

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 11, November 2015

Qualitative Evaluation of Distillates Produced from Aromatic Grape Cultivars Produced in Albania

KlotildaMarku¹, Renata Kongoli², Vlash Mara²

Ph. D Student, Faculty of Biotechnology and Food, Agricultural University of Tirana, Albania¹

Prof. dr: Faculty of Biotechnology and Food, Agricultural University of Tirana, Albania²

ABSTRACT: The production of alcoholic distillates in Albania is a part of the tradition that is being strengthened each day more. The study was taken in Durres in zone that is characterized from the soft mediterranean climate with the minimum annual temperatures that never goes under 2⁰C. For this study we have taken Pearl of csaba, Muschat Hamburg cultivated in Durres in 2010, 2011, they are two aromatic varieties from which we have produced alcoholic distillate. The study aims to identify the aromatic compounds in the fresh alcoholic distillate by using GC/MS and GC-FID in accordance with the CE directive n. 2870/2000. The results shows that the distillates produced by these cultivars appear to be in high quality and the identifying compounds of the quality show that they were within the limits imposed by the European standard. They have low content in methanol, higher alcohols and ethyl acetate, but they have high levels of terpenic content that gives to these distillates pronounced aroma flowers.

KEYWORDS: Muschat Hamburg, Geraniol, Nerol, Aromatic compound

I. INTRODUCTION

Albania has a highly advantageous geographical position for the cultivation of vineyards and the wine production, and therefore the alcoholic distillates is priority for our country. Grape distillate quality depends on many factors, but primarily on cultivar characteristics of grape, the grape processing manner, the alcoholic fermentation process as well as on the implemented distillation procedure (Versini et al., 1993, Nikićević et al., 2000, Mojmir, W., Berović, M., 2001, SanjaRadeka et al., 2008) [1]. Alcoholic distillates are composed by a number of volatile compounds that are directly responsible for their aroma and flavor. Major volatile compounds are usually formed during the fermentation process, and their formation is influenced by the cultivation conditions. All the compounds that are present in the alcoholic distillate arise during the fermentation process. These components comprise mainly fusel alcohols, fatty acids and esters and these organoleptic substances can be present in relatively large amounts (i.e., up to 3 g/L) [2]. The most abundant secondary compounds present in distilled spirits are the fusel alcohols and fatty acid esters, together with acetaldehyde and its acetal with ethanol [3]. In spirits and alcoholic beverages, low molecular mass carbonyls (C1–C6) are present as the by-products of yeast fermentation, intermediates in the formation of fusel oil and as a result of alcohol oxidation at various stages of beverage production. Their presence is undesirable as some of them are responsible for unpleasant organoleptic properties of alcoholic drinks [4]. Acetaldehyde is the most toxic metabolite created by alcohol metabolism originating from fermented raw materials [5]. Acetaldehyde levels in distillates can increase during ageing due to the chemical oxidation of ethanol and further oxidation of acetaldehyde can result in the formation of small amounts of acetic acid [6]. Methanol is formed by pectinolytic enzymes that split the methoxyl group from the pectin present in the crushed fruit. For this reason, the concentration of methanol in the final distillate spirit increases with the extraction time of the pomace [5,7]. Ethyl acetate has a significant effect on the organoleptic characteristics of wines and distillates. This ester is frequently described as having “fingernail polish remover” aroma properties and at a level of 150–200 mg/L can add spoilage “notes” to the wine. At lower concentrations, ethyl acetate contributes to fruity properties of the wine. Ethyl acetate derives mainly from bacterial spoilage of the marc distillates

