Classical oenological parameters and concentration of selected higher alcohols and esters in traditional fermented Slovakian and Bulgarian wines

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Summary

The study is focused on investigation of Slovakian and Bulgarian wines; their production, basic parameters, as well as assessment of selected higher alcohols and esters. Bulgarian wines – Chardonnay, Riesling, Cabernet Sauvignon and Sauvignon Blanc (2008–2010 vintages) were prepared. Their features were compared with those of Slovakian wines of the same vintage years and grape variety. Much lower concentrations of esters were detected in Bulgarian wines in comparison with the Slovakian wines; on the other hand, they contained more alcohols. Compared to samples of the Slovakian wines, significantly higher levels of 1-butanol were detected in Bulgarian Riesling. On the other hand, Slovakian Riesling and Sauvignon Blanc wines had on average twice the concentration of ethyl butanoate in comparison with respective Bulgarian wines. Based on radar charts, which were created using data of quantitative assessment of selected aromatic compounds, the highest score demonstrated in all the samples of Slovakian and Bulgarian wines was that of "pineapple" note. The pear, banana and acid notes were also typical for Slovakian wines, while the corresponding Bulgarian wines were mostly characterized by acid note; pear and banana notes were minor, or they were absent. Results of analyses were confirmed by a degustation commission.

Keywords:
alcohols; beverages; esters; sensory active metabolites

While data concerning composition of e. g. Italian, French and Spanish wines are available in scientific literature, Slovakian and Bulgarian wines are less studied. Slovakian wines gained recognition in Slovakia and world widely due to such contests as Vinalies Internationales Paris 2013, where they were awarded 9 gold and 34 silver medals. Chardonnay WMC (2011 vintage) by Mrva and Stanko (Trnava, Slovakia) was awarded a golden medal in this contest, which may be regarded as a significant success since it won over French Burgundy wines that are deemed to be of the top quality in this variety. Without dispute, Slovakian white wines take pride in very high quality thanks to unique natural conditions of Slovakia. This country offers large diversity of terroirs, which leads to a wide range of varieties and styles from dry Rieslings through precious ice wines to high-quality Tokay wines. Similarly, Bulgarian wines regularly take part in world wine competitions gaining various awards. They were awarded 3 gold and 10 silver medals in Vinalies Internationales Paris 2013 contest.

South Slovakian wine region covers the

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southernmost part of Slovakia. Western part of this region is placed on gravel and gravelous sand, offering conditions suitable for production of lower quality wines. On the other hand, the eastern part of this region offers conditions for growing grape varieties that require warm weather and sunshine. Vineyards are placed on high-quality loess hills of the Danube Lowland. South Slovakian wine region is home to the great Riesling. The region is further highly renowned for Chardonnay, Sauvignon Blanc, Pinot blanc, Pinot gris, Pinot noir, Cabernet Sauvignon, as well as Danube.

Wine is a natural product, which results from a number of biochemical reactions. These begin with ripening of the grapes and further continue through harvesting, alcoholic fermentation, clarification and bottling [1]. Based on this, wine aroma can be classified into three distinct categories. Firstly, the primary aroma of wines depends on both chemical composition of grapes [2, 3] as well as on the applied production technology [4]. However, a greater part of chemical substances found in wine are metabolic by-products of yeasts, which produce the secondary aroma [5]. The bouquet, originating in the process of wine aging, subsequently produces the tertiary aroma, i.e. the result of chemical changes connected with wine oxidation and releasing of aromatic compounds from wood that was used throughout the primary and secondary fermentation.

Fermentation process comprises saccharides conversion into ethanol, CO_2 and volatile compounds, such as higher alcohols, making up to 50% of all volatile substances, esters [6], aldehydes [7], organic acids, carbonyl compounds (aldehydes and vicinal diketones) and compounds containing sulphur [8]. Higher alcohols can be present in grape berries, but only scarcely in high amounts (except for hexanol). These add the herbal aroma to wines [9]. Higher alcohols are produced by *Saccharomyces cerevisiae* by means of two metabolic pathways. They originate either from amino acids, through Ehrlich pathway, or from glycolysis. Alcohols react with carboxyl acids producing esters as a result of enzymatic esterification during fermentation or chemical esterification [10, 11] over the long aging period of wine with low pH [12, 13].

