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The Impact of Grape Marc Distillation Process on the Major Volatile Compounds

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Abstract. The grape marc represents the product resulted after the pressing of grapes in the wine technology (clusters, skins, seeds and must). It contains many valuable compounds such as: carbohydrates, alcohol, tartaric salts and seed oils. In Romania grape marc is usually used to produce spirit. There were analyzed samples of grape marc spirits from the two stages of distillation process, first and second distillates, as were collected directly from the production process soon after the process ended. The aim of the study it was to evaluate the impact of distillation process on the major volatile compounds in grape marc spirit, resulted after the first and second distillation process. We investigated the ethyl alcohol content by electronic densimetry and 10 major volatile compounds (acetaldehyde, ethyl acetate, methanol, 1-propanol, 1-butanol, 2-butanol, isobutyl alcohol, isoamyl alcohol, amyl active alcohol and furfural) by Gas Chromatography coupled with Flame Ionization Detector. We used reference chemicals to identify these compounds and 3-pentanol as internal standard to quantify the volatiles. This analysis permitted to observe the differences between the two distillates. Acetaldehyde, ethyl acetate, methanol and higher alcohols have smaller amounts in the second distillation step. Furfural registered values below the method detection limit.

The factors which differentiate the two samples can be separation of fractions (heads, hearts and tails), temperature applied in the distillation process, quality of raw material and the fermentation process.

Keywords: grape marc spirit, GC-FID, distillation, volatile compounds

INTRODUCTION

Alcoholic beverages made from grape marcs are very popular in Mediterranean countries. The most famous geographical indications for producing grape marc spirit are: eau-de-vie de marc (French grape marc spirit), the Italian grappa, tsipouro (from Greece) and zivania from Cyprus (Danilatos and Harvala, 1981; Apostolopoulou *et al.*, 2005; Geroyiannaki *et al.*, 2007). Being a good method for revaluation of residues from the wine making industry, the producing of grape marc spirit can become a trend also in Romania.

The production of marc distillates includes several stages with impact to the chemical and sensory characteristics of the spirit. After the pressing of grape pomace for wine making, the resulted marc is subjected to alcoholic fermentation, when are formed the most important volatile aroma compounds. Among them are ethanol, ethyl esters, eugenol, acetic acid, acetaldehyde, fatty acid esters, ethyl acetate, amyl alcohols, high alcohols, aldehydes, acetals (Apostolopoulou *et al.*, 2005; Geroyiannaki *et al.*, 2007; Nunes *et al.*, 2008; Tešević *et al.*, 2009; Cortés *et al.*, 2010). When fermentation is completed, the ethanol and volatiles formed in the fermented marc are recovered in the distillation stage. Due to its boiling point and solubility in liquid and vapor phases, the behavior of each volatile compound is different. Therefore distillation can seriously damage the spirit quality if is not conducted properly.

During grape marc spirit production, the slow distillation process permits the proper separation of the distillate into three fractions called the head, the heart and the tail. The fractions from the beginning of the distillation process called heads and those from the end called tails, are usually separated from the spirit since they contain high amounts of compounds which contribute negatively to sensory and safety of distillate. Acetaldehyde has a low boiling point (21°C) and it is distilled in heads fraction (Rodriguez Madrera *et al.*, 2006), but can also appear in tails due to its miscibility with water. In the present study, all esters were expressed as ethyl acetate this being the main ester present in grape marc spirit. Ethyl acetate results after the fermentation and distillation by etherification reaction between acetic acid and ethanol. With a low boiling point (77°C) and a minor solubility in water is a typical volatile for head fractions, but also appears in the middle fraction. Methanol distills off throughout the entire distillation process, with an increased amount in the tail fraction, being the reason for tail fraction separation at the beginning of distillation. Methanol is formed when pectic substances hydrolyze under the influence of some pectolytic enzymes, especially, pectin methyl esterase (Geroyiannaki *et al.*, 2007).

