Comparison between the volatile substances in spirits beverages distilled by two different initial materials of Prunus domestica "Stanley" in an industrial environment

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Abstract. Analysis of the chemical composition of volatile substances in two distillates from Prunus domestica "Stanley" cultivated in the village of Rumyantsevo, Lovech, Bulgaria. Production is in an industrial environment, fermentation and distillation are carried out under equal conditions, but on different starting materials. One batch PDS-1 distilled from fermented mash and second batch PDS-2 distilled from fermented juice. The distillation apparatus is equipped with a rectifying column with 4 trays, as well as a water reflux condenser. Determination of congeners in both samples was done by gas chromatography principle OIV-MA-BS-14:2009. Methodology used for measuring alcohol content, cyanide derivatives, furfural and total acidity is according to the requirements of the OIV. In PDS-1 methanol (1094.7 g/hL a.a.) is almost 8% higher than in PDS-2 (1015.8 g/hL a.a.), it was found insignificant increase of furfural content in distillates of PDS-1 than in PDS-2. Concerning esters, aldehydes and higher alcohols the amount in PDS-1 is significantly higher than in PDS-2, respectively 203.06 g/hL, 14.2 g/hL and 484.6 g/hL in batch fermented with hard particles, and 14.2 g/hL, 8.6 g/hL, 267.9 g/hL in batch produced from fermented juice.

1 Introduction

Prunus domestica "Stanley" (European plum) is a specie known around the world, especially in Bulgaria. This variety could be used as fresh fruit or dried, also processed in distilled beverages, jams or other. The typical form of the fruit is oval, medium size, the skin colour ranges from pink to dark purple almost black, the pulp is yellow and very sweet when ripen well [1].

According to FAO data, 2019 worldwide registered plantations are little over 2 700 000 ha, including European and Japanese plum, but also some hybrids. Total production is around 12 600 000 tons, with a significant increase about 20% over the last century. Leading producing country its China, followed by Romania, Serbia, Chile, USA, Turkey, Italy, France and Spain. In Europe the largest production areas are Romania and Serbia, their products are intended mainly for direct consumption in both countries and for production of distilled beverages [2, 3].

In 1965 the area of plum gardens in Bulgaria reaches its maximum of 53 000 ha since then began to decrease and in 2004 fell to 10 967 ha. The plum plantations include two varieties "Kyustendil Blue Plum" and "Stanley". In the last 15 - 20 yeast Prunus domestica "Stanley" is predominant [4].

The economic importance of Prunus species is extremely high due their widespread use in the food industry. The fruits are utilized both fresh and processed, but a significant number of distilled beverages is also produced [5, 6].

Alcoholic beverages produced by plums are known from centuries with their tradition of production and are found under various names, they depend on the region in which are made, for example Palinka (Hungary), Slivovica (Serbia, central and southern parts of Europa), in Bulgaria it is called Rakia.

The plum distilled beverages are characterized by intensive fruity aromas, but often with atypical sharp taste [7]. Volatile compounds are very important for the quality and aroma of these beverages. Those compounds originate from the raw materials, but also could be formed during alcoholic fermentation, distillation and aging.

Distillation is an excellent method to eliminate faults occurred during pre-processing of raw material. However, there is extremely divers opinions on this topic, concerning which is the exact moment concerning the quality of final product. Some authors point out the raw material has the main influence on the profile of the fruit beverage [8 - 10]. Others say that the most important part during production of aromatic compounds is alcoholic fermentation. There is some that wrote about the distillation techniques as a main factor for managing aromas found in distilled beverages [11 - 13]. Some authors, on the other hand, emphasize the influence of the aging of distillates in creating their unique quality [14, 15]. However, the truth is somewhere between all these points of view. All researchers agree that each phase must be performed adequately to achieve premium quality products.

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The aim to this study is to determine the influence of the type of fermentation on the chemical composition of distillates obtained by fermenting Prunus domestica "Stanley".

2 Materials and methods

The study consists of several important stages affecting quality of the final product. These are - raw material, managing proper process of alcoholic fermentation and subsequent distillation. In the experimental part of this study, these three important parts will be discussed. The whole experimental work was conducted in an industrial environment. The technological shame is presented in Fig. 1 below.