The main objectives of this study include the basic characterization of Bulgarian and Slovakian wines, obtained over three consecutive vintages, together with quantitative assessment of selected higher alcohols and esters.

Further goal was to prove a significant impact ($p < 0.05$) of the country of origin, vintage and grape variety on the concentration of selected higher alcohols and esters in Bulgarian and Slovakian wines.

MATERIAL AND METHODS

Winemaking procedure

Selected Bulgarian wines were produced in a wine cellar from grapes of Chardonnay, Riesling, Sauvignon Blanc and Cabernet Sauvignon varieties (Department of Enology and Chemistry, Institute of Viniculture and Enology, Pleven, Bulgaria), which were harvested at optimal technological maturity.

Sampled grapes were processed in accordance to standard procedures of winemaking under the condition of microvinification. Musts of white varieties (Chardonnay, Riesling and Sauvignon Blanc) were inoculated at 0.1 $g \cdot l^{-1}$ with pure cultures of dried wine yeast *S. cerevisiae* Vitilevure B+C (Martin Vialatte Enologie, Epernay, France). The main alcoholic fermentation of musts proceeded for 7–14 days at a temperature of 20 °C. Musts of red variety (Cabernet Sauvignon) were macerated for 7–14 days at a temperature of 20 °C and were inoculated at 0.1 $g \cdot l^{-1}$ with pure cultures of dried wine yeast *S. cerevisiae* Vitilevure CSM (Martin Vialatte Enologie). When the main alcoholic fermentation was completed, malolactic fermentations took place, the wines were separated from pomace and treated with sulphur dioxide (20 $mg \cdot l^{-1}$). The fermentation of all musts was performed in triplicate. Wines coming from the 2008–2010 vintage were made from 4 grape varieties, 36 samples of young wines were prepared in total.

Slovakian wines, from South Slovakian wine region, including Riesling, Sauvignon Blanc, Chardonnay and Cabernet Sauvignon varieties (from the 2008–2010 vintages, 36 samples in total), were prepared in wineries in accordance to standard procedures using *S. cerevisiae* Oenoferm InterDry (white wines) or Oenoferm Klosterneuburg (red wines) from Erbslöh Getränketechnologie (Geisenheim, Germany). Fermentation temperature was 16 °C.

Determination of chemical composition

Five parameters (alcohol concentration, total acidity, volatile acidity, residual saccharides and saccharides-free extract) were determined according to the official International Organisation of Vine and Wine (OIV) methods [14]. The polyphenol concentration in the wine samples was measured using the Folin-Ciocalteu method, following the procedure described by Arnous et al. [15]. The pH was measured with a pH metre (SevenEasy, Mettler Toledo, Greifensee, Switzerland) by differential method [16].

Sample preparation and analysis by gas chromatography-mass spectrometry

The head space solid-phase microcolumn extraction (HS-SPMCE) method previously described by Hrivňák et al. [17] was used for sample extraction. The gas chromatography-mass spectrometry (GC-MS) method was used in order to assess concentrations of selected higher alcohols and esters.

The analysis was carried out using GC-MS QP2010 (Shimadzu, Kyoto, Japan) equipped with a modified inlet [18] that is used for SPMCE. A column VF-WAXms (Varian, Lake Forest, California, USA) with the length of 30 m, inner diameter of 0.25 mm and thickness of stationary phase of 0.25 μm was used. Analytes trapped in the microcolumn were desorbed for 1 min and injected in splitless mode (1:30). The oven temperature programme started at 40 °C, the temperature was held for 1 min, then increased to 220 °C at 5 $°C \cdot min^{-1}$ and held for 5 min. The injector temperature was set at 220 °C. Helium was used as a carrier gas and its pressure was 10 kPa during desorption and 60 kPa during the analysis. The electron ionization mode with electron energy –70 eV was used for ionization. Mass fragments were scanned in the range of m/z of 50–350.

Determination of aromatic compounds

Selected esters and higher alcohols were identified using NIST library (National Institute of Standards and Technology, Gaithersburg, Maryland, USA) and concentrations of these aromatic compounds were estimated from five-point calibration curves (0.001–10.00 $mg \cdot l^{-1}$) with correlation coefficients (r^2) of 0.9976–0.9998. Each wine sample was measured in three replicates and the results represented means of nine determinations (relative standard deviation < 5%). Data were collected by the software GCMS Postrun Analysis (Shimadzu).

