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Effect of alcoholic fermentation on the quality of grape brandies

Vera Vukosavljević[1], Ranković Vesna[2], Dragoljub Žunić[3], Saša Matijašević[3]

[1]Faculty of Agronomy, Cara Dušana 34 Čačak, Serbia (verav@kg.ac.rs)
[2]Centre of Viticulture and Viniculture, Kolonija EL 6, Niš, Serbia
[3]Faculty of Agriculture, Zemun, Nemanjina 6, Belgrade, Serbia

Abstract: Grape brandy is a product obtained by fermentation and distillation of crushed grapes of cultivated grapevine *Vitis vinifera*. Grape brandy quality depends on many factors such as: grapevine varieties, climate, soil, time and method of distillation, storage methods and other distillates. The grapevine variety 'Neoplanta' grown in the experimental field of the PD "Center for Viticulture and Enology" in Niš was used in the experiment. Tests were performed in the laboratory of the Centre. Healthy grapes of harvest maturity were squashed by a stalk-removing electric crusher. Fermentation was performed in plastic containers in the presence of the indigenous microflora of wine yeasts. This paper presents the influence of pH and inorganic nitrogen added to the fermentation medium on the content of volatile components and concentrations of higher alcohols.
Key words: grape brandy, grape, higher alcohols, variety, Neoplanta

Introduction

Grape brandy is a product made by fermentation and distillation of grape pomace of cultivated grapevine Vittis vinifera (Lučić 1986; Paunović and Đurišić

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1981). Grape brandy quality depends on many factors: grapevine variety, climate, land, agricultural practices, yield, fermentation characteristics, timing and methods of distillation, storage methods and other distillates (Nikićević *et al.* 2000; Paunović and Nikičević 1986; Petkov *et al.* 1998; Stanković *et al* 1998).

Water and ethanol are the main volatile ingredients of alcoholic beverages, followed by methanol and higher alcohols (Paunović 2000). Higher alcohols are formed during fermentation, and they affect the quality of a beverage and its sensory properties. In addition, higher alcohols contribute to the formation of flavor. Unfortunately, problems arising due to excessive consumption of beverages are partially attributed to higher alcohols which, considering their action, belong to drugs.

This research was conducted to study the impact of alcoholic fermentation on the concentration of higher alcohols in 'Neoplanta' grapevine brandy. Quality parameters of the grape brandies produced were determined by standard methods in accordance with the Rules on the Methods of Sampling and Performance of Chemical and Physical Analyses of Alcoholic Beverages (Regulations on Sampling Methods and Physical and Chemical Analyses of Spirits (1987). Higher alcohols were assessed by the gas-chromatographic method.

The GC method for the quantitative determination of volatile components in alcoholic beverages prescribed by the Office International de la vigne et du vin, Recueil des methodes internationales d'analyse des boissons spiritueses, des alcools et de la fracton aromatique boissons (OIV 1994) is an internal standard method, with 4-methyl-2-pentanol as the internal standard, column Carbowax 1540 isothermal temperature regime of 40 ° C, linear increase of 4 ° C / min to 200 ° C. Some analysts determine higher alcohols in wine using column Carbowax 1500, with n-butanol as the internal standard, and temperature is controlled by increasing injector temperature to 8 ° C after leaving the peak (Lee and Cooly 1981). Retention times of methanol 0.77, ethanol 1.49, n-propanol 3.23, isobutanol 6.53, n-butanol - 8.16 internal standard, isoamylalcohol 14, 19. In some studies, the GC method with flame ionization detector was used to determine the parameters (ethyl acetate, 2-butanol, 1-propanol, 2-methyl-1-propanol, 21-ol, 1-butanol, 2- methyl-1-butanol, 3-methyl-1-butanol) under similar conditions (Boscolo *et al.* 2000; Miranda *et al*. 1985).

Materials and methods

Grapes of grapevine cultivar 'Neoplanta' grown in the experimental field of the PD "Center for Viticulture and Enology" in Niš were used in the experiment. Tests were performed under laboratory conditions at the Centre. Healthy grapes of harvest maturity were mashed by a stem-removing electric crusher. The fermentation of the whole grape pomace was performed in plastic containers in the presence of the indigenous microflora of wine yeasts. Distillation and

redistillation of fermented pomace were performed using discontinuous-type distillation apparatus of 10L volume. The first distillation was designed to maximize the exploitation of alcohol without separation into fractions. Redistillation involved separation into fractions, as follows:

- The first faction - 1% of the still,
- Heart binding constraint - central stream which has an average of 55vol% alcohol
- Weak brandy - last distillate stream to the maximum alcohol exploited.

The obtained distillates were stored in glass balloons, and after 6 months physically and chemically partially stabilized brandies were analyzed.

The experiment was set up in six variants according to the design given in Table 1.

