

Jasna Mrvčić¹, Antonija Trontel¹, Karla Hanousek Čiča¹, Nada Vahčić¹, Original scientific paper
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Chemical and sensorial characteristics of traditional fruit spirits from Southeast Europe

Abstract

Spirits have proliferated and become an indispensable part of most gastronomic cultures around the world. The production and consumption of fruit brandies, especially plum and grape brandies as well as pear and apple brandies, have a long tradition in the countries of Southeast Europe. The aim of this study was to evaluate 47 fruit brandies produced in small distilleries and industrial plants from five countries. The content of the most common volatile compounds (methanol, higher alcohols and fatty acid esters) and the sensory quality of the fruit brandies were analysed. Principal component analysis (PCA) was performed using the concentrations of the main volatile compounds in the spirit samples and sensory evaluation to identify similarities or differences between the spirit samples based on distillery size. The methanol concentration in all samples was below the EU legal limit. Methanol concentration was highest in Williams pear spirits and lowest in grape pomace spirits. The PCA sample distribution confirms the good quality of samples from both small distilleries (SD) and industrial plants (IP), with some exceptions - samples with identified defects produced in some small distilleries. The results of the sensory evaluation show high sensory quality of fruit spirits from this part of Europe.

Keywords: fruit spirit, higher alcohols, fatty acids esters, metanol, sensory evaluation

Introduction

The lands of Southeast Europe have a long and rich tradition of fruit growing and the production of fruit brandies and liqueurs. Today's spirit production in these areas is characterized by an increase in the number of small distilleries, the development of local products and souvenir products, and the growth of gastronomic tourism. The development of local spirits production is often a story of people handcrafting raw materials and refining their distilling skills to create their own unique regional products.

Fruit spirit is an alcoholic beverage made exclusively by the alcoholic fermentation of fruit or must from such fruit, with or without stones, and distilled with an ethanol content of less than 86 % vol. so that the distillate has a odor and flavour derived from the raw materials distilled. The production of plum brandy, grape brandy, pear brandy and apple brandy is particularly characteristic of this area. There are various producer groups on the market. Most large-scale producers are fruit and wine growers for whom the production of spirits are a complementary activity linked to the production of fruit spirits due to the low quality of the fruit or the low purchase prices. In contrast, some fruit growers extend their core business to the production of high-quality distillates. The third group is small producers who produce spirits for their own

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consumption or, more recently, for the consumption of their guests in the context of rural and island tourism. Different and often unsuitable production methods, the use of fruit varieties unsuitable for processing into spirits, and the lack of knowledge about the correct technology of spirits production can be cited as reasons for the ultimately poor quality of spirits. Although most producers who make spirits using the traditional method are convinced that their spirits are the best, experience often shows shortcomings and poor quality of these products. In order to assess the quality of fruit spirit production, it is important to determine the content of methanol, the maximum limit of which is required by law (Regulation EC No 110/2008), as well as the concentration of higher alcohols and esters as the most common volatile compounds in the distillate.

The aroma compounds of fruit spirits are formed in all production phases (Tešević at al., 2005): during fruit ripening (primary aroma), during fermentation (secondary aroma), during distillation (tertiary aroma) and during maturation (quaternary aroma). Therefore, all of these stages must be done correctly, whether they are done by small or industrial producers. But there are significant differences in the method of distillate production by traditional vs. industrial processes. In the traditional process, fruit brandies are produced from autochthonous varieties that have a long tradition of cultivation in these areas and provide distillates with a very specific and recognizable character. Very often the mash is fermented in wooden vats with yeasts spontaneously present on the fruit, without any fermentation control. Moreover, traditional plum brandy production still uses a simple still and often a single still with an inadequate distillation cut. As a result, a fruit spirit with a high concentration of high total acids, aldehydes, total esters and ethyl carbamate is obtained (Spaho and Blesić, 2005). During the last two decades, column distillation has slowly entered the production of spirits in small distilleries and two different types of stills are now commonly used in the production of fruit spirits: the Charentais alembic pot (French style; simple distillation pot still) and the batch distillation column (German style) (Spaho, 2017). The aim of this study was to evaluate the chemical and sensory characteristics of 47 fruit spirits produced in small distilleries and industrial plants from five countries Southeast Europe. The most abundant volatile compounds in fruit spirits, higher alcohols, esters and methanol of fruit spirits, were analysed.