The impact of individual aromatic compounds on the overall sensory impression of wines was graphically processed. At the beginning, aromatic compounds were divided into groups according to their characteristic aroma, on the basis of information from literature [19]. Odour description of selected aromatic compounds and their average areas in GC-MS chromatograms were used for generation of radar charts. The results were compared with results obtained by sensory analysis, but this outcome is only of illustration value.

Statistical analysis

An analysis of variance (ANOVA) was applied to the experimental data for the determination of statistical differences between the analysed samples; results were considered significant if the associated p value was < 0.05. The significance of the differences was determined by Multiple Range Tests. The statistical analysis was performed using the software StatGraphic Plus 3.0. (Statpoint Technologies, Warrenton, Virginia, USA).

Sensory evaluation of wine samples

In total, 15 staff members coming from the same working place as authors participated in the sensory descriptive analysis. Wines were sensorially evaluated and were assigned scores on a 100-point scale in accordance to the tasting protocol proposed by OIV [20].

Degustators were asked to describe the odour of tested wines by choosing one odour characteristic in the aroma list. The following twelve odour characteristics (exotic fruits, red fruits, citrus, fruity, distillate, spice, honey, roses, acidic, stone fruits, freshly cut grass, forest fruits) considered as the most appropriate to describe the wine samples, were further selected based on the literature [21].

RESULTS AND DISCUSSION

Classical oenological parameters of Slovakian and Bulgarian wines

Slovakian varietal wines (Riesling, Chardonnay, Sauvignon Blanc and Cabernet Sauvignon) were compared with Bulgarian wines of the same varieties. Tab. 1 shows the average values of the basic oenological parameters of Bulgarian and Slovakian wines.

The Slovakian wines were classified according to residual saccharides concentration as dry (0.6–3.4 $g \cdot l^{-1}$), semi-dry (5.7–10.4 $g \cdot l^{-1}$), semi-sweet wines (12.4 $g \cdot l^{-1}$), while all samples of Bulgarian wines were dry (1.2–3.03 $g \cdot l^{-1}$) [22].

The ethanol concentration in Slovakian wines varied significantly among samples (10.8–14.5% v/v). On the other hand, difference in alcohol concentration was not that distinct in Bulgarian wines (12.1–13.3% v/v). Comparing wines obtained over three consecutive vintages, the highest alcohol concentration was detected in all Bulgarian samples of Cabernet Sauvignon (12.9–13.3% v/v). The lowest concentration of ethanol was detected in Riesling wines (correspondingly 12.1% v/v and 12.3% v/v) in two consecutive vintages (2008 and 2009) except for year 2010 in which Chardonnay

Tab. 1. Classical oenological parameters of the studied wines.

Origin	Variety	Vintage	Alcohol [%]	Residual saccharides [g·l-1]	Saccharides-free extract [g·l-1]	Total acidity [g·l-1]	Volatile acidity [g·l-1]	pH
Bulgaria	Riesling	2008	12.1	1.37	20.38	6.30	0.57	3.10
		2009	12.3	1.40	18.80	8.55	0.42	3.13
		2010	12.7	2.31	18.69	6.23	0.54	3.08
	Chardonnay	2008	12.2	1.80	21.50	6.45	0.54	3.18
		2009	12.6	2.46	20.24	7.30	0.75	3.26
		2010	12.4	1.27	18.53	6.90	0.62	3.14
	Sauvignon Blanc	2008	12.5	1.67	24.53	5.40	0.42	3.35
		2009	12.3	1.40	20.40	8.00	0.48	3.00
		2010	12.7	1.20	18.80	8.25	0.68	3.04
	Cabernet Sauvignon	2008	12.9	1.20	30.50	5.40	0.48	3.39
		2009	12.9	2.10	27.90	6.08	0.36	3.42
		2010	13.3	3.03	25.30	6.50	0.60	3.26
Slovakia	Riesling	2008	12.6	0.60	17.50	6.20	0.27	3.17
		2009	11.6	1.30	22.90	7.40	0.32	3.10
		2010	11.1	1.60	20.60	7.56	0.24	3.23
	Chardonnay	2008	12.0	1.00	20.60	7.00	0.32	3.32
		2009	11.7	1.50	22.70	7.80	0.38	3.00
		2010	10.8	7.60	21.10	7.10	0.14	3.27
	Sauvignon Blanc	2008	13.0	0.80	20.30	7.60	0.33	3.56
		2009	13.2	3.40	24.00	7.20	0.58	3.72
		2010	14.5	5.70	23.40	6.03	0.69	3.76
	Cabernet Sauvignon	2008	12.4	1.90	27.90	6.00	0.56	3.35
		2009	14.1	10.40	41.60	7.40	0.39	3.42
		2010	13.5	12.40	44.20	6.99	0.37	3.70

