

AROMATIC COMPOUNDS OF BRANDIES PRODUCED FROM THREE APRICOT VARIETIES CULTURED IN SERBIA

AROMATIČNE MATERIJE RAKIJA PROIZVEDENIH OD NEKIH SORTI KAJSIJE UZGAJANIH U SRBIJI

Vladimir S. PUŠKAŠ, Uroš D. MILJIĆ, Vesna M. VUČUROVIĆ, Ana B. MUZALEVSKI
University of Novi Sad, Faculty of Technology, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia
e-mail: puskasv@uns.ac.rs

ABSTRACT

This study investigated the effect of certain apricot varieties cultured in Serbia on the quality of produced brandies, primarily in terms of the content and relationships of aromatic substances. In this study, fruits of three apricot varieties (NS 6, NS rodna and Ambrozija) were used for production of brandies. Primary fruit processing and distillation were carried out in a distillery of industrial capacity. High differences in the quantity of 14 identified aromatic components of the distillates produced from three apricot varieties were recorded. Ethyl decanoate was present in all three distillates in significantly larger amounts compared to other esters. Ethyl isobutyrate was found in a small amount (0.32 mg/L) in the distillate produced from Ambrozija variety, while in the distillates from other varieties this compound was not detected. The distillates produced from varieties NS6 and NS rodna contained significantly higher amounts of ethyl lactate (12.50 to 13.46 mg/L) compared to the distillate from Ambrozija variety (8.87 mg/L). The content of linalool determined in NS6 distillate was three times higher (22.12 mg/L) in comparison to the distillate from Ambrozija (7.31 mg/L).

Key words: aromatic compounds, apricot variety, distillate, brandy.

REZIME

Kajsija (*Prunus armeniaca* ili *Armenicea vulgaris lam*) pripada rodu *Prunus*. Vodi poreklo iz severo-istočne Kine. Sorte kajsije, koje se gaje u južno-evropskim i našim krajevima, imaju kratak vremenski period sazrevanja, 25 - 30 dana. Plod kajsije poseduje aromu, koja destilacijom prelazi u rakiju i daje joj specifična organoleptička svojstva. U svežim kajsijama identifikovano je oko 100 isparljivih jedinjenja, među kojima su terpeni alkoholi, laktoni, neki fenoli, aldehidi i terpeni ketoni. Aromatične materije rakije od kajsije čine mnogobrojne komponente od kojih neke deluju sinergistički, pa svojim prisustvom pojačavaju ukupnu aromu destilata. Ovo se posebno odnosi na alkohole sa brojem atoma ugljenika 6 - 10 i enantne estre, koji se u destilatima nalaze u malim količinama, imaju jak miris i tako pojačavaju aromu i doprinose da ona bude složenija i harmoničnija. U radu je ispitan uticaj sorte kajsije na kvalitet proizvedene rakije, pre svega u pogledu sadržaja i odnosa mirisnih materija. Za proizvodnju ispitanih rakija upotrebljeni su plodovi tri sorte kajsije (NS 6, NS rodna i Ambrozija). Primarna prerada voća i destilacija je izvršena u destileriji industrijskog kapaciteta, pod identičnim uslovima prerade za sve tri ispitivane sorte voća. Etil-izobutirat je utvrđen u maloj količini (0,32 mg/l) u destilatu proizvedenom od sorte Ambrozija, dok u destilatima od druge dve sorte nije detektovan. Destilati proizvedeni od sorti NS6 i NS rodne, sadržali su značajno veće količine etil-laktata 12,50 – 13,46 mg/l u odnosu na destilat od sorte Ambrozija (8,87 mg/l). Utrvđen sadržaj linalola je trostruko veći u destilatu NS6 (22,12 mg/l) u odnosu na destilat Ambrozije (7,31 mg/l).

Ključne reči: aromatična jedinjenja, sorte kajsije, destilat, rakija.

