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Gas-Chromatographic Analysis of Major Volatile Compounds Found in Traditional Fruit Brandies from Transylvania, Romania

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Abstract

In the current study, the major volatile compounds from three categories of traditional fruit brandies (plum, apple and pear) were characterized by gas-chromatography (GC-FID). There were collected 26 samples from different locations of Transylvania (Romania), all made by traditional technologies involving fermentation in barrels and distillation in copper stills. The major volatile compounds, besides ethanol, identified and quantified were: acetaldehyde, ethyl acetate, methanol, 1-propanol, 2-butanol, *iso*-butylic alcohol, alcool amyl active, *iso*-amylic alcohol, 1-butanol and furfural. For each type of brandy, positive but no significant correlations between methanol and furfural concentrations in plum and apple brandy were noticed. To evaluate the differences in composition regarding the geographical origin of plum brandies and to analyze the composition of plum, apple and pear brandies it has been compared the mean values (MVP, MVA and MVPe) obtained for each volatile. For plum brandies it has been observed differences among the mean values of each volatile, in samples originating from counties Cluj, Bistriţa-Năsăud and Maramureş. For methanol, acetaldehyde and 1-propanol the MVP Cluj values were significantly higher than MVP Bistriţa-Năsăud. For *iso*-butylic alcohol, amyl active alcohol, *iso*-amylic alcohol the MVP Cluj values were significantly higher than for Bistriţa-Năsăud and Maramureş, while for ethyl acetate and furfural the MVP Bistriţa-Năsăud were significantly higher than MVP Cluj and MVP Maramureş. When compared the mean values of volatiles in plum *vs* apple *vs* pear brandies, for ethyl acetate, methanol, 2-butanol, 1-propanol and 1-butanol, the MVPe values were significantly higher than MVA, for furfural, amyl active and *iso*-amylic alcohols, while for acetaldehyde the MVPe values were significantly higher than MVP. Methanol represented the major volatile component, characteristic to fruit brandies, released by enzymatic degradation of methoxylated pectins. Therefore, this molecule can be considered not only a parameter of distillate safety but also an indicator of natural origin of distillate and traditional processing.

Keywords: ANOVA, correlation coefficient, direct injection, Duncan, GC-FID

Introduction

Romania has an old and rich tradition in fruit growing and traditional distilled beverages, their assortment being enlarged significantly in the last decades. The traditional method used to obtain fruit brandies is the distillation of fruit pulp in copper stills with open fire, maturing and conditioning in oak barrels (Pomohaci, 2002).

The most important Romanian traditional fruit distillate is plum brandy known as "ţuica" (denominated by Romanian legislation), obtained exclusively from plums and "pălinca", a brandy obtained from a mixture of fruits.

The fruit fermentation is made in wood barrels or in stainless steel recipients. Distillation is made in copper stills under open fire or in distillation installation. Usually distillation is repeated twice, the final alcoholic concentration of these products is between 24 to 86% v/v, for "ţuica" and 40-70% v/v, for "pălinca". In Romania, there are different types of fruit brandies and according to the region, it can be find different alcoholic concentrations of these drinks. For example, in the south of the country "ţuica" has values around 30% v/v (single distillation), but in Transylvania region, its values are around 50% v/v (in most cases obtained by double distillation process).

No matter the production process applied, the flavor and taste of these traditional beverages may be an indicator of the fruit or fruits used as raw materials.

The storage and the maturing are achieved in wood barrels, stainless steel or glass recipients for at least three months. The yellow or gold-yellow color of these traditional distillates can be obtained exclusively by maturing in wood barrels (the most used being the oak barrels), without any colorants or pure alcohol of industrial origin adding.

The preparation and fermentation of raw material, distillation technology and maturation are main factors responsible for the specific bouquet of fruit brandies.

Some of volatiles found in fruit distillates, such as methanol, furfural, *iso*-butylic alcohol and acetaldehyde have toxic potential. This is the reason why the European Commission established a maximum admissible value for methanol in fruit brandies being 1200 mg/100 ml anhydrous alcohol (anh. alc.). In the case of ethyl alcohol of agricultural origin, the limits of these toxic compounds are more restrictive (acetaldehyde-maximum 0.5 mg/100 ml anh. alc.; methanol-30 mg/100 ml anh. alc.; furfural-not detectable) (REG.110/2008).

