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CONTENT OF HARMFUL CHEMICAL COMPOUNDS THAT MAY PERSIST IN PLUM SPIRITS

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Abstract: In Bosnia and Herzegovina plum spirits are often made in small quantity production batches, involving pot still alembic vessels. In many cases the producer will utilize plums still retaining their stone during the fermentation process which results in important contributions to the overall complexity of final spirit aroma. Plum spirits are characterized by an intense fruity aroma. However, these spirits can also contain some harmful compounds. In this study were determined the concentration of the methanol and hydrocyanic acid (HCN) that are toxic and acetaldehyde and furfural that are harmful just if they are present in higher concentration. Plum spirits were obtained using three plum variety: Pozegaca, Stanley and Bilska rana (Buchler). The behavior of these major harmful compounds was followed during distillation, with their respective contents measured in the heads, hearts, and tails fractions. The most abundant compound was methanol, which is concentrated in the heart fraction, reaching a maximum value of 9668 $mg \cdot L^{-1}$ absolute alcohol, in the heart fraction of Bilska rana spirit. The concentration of HCN and furfural was influenced by the plum cultivar, the spirits made from the Stanley cultivar contained higher concentrations of these two compounds. The concentrations of harmful compounds are seen not to exceed the allowed limit if an adequate fraction of the heart and tail fractions are removed.

Keywords: *acetaldehyde, distillation fractions, furfural, hydrocyanic acid, methanol, plum spirits*

INTRODUCTION

A range of chemical compounds are responsible for the sensory qualities of fruit spirits. Together with compounds giving pleasant and typical fruity aromas, fruit spirits may contain undesirable and / or harmful compounds. Some of harmful compounds, which do not contribute to any positive attribute of spirits, however, deleterious to health, are methanol, ethyl carbamate (EC) or urethane and hydrocyanic acid (HCN). Given their toxicity, their concentrations are strictly regulated by legislative mandates. Thus, EU Regulations (No. 110/2008) for fruit spirits, allows for a maximum level of methanol in a range of from 1000 g $h \cdot L^{-1}$ a.a. (hectoliters of absolute alcohol) to 1350 g $h \cdot L^{-1}$ a.a. depending upon the type of fruit [1]. The allowable concentration of HCN is also regulated in stone-fruit spirits to a maximum of 7 g $h \cdot L^{-1}$ a.a.

Fruit spirits also contain many chemical compounds that have a toxic effect in humans at high concentrations, which in small quantities, contribute to desirable sensory attributes and to the aroma profile of spirts. Some compounds in this group are acetaldehyde, ethyl acetate, higher alcohols (fusel oils), and furfural. Their individual concentrations are not separately regulated by EU mandates but are regulated by a maximally permissible level of the total amount of the combined volatile ingredients that may be present in the fruit spirits.

In this paper, we address methanol and HCN as toxic components and acetaldehyde and furfural, if they are present in higher concentration, as undesirable components.

Methanol occurs naturally in all fruit spirits and could serve as a parameter for the proof of authenticity and naturalness [2 – 5]. Although, it is not a direct fermentation by-product, methanol is formed during alcohol fermentation by the enzymatic breakdown of plant-derived pectin [2]. Methanol can also be produced, post-fermentation, or even by inadequate distillation procedures [6]. Methanol is a colorless volatile compound with only a mild alcohol odor [7]. It is rather difficult to detect methanol in spirits simply via sensory evaluation [3, 8]. This is due to methanol not having a unique defining aroma and thus, it does not affect the sensory profile of spirit.

Ingestion of higher concentrations of methanol can cause many health problems and in extremely higher concentration methanol can even cause death [9]. Human toxicosis has been reported at doses as low as 1.25 mL·kg^{-1} of body weight [9]. Methanol is readily absorbed after ingestion or via inhalation and, more slowly, through the skin, with subsequent entry into the blood stream [10]. In the body, methanol is metabolized in the liver, and converted first to formaldehyde by alcohol dehydrogenase and then the formaldehyde is further metabolized into formic acid by acetaldehyde dehydrogenase. Fundamentally, methanol itself is relatively non-toxic, it is methanol's resultant metabolites that can produce severe acidosis which is ultimately responsible for the clinical symptoms [10]. Methanol toxicity is presented by nausea, vomiting, abdominal pain, headache, vertigo, restlessness, incoordination, weakness, or delirium. More severe cases can present with visual loss, parkinsonism, convulsions, stupor, coma, or death [11]. Toxic symptoms develop over 12 to 48 hours [11]. The lethal dose of methanol in humans is not fully established. It is, however, thought that the human lethal dose through oral ingestion is approximately 300-1000 mg·kg^{-1} [11].

