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The impact of *Quercus pubescens* wood chips on chemical and sensory characteristics of a Serbian 'Kadarka' red wine during aging: A comparison with other oak species (*Q. petraea*, *Q. alba*, and *Q. pyrenaica*)

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Summary

'Kadarka' (*Vitis vinifera* L.) is a red grape variety considered native for the countries on the lower reaches of the Danube River (east of Europe). However, there is very limited knowledge about the evolution of the wines produced from this variety during aging in contact with oak wood. Thus, the aim of this work was to investigate under laboratory conditions the changes in phenolic, volatile, and sensory profile of a 'Kadarka' wine during 180 days in contact with 4 different oak chip species: *Q. petraea* (French and Hungarian origin), *Q. alba*, *Q. pyrenaica* and *Q. pubescens*. In addition, there is scarce knowledge about the use of *Q. pubescens* species in enology. So, another objective was to assess its impact on wine composition and sensory properties. Independently of the oak chip species used, the results obtained demonstrated a decrease of anthocyanin content and an increase of gallic, caffeic and *p*-coumaric acids during 180 aging days for all wines with oak chips contact. Significantly higher amounts of vanillin in wines aged in contact with *Q. petraea* from France and *Q. alba* chips was detected, while wine aged in contact with *Q. pubescens* chips showed significantly higher amounts of furan derivatives, *trans*-β-methyl-γ-octalactone and eugenol. From a sensorial point of view, a tendency for higher scores for overall appreciation was obtained for wines aged in contact with *Q. petraea* chips. The outcomes of this work improved the knowledge of the Kardaka wine characteristics and their evolution in contact with different oak chips and also expanded the knowledge about the use of *Q. pubescens* in enology.

Keywords

Kadarka wine, oak chips, phenolic composition, *Quercus pubescens*, sensory profile, volatile compounds

Introduction

In the last twenty years, the possibility of oak wood fragments use in wine production, including during the aging process, has emerged. In Europe, only after the publication of EEC regulation in 2006 and later modified by the EEC Regulation Nº 2019/934 of 12 March 2019 (Appendix 7), the use of pieces of oak in enology, was possible. According to this regulation, only wood from the *Quercus* genus could be used at different toasting levels or without toasting. Thus, today a great variety of oak wood pieces can be found on the market, with different particle sizes, shapes (chips, cubes or beans, powder, shavings or granulates, dominoes, and blocks or segments), and toasting levels. Those oak fragments are particularly made from three main oak wood species, *Quercus robur* and *Quercus petraea* from French and Eastern Europe forests, and *Quercus alba* from the USA (Fernández de Simón *et al.*, 2010, Jordão *et al.*, 2007, 2012, 2006). Nevertheless, limited availability of these three main oak wood species as raw materials makes potential use of other less commercially known oak species an interesting option for the aging of red wines. Thus, in last years other oak wood species have been used in oenology, namely *Quercus faginea* (Fernández de Simón *et al.*, 2003), *Quercus frainetto* (Vivas, 2005), *Quercus oocarpa* (Vivas and Glories, 1996), *Quercus pyrenaica* (de Coninck *et al.*, 2006, Fernández de Simón *et al.*, 2008, Gonçalves and Jordão, 2009, Tavares *et al.*, 2017), *Quercus humboldtii* (Martínez-Gil *et al.*, 2018), *Quercus pubescens* (Costa *et al.*, 2020) and *Quercus ilex* (Valdés *et al.*, 2021).

Several works describe the impact of the use of different oak wood chip species on red wine composition and sensory properties. Thus, according to the literature, the main factors affecting the chemical and sensorial characteristics of wine aged in contact with oak wood imply: the species and origin of oak wood, morphological characteristics of the wood, wood toasting level, wood surface to wine volume ratio, and the contact time (de Coninck *et al.*, 2006, Gonçalves and Jordão,

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2009, Nunes *et al.*, 2017, Tavares *et al.*, 2017). For Gambuti *et al.* (2010) wood type has a significant influence on chromatic characteristics, on low-molecular weight phenolics and on astringency of red wines. However, according to several authors (Pérez-Magariño *et al.*, 2009, Laqui-Estaña *et al.*, 2019, Nikolantonaki *et al.*, 2019) the effect of wood on the wine composition and on the extraction of oak wood components does not entirely depend on the initial wood composition and aging time. In fact, it is also associated with the original and intrinsic characteristics of the wine itself. Thus, this effect also depends on the type of wine, *i.e.*, mainly the grape variety used. Most previously published studies have been conducted on monovarietal red wines from different widely-grown international red grape varieties, such as 'Cabernet franc' (Izquierdo-Cañas *et al.*, 2016), 'Cabernet Sauvignon' (Gambuti *et al.*, 2010, Laqui-Estaña *et al.*, 2019), 'Merlot' (Gambuti *et al.*, 2010, Schumacher *et al.*, 2013) and 'Syrah' (Gonçalves and Jordão, 2009). Although significantly less represented, studies on red wines made from several native red grape varieties such as, 'Monastrell' (Pérez-Prieto *et al.*, 2002), 'Tempranillo' (Valdés *et al.*, 2021), 'Touriga Nacional' (Tavares *et al.*, 2017, Costa *et al.*, 2021) and 'Agiorgitiko' (Kyraleou *et al.*, 2016) also gave contribution to the knowledge of this subject. Thus, it is also important to expand the research about the potential impact of different oak wood chip species on other red wines made from less known native grape varieties. This can also contribute to the quality and diversity of wines in less known wine-producing countries, such as Republic of Serbia. This country has a great diversity of native and regional vine varieties. One of these native grape varieties is 'Kadarka' (*Vitis vinifera* L). According to Csóka *et al.* (2013), this red grape variety is also considered indigenous in Hungary. After the phylloxera vine-pest in 1875, 'Kadarka' variety was planted only in sandy soil. Thus by 2002 its ratio decreased to 1.1% compared to the former 67% at the beginning of the 19th century. In 2007, Hungary, Romania and Serbia agreed with the details involved in the production, cultivations mode, registration of the producers of this grape variety and also the applicable trade legislation (Janyik, 2010). In general, red wines produced from this grape variety show lower phenolic content (500-1100 mg·L^{-1} gallic acid equiv.) compared to the international red varieties, such as, 'Cabernet Sauvignon', 'Cabernet Franc' or 'Merlot' (Pour Nikfardjam and Pickering, 2008, Balga, 2014). In addition, wines produced from this grape variety are characterized by red fruit flavours, freshness and delicate taste and also mild tannin structure (Miljić and Puškaš, 2020). On the other hand, no studies exist about the use of different oak wood species during the aging process of Kadarka wines, and consequently on their impact on chemical and sensory characteristics of these wines. In fact, the scientific knowledge regarding the application of different wood species in Serbian alcoholic drinks (including in wines) is in general very limited. Only a few studies were published about the use of different wood species in apple and plum brandies aging (Pecić *et al.*, 2012, Smailagić *et al.*, 2021).

In this context, the research presented herein was undertaken to investigate the changes in phenolic, aromatic, and sensory profile of Kadarka wine as a result of the contact with different oak wood chip species during 6 months under laboratory conditions. For this purpose, oak wood chips from 4 different species were used: *Quercus petraea*, *Quercus alba*, *Quercus pyrenaica* and *Quercus pubescens*. Regarding Pubescent oak (*Q. pubescens*), it should be also noted that there is a very limited knowledge of its use in enology. According to Bordács *et al.* (2019), *Q. pubescens* is one of the most abundant tree species in central and south eastern European forests, as well as in Anatolia. This oak species is traditionally used for production of wine and fruit spirit barrels in Serbia. However, it was only very recently that a first study about the use of this oak species from Serbia during the aging of a Portuguese red wine was published (Costa *et al.*, 2020).

Thus, the aim of this study is to contribute to the better understanding of the impact of different oak species use on the composition of Kadarka red wines, and at the same time to deepen the knowledge about the use of *Q. pubescens* oak species in enology.

Material and Methods

Red wine and oak wood chip species

The red wine used in this experiment was a varietal wine made from 'Kadarka' *Vitis vinifera* red grape variety cultivated in Serbia (synonyms Skadarka, Gamza, Cherna and Ceterska). The grapes (around 10 tons) were harvested manually (hand-picked) in 2018 at the technological stage of ripeness (24 °Brix; pH = 3.50 and total acidity of 5.7 g·L^{-1} tartaric acid) from a vineyard located in the Subotica wine region (northern of Serbia). The winemaking process at Tonković winery followed the standard red wine technology production with a maceration time of 7 days at 25 ± 2°C. After destemming and crushing, the sulfitation of the grape must by the use of potassium metabisulfite (0.07 g·L^{-1}) was followed by alcoholic fermentation, which was carried out in stainless steel tank (8,200 L) using a commercial *Saccharomyces cerevisiae* yeast strain (Zymaflore FX10 Laffort, France), previously rehydrated and inoculated at 25 g·hL^{-1}. During alcoholic fermentation, an organic nutrient based on yeast autolysates (Nutristart Org, Laffort, France) was added in the amount of 25 g·hL^{-1} after the one-third of sugar has been fermented. After the end of alcoholic fermentation, the pomace was pressed. The wine underwent malolactic fermentation using a commercial *Oenococcus oeni* strain Uvaferm Alpha (Lallemand, France) at 18°C during 7 days. Wine was racked from lees 15 days after the end of malolactic fermentation, and then sulfited (10 g·hL^{-1} potassium metabisulfite). The red wine produced was kept in the stainless-steel tank under controlled conditions (12 ± 0.5°C) for 4 months and analyzed for the free SO_2 level regularly until used in this experiment. Table 1, shows the main physicochemical and phenolic characteristics of the Kadarka red wine used in the experimental work before the contact with the different oak wood chip species studied.