Values represent means of nine replicate determinations (maximum relative standard deviation ± 5%).
The residual saccharides are expressed as grams of a mixture of glucose and fructose per litre. Total acidity is expressed as grams of tartaric acid per litre. Volatile acidity is expressed as grams of acetic acid per litre.

wines (12.4% v/v) had the lowest alcohol concentration.

Red wines Cabernet Sauvignon (25.3–44.2 g·l-1) had higher levels of saccharide-free extract in comparison with white wines (17.5–24.5 g·l-1).

The pH of wine is important since it affects the quality of the product in terms of its taste, colour, oxidation status, chemical stability and other factors. Wines optimally have a pH up to 3.4 [23]. Among Slovakian wines, Sauvignon Blanc wines and Cabernet Sauvignon 2010 had pH higher than this value (3.56; 3.72; 3.76 and 3.7), which caused loss of their fullness and freshness. Such wines are known to be susceptible to microbial contamination [23].

The levels of total acidity varied among samples of Bulgarian wines (5.4–8.55 g·l-1), while Slovakian wines contained 6.2–7.8 g·l-1 of the total acids. Alongside, it must be pointed out that tested wines with the highest levels of total acidity did not have the lowest pH. This result agrees with findings of Beelman and Gallander [24] who demonstrated poor correlation between pH and total acidity of wine.

Commission Regulation (EC) No 606/2009 [25] established the limits for volatile acidity of white wines (1.08 g·l-1) and of red wines (1.2 g·l-1). The studied Slovakian wines had acceptable volatile acidity as expected, ranging from 0.14 g·l-1 to 0.69 g·l-1. Similarly, Bulgarian wines had acceptable concentration of volatile acids (0.36–0.75 g·l-1).

Selected higher alcohols and esters in wines

The typical wine odour is provided by aromatic compounds [26]. The best known higher alcohols and esters present in alcoholic beverages are secondary metabolites produced by yeasts throughout the fermentation process. The selected aromatic compounds in 12 Slovakian and Bulgarian wines prepared in triplicate were measured by GC-MS. Three higher alcohols (1-butanol, 1-hexanol and 1-heptanol) and 10 esters (*n*-propyl acetate, isobutyl acetate, ethyl butanoate, butyl acetate, isopentyl acetate, pentyl acetate, ethyl hexanoate, hexyl acetate, ethyl octanoate and ethyl decanoate) were determined in wine samples. Esters are desirable aromatic constituents of a pleasant wine, which contribute to its fruity and flowery nuances [27]. Concentrations of studied aromatic compounds in Slovakian and Bulgarian wines are shown in Tab. 2 and Tab. 3.

Acetate esters are produced by reaction of acetyl-CoA with higher alcohols that are formed by degradation of saccharides or amino acids [19, 28]. Isobutyl acetate, *n*-propyl acetate, butyl acetate, isopentyl acetate, pentyl acetate and hexyl acetate were detected as the acetate esters. Butyl acetate and pentyl acetate were not detected in all Slovakian wines.

Slovakian varietal wines Riesling 2008 contained the highest levels of ethyl octanoate (5.12 $mg\cdot l^{-1}$), while Riesling 2009 had the highest concentration of 1-heptanol (3.35 $mg\cdot l^{-1}$) and Riesling 2010 had the highest concentration of isopentyl acetate (5.8 $mg\cdot l^{-1}$).