Table 1. Experimental variations

Experimental variant	Experimental conditions
Variant 1	fermentation at 20 ° C
Variant 2	fermentation at 30 ° C
Variant 3	pH adjustment to pH 3 by addition of H2SO4 to the medium, fermentation at 20 ° C
Variant 4	pH adjustment to pH 3 by addition of H2SO4 to the medium, fermentation at 30 ° C
Variant 5	addition of 0.6 g $(NH4)_2HSO4$ per kg of pomace, fermentation at 20 ° C
Variant 6	addition of 0.6 g $(NH4)_2HSO4$ per kg of pomace, fermentation at 30 ° C

The quality parameters of grape brandies produced were determined by standard methods laid down in the Rules on the Methods of Sampling and Performance of Chemical and Physical Analyses of Alcoholic Beverages. Higher alcohols were analyzed by gas-chromatography.

The applied method is a GC internal standard, with 1-butanol as the internal standard. Analysis was performed on a Varian 3400 with flame ionization detector (FID). Operating conditions were as follows: nitrogen flow rate 20ml / min, the flow rate of hydrogen 20ml / min, air flow rate 200ml / min, column Carbowax 20M, injector temperature 120 °C, 160°C temperature detectors, temperature conditions: starting temperature of 40 ° C, linear increase of temperature 40 ° C to 160 ° C, 8 °C / minute to 160 ° C without holding the final temperature, the amount of injected sample 1µl. The qualitative and quantitative

determination of 1-propanol, isobutanol, isoamyl alcohol and amyl alcohol was performed.

Results and Discussion

The chemical composition of grape brandies is shown in Table 2.

The chemical quality parameters of the experimental grape brandies are in accordance with legal regulations, the Ordinance on the Quality of Alcoholic Beverages, Official Gazette 4/2003.

Experimental results showed that the total acid content and esters of methanol were lower in the variant involving fermentation at 20 ° C (variants 1, 3 and 5), compared to variants in which fermentation took place at 30 ° C (variants 2, 4 and 6) (Flanzy *et al.* 1968; Jović 1992; Lee and Cooly 1981). The concentration of total aldehyde and furfural was higher in grape samples undergoing fermentation at a higher temperature, 30 ° C (Variant 2) (Flanzy *et al*.1968; Lee and Cooly 1981 and Miranda *et al.*1985).

The concentration of higher alcohols generated during fermentation depends on a number of factors, such as amino acid composition, the concentration of ammonium salt in the fermented mixture, fermentation temperature, yeast, etc.

At lower nitrogen content up to 300 mg / l, the amount of higher alcohol rises to the maximum, when it starts to decrease until the end of fermentation, despite the further increase in nitrogen. This rule applies to higher alcohols having corresponding amino acid precursors. In the case of 1-propanol, which has no corresponding amino acid precursor, the formation continues with increasing nitrogen up to 500 mg / l. This is interpreted as the predominant formation of sugar.

It is believed that the relationship between the amount of amino acids (more than twenty were identified in the grapes) and higher alcohols in wine is strongly determined by varietal specificity. The amino acid composition indicates the metabolic processes occurring during the growing season and grape maturation. The amino acid composition provides information about the time of separation of wine from the litter (Pekka 1996). Paunovic R. quoting Rodopula (Paunović 2000) states that the increase of the concentration of amino acids is related to generated higher alcohols; 1-propanol and isobutanol increase, and the amount of pentanol declines. The experimental results confirm that the addition of inorganic nitrogen led to a reduction in the concentration of higher alcohols compared to the control (Puškaš 2002).

Table 2. Chemical composition of experimental 'Neoplanta' grape brandies

Experimental variant / Investigation Parameter	Variant 1	Variant 2	Variant 3	Variant 4	Variant 5	Variant 6
Relative density at 20º/20ºC	0.9205	0.9191	0.9122	0.9196	0.9192	0.9228
Alcohol, vol%	55.59	56.25	59.42	56.02	56.21	54.50
Total acids, mg/L	442.3	69.8	221.2	128.0	279.4	46.6
Esters, mg/Laa	3466.0	1120.0	4839.0	1193.0	2119.0	694.0
Methanol, g/Laa	1.65	1.40	2.44	1.36	2.03	1.71
Total aldehydes, mg/Laa	107.5	258.0	129.3	259.0	91.1	125.3
Furfural, mg/Laa	1.3	3.2	0.9	2.9	1.0	1.1
Total higher alcohols, mg/Laa, GC-method	2870.40	3545.41	2688.21	3372.92	2669.64	3170.85
Propanol mg/Laa	208.68	137.92	127.46	107.97	200.88	181.97
Isobutanol mg/Laa	453.31	628.89	492.13	596.14	445.88	547.26
Isopentanol mg/Laa	2004.74	2717.25	2023.47	2564.97	1988.29	2321.41
Pentanol mg/Laa	203.67	64.35	45.15	103.84	34.59	120.21
Isopentanol/isobutanol	4.4	4.3	4.1	4.3	4.4	4.2
Isobutanol/propanol	2.2	4.5	3.8	5.5	2.2	3.0
Isopentanol/propanol	9.6	19.70	15.9	23.7	9.9	12.8

The minimum concentration of higher alcohols was determined in Variant 5 which involved the addition of inorganic nitrogen and fermentation at 20 ° C, followed by Variant 3 for which pH of the fermentation medium was adjusted.