The wood chip species used in this research were: Pubescent oak (*Quercus pubescens*) from Djordjevic Cooperage (Vranje, Serbia), Iberian oak (*Quercus pyrenaica*) from J.M. Gonçalves Cooperage (Palaçoulo, Portugal) and French, Hungarian (both from *Quercus petraea* species) and American (*Quercus alba*) oaks obtained from Trust Cooperage (Szigetvár, Hungary).

Table 1: General physicochemical and phenolic characteristics of the Kadarka red wine used in this experimental work

Parameters	Values*
Alcohol strength (% v/v)	14.28 ± 0.06
Reducing sugars ($g \cdot L^{-1}$)	2.4 ± 0.1
Total extract ($g \cdot L^{-1}$)	31.5 ± 0.1
pH	3.57 ± 0.05
Total acidity ($g \cdot L^{-1}$ tartaric acid eq.)	5.6 ± 0.0
Volatile acidity ($meq \cdot L^{-1}$ acetic acid eq.)	5.1 ± 0.1
Free SO_2 ($mg \cdot L^{-1}$)	21 ± 2
Total SO_2 ($mg \cdot L^{-1}$)	80 ± 2
Ash ($g \cdot L^{-1}$)	2.24 ± 0.10
Total phenols ($mg \cdot L^{-1}$ gallic acid eq.)	2600 ± 19
Total flavan-3-ols ($mg \cdot L^{-1}$ (+)-catechin eq.)	1489 ± 15
Total anthocyanins ($mg \cdot L^{-1}$ malvidin-3-monoglucoside eq.)	308 ± 11
Monomeric anthocyanins ($mg \cdot L^{-1}$ malvidin-3-monoglucoside eq.)	145 ± 5

*Average values obtained from triplicate analysis

According to information provided by the cooperages, wood surface of medium toasted oak chips underwent 170-180°C for 20 min. All oak chips used had a medium particle size of 7-8 mm.

Experimental conditions

For each oak wood chip species studied at laboratory scale, three 0.7 L glass bottles were filled with the wine and closed with natural cork stoppers after a measured amount of chips was added. The red wine samples were stored in contact with the wood chip species (1.5 $g \cdot L^{-1}$) during 1, 3 and 6 months at cellar temperature (16 ± 2°C) in the absence of light and stirred manually once a week for 1 min. The experimental work was performed in duplicate which means that the first two wine samples in contact with certain chips were opened after 1 month, the next two after 3 months and the last two after 6 months of aging. For each essay, after the bottles were opened, the oak wood chips were removed and then the wines were analyzed. A control red wine (without wood chip contact) was also considered for each sampling date and stored in the same way as other experimental wine samples. Before laboratory analysis, the wine samples were filtered with a Whatman-Cytiva Europe (Marlborough, MA, USA) cellulose filter with a pore diameter of 0.45 µm. The concentration of wood chips used in this experimental work (1.5 $g \cdot L^{-1}$) took into account works carried out on red wines previously published by other authors (de Coninck *et al.*, 2006, Tavares *et al.*, 2017, Costa *et al.*, 2020)

General wine physicochemical characterization

The general Kadarka wine physicochemical characterization (reducing sugars, total extract, alcohol strength, pH, total and volatile acidity, total and free sulfur dioxide) was performed using a FTIR WineScan® (Foss Analytics, Hillerød, Denmark) previously calibrated. Ash content was performed according to the official OIV method (OIV, 2021). The analyses of both bottles of wines aged with the same oak chip species were done in triplicate, and the results represent the average values.

Global phenolic parameters

During the aging process of Kadarka wines in contact with the different oak wood chip species, several global phenolic parameters were analyzed. Thus, Folin-Ciocalteu's method (Singleton *et al.*, 1999) was used for determination of the total polyphenolic content with gallic acid used as a standard. The quantification of total flavan-3-ols was performed using the vanillic method described previously by Revilla *et al.* (1991) with (+)-catechin used as a standard. For total anthocyanins, the method based on their ability to discolor after addition of SO_2 (in the $K_2S_2O_5$ form) at pH 1 was used (Ribéreau-Gayon and Stonestreet, 1965). Monomeric anthocyanins' content was determined by the pH differential method (Fuleki and Francis, 1968). For both anthocyanin determinations malvidin-3-monoglucoside was used as a standard. All analyses were done in triplicate.

Individual phenolic compounds analysis by HPLC

For the individual phenolic acids and (+)-catechin analysis, a HPLC-DAD Dionex Ultimate 3000 Chromatographic System (Sunnyvale, California, USA) equipped with a quaternary pump Model LPG-3400 A, an auto sampler Model ACC-3000, a thermostatted column compartment (adjust to 35°C) and a multiple Wavelength Detector MWD-300 were used. The column (250 × 4.6 mm, particle size 5 µm) was a C18 Acclaim® 120 (Dionex, Sunnyvale, California, USA) protected by a guard column of the same material. The elution conditions used were implemented based on the methodology described by Guise *et al.* (2014). Thus, solvent (A) was 5% aqueous formic acid and solvent (B) was pure methanol. The elution program was the following: 5% (B) from zero to 5 min followed by a linear gradient up to 65% (B) until 65 min and from 65 to 67 min

down to 5% (B). The flow was 1 mL·min^{-1} and detection was performed from 200 to 650 nm with a sample injection volume of 25 µL.

The quantification of (+)-catechin and each individual phenolic acid was performed by external calibration curves obtained using standards of (+)-catechin, caffeic acid, coumaric acid, ferulic acid and gallic acid. All pure compounds were purchased from Extra-Synthese (Genay, France). *Trans*-caftaric acid and caffeic acid ethyl ester were expressed as caffeic acid equivalents. Coutaric acid was expressed as coumaric acid equivalents. All analysis were done in triplicate.

Volatile composition analysis by SPME-GC-MS

The determination of volatile components extracted from oak wood chips to the Kadarka wines was carried out using a Shimadzu GC-MS QP2010 Ultra instrument (Kyoto, Japan) accoupled to an AOC-5000 Plus autosampler with SPME head and fiber cleaning unit.

The pre-treatment of the samples included SPME extraction. Thus, 2 mL of wine sample was mixed with 1.5 g NaCl, 4 mL of ultrapure water and 10 µL internal standard (3,4-dimethyl-phenol) stock solution. For vanillin determination, an 85 µm polyacrilate SPME fiber was used, while for the remaining volatile compounds extracted, a 65 µm PDMS/DVB SPME fiber was used. The extraction process was performed according to the modified procedure described previously by Cincotta *et al.* (2015): pre-incubation time 600 s, incubation temperature 70°C, extraction time 2400 s and desorption time 300 s for vanillin determination, while pre-incubation time 600 s, incubation temperature 50°C, extraction time 1200 s and desorption time 300 s was used for the remaining wood volatile compounds analyzed.

The GC-MS equipment was equipped with a Zebron ZB-WAX plus column (30 m × 0.25 mm × 0.25 µm). According to the modified method previously published by Pérez-Olivero *et al.* (2014), the column temperature was programmed from 40°C (held for 5 min) to 80°C at 10°C·min^{-1}, then at 8°C·min^{-1} to 240°C (held for 3 min). The carrier gas was helium with a constant flow of 1.2 mL·min^{-1}. Total program in spitless mode lasted 32 min. The mass spectrometer was operated in electron impact mode (EI) and the masses were scanned over an *m/z* range of 40-300 amu (2-20 min) and 40–400 amu (20-35 min). The injection temperature was 240°C and the temperatures of ion source and interface were 220°C and 240°C, respectively.

The standards used in the determination of the wood volatile components detected in red wines were as follows: furfural, 5-methyl-furfural, guaiacol, *trans*-β-methyl-γ-octalactone, *cis*-β-methyl-γ-octalactone, 4-methylguaiacol (creosol), eugenol, vanillin and 3,4 dimethyl-phenol as internal standard, all of them from Sigma Aldrich (Saint Louis, USA). All analyses were done in triplicate.

Sensory evaluation

The evaluation of sensory properties of Kadarka wines aged in contact with the different oak wood chip species was carried out using the Buxbaum model of positive ranking (Amerine and Roessler, 1983). A panel of five qualified tasters available at the moment of analysis (officially certified and authorized for wine sensory analysis by Serbian Ministry of Agriculture) performed sensory evaluation using a 20 points scale. It is important to point out that although the number of wine tasters could be at some cases considered low, the number of officially certified and authorized wine tasters in Serbia is very limited.

The wines were evaluated after 30 and 180 days in contact with the different oak wood chip species and were presented to panelists in different randomized order at 20-22°C, in ISO standard wine glasses, in isolated booths, and under daylight-type lighting. Two sessions were employed in two consecutive days, where the panelist evaluated all wines each day. Separate unopened bottles were used for the replication sets held on different days.

The aroma was rated up to 4 points, and overall flavor (both taste and retronasal aroma experience) up to 12 points. The minor unit of the scale was 0.1. The higher marks mean the evaluated parameter was better rated. Moreover, an additional table was placed at the bottom part of the evaluation sheet and it was used for the assessment of the most dominant aroma descriptors recognized in wines aged in contact with different oak wood chip species. The sensorial attributes used were grouped in the following way: color ("red" and "brown"), aroma ("fruity", "floral", "vanilla", "boisé", "coconut", "sawdust", "coffee" and "balance"), taste ("body", "bitterness", "astringency", "persistence" and "balance") and overall appreciation. The tasters awarded each sensory attribute on a scale of 1 to 5 (1 = "absence"; 2 = "little intensity"; 3 = "moderate intensity"; 4 = "intense"; 5 = "high intensity"). Overall appreciation was also scored on a scale of 1 to 5 (1 = "bad"; 2 = "pleasant"; 3 = "good"; 4 = "very good"; 5 = "excellent").

