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Original article

Aromatic Profile of Grapes from White and Red Varieties[1]

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Abstract

The aromatic composition of grapes from the white varieties Dimyat clone 6/46, Aligote clone 4/10, Muscat Ottonel clone 7/46, Misket Vrachanski clone 9/5, Plevenska Rosa and the red varieties Pamid clone 5/76, Gamza clone 52-9-4, Gamza clone 52-9-5, Kaylashki Rubin, grown in the soil and climatic conditions of Pleven, Central Northern Bulgaria was studied. Twenty-one flavor-determining components influencing the aromatic profile of the wine (9 esters, 7 terpenes and 5 higher alcohols) were identified. The number of the analyzed groups of compounds was the greatest in the white aromatic varieties (Muscat Ottonel, Misket Vrachanski, Plevenska Rosa), being their specific feature. The content of esters in white and red varieties was similar, unlike the terpenes and the higher alcohols, the sum of which was higher in the white ones. In the experimental samples the quantity of esters was prevailing with the highest concentration of ethyl butanoate, diethyl succinate, ethyl decanoate. The 2-phenylacetate content was the lowest. From the terpenes group, in the white varieties the representatives of linalool, nerol and geraniol predominated qualitatively, while in the red ones linalool and the isomers of linalool oxide were prevailing. From the identified higher alcohols the highest concentrations found were of 3-methyl-1-butanol and 2-methyl-1-butanol.

Keywords: Grapes, Gas chromatography, Esters, Terpenes, Higher alcohols.

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INTRODUCTION

Wine has a complex and diverse chemical composition, as the aroma is the most important for its quality and characteristics. It has a composite nature being the combination of a large number of volatile organic compounds in different concentrations. The volatile substances forming the wine aroma are of various origins and evolve through the wine making stages. Many of them pass from the grapes, where they are synthesized during the ripening and are modified in the vinification process. Others are the product of the yeast metabolism, produced during the alcohol fermentation and form the so-called fermentative aroma (Lengyel and Panaitescu, 2017). Throughout the wine aging and maturing, as a result of ongoing biochemical reactions, a large number of compounds defining its “bouquet” are formed.

Not all volatile compounds contribute equally to the wine aroma. That depends on their quantity and threshold concentration. The content of esters, aldehydes, higher alcohols and terpenes is the highest. Fatty acids, norisoprenoids, volatile phenols and benzenoids also participate in lower concentrations (Ilc et al., 2016; Slegers et al., 2017).

The esters and terpenes are the most important for the aromatic composition of wines. The esters are formed as a result of ongoing esterification processes during the grapes ripening and through almost all stages of the technological process. They have low thresholds of perception and various aromatic nuances (Tao and Li, 2009). The aldehydes and the higher alcohols are mainly the product of the yeast metabolism and in high concentrations adversely affect the wine aromatic profile. The majority of the terpenes come from the grapes and have a decisive role in forming the floral aroma of the Muscat varieties. The prevailing terpene alcohols are α-terpineol, linalool, nerol, geraniol, β-citronelol (Chobanova, 2012; Blagoeva et al., 2016).

The ratio of the individual aromatic components in the grapes and the wine, respectively, is individual and characteristic of each variety. For example, in wines from the red variety Stanushina, Nedelkovski et al. (2017) determined 19 aromatic substances, identifying 5 alcohols, 11 esters, 1 terpene, 1 furan, and 1 fatty acid. Ilc et al. (2016) investigated 141 volatile components in grapes and wine from different varieties and compared quantitatively 43 of them. Slegers et al. (2017) specified the content of 40 aromatic compounds in white wines from interspecies hybrid varieties.

Certain conditions – natural and technological also have an impact on the aromatic composition of grapes and wines. Ponts et al. (2017) pointed out the importance of the environmental factors and climate changes on vine physiology, the grape ripening process and the formation of flavoring components and their predecessors. Wine-making technology also uses a variety of practices such as grape must maceration and aromatic enzymes to enhance the varietal aroma of the final product (Blagoeva et al., 2013). The enzyme systems with β-glucosidase activity degrade the glycosidic bonds in the molecules of the non-volatile aroma precursors. That determined them as “aroma-releasing” and their use increase the concentration of free and linked terpenes in must (Codresi et al., 2012 [1, 2], Lengyel et al., 2013).

The objective of this study was to investigate the aromatic composition of grapes of 5 white and 4 red varieties grown in the soil and climatic conditions of the Pleven region, Central Northern Bulgaria.