INTRODUCTION

Apricot (*Prunus armeniaca*, or *Armenicea vulgaris lam*) belongs to the genus *Prunus*. It originates from north-eastern China. An average year production of apricots in Serbia is around 30,000 t (Faostat, 2013). More than 80 % of world apricot production is comprised of less than 30 varieties. In Serbia, the following apricot varieties are usually grown: Ambrozija (S. Ambrogio), Breda, Kečkemetska ruža (Kečkemeti rozsa), Mađarska najbolja (Ungarische Beste), Holubova (Holubova Merunka), Crvena rana, Novosadska rodna, NS-6 etc. (Đurić and Keserović, 2007). The fruits are used for table consumption, drying and processing (Babić et al., 2002; Babić et al., 2003). A significant amount of apricot fruits produced in Serbia, as well as Hungary, Romania and other countries from the region, is processed into brandy, a distillate of apricot fermented pomace.

Apricot fruits to be processed into brandy should be soft and should have the largest amounts of aromatic substances and sugar. Therefore, they must be fully ripe or slightly overripe before harvesting. Apricot fruit has unique flavour, which

through the distillation process is transferred into brandy, giving it specific organoleptic characteristics. The composition and amount ratio of aromatic components in brandy varies depending on the variety, degree of fruit ripeness during processing, primary processing and alcoholic fermentation conditions (pH, temperature, enzymes, yeasts etc.), the distillation process, as well as the distillate ageing (Genovese et al., 2004; Nikićević and Paunović, 2013). According to the stage of processing and production when aromatic substances occur, they are divided into: primary (originating from fruit), secondary (originating from fermentation), tertiary (originating from distillation) and quaternary (originating from distillate ageing).

In fresh apricots about 100 volatile compounds are identified, including the terpene alcohols, lactones, some phenols, aldehydes and terpene ketones (Guillot et al., 2006). Numerous components which determine the aroma of apricots can act synergistically, enhancing the overall flavour of the distillate (Nikićević and Paunović, 2013; Puškaš et al., 2013). This especially refers to alcohols with 6-10 carbon atoms and enanthic (heptanoic) esters, which are found in small quantities in the distillates, but which have a strong odour and enhance the

flavour and contribute to its complexity and harmoniousness. Heptanoic esters, higher alcohols (from hexanol to decanol) and alcohols and esters of terpene structure are characterized by a complex floral-ester odour. Ethyl acetate and other aliphatic esters are characterized by fruity-ester aromas. The total amount of volatile compounds in spirit drinks is within the range 0.6-1.4 g/L (Buglass, 2011).

The aim of this study was to evaluate the suitability of certain apricot varieties cultured in Serbia for production of high quality brandy. The suitability was primarily assessed in terms of the content and relationships of the most important aromatic substances determined in the produced brandies.

MATERIAL AND METHOD

Distillates examined in this paper were produced and analysed in Promont distillery, Novi Sad, Serbia. The process of the distillate production is described in the following paragraphs.

Raw material for brandy production included fruits of three apricot varieties (NS 6, NS rodna and Ambrozija). The dry matter content in the liquid phase of pomace after crushing was 13 % for NS 6, 12 % for NS rodna, and 14 % for Ambrozija. The pH was adjusted to 3.25 prior to yeast inoculation using sulfuric acid. After the preparation of pomace, commercial rehydrated active dry yeast *Saccharomyces cerevisiae* (Fermol Aroma, AEB Group, Italy) was inoculated in the amount of 25 g/hL. Alcoholic fermentation took place in stainless steel tanks (volume 20 000 L) at 18 °C. Fermentation lasted for 18 days for NS 6 and NS rodna varieties, while in the case of Ambrozija, fermentation lasted for 17 days. Distillation was carried out immediately after the end of the fermentations in the distillation unit Arnold Holstein SH (volume 500 L), equipped with rectification column with 4 floor. The distillates were stored in stainless steel tanks until the time of the analysis. The alcohol content in the distillates was set at 42 % v/v.

