ANTIRADICAL CAPACITY OF SOME RED WINES PRODUCED IN THE IASI VINEYARD IN RELATION TO THEIR PHENOLIC CONTENT

CAPACITATEA ANTIRADICALICĂ A UNOR VINURI ROŞII PRODUSE ÎN PODGORIA IAŞI ÎN RELAȚIE CU CONȚINUTUL FENOLIC AL ACESTORA

ZAIȚ Monica[1*], FILIMON V. R.[1], NECHITA Ancuța[1], DAMIAN Doina[1]
*Corresponding author e-mail: monica.zait95@gmail.com

Abstract: *In recent years great attention has been paid to food antioxidants and their association with multiple health benefits. Free radical scavenging activity is currently considered to be one of the most important characteristics of wine and is often associated with its polyphenolic content. The aim of this paper was the assessment of total phenolic compounds, anthocyanin and tannin contents of five wines (Cabernet Sauvignon, Merlot, Pinot gris, Arcaş and Busuioacă de Bohotin) produced in the NE of Romania - Iasi vineyard, from 2018 and 2019 harvests, in relation to their free radical scavenging activity (DPPH). High content of phenolic compounds (flavonoids and non-flavonoids) and their positive correlation with the free radical scavenging activity of the analysed samples suggests that rose and red wines are excellent source of compounds with antiradical capacity.*
Key words: free radical, scavenging activity, antioxidants, DPPH, phenolic compounds

Rezumat. *În ultimii ani a fost acordată o atenție deosebită antioxidanților alimentari şi asocierii acestora cu multiple beneficii pentru sănătate. În prezent, activitatea antiradicalică este considerată a fi una dintre cele mai importante caracteristici ale vinului şi este adesea asociată cu conținutul său polifenolic. Scopul acestei lucrări a fost evaluarea conținutului total de compuşi fenolici, antociani şi taninuri din cinci probe de vin (Cabernet Sauvignon, Merlot, Pinot Gris, Arcaş şi Busuioacă de Bohotin), produse în zona de NE a României - podgoria Iaşi, din recoltele anilor 2018 şi 2019, în raport cu capacitatea antiradicalică (DPPH) a acestora. Conținutul ridicat de compuşi fenolici (flavonoizi şi non flavonoizi) şi corelația pozitivă a acestora cu activitatea antiradicalică a probelor analizate sugerează faptul că vinurile rose şi roşii reprezintă o sursă excelentă de compuşi cu capacitate antiradicalică.*
Cuvinte cheie: radicali liberi, activitate antiradicalică, antioxidanți, DPPH, compuşi fenolici

INTRODUCTION

The overproduction of reactive oxygen species (ROS) has been reported to result in oxidative stress and is involved in the damage of cell structures that

[1]Research and Development Station for Viticulture and Winemaking Iasi, Romania

causes various disease states (Sanaa *et al.*, 2018). This can be largely counteracted by antioxidant defence systems.

In recent years, increasing attention has been paid to food antioxidants and their association with multiple health benefits. In general, it has been described that phenolic compounds are secondary antioxidants included in the category of free radical scavengers. Consumption of red wine has been proven to increase plasma/serum antioxidant activity and to protect LDL from oxidation. Consequently, the potent antioxidant activity of phenolic compounds in red wine has been proposed as an explanation for the French paradox (Davalos and Lasuncion, 2009). For these reasons free radical scavenging activity is currently considered to be one of the most important characteristics of wine and is often associated with its polyphenolic content. The aim of this paper was the assessment of total phenolic compounds, anthocyanin and tannin contents of five wines (Pinot gris, Busuioacă de Bohotin, Cabernet Sauvignon, Merlot and Arcaş) produced in NE of Romania - Iasi vineyard, in relation to their free radical scavenging activity.

