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POMACE BRANDY QUALITY OF CULTIVAR RIESLING WHITE FROM KUTJEVO VINEGROWING REGION

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Abstract

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The research on pomace brandy from grape pomace cultivar Riesling White from Kutjevo vinegrowing region was conducted in the year 2004. The experiment with pomace obtained after pressing mash (pomace K) was set in five variants with three repetitions (pomace fermentation with epiphyt microflora, fermentation of pomace supplemented with yeast, treatment of pomace before boiling with commercial preparation of pectolitic enzymes – three different enzymes). Two series of experiments were carried out in the year 2005: pomace obtained after pressing mash (series K) and pomace remaining after separation of the free-run juice (series J). In that year with two main variants (pomace fermentation with epiphyt microflora and fermentation of pomace supplemented with yeast), the experiment of pomace treatment with one of the applied preparations of pectolitic enzymes was repeated. The analysis of the chemical composition of pomace brandy comprised the determination of the alcohol, the total titratable acidity, the share of ester and the share of total aldehydes, the concentration of methanol, n-propanol, isobutanol, 2-butanol, isoamyl alcohol, n-hexanol, ethyl acetate and ethyl lactate. Based on the average values of basic chemical compounds, pomace brandies of all experimental variants obtained from Riesling White pomace in the year 2004 and 2005 satisfied the criteria of quality according to the *Pravilnik o jakim alkoholnim i alkoholnim pićima* and regulatory rules, *Definition, Description and Presentation of Spirit Drinks: Council Regulation No 1576/89,* with the exception of pomace brandies produced in the year 2005 from pressed pomace fermented with epiphytic yeasts, as well as brandies of the same pomace treated with pectolitic enzyme before fermentation conducted with epiphyt yeasts. In these pomace brandies methanol concentration was above the allowed marginal values. The chemical composition of pomace brandies differed significantly in particular years as well as in relation to the experimental series.

Key words: pomace brandy, pomace, pectolitic enzymes, distillation, methanol

Introduction

Pomace brandy, brandy produced by the distillation of fermented grape marc is of distinctive sensory properties and chemical composition that distinguish it from the beverages obtained by the distillation of wine, as well as those produced by the distillation of fermented crushed grapes. The composition and sensory properties of brandy result from the specific structure of pomace, its chemical and microbiological composition which is different from the composition of the mash and wine. Pomace consists of solid parts of grapes in which the proportion of seeds is around 25%, skins 50% and stems around 25% (Silva et al., 2000).The factors important for the quality of pomace are health status and the degree of grape ripeness (Da Porto and Zironi, 1997; Silva et al., 2000), aromatic properties of cultivars (Versini, 1992a), as well as the technology of vinification (Radovanovic, 1986; Paunovic and Danicic, 1967; Paunovic and Djurisic, 1983; Da Porto and Zironi, 1997; Silva et al., 2000; Cortés et al., 2005; Apostolopoulou et al., 2005). In accordance with the regu-

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lations (Pravilnik o jakim alkoholnim i alkoholnim pićima; Definition, Description and Presentation of Spirit Drinks: Council Regulation No 1576/89), pomace brandy must contain at least 37.5% vol. of alcohol, volatile matter content of at least 140 g/hl a.a. and methanol up to 1000 g/hl a.a. The share of ethanol is of the key importance for the flavor and body of pomace brandy, however, it contributes a little to its aroma (Silva et al., 2000). The share of alcohol in Italian *grappa* is at least 37.5% vol., but it usually reaches 50% vol. (Versini and Odello, 1990). Methanol is the natural ingredient of brandies produced from grape. Because of its toxicity, concentration of methanol in the spirit drinks is limited by regulations. Various factors that affect the concentration of methanol in grape marc have been reported in professional literature. They are associated with the cultivar (Versini, 1992a), the intensity of action of pectolitic enzymes (Silva et al., 2000), pH levels (Da Porto, 1997), the structure of mash and the share of the liquid phase (Paunovic and Djurisic, 1981), boundary of separating the first distillate flow (Silva and Malcata, 1999), as well as the effective separation of the last distillate flow (Apostolopoulou et al., 2005).