In Slovakian Chardonnay wines obtained over the period of three years, isopentyl acetate was detected in the highest concentration (3.43–7.58 $mg\cdot l^{-1}$).

Sauvignon Blanc 2008 and 2009 had the highest levels of 1-hexanol (3.6 and 3.48 $mg\cdot l^{-1}$). Isopentyl acetate prevailed in Sauvignon Blanc 2010 as well as in Chardonnay wines (6.72 $mg\cdot l^{-1}$).

Cabernet Sauvignon 2008 and 2009 had the highest concentration of 1-hexanol (10.03 $mg\cdot l^{-1}$ and 8.63 $mg\cdot l^{-1}$), Sauvignon Blanc 2008 and 2009 were similar to these. Cabernet Sauvignon 2010 had the highest concentration of 1-butanol (9.24 $mg\cdot l^{-1}$).

On the other hand, 1-butanol was not detected in other analysed varietal wines produced in 2009 and 2010; similarly very low levels were detected in wines produced in 2008 (0.16–0.25 $mg\cdot l^{-1}$). Significant differences were determined in concentrations of *n*-propyl acetate, where no impact of particular vintage or variety on its production was found. Some studies showed that acetate esters, even at low concentration, had a synergistic or additive effect on the aromatic complexity of wines in the presence of other aroma compounds [29].

Concerning Bulgarian wines, butyl acetate and pentyl acetate were detected only in one wine sample, that of Cabernet Sauvignon 2008 (0.14 $mg\cdot l^{-1}$ and 0.06 $mg\cdot l^{-1}$, respectively). In 2008 and 2009, the wines contained higher amounts of ethyl octanoate in comparison with the same type of wine produced in 2010, except for Chardonnay from the 2008 vintage, in which its concentration decreased.

Fatty acids ethyl esters, such as ethyl octanoate, can be produced enzymatically during fermentation and from acetyl-CoA that is formed during synthesis or degradation of fatty acids. Their concentration depends on yeast strains involved in fermentation, saccharides content, fermentation temperature, aeration degree and other factors [28].

In general, the major compounds produced during the fermentation of musts of grape berries of Riesling and Sauvignon Blanc (year 2010) included isopentyl acetate (0.98 $mg\cdot l^{-1}$ and 2.20 $mg\cdot l^{-1}$) and ethyl octanoate (0.93 $mg\cdot l^{-1}$ and 2.60 $mg\cdot l^{-1}$). Concentration of isopentyl acetate increased 2.4 times in Riesling and Sauvignon Blanc, and 3 times in Chardonnay (the 2009 vintage), compared to the same wine types produced in 2010.

Based on the obtained results, we could state that Chardonnay and Sauvignon Blanc wines produced in 2009 had the highest concentration of *n*-propyl acetate (0.27 $mg\cdot l^{-1}$ and 0.23 $mg\cdot l^{-1}$). Significantly lower concentration of *n*-propyl acetate was detected in Sauvignon Blanc 2010 (0.07 $mg\cdot l^{-1}$), while other wine samples contained no *n*-propyl acetate.

The higher alcohols are produced by yeasts during the fermentation either by anabolism from glucose or catabolism from amino acids (valine, leucine, isoleucine and phenylalanine). As secondary products of yeasts, they are consequently released to the medium and they are responsible for the "fermentative" aroma of wines [30].

No 1-butanol was detected in Chardonnay 2008. Its concentration increased 1.6 times in Cabernet Sauvignon wines (the 2008 and 2009 vintages) and twice in Chardonnay from the 2009 vintage, compared to the same wine samples produced in 2010. The major compound detected in Cabernet Sauvignon 2010 was 1-hexanol (7.81 $mg\cdot l^{-1}$). The three-year average showed the highest level of 1-hexanol in Cabernet Sauvignon wines from the 2010 vintage (7.81 $mg\cdot l^{-1}$). 1-hexanol characterized by "vegetal" notes is enzymatically formed in the pre-fermentation stage and it is considered an off-flavour [31, 32].

When comparing Bulgarian and Slovakian wines, high levels of 1-butanol were detected in Bulgarian Riesling (0.69–3.0 $mg\cdot l^{-1}$), while in

Tab. 2. Concentration of selected aromatic compounds in Slovakian wines.