Beside ethanol, from all major volatile substances, methanol has the highest amount in fruit distillates. In most cases, it is ingested by the consumers in low doses when consuming alcoholic beverages.

Methanol is found in high amounts in raw distillate (resulted after the first distillation) as well in the final brandy. This happen because the methanol concentration is directly related to the quantity of pectins present in fruits (peels, seeds) which are methoxylated during fruit ripening. By the effect of pectases, the demethylation can occur and methanol is released together with pectic acid and pectol.

After re-distillation, methanol is concentrated in overhead, and then it can be reduced and the final distillate to contain concentration in accordance with the maximum admissible levels. It is formed when pectic substances hydrolyse under the influence of some pectolytic enzymes (especially, pectin methyl esterase). The distillates produced from different fermented fruits have generally higher amount of methanol in comparison with those obtained by other techniques (ethyl alcohol from cereal processing), due to the degradation of methoxylated pectins found in fruit flesh. This is the reason why methanol is present in fruit distillates and may indicate the origin of raw material (Moales *et al.*, 2010) or the authenticity of a natural fruit brandy vs a brandy containing fruit synthetic essence and refined ethanol (Nikićević and Tešević, 2005).

Furfural, derived from fruit carbohydrates, contribute to the aroma and flavor of fruit distillates. By ingestion, furfural may be toxic to human organism, inducing pain, sore throat, diarrhea, vomiting and headache. Furfural can have harmful effects by inhibition of enzymatic substrates in fermentation process (Modig *et al*., 2002).

The classical distillation method (which integrates the copper still) with direct heating can create harmful effects such as mashes with a burnt-bitter taste caused by furfural formation. This effect is hardly removable (Berglund, 2004). The caramel color can be also an explanation of furfural presence (Quesada Granados *et al.*,1996).

Acetaldehyde is a result of ethanol dehydrogenation and can occur during fermentation, as a minor volatile. It has toxic effects when ingested, causing diarrhea, dizziness, nausea and vomiting.

Significant data were reported the last years, regarding the volatiles in traditional brandies from Central and East, South-East European countries (Tab. 1).

Slivovice, another name of a traditional plum brandy, togheter with other distilled beverages were characterized and classified by total luminescence and synchronous fluorescence spectroscopy (Tóthová *et al.*, 2008).

Few data about the quality of Romanian fruit distilates are reported. Recently, the chemical analysis of distillated beverages has been made by Beceanu and Nicula (2009); Beceanu *et al.* (2010) for some traditional and commercial distilled alcoholic beverages made in Romania.

In this study, the aim was to fingerprint and quantify the specific volatile compounds found in three categories of home-made fruit brandies. The brandies were made by the distillation of different fermented fruits of plum, apple and pear.

Tab. 1. The reported volatiles identified in different types of distillates and the applied techniques

Type of distillate	The volatile compound determinated	Techniques of analysis	References
Traditional fruit distillates	Methanol	GC-MS	Moales *et al.* (2010)
Plum brandy	Methanol	GC-FID	Nikićević and Tešević (2005)
Commercial brandies and wine spirits	Furfural	HPLC	Quesada Granados *et al.* (1996)
Slivovitz (plum brandy)	1-propanol, 2-propanol, ethyl acetate, 2-methyl-1-propanol etc.	GC-MS and SPME-GC-MS	Korhonova *et al.* (2006)
Apple brandy	Aroma fraction (furfural, ethyl acetate etc.)	HRGC-FID and HRGC-MS	Versini *et al.* (2009)
Whey spirit	Major volatile compounds (acetaldehyde, ethyl acetate, *iso*-amyl alcohol, 1-propanol, 2-butanol, furfural, 1-butanol, etc.)	GC-FID	Dragone *et al.* (2009)
Hellenic alcoholic beverages from white grapes	Major volatile compounds (methanol, acetaldehyde, 2-butanol, 1-propanol, 1-butanol, ethyl acetate, etc.)	gas/liquid chromatography	Christopoulou-Gerogiannaki *et al.* (2007)
Brandy de Jerez	Aromatic profile (furfural, 1-propanol, *iso*-butanol, 1-butanol, etc.)	GC-MS	Martínez Montero (2006)
Plum brandy	Methanol, higher alcohols, esters, ethyl acetate, benzaldehyde	GC	Popović *et al.* (2009)
Plum brandy	Methanol, ethanol, higher alcohols	GC-MS and GC-FID	Tešević *et al.* (2005)
Drenja (alcoholic beverage made from cornelian cherry)	Specific aroma compounds (alcohols, esters, monoterpene, lactones, volatile phenols, acetal compounds)	GC-MS	Tešević *et al.* (2009)
Turkish Raki beverage	Methanol, acetaldehyde, ethyl acetate, 1-propanol, 2-butanol, 1-pentanol, ethyl lactate, etc.	GC-MS	Ertan Anli *et al.* (2007)

