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Antioxidant constituents and antioxidant activity of some red wine and red table grape varieties, cultivated in different regions of Bulgaria

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Abstract

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Foods that have a positive effect on human health are becoming more and more popular nowadays. Such foods are the grapes - rich in phenolic compounds, which are known as very potent bio-antioxidants. This paper presented a research made for the first time- twelve red wine varieties (Rubin, Kaylashki Rubin, Storgozia, Mavrud, Nikopolski Mavrud, Melnik 55, Bouquet, Cabernet Sauvignon, Merlot, Syrah, Mourvedre and Malbec) and eight red table varieties (Velika, Dunav, Siyana, Hybrid V5-1, Muskat Hamburg, Moldova, Palieri and Black Pearl), cultivated in different regions of Bulgaria were tested for their antioxidant activity (AA) and contents of total phenols (TPC), *trans*-resveratrol (t-RVT) and quercetin (QU). In the grape skins the parameters ranged: t-RVT- from 2.05 ± 0.21 to 14.34 ± 1.35 and from 1.44 ± 0.17 to 23.71 ± 2.53 mg/kg FW; QU- from 0.27 ± 0.03 to 1.98 ± 0.18 and from 0.63 ± 0.07 to 2.12 ± 0.20 mg/kg FW; TPC – from 17 ± 2 to 371 ± 33 and from 21 ± 2 to 444 ± 43 mmol GAE/kg dm and AA – from 23.2 ± 1.9 to 59.9 ± 5.5 and from 32.4 ± 2.8 to 66.4 ± 6.3 mmol TE/kg dm for wine and table grapes, respectively. The table grape varieties had higher mean values of the parameters examined than the wine grape varieties. South Bulgaria have grape varieties with higher values of the antioxidant parameters with comparison to North Bulgaria. But, Danubian region, North Bulgaria, have wine and table grape varieties with very good antioxidant parameters and can‘t be ignored. The reason for this is the agrometeorological conditions. The correlations between the determined values were positive with very high correlation coefficients.

Keywords: wine grapes; table grapes; antioxidant activity; total phenols, *Trans*-resveratrol; quercetin

Introduction

Despite the ban by the European Commission in 2007 of using “superfoods” (a marketing term for food with supposed health benefits) in the labeling, foods that have a positive effect on animal and human health are becoming more and more popular nowadays. Such foods are these with antioxidant contents (Atanasov et al., 2017; Tzanova et al., 2017, 2018). Many plants and their products are rich in phenolic compounds, which are known as bio-antioxidants with high potential (Leifert et al., 2008; Garcia-Alonso et al., 2009; Flamini et al., 2013; Ongaratti et al., 2014). Small molecules of that kind, produced *de novo* by the grapes as protection in response to diverse biotic and abiotic factors, e.g. Bacteria, fungi and UV-irradiation, are *trans*-resveratrol and quercetin (Dixon, 2001). *Trans*-resveratrol belongs to the stilbenes polyphenol subgroup. This stilbene is alleged to be potentially responsible for the “French paradox” – the French suffer relatively seldom from cardio-vascular system disease, although their diet is rich in saturated fats (Kopp, 1998). Some selected natural and synthetic compounds are proven to work in synergy with *trans*-resveratrol. One of them is quercetin. It is categorized as flavonol, one of the six subclasses of flavonoid compounds. In addition, quercetin increases the protective effect of *trans*-resveratrol as powerful antioxidant (Mikstacka et al., 2010), an anti-inflammatory (Khandelwal et al., 2012), a cardiovascular (Pace-Asciak et al., 1995) and an anti-obesity agent (Arias et al., 2016).

It's long been known that *trans*-resveratrol is abundant in grape skin (Creasy & Coffee, 1988; Jiménez et al., 2007) and present in higher concentration in red grape varieties compared to white varieties (Sieman & Creasy, 1992; Gatto et al., 2008). The maceration is a very important stage in the red wine production. During maceration are extracted not only substances giving good organoleptic qualities, but also many bio-antioxidants. In this aspect, red grapes and red wines are the main dietary sources of *trans*-resveratrol (Burns et al., 2002).

Bulgarian table grapes and wines are presented on the international market for a long time, but the data about the antioxidant properties, content of phenols, *trans*-resveratrol and quercetin are deficient. The aim of the present study is to determine their content in some red wine and red table varieties, cultivated in different regions of Bulgaria.