Aromatic compounds [mg·l-1]	Variety of wine and year of vintage											
	Riesling			Chardonnay			Sauvignon Blanc			Cabernet Sauvignon		
	2008	2009	2010	2008	2009	2010	2008	2009	2010	2008	2009	2010
n-Propyl acetate	ND	ND	0.37	0.04	0.21	ND	0.05	ND	ND	ND	ND	ND
Isobutyl acetate	0.15	0.07	0.13	0.03	0.09	0.16	0.08	0.09	0.17	0.13	0.09	0.14
Ethyl butanoate ab	0.96	0.61	0.86	0.56	0.59	0.55	0.89	0.69	0.87	0.25	0.27	0.38
Butyl acetate c	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Isopentyl acetate c	1.50	0.59	5.80	4.17	3.43	7.58	3.19	1.75	6.72	1.82	0.61	1.73
1-Butanol	0.17	ND	ND	0.16	ND	ND	0.25	ND	ND	ND	ND	9.24
Pentyl acetate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethyl hexanoate ab	1.20	1.27	1.85	0.80	0.92	1.24	1.07	1.05	1.69	0.63	0.57	0.57
Hexyl acetate	0.71	ND	0.36	0.08	0.10	0.48	0.85	0.10	0.63	ND	ND	0.02
1-Hexanol ac	5.08	2.36	2.52	1.73	1.48	2.52	3.6	3.48	3.79	10.03	8.63	5.97
Ethyl octanoate ac	5.12	1.91	3.01	2.18	1.39	2.32	2.47	1.43	2.73	0.9	0.52	0.72
1-Heptanol ab	3.63	3.35	0.52	0.84	1.08	2.69	0.09	2.00	1.41	ND	6.47	0.50
Ethyl decanoate ac	1.23	0.90	0.83	1.93	0.35	1.08	1.02	0.48	0.82	0.08	ND	0.09

Values represent means of nine replicate determinations (maximum relative standard deviation ± 5%).
Letters in superscript indicates statistically significant difference: a – among samples depending on variety, b – among samples depending on country of origin, c – among samples depending on vintage.
ND – not detected (value under the detection limit of 0.0005–0.03 mg·l-1).

Slovakian Rieslings 1-butanol either was not detected or its maximum concentration was merely 0.25 mg·l-1.

In proportion to this, samples of Bulgarian Chardonnay wines (1.77–3.65 mg·l-1) had concentrations of 1-butanol higher than Slovakian wines except for wines produced in 2008, where this compound was not detected at all.

In contrast, Slovakian Riesling wines (1.2–1.85 mg·l-1) had higher concentrations of ethyl hexanoate compared to Bulgarian counterparts (0.74–0.87 mg·l-1).

The concentration of ethyl butanoate was on average twice as high in two Slovakian varietal wines (Riesling 0.61–0.96 mg·l-1 and Sauvignon Blanc 0.69–0.89 mg·l-1) compared to respective Bulgarian wines (0.22–0.32 mg·l-1 and 0.29–0.48 mg·l-1). In addition, higher concentrations of this compound were also identified in Slovakian Chardonnay wines compared to Bulgarian wines, however, with a smaller difference than in the previous example.

Odour characteristics of wine samples

The results obtained from GC-MS analysis were also expressed in radar charts as odour characteristics. Results presented in this way could be easily compared with results obtained by sensory evaluation.

The highest score, demonstrated in all samples of Slovakian and Bulgarian wines, was that of "pineapple" note. This fact can be explained by the highest concentration of ethyl acetate from all acetates with fruity odour. The pear, banana and acid notes were also typical for Slovakian wines, Chardonnay and Cabernet Sauvignon wines, while the corresponding Bulgarian wines (Fig. 1, 2) were mostly characterized by acid note; pear and banana notes were minor, or they were absent (other results are not graphically presented).

Much smaller concentrations of esters were detected in Bulgarian wines compared to Slovakian wines; on the other hand, the former contained more alcohols. Results of these analyses were also confirmed by degustation (Tab. 4), which evaluated Bulgarian wines as less aromatic but more reminiscent of distillate.

