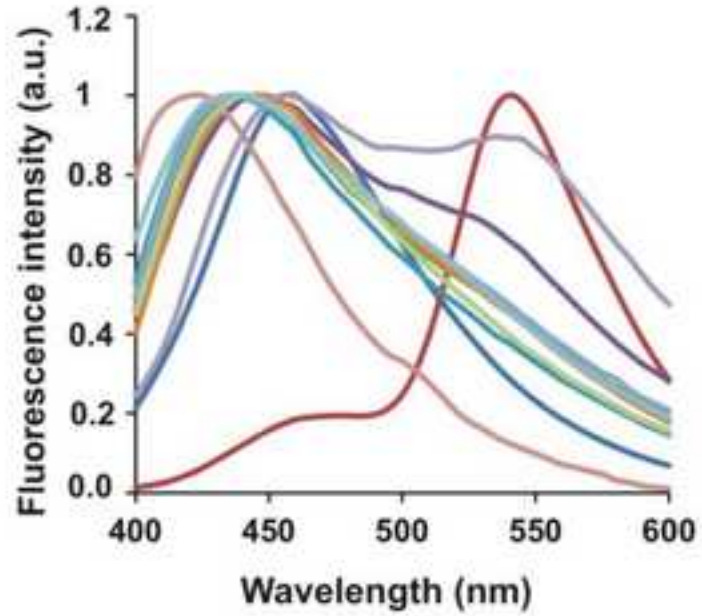
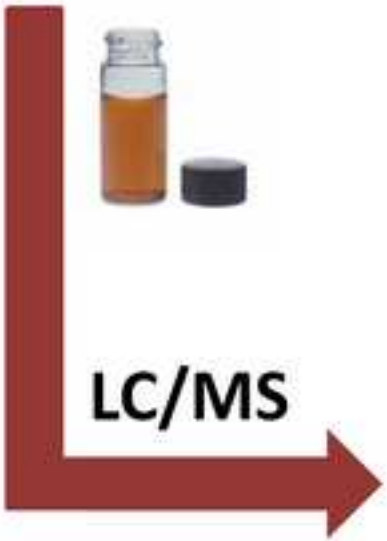
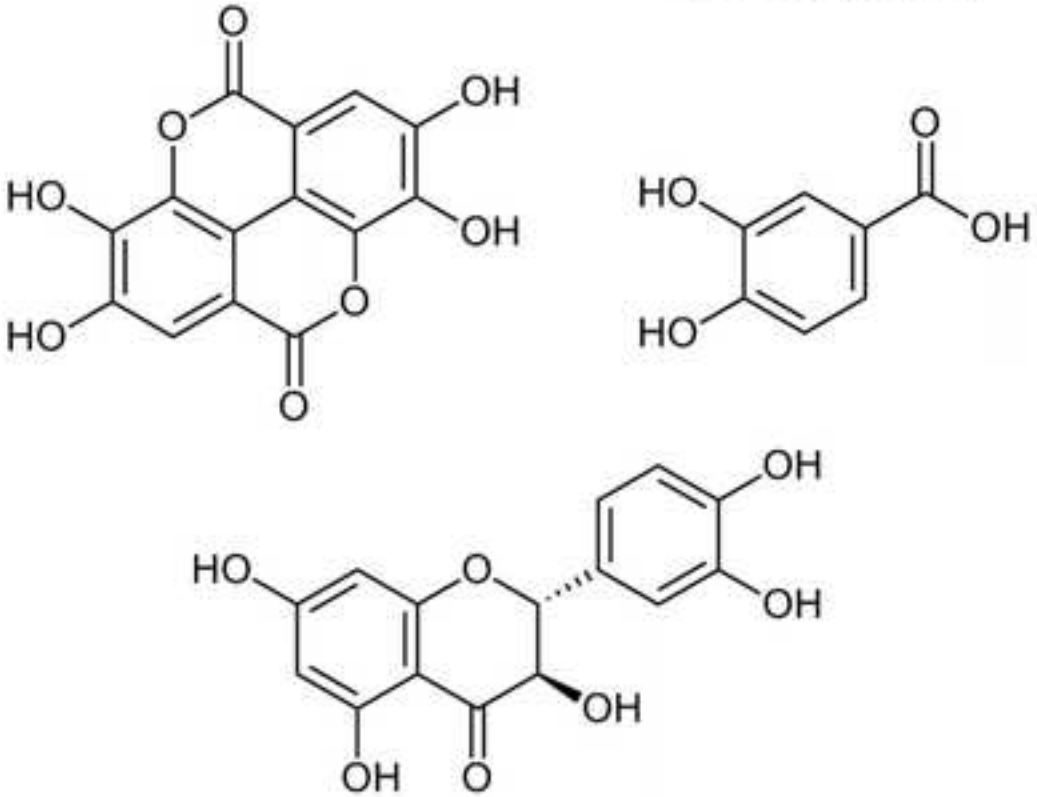
Graphical Abstract







Highlights

- Polyphenolic profile was shown to be an useful tool to identify the wood used in cooperage
- Specific flavonoids were suggested as indication of heartwood botanical origin
- Color of analyzed wood samples was affected by the botanical origin of wood samples
- Shape and maxima positions of fluorescence spectra varied more among wood samples than among corresponding wood extracts
- Principal component analysis based on emission spectra discriminated black locust and cherry from the other wood samples, due to presence of flavonoids

Phenolic profile, chromatic parameters and fluorescence of different woods used in Balkan cooperage

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ABSTRACT

The aim of this research was to study phenolic compounds of diverse botanical species of wood commonly used in cooperage in Balkan countries. Several botanical species have been considered including mulberry (*Morus alba* L.), myrobalan plum (*Prunus cerasifera Ehrh.*), black locust (*Robinia pseudoacacia* L.), wild cherry (*Prunus avium* (L.) L.), and oak *(Q. petraea* (Matt.) Liebl., *Q. robur* L., *and Q. cerris* L.). A total of 37 compounds were quantified, demonstrating the presence of phenolic acids, flavonols, flavones, flavanones, flavanonol taxifolin, stilbenoids, and coumarins. Taxifolin was the most abundant in wild cherry (8455.70 mg kg^{-1}), while ellagic acid predominated in oak wood (8872.05 – 10099.32 mg kg^{-1} in sessile oaks, and up to 15958.80 mg kg^{-1} in pedunculate oak from Slavonia). The highest content of protocatechuic acid (533.39 mg kg^{-1}) was found in myrobalan plum. Also, isoflavones were characteristic of wild cherry, while mulberry was abundant in stilbenoids. Total phenolic content, as well as antioxidant, chromatic, and fluorescence properties were studied. The spectral shapes and maxima of fluorescence emission spectra of bare wood samples were compared with those of the corresponding wood extracts. The Principal Component Analysis (PCA) was applied in order to find patterns in emission spectra for differentiation among wood samples.

Keywords: Wood cask; Phenolics; LC-MS; CIELab; Spectrofluorometry; PCA

1. Introduction

The wood industry is economically significant sector of Balkan countries. During 2016, Balkan countries (Albania, Bulgaria, Bosnia and Hercegovina, Croatia, Greece, Macedonia, Montenegro, Slovenia, and Serbia) exported over 872 hundred m^3 industrial round wood (non-coniferous) (FAOSTAT, 2018). The wood waste generated in final products processing, such as the manufacture of barrels, is estimated on more than 60% volume of tree cut. During 2017, Serbian producers exported 137 tons of wooden barrels (Trade Map, 2018), so more than 200 tons of wood waste is available annually in Serbia from this production.

Chemical composition of wood depends upon various factors including species, age, height, and their growth environment, but also tree part (root, stem, or branch), type of wood, geographic location, climate, and soil conditions (Doussot et al., 2002).

The chemical constituents of dry wood species are divided in two groups: structural substances and non-structural substances. Structural substances are cellulose, hemicelluloses, and lignin, which are the main chemical constituents of wood. They are complex polymers insoluble in water-alcohol mixture (Le Floch et al., 2015). Non-structural substances are mostly low-molecular-mass compounds, e.g. extractives, some water-soluble organics, and inorganics. Extractives are non-cell wall small molecules that can be extracted from wood by solvents, and are aliphatic and alicyclic compounds, and phenolic compounds (Valette et al., 2017).

Some of the wood constituents are partially soluble, but many of them are decomposed during the maturation of spirits and migrate into the alcohol-water solution. The amount of extracted wood compounds strongly depends on its initial concentration in different botanical species.