Materials and Methods

Sampling

The grapes were grown in different viticulturally regions of Bulgaria (Tables 1 and 2). The regions provided good soil and climatic conditions to produce the general red wine and table grape varieties. During the vegetation season of 2017 no extreme climatic occurrences were observed.

Twelve wine grape varieties were included in the present study. Mavrud is an old local one. Rubin, Storgozia, Nikopolski Mavrud, Melnik 55 and Bouquet were created by the methods of intra- and interspecies hybridization. Cabernet Sauvignon, Merlot, Syrah, Mourvedre and Malbec were introduced varieties. Conventional methods of pest control were used during growing season, except for the Melnik 55 and Mavrud varieties which were grown organically.

The number of the tested red table grape varieties were eight (Table 2): Hybrid V5-1, Velika, Dunav and Siyana were created by the methods of interspecies hybridization. Black Muskat (Muskat Hamburg), Moldova, Palieri and Black Pearl (Perla nera) were introduced varieties. Conventional methods of pest control were used during growing season.

From every variety three representative sample were collected in the period from the middle of August to the beginning of October at the moment of reaching consumption

Table 1. Varieties and regions of tested red wine grapes

Region	Varieties	IN*	Location	Climatic conditions**
Danubian Plain (North-Bulgarian)	Merlot Cabernet Sauvignon Syrah Rubin Kaylashki Rubin Storgozia Bouquet	W1	Institute of viticulture and enology, the town of Pleven N: 43.407778° E: 24.620278°	See level: 116 m a.s.l. Moderate continental climate Time without freezing: 203 days Av. Jan. Temp.: -2.2°C Av. July Temp.: +23.0˚C Growing degree days: 3911°C
Rose Valley (Sub-Balkan mountain)	Merlot Mavrud Melnik 55 Bouquet	W2	Village of Elenovo, Nova Zagora municipality N: 42.366667° E: 26.15°	See level: 212 m a.s.l. Moderate continental climate Time without freezing: 229 days Av. Jan. temp.: +1.2°C Av. July tem.: +22.8°C Growing degree days: 3712°C
Thracian Lowland (South-Bulgarian Region)	Merlot Cabernet Sauvignon Syrah Mourvedre Malbec	W3.1	Village of Mogilovo, Chirpan municipality N: 42.333333° E: 25.4°	See level: 312 m a.s.l. Moderate continental climate Time without freezing: 194 days Av. Jan. Temp.: -0.8°C Av. July Temp.: +23.4°C Growing degree days: 3820°C
	Cabernet Sauvignon Nikopolski Mavrud	W3.2	Village of Kolyu Marinovo, Bratya Daskalovi municipality N: 42.383333° E: 25.166667°	See level: 403 m a.s.l. Continental climate Time without freezing: 194 days Av. Jan. Temp.: +1°C Av. July Tem.: +22°C Growing degree days: 3742°C

*Identification number of the region & location; **acc. weather maps, available at: www.meteoblue.com

Table 2. Varieties and regions of tested red table grapes

Region	Varieties	IN*	Location	Climatic conditions**
Danubian Plain (North-Bulgarian)	Black Muskat/ Muskat Hamburg Moldova Hybrid V5-1	T1	Institute of viticulture and enology, the town of Pleven N: 43.407778° E: 24.620278°	See level: 116 m a.s.l. Moderate continental climate Time without freezing: 287 days Av. Jan. Temp.: -2°C Av. July Temp.: +24.5˚C Growing degree days: 3911°C
Rose Valley (Sub-Balkan mountain)	Black Muskat/ Muskat Hamburg Palieri Black Pearl/ Perla nera Moldova Velika Dunav Siyana	T2	Village of Topolchane, Sliven municipality N: 42.65° E: 26.43333°	See level: 165 m a.s.l. Intermediate continental climate Time without freezing: 289 days Av. Jan. Temp.: +1.4°C Av. July Temp.: +23.6°C Growing degree days: 3167°C
Thracian Lowland (South-Bulgarian Region)	Velika	T3	Village of Nayden Gerovo, Saedinenie municipality N: 42.35° E: 24.483333°	See level: 263 m a.s.l. Intermediate continental climate Time without freezing: 286 days Av. Jan. Temp.: -1.5°C Av. July Temp.: +23.5°C Growing degree days: 3290°C

*Identification number of the region & location;
**acc. weather maps, available at: www.meteoblue.com

ripeness (for the table grapes) and from the middle of September to the beginning of October in 2017 at the moment of reaching technological maturity (for the wine grapes). Small portions of the base, middle and top of the grape cluster, located at the base, middle and top of the vine were been picked (Katerov et al., 1990). Grapes free from visible blemish or disease were selected. Every sample consisted of 3 - 5 kg of grape berries. After sampling the grapes were peeled and immediately frozen, transported in refrigerator and stored for a maximum of 7 days at -12°C prior to the analysis.