Hydrocyanic acid (HCN) is formed by the enzymatic hydrolysis of cyanogenic glycosides produced by various plant species as secondary metabolites [12]. Under normal growing conditions the cyanide in the plant is bound as a relatively nontoxic

glycoside and no free HCN is present in plant tissues [13]. Amygdalin is a cyanogenic glycoside located in fruit seeds and stones [14]. Since the proportion of stone in stone fruits is much higher than that of the seeded fruits, controlling the content of HCN is especially important for the production of stone fruit spirits [15]. Balcerek and Szopa [12] show that the highest rate of HCN production occurs on the first day of the fermentation. They note that spontaneous fermentation of fruit mash results in much higher production of HCN relative to fermentations using cultured *S. bayanus* wine yeast. The presence of amygdalin in the seed kernels is not harmful unless the seed or stone is crushed and followed by enzymatic hydrolysis of the cyanogenic compounds by β-glucosidases [15]. The final products of this process of decomposition are HCN and benzaldehyde. Benzaldehyde is a quite desirable aroma compounds responsible for the bitter almond character of spirits [16 – 18]. Thus, one product of amygdaline hydrolysis is desirable, and the other is toxic. Regarding stone fruit use as a raw material for production of spirits then becomes one of a compromise between sensory quality and safety.

Acetaldehyde is produced during alcohol fermentation as a secondary metabolic byproduct. Its concentration reaches a peak value during the early fermentation phases and is then partly remetabolized by yeast [19]. It is also formed via the oxidation of ethanol and then, in turn, acetaldehyde is converted to acetate [20]. Acetaldehyde is regarded as possibly being carcinogenic to humans. Acetaldehyde is more toxic than ethanol, with a proposed ethanol carcinogenic mechanism strongly linked with its transformation into acetaldehyde [21]. A high concentration of acetaldehyde (>125 $mg \cdot L^{-1}$) negatively influences the sensory profile of spirits and other alcoholic beverages [22]. Boffetta *et al*. [23] emphasized the importance of monitoring the acetaldehyde content of alcoholic beverages, because the intake of acetaldehyde in alcoholic beverages, in central Europe is a contributing factor in alcohol-related disease, especially that of upper digestive tract cancers [23].

Furfural is another aldehyde and is formed by dehydration of pentose under acidic conditions. Furfural is not present in musts and is formed during distillation by heating or by the complex Maillard reactions [3]. Furfural is formed specifically by direct heating in copper alembics [24], mainly from the pyrolysis of organic matter deposited at the bottom of the still [25]. Since it is made exclusively from plant material and pentose sugar content, it can serve as an indicator of authentic natural raw material spirit production. Furfural is also formed during the aging process through the action of acids on pentoses and its polymers, notably hemicelluloses [26]. In relation to health, the harmful effects of furfural ingestion are related to skin, eye and respiratory tract irritation, headaches, loss of taste, skin allergies, respiratory difficulties, vomiting, thirst sensation and, with long term exposure affecting the central nervous system, the liver or blood [24].

To reduce the concentration of these harmful compounds, it is necessary to make some possible preliminary interventions including the reduction of these compounds in so-called safe status. There are many factors of influence relating to the potential concentration of harmful compounds in spirits and in this paper the aim is to investigate the effects of using different plum cultivars and distillation cut on the content of harmful compounds.

MATERIALS AND METHODS

The detailed descriptions of the production methods, fermentation, distillation, and the analysis of volatile compounds obtained from the plum spirits analyzed in this report were presented in previous paper [27].

Fruits

Three plum cultivars: Pozegaca (autochthonous or local cultivar), Stanley and Bilska rana (Buchler) were used for the plum spirits production. These cultivars are often used for the traditional plum spirits production [27]. The fruits obtained from Pozegaca trees are characterized by a very intensive and pleasant plum aroma, as well as a high content of sugar, which has contributed to the fact that Pozegaca plum spirits are well-known even beyond the borders of the West Balkan countries. Unfortunately, during the last several decades, cultivation and production of Pozegaca in Bosnia and Herzegovina has significantly decreased because of the rapid spread of plum pox virus (Sharka), for which this cultivar is very susceptible. Stanley and other genotypes derived from the breeding programs conducted at the Fruit Research Institute in Cacak, Serbia are today dominant in plum cultivation. Bilska rana remains as a sustained crop in the north-east of Bosnia and, thanks to early maturation this cultivar is also popular for spirits production in this part of country. All the cultivars evaluated in this study were collected from orchards in Gradacac and Celic, towns located in the northeast of the Bosnia and Herzegovina.