Materials and methods

Provenience of beverage samples

The samples were collected, directly from the producer; 26 samples of homemade fruit distillates (plum brandy, apple brandy and pear brandy) processed between 2008, October and 2010, September, originating from different counties of Transylvania (Romania) such as: Maramureş, Cluj, Bistriţa-Năsăud, Alba, Bihor (Tab. 2).

Alcohol concentration and the relative density

The determination of the alcoholic concentration and relative density were made 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 density was displayed with 5 decimals and alcoholic concentration with 2 decimals.

Volatile compounds analysis

Analysis of major volatile compounds in fruit brandies was adapted after the EU reference method for volatile compounds. For the determination of the major volatile compounds, the samples were injected directly into the gas chromatograph column, from a GC-FID Agilent Tehnologies Gas chromatograph, 6850A, without preliminary treatment.

Each sample was injected twice in the GC-FID. One microliter from each sample was introduced on 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°C. The injector temperature was 240°C-automatic injection; the carrier gas was helium and the detector (FID) temperature was 250°C (Tab. 3). The total time analysis was 30.63 min.

The main components (methanol, acetaldehyde, ethyl acetate, 1-propanol, 2-butanol, *iso*-butilic alcohol, amyl active alcohol, *iso*-amylic alcohol, 1-butanol), were identified by comparing their retention times with those of authentic compounds.

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, *iso*-butylic alcohol, *iso*-amylic alcohol, amyl active alcohol, ethyl acetate, 3-pentanol) with purity over 99% were provided by Merck and Sigma Aldrich Company.

Tab. 2. The location, type and codification of the beverage samples

Code	Type of fruit distillate	Producer localization		Production year
		Couty	Village	
P1	Plum brandy	Cluj	Tioltiur	2009
P2	Plum brandy	Cluj	Petreşti	2009
P4	Plum brandy	Cluj	Ciucea	2009
P6	Plum brandy	Cluj	Morlaca	2009
P17	Plum brandy	Cluj	Bârlea	2007
P18	Plum brandy	Cluj	Negreni	2009
P3	Plum brandy	Bistriţa-Năsăud	Beclean	2009
P12	Plum brandy	Bistriţa-Năsăud	Năsăud	2009
P13	Plum brandy	Bistriţa-Năsăud	Rebrişoara	2009
P14	Plum brandy	Bistriţa-Năsăud	Salva	2009
P15	Plum brandy	Bistriţa-Năsăud	Runc	2009
P16	Plum brandy	Bistriţa-Năsăud	Feldru	2010
P5	Plum brandy	Maramureş	Seini	2008
P7	Plum brandy	Maramureş	Săliştea de Sus	2009
P8	Plum brandy	Maramureş	Vişeu de Jos	2009
P9	Plum brandy	Maramureş	Vişeu de Sus	2009
P10	Plum brandy	Maramureş	Moisei	2009
P11	Plum brandy	Maramureş	Leordina	2009
M19	Apple brandy	Bistriţa-Năsăud	Coşbuc	2010
M20	Apple brandy	Alba	Ocoliş	2008
M21	Apple brandy	Cluj	Câţcău	2009
M22	Apple brandy	Bihor	Tulca	2008
PE23	Pear brandy	Cluj	Negreni	2009
PE24	Pear brandy	Maramureş	Şişeşti	2006
PE25	Pear brandy	Bistriţa-Năsăud	Runc2	2009
PE26	Pear brandy	Cluj	Aiton	2008

Tab. 3. The temperature program used for the GC-FID analysis of all types of fruit brandies

Steps	Rate	Final temperature	Final time
1	12°C/min	35-58°C	4 min
2	3°C/min	58-85°C	0 min
3	30°C/min	155°C	3 min
4	200°C/min	230°C	5 min

Statistical analysis

The results obtained from the individual experiments were used to calculate the mean values for plum, apple and pear brandy samples. Analysis of variance (ANOVA) and Duncan's multiple range tests were performed to analyse the results. Significance of differences was defined at the 5% threshold ($P<0.05$). All statistical analysis was carried out using Graph Pad Version 4.0 (Graph Pad Software Inc; San Diego, CA, USA).

