

FRI-LCR-1-BFT(R)-01

CHEMICAL COMPOSITION, PHENOLIC COMPLEX AND ANTIOXIDANT ACTIVITY OF WHITE WINES PRODUCED IN CONTACT WITH OAK WOOD

Assoc. Prof. Tatyana Yoncheva, PhD

Assoc. Prof. Dimitar Dimitrov, PhD

Department of Vine Selection, Enology and Chemistry

Institute of Viticulture and Enology – Pleven, Bulgaria

Agricultural Academy

E-mail: t_ion@abv.bg

E-mail: dimitar_robertov@abv.bg

Abstract: *The oak wood impact, during aging in a barrel, on the characteristics of three white wines of the Chardonnay and Riesling varieties was studied. The samples were from different vintages, producers and regions of Bulgaria. They were produced in contact with different species of wood and duration of storage. Their chemical composition was determined in terms of the main chemical indicators, phenolic complex and antioxidant activity. The influence of the barrel was established mainly on the wines' phenolic content and antioxidant potential. Chardonnay, 2020 vintage stood out for its richer phenolic composition and higher content of the investigated phenolic components (total phenolic compounds TPC, flavonoid phenolic compounds FPC, non-flavonoid phenolic compounds NPC, total phenolic index TPI). The sample was aged in Bulgarian barrels for 24 months. Of the wines, 2021 vintage, a higher concentration of TPC and NPC was found in Chardonnay, and more FPC and TPI in Riesling. The Riesling and Chardonnay samples from the Danube Plain showed similar antioxidant activity, while Chardonnay, 2020 vintage, had the lowest potential, despite the identified higher phenolic content.*

Keywords: *White wine, Oak wood, Chemical composition, Phenolic complex, Antioxidant activity.*

INTRODUCTION

The use of oak wood in various forms in white wines production had been increasingly popular practice among winemakers. Their chemical composition and sensory profile had been changing due to the ongoing intensive extraction, oxidation-reduction, condensation and other processes. Polyphenolic and volatile aromatic substances passed from the wood to the wine, made better its aroma and taste, and enhanced its antioxidant capacity (Navojnska et al., 2012; Dumitriu et al., 2019).

Traditionally, oak barrels had been used to store and age wines. The basic processes taking place in winemaking could also occur efficiently in them (Chira, 2018). Along with this classical method of aging, accelerated ways to improve the quality of wines were also applied in practice, by adding wood in the form of staves, planks, sticks, cubes, granules, chips of different sizes and degree of toasting (Kyraleou et al., 2016; Rubio-Breton et al., 2018). The choice of the wood species and the contact time would depend on the variety specifics, the applied technology for its heat treatment and winemaking (Chira and Teissedre, 2014; Zamora, 2022).

In the technological process for white wines production, the barrels might be used in several cases, at the following stages – fully carrying out of the alcoholic fermentation with subsequent aging of the wines, fully carrying out only of the fermentation in the barrel and separation after the process completion, contact of the wine with the barrel only for storage and aging (Alañon et al., 2018; Zamora, 2022).

The wood impact was primarily on the phenolic composition of white wines and their colour intensity. It was observed a rise in the total phenolic index, the content of polyphenols, flavonoid and non-flavonoid phenols. The amount of some specific phenolic components such as gallic and ellagic acid was increased. Wines aged in oak barrels also had a higher ratio of polysaccharides and more intense yellow colour (Rodrigues et al., 2012; Nunes et al., 2017).

Wine contact with wood also had a positive effect on its antioxidant properties, due to the presence of more extracted polyphenols. The content of these components determined its antiradical features. The amount of extractable total phenols and ellagitannins depended greatly on the size and shape of the wood used and therefore this factor also affected their concentration and the wines' antioxidant activity (Jordao et al., 2012; Nikolantonaki et al., 2019; Bartkovsky et al., 2020; Romanet et al., 2023).

The objective of this study was to determine the effect of oak wood on the chemical composition, phenolic complex and antioxidant activity of Chardonnay and Riesling white wines.

EXPOSITION

Material and Methods

The study was carried out in 2023 at the Institute of Viticulture and Enology (IVE) – Pleven, Bulgaria. The object of the study were 3 white dry wines, provided by different producers made in contact with oak wood, aged in a barrel with various duration:

- Chardonnay, 2020 vintage, from the Thracian Lowland – the wine was aged in new Bulgarian oak barrels, with a medium degree of toasting; duration of contact 24 months (according to the producer).