Extraction

The procedure of extraction, described by Tzanova & Peeva (2018) was applied to prepare the samples for determination of *trans*-resveratrol (t-RVT), quercetin (QU), total phenolic content (TPC) and antioxidant activity (AA). Briefly, the frozen grape skins were thawed at room temperature, 10 g were weighed to the nearest ± 0.0001 g, and homogenized with mechanical tissue homogenizer in 60 ml 1% HCl in methanol for 5 min protected from light. The suspended samples were left in darkness at room temperature overnight and then filtered through a 0.45 μm membrane. The filters were rinsed twice with 10 ml solvent mix. The extracts were collected and adjusted to 100 ml with 1% HCl in methanol. The methanol extracts were stored overnight at -12°C prior to the HPLC analysis. A small quantity of each extract was transferred into a screw capped vial and placed in the HPLC system auto sampler.

Quantification of trans-resveratrol and quercetin

The quantification of t-RVT and QU was carried out using the HPLC method developed by Tzanova & Peeva (2018). Thermo HPLC with a C18 column Hypersil Gold (5µm; 150 mm × 4.6 mm) system composed of a Surveyor LC Pump Plus, Surveyor Autosampler Plus, and Surveyor photodiode array detector PDA Plus was used. Typical chromatogram of sample solution was presented in Figure 1. The concentrations of the analytes were expressed as mg/kg fresh material (FM).

TPC determination

The determination of total phenol content (TPC) was carried out by using Folin method (Anesini et al., 2008) applied

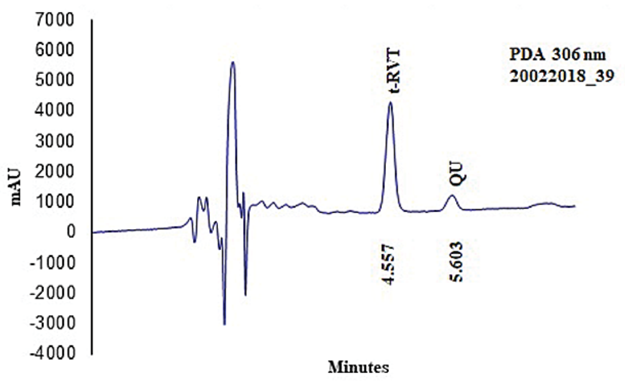

Figure 1. Typical chromatogram of sample solution of grape skin extract

to the methanol grape extracts with final concentration of 1 mg/ml DM. Each sample was analyzed in triplicate. Gallic acid (Sigma-Aldrich, St. Louis, MO) solutions in methanol ranging from 10 to 100 µg/ml were used for calibration curve ($R^2 = 0.9991$). TPC of each sample was expressed as mmol gallic acid equivalents (GAE) in 1 kg dry matter (DM) of the starting material.

Determination of antioxidant activity by DPPH method

Antioxidant activity (AA) was quantitatively assessed by measuring of the radical scavenging potential of the extract by the DPPH method. The method described by Serpen *et al.* (2007) was applied to measure the radical scavenging potential of the prepared methanolic grape extracts with final concentration of 1 mg/ml DM. The results for the radical scavenging capacity were compared with that of Trolox and calculated by regression analysis from the linear dependence between concentration of Trolox solution in methanol, ranging from 2 to 60 µmol/l ($R^2 = 0.9994$), and absorption at 517 nm. Trolox standard was purchased from Sigma-Aldrich (St. Louis, MO). The results were expressed as mmol Trolox equivalent (TE) in 1 kg DM of the starting material.

Statistical analysis

The statistical analysis was performed using Statistica 6 for Windows. All analytical determinations were performed in triplicate and the mean values ± standard deviation (SD) was reported. Tukey post-hoc multi comparison tests and Pearson regression were used for data analysis. Pirouette 4.5 software (Infometrix, Woodinville, WA) was used for Principal Component Analysis (PCA).