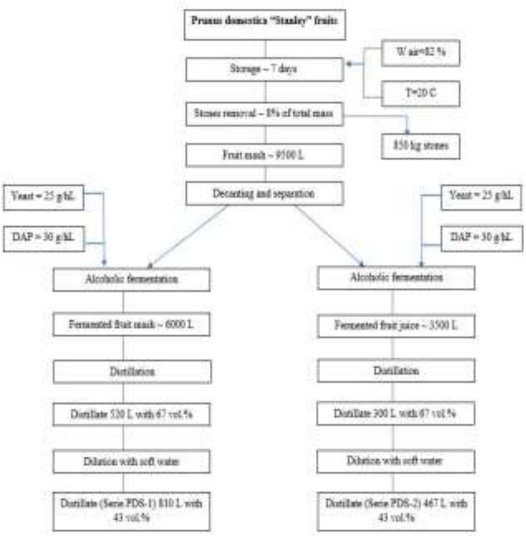

Fig. 1. Technological scheme of distillate produced from Prunus domestica "Stanley"

2.1 Experimental part

2.1.1 Raw fruit material

In this research 10 440 kg Prunus domestica "Stanley" were harvested in period between 18 - 20 September 2021. The origin of raw material is the village Rumyantsevo, Lovech region located in the Central Balkan Mountains, which is also one of the main areas of plum production in Bulgaria. There are favourable agro-climatic conditions affected the wine distribution of plums. In this location are situated some of the major producers of plums for direct consumption or for processing into jams, juices or high alcoholic beverages. This region includes hilly areas of the towns of Teteven, Lovech, Troyan, Sevlievo, Gabrovo, Dryanovo and Elena [4].

At the beginning of experiment sugar content, total acidity and pH of fresh fruits were analysed. Dry material and each one of fermentable sugars were tested as well. The results are shown in Table 1 below.

Table 1. Physicochemical analysis of fresh fruits Prunus domestica "Stanley"

Fresh fruit sample of Prunus domestica "Stanley"	
Total sugars, g/L	112.3
Total acidity, g/L	7.52
pH	3.57
Dry material, %	18.53
Glucose, %	3.98
Fructose, %	2.73
Sucrose, %	4.52

2.1.2 Alcoholic fermentation

Before fermentation begins prunes have been left to soften for a period of seven days in ventilated and cool place. The aim is to remove the stones from the flesh more easily. For this purpose, a stone fruit crusher with capacity 1.2 t/h has been used the stones were around 9% of the total mass of prunes - 950 kg. The obtained batch after crusher goes in stainless steel tank to settle down for easy decanting and separation of both materials – juice and mash. After this procedure separated products go under alcoholic fermentation in stainless sleet fermenters equipped with cooling jackets for thermoregulation.

To manage the quantity of microorganism in the fermented juice and in the fermented mash after mechanical treatment was performed cooling of both batches and using higher dose of lyophilized yeast. This enhanced the chance to protect the masses from developing undesirable microorganisms.

For better and trouble-free alcoholic fermentation, a lyophilized *S. cerevisiae* yeast at a dose of 25 g/hL was added to the mash and juice during the filling of fermenters. The yeast strain was chosen depending on type of desired product. It was preferable to be a neutral strain with fructophilic character. The strain has low nitrogen demands and good fermentation kinetics. After the first five days, DAP was added at a dose of 30 g/hL. The aim was to avoid reduction of aromas and giving the yeast some nutrients to finish alcoholic fermentation without any deviations in taste or flavour of the fruit wine.

DAP was added at a later stage of fermentation because if added in the beginning or during the inoculation of the mash and juice, it could inhibit the uptake of amino acids from fruit by the yeast cells. As is well known, the transport of amino acids from the fermenting environment into the yeast cells is inhibited when the alcohol level increases. This is the correct moment to use DAP as the main source of nitrogen, which will be from this inorganic compound.

During the process twice a day was performed pumping over for the mash, from the lower part of the tank juice was pumped to the cap. The aim is better homogenization and prevention of developing undesired microorganisms such as acetic bacteria over the cap.