Materials and methods

Samples

A total of 47 fruit spirits were analysed, of which 12 were industrial samples and 35 from small distilleries. The samples were collected on a voluntary basis through a public call for international spirits evaluation. The samples came from 5 countries Southeast Europe, mainly from Croatia (25) and Serbia (15), then from Bosnia and Herzegovina (4), Slovenia (2) and Montenegro (1). The samples were delivered in a volume of 1 L. All samples were coded before analysis. For data processing, samples were grouped into 7 categories depending on the raw material (Q - quince spirit; WP - Williams pear spirit; GB - grape spirit; APP - apple spirit; SFB - stone fruit spirit (excluding plum spirit); BF - berry spirit; PB - plum spirit). Moreover, the samples are divided into 2 groups according to the size of the distillery (SD - small distilleries; IP - industrial plants).

GC-FID analysis of volatile compounds

All samples used for HS-GC-FID analysis were diluted to alcohol content of 5 % v/v and transferred to 50 mL volumetric flask containing 5 µL of internal standard (butan-1-ol). Ten millilitres of sample were placed into a 20 mL headspace vial (Macherey-Nagel GmbH & Co. KG, Germany) and sealed with PTFE/silicone septa (Macherey-Nagel GmbH & Co. KG, Germany).

The column ZB-5MS 60 m x 0,25 mm I.D. x 0,50 μm df (Zebron, Phenomenex, USA), HS 40XL headspace sampler (Perkin Elmer) and gas chromatograph PE Autosystem XL (Perkin Elmer) was used for volatile compounds determination in fruit spirit samples. The alcohols detected were methanol, ethanol, propan-1-ol, 2-methylpropan-1-ol, 2-methylbutan-1-ol and 3-methylbutan-1-ol. Esters detected in the samples were ethyl ethanoate, ethyl butanoate, 3-methylbutyl ethanoate, ethyl hexanoate and ethyl octanoate. Identification of volatiles was based on external standard.

Sensory analyses

The sensory analysis was performed by an expert panel composed of five testers (3 women and 2 men) with rich experience in sensory analysis of fruit spirits. The samples were presented to the panel in tasting glasses, at room temperature and in a tasting room. Scoring was anonymous using the modified Buxbaum method for sensory evaluation (Nikićević, 2005). After tasting, the results of all testers for each sample were summed up and the median score was calculated. Medals are awarded at many fairs and distillery exhibitions: a medal is not awarded if the score is 14.00, a bronze medal (BM) from 14.01-16.00, a silver medal (SM) from 16.01-18.00, and a gold medal (GM) from 18.01-20.00. Within the gold medal award, special recognition in the form of a large gold medal (GGM) is given to the samples that scored more than 18.20 points (Nikićević, 2005).

Statistical analyses

The results obtained were analysed using XLstat (Addinsoft). The statistical significance of the difference between the spirit categories for volatile compound content was evaluated using analysis of variance (One-way ANOVA), followed by Tukey's test. Statistical differences were considered significant at $p < 0.05$. Principal component analysis (PCA) on sensory descriptors and chemical parameters was also used to group samples based on distillery size.

Results and discussion

Methanol content in fruit spirits

The most common volatile compounds that determine the quality and sensory character of fruit spirits are higher alcohols, fatty acid esters, ethanal, and methanol. The visualization of the data analysis of methanol in the analysed distillates and the difference in methanol content between the categories of spirits is shown in Figure 1.