Results and discussion

Ethanol concentration based on relative density determination

The values obtained for the alcoholic concentration based on relative density measurement were represented in Tab. 4 . All ethanol concentrations were calculated from relative density by specific formulas (not shown).

The mean value of ethanol concentration in plum brandies was 51.21%, while 50.24% for apple brandy. In pear brandy the mean value was 45.05%, significantly inferior (P<0.05).

GC-FID analysis

The GC-FID chromatograms of two representative samples (P7 and M20) are presented in Fig. 1 A and B. The major peak corresponding to ethanol (t_R =8.11 min) was eliminated, in order to illustrate the other components better.

The main volatile compounds were identified 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

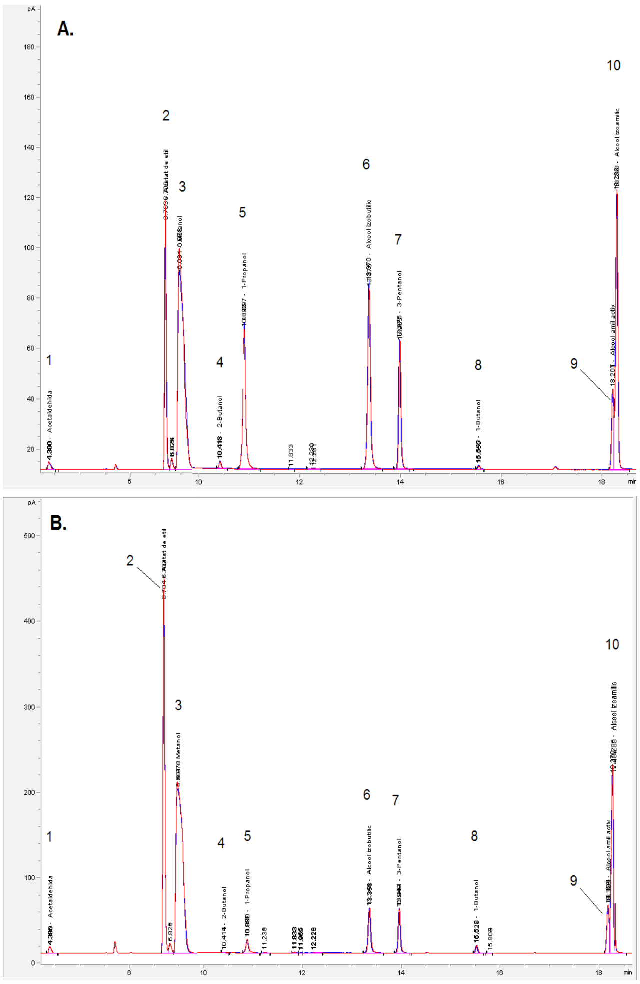

Fig. 1. The GC-FID chromatogram of major volatile compounds in sample P7 (A) and sample M20 (B) . Peak identification: 1=Acetaldehyde; 2=Ethyl acetate; 3=Methanol; 4=2-Butanol; 5=1-Propanol; 6=*Iso*-butylic Alcohol; 7=3-Pentanol (IS); 8=1-Butanol; 9=Amyl Active Alcohol; 10=*Iso*-amylic Alcohol

and mean values for each volatile found in plum (MVP), apple (MVA) and pear (MVPe) brandies are presented in Tab. 4-7.

For plum brandies (Tab. 5) it has been observed differences among the mean values (MVP) of each volatile, in plum brandies originating from 3 counties, Cluj, Bistrița-Năsăud and Maramureş, For acetaldehyde and 1-propanol the MVP Cluj values were significantly higher than MVP Bistrița-Năsăud. Also, methanol MVP from Cluj were significantly higher (P<0.05) than MVP Maramureş and Bistrița-Năsăud. As an explanation for the presence of acetaldehyde can be the fact that aldehydes, especially acetaldehyde or ketones, are produced during in marc fermentation (Geroyiannaki *et al.*, 2007; Garcia Llobodanin, 2008), their concentration level being higher if the copper still was not utilized properly or because of their higher