Results and Discussion

The results obtained for the red wine and red table grape varieties tested in this study were presented in Tables 3 and 4, respectively.

Antioxidant constituents and activity of wine grape varieties

The attractive compound, *trans*-resveratrol, in the skins of red wine grapes ranged from 2.05 ± 0.21 mg/kg FM to 14.34 ± 1.35 mg/kg FM (Table 3). The superior variety was Malbec (t-RVT content 14.34 ± 1.35 mg/kg FW) from W3.1 region, followed by Syrah (t-RVT content 13.77 ± 1.42 mg/kg FW) from W3.1 region; Mavrud (t-RVT content 12.58

Table 3. Content of trans-resveratrol (RVT); of quercetin (QU); of total phenols (as GAE) and antioxidant potential (as TE) of wine grape varieties, produced in Bulgaria (vintage 2017)

Variety	IN	t-RVT mg/kg FM	QU mg/kg FM	mmol GAE eq/ kg dm	mmol TE/kg dm
Mavrud	W2	12.58 ± 1.88	1.98 ± 0.18	300 ± 29	53.9 ± 4.8
Nikopolski Mavrud	W3.2	8.54 ± 0.79	0.48 ± 0.05	129 ± 11	48.6 ± 3.5
Melnik 55	W2	4.42 ± 0.26	0.32 ± 0.04	41 ± 5	36.3 ± 2.6
Merlot	W1	3.77 ± 0.35	0.62 ± 0.06	81 ± 7	36.4 ± 3.2
	W2	2.31 ± 0.17	0.62 ± 0.07	18 ± 2	23.2 ± 1.9
	W3.1	3.92 ± 0.25	0.81 ± 0.08	46 ± 5	37.7 ± 2.4
Cabernet Sauvignon	W1	2.05 ± 0.21	0.67 ± 0.06	17 ± 2	24.1 ± 2.0
	W3.1	2.52 ± 0.18	0.75 ± 0.09	44 ± 5	25.4 ± 2.1
	W3.2	3.97 ± 0.40	0.82 ± 0.08	118 ± 13	41.4 ± 3.9
Syrah	W1	9.96 ± 0.95	0.84 ± 0.09	114 ± 10	42.2 ± 4.1
	W3.1	13.77 ± 1.42	1.24 ± 0.11	218 ± 19	59.9 ± 5.5
Bouquet	W1	8.94 ± 0.91	0.59 ± 0.06	96 ± 8	49.4 ± 4.5
	W2	10.4 ± 1.07	1.55 ± 1.47	192 ± 18	53.7 ± 4.8
Malbec	W3.1	14.34 ± 1.35	1.85 ± 0.17	250 ± 22	58.0 ± 5.3
Mourvedre	W3.1	3.82 ± 0.32	0.44 ± 0.05	136 ± 15	36.5 ± 3.3
Kaylashki Rubin	W1	3.59 ± 0.31	0.27 ± 0.03	20 ± 3	37.1 ± 3.5
Rubin	W1	12.29 ± 1.20	1.45 ± 0.13	371 ± 33	57.8 ± 6.0
Storgozia	W1	2.34 ± 0.19	0.68 ± 0.07	22 ± 2	35.6 ± 3.4
Mean value		6.84	0.89	123	42.1
SD		4.39	0.51	105	11.7
t- value		6.61	7.38	4.96	15.23
p- value		< 0.01	< 0.01	< 0.01	< 0.01

Table 4. Loadings of calculated PCA of the wine and table grape varieties.

Values	Factor 1 (99.9%)	Factor 2 (0.1%)	Factor 3 (0.0%)	Factor 4 (0.0%)	Factor 5 (0.0%)
t-RVT	0.002286	0.043739	0.211311	**0.976334**	-0.014194
QU	0.000301	0.004170	0.015835	0.010921	**0.999806**
mmol GAE/kg	0.042850	**0.993625**	-0.101769	-0.022621	-0.002299
mmol TE/kg	0.012342	0.094095	**0.971943**	-0.214800	-0.013444
Growing degree days	**0.999003**	-0.043883	-0.008132	0.001389	0.000034

± 1.88 mg/kg FW) from W2 region and Kaylashki Rubin (t-RVT content 12.29 ± 1.20 mg/kg FW) from W1 region. So, the best wine grape variety was an introduced one, but the following varieties had very close values in this respect.