Selection of wood type for casks production depends on several factors including local tradition, desirable sensory contribution for different spirits, and availability and costs of materials (Mosedale and Puech, 1998). However, oak is by far the most commonly used wood for casks production, mainly because of its good mechanical properties (strength, hardness, and flexibility) and low permeability to liquids. Among 250 species of the genus *Quercus*, the sessile oak (*Quercus petraea* (Matt.) Liebl.) and the pedunculate oak (*Quercus robur* L.), are commonly used in Europe, while *Quercus alba* L. is mostly used in the North America (De Rosso et al., 2009).

Balkan countries, including Serbia, have long tradition in the production of wood casks for fruit brandies. The quality of cask depends on many factors defined by individual producers, such as wood selection and wood preparation. Given that the availability of wood from some localities can be limited, local producers of casks extended the list of preferred types of wood for cooperage. In Serbia, other wood species besides oak are in usage, such as wild cherry (*Prunus avium* (L.) L.), black locust (*Robinia pseudoacacia* L.), mulberry (*Morus alba* L.), and plum (*Prunus* spp). Natural seasoning process (drying) is also important since it induces diverse changes such as degradation of wood polymers together with oxidation reactions (Mosedale and Puech, 1998). Local producers in Serbia frequently use naturally seasoned staves (without toasting treatment) for cask production. The natural seasoning is a complex process, but highly recommended for the quality of the final product (de Simón et al., 2010).

The aim of this research was to study phenolic composition of commercial wood staves commonly used in Serbian cooperage. Several botanical species have been considered, including mulberry (*Morus alba* L.), Myrobalan plum (*Prunus cerasifera Ehrh.*), black locust (*Robinia pseudoacacia* L.), wild cherry (*Prunus avium* (L.) L.), and oak *(Q. petraea* (Matt.) Liebl., *Q.*

84 *robur* L., *and Q. cerris* L.). So far, mulberry and Turkey Oak (*Q. cerris* L.) were not extensively
85 investigated in order to characterize polyphenols. Also, according to literature, no comprehensive
86 research data could be found on phenolics present in myrobalan plum heartwood. Although,
87 some reports on the most appreciated Balkan oaks from Kučaj (East Serbia) and Slavonia
88 (Croatia) could be found in literature (Pecić et al., 2012; Kyraleou et al., 2015), other oak
89 samples with defined geographical origin from the Balkan region were not under investigation
90 until now.

91 In order to characterize wood extracts, total phenolic content and antioxidant capacity
92 were determined, and phenolic profiles were analyzed using ultra-high performance liquid
93 chromatography-diode array detector-triple-quadrupole mass spectrometer (UHPLC–DAD
94 MS/MS). Further, the wood colorimetric parameters were measured and the relationship of
95 analyzed phenolic compounds with the color was investigated. Finally, having on mind that
96 phenolic compounds and coumarins are well known fluorophores (Sádecká et al., 2016), the
97 fluorescence spectra were recorded to observe the differences among the samples based on
98 phenolic composition of the studied types of wood used for cask production, as well as on
99 phenolic composition of corresponding ethanolic extracts.

100

101 **2. Material and methods**

102 *2.1. Reagents and Standards*

103 Acetonitrile and acetic acid (both of MS grade), methanol (HPLC grade),
104 Folin−Ciocalteu's reagent, sodium acetate trihydrate, glacial acetic acid, and sodium carbonate
105 (anhydrous) were purchased from Merck (Darmstadt, Germany), and 2,2-diphenyl-1-
106 picrylhydrazyl (DPPH) and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox)

were purchased from Sigma-Aldrich (Steinheim, Germany). Ultrapure water (Thermofisher Scientific, Bremen, Germany) was used to prepare standard solutions and blanks. Syringe filters (13 mm, PTFE membrane 0.45 μm) were purchased from Supelco (Bellefonte, PA, USA). Polyphenolic standards were purchased from Sigma-Aldrich (Steinheim, Germany).

2.2. Samples

In this research, the heartwood staves of eleven different wood samples were analyzed (Table 1). During 12 months, the staves were seasoned in the open air at cooperage industry VBX-SRL. D.O.O. from Kraljevo, Central Serbia. Two samples (sessile oak from Kuršumlija and Turkey oak), were staves without natural seasoning treatment. During natural seasoning the relative humidity in staves is decreased in order to stabilize the dimension and optimize organoleptic characteristics. Additionally, the content of water-soluble compounds and ellagitannin are decreased during this treatment (Mosedale and Puech, 1998; Doussot et al., 2002).

2.3. Extract preparation

The extraction was carried out by a procedure reproducing the conditions of spirits maturation. Before extraction, the staves were grinded in a mill for wood, and the granulation of the obtained sawdust was in the range of 0.5-1.5 mm. The sawdust (100 g) was extracted with 1000 mL of ethanol (60%, v/v), in glass bottles, with constant stirring in a laboratory shaker at a speed of 100 rpm for 7 days in dark at room temperature (20 ± 2ºC). In order to separate solid

129 parts, extracts were filtered through a filter paper (80 g/m^2) and kept in refrigerator (4°C) for
130 further analysis. All samples were prepared in triplicate.
131
132 *2.4. Determination of total phenolic content and antioxidant capacity*
133 Determination of total phenolic content (TPC) of wood extracts was conducted by the
134 Folin-Ciocalteu method described by Singleton and Rossi (1965). The antioxidant capacity was
135 determined by DPPH method modified by Veljović et al., (2017). The results were expressed as
136 g gallic acid equivalents (GAE) per liter of the extract for TPC, and mmol Trolox equivalents
137 (TE) per liter of the extract for antioxidant capacity. All measurements were done in triplicate
138 and data were expressed as mean value ± standard deviation (SD).
139
140 *2.5. UHPLC–DAD MS/MS analysis of polyphenolic compounds*
141 The separation, determination, and quantification of the compounds of interest in each
142 sample were performed using a Dionex Ultimate 3000 UHPLC system equipped with a diode
143 array detector (DAD) that was connected to TSQ Quantum Access Max triple-quadrupole mass
144 spectrometer (ThermoFisher Scientific, Basel, Switzerland). The elution was performed at 40°C
145 on a Syncronis C18 column. The mobile phase consisted of water + 0.01% acetic acid (A) and
146 acetonitrile (B), which were applied in the following gradient elution: 5% B in the first 2 min, 2–
147 12 min 5–95% B, 12.0–13.0 min from 95% to 5% B, and 5% B until the 20th min. The flow rate
148 was set to 0.3 mL/min and the detection wavelengths to 254 and 280 nm. The injection volume
149 was 5 μL. A TSQ Quantum Access Max triple-quadrupole mass spectrometer equipped with an
150 heated electrospray ionization (HESI) source was used with the vaporizer temperature kept at
151 250°C, and the ion source settings as follows: spray voltage 4500 V, sheet gas (N_2) pressure 27

AU, ion sweep gas pressure 0 AU and auxiliary gas (N_2) pressure 7 AU, capillary temperature 275°C, skimmer offset 0 V, and capillary offset -35 V. The mass spectrometry data were acquired in the negative ionization mode, in the *m*/*z* range from 100 to 1000. Multiple mass spectrometric scanning modes, including full scanning (FS), and product ion scanning (PIS), were conducted for the qualitative analysis of the targeted compounds. The collision-induced fragmentation experiments were performed using argon as the collision gas, and the collision energy was varied depending on the compound. The time-selected reaction monitoring (tSRM) experiments for quantitative analysis were performed using two MS^2 fragments for each compound that were previously defined as dominant in the PIS experiments (Gašić et al., 2015). Xcalibur software (version 2.2) was used for instrument control. The phenolics were identified by direct comparison with commercial standards. The total amounts of each compound were evaluated by calculation of the peak areas and expressed as mg L^{-1}.

2.6. CIELab chromatic parameters

Color measurements of wood extracts were performed using a portable tristimulus Chroma Meter model CR-400 (Konica Minolta, Osaka, Japan). Results were expressed in Commission Internationaled'Eclairage L*, a*, and b* color space coordinates. Following parameters were measured using a D_{65} light source and the observer angle of 2°: L* (lightness), a* (+a* = redness, -a* = greenness), b* (+b* = yellowness, -b* = blueness), C* (chroma or saturation), and h (hue angle). The tristimulus values of CIELab readings were calibrated against a standard white plate (Y = 84.8; x = 0.3199; y = 0.3377). Measurements were done in triplicate and data were expressed as mean value ± standard deviation (SD).