Material and Methods

The study was carried out at the Institute of Viticulture and Enology (IVE) – Pleven, Central Northern Bulgaria. The region is characterized by a typical continental climate, and the soils include all types of chernozems. The object of the study was the grapes, 2013 vintage, from the white varieties Dimyat clone 6/46, Aligote clone 4/10, Muscat Ottonel clone 7/46, Misket Vrachanski clone 9/5, Plevenska Rosa and the red varieties Pamid clone 5/76, Gamza clone 52-9-4, Gamza clone 52-9-5, Kaylashki Rubin. Plevenska Rosa and Kaylashki Rubin varieties have been selected by interspecific hybridization and are characterized by increased resistance to diseases and low winter temperatures.

The plantations of the studied varieties were fruit-bearing, grown at the Institute’s Experimental Base. Every year in the period March–April the necessary agricultural procedures were carried out for vine pruning and loading. In August–September, the grapes ripening dynamics was monitored. The grapes were picked up at the time of the technological maturity. The raw material was processed at the Experimental Winery in accordance with the classic practice for the production of white and red wines under micro-vinification conditions (Yankov, 1992). After crushing the grapes, the must was clarified by sulphiting (50 mg/dm^3 SO_2) and the main chemical indicators were analyzed.

The must composition from the studied varieties and clones was determined according to the generally accepted methods in wine-making practice (Ivanov et al., 1979):

sugars, g/dm^3 – areometer of Dujardin;

glucose, g/dm^3 – iodometric method;

fructose, g/dm^3 – calculation method;

titratable acids, g/dm^3 – titration with NaOH;

pH - pH-meter;

glucoacidometric index (GAI) – calculation method as the ratio of sugars (%) and titratable acids (g/dm^3).

An identification and quantification of 21 flavor-determining compounds (9 esters, 7 terpenes and 5 higher alcohols) in the grape juice was made by means of a gas chromatograph with a mass spectrometer.

The samples preparation for analysis was as follows: 100 µl of BC (internal standard, 3-octanol, 50 mg/L) was added to 5 ml of grape must. The resulting mixture was subjected to liquid-liquid extraction (10 min in ultrasonic bath at T=°C) with dichloromethane (3 x 5 ml). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to dryness in vacuum.

The aroma components in the tested samples were determined by GC-MS analysis. The samples were injected into a system consisting of Agilent GC 7890 gas chromatograph and Agilent MD 5975 mass spectrometer. HP-5MS column was used with parameters: length 30 m, diameter 0.32 mm, and film thickness 0.25 µm with the following temperature program: initial temperature 40°C for 4 min, increase to 250°C with 5°C/min, holding 10 min; injector and detector temperatures 250°C; gas-carrier helium at a flow rate of 1.0 ml/min; scanning range of the mass spectrometer m/z = 39-400; sample injection volume of 1 µl in splitless mode. The compounds were identified by comparing the relative indices per Kovacs (RI) with mass spectral data from the NIST 08 library (Kovacs et al., 1999).

Results and Discussion

In 2013, the weather conditions (hot summer without precipitation) favoured the normal ripening process, the good sugar accumulation and the sanitary status of the grapes from the studied varieties and clones. It had an optimal composition for obtaining high quality wines (Table 1). Under the conditions of cultivation in the region of Pleven the white varieties, Plevenska Rosa and Muscat Ottonel 5/76 were the earliest ripening, and Dimyat 6/46 – the latest. The red varieties matured approximately in the same period, as Kaylashki Rubin was the latest ripening.

Table 1. Grapes chemical composition from the studied varieties and clones

Variety, Clone	Date of harvest	Sugars, g/dm^3	Glucose, g/dm^3	Fructose, g/dm^3	Titratable acids g/dm^3	GAI	pH
White varieties							
Dimyat clone 6/46	23th September	184.00	88.80	95.20	6.58	3.18	3.27
Aligote clone 4/10	11th September	212.00	98.00	114.00	6.08	3.32	3.24
Muscat Ottonel clone 7/46	29th August	198.00	82.00	116.00	5.76	3.44	3.26
Misket Vrachanski clone 9/5	16th September	198.00	84.80	113.20	5.73	3.46	3.26
Plevenska Rosa	29th August	213.00	93.00	120.00	5.88	3.62	3.25
Red varieties							
Pamid clone 5/76	13th September	186.00	75.00	111.30	5.24	3.44	3.19
Gamza clone 52-9-4	19th September	219.00	92.10	126.90	5.50	3.98	3.24
Gamza clone 52-9-5	19th September	222.00	82.54	139.46	6.00	3.70	3.21
Kaylashki Rubin	25th September	262.00	121.35	140.65	5.85	4.47	3.27

From the studied white varieties and clones, the highest sugar rates were recorded in Aligote 4/10 (212.00 g/dm^3) and Plevenska Rosa (213.00 g/dm^3), and the lowest in Dimyat 6/46 (184.00 g/dm^3). The content of monosaccharides – glucose and fructose was also identified in the grape juice. Their ratio was less than 1, with fructose predominance. The titratable acids were in the range from 5.73 to 6.58 g/dm^3, as they were lower in the aromatic varieties Muscat Ottonel 7/46, Misket Vrachanski 9/5 and Plevenska Rosa, that was their varietal feature.