The main factors influencing the synthesis and accumulation of t-RVT were already specified: varieties (Pascual-Marti et al., 2001; Bavaresco et al.; 2007a; Gatto et al., 2008; Vincenzi et al., 2013) and variety clones (Gatti et al., 2014); regions, terroir (Gatto et al., 2008) and fungal infection (Šubíková, 1991). Okuda & Yokotsuka (1996) studied a large number of grape varieties, grown in Japan. The concentration of t-RVT in the grape skins ranged from 0.5 to 14.1 mg/kg FM, with an average concentration of 4.12 mg/kg of FM. The authors found values that did not differ significantly from those in the literature referring to other regions of grape and wine production in the world. So, compared to these results, the tested red wine grape varieties grown in Bulgaria, contained similar or higher t-RVT concentration.

A number of authors confirmed that more disease-resistant genotypes were characterized by a higher content of stilbene than the sensitive ones (Creasy & Coffee, 1998; Jeandet et al., 1991; Romero-Perez et al., 2001; Bavaresco, 2003; Li et al., 2003). In this study the superior wine grape variety, Malbec, isn't resistant to disease. So, other factors, like soil, climate and technological practice had a positive impact on the stilbene synthetase (STS) activity. Bouquet also isn't resistant against fungal disease and had relative high t-RVT content (8.94 ± 0.91 mg/kg FM from W1 region and 10.4 ± 1.07 mg/kg FM from W2 region). Bouquet is a hybrid variety of Mavrud vs. Pinot Noir, and Mavrud variety is characterized by high STS expression. So, the variety clone was crucial factor for the t-RVT synthesis. Haygarov et al. (2017) determined t-RVT content in the pomace from some local grape varieties, cultivated in Danubian plain, Pleven, Bulgaria (matching W1 region in the present study). Among the selected varieties were Storgozia, Rubin, Kaylashki Rubin and Bouquet. The stilbene concentration found by the authors decreased in the given order- from 2.41 mg/l (Rubin) to 1.14 mg/l (Bouquet). In the present study the t-RVT content in the grape skins decreased in the following order: Rubin, Bouquet, Kaylashki Rubin and Storgozia varieties. Videnova published (2016) data from the study of the *trans*-resveratrol content in juice obtained from different white and red grape varieties (vintage 2013) from Bulgaria without maceration. Among the tested varieties were Melnik 55 and Mavrud, and according to the results Melnik 55 had a higher t-RVT content than Mavrud grapes.

Great attention was devoted worldwide to the varieties Syrah, Merlot and Cabernet Sauvignon. However, the results reported in the scientific literature were ambivalent. Regarding the t-RVT content, Syrah was often the prefered one of the tested wine grape varieties (Hui, 2007; Brill, 2013; Peeva et al., 2017). Most researchers found higher amounts of *trans*-resveratrol in Merlot than in Cabernet Sauvignon grapes without considering any other parameters (Romero-Perez et al., 2001; Vincenzi et al., 2013; Zhu et al., 2012; Du et al., 2012; Geana et al., 2015; Yaman et al., 2016). Rockenbach et al. reported (2011) higher t-RVT and QU content in Merlot grape pomace, but higher TPC and greater radical scavenging activity of Cabernet Sauvignon grape pomace, varieties "widely produced in Brazil". Zhu et al. (2012) found higher stilbene content in Merlot grape skins than in Cabernet Sauvignon from East Asian and North American regions, but the second variety was characterized by larger TPC in its grape skins. Iacopini et al. (2008) tested seven grape varieties from Italia and reported higher t-RVT and TPC content in Cabernet Sauvignon than in Merlot grape skins, and QU content values were similar – around 0.6 - 0.7 mg/kg FW. So, the results obtained in the present study confirm this conclusion: Syrah demonstrated very high t-RVT concentration levels, and Merlot - higher than Cabernet Sauvignon from the same region. For example, for W3.1 region, Syrah had 13.77 ± 1.42, Merlot - 3.92 ± 0.25 and Cabernet Sauvignon – 2.52 ± 0.18 mg/kg FW. The QU were similar, and the TPC assayed as mg GAE/kg dm differed greatly in one and the same wine region, W1: 114 ± 10 (Syrah); 81 ± 7 (Merlot) and 14 ± 2 (Cabernet Sauvignon).