175 *2.7. Fluorescence of the wood samples and corresponding extracts*

176 The fluorescence spectra of the wood and wood extract samples were recorded using an
177 Fl3-221 P spectrofluorometer (JobinYvon, Horiba, France), equipped with a 450W Xe lamp and
178 a photomultiplier tube. The wood samples were placed in the solid sample holder, in front-face
179 configuration. The illumination's incident angle was set to 35°, to minimize light reflections,
180 scattered radiation, and depolarization phenomena. The Rayleigh masking was applied in order
181 to reduce Rayleigh scattering from the solid sample which limits the sensitivity and accuracy of
182 the measurement. The extracts were measured in the cuvette with 10 mm optical path and 1 mL
183 volume, in right angle configuration.

184 Fluorescence steady-state emission spectrum of either wood or wood extract may be a
185 sum of two or more individual components corresponding to various fluorophores - emitting
186 structural entities. In order to determine the number and emission profiles of components in an
187 integral spectrum, measurement of series of emission spectra at different excitation wavelengths
188 in a wavelength range is performed, thus obtaining excitation-emission matrices (EEMs) that are
189 subsequently analyzed by using advanced statistical methods. The ranges of the excitation
190 spectra was 250-450 nm and 310-385 nm for the wood and extract samples, respectively, while
191 the range for the recorded fluorescence emission spectra was 335-595 nm and 400-600 nm for
192 the wood samples and extracts, respectively. The integration time was 0.5 s, and the wavelength
193 increment in excitation measurements was 5 nm, and emission increment was 1 nm. A spectral
194 band width of 2 nm was employed for both the excitation and emission slits.

195

196 *2.8. Statistical analysis*

Tukey's test was used to detect the significance of differences ($p \leq 0.05$) between mean values (NCSS software package, www.ncss.com). Principal Component Analysis (PCA) was realized using the PLS_Tool Box software package for MATLAB (Version 7.12.0). All data were group-scaled prior to PCA. The singular value decomposition algorithm (SVD) and a 0.95 confidence level for Q and Hotelling T2 limits for outliers were chosen. For each sample the average of the 10 emission spectra recorded for various excitation wavelengths was used as input value in PCA, in order to take into account contribution of all fluorophores present in the sample.

3. Results and discussion

3.1. Total phenolic content and antioxidant capacity

The results of total phenolic content (TPC) and antioxidant capacity (DPPH) are presented in the Table 2. Considering all the analyzed samples, the TPC was in the range from 5.31 (Turkey oak) to 107.69 (mulberry) g kg^{-1} gallic acid equivalents (GAE). Mulberry, myrobalan plum, and black locust wood extracts were characterized with higher TPC values in comparison with traditional oak woods. Mulberry showed the highest level of total polyphenols (107.69 g kg^{-1} GAE), while total phenolic content in myrobalan plum, black locust, and wild cherry wood samples were 81.71 g kg^{-1} GAE, 74.28 g kg^{-1} GAE, and 49.69 g kg^{-1} GAE, respectively. As reported by de Simón et al., (2014) oak heartwood contains high level of lignin derivatives, ellagitannins, ellagic acid, and gallic acid, but it does not contain other kinds of phenolic compounds. Therefore, lower TPC in oaks than in other botanical species were expected since the content of oak phenol compounds significantly increases by lignin degradation during aging process (Zhang et al., 2015).

Among oak samples, pedunculate oak from Slavonia (55.51 g kg^{-1} GAE) had the highest TPC, followed by pedunculate oak from Gornji Radan (54.21 g kg^{-1} GAE). In the other oak samples TPC varied between 30.30 g kg^{-1} GAE (sessile oak, Kuršumlija) and 39.46 g kg^{-1} GAE (sessile oak, Kučaj). Turkey oak had significantly lower TPC (5.31 g kg^{-1} GAE) than other wood samples. In general, it can be assumed that the type of oak wood influenced TPC values, since it was observed that sessile oaks had lower content of total phenolics (30.30 – 39.46 g kg^{-1} GAE) than pedunculate oak (37.51 – 55.51 g kg^{-1} GAE), also confirmed by Alañón et al., (2011). However, the influence of geographical origin could also be important since the samples of sessile oak from various geographic regions had significantly different TPC.

The DPPH follows almost the same order as TPC, ranging from 28.14 (Turkey oak) to 844.93 mmol TE kg^{-1} (mulberry), also confirmed by high correlation coefficient (R = 0.951). All the wood extracts showed notable antioxidant capacity, with exception of Turkey oak. The antioxidant capacities of mulberry and myrobalan plum wood extracts were significantly higher than other samples, and were 844.93 and 612.95 mmol TE kg^{-1}, respectively.

3.2. Phenolic profiles

In total, thirty-seven compounds were quantified by liquid chromatography in all wood ethanolic extracts and data are shown in Table 3. As for the phenolic acids, the most abundant was ellagic acid. It was found in all samples, with the highest amount determined in oak wood samples, both sessile and pedunculate, in the range from 8872.05 (sessile oak from Ravna Gora) to 10099.32 mg kg^{-1} (sessile oak from Kučaj). It is interesting to note that, in pedunculate oak from Olovo, the amount of ellagic acid was significantly lower (3039.41 mg kg^{-1}), and in pedunculate oak from Slavonia oak significantly higher (15958.80 mg kg^{-1}) than in the other

242 sessile and pedunculate oak samples. The lowest amount of ellagic acid was found in Turkey oak
243 (205.15 mg kg^{-1}).

244 Ellagic acid possesses a number of potential activities such as antimutagenic,
245 antibacterial, antiviral, antiallergic, anti-inflammatory; antidiabetic, cardioprotective, and
246 hepatoprotective activities (García-Ninõ and Zazueta, 2015). Gallic acid was found in black
247 locust (58.74 mg kg^{-1}) and in both sessile and pedunculate oak samples, in the range from 17.38
248 mg kg^{-1} (Olovo) to 117.70 mg kg^{-1} (Slavonia). The amount of gallic and ellagic acid were
249 significantly higher in oak samples than in wild cherry wood, which was in accordance with the
250 results of Alañón et al., (2011).

251 Protocatechuic acid was present in all samples except in the sessile oak from Ravna Gora.
252 Myrobalan plum had significantly higher content of protocatechuic acid (533.39 mg kg^{-1}) than
253 other samples. Mulberry and wild cherry were also abundant in protocatechuic acid (201.85 mg
254 kg^{-1} and 83.16 mg kg^{-1}, respectively). The oaks had the protocatechuic acid in range between
255 9.79 mg kg^{-1} (sessile oak, Kuršumlija) and 35.86 mg kg^{-1} (pedunculate oak, Gornji Radan). *p*-
256 Hydroxybenzoic acid was found in all samples except in sessile and pedunculate oaks. The
257 largest quantity of this compound was found in mulberry (260.04 mg kg^{-1}), followed by black
258 locust (164.78 mg kg^{-1}), while the lowest amount was found in Turkey oak (19.58 mg kg^{-1}). *p*-
259 Coumaric acid and ferulic acid were found only in the extract of mulberry and wild cherry. In
260 wild cherry, higher concentration of protocatechuic, *p*-coumaric, caffeic acid, and ferulic acid,
261 and lower concentration of coniferyl aldehyde than in oak were found, which was opposite to the
262 results of Alañón et al., (2011). The reason for discrepancy could be explained by different
263 process of extraction but also could be due to different geographical origin of the wood. Madrera

et al., (2010) also examined the concentration of protocatechuic acid in wild cherry wood, and the reported value was 1.13 mg L^{-1}.

According to the obtained results, flavonols were found in significant quantities only in the wild cherry and mulberry. The most abundant flavonols in wild cherry wood were quercetin (187.11 mg kg^{-1}), kaempferol (140.14 mg kg^{-1}), and galangin (54.23 mg kg^{-1}). High amount of kaempferol was also found in mulberry wood (57.31 mg kg^{-1}). Among oak samples, pedunculate oak from Olovo did not contain any of the studied flavonols. Other oaks contained quercetin in the range from 9.35 mg kg^{-1} (Gornji Radan) to 9.90 mg kg^{-1} (Kuršumlija), and only oaks originating from Kuršumlija and Slavonia contained flavonols other than quercetin.