Methanol is an ever - present compound in spirits, regardless of the fruit raw material from which they are made, due to the action of pectin methylesterase on fruit pectin. The concentration of methanol was below the EU legal limit (Figure 1) in all samples. Furthermore, the analysis ANOVA with Tukey's test showed that Williams pear spirit and pomace spirit have significantly ($p < 0.05$) different methanol concentrations than the other spirit categories. The methanol concentration was highest in Williams pear spirits, while it was lowest in pomace spirits. Methanol concentrations in WP ranged from 777.72-1271.38 g/hL a.a., but the regulation for this category of spirits allows methanol concentrations up to 1350 g/hL a.a. (Regulation EC No 110/2008). In general, the average methanol concentrations in all categories were in the range of 400-650 g/hL a.a. with some exceptions. One sample from berry spirit category as well as one sample from apple spirit has a high methanol concentration, well above the average for their own category, but it is a spirit made from pomace. Pomace is rich in pectin and higher concentrations of methanol are to be expected, especially if apple pomace has been treated with pectinase.

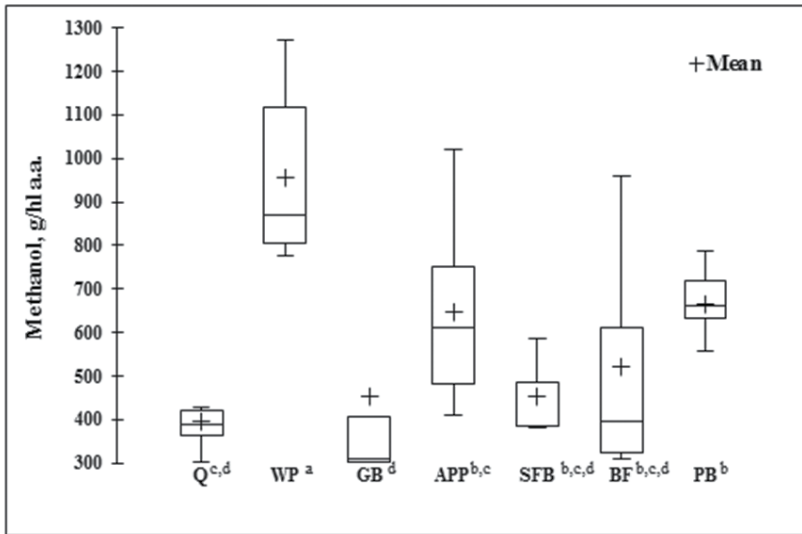


Figure 1. Box plots visualization of data analysis of methanol in fruit spirits (Q - quince spirit; WP - William pear spirit; GB – grape spirit; APP – apple spirit; SFB – stone fruit spirit; BF - berry spirit; PB - plum spirit). The different letters (a,b,c,d) represent a significant difference between the categories ($p < 0.05$).

Slika 1. Vizualizacija koncentracije metanola u voćnim destilatima (Q – rakija od dunje; WP - rakija wiljamovka; GB - rakija od grožđa; APP - rakija od jabuka; SFB - destilati od košunjičavog voća; BF - rakija od šljiva). Različita slova (a,b,c,d) predstavljaju signifikantnu razliku između kategorija ($p < 0.05$).

Zhang et al. (2011) and Madrera et al. (2013) showed that the use of the enzyme pectinase in the production process significantly increased the methanol concentrations of apple spirits produced from apple mash and juice, especially from apple pomace. Except for the above samples, the methanol concentration agreed with the data available in the literature. The median methanol concentration in the PB category was 661 g/hL a.a. (with little variation within the category), according to Dimitrov et al. (2016) and Popović et al. (2019). In contrast, Coldea et al. (2011) detected slightly higher concentrations of methanol in traditional plum and apple brandies from Romania, about 900-1000 g/hL a.a., depending on the fruit variety. Spaho et al. (2019) demonstrated different methanol concentrations in apple distillate depending on the distillation apparatus used. Methanol concentrations were 540 and 830 g/hL a.a., respectively, for alembic and batch distillation column and decreased slightly during 18 months of aging in oak barrels. Higher methanol concentrations in plum, apple and pear brandies compared to grape brandies (Figure 1) are a normal trend. The reason for this is the higher pectin content in plum, apple and pear fruit. The higher pectin content usually results in the formation of a higher amount of methanol in the final product. An exception to this trend is quince brandy, in which a lower methanol concentration was found (Figure 1). Although the content of pectin substances in quince is high, in the range of 1.75-3.51 g/100 g (Rop et al., 2011), the wine obtained by quince fermentation does not have a high methanol concentration (Nikićević et al., 2018). Possner et al. (2014) analysed the methanol content of fruit juices and smoothies in