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 11, November 2015

and imparts an acidic character to the spirit when its concentration is higher than 180 g/hL anhydrous alcohol [8,7,10]. Higher alcohols constitute the group with the highest concentration in the distillates and give a flavoring aroma and an essential character [8,7]. The levels of these compounds are influenced by several factors, such as grape variety, the conditions of fermentation and the distillation techniques, the majority of the higher alcohols is concentrated in the first fraction of the distillate [5]. The most important higher alcohols of the alcoholic distillate are 2-propanol, n-propanol, 1-pentanol, 2-pentanol, 3-pentanol, n-butanol, 2-butanol, 3-methyl-1-butanol, 2-hexanol, and 2-heptanol [11]. Ethyl lactate is produced mainly by lactic acid bacteria and is considered in low concentrations to stabilize the distillate flavor characteristics [8]. The group containing the highest number of different compounds that contribute to the flavor of the distillates and account for a pleasant aroma, indicative of the quality of the spirit, is the fatty acid esters [12,7,13]. Isoamyl acetate is an ester of acetic acid and is mostly responsible for the flower and fruity characteristics of the distillates [8,14,7]. 1-Hexanol is an alcohol originating only from raw material and is not an alcoholic fermentation product [10]. In this study the principal volatile compounds of the alcoholic distillates Pearl of Csaba and Muschat Hamburg are identified with GC/MS and GC-FID in accordance with the CE directive n. 2870/2000, by using a direct injection method.

II. MATERIALS AND METHODS

Muschat Hamburg and Pearl of Csaba are two aromatic varieties and they are characterized from the pronounced aroma flower. For this study we have used the harvest of two years 2010 and 2011. These two years are characterized by a sustainable weather without precipitation in the period of maturity and harvest, the annual temperatures in 2010 was 16,75°C and in 2011 was 17,5°C. One week before the harvest we check the vineyard by measuring the quantity of sugar, the acidity and the level of expression of the aroma. The samples (100 kg grape) are taken by respecting the vineyard sampling method of the average to have accurate assessment. After the harvest the grape undergoes to the crushing with deprivation of the branes and then undergoes to the fermentation without using SO₂. Fermentation is monitored every day by measuring two elements: the density and temperature, after preparing the fermented material it goes to fractional distillation by using traditional alembic distillation system. As we know the alcoholic distillate is composed by a large number of components out of which we can assess the quality of the beverage. The study aims to identify these compounds with the GC-MS and GC-FID technique. We have to identify these compounds by their retention time and by reading their chromatograms.

Chemicals and standards:

For this study we use REG-CE 2870/2000 and we have to use exclusively reagents with purity of more than 97% with ISO 3696. The method indicates that the reagents necessary for the identification are: Absolute Ethanol (CAS 64-17-5), methanol (CAS 67-56-1), Propan-1-ol (CAS 71-23-8), 2-methylpropan-1-ol (CAS 78-33-1), 2-methylbutan-1-ol (CAS 137-32-6), 3-methylbutan-1-ol (CAS 123-51-3), ethyl acetate (CAS 141-78-6), Butan-1-ol (CAS 71-36-3), Butan-2-ol (CAS 78-92-2), Acetaldehyde (CAS 75-07-0), Acetal (CAS 105-57-7). With the internal standards: pentan-3-ol (CAS 584-02-1) and methyl nonanol (CAS 1731-84-6). Ethanol 40% v/v. For the preparation and storage of calibration solutions we follow the procedure expressed in the method.

The technique of gas chromatography is very important to identify the components in the alcoholic distillate, these components are determined by direct injection of this distillate, into the gas chromatographic (GC) system without need of extraction after adding of an internal standard. To identify all the components we have used two detectors FID and MS. For the detection by using a flame ionization detector (FID) the used column is (6ft x 2mm i.d, packed 5% Carbowax 20 M on 80 – 100 Carbopak B. Gas flow: He, 300- 30 ml/min). For the detection by using MS Perkin Elmer TurboMass gold, scan: 33-300 m/z, source: 200°C, elmer energy: 70eV, solvent delay: 0,9min, transfer line: 250°C. According to the internal standard used to determine the quantity of each component present in the alcoholic distillate, chromatographic conditions and methods of use. Appropriate for this definition is the method defined by REG-CE 2870/2000, that all reagents should have purity over 97%. The identification of chromatographic peaks was also confirmed by comparing retention times with those of pure compounds. Quantitative analyses were made by

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 11, November 2015

employing the corresponding response factor in the reference solution, according to the internal standard method. Determinations were made in triplicate.

