additionally, the utilization of alternative wood fragments species from local regions to hasten aging, such as Eastern Europe or Mediterranean countries, has the potential to be another novel trend introduced into global cooperage [2,14]. Furthermore, the wood fragment made of local oaks and wood alternatives is commonly used for aging brandies in Balkan countries, mostly in homemade production, with expansion in the local industry. To our knowledge, the influence of utilized local wood fragments on the volatile profile of aged brandies has not been investigated, although a report on Slavonija oak chips can be found in the literature [15].

The present study aimed to study the volatile composition of heartwood of different wood species using model spirit solutions as well as to determine the wood samples' surface and the total lignin content. Volatile profiles of experimentally aged brandy samples were examined to collect data for differencing brandies aged by wood fragment addition used to hasten the brandies' aging process.

MATERIALS AND METHODS

Wood samples

In this study, eight different wood stave samples utilized in Balkan cooperage were investigated. They were produced by local wood cask producer VBX-SRL. D.O.O. from Kraljevo, Central Serbia. Considered staves were made of the heartwood from several botanical species, including mulberry (M) (*Morus alba* L.), Myrobalan plum (MP) (*Prunus cerasifera* Ehrh.), black locust (BL) (*Robinia pseudoacacia* L.), wild cherry (C) (*Prunus avium* (L.) L.), and oak (*Quercus petraea* (Matt.) Liebl. (SRO), and *Q. robur* L. (PSO, PGO, POO)). Besides wood samples originating from the territory of the Republic of Serbia, two samples: Slavonija oak (PSO) and Olovo (POO) oak were obtained from Croatia and Bosnia and Herzegovina, respectively. Before analysis, the wood staves were grounded in a wood mill, to enhance the extraction of volatiles from wood samples. The granulation of the obtained sawdust was in the range of 0.5–1.5 mm [16].

Wood analysis

ATR-FTIR spectroscopy

The wood samples' surface chemistry was characterized using an ATR-FTIR spectrometer IR-Affinity (Shimadzu, Japan). The spectra were obtained in the wavenumber range of 4000–600 cm^{-1} at a resolution of 4 cm^{-1}.

Determination of the lignin in wood samples

The lignin content in wood samples was determined according to the procedure reported by Soutar and Bryden [17]. In brief, sample (2 g) was added to 25 ml 72% H_2SO_4, steeped for 75 min at room temperature, diluted with 600 ml water, reflux for 2 h, filtered through a weighted Gooch crucible, washed acid-free with water, dried at 105 °C, cooled and weighed. The lignin content was calculated from the ratio between the mass of lignin and the mass of the wood sample (determined before the treatment with H_2SO_4).

Determination of moisture sorption in wood samples

The moisture sorption (M, %) was determined by the thermogravimetric method using the Infrared Moisture Analyzer (Sartorius MA35). Before moisture sorption measurement, milled wood samples were exposed to 65% relative air humidity for 24 h. The average of three measurements for each sample was considered.

Preparation of wood extracts in a model spirit solution

The extraction was carried out by a widely extended procedure using wood pieces after double distillation to simulate the aging of spirits in the cask. Hydroalcoholic wood extracts were obtained according to the methodology reported by Smailagić *et al.* [16]. In short, wood sawdust (100 g), with a granulation between 0.5 and 1.5 mm, was extracted with 1000 mL of ethanol (60%, v/v), with constant stirring in a laboratory shaker at a speed of 100 rpm for 7 days in dark at room temperature (20 ± 2 °C). Extracts were filtered through filter paper (80 g/m^2) and kept in the refrigerator (4 °C) for further analysis. All extracts were prepared in triplicate.

GC-FID and GC-MS analysis of the wood extracts

Qualitative and quantitative analyses of the wood extracts in a model spirit solution were conducted using GC-MS and GC-FID, respectively. All wood extracts were prepared using liquid-liquid extraction, according to the procedure described by Veljović *et al.* [18]. Briefly, a 50 mL aliquot of each extract was diluted with 100 mL of distilled water and then mixed with 20 mL of internal standard solution (methyl-10-undecanoate diluted in dichloromethane (0.01 mg/mL)) and 10 g of NaCl. Each resultant mixture was stirred on a magnet stirrer in iodometric closed flasks (Erlenmeyer Polishing) for one hour. After mixing, the organic layer was separated from the water layer. The upper organic layer was dried with Na_2SO_4 and then filtered and evaporated on a vacuum-evaporator (45 °C, 10 kPa) (Heidolph Hei-VAP Value rotary evaporator, Schwabach, Germany) to a volume of 2 mL. After preparation, the samples were stored in a refrigerator (4 °C) until analysis.