Spirit production

Immediately after harvest, the plums were transported to a pilot plant, located at the Faculty of Agriculture and Food Science, University of Sarajevo. Upon delivery, plums were carefully crushed so that the stones were not broken, and the stones were not removed. The main chemical parameters (acidity and extract content of fruit mash) were measured in mashes. The results are presented in Table 1.

Table 1. *Extract content (Brix) and acidity (pH) of fruit mash from three plum cultivars*

Cultivars	Pozegaca-P	Stanley - S	Bilska rana (BR)
Brix ^{O}	15	14	14
*p*H	3.5	3.8	3.4

After the plums were processed, the plum mashes were placed in six plastic containers with a charge of 50 L per each cultivar, the *p*H was adjusted to ~3.0 by the addition of phosphoric and lactic acids. The mashes were inoculated with a commercial dry yeast 'Uvaferm' (Danstar Ferment AG, Denmark), a strain of *Saccharomyces cerevisiae* and left to ferment at a daily room temperature of 19 ± 1 °C until the concentration of extract decreased and sticked to 4 °Brix. After the fermentation finished, a two-stage distillation was conducted by using a traditional pot still so-called alembic pot, 10 L volume. It consists of a copper boiler, a hat, a copper pipe (pipe is not like swan neck) and a condenser. After the first distillation was completed, approximately 46 L of raw distillate were obtained per plum variety with yields of around 24 % vol. of alcohol. The

volume and alcohol content of raw distillates depended on plum variety used so, the raw distillate of Pozegaca cultivar had slightly higher yield. The first distillation was performed without the cutting of spirit fractions. In the re-distillation, three fractions were then separated. The volume of head fraction was 1.5 % of the volume of the raw distillate on the basis of sensory evaluation. The fractions of the heart cut collected until ethanol decreased to 40 % vol., because it is the usual level of alcohol for cutting hearts in the production of plum spirits in Bosnia and Herzegovina. Tail fractions were collected from 40 % vol. of ethanol until 3 % vol remained. All the distillations were performed in triplicate.

Chemical analysis

A total of twenty-seven samples were prepared for analysis (3 plum variety x 3 fractions x 3 repetitions). The content of methanol and acetaldehyde were determined using a gas chromatography system, a Varian 3400 (USA) with flame ionization detector (FID) equipped with 6.6 % Carbowax 20 M (4 m x 2 mm) column on Carbopack B80/120 according to method described in Spaho *et al.* [27].

The total free HCN content in the spirits samples was determined by a spectrophotometric method with a spectrophotometer UV-1700 Shimadzu (Japan). The method described in EFSA journal (2007) by Pielech-Przybylska *et al*. [18]. In this spectrophotometric measurement, the cyanide is converted to cyanogen chloride, by reaction with chloramine-T at a *p*H less than 8. After reacting with chloramine-T and pyridine, the glutaconic dialdehyde formed is determined by colorimetry based on the violet-blue coloration it gives with 1,3-dimethyl-barbituric acid. The color of the formed complex was measured at a wavelength of 580-585 nm. The hydrocyanic acid then expressed in milligrams per liter of absolute alcohol ($mg \cdot L^{-1}$ a.a.).

The furfural content was also measured spectrophotometrically. First, a series of standard furfural solutions with known concentration was prepared. In 1 mL of standard furfural solutions, and all spirits samples, were added 10 mL aniline in the presence of acetic acids. A bright pink color developed by the reaction of furfural and aniline in acetic acid solutions. The intensive pink color indicates the high content of furfural and straw yellow color means low content of furfural. The presented vales are derived from spectrophotometric measurements of colored complex intensity at 518 nm [28].