III. RESULTS AND DISCUSSION

All the compounds are identified by their retention time the GC chromatogram with direct injection for the two tipe of grape distillates are given below in Fig.1 is the GC-FID chromatogram and in Fig.2 is the GC-MS chromatogram. The concentrations of the volatiles were calculated as milligrams in 100% ethanol (mg % mL p.a.) for all the samples and the average amount of the volatile compounds are given in the graphics below.

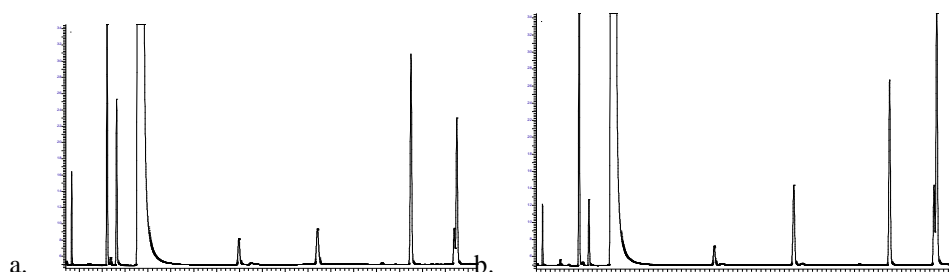


Fig 1. GC-FID chromatogram (a- Pearl of csaba, b- Muschat Hamburg)

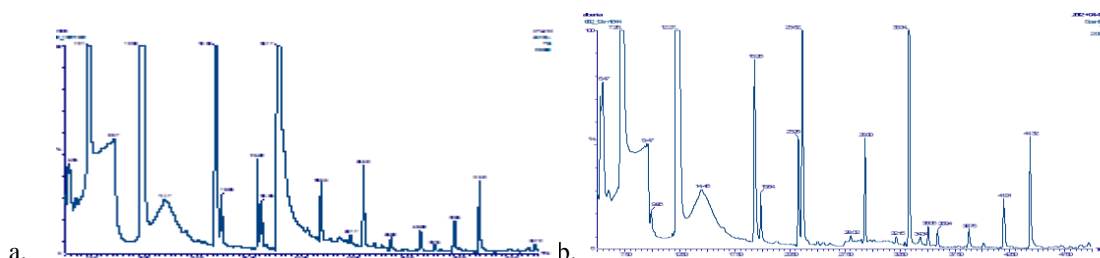


Fig 2. GC-MS chromatogram (a- Pearl of csaba, b- Muschat Hamburg)

Table 1. Physico-chemical indicators of Pearl of csaba (2010-2011) and Muschat Hamburg (2010-2011) distillates.

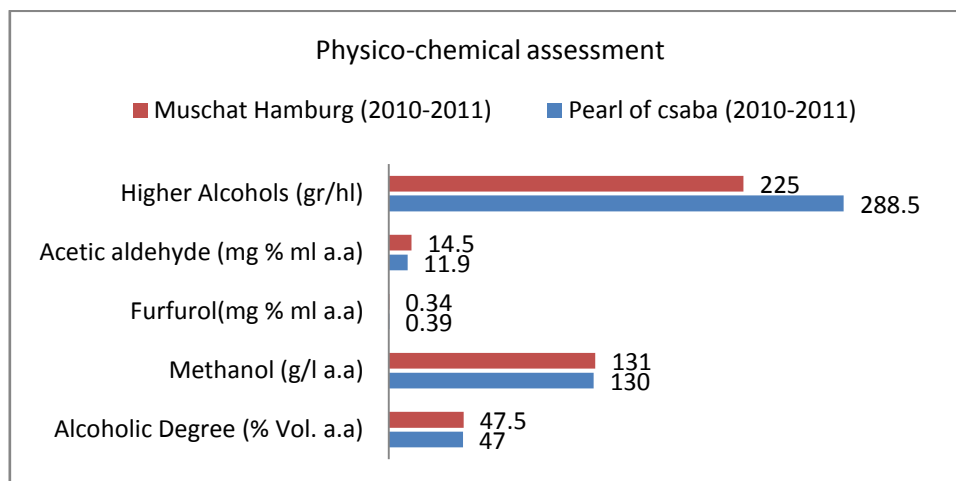
	Physico-chemical indicators	Pearl of csaba (2010-2011)	Muschat Hamburg (2010-2011)
1	Alcoholic Degree (% Vol. a.a)	47±0	47.5±0.71
2	Methanol (g/l a.a)	130±0	131±1.4
3	Furfurol(mg % ml a.a)	0.39±0.07	0.34 ± 0.05
4	Acetic aldehyde (mg % ml a.a)	11.9±2.69	14.5 ± 0.71
5	Higher Alcohols (gr/hl)	288.5±12.03	225 ± 4.24