GC-MS was used for the identification of wood compounds. The injections of prepared extracts (1 µl) were carried out in splitless mode. For GC-MS analyses, an Agilent 7890N gas chromatograph with an HP5-MS capillary column (30 m × 0.25 mm × 0.25 µm) was used. The following temperature program was employed: 60 °C for 0 min; then 3 °C/min to 280 °C and then held for 20 min. Helium was used as a carrier gas with a flow rate of 1 mL/min. The GC was coupled to a Hewlett-Packard 5972 MSD operated at 70 eV and scanning masses in the 40-550 range. The obtained peaks were identified by comparison of their retention times (calculated relative to n-alkanes) with the literature data as well as by comparison of the mass spectra fragmentation pattern with the mass spectra in the databases (NIST/EPA/NIH mass spectral library NIST2000, Wiley/NBS registry of mass spectral data, 7th ed., electronic versions) [19,20].

GC-FID was used for semi-quantitative analyses of wood compounds. For GC-FID analyses, an Agilent 4890A gas chromatograph with an HP5-MS capillary column (30 m × 0.25 mm × 0.25 µm) was used. The employed temperature program was the same as that used for GC-MS analyses. Hydrogen was used as carrier gas (1 mL/min). The GC was coupled to a FID detector operating at 300 °C. The results of GC-MS analyses were expressed as milligrams of methyl-10-undecanoate equivalents per liter of analyzed wood extracts [18]. The limit of detection was established using the US EPA 3σ approach.

Statistical analyses

Tukey's test was used to compare the mean values of lignin content, done in triplicate, with the level of statistical significance set at 0.05 (Statistica v. 12). Principal Component Analysis (PCA) of ATR-FTIR spectra was realized using PAST software [21]. For all PCA analyses, the spectra (1800–800 cm^{-1}) were preprocessed Spectragryph software [22] as follows: the spectra were smoothed using Savitzky-Golay filters with 5 points and a second-order polynomial function, baseline corrected, while the intensities were normalized (Standard Normal Variate-SNV).

RESULTS AND DISCUSSION

Characterization of the wood samples

The wood samples were characterized in terms of their surface chemistry (ATR-FTIR) and lignin content. The FTIR analysis, a rapid and non-destructive method, was performed to distinguish differences in the chemical composition of the wood samples. Fig. 1 shows the spectra of analyzed samples separated into two groups: the FTIR spectra of samples that originated from various tree species (Fig. 1a) and the FTIR spectra of wood samples from various oak varieties (Fig. 1b).

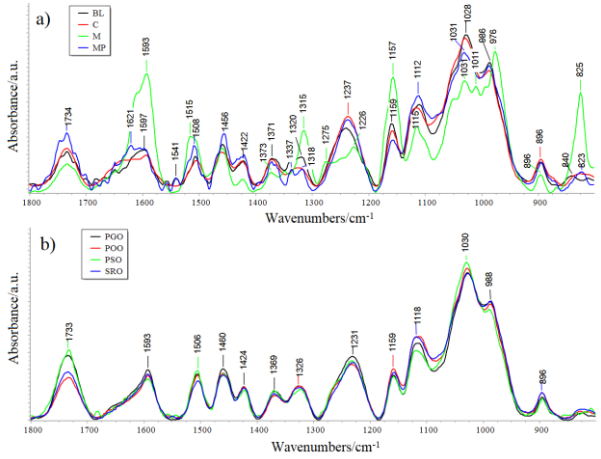

Figure 1. FTIR spectra of tested wood samples: a) Different wood samples from various tree species; b) Oak wood samples.