Statistical analysis

To establish whether a significant difference existed between the mean concentrations of the compounds in the different plum cultivar and three fractions of distillations, we used one-way analysis of variance (ANOVA) using $p < 0.05$ to test the null hypothesis. The ANOVA was followed by a least significant difference (LSD) test to verify the statistical difference at the 0.05 significance level. Principal component analysis (PCA) was used to determine the relationships among harmful compounds and spirits obtained from three plum variety. All statistical analyses were performed with the statistical package StatBox 6.7 (Grimmersoft, Paris, France). Hierarchical-clustering analysis (HCA) was generated in order to examine the similarity in the harmful compounds among the three fractions of spirits from the three plum cultivars.

RESULTS AND DISCUSSION

After water and ethanol, methanol is the most concentrated component in spirits [4, 29, 30]. The concentration of methanol in distilled spirits is of major concern because distillation concentrates methanol. Thus, it can be present at high levels in the final spirits. The concentration of methanol in fruit spirits is influenced by many factors: the type and quality of the raw material (polymers of galacturonic acid are located in the cell walls of plant tissues; therefore, methanol concentration is directly correlated with the pectin content of the fermented material), acidification of fruit mash and other conditions of the fermentation process, storage time between fermentation and distillation and, finally, the details of the distillation process [5, 7, 31]. The mean concentrations (n = 3) of the methanol in plum spirits samples are presented in Table 2 and as it could be seen the concentration of methanol was influenced by plum cultivar used. Presumably, different concentrations of methanol in spirits of different plum cultivars were derived from different concentrations of pectin in the raw materials. The results of LSD test show that significantly the lowest concentration of methanol measured was in the spirits made from the Stanley cultivar, the spirits from Pozegaca and Bilska rana cultivars both contained higher concentrations of methanol (Table 2).

Table 2. *The mean concentration (n=3) in mg·L^{-1} of absolute alcohol of methanol with results of one way-ANOVA and LSD test in head (I), heart (II), and tail (III) fractions of spirits from different plums cultivars*

Compound - Fraction	Pozegaca	Stanley	Bilska rana	Mean per fraction
Methanol I	8639.00 ± 45.3	6745.00 ± 48.8	8796.00 ± 8.9	8060.00^{A}*
Methanol II	9369.00 ± 90.6	6879.00 ± 212.7	9668.00 ± 82.6	8638.67^{A}
Methanol III	7310.00 ± 87.0	5676.00 ± 367.4	7172.00 ± 78.2	6719.34^{B}
Mean per cultivar	8439.33^{a}**	6433.33^{b}	8545.33^{a}	

*Means per fraction in columns with different superscript letters are significantly different ($p < 0.05$) according to the one-way ANOVA and the LSD post-hoc test. ($p < 0.05$). **Means per cultivar in rows with different superscript lowercase letters are significantly different ($p < 0.05$) according to the one-way ANOVA and the LSD post-hoc test. ($p < 0.05$).

Of note, the drupes of Stanley were larger with a higher proportional stone content relative to the other two cultivars. This is in accordance with results of Silbereisen *et al.* [32]. Thus, a lower content of fruit flesh and skin resulted. Since methanol is largely formed by the hydrolysis of pectin [33], the lower the content of fruit, the lower the content of methanol.

The concentration of methanol increases during redistillation in the alembic pot stills [34]. Compared with the head, heart and tail fractions, concentration of methanol had significantly lower content in tail fraction (Tabel 2). Due to its higher solubility in water compared to alcohol, methanol tends to concentrate the vapor fraction of the tails during double stage distillation in alembic pots [34, 35]. Therefore, methanol will concentrate in the fractions at the end of distillation runs, when vapors are richer in water [33, 36]. In this experiment with described equipment and distillation techniques, higher concentrations of methanol in the heart fractions for all the spirit samples were measured. A peak in the concentration of methanol in the heart fraction has also been documented in other studies [22, 36, 37]. The heart fraction was cut from the tail at 40 % vol of alcohol and apparently part of the methanol was withdrawn from the tail.

So, these differences may be attributed to the cut-off point for the tails congeners. This suggests that fractional cut-off at higher concentration of ethanol, instead of at 40 %, leading then to the tails cut would result in a lower methanol content in the heart fraction as reported in the study of Jamakovic and Spaho [36]. Pineau *et al.* [33] stated that high ethanol-specific methanol contents in the last part (i.e., "tail") of distillation are problematic if this fraction is kept in the final product or redistilled. Balcerek *et al.* [22] also stated that in distillation variants in which the hearts contained the highest alcohol contents the concentration of methanol was the lowest, while the tail fractions contained the highest concentrations of methanol.