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

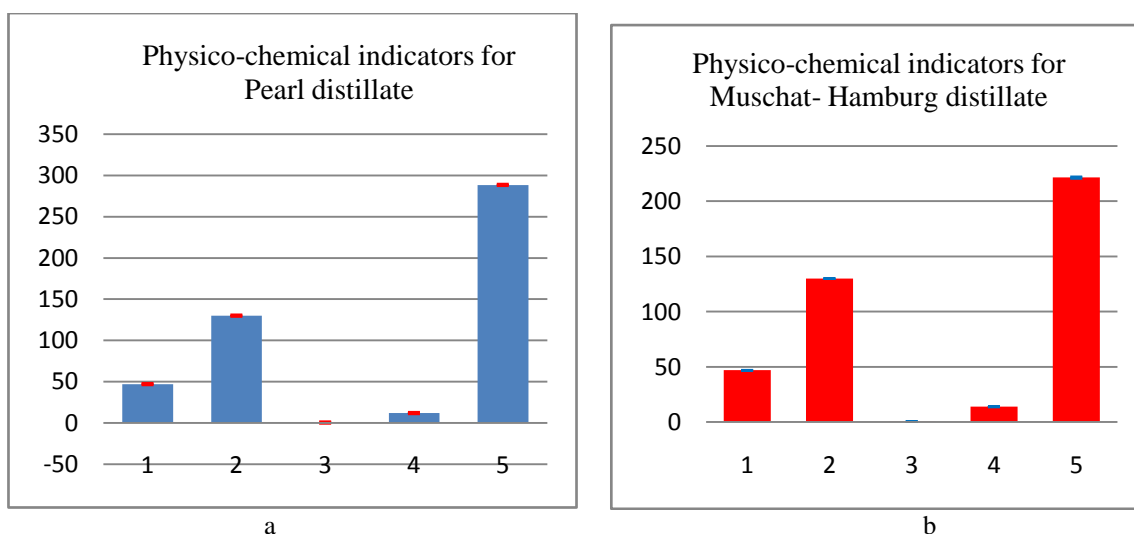
Vol. 4, Issue 11, November 2015

Chart.1 Physico-chemical assessment of the distillates produced from Pearl of csaba (2010-2011) and Muschat Hamburg (2010-2011)



The Regulation Council (37.5–50% v/v) established that the alcoholic degree of distillates for human consume have to be (37.5–50% v/v) so we can evaluate that our distillates with the alcoholic degree 47.5 ± 0.71 for Muschat Hamburg distillate and $47. \pm 0$ for the Pearl distillate is iswith in the margine. The acetaldehyde is formed during spontaneous or microbial mediated oxidation during the alcoholic fermentation of raw material, according to European regulations (No.1576/89)8 the acetaldehyde concentration must be lower than 73 g/hl a.a to 500 g/hl a.a. The two distillates that we have study have a lower content of this component because of fermentation technique and the cultivars so for Pearl distillate it is 11.9 ± 2.69 g/hl a.a and for Muschat Hamburg 14.5 ± 0.71 g/hl a.a. The toxicity of the alcoholic distillate is given by the methanol content so in this study for Pearl distillate the methanol content is 130 ± 0 g/hl a.a and for Muschat Hamburg is 131 ± 1.4 g/hl a.a these levels of methanol are really very lower infront of the standart normative 950 g/hl a.a. The higher alcohol content in the Pearl distillate is 288.5 ± 12.03 g/hl a.a and this higher than these components at Muschat Hamburg distillate 225 ± 4.24 g/hl a.a.