If we consider the temperature factor, the content of higher alcohols was lower in variants subjected to fermentation at 20 ° C (Variants 1, 3 and 5). The highest concentration of propanol increases at the fermentation temperature of 18°C (Paunović 2000). The concentration of propanol in the experimental grape

brandy for variants in which fermentation took place at 20 ° C (Variants 1, 3 and 5) was expectedly higher than in variants subjected to fermentation at 30 ° C.

Propanol content was higher in the variant with inorganic nitrogen added (Variants 5 and 6) and fermentation of pentanol until the concentration was higher in the variant where fermentation took place at 30 ° C (Paunović, (2000).

Variants involving pH adjustment of the fermentation medium (Variants 3 and 4) resulted in reduced content of higher alcohols compared to the control.

The highest content of isobutane and isopentanol was determined in Variant 2 during fermentation at 30 °C, without correction of the fermented medium, and lowest in Variant 5 which involved fermentation at 20 °C with the addition of inorganic nitrogen.

The minimum content of pentanol was determined in Variants 5 and 3 - 34.59 mg / La.aa and 45.15 mg / La.aa, respectively.

The ratio of isopentanol / isobutanol in experimental grape brandies ranged from 4.1 (Variant 3) to 4.4 (Variants 1 and 5). The ratio of isobutanol / propanol ranged from 2.2 (Variants 1 and 5) to 5.5 (Variant 4), isopentanol / propanol 9.6 (Variant 1) to 23.7 (Variant 4). The ratios of tested higher alcohols are consistent with research in this field. The ratio of isobutanol / propanol in Variant 4 was 5.5, maximum ratio 4, isopentanol / ropanol 23.7, previous maximum determinations 20 (Petkov *et al.*; Stanković *et al.* 1998). The resulting deviations in Variant 4 were expected because this grape fermentation occurred at 20 ° C with the addition of inorganic nitrogen.

Conclusion

These results suggest the following:

Chemical quality parameters of experimental grapes are in accordance with legal regulations, the Ordinance on the Quality of Alcoholic Beverages, Official Gazette 4/2003.

The experimental samples of grape brandies obtained by fermentation at 20 ° C have a lower content of acids, esters and methanol compared to corresponding solutions at 30 ° C.

The concentration of total aldehyde and furfural were higher in variants in which fermentation occurred at 30 ° C.

The lowest concentration of higher alcohols was determined in the experimental variant involving the addition of inorganic nitrogen and fermentation at 20 ° C, followed by Variant 3 involving pH adjustment.

The content of higher alcohols was lower in variants with fermentation occurring at 20 ° C.

Variants involving pH adjustment of the fermentation medium led to a reduced content of higher alcohols compared to the control.

The highest contents of isobutanol and isopentanol were determined in Variant 2, fermentation at 30 ° C, without correction, and lowest in Variant 5, fermentation at 20 ° C, addition of inorganic nitrogen.

The minimum content of pentanol was determined in variants involving fermentation at 20 ° C, pH adjustment and inorganic ammonia addition.

The ratio of isobutanol / propanol ranged from 2.2 to 5.5, isopentanol / propanol 9.6 to 23.7.

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UTICAJ ALKOHOLNE FERMENTACIJE NA KVALITET RAKIJE LOZOVAČE

Vera Vukosavljević[1], Ranković Vesna[2], Dragoljub Žunić[3], Saša Matijašević[3]

[1]Agronomski fakultet u Čačku, Cara Dušana 34 Čačak, Srbija
[2]Centar za vinogradarstvo i vinarstvo, Kolonija EL 6, Niš, Srbija
[3]Poljoprivredni fakultet,Zemun, Nemanjina 6, Beograd, Srbija

Rezime

Lozovača ili lozova rakija predstavlja proizvod koji se dobija fermentacijom i destilacijom celog kljuka grožđa plemenite vinove loze *Vitis vinifera.* Kvalitet rakije lozovače zavisi od velikog broja faktora: sorte vinove loze, klime, zemljišta, vremena i načina destilacije, načina čuvanja destilata i dr. Za realizaciju ovog eksperimenta korišćeno je grožđe sorte vinove loze 'Neoplanta' koja se gaji na oglednom imanju PD »Centar za vinogradarstvo i vinarstvo« u Nišu. Ispitivanja su izvedena u laboratorijskim uslovima Centra. Zdravo i tehnološki zrelo grožđe je izmuljano električnom muljačom koja odvaja peteljke. Fermentacija celokupnog kljuka grožđa je izvršena u plastičnim vrionim posudama u prisustvu autohtone mikroflore vinskih kvasaca.

U radu je prikazan uticaj pH vrednosti i neorganskog azota dodatog u fermentacionu smešu na sadržaj isparljivih komponenti i koncentraciju viših alkohola.

Ključne reči: lozova rakija, grožđe, viši alkoholi, sorta, Neoplanta