- Chardonnay, 2021 vintage, from the Danube Plain – the batch was a combination of wine where 33.3% was aged in Bulgarian oak barrels and 66.7% was aged in French oak barrels; the barrels had a light and medium degree of toasting; duration of contact 6 months (according to the producer).

- Riesling, 2021 vintage, from the Danube Plain – the batch was a combination of wine where 37.5% was aged in Bulgarian oak barrels and 62.5% was aged in French oak barrels; the barrels had a light and medium degree of toasting; duration of contact 6.5 months (according to the producer).

The experimental samples were analysed for the main chemical parameters, phenolic complex and antioxidant activity. A comparison was made and differences were found in the studied parameters depending on the wood species used and the contact time.

1. Chemical composition

For identifying the wines' chemical composition, generally accepted methods in winemaking practice were used (Ivanov et al., 1979). The following indicators were analysed:

- alcohol, vol. % - distillation method, Gibertini apparatus with densitometry by the distillate density

- residual sugars – Schrool' s method

- total extract (TE), g/dm³ - Gibertini apparatus with densitometry by density of alcohol-free sample

- sugar-free extract, g/dm³ - calculation method (the difference between TE and sugars)

- titratable acids, g/dm³ - titration with 0.1n NaOH with bromothymol blue indicator

- tartaric and malic acid, g/dm³ – Pochinok's method

- volatile acids, g/dm³ – distillation method with subsequent titration with 0.1n NaOH with phenolphthalein indicator

- pH – pH-meter

2. Phenolic composition (Ivanov et al., 1979; Chobanova, 2007).

The following indicators of the wines' phenolic composition were determined:

- total phenolic compounds (TPC), g/dm³ gallic acid - Singleton and Rossi method with Folin-Ciocalteu reagent and spectrophotometric measurement of light absorption at λ 750 nm.

- flavonoid phenolic compounds (FPC), mg/dm³ catechin equivalent and non-flavonoid phenolic compounds (NPC), mg/dm³ caffeine equivalent – Somers method with analytical and calculation part.

- total phenols index (TPI), [abs. unit] – determined spectrophotometrically by measuring the light absorption at λ 280 nm.
- colour intensity I, [abs. unit] – Glories method, represented the measurement of light absorption at λ 420 nm.

3. Antioxidant activity (AA)

The wines' antioxidant activity was determined by the method of Wang et al. (1996), as antiradical activity against the stable product DPPH• (2,2-diphenyl-1-picrylhydrazyl) (Sigma Aldrich, Germany). For this purpose, the tested wine was diluted immediately before the analysis with distilled water to a total extract content equal to 600 mg/dm³ and 400 mg/dm³, respectively. In a test tube it was mixed 0.5 cm³ of the sample and 2.5 cm³ of the freshly prepared solution (100 μ m) of DPPH• in ethanol. Thus, the TE:DPPH ratio in the reaction medium assumed values of 3:1 and 2:1, respectively. Similarly, a control sample was prepared with distilled water instead of wine. The values of the molecular absorption of light (spectrophotometrically at a wavelength of 515 nm) of the control and the experimental sample, denoted by A_K and A_0 , respectively, were measured. The measurements were carried out at reaction time of 5 and 15 min, counted from the moment of mixing the reagents. The antiradical activity was calculated by the formula:

$$AA = 10^2(A_K - A_0).A_K^{-1} \quad (1)$$

4. Statistical processing of the results.

The obtained data from triplicate performance of the chemical analyses were subjected to statistical processing, represented by mean value and standard deviation (\pm SD). Excel 2007 software (Microsoft Office) was used for the determination.

RESULTS AND DISCUSSION

1. Determination of the chemical composition of the studied white wines.

The chemical composition of white wines fermented or aged in contact with oak wood had been changed, modified and enriched considerably due to the extraction processes and the passing of a number of components from the wood to the liquid (Navojnska et al., 2012; Baron et al., 2018; Bartkovsky et al., 2020; Zamora, 2022).

The results of the chemical analysis of the studied white wines according to the main indicators of the composition are presented in Table 1.

Table 1. Chemical composition of the studied white wines.