Fresh grape marc distillate contains solely the middle fraction, known as heart. This part contains the majority of ethanol and the valuable volatiles such as ethyl acetate, ethyl butyrate, ethyl esters of fatty acids, acetaldehyde, methanol, furfural, 2-phenethyl acetate, higher alcohols, furaldehyde, phenols, fatty acids, acetic esters, hydroxi- and dicarboxylic acid esters (Cortés *et al.*, 2010; García-Llobodanin *et al.*, 2011; Lukić *et al.*, 2011; Rodríguez Madrera and Mangas Alonso, 2011; Rusu *et al*., 2011**)**. Hearts are distilled once again for a better separation of the volatiles. Furfural is responsible for the aroma and flavor of fruit brandies. It has a high boiling point (160^{o}C). The caramel color of the not maturated fruit spirit can be explained by the presence of furfural (Quesada Granados *et al.*, 1996; Rodriguez Madrera *et al.*, 2006). Higher alcohols, found in tail fractions, contribute to the aroma of the final spirit. They amount in grape marc spirit depends on their percentage in the raw material used in distillation. Usually, fruit spirits are aged in wood barrels for maturation before consumption. During aging process is formed the specific bouquet resulted from the interaction between spirit with wood extracts. Due to the toasting woods used in the aging process, furfural can be also formed.

In the present study, it was monitored the evolution of major volatiles in grape marc spirit as well as their changes during distillation. Gas chromatography coupled with Flame-Ionization Detection (GC-FID) was used for these determinations.

MATERIALS AND METHODS

Provenience of samples. In order to perform this study, two samples of grape marc spirit were produced in USAMV Cluj-Napoca pilot station (one resulted after the first distillation stage, sample -D1 and another after the second distillation process, sample -D2) in May 2013. All production stages were monitorized.

Samples preparation. Red grapes varieties were harvested during September 2012. The grapes are first destemmed and crushed then the must is transferred to a fermentation vat. During devatting the wine is run off and separated from the marc, the solid residue composed largely of seeds and skins. Devatting takes place when most of the sugar content has been converted into alcohol. The liquid still remained in the marc is separated by pressing. After having pressed the grapes in the winemaking process, the grape pomace is stored for six months in order to promote spontaneous anaerobic fermentation of residual sugars. The various volatile organic components thus formed are then recovered by distillation after having added water, in alembic made of copper. The distillation process took place in two

stages. The distillate resulted was cooled with water to facilitate the condensation of the spirit. A quantity of around 1 L of distillate resulted at the beginning of the boiling, heads fraction was separated. The most important part of the distillate, called heart is collected separately. The last fraction of the distillate, named tails is cut from distillation process. The intermediate product it has an alcohol content around 42,32% v/v. The operation of distillation is repeated in the second stage; the grape spirit resulted has an alcohol content around 72% v/v. Both fractions were then diluted with water and resulted samples D1 and D2.

Alcohol concentration and the relative density. The alcohol content and relative density analyses were analyzed by the electronic densitometer type DDM2911, with digital display and measuring cell connected to an incorporated temperature regulator, made by Rudolf Research Analytical, series: 2045, measuring domain: 0-3 g/cm^3. The measurement result was an average of five values obtained for alcohol concentration and respectively, for the relative density. The density was displayed with 5 decimals and alcoholic concentration with 2 decimals.

Volatile compounds analysis. Analysis of major volatile compounds of the two fractions of distillate was adapted after the EU reference method for volatile compounds found in alcoholic beverages. For the determination of the major volatile compounds, the samples were injected directly into the gas chromatograph column, from a GC-FID Agilent Technologies gas chromatograph, 6850A, without preliminary treatment. Each sample was injected twice in the GC-FID. One micro liter from each sample was introduced in the capillary chromatography column ZB-WAX plus (characteristics: 60 m length, 0.25 mm diameter, 0.25 μm film thickness, stationary phase: cross linked polyethylene glycol) produced by Zebron Company. Inside the oven, the initial temperature was 35^{o}C. The injector temperature was 240^{o}C, automatic injection. The carrier gas was Helium. Detector (FID) temperature was 250^{o}C (Rusu *et al.*, 2011).

The temperature program is represented in *Table1*. The total analysis time of each sample was 30.63 min.

Tab. 1

Temperature program used for the GC-FID analysis of all beverages

Ramps	Rate	Final temperature	Final time
1	12^{0}C/min	35-58^0 C	4 min
2	3^{0}C/min	58-85^{0}C	0 min
3	30^{0}C/min	155^{0}C	3 min
4	200^{0}C/min	230^{0}C	5 min

The main components (methanol, acetaldehyde, ethyl acetate, 1-propanol, 2-butanol, isobutylic alcohol, amyl active alcohol, isoamylic alcohol, 1-butanol), were identified by comparing their retention times with those of authentic compounds (see *Chemicals and reagents*). For quantitative evaluation it was applied the internal standard method, with a known amount of 3-pentanol, as internal standard (IS). As such, a solution containing 0.1 ml 3-pentanol was added to 10 ml of every each sample. For all volatiles, the quantitative evaluation was based on automatic calculation, based on peak area integration, while for furfural the integration was done, manually.