MATERIAL AND METHOD

For conducting the study were used the wines obtained from grapes of five *Vitis vinifera* L. varieties: Cabernet-Sauvignon, Merlot, Arcaș (Cabernet Sauvignon × Babească neagră), Busuioacă de Bohotin and Pinot gris, in the years 2018 and 2019, growing in the experimental field of the Research-Development Station for Viticulture and Winemaking Iasi, Romania. Grapes were harvested at technological maturity, destemmed, mechanically crushed, macerated (5 days) and pressed. The wine was fermented using *Saccharomyces cerevisiae ssp. bayanus* yeast strain *(*Fermactive CB, Sodinal, France*)* and fining was done with bentonite (Spherobent super, 0.9 g/L). The wines were filtered and stabilized with SO_2. Physical and chemical features of wines were analysed according to the Compendium of international methods of wine and must analysis (OIV, 2012). Colour parameters (proportion of red, yellow, blue, colour intensity, colour hue, and brilliance of red wines) were calculated according to the method described by Glories (1984), measuring the absorbance at 420, 520 and 620 nm using an Analytik Jena Specord 200 plus spectrophotometer. Total phenolic, flavonoid and non-flavonoid fractions were determined by the colorimetric method using the Folin-Ciocâlteu reagent (Merck, Germany) (Singleton and Rossi, 1965) and expressed as galic acid equivalent (GAE)/L ($x = 1.1317 \times DO - 0.0451$). Flavonoids were precipitated using an acidic formaldehyde solution (pH<0.8) (Tibiri, 2010). Anthocyanins were determined by pH variation method (AOAC, 2005).

The free radical scavenging activity of the wine samples was determined using 2,2-diphenyl-1-picrylhydrazyl free radical (DPPH) (Alfa Aesar, Germany), according to the protocol presented by Brand-Williams (1995). Sulphur dioxide, used as preservative, could influence the antiradical activity by locking anthocyanins. In order to free anthocyanin from their combinations an acetaldehyde 10 % solution was used.

Pearson's correlation coefficient (r) was used to measure the strength of the association between the antiradical activity and phenolic content.

RESULTS AND DISCUSSIONS

Wine physico-chemical parameters of wines have complied with the values mentioned by the current legislation (***, 2016). The alcohol concentration ranged between 10.6 % vol. (Arcaş, 2018) to 14.9 % vol. (Pinot gris) (tab. 1). All wines were dry (1.2 - 3.8 g/L sugars), so the sugar content was too low to affect the antiradical activity of the analysed samples.

Table 1

Physico-chemical features of wines

Variety	Arcaş		Busuioacă de Bohotin		Cabernet Sauvignon		Merlot		Pinot gris	
Year	2018	2019	2018	2019	2018	2019	2018	2019	2018	2019
pH	3.58	0.30	3.42	0.28	3.43	0.30	3.54	0.29	3.64	0.31
ρ 20°C (g/cm^3)	0.9933	0.9922	0.9927	0.9915	0.9935	0.9918	0.9922	0.9930	0.9916	0.9918
Alc. (% vol)	10.6	12.1	14.7	13.1	12.4	12.1	11.8	12.7	14.5	14.9
Total acidity (g TA /L)	5.62	6.3	6.38	6.52	5.39	6.75	5.92	4.57	5.25	5.4
Volatile acidity (g Ac.ac./L)	0.43	0.3	0.39	0.28	0.36	0.30	0.45	0.29	0.43	0.31
Free SO_2 (mg/L)	53	28	47	48	37	33	50	37	36	35
Total SO_2 (mg/L)	105	75	105	130	87	83	104	100	82	93
Sugars (g/L)	1.40	1.20	3.80	1.90	1.20	1.20	1.20	1.90	1.40	1.20
Dry extract (g/L)	22.40	19.60	28.60	22.20	22.40	19.60	22.70	21.60	25.50	21.90
N.rd. extract (g/L)	21.00	18.40	21.80	20.30	21.20	18.40	21.50	19.70	21.90	20.00

Note: TA - tartaric acid; Alc – Alcohol; Ac.ac - acetic acid; N.rd. - Non-reducing.

Red wines (Arcaş, Cabernet Sauvignon and Merlot) showed a higher free radical scavenging activity (54.52 - 88.87 %), comparing to rose wines (fig. 1).