Chart.2 Physico-chemical assessment at each distillate produced from Pearl of csaba (a) and Muschat Hamburg (b)



International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

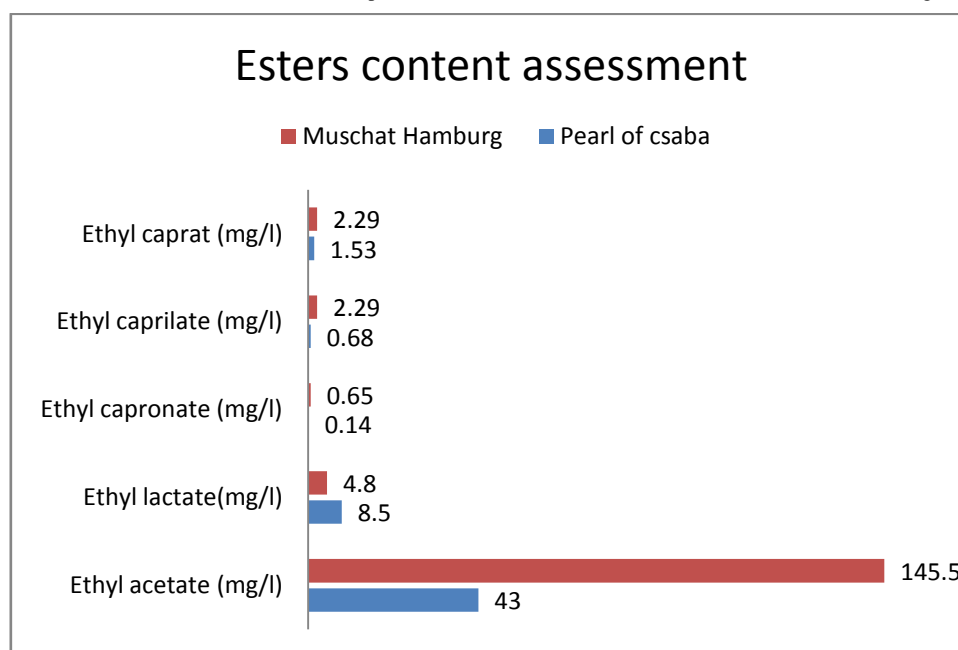
Vol. 4, Issue 11, November 2015

As we can see from chart 2 the physico-chemical assessment at each distillate produced from Pearl of csaba (a) and Muschat Hamburg (b) in two years does not have any significant change.

Table 2. Esters content at the distillates produced from Pearl of csaba (2010-2011) and Muschat Hamburg (2010-2011).

	Esters	Pearl of csaba (2010-2011)	Muschat Hamburg (2010-2011)
1	Ethyl acetate (mg/l)	43±1.42	145.5±0.71
2	Ethyl lactate(mg/l)	8.5±0	4.8± 0.28
3	Ethyl capronate (mg/l)	0.14±0	0.65±0.07
4	Ethyl caprilate (mg/l)	0.68±0.11	2.29±0.014
5	Ethyl caprat (mg/l)	1.53±0.04	2.29±0

Chart. 3. Esters content assessment of the distillates produced from Pearl of csaba (2010-2011) and Muschat Hamburg (2010-2011)