Chemicals and reagents. All used chemicals (ethanol, acetaldehyde, methanol, propanol, 1-butanol, 2-butanol, isobutylic alcohol, isoamylic alcohol, amyl active alcohol, ethyl acetate, 3-pentanol, furfural) with purity over 99% were purchased from Merck and Sigma Aldrich Company.

Statistical analysis. The results obtained from the individual experiments were used to calculate the mean values and standard deviation values for the two apple brandy fractions samples.

RESULTS AND DISCUSSIONS

Alcohol concentration based on relative density determination. *Table 2* represents the values obtained for the alcohol concentration based on relative density measurement.

Tab. 2

Alcohol concentration, determined from relative density

Sample code	Alcohol concentration, % v/v	Relative density, g/cm^3
D1	36.16	0.95392
D2	39.85	0.94829

The mean values of alcohol concentration in the two fractions of distillate were quite different due to the double distillation process applied. After the first distillation stage the value for alcohol concentration was smaller, 36.16 % v/v, than the second distillation stage, 39.85 % v/v.

GC-FID analysis. The GC-FID chromatograms of the distillates resulted after the first and second distillation stage are presented in *Figure 1 A* and *B*. The major peak corresponding to ethanol (t_R=8.11 min) was eliminated, in order to identification the other minor components. There were identified the main volatile compounds by their retention times and by comparison with pure standards. The internal standard used in all cases was 3-pentanol (peak 7). Based on the peak areas, for each sample it was calculated the concentration of each component, expressed as mg/100 ml anhydrous alcohol (anh. alc.). The individual and mean values for each volatile found in the samples resulted from the distillation process are presented in *Table 3*.

Tab. 3

Major volatile compounds identified in the samples collected from the two distillation stages

Sample name	Major volatile compound, mg/100 ml anh. alc.									
	Acetaldehyde	Ethyl Acetate	Methanol	Furfural	2-Butanol	1-Propanol	*Iso*-butylic Alcohol	1-Butanol	Amyl Active Alcohol	Iso-amylic Alcohol
D1	45.53	1625.81	735.89	0.00	0.69	30.91	79.62	2.40	33.91	129.27
	45.61	1624.50	744.07	0.00	0.69	31.15	79.94	2.42	34.14	129.88
MV*	45.57	1625.15	739.98	0.00	0.69	31.03	79.78	2.41	34.02	129.57
SD**	0.06	0.93	5.79	0.00	0.00	0.17	0.23	0.02	0.17	0.43
D2	30.94	1034.94	657.51	0.00	0.77	32.91	88.84	2.69	39.38	148.65
	30.98	1040.63	659.05	0.00	0.79	32.94	89.06	2.67	39.47	148.68
MV*	30.96	1037.79	658.28	0.00	0.78	32.93	88.95	2.68	39.43	148.67
SD**	0.03	4.02	1.09	0.00	0.01	0.02	0.15	0.01	0.07	0.03