The most abundant flavanone in all extracts was pinocembrin, with the exception of pedunculate oak from Olovo, having eriodictyol as the most abundant. In wild cherry, significant amounts of pinocembrin (1851.19 mg kg^{-1}), naringenin (409.20 mg kg^{-1}), and eriodictyol (89.54 mg kg^{-1}) were found in comparison with other samples. Sessile oak from Kuršumlija had significantly higher amount of pinocembrin (26.73 mg kg^{-1}) when compared with other oak samples, in the range from 0.33 (pedunculate oak, Olovo) to 4.18 mg kg^{-1} (sessile oak, Kučaj).

All flavones were found only in sessile oak from Kuršumlija and wild cherry wood. In wild cherry, the most abundant flavone was chrysin (716.10 mg kg^{-1}), followed by apigenin (233.97 mg kg^{-1}). Among flavones, chrysin was the most abundant flavone in all samples except in black locust, in which apigenin was the most abundant flavone, and in pedunculate oak from Olovo, where no flavones were found. Pedunculate oak from Gornji Radan and Slavonia, sessile oak from Ravna Gora, and Turkey oak did not contain any flavone other than chrysin. In addition, sessile oak from Kuršumlija contained significantly higher amount of chrysin (13.64 mg kg^{-1}) than the other oak samples, ranging from 0.22 mg kg^{-1} (pedunculate oak, Gornji Radan)

287 to 2.75 mg kg^{-1} (sessile oak, Kučaj). High amounts of vitexin (66.88 mg kg^{-1}), luteolin (55.99 mg
288 kg^{-1}), acacetin (61.49 mg kg^{-1}), and genkwanin (60.06 mg kg^{-1}) were also found in wild cherry
289 wood.

290 Flavanonol taxifolin was detected in all samples except in black locust, and it was the
291 most abundant in wild cherry wood extract (8455.70 mg kg^{-1}). Mulberry (4034.69 mg kg^{-1}) and
292 myrobalan plum (136.18 mg kg^{-1}) were also abundant in taxifolin. In oak, taxifolin was found in
293 the range from 0.99 mg kg^{-1} (Ravna Gora) to 4.07 mg kg^{-1} (Kuršumlija) in sessile oaks, and from
294 5.72 mg kg^{-1} (Slavonia oak) to 11.44 mg kg^{-1} (Olovo) in pedunculate oak. Taxifolin was detected
295 in the bark of the genus *Pinus* or *Larix* and in the seeds of the genus *Silybum*, but also in
296 different fruit bodies with the highest content in grapes, oranges, and grapefruit (Zu et al., 2014).
297 Its presence was reported in vinegars aged in cherry wood (Cerezo et al., 2010). Thus,
298 investigated wood species can be used as a promising raw material for taxifolin production,
299 especially having on mind many pharmacological effects that this compound exibits, including
300 chemopreventive, antiproliferative, antioxidant, and anti-inflammatory effects (Wu et al., 2017).
301 It can also be found in the market in its semi-synthetic form under the trade name of Venoruton®
302 (Menaa et al., 2014).

303 Isoflavones were characteristic of wild cherry wood extract. Daidzein was found
304 exclusively in wild cherry (0.77 mg kg^{-1}). Genistein was found in significant amount in wild
305 cherry (137.17 mg kg^{-1}), much higher than in sessile oak from Kuršumlija (1.65 mg kg^{-1}). Other
306 samples did not contain isoflavones.

307 Only mulberry was abundant in stilbenoids, and the most abundant stilbenoid was
308 oxyresveratrol (1731.73 mg kg^{-1}), while the contents of resveratrol and pterostilbene were lower
309 (121.55 mg kg^{-1} and 12.21 mg kg^{-1}, respectively). Among the three investigated stilbenoids, only

oxyresveratrol was found in black locust (44.55 mg kg^{-1}), Turkey oak (15.07 mg kg^{-1}), myrobalan plum (3.85 mg kg^{-1}), and sessile oaks from Kuršumlija (3.74 mg kg^{-1}) and Kučaj (3.30 mg kg^{-1}). As previously suggested, high amounts of stilbenoids contribute to identification of mulberry wood (Zhang et al., 2015). The presence of resveratrol in different parts of mulberry was confirmed previously in various *Morus alba* L. cultivars (Song et al., 2009, Wu et al., 2013; Choi et al., 2013). The content of resveratrol varied between 0.0021-0.0053 mg/g in the mulberry fruit, and between 0.0010-0.0068 mg/g in fruit marc. Resveratrol is a phytoalexin antioxidant, which has attracted substantial attention in the scientific community during the past two decades through the link with the "French paradox" (Menaa et al, 2014). It is a cancer chemopreventive agent, a cardioprotective agent, and shows antioxidant, antiinflammatory, neuroprotective, and antiviral properties (Tellone et al., 2019). Oxyresveratrol is a naturally occurring resveratrol analogue with an additional hydroxyl group on the aromatic ring that enables better water solubility. Similar to resveratrol, oxyresveratrol has various health-promoting activities including anti-inflammation, anti-obesity, anti-oxidation, anti-virus, cholesterol lowering, hepato- and neuro-protection in pre-clinical studies (Chen et al., 2016). In addition, it possesses skin-whitening and photoprotective effect, which could be applied in cosmetology and dermatology (Chen et al., 2016).

Two coumarins were characterized in the wood extracts. Aesculetin was found in wild cherry, mulberry, and Turkey oak (102.30, 29.15, and 12.87 mg kg^{-1} respectively), while low quantities of aesculin were found in myrobalan plum, mulberry, all pedunculate oaks, and in sessile oak from Ravna Gora. Black locust and sessile oaks from Kuršumlija and Kučaj did not contain any of investigated coumarins.

The highest content of coniferyl aldehyde, which is the product of lignin degradation (ethanolysis) was found in pedunculate oak from Olovo (20.13 mg kg^{-1}), while mulberry was characterized with the lowest content of it (0.99 mg kg^{-1}). In sessile and pedunculate oaks, the content of coniferyl aldehyde was between 7.26 mg kg^{-1} (Gornji Radan) and 20.13 mg kg^{-1} (Olovo), while it was not detected in sessile oak from Ravna Gora and Turkey oak. The highest amount of phloretin was found in wild cherry (17.16 mg kg^{-1}) while it was detected in small quantities in sessile oak from Kuršumlija, Turkey oak, myrobalan plum, and mulberry. It was not found in black locust and other oak wood samples.

Finally, from all the results presented, one general conclusion could be drawn on the relation between botanical origin of wood and corresponding phenolic profile. Namely, both qualitative profile and quantitative differences should be considered. Just a few phenolic compounds were identified in specific type of wood used for cask production. Hence, some of the identified and quantified compounds could be suggested as possible chemical indication of botanical origin of heartwood material. This is stressed out in the following section.

The uniqueness of the wild cherry wood phenolic profile is notable. Wild cherry was the only wood rich in flavanones and flavones. Sanz et al., (2012) found that flavanones prunin, naringenin, isosakuranetin, eriodictyol, and the flavanonols aromadendrin, and taxifolin contribute to polyphenolic profile of cherry wood. Chinnici et al., (2015) suggested several phenolic compounds as markers of cherry heartwood and wine aged in cherry wood (eriodictyol, sakuranetin, pinocembrin, and chrysin). These findings are in agreement with our results. Moreover, according to our investigation, quercetin, kaempferol, galangin, vitexin, luteolin, apigenin, acacetin, genkwanin, genistein, and aesculetin could be also considered as possible contributors to polyphenolic profile of wild cherry wood.

Only sessile and pedunculate oak wood samples did not contain *p*-hydroxybenzoic acid. On the other hand, the oak heartwood contained gallic acid and large quantities of ellagic acid, which could be useful for its identification, also suggested by other authors (Sanz et al., 2012). It is interesting to note that, similar to the oak samples, black locust wood was abundant in gallic acid but the amount of the ellagic acid was significantly lower. Turkey oak showed significantly lower amounts of all investigated individual polyphenols, which also stands for the values of TPC and DPPH, when compared with other oak samples. The most abundant phenolic compound was ellagic acid (205.15 mg kg^{-1}), but the amount was the lowest among the investigated samples.

Mulberry wood had specific and the most complex chemical composition, with 29 detected phenolic compounds of the 37 analyzed in this research. Comparing with the other investigated wood samples, mulberry had the largest concentration of *p*-hydroxybenzoic acid and oxyresveratrol. Among all investigated samples, resveratrol and pterostilbene were found only in mulberry, so these compounds can contribute to identification of this wood.