comparison with fruits and showed that more than 90 % of the potentially available methanol remained in the pomace and only about 2.5 % transferred to the aqueous phase of the juice. This means that a fruit juice, and thus also wine and distillate, can contain significantly less methanol than the corresponding fruit.

Berries are frequently used in the preparation of macerated fruit brandies and liqueurs. They are rarely used to produce fruit brandy, as the relatively low sugar content (4-8 %) results in a low ethanol yield. These fruits are suitable to produce liqueurs due to a significant content of phenolic compounds that diffuse into the macerate during maceration (Mrvčić et al., 2012; Hanousek Čiča et al., 2020). According to Alonso-Gonzalez et al. (2010, 2011) methanol concentrations of 114-350 g/hL a.a. were found in spirits from black mulberry, black currant, red raspberry and arbutus berry, which is slightly lower than the concentration in the BF category in this work. Overall, methanol levels are mainly dependent on spirit category, fruit variety, harvest year, fruit processing, and distillation methods (Popović et al., 2019; Zhang et al., 2011; Zhang et al., 2012; Spaho, 2017; Spaho et al., 2019).

Volatile compounds in fruit spirits

Volatile components of fruit spirits may be derived from the raw materials as well as being by-products of alcoholic fermentation, distillation, and aging. The higher alcohols are by-products of fermentation and depend on the source of sugar used in fermentation and the presence of amino acids. Fusel alcohols are the most abundant volatile components formed during fermentation via the Ehrlich pathway or via central carbon metabolism and contribute to essential aroma and flavour compounds in fermented beverages and foods. Depending on their concentration, they can have positive or negative sensory effects. Propan-1-ol, butan-1-ol, and 2-methylpropan-1-ol are described as having an alcoholic odour, while 2-methylbutan-1-ol and 3-methylbutan-1-ol are described as having a marzipan-like or banana-like aroma (Lambrechts and Pretorius, 2000). In appropriate concentrations, fusel alcohols impart a beneficial complexity and also serve as precursors for the formation of acetate esters. However, a high number of higher alcohols can affect the taste of the distillate and cause a strong, pungent odour and flavour, especially at concentrations above 350 g/hL a.a. (Spaho, 2017). In the samples analysed, the mean value of total higher alcohols was in the range of 300-400 g/hL a.a., with no significant differences between categories (Figure 2). In all samples, the most abundant higher alcohol was 3-methylbutan-1-ol (isoamyl alcohol). Lower 3-methylbutan-1-ol mean values were found in the plum brandy group compared to the other spirit categories but in consistent with the value of this alcohol in plum brandies from Čačanska Rodna, Stanley and Požegača plum varieties (Popović et al., 2019). Comparison with some other literature data suggests that the concentrations of higher alcohols found in the tested samples are generally acceptable (Spaho et al., 2013).