№	Indicators		Region of production	Alcohol vol. %	Total extract g/dm ³	Sugar g/dm ³	Sugar-free extract g/dm ³	Titratable acids g/dm ³	Volatile acids g/dm ³	pH
	Wine	Vintage								
1.	Chardonnay	2020	Thracian Lowland	13.20 ± 0.00	21.50 ± 0.00	0.29 ± 0.02	21.21 ± 0.02	5.28 ± 0.03	0.54 ± 0.00	4.05 ± 0.01
2.	Chardonnay	2021	Danube Plain	13.52 ± 0.00	22.80 ± 0.00	0.32 ± 0.00	22.49 ± 0.01	5.95 ± 0.04	0.36 ± 0.00	4.12 ± 0.01
3.	Riesling	2021	Danube Plain	12.56 ± 0.00	19.60 ± 0.00	0.54 ± 0.00	18.86 ± 0.35	5.25 ± 0.00	0.48 ± 0.00	4.04 ± 0.01

Chardonnay, 2021 vintage had the highest alcohol content (13.52 \pm 0.00 vol. %), and Riesling, 2021 vintage – the lowest (12.56 \pm 0.00 vol. %). The total and sugar-free extract of the samples were within the ranges typical of the respective variety. The rates of the indicators were

significantly higher in Chardonnay wines compared to Riesling. The results showed the specific varietal characteristics. The residual sugars varied from 0.29 ± 0.02 to 0.54 ± 0.00 g/dm³, which confirmed the full completion of the fermentation process. Higher titratable acids were recorded in Chardonnay, 2021 vintage. The acidity was almost similar in Chardonnay, 2020 vintage and Riesling, 2021 vintage. All samples had normal volatile acidity (from 0.36 ± 0.00 to 0.54 ± 0.00 g/dm³), and pH values (from 4.04 ± 0.01 to 4.12 ± 0.01) were higher than the usual rates.

The influence of the oak contact on the wines' chemical parameters was primarily on the sugar-free extract. Its amount increased due to the enhanced extraction of polyphenols and polysaccharides from the wood to the liquid (Lukic et al., 2015; Nunes et al., 2017).

2. Determination of the phenolic composition and antioxidant activity of the studied white wines.

The data on the analysed wines revealed a several times higher content of the studied phenolic compounds in Chardonnay, 2020 vintage. The three samples were aged in new barrels with a medium degree of toasting. Therefore, the differences found were the result of the varying duration of the wine contact with the wood. The sample Chardonnay, 2020 vintage stood out with its richer phenolic composition – TPC (1.23 ± 0.00 g/dm³), FPC (1059.83 ± 0.01 mg/dm³), NPC (332.92 ± 0.03 mg/dm³), TPI (18.46 ± 0.02 abs. units). This was due to the storage in Bulgarian barrels for 24 months. The longer impact of the wood on the wine was the reason for its phenolic profile enrichment with the studied groups of components.

Table 2. Phenolic composition of the studied white wines.

№	Indicators		Region of production	TPC, g/dm ³ gallic acid	FPC, mg/dm ³ catechin equivalent	NPC, mg/dm ³ caffeine equivalent	TPI, [abs. unit]	Colour intensity I, [abs. unit]
	Wine	Vintage						
1	Chardonnay	2020	Thracian Lowland	1.23 ±0.00	1059.83 ±0.01	332.92 ±0.03	18.46 ±0.02	0.43 ±0.02
2	Chardonnay	2021	Danube Plain	0.57 ±0.01	205.66 ±0.06	160.97 ±0.46	10.92 ±0.01	0.41 ±0.01
3	Riesling	2021	Danube Plain	0.38 ±0.01	468.02 ±0.04	155.70 ±0.11	12.03 ±0.01	0.34 ±0.02

The samples from the Danube Plain region belonged to the same vintage, they were produced in a similar way, with approximately the same duration of contact with the oak wood. The differences between them in the content of total and flavonoid phenolic compounds were more significant, which was probably due to the varietal phenolic content. In Chardonnay, 2021 vintage, a higher ratio of TPC (0.57 ± 0.01 g/dm³) and NPC (160.97 ± 0.46 mg/dm³) was found, while in Riesling, 2021 vintage – more FPC (468.02 ± 0.04 mg/dm³) and TPI (12.03 ± 0.01 abs. units) (Table 2).

The contact with the oak wood had a positive effect on the white wines' phenolic profile. The oak wood had been a source of specific phenols, which were extracted to varying degrees upon contact with the wine. The wines were enriched with polyphenols, as the ratio of mainly the gallic and ellagic acid and the flavonoids went up. The form in which the wood was used, its botanical and geographical origin, the dosage, and the stage at which it was applied in the production were essential (Galdo et al., 2019; Bartkovsky et al., 2020).

The increased phenolic content in wines that had been in contact with wood, in most cases, led to enhancing of their antioxidant properties.

The antioxidant activity of the studied white wines are presented in Figures 1, Figure 2 and Figure 3.