Statistical analysis

The data are presented as mean ± standard deviation. The statistical difference between mean values of parameters studied was estimated by analyses of variance (ANOVA, one-way). Duncan multiple range test (p<0.05) was applied to the data determine significant differences between Kadarka wines. In addition, a principal component analysis (PCA) was also used to analyze the data and to study the relationships between the red wines aged in contact with the different oak wood chip species, and also the chemical (phenolic and volatile composition) and sensory characteristics after 30 and 180 aging days. All analysis were performed using Statistica software version 12.0 (StatSoft Inc., Tulsa, USA).

Results and Discussion

Evolution of general phenolic parameters

Wine maturation in contact with oak wood modifies its phenolic composition due to extraction of different oak wood compounds, such as several phenolic acids and ellagitannins

(Chira and Teissedre, 2015, Nunes *et al.*, 2017, Nunes *et al.*, 2020, Costa *et al.*, 2020, Costa *et al.*, 2021). The results for general phenolic parameters (total phenols, total flavan-3-ols, total and monomeric anthocyanins) of Kadarka wine after 30, 90 and 180 aging days in contact with different oak chips are shown in Table 2. After the first 30 aging days, the content of total phenolic compounds in the different wines was in general similar compared to the control wine. The exceptions were found in wine aged in contact with French oak chips, where a significant increase of total phenols was detected (an increase of 8% which corresponded a 2700 mg·L^{-1} gallic acid equivalents), and in the wine aged in contact with *Q. pyrenaica* wood chips showing the lowest value (2270 mg·L^{-1} gallic acid equivalents). The value of this parameter in control wine constantly declined during 180 aging days, which corresponded to a total decrease of 14% since the beginning of aging. A similar trend was detected also for the wines aged in contact with *Q. petraea* (from France) and *Q. alba* chips (decrease of 15 and 11%, respectively). Therefore, although the content of total phenolic compounds has been the highest in Kadarka wine after 30 days in contact with *Q. petraea* (from France) chips (2700 mg·L^{-1} gallic acid equivalents), after 180 aging days the highest values were found in wine samples aged in contact with *Q. pubescens* chips (2390 mg·L^{-1} gallic acid equivalents, respectively). In addition, among the wine samples aged with four other oak chips there was no significant difference in the content of total phenols (values varied between 2250 and 2300 mg·L^{-1} gallic acid equivalents). These results could indicate that *Q. pubescens* wood may have higher levels of phenolic compounds compared to the other oak wood species used in this work. This is important since among oak species used in this study, the least information on its enological use is available for Pubescent oak. In addition, it is important to note that phenolic compounds extraction from wood to wines is dependent on several factors such as, the natural wood richness in phenolic compounds, wood structure (for example, the favourable porosity of each wood species could determine the easier extraction of phenolic compounds from wood to wine) and the interaction between oxygen and the wood components could also promote the release of certain wood phenolic compounds into the wine (Canas *et al.*, 2000, Jordão *et al.*, 2007, Garcia *et al.* 2012). Several authors also reported previously no differences in total phenolic content evolution in wines stored in contact with different oak wood chip species (De Coninck *et al.*, 2006, Tavares *et al.*, 2017), while other works demonstrated different wine total phenolic content during aging process according to the wood chip species used (Chinnici *et al.*, 2015, Costa *et al.*, 2021). Thus, there

Table 2: General phenolic parameters quantified in Kadarka red wines aged in contact with different oak chip species after 30, 90 and 180 days

Wines	Total phenols (mg·L^{-1} gallic acid eq.)	Total flavan-3-ols (mg·L^{-1} (+)-catechin eq.)	Total anthocyanins (mg·L^{-1} malvidin-3-monoglucoside eq.)	Monomeric anthocyanins (mg·L^{-1} malvidin-3-monoglucoside eq.)
30 aging days				
CW	2530 ± 25^{c*}	1436 ± 14^{d}	282 ± 4^{c}	131 ± 1^{b}
FR	2700 ± 14^{d}	1088 ± 20^{b}	257 ± 8^{b}	121 ± 6^{a}
AMR	2530 ± 34^{c}	1093 ± 8^{b}	254 ± 6^{b}	125 ± 3^{a}
POR	2270 ± 18^{a}	1269 ± 17^{c}	255 ± 4^{b}	122 ± 3^{a}
HU	2460 ± 12^{bc}	921± 13^{a}	277 ± 9^{c}	129 ± 5^{ab}
SRB	2420 ± 33^{b}	931 ± 10^{a}	238 ± 10^{a}	125 ± 2^{a}
90 aging days				
CW	2470 ± 15^{c*}	528 ± 8^{c}	233 ± 8^{bc}	98 ± 6^{b}
FR	2510 ± 21^{c}	576 ± 12^{d}	214 ± 5^{b}	76 ± 3^{a}
AMR	2490 ± 14^{c}	434 ± 4^{a}	242 ± 5^{c}	74 ± 5^{a}
POR	2220 ± 17^{a}	462 ± 13^{ab}	181 ± 12^{a}	80 ± 2^{ab}
HU	2340 ± 27^{ab}	479 ± 11^{b}	248 ± 8^{c}	71 ± 5^{a}
SRB	2390 ± 11^{b}	530 ± 7^{c}	233 ± 7^{bc}	75 ± 2^{a}
180 aging days				
CW	2290 ± 19^{a*}	429 ± 11^{ab}	179 ± 2^{b}	83 ± 3^{b}
FR	2300 ± 25^{a}	566 ± 5^{d}	173 ± 2^{ab}	68 ± 3^{a}
AMR	2250 ± 21^{a}	457 ± 8^{b}	167 ± 3^{a}	68 ± 5^{a}
POR	2280 ± 9^{a}	510 ± 5^{c}	161 ± 8^{a}	70 ± 2^{a}
HU	2360 ± 26^{ab}	426 ± 10^{ab}	174 ± 3^{ab}	65 ± 5^{a}
SRB	2390 ± 20^{b}	416 ± 9^{a}	170 ± 5^{ab}	64 ± 6^{a}

CW – control sample (no oak chips contact); FR – ***Q. petraea*** chips from France; AMR – ***Q. alba*** chips from USA; POR – ***Q. pyrenaica*** chips from Portugal; HU – ***Q. petraea*** chips from Hungary; SRB – ***Q. pubescens*** chips from Serbia. Two bottles of wines aged with the same oak chip species were analysed in triplicate, and the results represent the average values ± standard deviation;
*values with same letter (in column) for each phenolic parameter and aging time are not significantly different (Duncan test $p < 0.05$).

is a great diversity of results that are very dependent on the numerous factors that determine the extraction of wood phenolic components to wines during the aging process.

For total flavan-3-ols more pronounced changes were detected than regarding total phenols content during 180 aging days (Table 2). In fact, a clear decrease of total flavan-3-ols content was detected for all Kadarka red wines during the aging time. This tendency was particularly evident after 90 aging days. However, between 90 and 180 aging days all red wines showed a slight decrease of the flavan-3-ols content. Thus, compared to the value of this parameter in control wine (1463 mg·L^{-1} (+)-catechin equivalents) after 30 aging days, wines aged in contact with oak wood chips showed a decrease from 12 (wine with *Q. pyrenaica* chips contact) to 35% (wine with *Q. pubescens* and *Q. petraea* from Hungary chips contact). After 90 aging days, the content of flavan-3-ols was almost three times lower in control wine and in the wine aged in contact with *Q. pyrenaica* chips, while for the wines aged in contact with the remaining oak chip species the values were two times lower. Rubio-Bretón *et al.* (2018) also reported a decrease in the content of flavan-3-ols ((+)-catechin and (-)-epicatechin) in wines aged in contact with oak chips. The reduction of flavan-3-ols was attributed to oxidative processes, polymerization and condensation reactions with other compounds during aging. In addition, it is also possible that adsorption of flavan-3-ols to wood surface may also occur (Barrera-García *et al.*, 2007). According to Drinkine *et al.*, (2007) through bottle storage flavanols-3-ols may be subjected to hydrolysis, freeing their flavanol subunit and ethyldiene bridged flavanol-phloroglucinol, subsequently hydrolyzed to ethyldienediphloroglucinol as residue. This liberation of flavanols leads to their availability for further reaction with aldehydes and anthocyanins to form anthocyanin/pyranoanthocyanin pigments (Jourdes *et al.*, 2009). In addition, these compounds can also be repolymerized by H_2O_2 because of oxidation and, if they increase excessively in size, will sediment in the bottom of the bottle during wine aging (Echave *et al.*, 2021).

After 180 aging days, among Kadarka wine samples aged in contact with the different oak chip species, the highest concentration of flavan-3-ols was quantified in wine aged in contact with *Q. petraea* (from France) chips (566 mg·L^{-1} (+)-catechin equivalents), while the lowest values were found in wines aged in contact with *Q. pubescens* and *Q. petraea* (from Hungary) chips (416 and 426 mg·L^{-1} (+)-catechin equivalents, respectively). These wines showed similar total flavan-3-ols values to control wine. Some authors reported the individual flavan-3-ols content in several wood species, including oak. Vivas *et al.* (2006) revealed the presence of several dimeric procyanidins in *Q. petraea* and *Q. robur* heartwood, while other authors also quantified few procyanidins in *Quercus hartwissiana* heartwood (Balaban Ucar and Uçar, 2011).