In relation to content of antioxidant compounds, when compared the North to the South Bulgarian wine grape regions, the South Bulgarian were superior, especially Thracian Lowland, W3.1 region, which had the best introduced wine grape varieties; and W2 region in Rose Valley that had the best local wine grape variety (Table 3). An important factor is agrometeorological conditions and often the climate was the key factor (Bavaresco et al., 2007a). Therefore, the geographical position of the vineyard and the meteorological indication at the exact time of the specified location must be indicated (Goldberg et al., 1995; Goldberg et al., 1996). The temperature conditions during ripening period is also of great importance (Bertamini & Mattivi 1999; Li et al., 2006; Bavaresco et al., 2007b). The correlation between t-RVT contents and temperature levels during ripening was confirmed to be inverse. So, that could probably explain the differences between the North and the South regions: the W1 region was characterized by 3911˚C growing degree days, compared to 3712 ˚C growing degree days of W2 region and to 3820 ˚C growing degree days of W3.1 region, where the t-RVT concentration levels determined were higher (Tables 1).

According to principal component analysis (PCA), the major component (Factor 1) was mainly determined by the value of growing degree days, and described 99.9% of the variation (Table 4). The most important parameter for the second PC is GAE, for the third - TE, for the fourth - t-RVT and for the fifth – QU. The results obtained by the PCA separated the tested wine grape varieties into 2 groups (Figure 2).

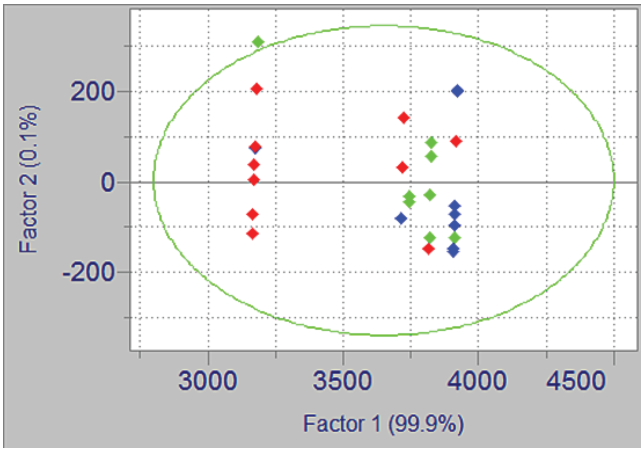

Figure 2. PCA 2D scores plot
(Red – Region 2, Blue – Region 1, Green – Region 3)

The results obtained in this study confirmed the results obtained by other researchers: the accumulation of *trans*-resveratrol in the skin of red grapes is higher than that of quercetin (Careri et al., 2003; Iacopini et al., 2008). QU content in the grape skins ranged from 0.27 ± 0.03 mg/kg FW (Rubin, from W1 region) to 1.98 ± 0.18 mg/kg FW (Mavrud from W2 region). The fact that the production of resveratrol is inversely related to anthocyanin (including quercetin) biosynthesis in grape berries, has been known for a long time. Jeandet et al. (1995) investigated the accumulation of resveratrol and common anthocyanin in the skin of the grapes during the maturation period. They found immature clusters showed t-RVT production capacity much greater than that of fruits harvested in technological maturity. Data on the correlation between t-RVT and QU accumulation in grape skins is scarce, especially regarding the varieties grown in Bulgaria. Tzanova & Peeva (2018) tested red grape varieties vintage 2016 and found a positive correlation between the t-RVT and QU concentration levels in the skins. The authors determined 4-fold higher t-RVT concentration in Rubin than Storgozia grape skins (compared to the present study- 6-fold higher concentration in favor of Rubin) and quercetin in amounts of 0.72 ±0.08 mg/kg and 0.85 ±0.06 mg/kg in Rubin and Storgozia, respectively.

Data about total phenolic compounds in wine grape varieties grown in Bulgaria are scarce. In the present study TPC in the grape skins ranged from 17 ± 2 mmol GAE/kg dm (Merlot from W1) to 371 ± 33 mmol GAE/kg dm (Kaylashki Rubin from W1). So, the superior variety regarding TPC was found to be a wine grape variety from North Bulgarian region.