The concentration of HCN and the results of the statistical analysis are presented in Table 3. In this experiment, the concentration of HCN in the measured heart fractions was higher in comparison to results obtained in other studies by Balcerek *et al*. [17], Pielech-Przybylska *et al.* [18] and Satora and Tuszynski [38]. However, our results were in accordance with those found in other studies [12, 14].

Table 3. *The mean concentration (n=3) in mg·L^{-1} of absolute alcohol of HCN, with results of one way-ANOVA and LSD test in head (I), heart (II), and tail (III) fractions of spirits from different plums cultivars*

Compound-Fraction	Pozegaca	Stanley	Bilska rana	Mean per fraction
HCN I	20.22 ± 4.3	28.32 ± 3.7	16.57 ± 2.5	21.70^{A}*
HCN II	7.19 ± 1.5	10.21 ± 2.8	6.83 ± 1.7	8.08^{B}
HCN III	2.82 ± 0.8	7.47 ± 2.6	3.03 ± 0.3	4.44^{C}
Mean per cultivar	10.08^{ab}**	15.33^{a}	8.81^{b}	

*Means per fraction in columns with different superscript letters are significantly different ($p < 0.05$) according to the one-way ANOVA and the LSD post-hoc test. ($p < 0.05$). Means per cultivar in rows with different superscript lowercase letters are significantly different ($p < 0.05$) according to the one-way ANOVA and the LSD post-hoc test. ($p < 0.05$).

The highest concentration of HCN (Table 3) in the head fractions regardless of plum cultivar was observed. The tail fractions had the lowest concentration of HCN. The boiling point of HCN is 26.5 °C and it is expected to concentrate more in the initial fractions. However, in the first distillation of fermented mash, HCN is in bound form and thus, is difficult to separate HCN in the initial heads fraction because it distils more into middle fraction. But in second distillation, when distils raw distillates, HCN is free and during distillation it follows its boiling point and accumulates significantly in the first fraction. The results of Balcerek *et al.* [22] illustrate that the highest concentrations of HCN are found in the heads fractions, while the content values in the heart fraction were in the range of 3.9 mg·L^{-1} a.a. to 4.7 mg·L^{-1} a.a.

Schehl *et al.* [15] reported that HCN concentration is influenced by the fruit type and showed higher concentrations of HCN in cherry mashes than in plum mashes. This result was not surprising as the proportion of stones in cherry fruit is higher than that in plums. In this study, spirits made with Stanley plum had the highest concentration of HCN, which we attribute to the higher proportion of stone in the fruit. Spirits from Bilska rana had statistically lower concentration of HCN in compared to spirits from Stanley cultivar. The differences in concentration of HCN in spirits from different plum cultivars are may be due to the variability in the amounts of crushed stones present during fermentation. Reducing the HCN content in fruit spirits is necessary not only because of its toxicity but also because HCN is one of the precursors of ethyl carbamate [39]. Ethyl carbamate (EC) is a genotoxic and carcinogenic compound [40]. It can be

formed by the reaction of urea with ethanol. Also, cyanogenic glycosides such as amygdalin in stone fruits are precursors of EC that are formed from enzymatic reactions and the thermal cleavage of amygdalin. Cyanate is formed from the oxidation of HCN catalyzed with copper. Heating hastens EC formation as well as storage and light [40]. According to Riachi *et al.* [41], heads and tails contain higher EC contents than hearts.
As the predominant aldehyde in spirits, acetaldehyde accounts for over 90 % of the total aldehyde content [3, 17]. When present in low concentrations it contributes to fruit aromas such as cherry and overripe or green apples [3]. At higher concentrations aldehydes can be related to aroma attributes reminiscent of "green apple," "overripe bruised apple," and "grassy," "pungent," "nutty" and "sherry" notes. Acetaldehyde is a typical representative of heads compound congeners giving a sharp tone to the first fraction. The measured acetaldehyde concentrations were highest in the head fractions (Table 4).