Determination of methanol, ethanol and higher alcohols concentration was conducted by gas chromatographic analysis, performed using a gas chromatograph Agilent 7890A equipped with flame ionization detector (FID) and a split/splitless injector. A capillary column HP-INNOWax (polyethylene glycol; 30 m x 250 µm i.d., with 0.25 µm film thickness) was used for separation of components. Sample volume of 1 µL was injected directly into the column. The detector and injector temperatures were 280 °C and 220 °C, respectively. GC oven temperature program was: 35 °C (5 min) to 240 °C (2 min) at the rate of 5 °C/min. The carrier gas was helium at a 150 mL/min flow, while flow speed of hydrogen and air was 30 mL/min and 400 mL/min, respectively.

Determination of other volatile components (aromatic compounds) of apricot brandy requires a pre-treatment of the sample. This includes Soxhlet extraction for 2 hours, according to the following procedure: 50 mL of brandy sample mixed with 50 mL of distilled water, 50 mL of methylene chloride (a solvent) and 200 µL of methyl undecanoate (1 mg/mL, an internal standard), while injection volume was 1 µL. The extract was concentrated to the volume of 1 mL by vacuum evaporation (2 hours at 20 °C). A gas chromatograph Agilent 7890A, equipped with flame ionization detector (FID) and a split/splitless injector was used. The separation was carried out using Agilent 19091J-215 HP-5 (5 % phenyl methyl siloxan) capillary column, 50 m x 320 µm i.d., with 1.05 µm film thickness. The detector and injector temperatures were 300 °C and 250 °C, respectively. GC oven temperature was programmed from 50 °C to 300 °C at the rate of 2 °C/min. The carrier gas was helium (45 mL/min), while flow speed of hydrogen was 30 mL/min and that of air 400 mL/min.

RESULTS AND DISCUSSION

The analysis of the produced distillates showed that the content of certain volatile components depends largely on the variety of apricots used. The obtained results are shown in Table 1.

Table 1. Content of the main components in the distillates produced from the studied apricot varieties

	NS 6	NS RODNA	AMBROZIJA
Ethanol (% v/v)	41.61	41.97	41.85
Compound (mg/L a.a.)			
Acetaldehyde	148	101	147
Ethyl acetate	592	588	592
Methanol	6372	6609	7329
1-Propanol	930	623	574
Isobutanol	798	1015	1184
1-Butanol	53	50	64
3-Methyl-1-butanol	1869	2768	3028
1-Hexanol	46	42	41
Furfural	5	13	15
Benzaldehyde	25	26	23
1-Nonanol	-	-	43
1-Decanol	-	47	-

From the obtained results, it is evident that the distillates produced from NS rodna and Ambrozija varieties contained significantly higher amounts of 3-methyl-1-butanol, the isomer of amyl alcohol with a characteristic odour similar to banana. However, since it is a higher alcohol, a by-product of alcoholic fermentation, the differences in the content of this compound may be linked to differences in the content of its precursor (amino acids isoleucine) in fruits or the presence of specific microbiota on the surface of fruits, which contributed to formation of larger quantities of this compound. In a similar way one can explain the differences in the presence of nonanol only in the distillate from Ambrozija variety and decanol in the distillate from NS rodna variety. Nonanol and decanol are some of the components of orange oil, with a characteristic intense citrus and floral scent. Higher alcohol 1-hexanol, the contents of which are very similar in all distillates, has the aroma that resembles the odour of enanthic esters. The content of some other compounds which are by-products of fermentation (such as ethyl acetate, acetaldehyde) and which have an intense smell was not significantly different in the distillates from the studied apricot varieties.