The grapes sugar content from the red varieties varied from 186.00 g/dm^3 (Pamid 5/76) to 262.00 g/dm^3 (Kaylashki Rubin). In all samples the monosaccharide fructose was prevailing in quantity. The titratable acids were within the typical range for the relevant variety. Pamid 5/76 grapes had the lowest sugars ratio and acidity that was specified by its varietal potential.

On the basis of the sugars and titratable acids ratio in the grapes from the studied varieties and clones, their GAI was also determined, which was indicative of the raw material quality. The calculated rates were higher than 3, as in Kaylashki Rubin they were as high as 4.47. It was a proof that grapes were suitable for making white and red wines of optimal quality with regard to their chemical composition and organoleptic features. The recorded pH rates in the grape juice were within the normal range for the studied varieties and corresponded to the found acid content.

Identification and quantification of the aromatic compounds in the grape must from the studied varieties and clones was made. Twenty-one components influencing the aromatic profile of the wine were found: 9 esters (ethyl acetate, ethyl lactate, ethyl butanoate, isoamyl acetate, ethyl hexanoate, diethyl succinate, ethyl octanoate, 2-phenylacetate, ethyl decanoate), 7 terpenes (trans (E)-linalool oxide, cis (Z)-linalool oxide, linalool, α-terpineol, citronelol, nerol, geraniol) and 5 higher alcohols (butanol, 3-methyl-1-butanol, 2-methyl-1-butanol, 2-phenylethanol, 1-hexanol).

The aromatic profile of the must from the studied varieties and clones is presented in Table 2, Table 3, Figures 1-4.

Table 2. Grapes aromatic profile from the studied white varieties and clones

	Dimyat clone 6/46	Aligote clone 4/10	Muscat Ottonel clone 7/46	Misket Vrachanski clone 9/5	Plevenska Rosa
Esters, mg/dm³					
Ethyl acetate	0.166	0.156	0.204	0.208	0.191
Ethyl lactate	0.217	0.178	0.245	0.252	0.213
Ethyl butanoate	0.301	0.332	0.368	0.382	0.374
Isoamyl acetate	0.109	0.118	0.143	0.157	0.150
Ethyl hexanoate	0.155	0.188	0.203	0.221	0.210
Diethyl succinate	0.335	0.353	0.388	0.402	0.398
Ethyl octanoate	0.117	0.126	0.138	0.142	0.140
2-phenylacetate	0.102	0.114	0.126	0.129	0.127
Ethyl decanoate	0.335	0.401	0.516	0.534	0.468
Amount Esters	**1.837**	**1.966**	**2.331**	**2.427**	**2.271**
Terpenes, mg/dm³					
trans (E) - linalool oxide	0.045	0.053	0.059	0.061	0.060
cis (Z)-linalool oxide	0.042	0.047	0.055	0.057	0.059
Linalool	0.124	0.145	0.181	0.199	0.184
α-terpineol	0.014	0.017	0.019	0.021	0.021
Citronelol	0.086	0.088	0.091	0.094	0.093
Nerol	0.101	0.103	0.109	0.114	0.112
Geraniol	0.103	0.105	0.117	0.121	0.122
Amount Terpenes	**0.515**	**0.558**	**0.631**	**0.667**	**0.651**
Higher alcohols, mg/dm³					
Butanol	0.015	0.017	0.020	0.022	0.021
3-methyl-1-butanol	0.257	0.260	0.265	0.270	0.268
2-methyl-1-butanol	0.278	0.280	0.285	0.288	0.287
2-phenylethanol	0.192	0.195	0.200	0.202	0.201
1-hexanol	0.141	0.145	0.148	0.150	0.149
Amount Higher alcohols	**0.883**	**0.897**	**0.918**	**0.932**	**0.926**

From the data presented in Table 2, it could be seen that in the musts of the studied white varieties and clones, the esters quantitatively predominate. In wine they are formed chemically and biologically, but their quantity in grapes was determined by the esterification processes occurring during ripening and the factors influencing it. The highest concentration observed was of ethyl decanoate, diethyl succinate. The lowest rate had 2-phenylacetate. The results revealed that the sum of esters in the aromatic varieties was significantly higher compared to the non-aromatic. It was found greater amount of nearly all identified esters in Muscat Ottonel 7/46, Misket Vrachanski 9/5 and Plevenska Rosa in comparison with Dimyat 6/46 and Aligote 4/10. Totally, Misket Vrachanski 9/5 must had the highest rate of esters (2.427 mg/dm^3), and the least – Dimyat 6/46 (1.837 mg/dm^3).