The fermentation process of the mash has been performed for twelve days; fermentation of juice was longer it took seventeen days to finish it. The end of this stage was ascertained by measuring the density of the fermenting mass and also by performing a chemical analysis showing the amount of residual sugars in both batches.

The temperature was maintained between 18 - 22℃ until the end of alcoholic fermentation. As a result, 6000 L and 3500 L with 6 vol.% fermented materials were obtained.

2.1.3 Distillation process and equipment

The distillation apparatus used for the experiment has a working volume of 700 L, it is heated by an oil jacket powered by electric heater in it. The apparatus is equipped with a rectifying column with 4 trays, as well as a water reflux condenser. This system is designed for batch distillation and only one distillation is required to achieve higher alcohol content and division into fractions: primary (head), middle (heart) and final fraction (tail).

Some of the volatile substances formed during the distillation have very pleasant aromas, this requires a very careful rectification process, the purpose is no to purify much the obtained distillate, but to have the typical aromas from raw material [16-19].

Due to the used distillation apparatus following fractions have been collected:

- 0.5 - 1% head per 100 L of distilled material
- 8 - 12% heart per 100 L of distilled material
- 4 - 8% tails per 100 L of distilled material

For this specific experiment 3500 L of fermented liquid phase and 6000 L of fermented fruit mash were distilled. The two materials subjected to distillation have an alcohol content of 6 vol.% and two series with distilled beverages were obtained:

- PDS-1 which contains 520 L distillate with 67 vol.% procured from distillation of plum mash;
- PDS-2 which contains 300 L distillate with 67 vol.% produced from distillation of fermented liquid phase;

Both distillates before analysing were diluted to 43 vol.% with softened water before being analysed, thus the amounts of distillates are as follows:

PDS-1 series - 810 L distillate with 43 vol.%;

PDS-2 series - 467 L distillate with 43 vol.%;

To collect the data reported in the results subsection, three repetitions of the experimental part have been made.

2.2 Analytical methods

The ethanol content was determined by measuring the relative density of the distillates [20].

Total acidity was determined by titration with bromothymol blue as an indicator and comparison with an end-point cooler standard [21].

HCN was determined by colorimetry principle with 1.3-dimethyl barbituric acid and the blue colour it gives [21].

Furfural was determined by high-performance liquid chromatography (HPLC), with detection by ultraviolet spectrophotometry at several wavelengths, and by spectrofluorimetric [21].

Congeners were determined by gas chromatography (GS) spirits were directly injected into a system, with an internal standard added to the distillate prior to injection [21].

3 Results

According to regulation (EU) 2019/787 of the European Parliament and of the council of 17 April 2019 fruit spirit has:

- Volatile substances content ≥ 200 g/hL of 100% vol. alcohol;
- HCN content < 7 g/hL of 100% vol. alcohol;
- Maximum ethanol content shall be ≤ 1200 g/hL of 100% vol. alcohol;

In Table 1 were shown parameters of raw material before fermentation starts. After alcoholic fermentation before distillation process the same parameters were checked again for both mash and juice. Fermented mash had insignificantly higher index of sugar and acidity content. It could be easily seen that almost all of the sugars were fermented, during the fermentation total acidity and pH were largely unaffected. The changes in these parameters are described in Table 2.

Table 2. Physicochemical analysis of fermented mash and juice of Prunus domestica "Stanley"

Parameters	Sample	
	Fermented mash	**Fermented juice**
Total sugars, g/L	6.68	6.53
Total acidity, g/L	7.46	7.41
pH	3.572	3.584

In distilled beverage production some specific EU regulations should be followed for each type of product. Quality parameters connected to the safety of the spirits are ethanol, higher alcohols, methanol, esters, aldehydes, furfural and HCN. Increased quality of the beverages is connected to the higher amount of total volatile substances in it.

It is known that distillation columns lead to increase esters and higher alcohols in the final beverage, in the same time a significant decrease of aldehyde content is observed and less methanol is produced. In this study a column was used and expected results were to have more aromatic beverage with less undesired aromas and flavours caused by higher methanol and aldehyde content.

Table 3 presents the data for the analysed distillates from each series. PDS-1 signify distillate of fermented mash and PDS-2 distillate of fermented juice.