The contents of aromatic components were also highly different in the distillates produced from three studied apricot varieties. It was shown that the amounts of aromatic components in the distillates were largely dependent on the apricot variety, i.e. on the chemical composition of raw materials. The results of the analysis of aromatic compounds content in the produced distillates are shown in Table 2. Ester ethyl isobutyrate, a compound with a characteristic odour similar to pineapple, was determined only in the distillate from Ambrozija variety, in the amount of 0.32 mg/L. Because of the pleasant aroma, this compound is considered as a desirable component of the distillate aromatic complex. Ethyl lactate, an ester present in many foods, giving a creamy scent with tones of fruits and coconuts, was found in all three distillates. The distillate of Ambrozija variety contained slightly lower amounts of ethyl lactate (8.87 mg/L), compared to the distillates from other two varieties (12.5-13.5 mg/L). Valeric esters have characteristic fruity scents. For example, ethyl isovalerate has a smell of apple, and it was present in all three distillates, but in small amounts.

Table 2. The content of aromatic components of the distillates produced from the studied apricot varieties

Compound (mg/L)	NS 6	NS RODNA	AMBROZIJA
Ethyl isobutyrate	-	-	0.32
Ethyl lactate	12.5	13.46	8.87
Ethyl isovalerate	0.96	1.41	1.37
Isoamyl acetate	-	1.02	-
Ethyl hexanoate	1.12	-	1.37
Linalool	22.12	18.53	7.31
1-Phenylethanol	-	2.63	1.68
Ethyl octanoate	16.34	14.8	18.39
α -Terpineol	14.01	13.56	6.18
β -Citronellol	-	0.65	-
Geranyol	2.09	1.81	-
Ethyl decanoate	69.8	57.79	60.67
Ethyl laurate	36.98	24.85	25.77
Ethyl palmitate	8.53	7.73	6.94

Isoamylacetate, ester which is responsible for the odour tones of banana and pear, was present only in the distillate from NS rodna variety (1.02 mg/L). Ethyl hexanoate, characteristic for a grape aroma, was determined in small amounts in NS 6 and Ambrozija distillates (1.12-1.37 mg/L).

Linalool is a terpene alcohol found in many fruits and herbs, and it gives a pleasant floral aroma. The limit of sensory detection of linalool is around 6 μ g/L. The concentration of this compound was the lowest in Ambrozija distillate (7.31 mg/L), while higher amounts were determined in the other two distillates: 22,12 mg/L (NS 6) and 18,53 mg/L (NS rodna). Phenylethanol, an aromatic alcohol, can be found in many essential oils, giving a pleasant floral aroma. It was detected in small amounts. Ethyl octanoate (ester with a pleasant pineapple aroma) was equally represented in all three distillates. α -Terpineol gives the smell of lilac, and the limit of sensory detection of this compound is 330 μ g/L. It was present in all three distillates in significant amounts. The concentration of α -terpineol in the distillate of Ambrozija variety (6.18 mg/L) was almost two times lower compared to other two distillates. β -citronellol gives a pleasant floral aroma to distillates, and it was present only in the distillate from NS rodna variety in a very low amount (0.65 mg/L). Geraniol, a compound which gives a floral scent to distillates, was detected in the distillates from NS 6 and NS rodna varieties in amounts substantially greater than the sensory detection limit (40 μ g/L).

Ethyl decanoate, a fruity flavour compound, was present in a three distillates in significantly larger amounts compared to other esters. A similar trend, but in lower quantities, was determined also for ethyl laurate, a compound with a characteristic apple odour. Ethyl palmitate, an ester of ethanol and palmitic acid, was determined in approximately equal amounts in all distillates, giving them a milky, creamy scent.

CONCLUSION

The contents of certain aromatic components were highly different in the distillates produced from three studied apricot varieties. It was shown that the chemical composition of the raw material, i.e. the apricot variety, has strong influence on the aromatic profile of the distillates. The most evident differences were recorded for linalool, α -terpineol and ethyl laurate contents. Although higher alcohols are by-products of alcoholic fermentation, the differences in the content of these compounds may be attributed to differences in the content of its precursor (amino acids) in fruits or the presence of specific microbiota on the surface of fruits. These factors contribute to formation of larger quantities of higher alcohols.

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