Table 4. *The mean concentration (n=3) in mg·L^{-1}of absolute alcohol of acetaldehyde with results of one way-ANOVA and LSD test in head (I), heart (II), and tail (III) fractions of spirits from different plums cultivars*

Compound - Fraction	Pozegaca	Stanley	Bilska rana	Mean per fraction
Acetaldehyde I	2059.19 ± 254.3	1968.71± 273.9	1722.78± 432.9	1916.90^{A}*
Acetaldehyde II	247.48 ± 35.5	150.13 ± 33.9	201.22 ± 38.2	199.61^{B}
Acetaldehyde III	33.23 ± 4.3	15.90 ± 3.6	20.60 ± 4.9	23.25^{C}
Mean per cultivar	779.97^{a}*	711.58^{ab}	648.2^{b}	

*Means per fraction in columns with different superscript letters are significantly different ($p < 0.05$) according to the one-way ANOVA and the LSD post-hoc test. ($p < 0.05$). Means per cultivar in rows with different superscript lowercase letters are significantly different ($p < 0.05$) according to the one-way ANOVA and the LSD post-hoc test. ($p < 0.05$).

As expected for a successful distillation process, the head fraction must be recovered as clean and free of acetaldehyde as possible levels thus low in the final packaged spirits. Interestingly, even though acetaldehyde has a low boiling point (20.2 °C), the measured concentrations were low (from 15.90 to 33.23 mg·L^{-1} a.a.) even in the tails fraction. Our results are consistent with those of Silva and Malcata [42] and Madrera *et al.* [43]. We suggest that acetaldehyde in the tails is a result of both the miscibility of acetaldehyde and water and its continuous formation during the course of distillation [43].
The effect of the plum cultivar used influences the total concentration of acetaldehyde in final plum spirits. Those spirits made from the Pozegaca plum had the highest value of the aldehyde, however, this value was not statistically, significantly different compared to values measured in the spirits from Stanley cultivar just from spirits made from the Bilska rana cultivar.
Concentration of furfural in distillation fractions obtained from different plum cultivar was showed in Table 5. Furfural rises during distillation due to the dehydration of pentose sugar and pentosan (polymers). In low concentration furfural can increase the aroma intensity of bitter almond but in higher concentration it is responsible for burnt-bitter tastes and "hotness" of spirits [3]. It is a typically found in the tails fraction [44].

Table 5. *The mean concentration (n=3) in mg·L^{-1} of absolute alcohol of furfural with results of one way-ANOVA and LSD test in head (I), heart (II), and tail (III) fractions of spirits from different plums cultivars*

Compound - Fraction	Pozegaca	Stanley	Bilska rana	Mean per fraction
Furfural I	nd	nd	nd	nd***
Furfural II	2.23 ± 2.3	1.73 ± 1.1	2.13 ± 1.5	2.03^{A}*
Furfural III	27.67 ± 5.3	23.07 ± 3.6	26.00± 9.9	25.58^{B}
Mean per cultivar	14.95^{a}*	12.4^{b}	14.07^{a}	

*Means per fraction in columns with different superscript letters are significantly different ($p < 0.05$) according to the one-way ANOVA and the LSD post-hoc test. ($p < 0.05$). Means per cultivar in rows with different superscript lowercase letters are significantly different ($p < 0.05$) according to the one-way ANOVA and the LSD post-hoc test. ($p < 0.05$). ***nd: not detected.

Statistically higher concentration of furfural was measured in the tails fractions (Table 5). Stanley plum has the statistically lowest amounts of furfural of any of the cultivars. We suggest that the reason for the lower content of furfural and methanol in spirits made from the Stanley cultivar is the smaller proportion of fruit flesh in Stanley than is found in the other plum varieties.

Principal component analysis (PCA)

The principal component analyze was used for obtained data. The goal was to interpret the relationships between plum cultivars used and the fractional cuts of distillation.
The concentration of harmful components is more influenced by how the distillation fractional cuts are made rather than for the plum varieties used (Figure 1).