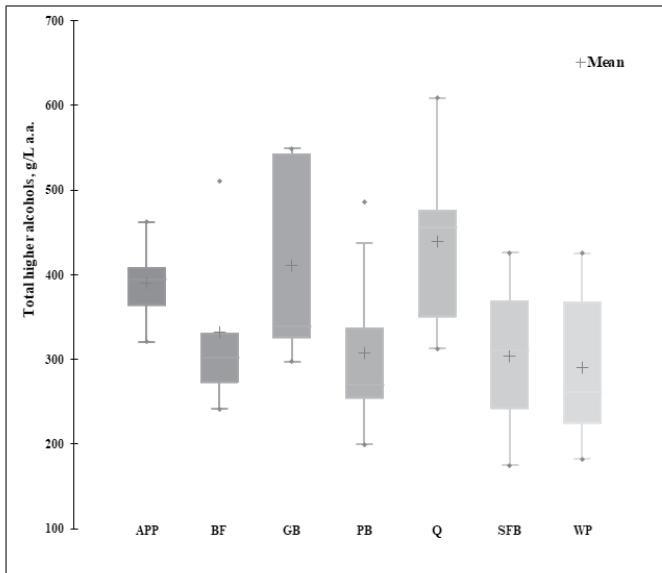


Figure 2. Box plots visualization of data analysis of spirit total higher alcohols (Q - quince spirit; WP - William pear spirit; GB – grape spirit; APP – apple spirit; SFB – stone fruit spirit; BF - berry spirit; PB - plum spirit).

Slika 2. Vizualizacija koncentracije viših alkohola u voćnim destilatima (Q – rakija od dunje; WP - rakija wiljamovka; GB - rakija od grožđa; APP - rakija od jabuka; SFB - destilati od koštunjica; BF - rakija od šljiva).

In the samples analysed, the mean value of total esters ranged from 100-500 g/hL a.a. with no significant difference between categories (Figure 3). Ethyl ethanoate was the most abundant ester in all samples. Apart from ethyl ethanoate as the most important ester, the others are found in low concentrations. The importance of ethyl ethanoate is such that the ratio of total ester to ethyl ethanoate is used as an indicator of the quality of spirits. The higher this ratio, the higher the quality of the final product (Spaho, 2017). In small amounts, ethyl ethanoate contributes to the pleasant and fruity smell of distillates. In high concentration, it provides a sticky odour or smell of nail polish remover, which is one of the most relevant off-odors in spirits. This ester has a very high volatility and high solubility in ethanol and therefore tends to distill during the first fractions. To optimize the ester aroma, distillation strategies focus on separating the ethyl ethanoate during the head fraction and keeping the rest of the esters in the heart fraction. High concentrations of ethyl ethanoate are indicative of prolonged storage of the raw material and probable spoilage by acetic bacteria, but could also be influenced by the distillation process (Spaho, 2017). Distillates obtained from alembic pot still showed higher amount of ethyl ethanoate compared to distillates obtained from distillation column (Spaho, 2017). Also, inadequate separation of the first fractions or microbiological spoilage, usually in small distilleries (Figure 4, highlighted), can lead to an undesirable concentration of ethyl ethanoate in the distillate and undesirable sensory characteristics. Elevated levels of butan-2-ol, the fermentation product formed by some *Lactobacillus* strains, detected in the same samples (Figure 4, highlighted), could be an indicator of bacterial spoilage.

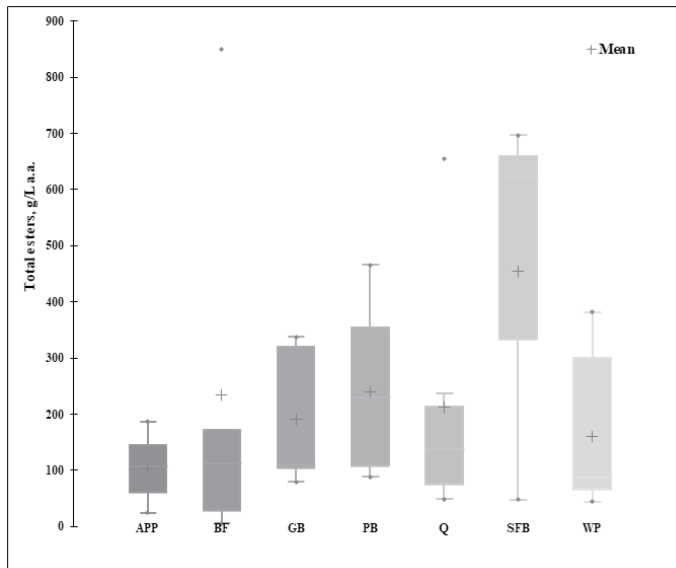


Figure 3. Box plots visualization of data analysis of spirit total esters (Q - quince spirit; WP - William pear spirit; GB - grape spirit; APP - apple spirit; SFB - stone fruit spirit; BF - berry spirit; PB - plum spirit).