The next most important group of compounds determining the aromatic profile of must were terpenes, although their concentration in the tested samples was rather lower compared to the other identified components. In grapes from the aromatic varieties, the quantity of terpenes was significantly higher than in the non-aromatic ones. The reason was that the terpenes were namely the compounds determining the specific Muscat aroma. It was the most pronounced in Misket Vrachanski 9/5 variety that was also confirmed by the higher concentration of terpenes (0.667 mg/dm^3). The representatives of linalool, geraniol and nerol, which also had the most significant influence on the formation of the aromatic profile, were prevailing quantitatively in the grape juice of all white varieties.

The group of the higher alcohols was the smallest, with respect to the representatives identified in the study. The reason was that they were mainly a product of the yeast metabolism during the alcoholic fermentation and only small concentrations were contained in grapes. The tendency in the must of the aromatic varieties was repeated – their rate to be higher as the highest content was recorded again in Misket Vrachanski 9/5 (0.932 mg/dm^3). In all varieties, the highest concentrations found were of 2-methyl-1-butanol and 3-methyl-1-butanol. Only the butanol had some traces.

Table 3. Grapes aromatic profile from the studied red varieties and clones

	Pamid clone 5/76	Gamza clone 52-9-4	Gamza clone 52-9-5	Kaylashki Rubin
Esters, mg/dm^3				
Ethyl acetate	0.237	0.243	0.244	0.250
Ethyl lactate	0.228	0.230	0.232	0.241
Ethyl butanoate	0.414	0.420	0.426	0.437
Isoamyl acetate	0.169	0.177	0.179	0.180
Ethyl hexanoate	0.225	0.228	0.229	0.231
Diethyl succinate	0.455	0.463	0.464	0.471
Ethyl octanoate	0.150	0.153	0.154	0.157
2-phenylacetate	0.103	0.087	0.088	0.089
Ethyl decanoate	0.364	0.370	0.372	0.370
Amount Esters	**2.345**	**2.371**	**2.388**	**2.426**
Terpenes, mg/dm^3				
trans (E) - linalool oxide	0.017	0.015	0.015	0.014
cis (Z)-linalool oxide	0.018	0.017	0.017	0.016
Linalool	0.089	0.085	0.082	0.080
α-terpineol	0.009	0.009	0.008	0.008
Citronelol	0.012	0.011	0.011	0.010
Nerol	0.011	0.010	0.009	0.009
Geraniol	0.008	0.007	0.007	0.006
Amount Terpenes	**0.164**	**0.154**	**0.149**	**0.143**
Higher alcohols, mg/dm^3				
Butanol	0.026	0.027	0.027	0.020
3-methyl-1-butanol	0.278	0.279	0.279	0.280
2-methyl-1-butanol	0,291	0.293	0.295	0.296
2-phenylethanol	0.151	0.153	0.153	0.154
1-hexanol	0.029	0.031	0.033	0.035
Amount Higher alcohols	**0.775**	**0.783**	**0.787**	**0.785**

The results for the aromatic composition of the red varieties grapes are presented in Table 3. The data from the chromatographic analyzes showed that the sum of the esters in the juice from the studied red varieties was higher and similar to that of the white aromatic varieties. The highest rate was reported for Kaylashki Rubin (2.426 mg/dm^3), and the lowest for Pamid 5/76 (2.345 mg/dm^3). From the identified and quantified esters in all experimental samples it was observed the prevalence of diethyl succinate, followed by ethyl butanoate and ethyl decanoate. Both in the white and red varieties it was repeated the trend for the lowest concentration to be of 2-phenylacetate.

For the terpene composition of the grape juice it could be seen from Table 3, that in the red varieties, the sum of the terpenes was three times smaller compared to the white ones. Quantitative predominance of linalool and the isomers of linalool oxide was observed. Only traces were present from the remaining identified terpenes. The highest sum of terpenes was found in Pamid 5/76 (0.164 mg/dm^3), and the lowest in Kaylashki Rubin (0.143 mg/dm^3).

