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COMPARASION OF THE AROMA ACTIVE COMPOUNDS IN RAW SPIRITS OBTAINED FROM DIFFERENT APPLE VARIETIES

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Abstract: Raw spirits were produced through distillation of apple wines obtained by fermentation of selected varieties of apples. Two types of apple wine were obtained using different apple varieties. In the first case, the wine was obtained from two types of apples: Red Elstar and Vilmuta. In the second case, the wine was obtained from mixture composed of four types of apples: Idared, Golden Delicious, Jonagold and Melrose. The aromatic profiles of obtained raw spirits were strongly influenced of desirable aromas of ethyl esters which contribute to the flavour of the destillates with a pleasant fruity and flowery smell, indicative of the quality of the spirit. A headspace solid phase microextraction (HS-SPME) as the extraction technique and gas chromatography coupled with mass spectrometry was utilized for the determination of volatile compounds. It was shown that raw spirits obtained from mixed combination of Red Elstar and Vilmuta have more intense aroma than obtained from second mixture (Idared, Golden Delicious, Jonagold and Melrose). Ethyl nonanoate, ethyl 9-hexadecanoate, ethyl palmitate and 9,12-octadecanoic acid ethyl ester were detected only in raw spirits obtained from Red Elstar and Vilmuta. The aroma profile of the fractions obtained during the distillation was also investigated. The most intensive aroma was detected in the first fractions (heads). On the other side, the content of ethyl esters in middle fractions was lower than that in the first fractions.

Keywords: raw spirits, apple varieties, ethyl esters, headspace solid phase microextraction

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Introduction

The presence, content and composition of volatile substances in agricultural distillates (raw spirits) have a substantial influence on their quality. The aroma of the raw spirit depends on the type and quality of the raw materials as well as the hygienic and fermentative conditions during processing. The volatile aroma was also influenced by the distilling stage (head, heart and tail) (Zheng at al., 2014). The chemical composition of volatile byproducts such as carbonyl compounds, alcohols, esters, acids, and acetals are often diverse and contribute to the peculiar flavor of the spirit. Esters are well-known aroma compounds occurring at relatively high content and exhibiting a low odor threshold and therefore are quite relevant for the beverage sensory properties (Nascimento et al., 2008; Plutowska et al., 2008).

Apple brandy is a spirit obtained by the distillation of cider or apple wine. The apples can be classified as table, commercial, or cider apples, but all are suitable for alcohol production (Kosseva, 2017). The volatile components of freshly distilled Calvados and Cognac have been extensively investigated, and 331 compounds, of which 162 can be considered as trace compounds, were characterized. The aroma quality of apple brandy is influenced by the cider maturation (Rodríguez-Madrera et al., 2010). It was found that the most mature cider gave a distillate of superior aroma (with more sweet and spicy character), with higher levels of ethyl acetate, ethyl lactate, and ethyl succinate, and volatiles derived from bacterial metabolism (which is more prevalent in extensively matured cider), such as 2-butanol, 4-ethylguaiacol, eugenol, and 2-propen-1-ol.

The aim of this study was to examine the effects of different types of apple varieties on aroma profiles of obtained raw spirits. A procedure for qualitative determination of fatty acid ethyl esters, in raw spirits of different quality or produced from various raw materials, by means of headspace solid phase microextraction (HS-SPME) as the extraction technique and gas chromatography with mass spectrometry (GC-MS) as the determination technique. These esters are known to be the most abundant esters in spirits, and their presence is commonly related to the pleasant fruity bouquet of alcoholic beverages.

Materials and methods

Raw spirits were obtained by one step distillation of apple wines obtained by fermentation of apple juice obtained from mixed varieties of apples: i) two types of apple varieties (Red Elstar and Vilmuta) were used at a weight ratio of 1:1; ii) four types of apple varieties (Golden Delicious, Idared, Melrose and Jonagold) at

a weigt ratio of 1:0.9:0.6:0.5, respectively (Table 1). The apples were washed and then ground in fruit mill. Obtained fruit pulp was put on hydraulic press to separate fresh juice from solid part.

Apple juice was fed into 100 L stainless steel fermenter (Fig. 1) with self-contained cooling. The fermentation was performed at 17 °C.

Figure 1. Fermenter used for fermentation of apple juice (location: Laboratory for Unit Operation and Biochemical Engineering; Faculty of Agronomy, Čačak)