Wine samples had an average concentration of 1-hexanol in the range of (not detected)–10.03 mg·l-1. The compound 1-hexanol may greatly contribute to wine aroma, at concentrations above the threshold (4 mg·l-1) it makes a faint impression and its odour is described as that of fat and freshly cut grass [33]. Additionally, at concentrations exceeding 8 mg·l-1, it gives off a vegetable or herbal scent [34]. Degustation commission described the aroma of Bulgarian varietal Sauvignon Blanc wines (vintage 2008) as that of freshly cut grass, which corresponded with the concentration of 1-hexanol being higher than

Tab. 3. Concentration of selected aromatic compounds in Bulgarian wines.

Aromatic compounds [mg·l^{-1}]	Variety of wine and year of vintage											
	Riesling			Chardonnay			Sauvignon Blanc			Cabernet Sauvignon		
	2008	2009	2010	2008	2009	2010	2008	2009	2010	2008	2009	2010
n-Propyl acetate	ND	ND	ND	ND	0.27	ND	ND	0.23	0.07	ND	ND	ND
Isobutyl acetate	0.07	0.12	0.06	0.11	0.14	0.04	0.26	0.14	0.10	0.23	0.08	0.08
Ethyl butanoate ^{ab}	0.32	0.28	0.22	0.25	0.43	0.16	0.42	0.48	0.29	0.33	0.32	0.21
Butyl acetate ^{c}	ND	ND	ND	ND	ND	ND	0.14	ND	ND	0.14	ND	ND
Isopentyl acetate ^{c}	2.30	2.34	0.98	1.17	3.21	1.04	0.65	5.35	2.20	0.63	0.53	0.69
1-Butanol	3.00	1.72	0.69	ND	3.65	1.77	1.99	2.20	0.61	2.41	2.57	1.45
Pentyl acetate	ND	ND	ND	ND	ND	ND	0.05	ND	ND	0.06	ND	ND
Ethyl hexanoate ^{ab}	0.74	0.78	0.87	0.46	0.56	0.38	0.64	1.06	0.82	0.42	0.40	0.74
Hexyl acetate	0.04	0.05	ND	ND	0.03	ND	ND	0.11	0.06	ND	ND	ND
1-Hexanol ^{ac}	0.63	ND	0.46	1.35	ND	0.28	4.01	ND	1.02	3.12	2.95	7.81
Ethyl octanoate ^{ac}	2.64	3.90	0.93	0.86	2.01	0.96	1.17	2.25	2.60	0.89	0.74	0.49
1-Heptanol ^{ab}	ND	ND	ND	ND	0.20	ND	ND	ND	0.21	ND	ND	ND
Ethyl decanoate ^{ac}	1.61	1.34	0.19	0.17	0.34	0.32	0.22	0.72	0.69	0.12	ND	0.11

Values represent means of nine replicate determinations (maximum relative standard deviation ± 5%).
Letters in superscript indicates statistically significant difference: a – among samples depending on variety, b – among samples depending on country of origin, c – among samples depending on vintage.
ND – not detected (value under the detection limit of 0.0005–0.03 mg·l^{-1}).

4 mg·l^{-1}. The concentration of 1-hexanol exceeding 8 mg·l^{-1} was identified in two samples of Slovakian Cabernet Sauvignon (vintages 2008 and 2009), however, it had no negative impact on the final aroma of these two samples.

Most ethyl esters and acetates are present in white wines in higher concentrations, contributing to sweet-fruit aromas. Esters of acetic acid, namely, ethyl acetate and isopentyl acetate, are the main sensory active metabolites [33]. Higher concentrations of isopentyl acetate have positive impact on aromatic profiles of wines [35] and they could emphasise uniqueness and originality of wines. Higher concentrations of isopentyl acetate (3.4 mg·l^{-1}) were detected in all samples of Slovakian Chardonnay, Riesling and Sauvignon Blanc wines produced in 2010, which were evaluated by tasters as having fruity aroma. As specified above, Bulgarian wines reminded of distillate, and thus the higher concentration of isopentyl acetate, that was detected in Sauvignon Blanc 2009, was not manifested.