The FTIR spectra of all samples have major bands that are related to their primarily chemical compounds such as cellulose, hemicellulose, and lignin as well as other less abundant compounds in the wood (e.g. aromatic compounds). The main wood compound is cellulose and its bands are identified in all analyzed spectra: ~1157 cm^{-1} (symmetric C-O-C stretching vibrations) [23]; ~1030 cm^{-1} (C-C and C-O vibrations), ~1115 cm^{-1} (C-O), (C-C) [24]; 896 cm^{-1} (C-H vibrations, cellulose and hemicellulose) indicates presence of the β-glycosidic linkages between the cellulose glycosidic units [23, 25–26]. Also, spectra exhibit several common bands that could be related to various wood compounds: ~1733 cm^{-1} (C=O groups); ~1460 cm^{-1} (CH_2 scissoring vibrations, most probably from cellulose); ~1423 cm^{-1} (asymmetric C-H deformation) [23]. Also, the bands near 1423–1460 cm^{-1} can be associated with the C-H bend (aromatic skeletal vibration and asymmetric C-H deformations) [27] and C=C-C aromatic ring stretch modes of lignin [28].

Lignin as well as other aromatic compounds can be identified by bands at around 1596–1593 cm^{-1} and ~1505 cm^{-1} due to skeletal vibrations of the aromatic ring (C=C vibrations), while some of these bands could not be clearly visible in the case of the mulberry; this sample exhibits more intense band at 1515 cm^{-1} (most probably from lignin and other aromatic compounds) [23]. Also, the presence of lignin in the samples was detected by the bands at around 1370 cm^{-1} (symmetric C-H deformation). However, this band in the case of mulberry is broader and shows low intensity compared to other samples. The bands with a maximum of around 1237 cm^{-1} are visible in all samples (sample mulberry shows a low-intensity band around this position) that, according to Gupta *et al.* [23], originates from ring breathing of guaiacyl 'G'. According to the same authors, the band at 1315 cm^{-1} is due to ring breathing of syringyl 'S' and could be clearly visible in the case of sample mulberry, while the oak samples cluster doesn't show any strong vibrations at this position. Also, the FTIR spectrum of mulberry shows a strong band at 825 cm^{-1} most probably due to C-H vibration of aromatic compounds [23] (C-H out-of-plane bends [29]).

The results of lignin content are presented in Fig. 2. Tukey's test showed a significant difference in lignin content among wood staves. Furthermore, the investigated samples possess large variability between their lignin content; it ranges from 23.58% to 40.93%, which can be explained by the parallel influence of multiple factors including botanical species, age, the sampling position, etc. [3,11]. Among all wood samples, the lowest lignin content is detected in the wild cherry wood (23.58%). Furthermore, the oaks have lignin content in the range between 29.91% (Bosna Olovo) and 34.37% (Slavonija). According to Peterson and Perumalla [30], the lignin content of a very diverse group of oaks, which differed in species, geographical location, and application, varied from 20.1 to 30.1%. Additionally, Puech [31] analyzed the lignin content of French and foreign oak, particularly intended for barrel production, and reported its content in the range from 25.3 to 28.5%. The lignin content in black locust (35.09%, Figure 2) is significantly higher than in hardwood of mature wood (20.9–25.8%) since the wood sample investigated in this research paper is much older than in Latorraca *et al.* [32].

The results of moisture content are presented in Fig. 3. Tukey's test showed no significant difference in moisture content among wood staves. Myrobalan plum (MP) is characterized by the highest porosity as well as the highest moisture content (8.45%) compared to the pedunculate oak (Gornji Radan) (PGO) and sessile oak (SRO) (7.10 and 6.38%, respectively). Although samples PGO and SRO belong to the same group of woods (i.e. oaks), the sample PGO (pedunculate oak) has smaller vessels and higher moisture content compared to the sample SRO (sessile oak).

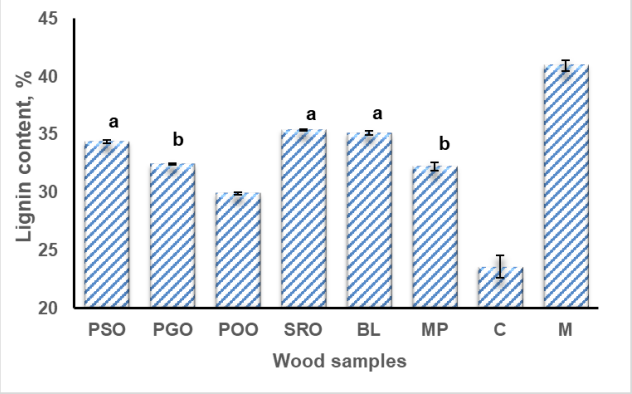

Figure 2. Lignin content of the analyzed wood fragment. The samples with the same letter are not statistically different ($\alpha = 0.05$).