According to our results, myrobalan plum showed the highest content of protocatechuic acid and 5-O-caffeoylquinic acid among investigated samples. Also, high amounts of taxifolin were found, so these compounds could be identified as important for myrobalan plum wood. In literature, scarce number of quantitative data are available on polyphenols characteristic for plum heartwood and this stands for Myrobalan plum, too.

3.3. Color of analyzed wood samples (CIELab results)

The color is one of the main characteristic influencing the sensory quality of aged spirits. Some of the compounds extracted from wood material can change the color of spirits. One of the

specific objectives of this research was to determine if the phenolic content and concentration of individual phenolic compounds in wood samples correlates with colorimetric CIELab parameters. The chromatic characteristics of the wood extracts were defined by the three chromaticity coordinates, lightness (L*), red/green color component (a*), and blue/yellow color component (b*), and by its calculated magnitudes: chroma (C*) and hue angle (h). The results of CIELab chromatic parameters are presented in Table 4. Tukey's test showed significant differences among different wood samples for individual chromatic components.

A wide range of L* was found among samples, from color darkness (19.98, in mulberry) to color lightness (51.52, in Turkey oak), most probably reflecting different qualitative and quantitative composition of colorants in studied wood extracts. Wild cherry wood showed high L* value (46.17), which can be explained by the extraction of compounds with low influence on the lightness of this wood extract.

Extraction of the compounds from wood material, mainly being phenolic compounds, affects the lightness of analyzed samples by decreasing L* value. Our results confirmed such trend; the mulberry wood extract, characterized with the highest TPC value, showed the lowest L* value. The significant influence of phenolic compounds on the L* parameter was also reported by Pecić et al., (2012). The extract of sessile oak from Ravna Gora showed the lowest value of L* parameter among all the oaks investigated. Herein, parameter L*was in the range from 31.83 to 41.56 for sessile, and from 38.20 to 41.94 for pedunculate oaks. The same trend was reported for the aged brandies (Pecić et al., 2012), where L* varied between 36.18 and 40.98, and from 36.41 to 46.86, for brandies aged in sessile and pedunculate oaks, respectively. The value of parameter a* was in the range from 5.73 (Turkey oak) to 27.43 (myrobalan plum). The wild cherry wood is recognizable by light color and many spirits producers suggest this

401 wood material for cask production to obtain spirits with affirmative color. However, our results
402 pointed to myrobalan plum and black locust wood extracts as important source of red colorants.
403 Values for pedunculate oaks were in the range from 14.55 to 18.01, and in sessile were in the
404 range from 14.99 to 21.43. Previously published values for plum brandies aged in oak cask were
405 in the range from 2.21 to 10.49 for pedunculate, and from 6.11 to 13.55 for sessile (Pecić et al.,
406 2012). These results are not in agreement with our results for oak staves, probably because of
407 duration of aging (plum brandies were aged much longer than the samples investigated in this
408 work) and different solvent (plum brandy versus water-alcohol mixture). The value of parameter
409 b* was positive for all the analyzed samples, so different intensity of yellow color, from light to
410 amber yellow was characteristic of all wood extracts. Mulberry extract had the lowest value of
411 b*, and it seems that the extracted compounds did not affect the intensity of yellow color. The
412 highest influence on the yellow color was found in the wild cherry wood extract, which could be
413 explained with the higher content of flavones and flavonols in comparison with other analyzed
414 samples (Table 3). Due to chemical modifications, such as O-glycosylation and O-methylation,
415 these flavonoids absorb light in the visible region of spectra, thus contributing to the yellow
416 color. The value of parameter b* was in the range from 33.14 to 36.95for pedunculate, while in
417 the range from 24.10 to 35.89 for sessile oaks. These results were in line with the results for
418 parameter b* of the old Serbian brandies (25.42-35.76) maturated in oak casks (Pecić et al.,
419 2012).
420 The results of our study indicate that the CIElab parameters were affected by the
421 botanical origin of wood samples, but also the species of oak wood had an effect on some of the
422 parameters.
423

3.4. Fluorescence of the wood samples and corresponding extract

Figure 1 presents overlaid averaged emission spectra for different wood samples and their extracts. Figure S1 shows the excitation-emission spectral series for the myrobalan plum wood sample (A) and corresponding extract (B), as an example. The spectral series recorded for various excitation wavelengths, reflected in the properties of the averaged spectra, enabled the study of the main emitting compounds in wood and in the corresponding extracts, which are the base for estimation of differences between the samples. The spectral shapes, number, and positions of the emission maxima differed among the samples. The seven samples of different variants of oak have similar shape and one maximum, in the range 435-455 nm (Figure 1A). Polyphenols including lignin are the main emitters in wood, with the maximum in the range 430-455 nm. The shift of the maximum position among various oak varieties indicates presence of the other emitters in higher amounts in some samples; such are the phenolic compounds of the type of chlorogenic acid, caffeic acid, coumarins, stilbenes which emit at 430 nm (Izquierdo et al., 2000; Lang et al., 1991). Mulberry wood has blue shifted maximum, at 420 nm, which may be addressed to a relatively low content of lignin in this wood species than in some other species (Rahman and Jahan, 2014). The black locust wood has considerably red shifted maximum, at 540 nm, and an additional low maximum at 465 nm (Figure 1A). The former maximum may be related to flavonoids, such as flavanones present in wood (Drabent et al., 1999). The latter maximum originates from polyphenols/lignin, which is present in a low amount in this wood species (Latorraca et al., 2011) and consequently its maximum is lower in comparison with the maximum of the oak samples. Flavanone derivatives bound in wood may be responsible for the orange emission with shoulder in blue region (Lang et al., 1991). The myrobalan plum wood has the maximum overlaying with the oak maxima, but has a shoulder at 525 nm (Figure 1A),

probably originating from the flavonoids present in this wood (Table 3). The wild cherry wood has two maxima, at 455 nm (overlaying with the oak maxima) and at 540 nm (overlaying with the black locust maximum). This wood may contain similar fluorophores to oak and black locust, namely lignin and flavonoids (Table 3).

The differences in spectral shape and maxima positions are lower among the wood extracts in comparison with the corresponding wood samples. The spectral shapes are simpler for wood extracts (Figure S1B, Figure 1B) than for wood samples (Figure S1A, Figure 1A), which may be addressed to the lower number of fluorophores (absence of lignin) present in the extract comparing with wood. The maximum positions of the oak extracts are in the range 420- 445 nm. As already stated, the wood extracts contain compounds, i.e. phenolic compounds produced in a process of lignin decomposition (Mosedale and Puech, 1998). These compounds are responsible for the emission maxima in the mentioned wavelength range. The wild cherry extract is close to them at 455 nm. Only the spectra of mulberry and black locust extracts are blue- and red- shifted, respectively, comparing with the other spectra, which can be addressed to the presence of larger concentration or higher fluorescence intensity of certain compounds. The 515 nm maximum of the black locust wood extract may be related to some of the flavanones or flavonols (Sudo et al., 2009), while the 360 nm maximum of the Turkey oak may originate from stilbenoids (Lang et al., 1991).

The PCA was used to classify wood samples according to the differences in characteristic emission spectrum. The dependent variables were the heartwood staves of different woods and corresponding wood extracts (oak, mulberry, myrobalan plum, black locust, and wild cherry). The independent variables were the recorded fluorescence emission spectra. The range for the recorded fluorescence emission spectra was 400-600 nm and 335-595 nm for the wood and wood

extracts, respectively. Principal component analysis of wood samples and wood extracts suggested that a two-component model explains 93.77% (PC1 accounted for 56.33% and PC2 for 37.44%) and 90.36% (PC1 accounted for 59.36% and PC2 for 31.00%) of total variance, respectively. The scores plot and loadings plot obtained for wood samples and wood extracts are shown in Figure 2.

The PCA scores plot of wood samples (Figure 2A-1) discriminated black locust and wild cherry from the other wood samples. From the loadings plot it was possible to identify wavelengths that were influential for the separation among samples. Black locust was separated from the other investigated wood samples along PC1. The PC loadings plot (Figure 2A-2) indicated that PC1 was strongly positively contributed by the recorded fluorescence at wavelength 540 nm. Black locust was characterized with fluorescence at wavelength 540 nm as maximum of emission spectra (Figure 2A). Since this red shift of its emission maximum comparing with the maxima of most other wood samples is related to the flavanones and other flavonoids in this wood species, one can say that these compounds are responsible for separation of black locust sample along PC1. On the other hand, wavelength 540 nm had the most negative impact on PC2 direction, whereas wavelength 505 nm had the most positive influence on PC2 (Figure 2A-3). The wavelength 505 nm was shown to be the most important variable for the separation of the wild cherry wood from the other wood samples along PC2. At this wavelength, the emission spectrum of wild cherry wood is substantially distinguished from the spectra of the other wood samples (Figure 1A).