* - Mean Value; ** - Standard deviation

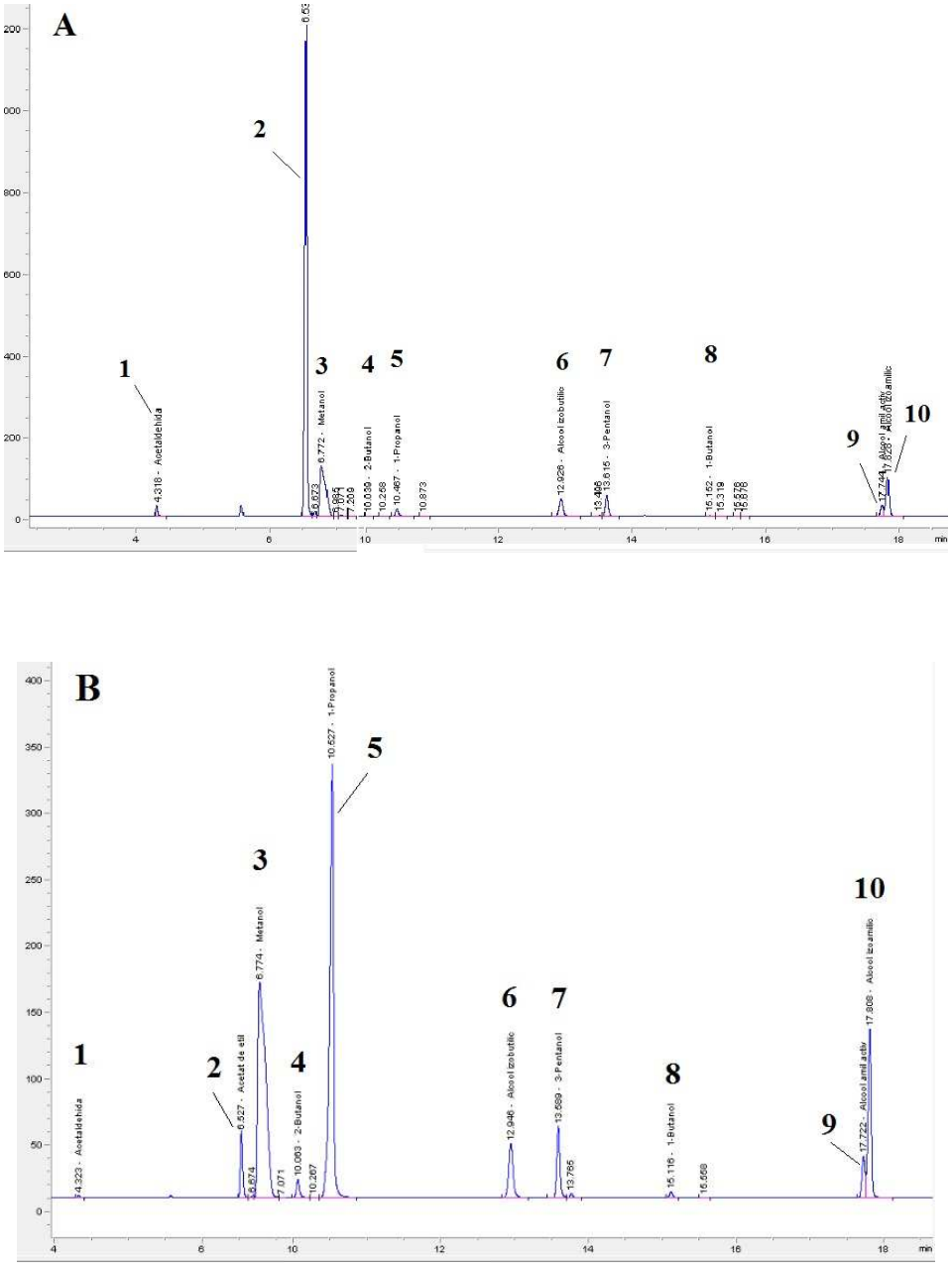

Fig. 1. The GC-FID chromatogram of major volatile compounds identified in first distillation stage sample (A) and second distillation stage sample (B).
Peak identification: 1=Acetaldehyde; 2=Ethyl acetate; 3=Methanol; 4=2-Butanol; 5=1-Propanol; 6=Isobutylic Alcohol; 7=3-Pentanol (IS); 8=1-Butanol; 9=Amyl Active Alcohol; 10=Isoamylic Alcohol.

As we can observe the first three major volatile compounds (acetaldehyde, ethyl acetate and methanol) have smaller amounts in the second distillation stage. The possible explanation may be the distillation impact by applying a good fraction separation in the distillation steps. In the second distillation process the temperatures applied were higher than the first one. Furfural was not detected in these samples. Higher alcohols have boiling points between 97-130^{o}C. Higher alcohols registered also higher values in the second distillation step were distillation temperature was also higher.

The volatile substance content is higher in the first distillate (2688.22 mg/100 ml anh. alc.) due to ethyl acetate and methanol which represent the most abundant compounds in both distillates.

When the correlation coefficient was calculated for all volatiles, it registered the value 0.98, meaning that there was no difference in the distillation procedure applied for the two fractions.

CONCLUSION

There were investigated the major volatile compounds found in two distillate fraction collected from the double distillation process in order to evaluate the impact of distillation process to the composition of grape marc spirit. It was identified and quantified ten major volatile compounds by GC-FID analysis. The temperature applied in the distillation process made possible a good fractionation of the volatile compounds. Due to the proper separation of the unwanted fractions in the two distillation steps (heads and tails), but also to the good quality of the raw material or the well conducted fermentation process, the first three major volatile compounds, acetaldehyde, ethyl acetate and methanol, have smaller amounts in the resulted grape marc spirit. Higher alcohols registered different evolution in the last distillation step. They were higher then in the first distillate. The possible explanation of this evolution can be the temperature, which was higher in the second distillation and make possible a better volatilization of these compounds.

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