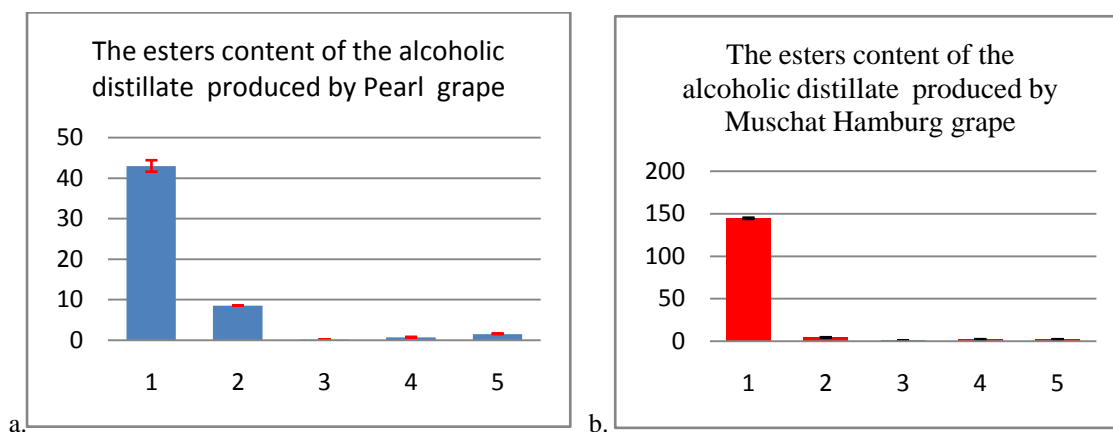
As we can clearly see from the results the main component that dominate the ester group is ethyl acetate. In Pearl distillate this component is really lower in content in front of the other distillate taken in study. The ethyl acetate itself gives some fresh aromas to the distillate, for Pearl distillate it is 43±1.42 g/hl a.a and for Muschat Hamburg 145.5±0.71g/hl a.a, the standarte normative of this component is 250 g/hl a.a. By itself ethyl acetate expresses the aromas of nail polish whether it would be over or the rate fixed by the European normatives at our distillates this puncher aroma will adversely affect on the aromatic quality of the alcoholic distillate, occurring in the levels shown in the graph, this element affects the fragrance of distillate having impact on his freshness also this allows the terpenoles to be identified better with their fragrances during organoleptic evaluation.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 11, November 2015

Chart.4. Esters content assessment at each distillate produced from Pearl of csaba (a) and Muschat Hamburg (b)

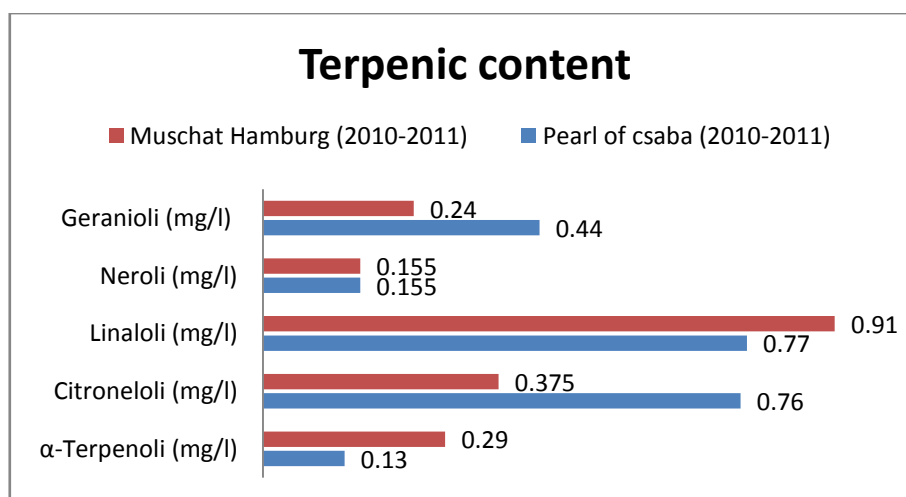


As we can see from chart 4 the esters content assessment at each distillate produced from Pearl of csaba (a) and Muschat Hamburg (b) in two years does not have any significant change, only ethyl acetate component shows the most difference between the two years.

Table 3. Terpenic content at the distillates produced from Pearl of csaba (2010-2011) and Muschat Hamburg (2010-2011).