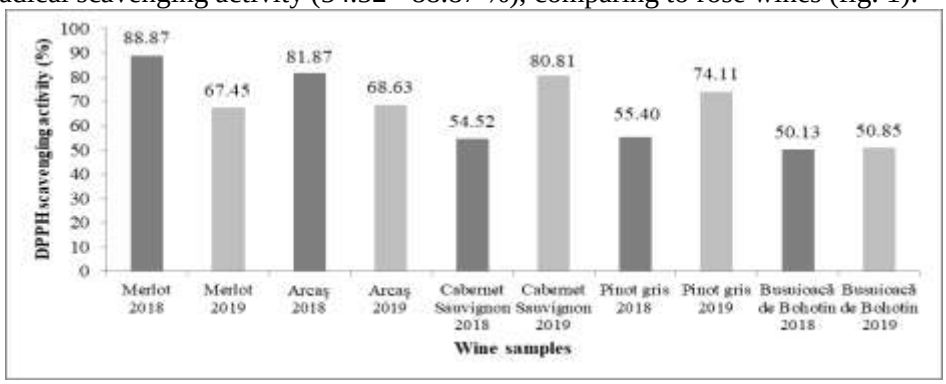

Fig. 1 DPPH scavenging activity (%) of wines made in Copou Iasi wine center

Colour is an attribute connected with many parameters, directly linked to wine quality, giving information on possible defects or poor storage conditions and also has a direct effect on consumer acceptability (Valentin *et al*., 2016). Colour composition of the analysed wines showed predominantly red and yellow hues.

The wines with the highest colour intensity were Merlot (2.21) and Arcaş (2.76). Rose wines presented higher values of colour brightness, ranging from 97.74 to 99.44 (tab. 2).

Table 2

Chromatic parameters of analysed wine samples

Variety	Year	Red (R%)	Blue (B%)	Yellow (Y%)	Colour intensity	Hue	Colour brightness
Arcaş	2018	42.09	5.56	52.34	1.74	1.24	62.99
	2019	56.05	3.45	40.50	2.76	0.72	65,00
Busuioacă de Bohotin	2018	27.44	12.17	60.39	0.48	2.20	97.74
	2019	39.08	3.43	57.49	0.29	1.47	98.99
Cabernet Sauvignon	2018	46.35	4.22	49.43	1.85	1.07	57.49
	2019	51.69	4.39	43.91	1.43	0.85	74.32
Merlot	2018	38.79	3.80	57.41	2.21	1.48	42.05
	2019	52.71	3.45	43.84	1.16	0.83	83.24
Pinot gris	2018	17.28	21.06	61.66	0.28	3.57	99.44
	2019	40.79	3.88	55.33	0.31	1.36	98.84

Red wines were rich in phenolic compounds (TPC), with higher values for Arcaş (2018), up to 2.42 g/L GAE, while rose wines showed values around 1.4 g/L GAE (tab. 3).

This paper explores the relationship between phenolic compounds, chromatic parameters and DPPH scavenging activity, using Pearson's correlation coefficient *r*. Thus, TPC showed a very strong correlation with flavonoid content (r=0.9754), a strong positive correlation with the tannin (r=0.8779), cathechin (r=0.8119) and anthocyanin (r=0.7493) content of wines. A moderate positive correlation of TPC with DPPH scavenging activity (r=0.5807) might imply that antiradical activity increases along with the concentration of phenolic compounds.

Although non-coloured, the non-flavonoid constituents are known to enhance and stabilize the colour of rosé/red wines by intra- and intermolecular reactions (Davalos and Lasuncion, 2009). This is reflected in the strong positive correlation with red colour percentage (R%) (r=0.7711) and moderate positive correlation with colour intensity, anthocyanin and catechin contents.

Flavonoids presented a very strong positive correlation with tannins (r=0.9205), a strong correlation with catechin (0.7219) and moderate positive correlation with anthocyanins (r=0.6622). Also, a moderate positive correlation of flavonoids with free radical scavenging activity was observed (r=0.5287).

Catechins showed a negative moderate correlation with the analysed parameters, excepting a positive moderate correlation with colour intensity (r=0.6804) and antiradical activity (r=0.6832). Also, tannins showed a weak correlation with chromatic parameters of wines and a positive moderate correlation with their DPPH scavenging activity (r=0.6108).