The data on the concentration of methanol in pomace brandy vary widely. The share of methanol in Greek pomace brandy (*tsipuro*), produced by traditional methods in small households, was from 86 to 143 mg% ml a.a. (Apostolopoulou et al., 2005). Silva et al. (2000) provided a comparative overview of the chemical composition of Portuguese, Spanish and Italian pomace brandies according to which the concentration of methanol in Portuguese pomace brandy was 3389.2 ± 1279.9 mg/l; in Spanish *orujo* 5169 mg/l; in Italian *grappa* 8869.2 ± 4338.3 mg/l, with the alcohol content of 45 ± 4.5% vol. in Portuguese pomace brandy, 58.1% vol. in Spanish *oruje* and 72.9 ± 7.7% vol. in Italian *grappa*. The increased methanol content (more than 2% vol.) can be found in pomace brandies produced in industrial conditions, which is explained as a consequence of the strong pressing of pomace using continuous presses or prolonged storage of fermented pomace during which a loss of alcohol occurred (Paunovic and Djurisic, 1983).

Cortés et al. (2005) reported that industrial pomace brandy produced from pomace pressed in a pneumatic press, had seven times higher concentration of methanol (an average of 5303 mg/l with 63.8% vol. of alcohol) from the pomace brandy produced in small households from pomace obtained by manual pressing of mash which contained an average of 704 mg/l of methanol with an average 52.7% vol. of alcohol. Most of the higher alcohols are formed in alcohol fermentation by yeasts and they are formed parallel with the formation of ethanol (Jackson, 1994). The share of hexanol in the distillate is connected with the varietal origin, (Versini, 1992a; Apostolopoulou et al., 2005) the degree of grape ripeness (Apostolopoulou et al., 2005), the strength of the pressing and prolonged storage of pomace (Cortés et al., 2005). Increased concentrations of amyl alcohols (described as "alcoholic," "sweet" and "suffocating" aromas) could have negative influence on the distillate aroma, as reported by Apostolopoulou et al. (2005).

According to the same source, 1-hexanol is considered to positively influence the aroma of distillate if its concentrations are lower than 20 mg/l. High concentrations of 1-hexanol seriously damage the sensory properties of distillates and are associated with "green" scents (Cantagrel et al., 1995). The presence of 2-butanol is considered harmful to the quality of the pomace brandy due to the unpleasant smell which is associated with this alcohol (Silva et al., 1996). The total concentration of higher alcohols in the pomace brandies studied by Paunovic and Đurisic (1983) ranged from 2220 to 6930 mg/l a.a., depending on the composition of pomace and fermentation conditions. Portuguese brandies had an average concentration of total higher alcohols from 1876.4 mg/l, Spanish *orujo* 1939 mg/l and Italian *grappa* 1799 mg/l (Silva et al., 2000) using the same sequence for the displayed alcohol strength of 45 ± 4. 5% vol., 58.1% vol., and 72.9 ± 7.7% volume. The concentration of 2-butanol in pomace brandy from Spain ranged from 0.00 to 16.9 mg/l for home-produced, while in industrial it was 0.00 to 44.9 mg/l (Cortés et al., 2005). In pomace brandies produced in industrial conditions the concentration of 2-butanol ranged from 80 to 946 mg/l (Paunovic and Đurisic, 1983).Concentrations of 1-hexanol in industrial pomace brandies ranged from 0.00 to 133 mg/l (Cortés et al., 2005).

Among comparatively analyzed pomace brandies the highest 1-hexanol content of 162 mg/l was found in *orujo* (Silva et al., 2000). Low concentrations of this alcohol (0.9 mg % ml a.a.) were reported for Greek brandies (Apostolopoulou et al., 2005).There is relatively little data on the movement of the total acidity of pomace brandy in contemporary professional literature. The average concentration of organic acids in the experimental pomace brandy produced in laboratory conditions was 0.17 g/l, and in pomace brandies produced in industrial conditions 0.45 g/l (Paunovic and Djurisic, 1983). Recognizable level of acetic acid was 200 mg/l (Diéguez et al., 2002).Ethyl acetate ester is the most important ester with respect to its intense smell and has a significant impact on the sensory properties of distillate (Silva et al., 1996; Apostolopoulou, 2005).The increased concentration of this ester indicates prolonged storage of pomace and possible acetic acid bacteria contamination. The data on the proportion of ethyl acetate in pomace brandy vary. The concentration of ethyl acetate in Portuguese pomace brandies ranged from 50.4 to 528 mg/l with an average concentration of 210 mg/l which, according to Silva et al. (1996), can be considered relatively

low for brandies. Ethyl lactate is considered to contribute to balance of taste and softness of the body of the distillate if it is present in low concentrations (Apostolopoulou et al., 2005).