Slika 3. Vizualizacija koncentracije ukupnih estera u voćnim destilatima (Q - rakija od duње; WP - rakija wiljamovka; GB - rakija od groždja; APP - rakija od jabuka; SFB - destilati od koštunjicačavog voća; BF - rakija od šljiva).

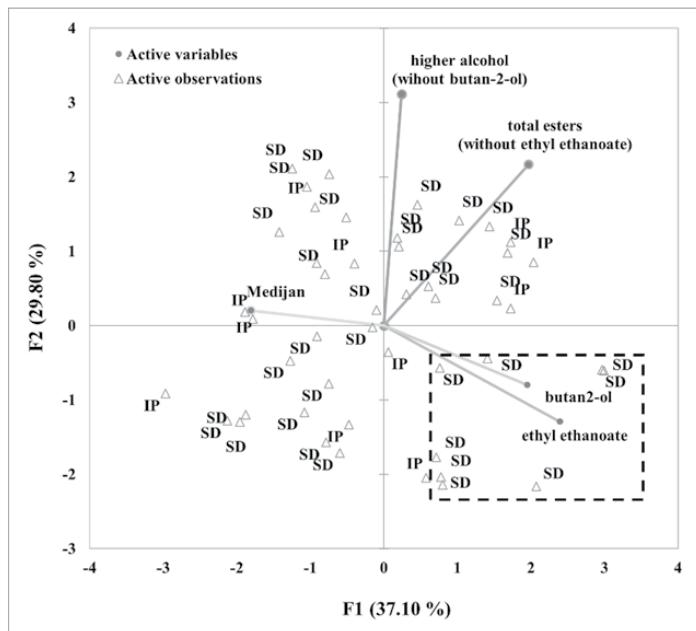


Figure 4. Samples scattering based on the distillery size (small distillery - SD; industrial plants - IP), volatile aroma compounds and sensory score. Highlighted - detected samples with increased amounts of compounds suggesting bacterial spoilage.

Slika 4. Razdvajanje uzoraka u prostor određen prvima dvjema glavnim komponentama prema veličini destilerije (mala destilerija - SD; industrijska postrojenja - IP), hlapivim spojevima i senzornoj ocjeni. Istaknuto - uzorci s povećanom koncentracijom spojeva koji upućuju na bakterijsko kvarenje.

Sensory analysis

The sensory properties of spirit are influenced by its chemical composition. Spiritus has a complex volatile composition consisting of numerous chemical compounds. Many of these compounds are present in odour-active concentrations and contribute to a wide range of perceptible aroma nuances. Analysis of ANOVA showed no significant difference ($p < 0.05$) in sensory evaluation between spirit categories as well as distillery size ($p < 0.05$). The sensory evaluation shows that the samples were sensory rated between 12 and 20 points. The largest number of samples were scored in the range of 16-18 points. The results show that almost 60 % of the samples evaluated here fall into this category (silver medal) and 10 % samples fall into range of 18-20 scores (gold medal), which shows the high sensory quality of fruit distillates from these areas. However, about 13 % of the samples are of poor quality. These samples (Figure 5, highlighted) were identified by the expert panel as poor quality samples, with high concentrations of butan-2-ol and ethyl ethanoate associated with bacterial spoilage of the marc.