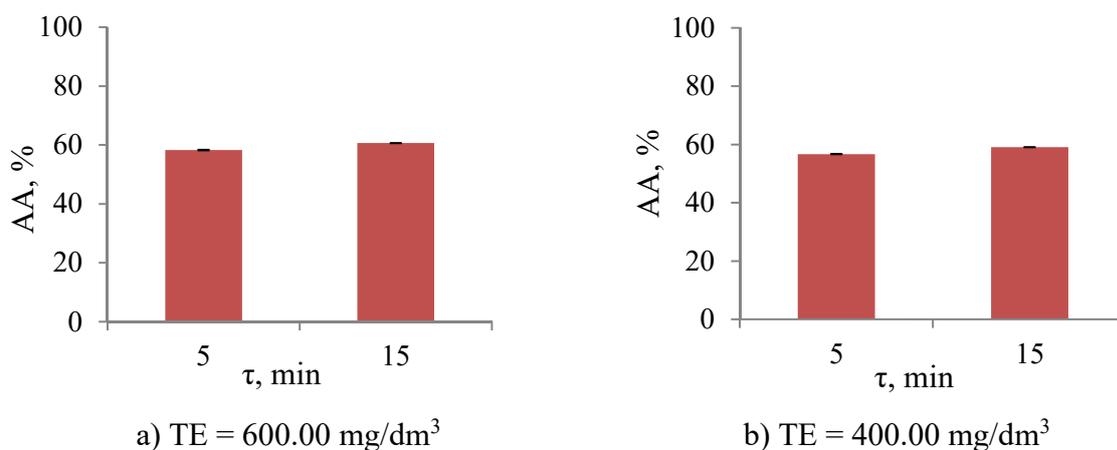


Fig. 1. Antioxidant activity of Riesling white wine, 2021 vintage.

The antioxidant activity of wines was defined in relation to the DPPH radical elimination. The obtained results indicated an almost similar potential of Riesling and Chardonnay wines from the Danube Plain, being slightly higher for Riesling, 2021 vintage. At TE=600.00 mg/dm³ after 5 min of the reaction with the radical, a radical scavenging activity of 58.28±0.09% was found. When the reaction time was increased to 15 min, a slight rise in the antioxidant activity was observed and it reached 60.63±0.01%, which was the highest achieved capacity for DPPH elimination of all white wines studied. When reducing TE to 400.00 mg/dm³, a slight, almost insignificant drop in the antioxidant capacity was observed. At 5 min of the reaction, 56.70±0.04% radical scavenging activity was found for this extract. When the reaction time was increased to 15 min, it went up slightly, reaching 59.06±0.01%.

Chardonnay wine, 2021 vintage, showed very similar but slightly lower antioxidant activity compared to Riesling. At TE=600.00 mg/dm³ and after 5 min of the reaction with the radical, a radical scavenging capacity of 56.08±0.09% was reported. When the reaction time was set to 15 min, a slight increase in the elimination percentage of DPPH radicals was observed and it reached 59.07±0.03%. No significant change was noticed in the antioxidant capacity of the wine of the investigated variety at TE=400.00 mg/dm³. Thus, 5 min after the reaction with the radical, an antiradical activity of 56.05±0.03% was revealed. In this case also as with the previous total extract, at 15 min a slight increase in antioxidant capacity was observed, reaching 58.15±0.02% elimination of the free DPPH radicals.

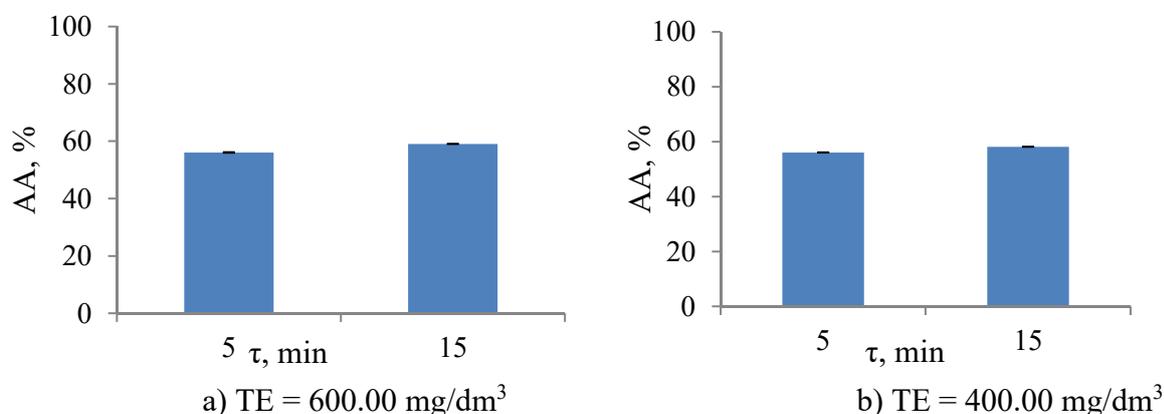


Fig. 2. Antioxidant activity of Chardonnay white wine, 2021 vintage.