Increased concentration of aldehyde in pomace brandies was connected with the spontaneous or induced microbial oxidation of ethanol (Silva and Malcata, 1999). By comparing the concentration of acetaldehyde in Portuguese, Spanish and Italian pomace brandies, the highest concentration of 933 mg/l was in *orujo* (Silva et al., 2000). Addition of water before boiling dry pomace influenced the concentration of acids, esters, aldehydes and methanol in pomace brandy (Paunovic and Djurisic, 1983). According to Silva and Malcata (1998), the addition of pectinase, the commercial chemical Ultrazym 100 G, contributed significantly to the increase of methanol content in pomace brandy, and it also had a statistically significant effect on the formation of n-propanol, isobutanol and isoamyl alcohol. Regarding the implementation of the alcoholic fermentation of pomace Silva et al. (2000) and Da Porto (1998) recommend inoculated alcoholic fermentation with the addition of selected yeasts. In the production of Portuguese pomace brandies authors proposed a mixed starter culture of the yeast *Saccharomyces cerevisie* and heterofermentative lactic acid bacteria *L. hilgardii*, which should be added to pomace before fermentation (Silva and Malcata, 2000).

Materials and Methods

The research has been conducted on the pomace brandy produced from grape pomace of the cultivar Riesling White from Kutjevo vinegrowing region. The research lasted for two years and comprised the harvests of the year 2004 and 2005. In the year 2004, the experiment was conducted with pomace obtained after pressing marc (pomace K) and it was set in five variants with three repetitions. The basic variants of the experiment of the year 2004 were as follows: variant A - pomace fermentation by epiphyt microflora and variant B - pomace fermentation with addition of *Uvaferm CM yeast* (*Lallemand*, France) in the amount of 30 g/100 kg of pomace. Other variants included the treatment of pomace by commercial preparations pectolitic enzymes, namely; variant C – by adding preparations *Lallzyme Cuvee Blanc (Lallemand,* France) to the pomace before fermentation in the amount of 2 g/100 kg of pomace, variant D – by adding preparations *Lallemand EX (Lallemand*, France) to the pomace before fermenration in the amount of 2 g/100 kg of pomace, variant E – by adding preparation *Ultrazym 100 G* (*Novozymes*, Switzerland) to the pomace before fermentation in the amount of 2 g/100 kg of pomace. Two series of experiments were conducted in the year 2005: the first with the pomace obtained after pressing the mash (series K) and the pomace remaining after the free run separation (series J). In the same year, with two basic variants, the experiment was repeated by treating the pomace with one of the applied preparations- pectolitic enzymes. Experiments were performed under the same conditions for each type of pomace in three variants and three repetitions. The variants of the experiment obtained after pressing marc (pomace K) were as follows: variant A*k* - pomace fermentation with epiphyt microflora, variant B*k* - pomace fermentation with *Uvaferm CM yeast* (*Lallemand*, France) in the amount of 30 g/100 kg of pomace, variant D*k* – by addition of preparation *Lallemand EX* (*Lallemand*, France) pomace before fermentation in the amount of 2 g/100 kg of pomace. Variants of the experiment with pomace obtained after separation of the free run pomace (pomace J) were: A*j* variant - the pomace fermentation with epiphyt microflora, variant B*j* - pomace fermentation with the addition of *Uvaferm CM yeast* (*Lallemand*, France) in the amount of 30 g/100 kg of pomace, variant D*j* – addition of preparation *Lallemand EX* (*Lallemand*, France) pomace before fermentation in the amount of 2 g/100 kg of pomace.

Harvested grapes were weighed and moved to the crusher-destemmer, stalks were separated and the obtained mash was moved to a pneumatic press. After separation of the must for the process of Riesling White vinification, residual pomace from the press was used as a raw material for the experimental production of pomace brandy. Pomace which remained after the separation of free run pomace was obtained without pressing, only by drawing off the must within the period of one hour with occasional turning of the basket. The total amount of pomace necessary for the particular series of experiments was weighed and divided by the experiment variations in plastic containers of 500 l. Upon homogenization and/or performed treatment, in accordance with the variants of the experiment, the pomace was distributed in plastic containers the capacity of which was 55 kg. In both years the containers filled with pomace were stored in the same air-conditioned rooms with an average temperature of 20°C for the period of 3 weeks, after which period alcoholic fermented pomace was distilled.

Distillation

In the experiment, double distillation was applied using simple copper still for distillation. First, the alcoholic fermented pomace was distilled, and then the selected fractions of the crude distillate (second and third fractions) combined and subjected to the second distillation. In the second distillation based on the analysis of the chemical composition of individual fractions of distillate, first and third fractions were

discarded, while the second fraction was used for the formation of brandy. Obtained distillates were diluted with demineralized water to the alcoholic strength of brandy of 50% vol. Brandy was formed for all the experimental variants with three repetitions, and it was stored in glass demijohns at the room temperature till the chemical analysis.