Anthocyanins showed the highest correlation with DPPH scavenging activity (r = 0.7486), a strong positive correlation with colour intensity (r=0.7075) and a moderate positive correlation with R% (tab. 4).

Table 3

Phenolic content of wines produced in Copou - Iasi wine centre

Variety	Arcaş		Busuioacă de Bohotin		Cabernet Sauvignon		Merlot		Pinot gris	
Feature / Year	2018	2019	2018	2019	2018	2019	2018	2019	2018	2019
DO 280	29.46	18.02	13.28	12.83	18.78	18.4	18.56	22.46	10.50	14.23
TPC (g/L GAE)	2.42	1.55	1.44	1.40	1.38	1.40	1.73	1.58	1.40	1.56
Non-FL. (g/L GAE)	0.40	0.41	0.31	0.35	0.37	0.33	0.39	0.36	0.14	0.30
FL. (g/L GAE)	2.02	1.14	1.13	1.05	1.01	1.07	1.35	1.22	1.24	1.25
Ant. (mg/L)	596.30	495.71	214.35	217.67	563.77	525.10	519.70	529.06	138.40	120.45
Cat. (mg/L)	21.8	9.82	2.51	2.59	10.11	11.49	11.14	9.18	1.87	4.35
Tan. (mg/L)	39.53	14.02	6.04	5.08	11.48	11.00	19.34	16.8	18.86	23.57

Note: GAE –galic acid equivalent; TPC – Total phenolic compounds; Non-FL – Non-Flavonoids; FL – Flavonoids; Ant – anthocyanins; Cat – Catechin; Tan –tannins.

Table 4

Correlation between phenolic content of wine, chromatic parameters and antioxidant activity

	TPC	*Non-FL*	*FL*	*Ant*	*Cat*	*Tan*	*R%*	*B%*	*Y%*	*C.I.*	*Hue*	*C.B.*	*AA %*
TPC	1												
Non-FL	0.4160	1											
FL	0.9754	0.2052	1										
Ant	0.7493	0.5947	0.6622	1									
Cat	0.8119	0.6267	0.7219	0.9397	1								
Tan	0.8779	0.1006	0.9205	0.5907	0.6836	1							
R%	0.1115	0.7711	-0.0670	0.4316	0.5082	0.0052	1						
B%	-0.1927	-0.8730	0.0043	-0.3939	-0.4386	-0.0156	-0.8614	1					
Y%	-0.0289	-0.5501	0.1023	-0.3809	-0.4678	0.0035	-0.9210	0.5956	1				
C.I.	0.3300	0.6993	0.1857	0.7075	0.6805	0.2035	0.6376	-0.4811	-0.6395	1			
Hue	-0.1929	-0.8711	0.0036	-0.4659	-0.5347	-0.0215	-0.9646	0.9464	0.7998	-0.5881	1		
C.B.	-0.2479	-0.6393	-0.1118	-0.5995	-0.5392	-0.1415	-0.5835	0.4257	0.5963	-0.9686	0.5168	1	
AA%	0.5807	0.3968	0.5287	0.7486	0.6832	0.6108	0.4081	-0.4318	-0.3145	0.5200	-0.4249	-0.4316	1

Note: CA – catechin; Ant – anthocyanin; Non-FL - non-flavonoids; FL – Flavonoids; TPC - Total phenolic compounds; Tan – Tannins; AA% - Antiradical activity (%); Y – Yellow; B – Blue; R – Red; CB – colour brightness; CI - colour intensity.

CONCLUSIONS

1. Merlot and Arcaş wines showed the highest colour intensity, due to a high polyphenolic content, especially anthocyanins, that presented a high correlation with DPPH free radical scavenging activity (r=0.7486) and positive correlation with red colour percentage (R%).

2. High content of phenolic compounds of the analysed samples and their positive correlation with the free radical scavenging activity suggests that red wine is an excellent source of compounds with important benefits for human health.

3. Experimental data showed that intense red-coloured wines might be healthier due to their rich phenolic compounds composition which helps the body fight against damage caused by reactive oxygen species.

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