The rate of higher alcohols in the grapes from the studied red varieties was similar but less compared to the white ones. The highest concentrations of 2-methyl-1-butanol and 3-methyl-1-butanol were found. Butanol and 1-hexanol were established only in traces.

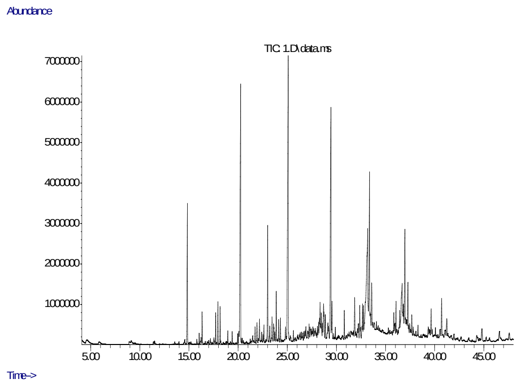

Figure 1. Chromatogram of grape must Dimyat clone 6/46 variety

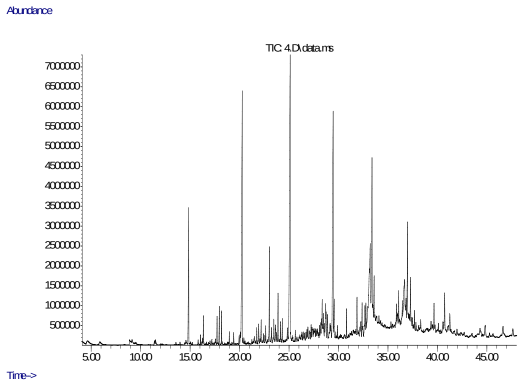

Figure 2. Chromatogram of grape must Misket Vrachanski clone 9/5 variety

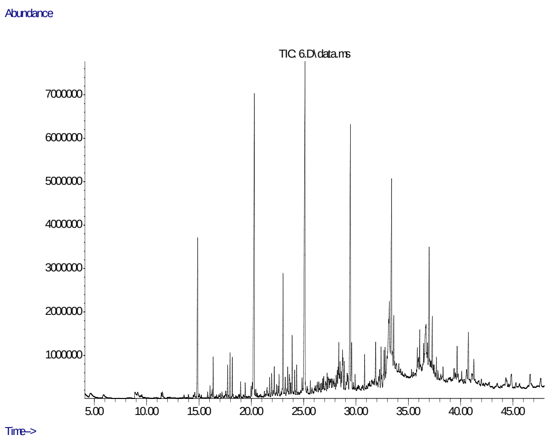

Figure 3. Chromatogram of grape must Pamid clone 5/76 variety

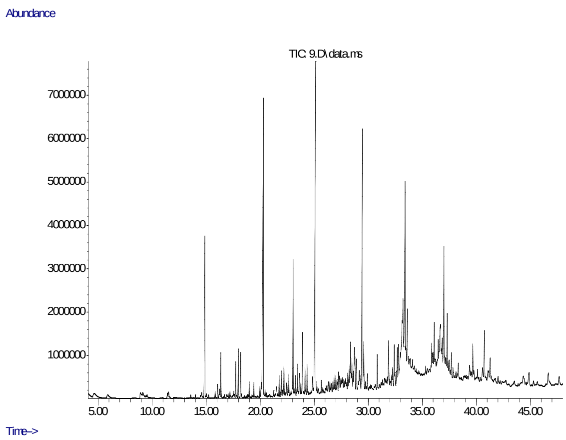

Figure 4. Chromatogram of grape must Kaylashki Rubin variety

Conclusion

Based on the results obtained for the aromatic profile of grape must from the studied white and red varieties, it could be summarized that the rates of the defined groups of components was the greatest in the white aromatic varieties (Muscat Ottonel, Misket Vrachanski, Plevenska Rosa), being their specific feature. The content of esters in white and red varieties was similar, unlike the terpenes and the higher alcohols, the sum of which was higher in the grape juice from the white ones.

In the analyzed samples the quantity of esters was prevailing with the highest concentration of ethyl butanoate, diethyl succinate, ethyl decanoate. The 2-phenylacetate content was the lowest. The white varieties had more terpenes and higher alcohols than the red ones, while the white aromatic varieties more than the non-aromatic. From the terpenes group, in the white varieties the representatives of linalool, nerol and geraniol predominated qualitatively, while in the red ones linalool and the isomers of linalool oxide were prevailing. From the identified higher alcohols the highest concentrations found were of 3-methyl-1-butanol and 2-methyl-1-butanol.

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