Physicochemical analysis methods

The share of alcohol, total titratable acidity, the proportion of esters and aldehydes in the samples was determined by the methods prescribed in the Regulations on Sampling Methods and Methods of Performing Chemical and Physical Analysis of Alcoholic Beverages (1987). The concentrations of methanol, n-propanol, isobutanol, 2-butanol, isoamyl alcohol (mixture of isomers 3-methyl-1-butanol and 2-methyl-1-butanol), n-hexanol, ethyl acetate, ethyl lactate were determined by gas chromatography (Recueil des methodes internationales d'analyse des boissons spiritueuses, des alcools et de la fraction aromatique des boissons) on a Hewlett Packard Model, 5890 Series II GC with flame-ionization detector and a split/splitless injector. The results of gas chromatographic analysis were processed by the integrator Hewlett Packard, Model HP 3396 Series II. For chromatographic separation the capillary column (Varian) CP-WAX 57 CB, was used measuring 50 m x 0.32 mm x 0.20 μm, with Restek Siltek guard column measuring 5 m x 0.25 mm. The conditions of chromatography regulated by The Regulations of the International Organization of Wine and Vine (O I V, Recueil des methodes internationales d'analyse des boissons spiritueuses, des alcools et de la fraction aromatique des boissons) were applied. The carrier gas was nitrogen at a flow rate of 30 ml/min. 0.5 μl of the sample with a split ratio of 1:50 was injected. 1-pentanol was used as internal standard.

Statistical methods

Statistical analysis was performed with two-way analysis of variance, and the significance level for all analyses an error of 5% was considered. Tukey's multiple comparison test was applied for testing the difference between the average of the effects of various types of fermentation and adding the additives before fermentation, which were significant in the analysis of variance. All the analyses were conducted with the Statistical Software Package SAS System for WinVer. 8.2 (SAS Inc., 1989).

Results

The average composition of brandies obtained from Riesling White pomace fermented with epiphyt yeasts (variant A) is shown in Table 1.

Composition of brandy obtained from pressed pomace

The average concentrations of methanol in brandies obtained from pressed pomace in the year 2005 were higher than the concentration of this alcohol in brandies from the year 2004 (Table 1). Lower concentrations of volatile substances (with the exception of ethanol and methanol) in pomace brandies obtained in the year 2005 were primarily the result of lower concentrations of volatile esters and lower acidity of pomace brandy variant A from that year. The average concentration of methanol in pomace brandy obtained from pressed pomace from the year 2005 exceeded the limit of maximum permissible concentration of the ingredient in pomace brandy (Pravilnik o jakim alkoholnim i alkoholnim pićima; Definition, Description and Presentation of Spirit Drinks: Council Regulation No 1576/89). The concentrations of total higher alcohols in pomace brandies of pressed pomace variant A were within the limits of movement of the higher alcohol content in pomace brandy quoted by Silva et al., 2000. Among the higher alcohols in the highest concentration (Table 1), isoamyl alcohol was present, followed by isobutanol, which is consistent with Portuguese and Spanish pomace brandy (Silva et al., 2000).

It should be noted that the concentration of total esters, as well as the total acidity of pomace brandy variant A obtained from pressed pomace in both years was within the limits of

Table 1
The concentration of volatile components in brandy from fermented grape marc graševine , variant A (2004-2005)

	2004	2005	
	K (*n*=3)	*K* (*n*=3)	*J* (*n*=3)
Alcohol %vol	49.37	49.7	48.62
Methanol	6751.30	10813.3	4,913
Total volatile substances	6530.60	5596.64	4,486
Σ higher alcohols	3484.97	3643.67	3,371
Isoamyl alcohol	1782.67	1981.67	2047.33
Izobutanol	765	883	646.67
n-propanol	527.33	418.67	577.67
n-heksanol	243.67	360.33	99.33
2-butanol	166.3	n.d.	n.d.
Total acidity*	453.33	120.67	98.67
Total esters**	2053.3	1284.3	639
Ethyl-acetate	1557.3	962.33	444.33
Ethyl-lactate	530	363.67	65
Total aldehydes***	539	548	377.33

* Expressed as acetic acid, ** Expressed as ethyl - acetate , *** Expressed as acetaldehyde

movement of the share of these ingredients presented by Silva et al. (2000) (Table 1). The average concentrations of total aldehyde in pomace brandies variant A derived from pressed pomace were at similar levels in both years of the experiment (Table 1) and they were below the limit values for the concentration of acetaldehyde in pomace brandies presented in references by Silva et al. (2000).