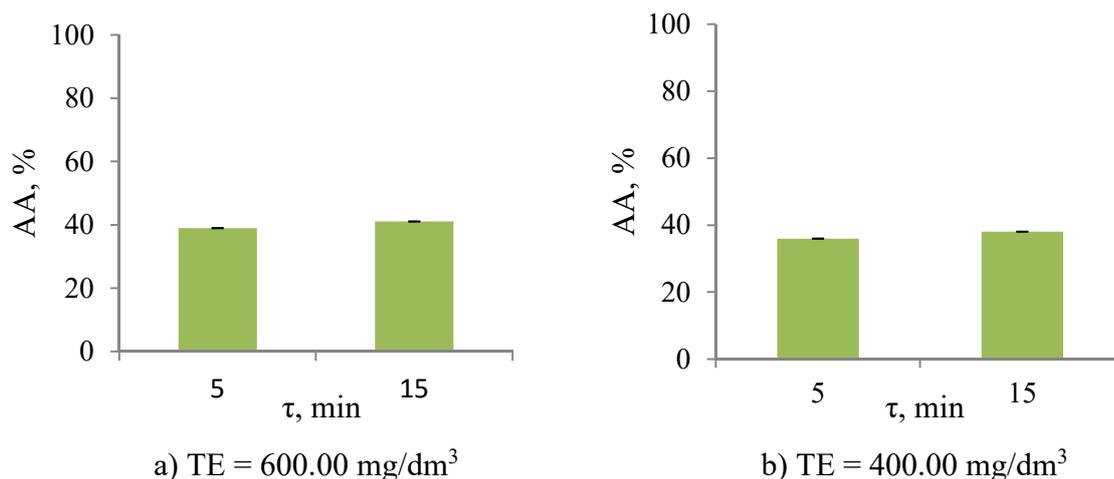


Fig. 3. Antioxidant activity of Chardonnay white wine, 2020 vintage.

Chardonnay wine, 2020 vintage, showed the lowest antioxidant activity. At TE=600.00 mg/dm³ and 5 min after the reaction, a radical scavenging capacity of 38.96±0.05% was reached. At 15 min of the reaction with the same extract, a slight increase in the activity was observed and it reached 41.06±0.03%. At TE=400.00 mg/dm³, a slight drop in the antioxidant capacity was noticed. At 5 min from the point of mixing the radical with the wine, an antiradical capacity of 35.97±0.03% was found, which was the lowest activity established among the studied wines for the different extracts. At 15 min of the reaction, a slight increase was observed with the same extract, and an elimination of free radicals of 38.04±0.01%.

Generally, the white wines' antioxidant activity was lower compared to the red wines, due to their production technology. Our data were consistent with the researches of Paixão et al. (2007), Marković et al. (2015) and Kharadze et al. (2018) who investigated the antioxidant potential of Spanish, Croatian and Georgian wines of different varieties made with oak wood, respectively. Our results also correlated with those of Bartkovsky et al. (2020), who determined the antioxidant capacity of Chardonnay white wines, aged in oak barrels for 6, 20 and 32 weeks, and also in contact with oak chips. Baron et al. (2018) found a 50% increase in the antioxidant activity of white wines of the Malverina variety, in contact with oak chips, compared to the control.

CONCLUSION

Based on the results obtained from the study on the influence of oak wood on the Chardonnay and Riesling white wines, it could be summarized:

- The chemical composition of the tested white wines were the result of the specifics of the respective variety and vintage and of the technological practices applied by the various producers. The Chardonnay wines had a higher total and sugar-free extract in comparison with the Riesling sample, which was due more to the varietal characteristics than to the influence of the wood.

- The differences in the phenolic composition were the result of varietal features, the species and amount of oak wood used, as well as the contact time. Chardonnay wine, 2020 vintage, stood out with its richer phenolic composition and higher content of the studied phenolic indicators (TPC, FPC, NPC, TPI), because of the storage in Bulgarian barrels for 24 months. In the samples, 2021 vintage, a higher ratio of TPC and NPC was found in Chardonnay, and more FPC and TPI in Riesling.

- The antioxidant profile of the samples characterized Riesling and Chardonnay, 2021 vintage, from the Danube Plain, as wines that had the highest antioxidant potential. The Chardonnay sample, 2020 vintage, had the lowest potential, despite the determined higher phenolic content.

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