The antioxidant activity established as radical scavenging capacity ranged from 23.2 ± 1.9 mmol TE/kg dm (Merlot from W2 region) to 59.9 ± 5.5 mmol TE/kg dm (Syrah from W3.1 region). Once again superior was an introduced variety from South Bulgarian region, W3.1.

In the present study, the correlation between *trans*-resveratrol and quercetin content was found to be positive, as well as their relationship to the antioxidant activity, measured by DPPH method. The correlation coefficients were found to be very high: for the influence of t-RVT, QU and TPC on the radical scavenging activity - 0.9166; 0.9615; 0.9634, respectively (Figure 3, panel A).

Antioxidant constituents and activity of table grape varieties

The table grape varieties were less studied in respect to antioxidants content. The results obtained by studying the selected table grape varieties were presented in Table 5.

The table grape varieties tested in the present study had higher mean t-RVT content than the wine grape varieties. The superior table variety is Velika with t-RVT content of 23.71 ± 2.53 mg/kg FW from T3 region, followed by Hybride V 5-1 (17.55 ± 1.85 mg/kg FW) from T1 region and Palieri (15.46 ± 1.62 mg/kg FW) from T2 region. The quercetin amount in the grape skins ranged from 0.63 ± 0.07 mg/kg FW (Dunav from T2 region) to 2.12 ± 0.20 mg/kg FW (Palieri from T2 region) and TPC –from 21 ± 2 mmol GAE/kg dm (Dunav from T2 region) to 444 ± 43 mmol GAE/kg dm (Velika from T3 region). The antioxidant activity as radical scavenging activity were from 32.4 ± 2.8 mmol TE/kg dm (Dunav from

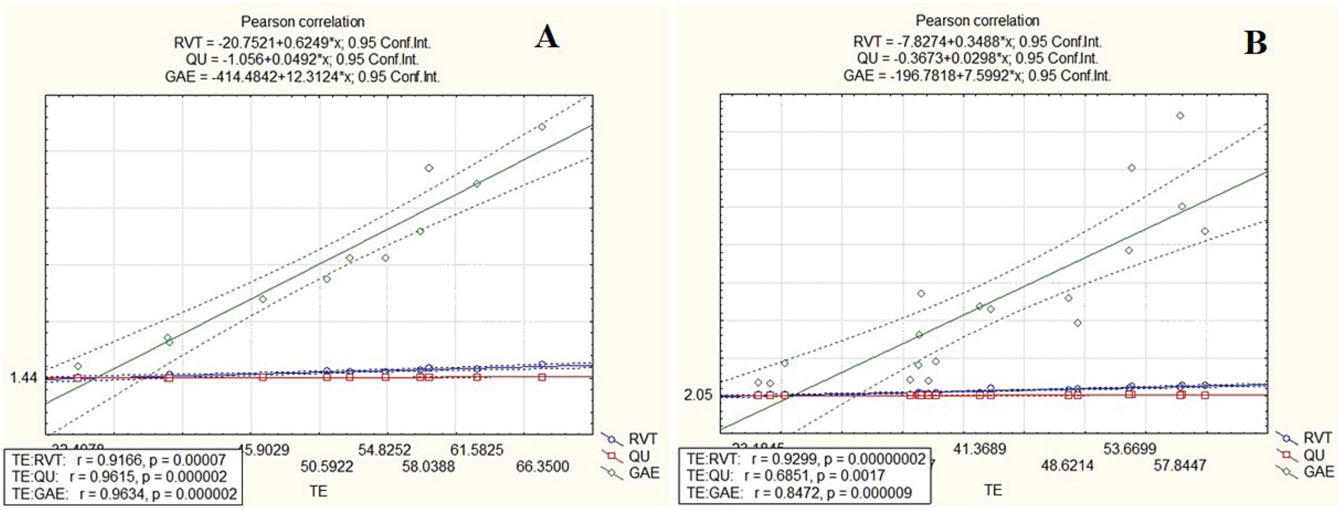

Figure 3. Pearson correlation between total phenol, trans-resveratrol and quercetin contents in wine (panel A) and table (panel B) grapes varieties, P ≤ 0.01 (2-tailed).

T2 region) to 66.4 ± 6.3 mmol TE/kg dm (Velika from T3 region). So, the best table grape variety in relation to the antioxidant properties, was Velika from T3 region.