In general, the content of total and monomeric anthocyanins (Table 2) decreased in all Kadarka wines during the aging period studied. The decrease in concentration of anthocyanins fractions was probably a consequence of condensation and polymerization reactions between anthocyanins and condensed tannins, involving in particular the establishment of acetaldehyde bridges (where acetaldehyde-mediated tannin-anthocyanin condensation), as well as the deposition of these compounds during wine aging (Tavares *et al.*, 2017). These reactions generate large, insoluble and precipitable polymers (Jordão *et al.*, 2019, Laqui-Estaña *et al.*, 2019).

Anthocyanins' decrease was generally more evident for the Kadarka wines aged in contact with the different oak wood chip species than in control wine. After 180 aging days, control wine showed the highest anthocyanin content among all wine samples and this was especially evident in terms of monomeric anthocyanin fraction (83 mg·L^{-1} malvidin-3-monoglucoside equivalents compared to remaining wines in which values varied between 64 and 70 mg·L^{-1} malvidin-3-monoglucoside equivalents). In general, the most pronounced decrease in the monomeric anthocyanins content was recorded in the period between 30 and 90 aging days. Previous published works also reported that wines aged in contact with wood chips showed lower values of total and individual monomeric anthocyanin content than wines without wood chips contact (Costa *et al.*, 2020, 2021, de Coninck *et al.*, 2006). Jordão *et al.* (2008) and (2019) reported in model wine solutions a more pronounced decrease of anthocyanins in the presence of ellagic acid and oak wood chip extracts. For these authors, during wine aging in contact with wood, namely oak, new pigments are formed by the polymerization and copigmentation of free monomeric anthocyanins with tannins. According to Quideau *et al.* (2005) the anthocyanin decrease may be related to other compounds present in wines, such as ellagitannins from oak wood, which may react with anthocyanins. In addition, other works reported the formation of several oligomeric and polymeric pigments resulting from reactions between malvidin-3-monoglucoside and (+)-catechin mediated by oak derived compounds, such as furfural, methyl-furfural, vannilin, and ellagic acid (De Freitas *et al.*, 2004; Pissarra *et al.*, 2005). Furthermore, some other new compounds are also formed during red wine aging in contact with oak wood, namely oaklins (Sousa *et al.*, 2005) and condensation reaction products obtained between c-glycosidic, ellagitannins and malvidin-3-monoglucoside (Lefeuvre *et al.*, 2004). Recently, oligomeric anthocyanins like dimers and the malvidin-3-O-glucoside trimer were identified by their ion masses and respective fragments in wines after 12 aging months in oak barrels (Prat-García *et al.*, 2021). All these new pigments formed will contribute to changes in the color of red wines during aging (Ribéreau-Gayon *et al.*, 2006).

Finally, the results obtained still indicate that after 180 aging days, anthocyanins content (total and monomeric forms) quantified in wines were independent of the oak wood chip species used. Thus, this result indicates that the oak wood chip species didn't influence the anthocyanin values among the wines.

Evolution of individual phenolic compounds

The content of (+)-catechin and phenolic acids determined in this study after 30 and 180 aging days is shown in Table 3. The 30 days long contact of Kadarka wine with different oak chip species did not cause differences in the content of (+)-catechin. However, after this aging time, wines aged in contact with oak chips showed significantly lower values (values var-

Table 3: Individual phenolic compounds quantified in Kadarka red wines aged in contact with different oak chip species after 30 and 180 aging days

Wines	Gallic acid (mg·L^{-1})	(+)-Catechin (mg·L^{-1})	*trans*-caftaric acid (mg·L^{-1})	Coutaric acid (mg·L^{-1}caffeic acid eq.)	Caffeic acid (mg·L^{-1})	*p*-Coumaric acid (mg·L^{-1})	Ferulic acid (mg·L^{-1})	Caffeic acid ethyl ester (mg·L^{-1} caffeic acid eq.)
	30 aging days							
CW	10.36±0.31^{a*}	37.47±3.57^{b}	63.89±2.40^{ab}	7.47±0.25^{a}	5.43±0.11^{a}	2.3±0.18^{a}	4.37±0.03^{a}	0.99±0.01^{a}
FR	12.29±0.30^{b}	30.16±0.57^{a}	62.56±1.00^{a}	7.32±0.17^{a}	5.22±0.17^{a}	2.23±0.11^{a}	4.33±0.03^{a}	0.93±0.02^{a}
AMR	12.51±0.11^{bc}	32.25±0.54^{a}	64.50±0.24^{ab}	7.55±0.03^{a}	5.38±0.03^{a}	2.28±0.03^{a}	4.35±0.01^{a}	0.97±0.01^{a}
POR	12.41±0.51^{b}	30.91±0.67^{a}	62.66±0.08^{a}	7.33±0.01^{a}	5.17±0.00^{a}	2.17±0.06^{a}	4.36±0.03^{a}	0.90±0.01^{a}
HU	12.39±0.08^{b}	28.91±1.12^{a}	61.81±1.02^{a}	7.23±0.11^{a}	5.21±0.13^{a}	2.36±0.06^{a}	4.34±0.01^{a}	0.92±0.01^{a}
SRB	12.82±0.16^{c}	29.63±0.70^{a}	64.22±1.55^{ab}	7.01±0.58^{a}	5.58±0.32^{a}	2.31±0.22^{a}	4.26±0.12^{a}	0.93±0.03^{a}
	180 aging days							
CW	7.97±0.25^{a*}	26.42±2.23^{c}	44.36±1.63^{a}	6.66±0.02^{a}	6.28±0.35^{a}	1.98±0.05^{a}	2.12±0.32^{a}	0.89±0.02^{a}
FR	19.79±0.40^{d}	19.64±1.31^{b}	52.58±1.93^{bc}	6.69±0.59^{a}	8.8±0.87^{b}	5.82±0.56^{d}	3.04±0.08^{a}	0.71±0.05^{a}
AMR	13.80±0.30^{b}	20.70±2.03^{b}	44.90±0.32^{a}	8.05±0.11^{ab}	9.25±0.16^{b}	3.04±0.08^{b}	3.05±0.10^{a}	0.96±0.09^{a}
POR	17.43±0.39^{c}	16.84±0.29^{a}	50.67±2.33^{b}	10.83±0.72^{b}	9.67±0.71^{b}	4.09±0.17^{c}	3.59±0.54^{ab}	1.76±0.05^{b}
HU	17.89±0.79^{c}	18.36±0.93^{ab}	51.81±1.02^{b}	6.65±0.48^{a}	9.88±0.64^{b}	4.43±0.41^{c}	4.10±0.15^{b}	1.13±0.12^{a}
SRB	16.66±0.47^{bc}	19.58±0.78^{b}	51.67±2.06^{b}	9.19±0.03^{b}	8.08±1.02^{ab}	4.72±0.56^{c}	4.39±0.25^{b}	0.96±0.12^{a}

CW – control sample (no oak chips contact); FR – *Q. petraea* chips from France; AMR – *Q. alba* chips from USA; POR – *Q. pyrenaica* chips from Portugal; HU – *Q. petraea* chips from Hungary; SRB – *Q. pubescens* chips from Serbia. Two bottles of wines aged with the same oak chip species were analysed in triplicate, and the results represent the average values ± standard deviation;
*values with same letter (in column) for each individual phenolic compound and aging time are not significantly different (Duncan test $p < 0.05$).

ied between 28.91 and 32.25 mg·L^{-1}) compared to the control wine (37.47 mg·L^{-1}). Similar tendency was detected also after 180 aging days, where control wine showed significantly higher values of (+)-catechin (26.42 mg·L^{-1}) compared to remaining wines aged in contact with oak wood chips (values varied between 16.84 and 20.70 mg·L^{-1}). These results could be explained by the participation of (+)-catechin in oxidative processes, polymerization, and condensation reactions with other compounds (particularly wood components). On the other hand, a partial adsorption of this flavan-3-ol monomer by the wood during the aging time could be also a reason for the reduction of their content in wines aged in contact with oak wood chips after 30 and 180 aging days. This tendency confirms previous results obtained by Rubio-Bretón *et al.*, (2018). Also, previous studies reported that monomeric phenols polymerize more rapidly in wines aged in contact with oak wood than in wines aged in tanks (Castellari *et al.*, 2001). In addition, there was no significant difference in the contents of the several phenolic acids quantified between control wine and wines aged during 30 days in contact with the different oak chip species used, except for gallic acid, where wines with oak chips contact showed the significantly higher values (ranged from 12.29 to 12.82 mg·L^{-1}). However, regardless of the oak chip species used no significant difference was found in the values of this hydroxybenzoic acid between the wines.

The analysis carried out after 180 aging days showed that gallic acid content further increased for up to 60%, with the highest values quantified in Kadarka wine aged in contact with *Q. petraea* (from France) chips (19.79 mg·L^{-1}) followed by the wine aged in contact with *Q. petraea* (from Hungary) and *Q. pyrenaica* chips (17.89 and 17.43 mg·L^{-1}, respectively). Between the wines aged in contact with oak chips the lowest values were found in wine aged in contact with *Q. alba* chips (13.80 mg·L^{-1}). Intermediate values were detected in the wine aged in contact with *Q. pubescens* chips (16.66 mg·L^{-1}). In support of these results, several authors (Jordão *et al.*, 2007, Cabrita *et al.*, 2011) reported that American oak (*Q. alba* specie) is naturally poorer in phenolics than French oak (*Q. petraea*). In addition, it is important to note that content of gallic acid in control wine was decreasing during all aging time studied.