Composition of non-pressed pomace brandy

The pomace brandies of variant A produced in the year 2005 from non-pressed pomace of Riesling White based on the average value of the surveyed elements (Table 1) meet the criteria of quality completely (Pravilnik o jakim alkoholnim i alkoholnim pićima; Definition, Description and Presentation of Spirit Drinks: Council Regulation No 1576/89.) The average ratio of methanol in these brandies was more than twice lower than in the pomace brandy from pressed pomace obtained in the same year under the same conditions of fermentation and distillation (Table 1). Paunovic and Djurisic (1981) also reported significant differences in the concentrations of methanol in pomace brandy obtained from the pressed pomace compared to pomace brandy that was not pressed. The average total concentration of higher alcohols in pomace brandy variant A derived from non-pressed pomace was not significantly different from those in the comparative pomace brandies from pressed pomace (Table 1). Even so, some (minor) differences in the concentration of isobutanol and propanol were noticeable, as well as significant differences in the concentrations of n-hexanol in compared pomace brandies. The average concentrations of n-hexanol in brandies obtained from non-pressed pomace were within the acceptable concentration limits of this alcohol in pomace brandy (Silva et al., 2000; Cortés et al., 2005).

The influence of fermentation conditions on the composition of pomace brandy

Composition of pomace brandy fermented with the addition of commercial yeast (Variant B)

Results of the average composition of pomace brandies obtained from Riesling White pomace fermented with added commercial yeast *Uvaferm CM* (variant B) are presented in Table 2. The chemical composition of pomace brandies obtained from pressed pomace (K) harvested in the year 2004 and 2005 is shown together with the chemical composition of pomace brandy produced from non-pressed pomace (J) harvested in the year 2005. All pomace brandies variant B (Table 2) meet the required criteria of quality (*Pravilnik o jakim alkoholnim i alkoholnim pićima*; *Definition, Description and Presentation of Spirit Drinks: Council Regulation No 1576/89*).

Table 2
The concentration of volatile components in brandy from fermented grape marc graševine, variant B (2004-2005)

	2004	2005	
	K (*n*=3)	*K* (*n*=3)	*J* (*n*=3)
Alcohol, % vol	48.32	49.57	47.12
Methanol	5820.70	9326	4494
Total volatile substances	7040	6416.01	6110.34
Σ higher alcohols	4761.33	4906.34	5250.34
Total acidity*	364	104.67	84.67
Total esters**	1483	899	436.33
Total aldehydes***	431.67	506	339

* Expressed as acetic acid, ** Expressed as ethyl - acetate, *** Expressed as acetaldehyde

The average concentrations of methanol in these brandies from the year 2005 were significantly higher than those in the compared pomace brandies from the year 2004 (Table 2).

The share of total volatile substances (except ethanol and methanol) was slightly lower in pomace brandies produced in the year 2005 as the result of lower concentrations of volatile esters and lower acidity. In the experiment which lasted for two years the pomace brandy variant B had a significantly lower content of methanol with respect to the pomace brandy variant A derived from the fermented pomace with epiphytic yeasts (Tables 3, 4, 6 and 7). Pomace brandies fermented by adding yeast had a significantly higher content of isoamyl alcohol, isobutanol, n-propanol with respect to the brandies of variant A regardless of the year of harvest and trial series (Table 4, 6 and 7). The formation of higher alcohols increased which is the characteristic feature of the yeast *Uvaferm CM*. It should be noted that the pomace brandies variant B from the year 2004 obtained from pressed pomace had a significantly lower content of 2-butanol from the pomace brandies variant A (Table 4). The pomace brandies of variant A and B obtained from pressed pomace in both years did not significantly differ in concentrations of n-hexane (Tables 4 and 6). Pomace brandies of variant B from the year 2005 obtained from the non-pressed pomace had lower content of hexane in comparison with brandies produced from pressed pomace (Table 7). The concentration of hexane in pomace brandies variant B derived from non-pressed pomace was significantly higher than those in comparable pomace brandies of variant A (Table 7).

Pomace brandies of variant B produced in the year 2004 had a significantly lower total acidity and concentration of total esters in relation to pomace brandies variant A of the same year (Table 5), which is understandable in relation to

Table 3
The concentration of volatile components in brandy from fermented grape marc graševine, variant C,D,E (2004-2005)

	2004 *K* (*n*=3) Variants			2005 Variant D	
	C	*D*	*E*	*K* (*n*=3)	*J* (*n*=3)
Alcohol % vol	49.14	49.62	49.24	49.97	45.99
Methanol	6682.30	6040.30	6194	10898	5156
Total volatile substances	6181	5626	5865	5672	4601
Σ higher alcohols	3465	3206	3433	3473	3677
Total acidity*	423.33	354.67	406.33	183.67	71
Total esters**	1982	1832.30	1811	1321.70	533.67
Total aldehydes***	310.33	232.67	214.67	694	319