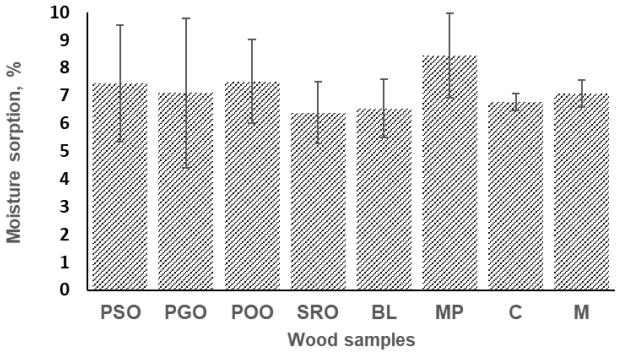

Figure 3. Moisture content of the analyzed wood fragment.

The PCA analysis (Figure 4a) confirmed that mulberry (M) showed the most distinctive spectrum among tested wood samples. As we pointed out, these differences in the mulberry spectrum primarily originated from the difference related to the lignin chemical compositions, i.e. its aromatic compounds. This is supported by loadings of PC 1, where the peaks that can be associated with the chemical composition of mulberry, such as those at 825, 972, 1157, 1311, 1519, and 1591 cm^{-1} are identified. The second group of samples separated by PC 2 is black locust (BL), Myrobalan plum (MP), and wild cherry (C), while the third group represents all studied oaks (PSO, PGO, POO, and SRO). The differences in the chemical structure between these two groups can be associated with the presence of less prominent chemical compounds, such as extractives, that in small concentrations may be crucial for the formation of specific brandy aromatic profiles.

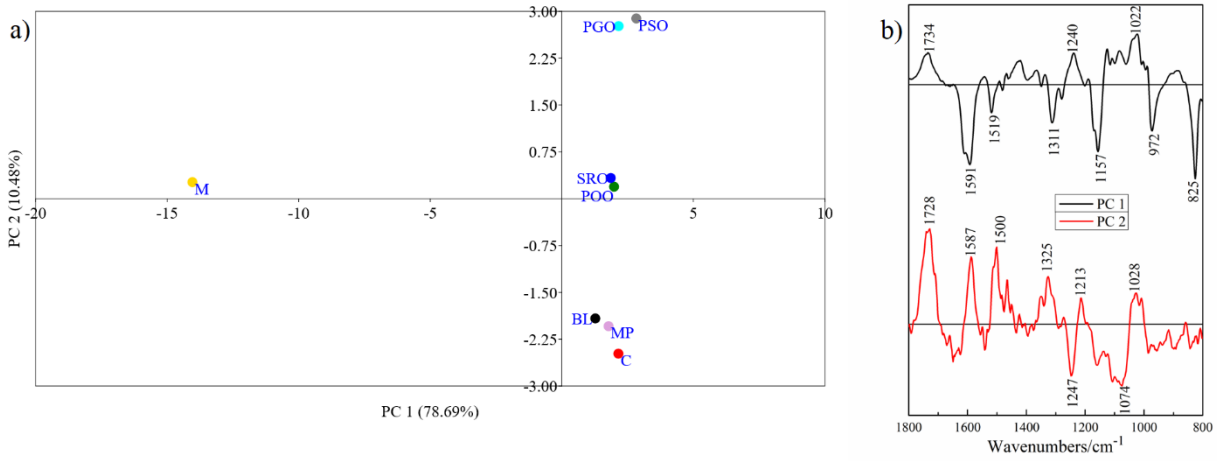

Figure 4. (a) Score plot of PCA for tested wood samples; (b) Loading plots of PC 1 and PC 2.