Tab. 4. Ethanol concentration, determined from relative density

Sample code	Alcoholic concentration (% v/v)	Relative density (g/cm^3)
P1	48.37	0.93330
P2	50.5	0.92916
P3	48.31	0.93342
P4	48.03	0.93395
P5	52.32	0.92551
P6	49.76	0.93061
P7	49.34	0.93142
P8	53.03	0.92406
P9	49.24	0.93162
P10	54.56	0.92089
P11	51.95	0.92626
P12	52.5	0.92514
P13	57.29	0.91506
P14	55.45	0.91902
P15	45.77	0.93815
P16	54.22	0.9216
P17	50.8	0.92859
P18	50.29	0.92956
MV	51.21a	0.93
SD	2.96	0.01
M19	50.19	0.92976
M20	52.76	0.92461
M21	47.94	0.93411
M22	50.06	0.93003
MV	50.24a	0.93
SD	1.97	0.00
PE23	48.16	0.9337
PE24	44.89	0.93974
PE25	47.02	0.93585
PE26	40.12	0.94784
MV	45.05b	0.94
SD	3.55	0.01

MV-mean value; SD-standard deviation. The values with different superscript letters (a, b, c) are significantly different (P<0.05)

Tab. 5. The major volatile compounds found in plum brandy as determined by gas-chromatography (GC-FID)

Sample code	Volatile compound (mg/100 ml anhydrous alcohol)									
	Acetaldehyde	Ethyl Acetate	Methanol	Furfural	2-Butanol	1-Propanol	*Iso*-butylic Alcohol	1-Butanol	Amyl Active Alcohol	*Iso*-amylic Alcohol
P1	13.70	223.26	1077.59	1.92	7.53	32.41	97.34	17.07	53.29	239.24
P2	12.99	691.67	1266.97	1.41	18.31	95.10	36.41	19.47	17.94	82.13
P4	5.25	125.55	954.31	1.56	0.66	72.29	128.81	1.95	54.65	219.96
P6	14.66	226.51	1244.35	2.28	8.65	175.09	49.30	11.59	20.71	73.22
P17	31.45	307.00	1100.76	3.58	0.17	132.81	42.24	6.78	22.73	93.62
P18	12.62	131.05	953.69	6.38	9.98	61.54	102.84	7.50	42.52	157.96
MVP Cluj	15.11a	284.17b	1099.61a	2.86b	7.55b	94.87a	76.16a	10.73b	35.31a	144.36a
SD	8.68	210.82	135.54	1.89	6.71	51.76	38.43	6.64	16.87	72.68
P3	20.93	298.55	964.96	6.93	0.09	141.55	69.41	4.04	34.48	119.87
P12	9.95	207.43	901.39	2.49	0.17	30.20	24.70	2.26	15.60	51.33
P13	17.01	353.84	1073.70	3.34	4.31	90.51	31.00	35.42	18.09	53.38
P14	6.44	293.03	913.01	3.17	10.55	37.28	45.82	17.55	41.44	127.67
P15	14.86	567.81	765.86	1.06	13.71	25.28	39.50	9.21	28.91	100.88
P16	12.42	128.21	953.73	2.06	0.64	150.97	40.13	9.17	24.16	87.19
MVP Bistrița-Năsăud	13.60b	308.14a	928.77b	3.18a	4.91c	79.30b	41.76c	12.94a	27.11c	90.05c
SD	5.16	149.90	100.47	2.01	5.89	56.98	15.46	12.23	9.85	32.48
P5	10.33	318.05	857.71	2.89	10.65	101.85	23.63	4.53	9.27	37.19
P7	8.39	115.60	504.18	2.06	3.16	87.46	96.66	1.69	31.47	111.96
P8	8.53	110.95	999.81	3.06	3.38	90.54	38.59	12.46	19.72	81.78
P9	24.11	255.02	1256.41	10.48	0.19	134.72	120.06	2.27	46.30	129.45
P10	21.15	414.58	450.50	0.00	50.32	31.68	71.71	20.43	47.08	184.61
P11	15.95	367.09	954.12	1.02	7.42	119.80	36.85	15.31	19.76	77.53
MVP Maramureş	14.74a	263.55b	837.12c	3.25a	12.52a	94.34a	64.58b	9.45c	28.93b	103.75b
SD	6.76	127.87	308.78	3.73	18.87	35.56	38.15	7.75	15.45	50.73
MVP	14.49c	285.29b	955.17b	3.09b	8.33b	89.50b	60.83a	11.04b	30.45b	112.72b
SD	6.62	157.61	221.23	2.52	11.78	46.58	33.90	8.76	13.98	56.42

MV-mean value; SD-standard deviation. The values with different superscript letters (a, b, c) are significantly different (P<0.05)

concentrations in plums. The plum brandy is well flavored due to a mixture of acetaldehyde, ethyl acetate and amyl alcohols, mainly responsible for the flavor and its quality depends significantly on their concentration (Apostolopoulou *et al.*, 2005).