Similar to the changes of total flavan-3-ols in Kadarka wine, the (+)-catechin quantified in all wines showed a decrease of the values during all aging times considered (Table 3). In fact, although previous results published (Jordão *et al.*, 2008) have clearly shown the contribution of certain oak wood components (particularly ellagitannins and ellagic acid) to the prevention of (+)-catechin and procyanidin B1 degradation in model wine solutions, this was not confirmed in our study by the use of a real wine. (+)-Catechin contents in wines aged in contact with different oak chips during 30 days varied from 28.91 to 32.25 mg·L^{-1}, while control wine showed the highest value (37.47 mg·L^{-1}). After 180 aging days, higher content of (+)-catechin was found in wines aged in contact with *Q. pubescens*, *Q. petraea* (from France) and *Q. alba* chips (19.58, 19.64 and 20.74 mg·L^{-1}, respectively).

Among Kadarka wines aged in contact with the different oak chip species, differentiation based on the phenolic acids content was only detected after 180 aging days. Thus, for the several hydroxycinnamic acids analyzed in this study, *trans*-caftaric acid was quantified in the highest

amount (61.81-64.22 mg·L^{-1} after 30 aging days, and 44.90-52.58 mg·L^{-1} after 180 aging days). A decrease for about 20% in *trans*-caftaric acid content was recorded from 30th till 180th day of wine aging. After 180 aging days, the content of this phenolic acid was significantly lower in control wine (44.36 mg·L^{-1}) and in wine aged in contact with *Q. alba* chips (44.90 mg·L^{-1}), compared to remaining wines. The amount of coutaric acid in Kadarka wines increased in samples aged in contact with *Q. pyrenaica* (from 7.33 to 10.83 mg·L^{-1} caffeic acid equivalents) and *Q. pubescens* (from 7.01 to 9.19 mg·L^{-1} caffeic acid equivalents) chips, while in other wines it was generally unchanged. After 180 aging days, these two wines showed the highest values of this phenolic acid.

The contents of caffeic and *p*-coumaric acids increased almost twice in all wines aged in contact with oak chips after 180 aging days. For control Kadarka wine, the content of these two phenolic acids remained practically constant with significantly lower values (8.08 mg·L^{-1}). After 180 aging days, the amount of caffeic acid was similar in all wines with oak chips contact, except for wine aged in contact with *Q. pubescens* chips, which showed the lowest values. Furthermore, wine aged in contact with *Q. petraea* (from France) chips had the highest content of *p*-coumaric acid followed by the wine aged in contact with *Q. pubescens* chips (5.82 and 4.72 mg·L^{-1}, respectively). An increase in the content of caffeic acid found in wines between 30 and 180 aging days was not only a result of this compound extraction from oak wood chips, but probably also a consequence of a hydrolysis of its ester (*trans*-caftaric acid) that takes place during wine aging. In support to this, a decrease in the amount of *trans*-caftaric acid was detected in all wines after 180 aging days. Similar changes in the content of these phenolic acids were also observed by other authors (Gómez Gallego *et al.*, 2013). Nevertheless, it is important to note that *p*-coumaric and caffeic acids are two of the most common hydroxycinnamic acids found in oak woods (Zhang *et al.*, 2015). However, other authors reported no changes in caftaric, caffeic and coutaric acids contents for red and white wines aged in oak wood barrels during several months (De Beer *et al.*, 2008, Nunes *et al.*, 2017). In addition, the values of caftaric, caffeic, *p*-coumaric, coutaric and ferulic acids quantified in our study for the Serbian Kadarka wine were similar to the values reported by other authors (Avar *et al.*, 2007) in several commercial Hungarian Kadarka wines.

For ferulic acid, in general a decrease of the values was found during the aging time for all wines. This trend could be explained by two simultaneous processes, one involving fertaric acid hydrolysis and the other the wood adsorption of fertaric and ferulic acids. However, after 180 aging days, wines aged in contact with *Q. petraea* (from Hungary) and *Q. pubescens* chips, showed a tendency for significantly higher values (4.10 and 4.39 mg·L^{-1}, respectively) compared to other wines. Thus, ferulic acid content quantified in all wines will be a balance between the hydrolysis and wood absorbed mechanisms and at the same time the ferulic acid that may have been extracted from the wood itself (in that case, it is important to note that after 180 aging days, control wine showed the lowest values for ferulic acid). According to Ibern-Gómez *et al.* (2001) ferulic acid is released from wood to wine and is formed from wood lignin degradation during toasting process. Finally, for caffeic acid ethyl ester, the values unchanged during the aging time, except for the wine aged in contact with *Q. pyrenaica* and *Q. petraea* (from Hungary) chips, where the values increased. At the end of the aging time, these two Kadarka wines showed the highest values (1.76 and 1.13 mg·L^{-1} caffeic acid equivalents, respectively).

Evolution of oak wood volatile compounds

Toasted oak contains significant amounts of several volatile compounds, such as *cis*- and *trans*- isomers of β-methyl-γ-octalactone, furfural and its derived compounds, phenolic aldehydes and volatile phenols. All these compounds have a significant impact on the wine flavor (Cabrita *et al.*, 2011, Jordão *et al.*, 2005, 2006, Ribéreau-Gayon *et al.*, 2006).

The results of wood volatile compounds in Kadarka wines aged in contact with different oak chips species after 30 and 180 aging days are shown in Table 4. It is evident that the extraction of wood volatile compounds was more intense during the first 30 days of wine wood chips contact. Almost 60-70% of the total amounts reported after the end of this experiment (180 days) had been extracted during the first 30 days of aging. The most dominant wood volatile compounds in Kadarka wines were furfural, vanillin and *cis*-β-methyl-γ-octalactone. In fact, apart from these 3 volatile compounds, the other wood volatile compounds (5-methylfurfural, guaiacol, *trans*-β-methyl-γ-octalactone, 4-methylguaiacol and eugenol) were presented in low amounts or below 1 µg·L^{-1} after 30 aging days.

The highest amount of analyzed wood volatile compounds in total, after 180 aging days was detected in wine with *Q. petraea* (from France) chips contact, while the lowest was found in wine aged in contact with *Q. pyrenaica* chips. In the case of the control wine (without oak chips contact), none of the compounds shown in Table 4 was detected, so this sample is not shown in the table. This fact would be expectable and confirms previous research works published (Herjavec *et al.*, 2007, Kyraleou *et al.*, 2016, Nunes *et al.*, 2020).

After 180 aging days, Kadarka wine aged in contact with *Q. petraea* (from France) and *Q. pubescens* chips showed the highest values of furfural (224 and 260 µg·L^{-1}, respectively), while wine aged in contact with *Q. alba* chips showed the lowest values (121 µg·L^{-1}). For 5-methylfurfural all wines showed values below the detection limit, except in wine aged in contact with *Q. pubescens* chips (values varied from 29 to 39 µg·L^{-1}, respectively after 30 and 180 aging days). Furan derivates, such as furfural and 5-methylfurfural are compounds formed during wood hemicellulose thermodegradation as a result of wood heat treatment which occurs in cooperage (Fengel and Wegener, 1989, Cadahía *et al.*, 2003, Jordão *et al.*, 2006). Although all oak chips used in this work were submitted to a similar toasting level (temperature and time), significantly higher values were found for furfural and 5-methylfurfural in Kadarka wine aged in contact with *Q. pubescens* chips. It could be assumed that this oak wood species probably shows a tendency to contain higher hemicellulose content in untoasted wood than the remaining oak wood species used. In addition, also the wood structure of this oak specie after toasting could help to facilitate the extraction of furan deriv-

Table 4: Oak wood volatile compounds quantified in Kadarka red in wines aged in contact with different oak chip species after 30 and 180 aging days (μg·L^{-1}).

Wines	Furfural	5-methylfurfural	Guaiacol	*trans*-β-methyl-γ-octalactone	*cis*-β-methyl-γ-octalactone	4-methyl-guaiacol	Eugenol	Vanillin
30 aging days								
FR	158± 9^{b*}	<1	<1	5 ± 2^{a}	41 ± 2^{c}	<1	<1	199 ± 17^{d}
AMR	96 ± 18^{a}	<1	<1	2 ± 1^{a}	48 ± 1^{d}	<1	<1	134 ± 10^{c}
POR	91 ± 21^{a}	<1	<1	<1	10 ± 1^{a}	<1	<1	77 ± 8^{b}
HU	103 ± 15^{a}	<1	<1	2 ± 0.5^{a}	39 ± 2^{c}	<1	2 ± 1^{a}	68 ± 11^{b}
SRB	195 ± 10^{c}	29 ± 6	2 ± 0.5	14 ± 2^{b}	22 ± 3^{b}	<1	5 ± 1^{b}	47 ± 7^{a}
180 aging days								
FR	224 ± 15^{c*}	<1	<1	13 ± 1^{b}	54 ± 1^{c}	<1	1 ± 1^{c}	284 ± 15^{c}
AMR	121 ± 15^{a}	<1	<1	6 ± 1^{a}	76 ± 1^{d}	<1	2 ± 1^{ac}	265 ± 15^{c}
POR	130 ± 15^{a}	<1	<1	<1	14 ± 1^{a}	<1	1 ± 1^{c}	104 ± 15^{b}
HU	160 ± 15^{b}	<1	<1	6 ± 1^{a}	60 ± 1^{c}	<1	6 ± 1^{b}	99 ± 15^{b}
SRB	260 ± 15^{d}	39 ± 5	<1	23 ± 1^{c}	38 ± 1^{b}	<1	10 ± 1a	83 ± 15^{a}

FR – *Q. petraea* chips from France; AMR – *Q. alba* chips from USA; POR – *Q. pyrenaica* chips from Portugal; HU – *Q. petraea* chips from Hungary; SRB – *Q. pubescens* chips from Serbia. Two bottles of wines aged with the same oak chip species were analysed in triplicate, and the results represent the average values ± standard deviation;

*values with same letter (in column) for each volatile oak wood compound and aging time are not significantly different (Duncan test $p < 0.05$); concentration for all oak wood volatile compounds in control wine were below the limit of detection; <1 means below the detection limit (μg·L^{-1}).

atives. However, until now, to our knowledge no studies were published about the volatile composition of this oak species for oenological propose.