GC-MS analysis

A total of forty-one compounds were quantified using gas chromatography (GC-MS), Table 1. According to volatile profiles, oaks' aged spirits significantly differ from aged spirits with alternative wood species (i.e. black locust, Myrobalan plum, wild cherry, and mulberry). Although the volatile profiles of analyzed oak-aged spirits are similar, they are opposite from existing published data. Namely, the coniferyl (23.14–26.60 μg/g) and sinapyl (23.56–25.82 μg/g) alcohols are the most abundant volatile compounds in oaks' aged spirits (Table 1). Opposite to this study, De Rosso *et al.* [33] and Flamini *et al.* [34] reported that coniferyl alcohol was found in a low amount within 50% hydroalcoholic oaks' extracts (model spirit), while there was no data about the content of sinapyl alcohol.

All identified compounds in oaks' aged spirits appear due to the lignin degradation and then their oxidation during aging. As it is well known, coniferyl and sinapyl alcohols are the main lignin compounds, whose presence in the wood fragments was confirmed by the ATR-FTIR (Figure 1). During aging, these alcohols are released and converted to aromatic aldehydes (coniferyl aldehyde, and sinapyl aldehyde) relatively quickly by oxidation and to respective acids by further oxidation [7]. In general, the differences between the present and previously published results occur because the decreasing of the coniferyl and sinapyl alcohols' content, and simultaneously increasing the amount of aromatic aldehydes and acids, is necessary to prolong the aging period. Thereby, the amount of vanillin (0.30–0.78 μg/g) and syringaldehyde (1.71–2.17 μg/g), as aromatic aldehydes whose formation depends on the oaks aging time, is lower. Moreover, the amount of syringaldehyde is lower (1.71 μg/g) in sessile oak (SRO) than in pedunculate oaks (PSO, PGO, and POO) (1.85–2.17 μg/g). On the other hand, the highest amount of vanillin has PGO (0.78 μg/g), while the lowest Slavonija pedunculate oak (PSO, 0.3 μg/g). The amount of coniferyl aldehyde (3.51 μg/g) and sinapyl aldehyde (7.95 μg/g) is higher in sessile oak (SRO) than in pedunculate oaks (2.19–2.47 μg/g and 4.49–5.40 μg/g, respectively). Besides vanillin and syringaldehyde, De Rosso *et al.* [33] found that oaks contain eugenol (aromatic terpene characteristic for oak-aged beverages) [3], methoxyeugenol, and *α*-terpineol. In our case, *α*-terpineol was not detected. Furthermore, Chira and Teissedre [15] reported the presence of *cis*- and *trans*-*β*-methyl-*γ*-octalactone (known as oak lactones) in oaks. The odor intensity of *β*-methyl-*γ*-octalactone *cis* isomer (woody, coconut odor) is about 2–12 times stronger in comparison with its *trans* isomer [37,38]. Herein, *β*-methyl-*γ*-octalactone *cis* isomer is more

Table 1. Quantitative data on wood extracts volatile compounds.