Nr	Terpenic content	Pearl of csaba (2010-2011)	Muschat Hamburg (2010-2011)
1	α -Terpenoli (mg/l)	0.13 \pm 0	0.29 \pm 0.014
2	Citroneloli (mg/l)	0.76 \pm 0.036	0.375 \pm 0.04
3	Linaloli (mg/l)	0.77 \pm 0.014	0.91 \pm 0.014
4	Neroli (mg/l)	0.155 \pm 0.01	0.155 \pm 0.01
5	Geranioli (mg/l)	0.44 \pm 0.014	0.24 \pm 0.014

Chart. 5. Terpenic content assessment of the distillates produced from Pearl of csaba (2010-2011) and Muschat Hamburg (2010-2011)



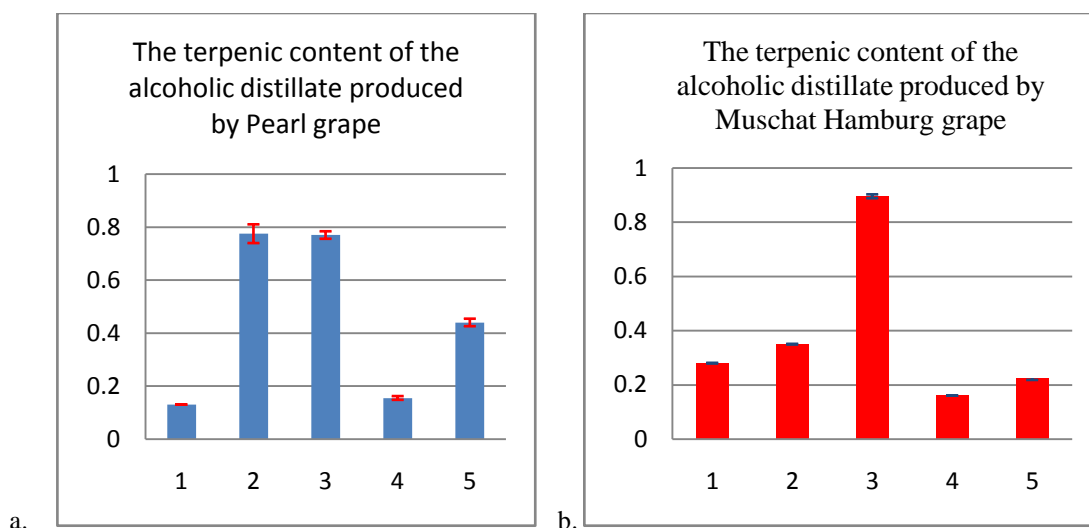
International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 11, November 2015

To evaluate the content of the terpenic compounds we have assessed the four main compounds that are characteristic of all aromatic grape cultivars: α -Terpenoli, Citroneloli, Linaloli, Neroli, Geranioli. According to the terpenic content we can say that the two cultivars are aromatic and the presence of the main aromatic compounds for Pearl of csaba such as Citroneloll 0.76 ± 0.036 (mg/l) is higher than Citroneloll 0.375 ± 0.04 (mg/l) of Muschat Hamburg, also Geraniol 0.44 ± 0.014 (mg/l) is higher than Geraniol 0.24 ± 0.014 (mg/l) of Muschat Hamburg. Linaloll for Pearl 0.77 ± 0.014 (mg/l) is lower than Linaloll 0.91 ± 0.014 (mg/l) of Muschat Hamburg. But the Nerol 0.155 ± 0.01 (mg/l) is the same amount for both of the distillates in the study.

Chart.6. Terpenic content assessment at each distillate produced from Pearl of csaba (a) and Muschat Hamburg (b)



As we can see from chart 6, the terpenic content assessment at each distillate produced from Pearl of csaba (a) and Muschat Hamburg (b) in two years does not have any significant change. At Pearl distillate only citronelol and geraniol component shows the most difference between the two years, whereas to the distillate produced from Muscat cultivar does not appear any visible change between two years of production.