For guaiacol and 4-methylguaiacol in all wines and for the two data points, the concentration of these two compounds were below of the detection limit, except for the wine aged in contact during 30 aging days with *Q. pubescens* chips, where 2 μg·L^{-1} of guaiacol was quantified. Both guaiacol and 4-methylguaiacol are formed by the pyrolysis of lignin (Sarni *et al.*, 1990) during the toasting of oak, with more guaiacol and 4-methylguaiacol produced at higher temperatures.

The *cis*- and *trans*-isomers of β-methyl-γ-octalactone are derived from oak wood, and the *cis*-isomer is an important contributor to wine flavor, responsible for oak aroma character such as "coconut", "vanilla", or "dark chocolate" in wines (Chatonnet *et al.*, 1990, Spillman *et al.*, 2004). In addition, *cis*-isomer is the most abundant form (Chatonnet *et al.*, 1990, Jordão *et al.*, 2005, 2006, Pérez-Coello *et al.*, 2000), which was confirmed by our results, where this form was the most abundant quantified in all Kadarka wines. As expected, wine aged in contact with *Q. alba* chips showed the highest values for *cis*-β-methyl-γ-octalactone (48 and 76 μg·L^{-1} after 30 and 180 aging days, respectively). According to several authors, American *Q. alba* species is characterized by high levels of lactones, especially in *cis* form (Jordão *et al.*, 2006, Prida and Puech, 2006). Wines aged in contact with *Q. pyrenaica* and *Q. pubescens* chips showed in both data point considered, the lowest values of *cis*-β-methyl-γ-octalactone (values varied from 10 to 38 μg·L^{-1}). However, it is important to note that wine aged in contact with *Q. pubescens* chips showed the highest values for *trans*-β-methyl-γ-octalactone in the two data points (14 and 23 μg·L^{-1}, respectively after 30 and 180 aging days). This result may mean that this oak wood species can be characterized by high levels of *trans*-β-methyl-γ-octalactone compared with the remaining oak wood species used. Similar trend was detected for eugenol. In fact, also Kadarka wine aged in contact with *Q. pubescens* chips showed the highest eugenol values after 30 and 180 aging days (5 and 10 μg·L^{-1}, respectively) compared with the remaining wines aged in contact with the other oak wood chip species.

Finally, for vanillin it was clear that during aging time, wines aged in contact with *Q. alba* and *Q. petraea* (from France) chips showed significantly higher values (values varied from 134 to 284 μg·L^{-1}) compared to remaining wines. The lowest values were quantified in wines aged in contact with *Q. pyrenaica*, *Q. petraea* (from Hungary) and *Q. pubescens* chips. According to Caldeira *et al.*, (2006) *Q. petraea* from France forests and especially *Q. alba* are characterized by higher vanillin content compared with Q. *pyrenaica* specie (for untoasted and toasted oak wood samples). This fact could explain the highest values of vanillin quantified in wines aged in contact with these two oak wood chip species. *Q. petraea* oak species from East Europe (which includes Hungary) is characterized by intermediate values of vanillin, usually between those determined in American and French oaks (Chira and Teissedre, 2015). However, Guchu *et al.* (2006) found in white wines aged in contact with toasted Hungary oak (*Q. petraea*) chips for 25 days more vanillin than those treated with toasted American oak chips (*Q. alba*).

Sensory evaluation

The wine sensory evaluation results for aroma, taste and overall flavor after 30 and 180 aging days are shown in Table 5. From a statistical point of view, the results indicated significant differences between the wines in the aroma, taste,

Table 5: Sensory evaluation of Kadarka red wines aged in contact with different oak chip species after 30 and 180 aging days

Wines	Aging time			
	30 days		180 days	
	Aroma (max 4 points)	Taste and overall flavor (max 12 points)	Aroma** (max 4 points)	Taste and overall flavor*** (max 12 points)
CW	2.8 ± 0.2^{a}*	10.5 ± 0.2^{a}	2.6 ± 0.2^{a}	10.6 ± 0.2^{a}
FR	3.3 ± 0.2^{b}	11.5 ± 0.2^{bc}	3.7 ± 0.2^{c}	11.0 ± 0.2^{b}
AMR	3.4 ± 0.1^{b}	11.1 ± 0.0^{b}	3.3 ± 0.1^{b}	11.4 ± 0.0^{c}
POR	3.0 ± 0.1^{a}	11.3 ± 0.1^{b}	3.5 ± 0.1^{bc}	11.0 ± 0.1^{b}
HU	3.7 ± 0.0^{c}	11.7 ± 0.1^{c}	3.8 ± 0.0^{c}	11.7 ± 0.1^{d}
SRB	3.5 ± 0.1^{b}	11.2 ± 0.0^{b}	3.1 ± 0.1^{ab}	11.2 ± 0.0^{b}

CW – control sample (no oak chips contact); FR – *Q. petraea* chips from France; AMR – *Q. alba* chips from USA; POR – *Q. pyrenaica* chips from Portugal; HU – *Q. petraea* chips from Hungary; SRB – *Q. pubescens* chips from Serbia. ± standard deviation;
*Values with same letter (in column) for each sensory parameter and aging time are not significantly different (Duncan test $p < 0.05$), the data represent the average values of the scores given by five members of the panel.
**Under term "Aroma", olfactory perception of the samples was considered.
***Under "Taste and overall flavor", taste and overall impression of flavor (combining retronasal olfactory as well as gustative elements of the flavor) was considered.

and flavor perceptions. After 30 aging days, the highest scores for aroma (3.7 points from a maximal of 4.0), taste and overall flavor (11.7 points from a maximal of 12.0) were obtained for Kadarka wine aged in contact with *Q. petraea* (from Hungary) chips. Similar result was also detected after 180 aging days. However, after this aging time, wine aged in contact with *Q. petraea* chips from France, was also awarded by the highest scores for aroma (3.7 points from maximal of 4.0). Nevertheless, the wine contact with the different oak chip species during 180 aging days induced a slight reduction of taste and overall flavor scores by the tasters (from 11.5 to 11.0 points). Probably, the increase of woody taste and overall flavor which induced a tendency for lower scores attributed by the tasters were a consequence of the oak chips concentration used (1.5 $g \cdot L^{-1}$) and longer aging times. This could imply that 180 aging days turned out to be a too long period of contact for this kind of lighter-body wine such is Kadarka wine.

Control wine aged without wood chips contact showed significantly lower scores for aroma (between 2.6 and 2.8 points) and overall flavor (between 10.5 and 10.6 points) compared to the wines aged in contact with different oak chip species, both after 30 and 180 aging days. In general, remaining wines aged in contact with different oak chips species showed similar scores.

Sensory profile of Kadarka red wines after 30 and 180 aging days in contact with different oak wood chip species is also show in the form of spider diagrams which are based on the average values of the different sensory descriptors used (Fig. 1).

In general, panelists did not differentiate wines aged in contact with different oak chips by used color descriptors ("red color" and "brown color"). However, it is important to note that control wine after 180 aging days showed the significantly higher scores for "brown color" and lower scores for "red color" descriptors. This could be addressed to more pronounced sensibility of Kadarka control wine to oxidation reactions compared to the wines aged with oak chips contact. Similar tendency was reported by Costa *et al.* (2020) between wines aged in contact with different oak wood chip species and control wine. In addition, several research works (Chinnici *et al.*, 2011, Gallego *et al.*, 2012) reported also that the use of wood promotes pigment stabilization, namely anthocyanin pigments, while maintaining the highest color intensity and the best chromatic attributes of wines.

Kadarka control wine after both 30 and 180 aging days showed also the lowest scores for the majority of aroma and taste descriptors (except for "fruity" and "floral" descriptors). In addition, this wine also shows the lowest score for "overall appreciation".