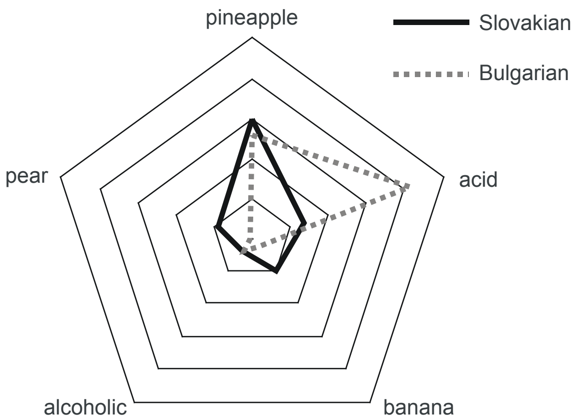

Fig. 1. Comparison of typical odour characteristics of individual aromatic compounds of white Chardonnay variety in Slovakian and Bulgarian wines.

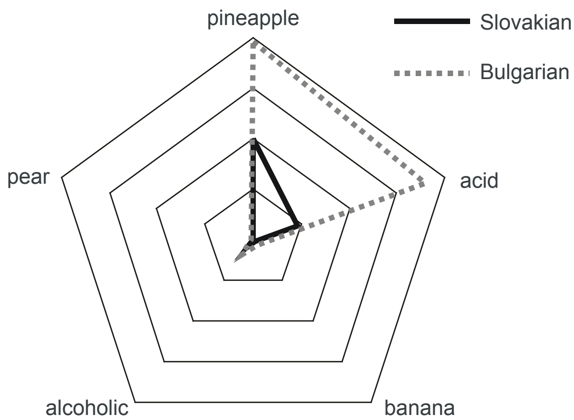

Fig. 2. Comparison of typical odour characteristics of individual aromatic compounds of red Cabernet Sauvignon variety in Slovakian and Bulgarian wines.

Tab. 4. Sensory description of Slovakian and Bulgarian wines using odour characteristics.

Odour attributes	Variety of wine and country of origin							
	Riesling		Chardonnay		Sauvignon Blanc		Cabernet Sauvignon	
	Slovakia	Bulgaria	Slovakia	Bulgaria	Slovakia	Bulgaria	Slovakia	Bulgaria
Exotic fruits	2	0	4	3	0	0	0	0
Red fruits	0	0	0	0	3	0	5	3
Citrus	1	0	0	0	0	0	0	0
Fruity	6	2	4	1	8	2	6	0
Distillate	0	7	0	4	0	3	1	6
Spice	5	3	3	0	0	0	2	4
Honey	1	0	1	1	0	0	0	0
Roses	0	0	0	0	0	0	0	0
Acidic	0	3	3	6	0	3	1	0
Stone fruits	0	0	0	0	0	0	0	0
Freshly cut grass	0	0	0	0	2	7	0	2
Forest fruits	0	0	0	0	2	0	0	0

Odour characteristics are provided by 15 degustators. Presented data express numbers of degustators who described the listed odour characteristic in the wine sample (produced in 2008–2010).

Statistical analysis of variance was used to differentiate the wines by evaluation scores such as vintage, variety and country of origin. Particularly vintage and variety had a great influence on amounts and concentrations of selected aromatic compounds.

Concentrations of *n*-propyl acetate, isobutyl acetate, ethyl butanoate, 1-butanol, pentyl acetate, ethyl hexanoate, hexyl acetate and 1-heptanol were not significantly influenced by variety or vintage.

Statistical analysis by Multiple Range Tests confirmed that concentrations of six aromatic compounds (Tab. 2, 3) were influenced by variety.

On the other hand, only three aroma substances (ethyl butanoate, ethyl hexanoate and 1-hexanol) were notably influenced by variety, regardless of the country of origin (One Way, ANOVA).

The concentrations of ethyl butanoate, ethyl hexanoate and 1-heptanol were significantly influenced by the country of origin.

CONCLUSION

The results obtained in this study will contribute to the Slovak databank of aromagrams, which contains over 15 000 data on aromatic compounds in Slovakian and foreign wines. This information can be helpful when considering adulteration of wine by aromatic concentrates. The aromatic profiles of Slovakian and Bulgarian wines are appreciated by winemakers and consumers since they can be identified as quality sensory traits of young wines. The presented work provides, for the first time, the comparison of oenological and aromatic properties of Slovakian and Bulgarian wines.

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