* Expressed as acetic acid, ** Expressed as ethyl - acetate , *** Expressed as acetaldehyde

Table 4
Results of analysis of variance of methanol and higher alcohols in brandies made from fermented pomace graševine variants A , B , C , D and E harvest in 2004

Varijant	Alcohol,	Methanol,		1-propanol,		Izobutanol,		Izoamyl alcohol,		2-butanol,		1-heksanol,	
	% vol	mg/l a.a.		mg/l a.a.		mg/l a.a.		mg/l a.a.		mg/l a.a.		mg/l a.a.	
A	49.37	6751.30	a	527.33	b	765.00	c	1782.67	c,d	166.33	a	243.67	b
B	48.32	5820.70	c	761.67	a	1051.33	a	2640.00	a	73.33	b	235.00	b
C	49.14	6682.30	a	498.33	d	763.00	c	1792.67	c,d	163.67	a	247.00	b
D	49.62	6040.30	c,b	485.00	d	717.00	d	1728.33	d	55.00	b	220.33	c
E	49.24	6194.00	b	503.67	c	759.33	c	1836.00	b,c	90.00	a,b	244.33	c
LSD	17,467	260.69		15,052		35.52		101.44		86,066		13.13	
Pr>F	0.6798	<.0001		<.0001		<.0001		<.0001		0.0551		0.0006	

Note: Mean values are denoted by the same letters do not differ statistically at $p < 0.05$

Table 5
Results of analysis of variance of total esters , ethyl acetate , ethyl lactate , total acidity and total aldehydes in brandies made from fermented pomace graševine A , B , C , D and E variants , vintage 2004

Varijant	Total esters,	Ethyl-acetate,	Ethyl-lactate,		Total acidity,		Total aldehydes,	
	mg/l a.a.	mg/l a.a.	mg/l a.a.		mg/l a.a.		mg/l a.a.	
A	2053.30	1557.00	530.00	c	453.33	a	539.00	a
B	1483.00	1146.00	473.33	c	364.00	c	431.67	a,b
C	1982.00	1741.30	526.33	c	423.33	a,b	310.33	b,c
D	1832.30	1343.00	696.00	a	354.67	c	232.67	c
E	1811.00	1491.00	607.67	b	406.33	a,b,c	214.67	c
LSD	345.22	407.10	66,885		58.72		165.1	
Pr>F	0.054	0.1071	0.0003		0.021		0.0094	

Note: Mean values are denoted by the same letters do not differ statistically at $p < 0.05$

Table 6
Results of analysis of variance components of fermented pomace brandy graševine A, B and D variants, the series (K) vintage , 2005

Varijant	Alcohol	Metha-nol,		Propa-nol,		Izobu-tanol,		Izoamyl alcohol,		Hek-sanol,	Total es-ters,		Ethyl - acetate,		Ethyl - lactate,		Total acidity,		Total al-dehydes,	
	% vol	mg/l a.a.		mg/l a.a.		mg/l a.a.		mg/l a.a.		mg/l a.a.	mg/l a.a.		mg/l a.a.		mg/l a.a.		mg/l a.a.		mg/l a.a.	
A	49.70	10813.30	a	418.67	b	883.00	b	1981.67	b	360.33	a 1.284.30	a	962.33	b	363.67	b	120.67	b	548.00	a
B	49.57	9326.00	b	719.67	a	1062.67	a	2738.00	a	386.00	a 899.00	b	629.00	c	216.33	c	104.67	b	506.00	a
D	49.97	10898.00	a	369.67	c	817.67	c	1888.33	b	397.00	a 1321.70	a	1113.33	a	347.00	a	183.67	a	694.00	a
LSD	0.7742	354.80		36,448		36.91		112.11		38,446	150.91		59,747		29,586		43,507		263.67	
Pr›F	0.42	0.0004		‹0.0001		0.0001		‹0.0001		0.1234	0.0026		‹0.0001		0.0006		0.0152		0.2312	

Note: Mean values are denoted by the same letters do not differ statistically at $p < 0.05$.