The most significant sensory differences among wines aged in contact with different oak chip species after 30 and 180 aging days were associated with certain aroma descriptors, such as "fruity", "boisé", "coffe", "vanilla", and "coconut", and also several taste descriptors, such as "astringency" and "body". The scores given by the tasters after 180 aging days for the wines aged in contact with the different oak wood chip species for "fruity" and "floral" aroma descriptors were in general lower than after 30 aging days. In addition, for aroma descriptors related with oak wood ("vanilla", "boisé", "coconut", "sawdust" and "coffee") it was clear that wines aged in contact with the different oak wood chip species showed the significantly higher scores compared with control wine. This point confirms the previous results showed in Table 4, where the volatile wood aroma compounds were only detected in wines with oak wood chips contact. For "vanilla" and "coconut" aroma descriptors the highest scores were obtained for 'Kadarka' wine aged in contact with *Q. alba* chips, which confirms also the data showed in Table 4, where this wine in general showed the highest content of *cis*-β-methyl-γ-octalactone and vanillin. Guchu *et al.* (2006) reported a positive

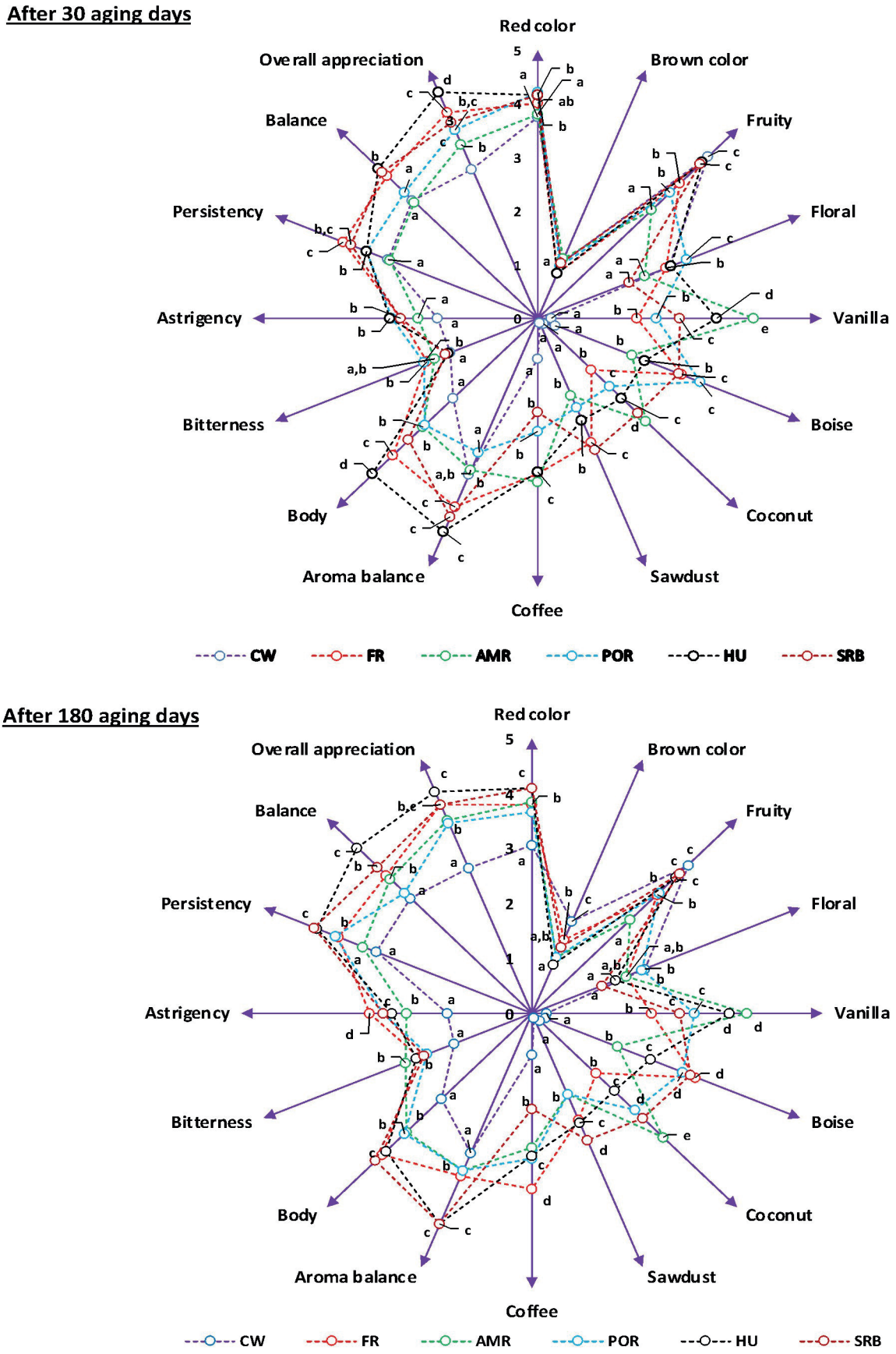

Fig. 1: Sensory profile of Kadarka red wines after 30 and 180 aging days in contact with different oak wood chip species. CW – control sample (no oak chips contact); FR – *Q. petraea* chips from France; AMR – *Q. alba* chips from USA; POR – *Q. pyrenaica* chips from Portugal; HU – *Q. petraea* chips from Hungary; SRB – *Q. pubescens* from Serbia.

* Values with same letter for each sensory descriptor are not significantly different (Duncan test $p < 0.05$).

contribution of *cis*-β-methyl-γ-octalactone to coconut sensory character of Chardonnay wines aged in contact with American *Q. alba* chip species.

The differences in scores for "aroma balance", "body", and "overall appreciation" were not so pronounced between all wines. However, after 30 and 180 aging days, wines aged in contact with *Q. petraea* from Hungary and *Q. pubescens* chips showed the highest scores for "aroma balance", "body", "balance" and "overall appreciation". Besides these wines, high scores for those sensory descriptors were also awarded to wine aged in contact with *Q. petraea* chips from France.

The results of sensory evaluation also showed that in general, the prolonged wood chips contact (180 aging days) did not have a negative impact on the majority of individual sensory descriptors analyzed. Cano-Lopez *et al.* (2008) reported better sensory characteristics of red wine samples aged with oak cubes than those aged in barrels, after both 3 and 6 months of contact. These authors suggest that the use of oak chips is a good alternative for short wine aging time. Another study by (Rubio-Bretón *et al.* (2018)) compared the use of chips and staves (with and without micro-oxygenation) as accelerated 'Tempranillo' wine aging strategies with the barrel aging. According to these authors, after 2 months of aging, gustative profile of red wines stored in contact with oak chips was evaluated as less structured, persistent, and astringent, as well as with a lesser retronasal aroma. However, after 4 months, wines aged in contact different oak wood chips, obtained the highest scores for the majority of gustatory parameters studied.

Principal components analysis applied to wine phenolic, aromatic and sensory characterization

Principal component analysis (PCA) was employed to better understand and explain the influence that the aging in contact with different oak chip species had on general phenolic parameters, oak wood volatile content and sensorial attributes of Kadarka wine (a total of 24 variables). PCA was carried out for the analytical data obtained after 30 and 180 aging days (Figs. 2 and 3, respectively). This statistical multivariate technique allows better understanding of the relationship between the variables due to the reduction of their linear combinations.

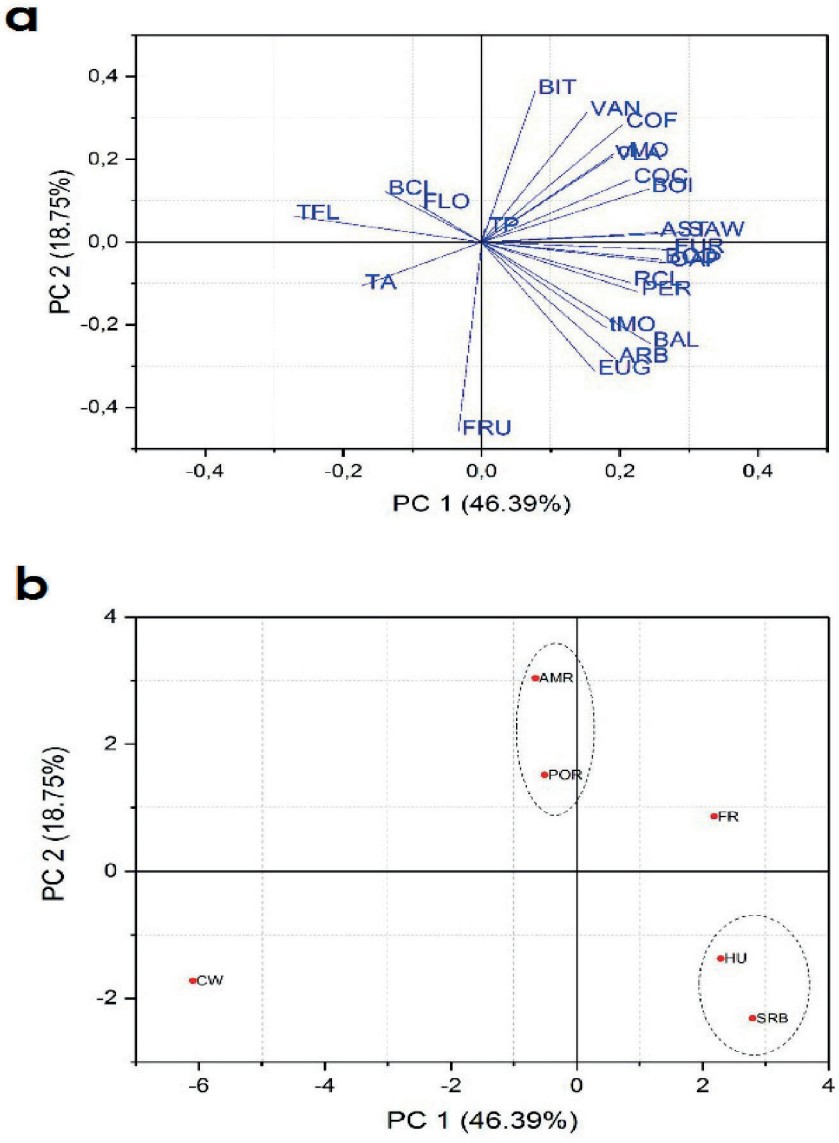

Fig. 2: Principal component analysis (PCA; PC1 and PC2) for general phenolic parameters, oak wood volatile compounds and sensorial attributes of Kadarka red wines after 30 aging days in contact with different wood chip species. (a) Projection of chemical parameters and sensorial attributes; (b) Projection of wine samples.

CW – control sample (no oak chips contact); FR – *Q. petraea* chips from France; AMR – *Q. alba* chips from USA; POR – *Q. pyrenaica* from Portugal; HU – *Q. petraea* chips from Hungary; SRB – *Q. pubescens* chips from Serbia.