As for the wood extracts, the PC score plot showed separation of black locust and Turkey oak extracts from the other investigated wood extracts (Figure 2B-1). Loadings plot (Figure 2B-2) indicated that recorded fluorescence at 515 nm had the most positive impact on PC1, while the

493 contribution of the recorded fluorescence at 385 nm was negative along PC1. Fluorescence at
494 wavelength 515 nm, which is the maximum of emission spectra of black locust extract (Figure
495 1B) was the major factor to separate black locust extract form the other wood extracts. Since this
496 maximum is related to some of the flavanones and/or flavonols (probably quercetin) in the
497 extract, one can say that these compounds are responsible for separation of the black locust
498 sample along PC1. The wavelength 385 nm was responsible for discrimination of the Turkey oak
499 sample. Further, fluorescence at wavelength 445 nm showed the highest positive influence on
500 PC2 (Figure 2B-3) and this was the most important variable to separate all wood extracts with
501 maximum of emission at about 445 nm (such as pedunculate oaks, sessile oaks, myrobalan plum,
502 mulberry, and wild cherry wood extracts) from black locust and Turkey oak extracts. Based on
503 the emission maxima, the major phenolic compounds produced by lignin decomposition in the
504 extracts of pedunculate oaks, sessile oaks, myrobalan plum, mulberry, and wild cherry wood, are
505 responsible for this separation.

506

507 **4. Conclusions**

508 The idea behind the work presented herein was to explore the possibilities of finding
509 traits that could point to diversity in wood used in cooperage industry. Commercial wood staves
510 commonly used in Serbian cooperage of several botanical species were considered, including
511 mulberry (*Morus alba* L.), myrobalan plum (*Prunus cerasifera Ehrh.*), black locust (*Robinia*
512 *pseudoacacia* L.), wild cherry (*Prunus avium* (L.) L.), and oak *(Q. petraea* (Matt.) Liebl., *Q.*
513 *robur* L., and *Q. cerris* L.). The results of the study unequivocally demonstrated the uniqueness
514 in phenolic profiles of the investigated wood samples and some of the identified compounds
515 were proposed as useful for identification of the specific wood. Alongside, wood extracts could

be considered unique in terms of the established colorimetric parameters and fluorescence properties, mainly based upon the content of specific flavonoids extracted from the wood material. Especially helpful were fluorescence emission spectra of bare wood samples as it was obvious that differences in spectral shape and maxima positions are lesser among the wood extracts in comparison with the corresponding wood samples. Altogether, these features could be useful for differentiation and fast screening of samples according to their botanical origin. Finally, the presented research study could be of broader relevance, since the cooperage industry has long tradition in Balkan countries, and it is important to avoid deception in this kind of production, especially when products are eligible for protected origin indication. Also, the possibility of utilization of wood as a source of compounds valued for potential nutraceutical properties is still unexplored field, and therefore the results presented herein could be considered as an added value.

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Ethical Approval This article does not contain any research involving human participants or animals.

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635 **Figure captions**

636

637 **Figure 1**.Overlay of the normalized emission spectra for different wood samples (A) and wood
638 extract (B). The spectrum of each sample is an average of the 10 spectra recorded for various
639 excitation wavelengths. Numbers correspond to samples in Table 1.

640 **Figure 2**.Principal component analysis of the fluorescence emission spectra: (A) wood and (B)
641 wood extract.

642 **Figure S1**.Fluorescence excitation-emission matrix for spectra of the Myrobalan plum wood
643 sample (A) and corresponding wood extract (B) with pronounced fluorophore maxima, as an
644 example.

Table 1

The botanical species, geographical origin, age of wood samples, and soil type.

No	Common names	Botanic species	Geographical origin	Wood age	Type of soil
1	Pedunculate oak	*Quercus robur* L. *(Q. pedunculata)*	Slavonija (Croatia)	> 60	Gajnjače
2			Gornji Radan (Serbia)	> 60	Rankers
3			Olovo (Bosnia and Herzegovina)	> 60	Rankers
4	Sessile oak	*Quercus petrea* (Matt.) Liebl. *(Q. sessiliflora)*	Kučaj (Serbia)	> 60	Red soil
5			Kuršumlija (Serbia)	> 60	Rankers
6			Ravna Gora (Serbia)	> 60	Rankers
7	Turkey oak	*Quercus cerris* L.	Kuršumlija (Serbia)	> 60	Rankers
8	Black locust	*Robinia pseudoacacia* L.	Kraljevo (Serbia)	> 40	Fluviosol
9	Myrobalan plum	*Prunus cerasifera* Ehrh.	Vrnjačka Banja (Serbia)	> 40	Vertisol
10	Cherry	*Prunus avium* (L.) L.	Ravna Gora (Serbia)	> 40	Rankers
11	Mulberry	*Morus alba* L.	Vrnjačka Banja (Serbia)	> 40	Vertisol

Table 2

The total phenolic content and antioxidant capacity of investigated wood extracts.

Sample No	TPC (g GAE kg^{-1})	DPPH (mmol TE kg^{-1})
1	55.51 ± 3.15^{d}	473.92 ± 13.99^{c}
2	54.21 ± 2.47^{d}	405.24 ± 10.87^{e}
3	37.91 ± 0.86^{e}	283.15 ± 12.01^{g}
4	39.46 ± 1.14^{e}	437.95 ± 13.73^{de}
5	30.30 ± 0.95^{g}	220.79 ± 6.18^{h}
6	37.10 ± 1.17^{eg}	333.73 ± 13.88^{f}
7	5.31 ± 0.15^{h}	28.14 ± 0.95^{i}
8	74.28 ± 1.73^{c}	451.47 ± 11.13^{cd}
9	81.71 ± 0.32^{b}	612.95 ± 13.43^{b}
10	49.69 ± 1.88^{d}	299.93 ± 8.41^{fg}
11	107.69 ± 6.05^{a}	844.93 ± 20.31^{a}

Different letters in the same column denote a significant difference according to Tukey's test, $p < 0.05$

Table 3

Quantitative data on phenolic acids and flavonoids found in wood extracts.

	1	2	3	4	5	6	7	8	9	10	11
Phenolic acids (mg kg^{-1})											
Gallic acid	117.70 ± 6.17^{a}	52.25 ± 1.24^{c}	17.38 ± 0.99^{f}	27.72 ± 1.78^{d}	22.99 ±1.83^{e}	26.4 ± 0.53^{d}	-	58.74 ± 3.15^{b}	-	-	-
Protocatechuic acid	34.76 ± 1.17^{d}	35.86 ± 0.98^{d}	20.13 ± 0.66^{g}	30.69 ± 2.03^{e}	9.79 ± 0.79^{i}	-	22.33 ± 1.32^{f}	15.62 ±0.21^{h}	533.39 ± 14.51^{a}	83.16 ± 9.36^{c}	201.85 ± 6.98^{b}
5-O-Caffeoylquinic acid	-	-	-	-	-	-	0.88 ± 0.09^{b}	-	15.18 ± 0.84^{a}	-	0.66 ± 0.02^{c}
p-Hydroxybenzoic acid	-	-	-	-	-	-	19.58 ± 1.12^{d}	164.78 ± 12.36^{b}	53.46 ± 3.48^{c}	51.70 ± 6.66^{c}	260.04 ± 13.03^{a}
p-Coumaric acid	-	-	-	-	-	-	-	-	-	22.44 ± 1.29^{a}	5.50 ± 0.75^{b}
Ferulic acid	-	-	-	-	-	-	-	-	-	8.03 ± 0.57^{a}	5.39 ± 0.11^{b}
Ellagic acid	15958.80 ± 459.63^{a}	9363.86 ± 236.14^{c}	3039.41 ± 94.58^{e}	10099.32 ± 335.23^{b}	8892.95 ± 215.46^{d}	8872.05 ± 198.55^{d}	205.15 ± 14.11^{j}	1131.46 ± 58.63^{f}	672.54 ± 22.94^{g}	267.74 ± 9.59^{i}	375.76 ± 12.22^{h}
Caffeic acid	1.32 ± 0.05^{d}	1.21 ± 0.07^{d}	1.10 ± 0.03^{e}	1.10 ± 0.03^{e}	0.88 ± 0.00^{g}	1.10 ± 0.04^{e}	-	1.43 ± 0.03^{c}	2.09 ± 0.23^{b}	2.64 ± 0.12^{a}	1.43 ± 0.05^{c}
Flavonols (mg kg^{-1})											
Rutin	-	-	-	-	-	-	0.44 ± 0.01^{a}	-	-	0.33 ± 0.00^{b}	-
Hyperoside	-	-	-	-	-	-	0.33 ± 0.01^{c}	-	-	0.55 ± 0.05^{b}	3.63 ± 0.13^{a}