Table 7
Results of analysis of variance components of fermented pomace brandy graševine A, B and D variants, the series (J), vintage 2005

Varijant	Alcohol	Metha-nol,		Propa-nol,		Izobu-tanol,		Izoamyl alcohol,		Hek-sanol,		Total es-ters,		Ethyl - acetate,		Ethyl - lactate,		Total acidity,		Total al-dehydes,	
		mg/l a.a.		mg/l a.a		mg/l a.a.		mg/l a.a.		mg/l a.a.		mg/l a.a.		mg/l a.a.		mg/l a.a.		mg/l a.a.		mg/l a.a.	
A	48.62	4913.00	a	577.67	c	646.67	b	2047.33	c	99.33	b	639.00	a	444.33	a	65.00	a	98.67	a	377.33	a
B	47.12	4494.00	b	917.67	a	1033.67	a	3173.00	a	126.00	a	436.33	c	211.00	c	0.00	b	84.67	a	339.00	a, b
D	45.99	5156.30	a	677.00	b	680.00	b	2201.67	b	118.33	a	536.67	b	374.67	b	61.33	a	71.00	a	319.00	b
LSD	27,826	338.46		44.89		44.39		94,517		7834.8		90,361		67,.503		11,208		34,772		43,129	
Pr>F	0.1343	0.0137		<0.0001		<0.0001		<0.0001		0.0016		0.0087		0.0016		0.0001		0.2029		0.0464	

Note: Mean values are denoted by the same letters do not differ statistically at $p < 0.05$

the expected effects of the flow of alcoholic fermentation with the addition of *starter* yeast culture. In the year 2005 pomace brandies of variant B had significantly lower levels of total esters, ethyl-acetate and ethyl-lactate than pomace brandies of variant A (Tables 6 and 7), while the difference in total acidity and total aldehydes between comparative variants was not significant in given year.

Composition of pomace brandies obtained from pomace treated with pectolytic enzymes before fermentation

The average composition of pomace brandies obtained from Riesling White pomace treated with pectolytic enzymes before fermentation conducted by epiphyt yeasts is shown in Table 3. Pomace brandies of all experimental variants derived from pomace treated with commercial preparations of pectolitic enzymes in terms of the average values of the basic elements of composition matched the prescribed quality requirements (*Pravilnik o jakim alkoholnim i alkoholnim pićima; Definition, Description and Presentation of Spirit Drinks: Council Regulation No 1576/89*) with the exception of pomace brandy variant D derived from pressed pomace in the year 2005, which had an average concentration of methanol above the permissible limit (10 898 m /l a.a.).

Pomace brandies obtained from pressed pomace in all treatments (variants C, D and E) from the year 2004 had a lower average concentration of methanol than the comparable pressed pomace brandies (variant D) from the year 2005 (Table 3). In the year 2004 pomace brandy of variant C had the highest average concentration of methanol, which was not significantly different from that in pomace brandies variant A (Table 4).

The average share of total volatile substances (other than ethanol and methanol) in pomace brandies variants C, D and

E from the year 2004 was slightly lower (Table 3) than the comparable brandies of variant A (Table 1), while in parallel brandies from the year 2005 share of total volatile matter was at a similar level. The average concentrations of total higher alcohols in brandies of variants C, D and E from the year 2004 did not significantly differ from those (Table 1) in samples of variant A. It is important to mention that the brandies of variant D from the year 2004 had significantly lower concentrations of n-propanol, isobutanol, 2-butanol and n-hexanol from the brandies of variant A. Similar to pomace brandies of variant A and B pomace brandies of variant D from the year 2005 obtained from pressed pomace had significantly lower total acidity, the average concentration of total esters, ethyl acetate and ethyl lactate in comparison to pomace brandies from the year 2004 (Tables 5 and 6).

Discussion

Excessive concentrations of methanol usually occur in the pomace brandies produced commercially, which is interpreted as a consequence of the strong pressing of pomace using continuous presses, or prolonged storage of fermented pomace during which the loss of alcohol occurred (Paunovic and Djurisic, 1983; Silva et al., 1996; Cortés et al., 2005). Due to the fact that in this experiment, in both years the processed pomace was obtained under equal conditions of pressing and the fact that brandies were produced at a unique scheme of the experiment, it has been assumed that the variation of methanol concentrations can be associated with different quality of the Riesling White grape in the comparative years. The research conducted by Herjavec (1989) indicated the variation of the concentration of methanol in wine produced from Riesling White in Kutjevo vinegrowing region in particular years. The average concentrations of n-hexanol in pomace brandies produced in the year 2005 were above the concentrations mentioned by other authors (Silva et al., 20000; Cortés et al., 2005; Apostolopoulou et al., 2005; Verisini et al., 1990).