Table 3. Volatile compounds (g/hL) found in distillates produced from fermented mash and juice of Prunus domestica "Stanley"

Volatile compounds, g/hL	**Sample**	
	PDS-1	**PDS-2**
Methanol	1094.7 ± 50.8	1015.8 ± 50.8
Furfural	7.21 ± 0.38	6.38 ± 0.38
Cynamide derivate (HCN)	< 0.02	< 0.02
Total acidity (as acetic acid)	6.39 ± 0.3	5.6 ± 0.3

Methanol is the second compound found in the distilled beverages, after ethanol. It is presented in each fraction, in heads and tails the quantity is much higher than in middle fraction. In the heart the amount of this substance depends on pre fermenting treatment of raw materials, the initial chemical composition of fruits, alcoholic fermentation and distillation regimes [22].

It could be easily seen the amount of methanol in both distillates is lower, despite that in the distillate produced from fermented mash PDS-1 methanol (1094.7 g/hL a.a.) is almost 8% higher than in PDS-2 (1015.8 g/hL a.a.) which is obtained after distillation of fermented juice. This increase could be in relation with higher amount of pectin in mash which is a precursor for methanol production. The enzymatic activities of Pectin methyl esterase during the fermentation may be another reason for endorsing the quantity of methanol which becomes a part of the plums mash. After alcoholic fermentation during distillation process this volatile compound is collected in higher quantities in distillate produced from fermented mash.

There is an insignificant increase of furfural content in distillates of PDS-1 (7.21 g/hL) than PDS-2 (6.38 g/hL) which could be related to the distillation of mash and eventual Maillard reactions of residual sugars in the pulp of the distilled material. During the distillation process stirring the mash would possibly affect the better consistency of the distilled material and avoid calcination, which is a prerequisite for development of Maillard reactions. The elevated amount of furfural in PDS-1 may be explained with prolonged period of distillation of the mash compared to the juice, this conduct to longer time and ability to degrade pentoses in the raw material. Another reason for higher content of this compound in PDS-1 may be the fermentation with hard particles and decomposition of carbohydrates during the process.

Furfural mainly is a result of dehydration of sugars, could be formed during the heating of fermented pentoses [23].

During distillation furfural is a result of acid hydrolysis or obtained by Maillard reactions. There is no data of humans for carcinogenic effect of furfural but it has a permissible exposure limit of 5 mg/L. This compound contributes the aromatic profile of distillates, if it is distributed in small amounts.

Hydrogen cyanide is obtained after hydrolysis of amygdalin found mostly in kernels of plums and small quantities in the pulp, also in other stone fruits. Before alcoholic fermentation if seeds of plums are removed the amount of HCN is significant decreased in produced beverage. HCN is compound distilled in higher percentage in the beginning of distillation process, with a visible decrease during prolonged process, and its depletion continuous almost until the end of the distillation of ethanol [24].

The results in this study for both series are < 0.02 g/hL of HCN which is explained by the removed seeds of the plums before alcoholic fermentation. This stage was strictly observed, whole kernels happened to be in the mash were removed by the hand during this operation. Quantity of amygdalin in pulps did not affect the final content of HCN in distillate produced of fermented mash. In a further study, the amount of amygdalin in the fruit pulp and its effect on the final product obtained by distillation of the mash could be analysed.

In Table 4 is presented collected data for esters and aldehyde content in both series of plum distillate.

Table 4. Esters and aldehydes (g/hL) found in distillates produced from fermented mash and juice of Prunus domestica "Stanley"

Volatile compounds, g/hL	**Sample**	
	PDS-1	**PDS-2**
Esters (as ethyl acetate)	203.06 ± 4.1	82.4 ± 4.1
Aldehydes (as acetaldehyde)	14.2 ± 0.54	8.6 ± 0.4

Esters are formed during alcoholic fermentation as a result of reaction between yeast, alcohols and acetyl-CoA. Formation of esters continuous during the distillation and maturation of alcoholic beverages via processes such as alcoholysis and trans-esterification [25]. Dominant esters in plum brandies are acetates and ethyl esters because ethanol and acetyl-CoA are cardinal catabolic product of glucose degradation. Esters affect the sweet fruity aroma of beverages.