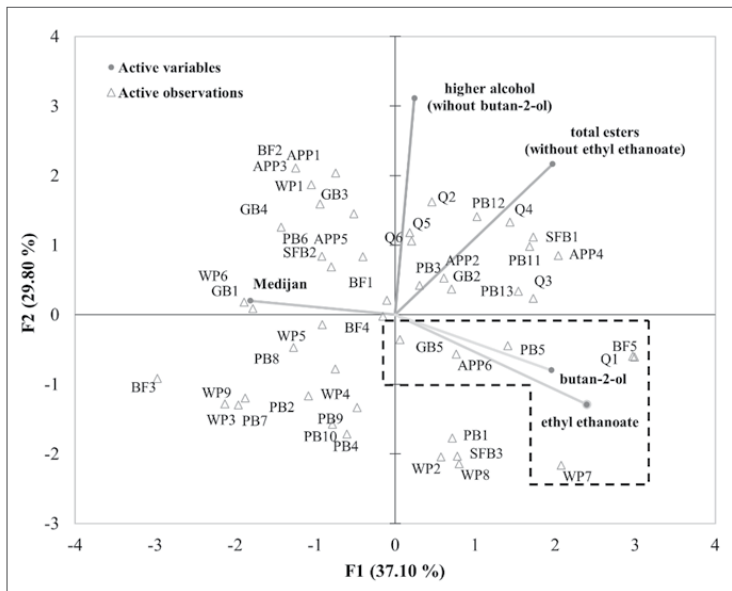


Figure 5. Samples scattering based on the volatile aroma compounds and sensory score. Highlighted - the samples recognized by testers as defective samples and out of the medal category.

Slika 5. Razdvajanje uzoraka u prostor određen prvim dvjema glavnim komponentama prema hlapivim spojevima i senzornoj ocjeni. Istaknuto – senzorno detektirani uzorci s mana-ma i izvan kategorije medalja.

Conclusion

The chemical and sensory evaluation showed the good quality of the samples from both the small distillery and the industrial plants. However, it is important to note that the samples with defects and high concentration of compounds indicating microbiological spoilage were samples from the small distillery. These results confirm that there are high quality products on the market, but also products based on traditional production without knowledge of correct production technologies and without control of fermentation and distillation processes. Success in spirits production depends on several factors: quality and timing of fruit or

Izvorni znanstveni rad

Kemijske i senzorne karakteristike tradicionalnih voćnih rakija jugoistočne Europe

Sažetak

Alkoholna pića su postala neizostavni dio većine gastronomskih kultura širom svijeta. Proizvodnja i potrošnja voćnih rakija, posebno rakija od šljiva i grožđa, kao i rakija od krušaka i jabuka, imaju dugu tradiciju u zemljama jugoistočne Europe. Cilj ovog istraživanja bio je procijeniti 47 voćnih rakija proizvedenih u malim destilerijama i industrijskim pogonima iz pet zemalja. Analiziran je sadržaj najčešćih hlapljivih spojeva (viši alkoholi, esteri masnih kiselina i metanol) te senzorna kvaliteta voćnih rakija. Kako bi se utvrdile sličnosti ili razlike između uzoraka alkoholnih pića na temelju veličine destilerije provedena je analiza glavnih komponenata (PCA) korištenjem koncentracija glavnih hlapljivih spojeva u uzorcima alkoholnih pića te senzorna procjena. Koncentracija metanola u svim uzorcima bila je ispod zakonske granice EU-a. Koncentracija metanola bila je najviša u rakijama od kruške Williams, a najniža u rakijama od grožđa. Distribucija uzoraka PCA potvrđuje dobru kvalitetu uzoraka iz malih destilerija (SD) i iz industrijskih postrojenja (IP), uz neke iznimke pojedinih uzoraka s utvrđenim nedostacima proizvedenih u nekim malim destilerijama. Rezultati senzorne evaluacije pokazuju visoku senzornu kvalitetu voćnih alkoholnih pića iz ovog dijela Europe.

Glavne riječi: voćna rakija, viši alkoholi, esteri, metanol senzorna evaluacija