The average ratio of 2-butanol in pomace brandies variant A produced from pressed pomace in the year 2004 was in the acceptable concentration (Silva et al., 2000). The assumption is that the lack of formation of 2-butanol in pomace brandy produced in the year 2005 resulted from the high acidity of pomace in that year as presented in references (Versini and Inama, 1981). It has been assumed that the lower total acidity, as well as lower levels of total esters and individual ethyl acetate and ethyl lactate in pomace brandies from the year 2005 was primarily the result of the high acidity of the pomace in that year, which according to Da Porto and Zironi (1997) was an important factor in preventing undesirable microbiological processes. The lower content of total esters, ethyl acetate, ethyl lactate and total aldehyde in pomace brandies obtained from non-pressed pomace (Table 1) could be connected with a homogeneous structure of non-pressed pomace and because of that a significantly reduced degree of aeration. Paunovic and Djurisic (1981) have also reported lower concentrations of total esters as well as concentrations of total aldehydes in pomace brandy obtained from the non-pressed pomace compared to pomace brandies obtained from pressed pomace. The average ratio of methanol in pomace brandy variant B derived from the pressed pomace in the year 2004 was for 931 mg/l a.a. lower than the concentration of methanol in the comparative pomace brandies variant A of the same year. It has been assumed that in the pomace fermented with added yeast was more separated liquid phase.

Due to the fact that the equal dilution ratio of pomace with water was applied before distillation, it was reasonable to expect a lower proportion of methanol in pomace brandies variant B, which was also indicated by Paunovic and Djurisic (1983). Significantly lower concentrations of methanol were in pomace brandies of variant D and E of that year (Table 4). In the year 2005 pomace brandy variant D derived from pressed pomace, as well as those derived from non-pressed pomace did not significantly differ in concentrations of methanol from comparable pomace brandy of variant A. According to previous studies (Silva and Malcata, 1998) addition of pectinase preparation *Ultrazym* 100 G in the amount of 2 g/100 kg of pomace had statistically significant effect on the increase of the proportion of methanol in pomace brandy. However, this experiment has brought mixed results. One of the possible interpretations of the obtained results is similar to that of the movement of methanol in brandies variant B. As the Table 3 shows it is evident that from the treated pomace brandies from the year 2004 the lowest average concentration of methanol was in pomace brandy variant D. When the same ratio of dilution of pomace with water has been applied it is reasonable to expect the same or lower proportion of methanol in these brandies compared to the control variant (A), as indicated in the results by Paunovic and Djurisic (1983). Compared with brandies of variant A, obtained from pressed pomace in the year 2005, brandies of variant D, also had significantly lower concentrations of n-propanol and isobutanol (Table 6). The pomace brandies of variants C and E obtained from pomace treated with pectolytic enzymes in the year 2004, were not significantly different from compared pomace brandies of variant A in term of total acidity, the share of total esters and ethyl acetate (Table 5). Pomace brandies of variant D in that year had significantly lower total acidity and significantly higher concentration of ethyl lactate. It is worth mentioning that the pomace brandies of variants C, D and E from the year 2004 had significantly lower content of total aldehydes in relation to pomace brandies of variant A.

Conclusions

Based on the average values of basic chemical compounds, pomace brandies of all experimental variants obtained from Riesling White pomace in the year 2004 and 2005, meet the criteria of quality according to (*Pravilnik o jakim alkoholnim i alkoholnim pićima; Definition, Description and Presentation of Spirit Drinks: Council Regulation No 1576/89*) with the exception of pomace brandy obtained in the year 2005 from the pressed pomace fermented with epiphytic yeast, as well as pomace brandy from the same pomace treated with pectolitic enzyme before fermentation conducted by epiphyt yeasts where the methanol concentration was above the permissible limits. The concentration of methanol in the pomace brandies obtained from Riesling White pomace varied considerably, both in relation to the experimental series, fermentation variant and according to particular years.

Pomace brandies of all experimental variants derived from pressed pomace in the year 2005 had significantly higher concentrations of methanol, lower total acidity, lower share of total esters, ethyl acetates and ethyl lactates in relation to pomace brandies from the year 2004. Pomace brandies of all experimental variants obtained from non-pressed pomace had twice as low methanol contents as the pomace brandies obtained from pressed pomace. Pomace brandies obtained from non-pressed pomace had significantly lower concentrations of total esters and individually ethyl acetate and ethyl lactate, and the lower concentrations of total aldehydes from pomace brandies obtained under the same fermentation conditions and distillation of pressed pomace. The concentration of n-hexane was twice as low in non-pressed pomace brandies in relation to pressed pomace brandies. Pomace brandies obtained from pomace fermented with addition of yeast had significantly lower concentrations of methanol, but higher total alcohol content compared to pomace brandies obtained from pomace fermented with epiphytic yeast. The average concentrations of total higher alcohols in brandies obtained from pomace treated with pectolytic enzymes were at the level of those in the control pomace brandies. Depending on the type of added enzyme preparation variation in concentration of some higher alcohols has been identified.

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