Compound (μg/g of wood)	Odor quality	Odor detection threshold (ppm, mg dm^{-3})	PSO	PGO	POO	SRO	BL	MP	C	M
Limonene	Orange peel-like ((R)-Limonene) [35,]	0.20[39]	n.d.	n.d.	n.d.	n.d.	n.d.	0.49	0.72	n.d.
Acetophenone	Citrusy, orange peel-like[36] Floral[40]	0.256[41]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.
Benzoic acid	Balsamic[35]		n.d.	n.d.	n.d.	n.d.	n.d.	0.30	n.d.	n.d.
Coumaran			n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.48
Vinylguaiacol	Smoky[40]	0.209[41]	0.08	0.19	0.17	0.26	n.d.	n.d.	n.d.	n.d.
o-Acetyl-*p*-cresol			n.d.	n.d.	n.d.	n.d.	0.26	n.d.	n.d.	n.d.
Eugenol	Clove[35,37] spicy, sweet[37]	0.0070[38]	0.08	0.54	0.48	0.03	n.d.	n.d.	n.d.	n.d.
Syringol	Flowery, clove[35] Spicy, phenolic[37] Burnt, smoke, burned wood[38]	0.58[38]	0.16	0.34	0.34	0.27	1.48	n.d.	n.d.	1.59
Methylresorcinol			n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.33
Resorcinol			n.d.	n.d.	n.d.	n.d.	10.07	n.d.	n.d.	62.00
β-Resorcinaldehyde			n.d.	n.d.	n.d.	n.d.	3.46	n.d.	n.d.	13.76
Resacetophenone			n.d.	n.d.	n.d.	n.d.	2.08	n.d.	n.d.	n.d.
trans-*β*-methyl-*γ*-octalactone	Coconut[c37] Sweet, flowery[38]	0.79[38]	0.17	0.25	0.24	0.72	n.d.	n.d.	n.d.	n.d.
cis-*β*-methyl-*γ*-octalactone	Coconut[37] Coconut, sweet[38]	0.067[38]	0.34	1.65	1.59	0.05	n.d.	n.d.	n.d.	n.d.
Vanillin	Vanilla[35-39]	0.022[38]	0.30	0.78	0.76	0.64	n.d.	n.d.	n.d.	n.d.
Isoeugenol (*cis*- or *trans*-)			n.d.	0.16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Homovanillyl alcohol			0.28	0.38	0.35	0.43	0.20	n.d.	n.d.	n.d.
Vanillyl propan-2-one			0.69	1.00	0.72	0.12	0.95	n.d.	n.d.	n.d.
Vanillic acid			n.d.	0.05	0.19	0.88	n.d.	n.d.	0.09	n.d.
Propiovanillone			0.32	0.36	0.32	0.09	n.d.	n.d.	n.d.	n.d.
3,4,5-Trimethoxy-phenol			n.d.	n.d.	n.d.	n.d.	n.d.	0.09	7.64	n.d.
Methoxyeugenol			0.32	0.56	0.26	0.79	0.67	n.d.	n.d.	n.d.
Homovanillic acid			0.50	0.50	0.38	0.44	n.d.	n.d.	n.d.	n.d.
Methyl homovanillate			0.33	0.32	0.27	0.44	n.d.	n.d.	n.d.	n.d.
Syringaldehyde	green, woody[32] green, woody, sweet[33]		1.85	2.17	2.04	1.71	0.94	0.20	n.d.	n.d.
Syringic acid			0.25	0.92	0.32	1.02	n.d.	n.d.	0.12	n.d.
Syringyl propan-2-one			0.73	0.73	0.50	0.86	n.d.	n.d.	n.d.	n.d.
Butyrosyringone			0.52	0.57	0.47	0.54	n.d.	n.d.	n.d.	n.d.
Coniferyl alcohol			26.6	25.73	24.47	23.14	9.75	n.d.	n.d.	0.36
Coniferyl aldehyde			2.47	2.21	2.19	3.51	2.14	n.d.	n.d.	1.55
4-hydroxy-3,5-dimethoxybenzoic acid			n.d.	n.d.	n.d.	n.d.	n.d.	0.18	n.d.	n.d.
Scopoletin			n.d.	n.d.	n.d.	n.d.	n.d.	0.03	n.d.	n.d.
Sinapyl aldehyde			5.40	4.89	4.49	7.95	4.88	n.d.	0.1	n.d.
Sinapyl alcohol			23.56	24.84	24.71	25.82	1.53	0.03	n.d.	n.d.
Dihydrosinapyl alcohol			0.09	0.53	0.58	0.51	n.d.	n.d.	n.d.	n.d.
Pinocembrin			n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.80	n.d.
Tectochrysin			n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	220.15	n.d.
2,6-Dimethoxybenzoquinone			n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.30	n.d.
Chrysin			n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	467.22	n.d.
Sakuranin			n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	896.65	n.d.
Naringenin			n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	75.91	n.d.
Total volatile compounds			65.04	69.67	65.84	70.22	38.41	1.32	1669.71	81.07

n.d. - not detected. Results are expressed as milligrams of methyl -10-undecanoate equivalents per liter of analyzed wood extracts

abundant in pedunculate oak samples (0.34-1.65 μg/g), while *trans* isomer is more abundant in sessile oak (0.72 μg/g). These two isomers, along with vanillin are major oak wood aroma compounds that have a great influence on wine aroma [30].