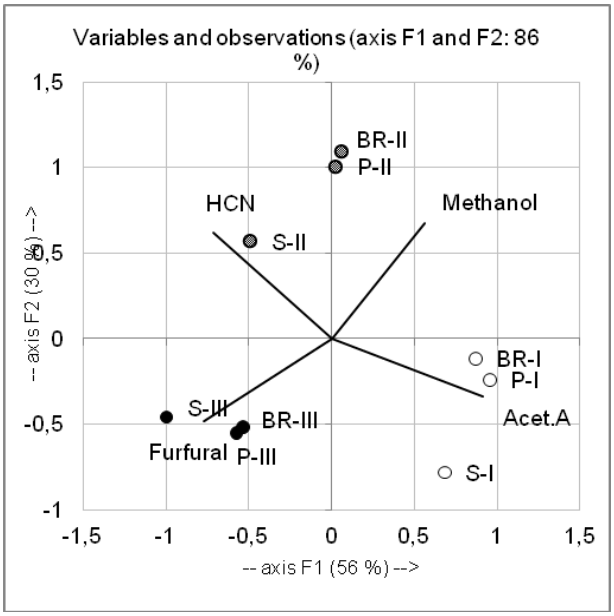

Figure 1. *Principal component analysis with plum spirits obtained by using different cultivar (Pozegac-P, Stanly-S, Bilska rana-BR) and three fractions (I-head, II- heart, III- tail)*

On the dendrogram (Figure 2), the head, hart and tail fractions from three plum cultivars were divided into clusters depending on content of harmful compounds. Largest similarity was found between head fractions of Pozegaca and Bilska rana spirits, followed by Stanley spirits. The fractions of distillation are clearly differentiated from each other.

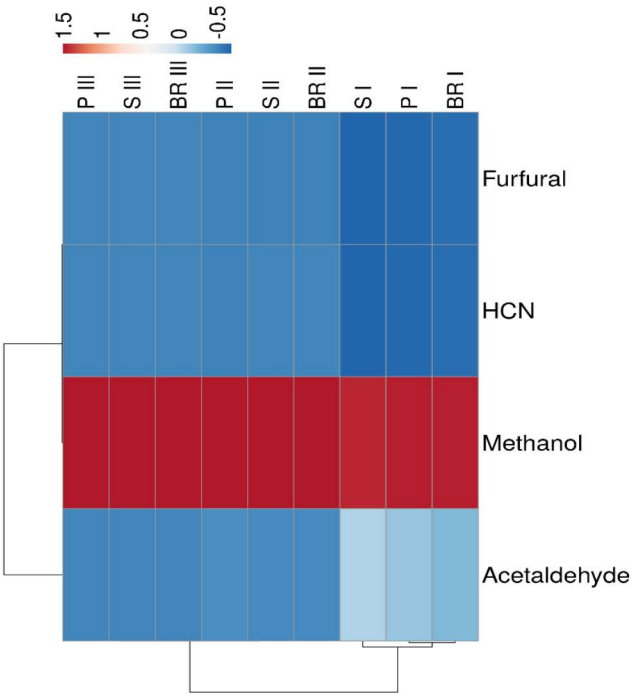

Figure 2. *Heatmap of the concentrations of compounds obtained by assigning values to colours along a scale of red/blue (red indicating a higher concentration/ blue – lower), as well as clustering of individual samples (Pozegac-P, Stanly-S, Bilska rana-BR; I-head, II- heart, III- tail)*

The fractions of head were characterized by higher concentration of acetaldehyde while the tail fractions were characterized by higher concentration of furfural, regardless used plum cultivars. That means that acetaldehyde and furfural can be removed in significant concentration from hearts by clean cuts off of head and tail fractions. The concentration of HCN and methanol separated the heart fraction from the other two fractions. The concentration of HCN was shown to be influenced by the plum cultivar, with the Stanley plum-based spirits characterized by the higher concentration of this compound. Thus, the heart fractions of Pozegaca and Bilska rana differ in higher methanol content compared to Stanley heart fraction. For all the compounds analyzed here, methanol is shown to be the potentially harmful component present in high concentrations in the heart fractions. The results show that it is difficult to separate methanol from the hearts fraction in our equipment as it does not cleanly separate and condense selectively into either the heads or tails fractions [3].

CONCLUSION

The results in study showed that the differences in the concentration of the harmful compounds found in the spirit distillates prepared here were due to the different distillation fractions and plum cultivar used. Thus, the choices in how and when to make the distinctions for heads, hearts and tails fractions are of great importance. The plum cultivars used was of lesser significance to the concentration of these specific congener levels in any spirit fraction. Sprits obtained from Pozegaca and Bilska rana cultivar were more similar in terms of methanol and furfural content.
With regard to their content of methanol, HCN, acetaldehyde and furfural, all the measured samples of plum spirits fulfilled EU requirements. This means that good manufacturing practices in the production of plum spirits using an alembic pot still can achieve products of suitable quality. In order to reduce the level of methanol in the plum spirits obtained on the alembic pot, we recommended to switch from heart to tail fractions above 40 % vol. of alcohol.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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