RCL – red color; BCL – brown color; FRU – fruity; FLO – floral; VLA – vanilla; BOI – boise; COC – coconut; SAW -sawdust; COF – coffee; ARB – aroma balance; BOD – body; BIT – bitterness; AST – astringency; PER – persistency; BAL – balance; OAP – overall appreciation; TP – total phenols; TFL – total flava-3-ols; TA – total anthocyanins; FUR – furfural; tMO – *trans*-β-methyl-γ-octalactone; cMO – *cis*-β-methyl-γ-octalactone; EUG – eugenol; VAN – vanillin.

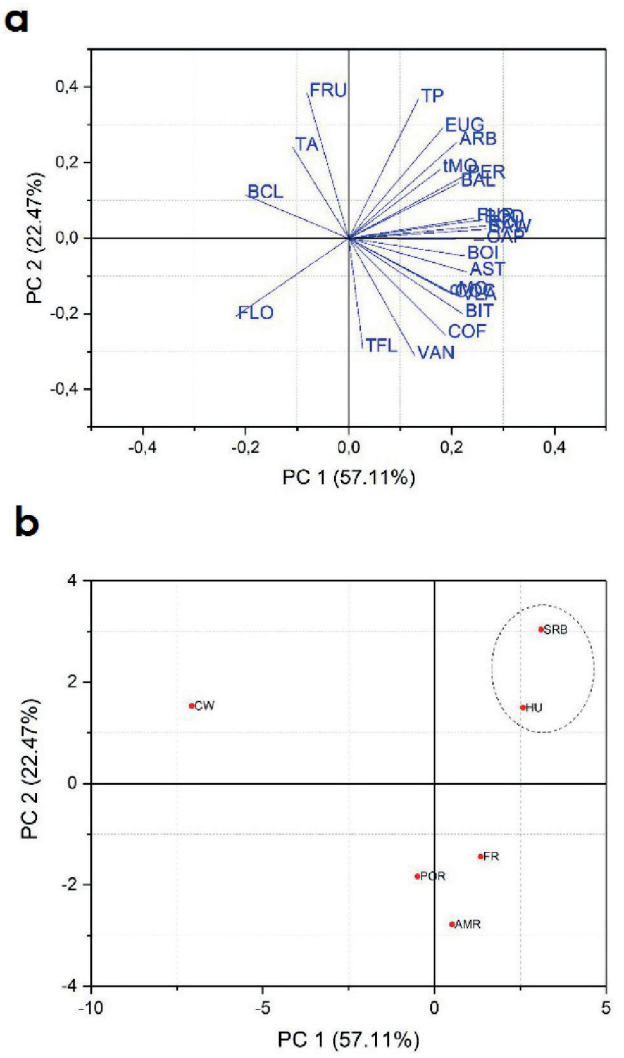

Fig. 3: Principal component analysis (PCA; PC1 and PC2) for general phenolic parameters, oak wood volatile compounds and sensorial attributes of Kadarka red wines after 180 aging days in contact with different wood chip species. (a) Projection of chemical parameters and sensorial attributes; (b) Projection of wine samples.

CW – control sample (no oak chips contact); FR – Q. petraea chips from France; AMR – *Q. alba* chips from USA; POR – *Q. pyrenaica* chips from Portugal; HU – *Q. petraea* chips from Hungary; SRB – *Q. pubescens* chips from Serbia.

RCL – red color; BCL – brown color; FRU – fruity; FLO – floral; VLA – vanilla; BOI – boise; COC – coconut; SAW -sawdust; COF – coffee; ARB – aroma balance; BOD – body; BIT – bitterness; AST – astringency; PER – persistency; BAL – balance; OAP – overall appreciation; TP – total phenols; TFL – total flava-3-ols; TA – total anthocyanins; FUR – furfural; tMO – *trans*-β-methyl-γ-octalactone; cMO – *cis*-β-methyl-γ-octalactone; EUG – eugenol; VAN – vanillin.

The PCA performed with the data obtained for Kadarka wines after 30 aging days (Fig. 2), showed that among five principal components obtained, the first two were accounting for more than 65% of the variance in the first two dimensions. Most of the separation occurred among the first principal component (PC1) which explained 46.39% of the variance. This factor was positively correlated with the majority of the sensory and analytical variables except with “brown color”, “fruity” and “floral” aroma sensory attributes, as well as with total flavan-3-ols and total anthocyanins. The second PC (PC2, 18.75% of the variance) was strongly positively loaded with “vanilla”, “boise”, “coconut”, “sawdust” and “coffee” aroma sensory attributes, as well as *cis*-β-methyl-γ-octalactone and vanillin volatile compounds (Fig. 2a).

Fig. 2b gives a spatial distribution of the Kadarka red wines aged in contact with the different oak wood chip species and control wine after 30 aging days in relation to the different phenolic, aromatic and sensory attributes considered. Four different groups were formed. A first group comprises wine aged in contact with *Q. petraea* chips from France, another group comprises the wines aged in contact with *Q. pubescens* and *Q. petraea* from Hungary chips, a third group is formed with the wines aged in contact with *Q. alba* and *Q. pyrenaica* chips, and the last, fourth group includes the Kadarka control wine. Wine from the first group is generally placed in positive part of the PC1 and PC2 and they are associated with “coffee”, “boise”, “coconut” and “bitterness” sensory descriptors and also with vanillin and *cis*-β-methyl-γ-octalactone content. Wines from the second group are placed in the positive part of component PC1 and negative part of PC2 being related with “red color”, “aroma balance”, “persistency”, “balance” sensory attributes, as well as *trans*-β-methyl-γ-octalactone and eugenol contents. Wines from the third group are placed in the negative part of component PC1 and positive part of PC2 and it is associated with “brown color” and “floral” sensory descriptors as well as total flavan-3-ols content. Finally, Kadarka control wine is placed in the negative part of both PC and it is positively correlated with “fruity” sensory attribute and total anthocyanins content.

The PCA performed with the sensory and analytical variables of Kadarka wines after 180 aging days in contact with different oak chip species revealed even better differentiation among wines (Fig. 3). It was shown that significantly more variations were explained by the first two PC than in the case of wine aging for 30 days (79.58% compared to 65.14%). Specifically, 57.11% and 22.47% of total variations were explained by PC1 and PC2, respectively. PC1 was loaded positively with all variables except with “brown color”, “fruity” and “floral” aroma sensory attributes, and total anthocyanins. Among all variables, the PC2 was positively correlated mostly with “fruity”, “aroma balance” and “persistency” sensory attributes, total phenols, total anthocyanins and eugenol contents, while negatively correlated mostly with “floral”, “coffee” and “bitterness” sensory attributes, total flavan-3-ols and vanillin contents (Fig. 3a).

Finally, the wines after 180 aging days in contact with oak chips can be almost entirely differentiated in separated groups in relation to the oak chip species used (Fig. 3b). Only the wines aged in contact with *Q. pubescens* and *Q. petraea* from Hungary chips could be considered as a distinct group positioned in positive parts of both PC and being positively correlated with “aroma balance’, “persistency”, “balance” sensory attributes, as well as total phenols, *trans*-β-methyl-γ-octalactone and eugenol contents. It is evident that these determining variables are almost the same as previously reported for the same wines after 30 aging days. Furthermore, wines aged in contact with *Q. petraea* from France, *Q. alba* and *Q. pyrenaica* chips are approximately placed in negative sections of both PC and mainly associated with “cof-

fee" and "bitterness" sensory attributes and total flavan-3-ols and vanillin content. At the end, control wine is related with "fruity", "brown color" sensory attributes and total anthocyanins content.

Conclusions

The necessity of this research is reflected in the fact that neither the aging of Kadarka wine produced from this old red grape variety of Balkan Peninsula in contact with different oak species nor the use of oak species grown in Serbia, particularly *Q. pubescens*, in enology have been sufficiently investigated.

Therefore, apart from differences in the trends of changes, the 180 days long aging of Kadarka red wines in contact with different oak chip species considerably affected the values of certain general phenolic parameters such as monomeric anthocyanins content whose decrease was more intensive in wine samples with oak chips contact than in control wine. In addition, compared to the wine aged without the contact with wood, the sensory profile of Kadarka wine was improved in terms of aroma, taste and overall flavor when stored in contact with oak chips.

The highest total amounts of volatile wood aroma compounds were determined in wines aged in contact with *Q. petraea* from France and *Q. alba* chips for 180 days. However, Kadarka wine aged in contact with *Q. pubescens* chips was characterized by significantly higher contents of several specific volatile wood aroma compounds, such as furfural, 5-methylfurfural, *trans*-β-methyl-γ-octalactone and eugenol, compared with remaining wines. This was an interesting result because there is a scare knowledge about the use of this oak specie in enology. On the other hand, the use of *Q. petraea* chips from Hungary induced the most pronounced complexity to the sensory profile of Kadarka wines which was confirmed by the highest marks for aroma and overall flavor.

Thus, the results of this research are interesting from a practical point of view, since they give an overview how Kadarka wines could evolve during aging in contact with different oak chip species. In addition, it was also possible to detect the impact of *Q. pubescens* chip species on Kadarka wine quality. In that case, the results obtained allow us to conclude that this oak species can give wines with similar characteristics to wines aged in contact with the most used oak wood species, namely from French and American origin. However, further research on the impact of different concentrations, chips sizes and contact times of this oak species on the chemical and sensory profiles of Kadarka wines and their evolution during bottle storage is certainly necessary under industrial conditions.

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Conflicts of interest

The authors declare that they do not have any conflicts of interest.

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