Acetaldehyde is a compound formed during fermentation and the quantity of it increase after distillation. It has a lower boiling point and form heads fraction, along with methanol, acrolein and some esters. These compounds are highly toxic and have unpleasant aromas and for this reason the fraction is separate after distillation. Acetaldehyde presents around 90% of total aldehydes in distilled beverages, aldehydes are formed during alcoholic fermentation of fruits as a by-product of yeast metabolism of consuming sugars and amino acids [26].

It is easily seen that in PDS-1 produced from fermented mash the quantity of esters is almost 3 times higher than in PDS-2 produced of fermented juice. Concerning aldehyde concentration, the mash fraction PDS-1 has around 1.5 times higher content of these congeners. Slight marzipan like aromas is found in the PDS-1 and this could be a signal that in the mash traces of seeds not separate from the pulp, in which is found benzaldehyde, its quantity may have led to overall increased aldehyde content. On the other hand, elevated concentrations of both esters and aldehydes in PDS-1 may be explained by poor separation of the middle fraction (hearts). It is known that there is a higher amount in the head fractions. A shorter separation period of heads may have led to higher amounts of these substances in the distillate.

Esters are formed intercellular in fermented yeast cells; the compounds are diluted in lipids and could diffuse from yeast membrane into fermenting mash. The increased number of esters in PDS-1 could be explained with this scientific regularity. Another reason that may affect the production of more esters in fermented mash is the elevation of temperatures during the alcoholic fermentation in period of two days. This elevation increases the process of yeast autolysis and excretion of esters in the mash.

Table 5. Higher alcohols content (g/hL) in distillates produced from fermented mash and juice of Prunus domestica "Stanley"

Volatile compounds, g/h.L	Sample	
	PDS-1	**PDS-2**
Higher alcohols	484.6 ± 13.4	267.9 ± 13.4
1-butanol	6.3 ± 0.1	1.8 ± 0.1
2-butanol	2.28	< 0.1
1-propanol	145.8 ± 3.7	73.6 ± 3.7
2-methyl-1-propanol	104.6 ± 2.2	43.0 ± 2.2
3-methyl-1-butanol	193.1 ± 6.3	125.4 ± 6.3
2-methyl-1-butanol	32.5 ± 1.2	24.2 ± 1.2

Higher alcohols have boiling point higher than the ethanol and form the tails fraction, they are also known as fusel oils. These compounds have strong aroma and taste and are obtained in high quantity in distillates. Their amount depends on the fruits and yeast strains used during alcoholic fermentation, as the compounds are by-product of metabolized sugars and amino acids by yeasts. [25]

In Table 5 are presented quantities of higher alcohols in both batches.

It is easily seen that PDS-2 contains 1.8 times lower concentrations than PDS-1. One of the reasons of increased content in PDS-1 could be the relation between turbidity of the middle during the fermentation and yeast activity. It is known that higher turbidity leads to better production of by-products from yeasts such as higher alcohols and through conversation of the amino acid threonine, leucine and valine in the medium.

The higher amount of 2-butanol could be a signal for undesired bacterial action, despite that there is no evidence of negative flavours in the beverage. Mostly the amount of these volatile compounds is influenced by the fraction separation which may be another reason for different amount of these volatile compounds in both batches.

4 Conclusion

In summary, the results of this study showed that an alcoholic fermentation of fruit mash after distillation gives a spirit beverage with much higher content of volatile substances such as esters, aldehydes, higher alcohols and even methanol. This is explainable with the fact that in the fermented and distilled medium has more of these congeners, and during the fermentation yeasts have better stimulus to produce more of substances, as well.

For an industrial production both distillates should be blended for better organoleptic profile. PDS-1 has complex and fruit driven flavours while PDS-2, produced from fermented and distilled juice, has much lighter and delicate expression. PDS-2 is much cleaner distillate that could be used as a good base for a blend.

Prunus domestica "Stanley" from village Rumyantsevo, Lovech region could be a source of decent raw material for spirits beverages produces in Bulgaria and should be further explored in future more extensive studies. Both batches obtained from these fruits have excellent parameters and organoleptic qualities.

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