The aroma profile was collected using headspace solid-phase micro-extraction followed by gas chromatography (Agilent Technologies 7890 B GC System, AIM, Littleton, CO, USA) coupled with mass spectrometry (Agilent Technologies 5977A MSD, AIM, Littleton, CO, USA). Briefly, the 0.2 mL of the sample (having 20 vol% of ethanol) was placed in a headspace vial. Each vial was sealed using a cap with PTFE/silicone septa and incubated at 27°C. Octanoic acid-methyl ester was used as internal standard at a concentration of 500 μg/L. The solid phase microextraction fiber (Polydimethylsiloxane (PDMS) 100 μm, Agilent Technologies, AIM, Littleton, CO, USA) was inserted into the head space of the vial containing the sample solution. The extraction was carried out for 70 min of fiber-exposed time. After sampling, the SPME fiber was withdrawn into the needle, removed from the tube, and inserted into the hot injector port (270 °C) of the GC system where the extracted analyte was desorbed and transferred to the analytical column (HP-5, Agilent Technologies, AIM, Littleton, CO, USA). A relatively long desorption time in the injector (10 min) was selected to avoid carryover between runs to ensure full desorption of analyte from the fiber. Ultra-high purity 5.0 grade helium (Messer Tehnogas AD, Belgrade, Serbia) was used

as a carrier gas at a flow rate at 1.2 mL/min along with the spitless injection. The oven temperature was programmed for an initial 30 °C for 5 min and was then increased in four steps: 30–40 °C at a rate of 3 °C/min and held for 2 min at this temperature; 40–100 °C at a rate of 5 °C/min, 100–180 °C and held for 2 min at this temperature; 180-280 °C at a rate of 25 °C/min, and held 1 min.

Volatile compounds were identified by comparison with the National Institute of Standards and Technology (NIST) database. The VOCs that showed mass spectra with match factor ≥80% were considered as identified substances.

Results and discussion

Fig. 1 shows GC profile of volatile organic compounds (VOCs) in raw spirits (heart) obtained from Red Elstar and Vilmuta (a) and Golden Delicious, Idared, Melrose and Jonagold (b). On the other side, the list of detected volatile organic compunds of chromatogram 2-a are shown in table 1.

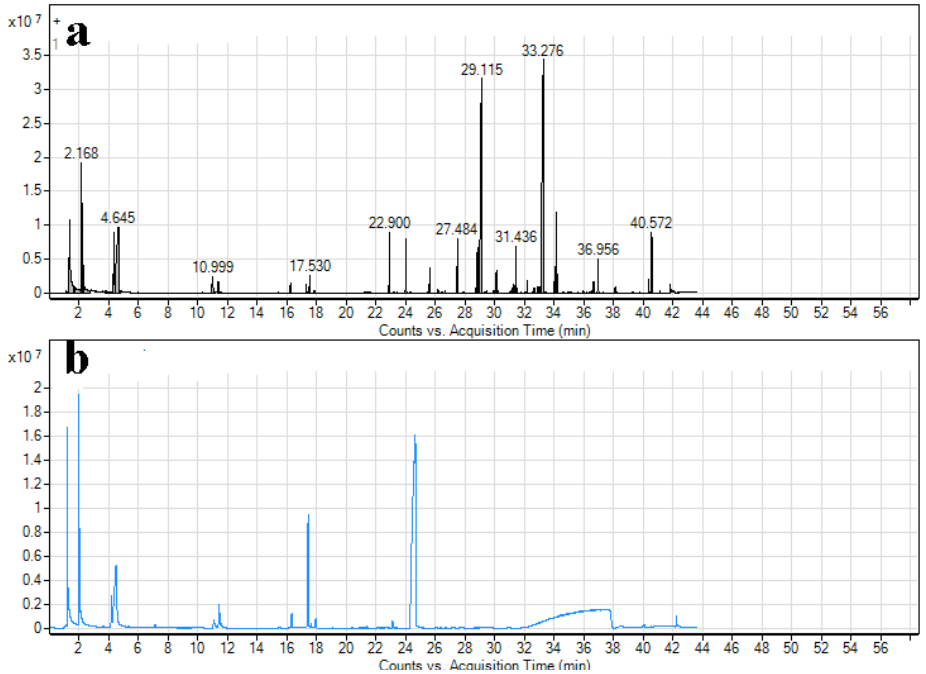

Figure 2. GC profile of volatile organic compounds (VOCs) in raw spirits (heart): a) the VOCs profile in distillate obtained from Red Elstar and Vilmuta; b) the VOCs profile in distillate obtained from Golden Delicious, Idared, Melrose and Jonagold.

Table 1. List of detected volatile organic compunds in raw spirit obtained from Red Elstar and Melrose

No	compounds	Retention time (min)	No	compounds	Retention time (min)
1.	ethanol	1.36	16	Isoamyl caprylate	30.1
2.	ethyl acetate	2.16	17	Octanoic acid, 2-methylbutyl ester	30.18
3	Isobutanol	2.3	18	Propyl decanoate	31
4	Acetal	4.33	19	α-Farnesene	31.4
5	Isopentyl alcohol	4.58	20	n-Capric acid isobutyl ester	32.16
6	Butyraldehyde, diethyl acetal	10.3	21	Octanoic acid, hexyl ester	32.9
7	1-Hexanol	10.98	22	Ethyl laurate	33.2
8	Isopentyl alcohol, acetate	11.38	23	Iso-Amyl n-decanoate	34.13
9	Ethyl caproate	17.3	24	Propyl dodecanoate	34.95
10	Hexyl acetate	17.85	25	Isobutyl laurate	35.95
11	Ethyl caprylate	24	26	Ethyl myristate	36.95
12	Acetic acid, phenethyl ester	25.6	27	Isoamyl laurate	38.1
13	Ethyl nonanoate	26.64	28	Ethyl 9-hexadecanoate	40.3
14	Ethyl trans-4-decanoate	28.82	29	Ethyl palmitate	40.5
15	Ethyl caprate	29	30	9,12-Octadecadienoic acid, ethyl ester	41.8