The main characteristic of wild cherry volatile profile, in comparison with other analyzed wood samples, was the high content of flavonoids, whose presence was also previously confirmed by HPLC-MS [16]. Five flavonoids including three flavanones (pinocembrin, naringenin, and sakuranin) and two flavones (467.22 μg/g chrysin and 220.15 μg/g tectochrysin) are exclusively detected in wild cherry (C). It is good to mention that the amount of sakuranin (896.65 μg/g) found in wild cherry is significantly higher than the two other flavanones. In another study, besides the aforementioned flavonoids, Vinciguerra *et al.* [42] identified three more flavanones (sakuranetin, pinostrobin, dihydrowogonin) and one dihydroflavonol (aromadendrin-7-methylether) in the heartwood of *Prunus avium*. Moreover, several flavonoids such as eriodictyol, sakuranetin, pinocembrin, and chrysin are suggested as markers of cherry hardwood and wine aged in cherry wood [16,43]. To our knowledge, sakuranin has not previously been detected in wild cherry wood, consequently. Additionally, it can be concluded that the hardwood of *Prunus avium* L. (wild cherry) species contains a significant amount of flavonoids compared with oak wood species, which is in agreement with the literature [2]. Wild cherry wood aged spirit (C) contains a high amount (7.64 μg/g) of 3,4,5-trimethoxy-phenol and a low amount of volatile compounds, which is in agreement with the previously published research [33,34].

Myrobalan plum has a significantly lower amount of volatiles (1.32 μg/g, Table 1) compared to the oaks (65.04–70.22 μg/g). Quantitatively, the most abundant volatile compounds in Myrobalan plum are terpene limonene (0.49 μg/g) and benzoic acid (0.30 μg/g). According to Bandeira Reidel *et al.* [44], limonene was detected as the most abundant compound in a stem of *P. cerasifera* 'Pissardii', while this compound was not detected in a stem of *P. cerasifera*. The presence of limonene was also confirmed in apple brandies aged with mulberry and sessile oak [5], which is opposite from our research, whereas limonene is detected in Myrobalan plum and wild cherry. The limonene, with citrus and herbal aroma notes, is the only detected terpene in all analyzed samples. Moreover, scopoletin was detected exclusively in Myrobalan plum-aged spirit. This is the opposite of literature data, where scopoletin was first considered as a marker for oak wood, but later it was detected also in chestnut and wild cherry wood [6].

Besides in black locust, the resorcinol is dominant compound in mulberry (M) with an amount of 62.00 μg/g, followed by a significant amount of *β*-resorcinaldehyde (13.76 μg/g), syringol (1.59 μg/g). De Rosso *et al.* [33] found a large amount of *β*-resorcinaldehyde in mulberry wood extract in a model spirit solution. Interestingly, the volatile profile of black locust (BL) differs from the results reported in the literature. In our case, the most abundant compound in black locust is resorcinol (10.07 μg/g), followed by coniferyl alcohol (9.75 μg/g), while the contents of coniferyl aldehyde and syringaldehyde were slightly lower (2.14 μg/g and 0.94 μg/g, respectively). Fernández de Simón *et al.* [46] also detected resorcinol, but not as the most abundant compound in black locust. De Rosso *et al.* [33] and Flamini *et al.* [34] found syringaldehyde as the dominant black locust compound as well as a large amount of vanillin, which is not found in the investigated black locust. On the other hand, Fernández de Simón *et al.* [45] observed coniferyl alcohol and sinapyl aldehyde as dominant compounds in seasoned black locust wood aged spirit. A high amount of *β*-resorcinaldehyde (3.46 μg/g) and no eugenol were found in the investigated black locust wood-aged spirit, which was in accordance with the findings of De Rosso *et al.* [33], and Flamini *et al.* [34]. In addition, the presence of methoxyeugenol, as in our case, was also confirmed by De Rosso *et al.* [33]. Generally, the composition of black locust wood extract in the model spirit solution is in accordance with the previous studies.

Herein, some volatile compounds were unique components of the volatile profile of certain alternative and oak species, which can contribute to the identification of specific wood species. Therefore, 2,6-dimethoxybenzoquinone and volatile flavonoids (pinocembrin, naringenin, sakuranin, chrysin, and tectochrysin) were quantified only in wild cherry wood. The coumaran and methylresorcinol are present only in mulberry (M), while *o*-acetyl-*p*-cresol and resacetophenone are present only in the black locust (BL). Benzoic acid, scopoletin, and 4-hydroxy-3,5-dimethoxybenzoic acid were found only in Myrobalan plum. Many compounds, such as oak lactones, vinylguaiacol, eugenol, vanillin, propiovanillone, homovanillic acid, methyl homovanillate, syringyl propan-2-one, butyrosyringone, and dihydrosynapic alcohol were found only in oak samples. Interestingly, isoeugenol was found only in oak from Gornji Radan (PGO).