Isorhamnetin 3-O-glucoside	-	-	-	-	-	-	-	-	-	-	0.22 ± 0.00
Kaempferol-7-O-glucoside	-	-	-	-	-	-	-	-	0.44 ± 0.00^{b}	-	3.08 ± 0.09^{a}
Quercetin	9.46 ± 0.00^{d}	9.35 ± 0.05^{e}	-	9.46 ± 0.05^{d}	9.90 ± 0.08^{c}	9.46 ± 0.03^{d}	-	10.12 ± 0.06^{b}	10.23 ± 0.26^{b}	187.11 ± 7.36^{a}	-
Kaempferol	0.66 ± 0.06^{c}	-	-	-	0.77 ± 0.06^{c}	-	-	-	-	140.14 ± 6.25^{a}	57.31 ± 3.14^{b}
Isorhamnetin	-	-	-	-	-	-	5.94 ± 0.13^{b}	-	-	-	6.16 ± 0.17^{a}
Galangin	-	-	-	-	0.44 ± 0.01^{b}	-	-	-	-	54.23 ± 1.28^{a}	-
Kaempferide	-	-	-	-	0.11 ± 0.00^{b}	-	-	-	-	8.58 ± 0.59^{e}	-
Flavones (mg kg^{-1})											
Vitexin	-	-	-	-	0.22 ± 0.00^{b}	-	-	-	-	66.88 ± 3.20^{a}	-
Luteolin	-	-	-	0.66 ± 0.01^{e}	1.98 ± 0.29^{c}	-	-	-	0.77 ± 0.03^{d}	55.99 ± 2.17^{a}	3.96 ± 0.34^{b}
Chrysin	0.66 ± 0.02^{g}	0.22 ± 0.01^{i}	-	2.75 ± 0.61^{d}	13.64 ± 0.97^{b}	1.10 ± 0.06^{f}	0.55 ± 0.01^{h}	1.32 ± 0.15^{e}	1.87 ± 0.42^{e}	716.10 ± 14.31^{a}	4.18 ± 0.23^{c}
Apigenin	-	-	-	-	1.21 ± 0.06^{d}	-	-	1.98 ± 0.21^{c}	0.44 ± 0.01^{e}	233.97 ± 8.99^{a}	2.97 ± 0.14^{b}
Acacetin	-	-	-	0.22 ± 0.00^{d}	1.21 ± 0.10^{b}	-	-	-	-	61.49 ± 1.52^{a}	0.22 ± 0.02^{c}
Genkwanin	-	-	-	0.22 ± 0.01^{c}	1.21 ± 0.07^{b}	-	-	-	-	60.06 ±	0.22 ± 0.01^{c}

										0.99[a]	
Flavanones (mg kg^{-1})											
Naringenin	-	-	-	0.33 ± 0.01[e]	2.64 ± 0.21[c]	0.11 ± 0.00[f]	0.33 ± 0.02[e]	-	1.21 ± 0.06[d]	409.20 ± 4.62[a]	5.39 ± 0.39[b]
Naringin	0.11 ± 0.00[d]	0.11 ± 0.01[d]	-	0.33 ± 0.04[b]	-	0.22 ± 0.00[c]	-	0.22 ± 0.02[c]	-	-	1.10 ± 0.11[a]
Eriodictyol	-	-	0.66 ± 0.05[c]	-	-	-	0.77 ± 0.04[c]	-	0.99 ± 0.09[b]	89.54 ± 2.96[a]	1.10 ± 0.07[b]
Pinocembrin	1.1 ± 0.09[h]	0.44 ± 0.01[j]	0.33 ± 0.01[k]	4.18 ± 0.47[d]	26.73 ± 0.89[b]	1.98 ± 0.11[g]	0.88 ± 0.08[i]	3.52 ± 0.12[e]	2.86 ± 0.26[f]	1851.19 ± 26.34[a]	6.71 ± 0.56[c]
Flavanonols (mg kg^{-1})											
Taxifolin	5.72 ± 0.19[g]	8.14 ± 0.30[f]	11.44 ± 0.98[d]	2.20 ± 0.15[i]	4.07 ±0.21[h]	0.99 ± 0.07[j]	9.90 ± 0.46[e]	-	136.18 ± 5.68[c]	8455.70 ± 32.35[a]	4034.69 ± 17.32[b]
Isoflavones (mg kg^{-1})											
Daidzein	-	-	-	-	-	-	-	-	-	0.77 ± 0.03	-
Genistein	-	-	-	-	1.65 ± 0.11[b]	-	-	-	-	137.17 ± 4.16[a]	-
Stilbenoids (mg kg^{-1})											
Resveratrol	-	-	-	-	-	-	-	-	-	-	121.55 ± 4.96
Oxyresveratrol	-	-	-	3.30 ± 0.10[e]	3.74 ± 0.31[d]	-	15.07 ± 0.58[c]	44.55 ± 1.56[b]	3.85 ± 0.23[d]	-	1731.73 ± 62.31[a]
Pterostilbene	-	-	-	-	-	-	-	-	-	-	12.21 ± 0.56
Coumarin (mg kg^{-1})											
Aesculin	0.44 ± 0.01[d]	0.22 ± 0.01[e]	0.11 ± 0.00[f]	-	-	0.44 ± 0.00[c]	-	-	1.87 ± 0.09[b]	-	2.31 ± 0.11[a]

Aesculetin	-	-	-	-	-	-	12.87 ± 0.56^{c}	-	-	102.30 ± 3.47^{a}	29.15 ± 1.34^{b}
Other (mg kg^{-1})											
Coniferyl aldehyde	13.86 ± 1.52^{b}	7.26 ± 0.35^{e}	20.13 ± 1.15^{a}	8.91 ± 0.20^{d}	9.90 ± 0.78^{c}	-	-	6.05 ± 0.41^{f}	2.64 ± 0.11^{h}	3.85 ± 0.09^{g}	0.99 ± 0.07^{i}
Phloretin	-	-	-	-	0.44 ± 0.07^{c}	-	0.33 ± 0.05^{c}	-	1.43 ± 0.13^{b}	17.16 ± 1.31^{a}	0.44 ± 0.08^{c}

Different letters in the same row denote a significant difference among wood extracts according to Tukey's test, $p < 0.05$.