As it was shown in Fig 2. and table 1, raw spirits obtained from Red Elstar and Vilmuta have more intense aromas than that obtained from mixed varieties of Golden Delicious, Idared, Melrose and Jonagold. Chromatogram 2a shows the presence of some ethyl-esters (ethyl nonanoate, ethyl 9-hexadecanoate, ethyl-palmitate, 9,12-octadecanoic acid ethyl ester) which were not detected in the sample obtained from mixed varieties of Golden Delicious, Idared, Melrose and Jonagold.

Fig. 3 shows aroma profiles of the fractions obtained during the distillation of apple wine obtained from mixed varieties of Golden Delicious, Idared, Melrose and Jonagold. Internal standar (octanoic acid-methyl ester, at concentration of 500 μg/L) was detected at retention time of 22 minute. The most intensive aroma was detected in the first fractions (heads), however, there were undesirable components such as hydrocyanic acid. This indicates that

alcohol-ester azeotrope and an ester-water azeotrope may be formed during distillation which allows esters evaporation at lower distillation temperatures. On the other side, the content of ethyl esters in middle fractions was lower than that in the first fractions. The lowest aroma profile was detected in at the end of distillation run (tails).

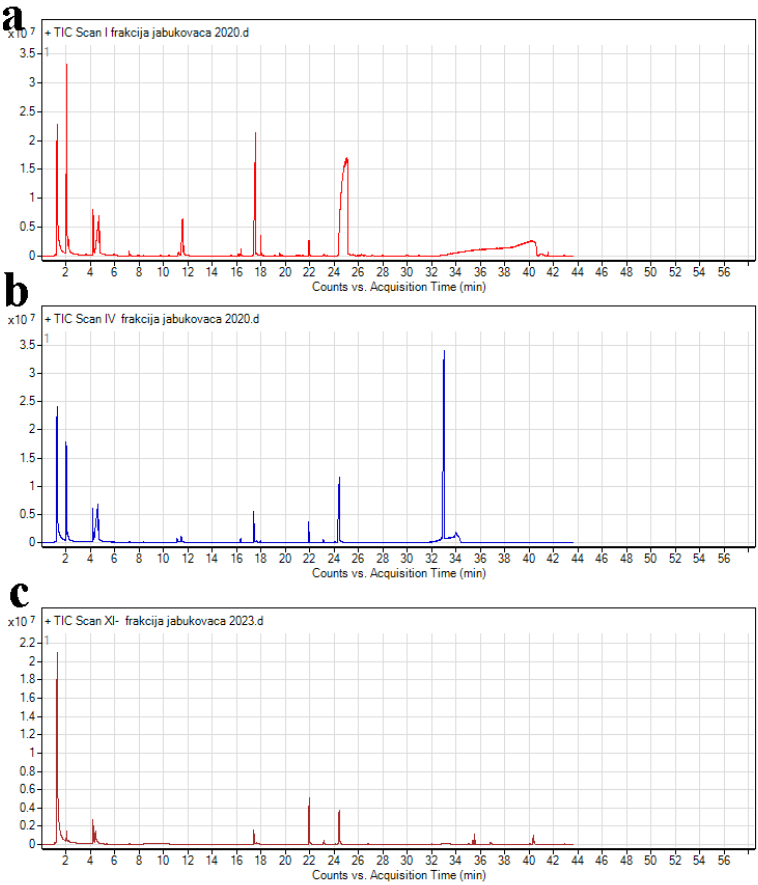

Figure 3. The volatile aroma profile at different the distilling stage: a) head, b) heart, c) tail.

Conclusion

Raw spirits were produced through distillation of apple wines obtained by fermentation of selected varieties of apples. The aromatic profiles of obtained raw spirits were strongly influenced of desirable aromas of ethyl esters which contribute to the flavour of the destillates with a pleasant fruity and flowery smell, indicative of the quality of the spirit. Aroma profile of raw spirit obtained from Red Elstar and Vilmuta have more intensive aroma profile than that obtained from Golden Delicious, Idared, Melrose and Jonagold. The presence of some esters including ethyl nonanoate, ethyl 9-hexadecanoate, ethyl-palmitate, 9,12-octadecanoic acid ethyl ester were detected in raw spirit obtained from Red Elstar and Vilmuta. The most intensive aroma profile was detected in the first fractions (heads) probably due to formation alcohol-ester azeotrope and an ester-water azeotrope. It was shown that solid phase microextraction coupled with gass chromatography/mass spectrometry allows qualitative analysis of aromas in raw spirits of different organoleptic quality. High precision and simple sample preparation enable the use of this method for routine investigations in both industrial and research laboratories.

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