CONCLUSION

The main idea of the current research was about the chemical degradation of lignin-based matrices in

the presence of hydroalcoholic solution, as well as surface chemistry and lignin content of local wood fragments traditionally used in Balkan countries for hastening brandies' aging. The ATR-FTIR spectra of the samples are similar, only the mulberry FTIR spectrum contains unique peaks due to its highest lignin content (40.93%). Wild cherry stood up from other wood species by the lowest lignin content, as well as the richness in flavonoids in its volatile profile. The profiling of volatile compounds released from local wood fragments can provide valuable data on local wood and aged spirits to improve the products' quality. In addition to GC-MS analyses, FTIR spectral analysis in combination with PCA can be promising as a potentially effective tool used to distinguish oak and alternative wood samples.

To conclude, with the presented results we are closing the loop. The outcomes from the current research, together with our previously published results on characteristic phenolic profiles of the same wood pieces, may be considered as a good starting point to consider the utilization of wood pieces of alternative wood species from local regions for hastening brandy aging to decrease the cost of aging technology. To the best of our knowledge, the wood particles (smaller than 2mm) used in this research could be used for aging, but the aging time must be optimized. Concerning the type of wood used in the aging process, mulberry wood stood out with the highest lignin content, and its aging potential can be further investigated. Collected data can pave the way to establish geographical indicators of famous aged fruit brandies to protect authenticity and locally sourced products, as well as reduce fraudulent production. Furthermore, this study could be the initial step for establishing regulation in the aging process of alcoholic brandy at the local and regional levels.

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NAUČNI RAD

HEMIJSKA KARAKTERIZACIJA RAZLIČITIH FRAGMENATA DRVETA I SASTAV ISPARLJIVIH JEDINJENJA U MODEL RASTVORU ALKOHOLNIH PIĆA

U ovoj studiji okarakterisane su različite vrste hrasta (hrast kitnjak i lužnjak) i alternativne vrste drveta (bagrem, džanarika, trešnja i dud) kao važan izvor isparljivih jedinjenja u alkoholnim pićima koja su odležavala u kontaktu sa drvetom. Danas se fragmenti navedenih vrsta drveta koriste za ubrzavanje procesa odležavanja rakija. ATR-FTIR spektri analiziranih uzoraka drveta su slični, jedino FTIR spektar duda sadrži jedinstvene pikove uglavnom zbog najvećeg sadržaja lignina u ovom uzorku (40,93%). Koristeći neselektivnu metodu gasne hromatografije (GC-MS), identifikovano je ukupno četrdeset i jedno isparljivo jedinjenje u model rastvoru alkoholnih pića. Profil isparljivih jedinjenja u ekstraktima alternativnih vrsta drveta u model rastvoru su se kvalitativno i kvantitativno značajno razlikovali u poređenju sa profilom hrasta. Najzastupljenija isparljiva jedinjenja u analiziranim ekstraktima hrasta bili su koniferil (23,14 μg/g–26,6 μg/g) i sinapil (23,56 μg/g–25,82 μg/g) alkohol. Rezorcinol i koniferil alkohol su bili najzastupljenija isparljiva jedinjenja u bagremu, sakuranin u divljoj trešnji, dok su rezorcinol i β-rezorcinaldehid bili najzastupljeniji u drvetu duda. Koliko nam je poznato, sakuranin do sada nije otkriven u drvetu divlje trešnje. Pored hemijskih karakteristika drveta, tehnologija korišćena tokom procesa odležavanja značajno utiče na profil isparljivih jedinjenja u rakijama koje su odležavale u kontaktu sa drvetom, tako da su navedena jedinjenja potencijalni hemijski markeri za razdvajanje između korišćenih vrsta drveta kao i tehnologija odležavanja.

Ključne reči: hrast, alternativne vrste drveta, isparljiva jedinjenja, model rastvor alkoholnih pića.