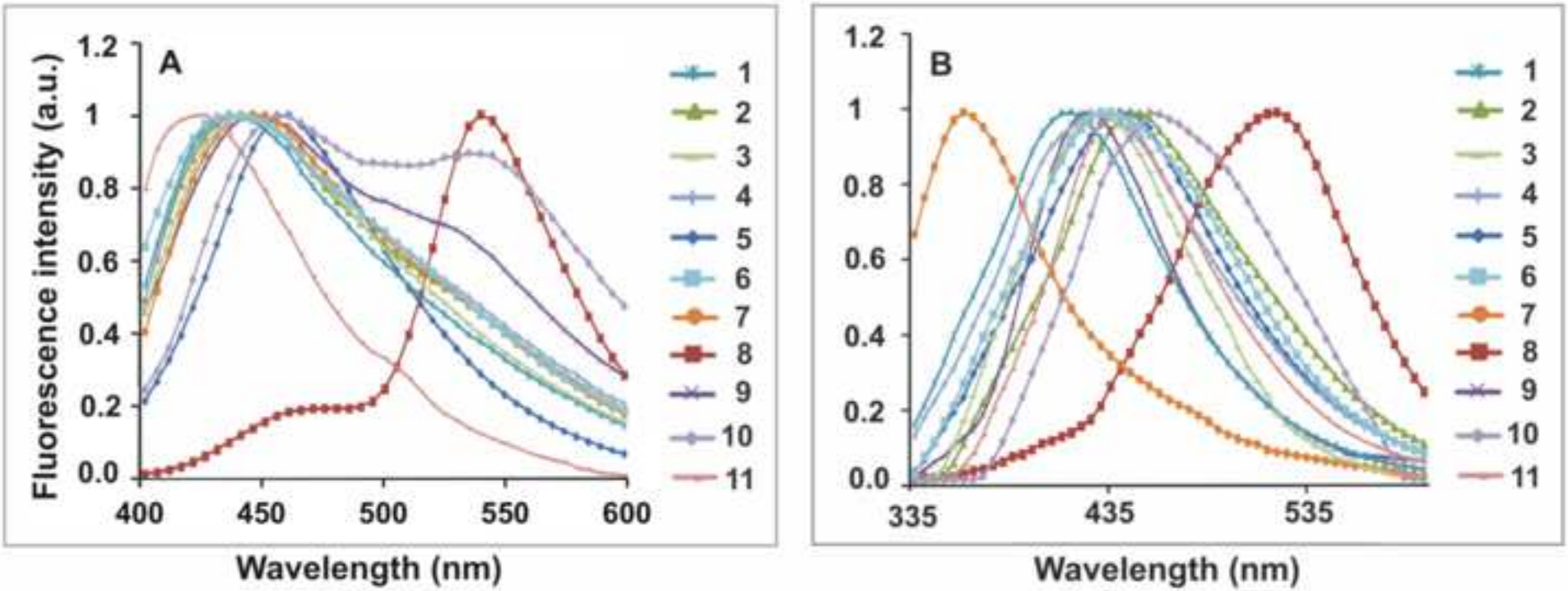
Table 4

CIELab chromatic parameters of the wood extracts.

No	L*	a*	b*	C*	h
1	38.20 ± 0.01^{f}	18.01 ± 0.01^{e}	33.14 ± 0.03^{e}	37.72 ± 0.02^{e}	61.48 ± 0.02^{f}
2	41.94 ± 0.01^{c}	14.55 ± 0.04^{h}	36.95 ± 0.03^{b}	39.71 ± 0.01^{b}	68.51 ± 0.06^{c}
3	40.87 ± 0.03^{e}	16.15 ± 0.06^{f}	35.88 ± 0.03^{d}	39.35 ± 0.01^{c}	65.76 ± 0.11^{e}
4	36.47 ± 0.01^{g}	19.97 ± 0.01^{d}	30.88 ± 0.02^{f}	36.78 ± 0.02^{g}	57.11 ± 0.01^{g}
5	41.56 ± 0.01^{d}	14.99 ± 0.05^{g}	35.89 ± 0.03^{d}	38.89 ± 0.01^{d}	67.33 ± 0.08^{d}
6	31.83 ± 0.02^{i}	21.43 ± 0.06^{c}	24.10 ± 0.04^{h}	32.25 ± 0.01^{i}	48.36 ± 0.12^{h}
7	51.52 ± 0.01^{a}	5.73 ± 0.02^{k}	36.81 ± 0.01^{c}	37.26 ± 0.01^{f}	81.16 ± 0.04^{a}
8	30.77 ± 0.01^{j}	24.63 ± 0.02^{b}	22.50 ± 0.01^{i}	33.36 ± 0.01^{h}	42.41 ± 0.02^{i}
9	32.33 ± 0.01^{h}	27.43 ± 0.02^{a}	25.19 ± 0.03^{g}	37.24 ± 0.02^{f}	42.56 ± 0.05^{i}
10	46.17 ± 0.02^{b}	14.12 ± 0.03^{i}	45.70 ± 0.02^{a}	47.84 ± 0.02^{a}	72.83 ± 0.04^{b}
11	19.98 ± 0.01^{k}	11.66 ± 0.04^{j}	4.03 ± 0.03^{j}	12.34 ± 0.03^{j}	19.06 ± 0.17^{j}

Different letters in the same column denote a significant difference according to Tukey's test, $p < 0.05$

Figure 1


A
B
Fluorescence intensity (a.u.)
1.2
1
0.8
0.6
0.4
0.2
0.0
400
450
500
550
600
335
435
535
Wavelength (nm)
Wavelength (nm)
1
2
3
4
5
6
7
8
9
10
11

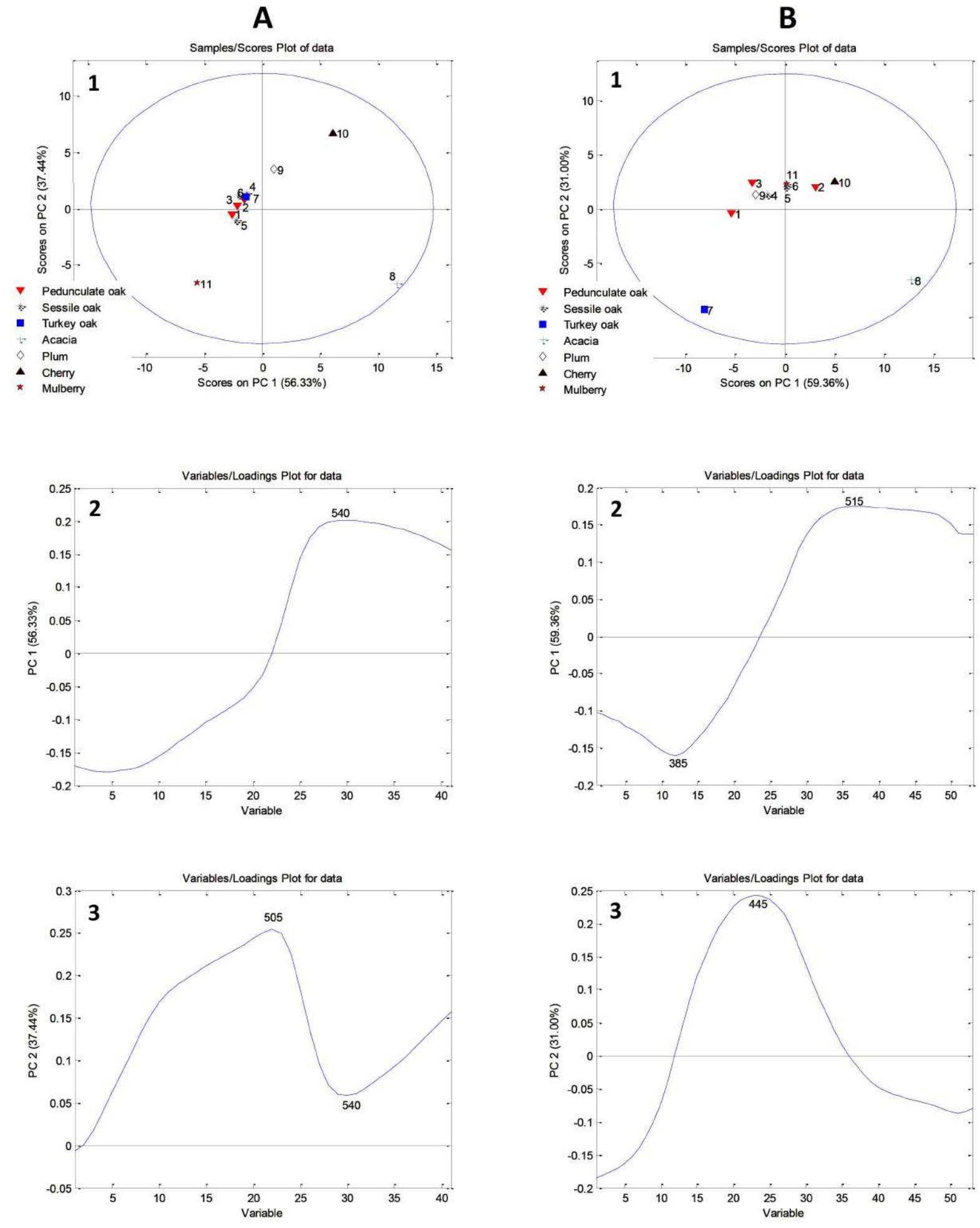

A
B
Samples/Scores Plot of data
1
Scores on PC 2 (37.44%)
Scores on PC 1 (56.33%)
Scores on PC 2 (31.00%)
Scores on PC 1 (59.36%)
Pedunculate oak
Sessile oak
Turkey oak
Acacia
Plum
Cherry
Mulberry
Variables/Loadings Plot for data
2
PC 1 (56.33%)
PC 1 (59.36%)
Variable
540
515
385
3
PC 2 (37.44%)
PC 2 (31.00%)
505
540
445

Figure S1

Click here to download Supplementary Interactive Plot Data (CSV): Figure S 1.tif