IV. CONCLUSIONS

The distillates produced in Albania from the two aromatic grape varieties Pearl of csaba and Muschat Hamburg appear to be in high quality and the identifying compounds of the quality show that they were within the limits imposed by the European standard. They have low content in methanol, higher alcohols and ethyl acetate, but they have high levels of terpenic content. As we can see by the results the distillates produced from the two cultivars have the same amount of nerol, Pearl contains less linaloll than Muschat Hamburg, but more Geraniol and citroneloll. These compounds give the flower aroma to the Peal distillate that is more expressed than the aroma flower of Muschat Hamburg.

REFERENCES

1. Versini, G., Dalla Serra, A., Falcetti, M., Sferlazzo, G.: "Role of clone, vintage year and period of harvesting on the aromatic potential of the Chardonnay grape". *Vitis*, Vol. 32., No 2, abstract p. 58, 1993.
2. Fitzgerald, G., James, K. J., MacNamara, K. and Stack, M. A., "Characterization of whiskeys using solid-phase microextraction with gas chromatography-mass spectrometry". *Journal of Chromatography A*, Vol. 896, p.p. 351-359, 2000.
3. MacNamara, K., Leardi, R. and Sabuneti, A., "Fast GC analysis of major volatile compounds in distilled alcoholic beverages. Optimization of injection and chromatographic conditions", *Analytica Chimica Acta*, Vol. 542, p.p. 260-267. 2005.
4. Wardencki, W., Sowinski, P. and Curylo, J.: "Evaluation of headspace solid-phase microextraction for the analysis of volatile carbonyl compounds in spirits and alcoholic beverages". *Journal of Chromatography A*, Vol. 984, p.p. 89-96. 2003.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 11, November 2015

5. Silva, M. L. and Malcata, F. X., "Relationships between storage conditions of grape pomace and volatile composition of spirits obtained therefrom". *American Journal of Enology and Viticulture*, Vol.49(1), p.p. 56–64. 1998.
6. Cole, V. C. and Noble, A. C., "Flavor chemistry and assessment. In: Fermented Beverage Production" A. G. H. Lea and J. R. Piggot, Eds. Blackie Academic and Professional: London, p.p. 361–385. 1997.
7. Silva, M. L. and Malcata, F. X., "Effects of time of grape pomace fermentation and distillation cuts on the chemical composition of grape marcs". *Zeitschrift für Lebensmittel-Untersuchung und Forschung A*, Vol. 208, p.p. 134–143, 1999.
8. Ferreira, V., Hernandez-Orte, P., Escudero, A., Lopez, R. and Cacho, J., "Semipreparative reversed-phase liquid chromatographic fractionation of aroma extracts from wine and other alcoholic beverages". *Journal of Chromatography A*, Vol. 864, 77–88. 1999.
9. Soufleros, E. and Bertrand, A., Study on "Tsipouro", "Traditional spirit made from grape pomace, precursor of ouzo". *Vigne et du Vin*, Vol. 21(2), p.p. 93–111. 1987.
10. Fidan, I. and Anli, R. E., Yüksek Alkollü İçkiler (Distilled Beverages, in Turkish). In: Kavaklıdere Kultur Yayınları, Vol. 6, p.p. 206 p, 2000.
11. Mateo, J., Aguirrezabal, M., Dominguez, C. and Zumalacarregui, J. M., "Volatile compounds in Spanish paprika". *Journal of Food Composition and Analysis*, Vol. 10, p.p. 225–232, 1997.
12. Soufleros, E. H., Mygdalia, S. A. and Natskouli, P., "Production process and characterization of the traditional Greek fruit distillate "Koumaro" by aromatic and mineral composition". *Journal of Food Composition and Analysis*, Vol.18, p.p. 699–716, 2005.
13. Silva, M. L., Malcata, F. X. and De Revel, G., "Volatile contents of grape marcs in Portugal". *Journal of Food Composition and Analysis*, Vol.9, p.p. 72–80, 1996.