In literature, the data were usually vary widely. For example, Costa et al. (2014) tested 24 grape varieties cultivated in two Portuguese wine regions and determined TPC from 1.78 ± 0.01 to 299.99 ± 5.04 mmol/kg dm. Du et al. (2012) compared wine grape and table grape varieties by TPC and radical scavenging capacity and concluded the tested wine grapes showed larger phenolic content and higher antioxidant activity than the table grapes studied.

The correlations between AA and t-RVT; between AA and QU; between AA and TPC of the tested red table grape varieties were positive with very high correlation coefficients: for the influence of t-RVT, QU and TPC on the radical scavenging activity they were 0.9299; 0.6851; 0.8472, respectively (Figure 4, panel B). The value of coefficient of correlation between AA and t-RVT was higher than the same between AA and QU, so the contribution of *trans*-resveratrol to the antioxidant activity was bigger than that of QU.

Babrikov et al. (2010) determined TPC and antioxidant activity by DPPH method of grape skin extracts from some

Table 5. Content of *trans*-resveratrol (RVT); of quercetin (QU); of total phenols (as GAE) and antioxidant potential (as TE) of table grape varieties, produced in Bulgaria (vintage 2017)

Variety	IN	t-RVT mg/kg FM	QU mg/kg FM	mmol GAE eq/ kg dm	mmol TE/kg dm
Black Muskat/ Muskat Hamburg	T1	1.44 ± 0.17	0.63 ± 0.06	72 ± 7	38.9 ± 3.7
	T2	1.95 ± 0.21	1.20 ± 0.11	139 ± 15	45.9 ± 4.4
Velika	T2	11.90 ± 1.22	1.66 ± 0.18	212 ± 20	54.8 ± 5.5
	T3	23.71 ± 2.53	1.93 ± 0.19	444 ± 43	66.4 ± 6.2
Dunav	T2	1.56 ± 0.17	0.63 ± 0.07	21 ± 2	32.4 ± 2.8
Moldova	T1	12.12 ± 1.26	1.45 ± 0.15	211 ± 22	52.21 ± 5.1
	T2	14.21 ± 1.45	1.92 ± 0.20	258 ± 25	57.5 ± 5.5
Siyana	T2	12.95 ± 1.31	1.61 ± 0.17	174 ± 17	50.6 ± 4.9
Black Pearl/ Perla nera	T2	7.13 0.80	0.82 ± 0.08	63 ± 7	39.1 ± 3.7
Palieri	T2	15.46 ± 1.62	2.12 ± 0.20	342 ± 35	61.6 ± 5.8
Hybrid V 5-1	T1	17.55 ± 1.85	1.83 ± 0.18	369 ± 36	58.0 ± 5.3
Mean value		10.91	1.44	209	50.7
SD		7.20	0.54	135	10.5
t- value		5.02	8.82	5.14	15.9
p- value		< 0.01	< 0.01	< 0.01	< 0.01

table grape varieties, cultivated in Bulgaria, including Palieri. The highest total phenolic compound and antiradical activity were established for Palieri variety - 8540 mg GAE / kg FM (equivalent to 50.2 mmol GAE / kg) dm and 10.5 mmol TE / kg FM. In the present study among the tested table grape varieties from one and the same region - T2, Palieri had the highest TPC and AA levels – 342 ± 35 mmol GAE / kg dm and 61.6 ± 5.8 mmolTE / kg dm, respectively.

Taking into account the influences of the value - growing degree days, the results obtained by the PCA separated the tested table grape varieties into 2 groups (Figure 2).

Conclusion

For the first time such an extensive research was made on the red wine grape and red table grape varieties, cultivated in different Bulgarian regions. Based on the results obtained in the present study, the main conclusions that could be drown were:

The table grape varieties had higher mean t-RVT content and AA than the wine grape varieties.

When we compare the North to the South Bulgarian viticultural regions, the South Bulgarian is superior. There are cultivated the best introduced wine grape varieties and the best local wine grape variety. But Dunabian region in North Bulgaria, has wine (e.g. Kaylashki Rubin) and table grape (e.g. Hybrid V5-1) varieties with very good antioxidant parameters and is not to be ignored. This was in relation to the agrometeorological conditions and the 'growing degree days' values had strong influence.

The correlations between the tested antioxidant parameters were positive with very high correlation coefficients. The contribution of *trans*-resveratrol to the antioxidant activity was greater than those of quercetin, especially according to the table grape varieties.

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