For *iso*-butylic alcohol, amyl active alcohol, *iso*-amylic alcohol the MVP Cluj values were significantly higher than MVP Bistrița-Năsăud and Maramureş, while for ethyl acetate and furfural, the MVP Bistrița-Năsăud were significantly higher than MVP Cluj and MVP Maramureş.

All the present data are in agreement with the recent literature reports (Tab. 9).

To evaluate the differences between the mean values of volatiles in different types of brandies it has been considered the statistical differences between plum-MVP (Tab. 5), apple-MVA (Tab. 6) and pear-MVPe (Tab. 7). For ethyl

Tab. 6. The major volatile compounds found in apple brandy as determined by gas-chromatography (GC-FID)

Sample code	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
M19	13.25	231.84	597.64	1.97	0.37	21.89	44.33	14.91	39.61	146.84
M20	18.63	473.50	1189.29	3.06	0.39	21.42	56.68	8.26	50.56	196.59
M21	14.98	215.68	1020.89	6.87	4.39	24.87	43.07	4.99	44.12	166.43
M22	12.88	63.15	810.97	2.74	0.31	136.18	43.33	4.37	20.15	75.28
MVA	14.93^{b}	246.04^{c}	904.70^{c}	3.66^{a}	1.36^{c}	51.09^{c}	46.86^{c}	8.13^{c}	38.61^{a}	146.29^{a}
SD	2.63	169.62	256.62	2.19	2.01	56.75	6.57	4.83	13.10	51.57

MV-mean value; SD-standard deviation. The values with different superscript letters (a, b, c) are significantly different (P<0.05)

Tab. 7. Major volatile compounds found in pear brandy as determined by gas-chromatography (GC-FID)

Sample code	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
PE23	26.09	203.52	973.61	4.69	44.80	34.66	63.79	9.51	29.67	117.59
PE24	15.83	388.87	818.34	1.51	104.70	212.20	52.51	8.53	20.23	71.05
PE25	27.71	136.32	880.69	2.56	19.58	59.01	59.93	17.16	41.31	145.48
PE26	10.04	521.75	1290.06	1.96	75.29	161.72	36.28	12.59	19.16	94.87
MVPe	19.92[a]	312.62[a]	990.68[a]	2.68[c]	61.09[a]	116.90[a]	53.13[b]	11.95[a]	27.59[c]	107.25[c]
SD	8.43	175.63	209.54	1.41	36.93	84.07	12.17	3.88	10.29	31.79

MV-mean value; SD-standard deviation. The values with different superscript letters (a, b, c) are significantly different ($P<0.05$)

acetate, methanol, 2-butanol, 1-propanol and 1-butanol the MVPe values were significantly higher than MVA. For furfural, amyl active alcohol and *iso*-amylic alcohol the MVA values were significantly higher than MVPe. For acetaldehyde the MVPe values significantly higher than MVP. Also, in this case, the present data are in agreement with the reported data (Tab. 9).

Tab. 8. The values of the coefficients of correlation between the mean concentrations of methanol-furfural and methanol-ethanol in the plum, apple and pear brandies

Sample	*r* values (methanol-furfural)	*r* values (methanol-ethanol)
Plum brandy	+0.296	-0.057
Apple brandy	+0.280	+0.335
Pear brandy	-0.049	-0.785

Correlations between methanol, furfural and ethanol concentration

Based on the mean values of methanol, furfural and ethanol concentrations, there were calculated the correlation coefficients (Pearson's correlation coefficient), for each type of brandy, considering the relations between methanol release, ethanol and furfural as markers of carbohydrate fermentation and thermal degradation (Tab. 8).

Positive, but no significant correlations between methanol and furfural concentrations in plum brandy and apple brandy, while slight negative correlations (non significant as well) for methanol versus ethanol in pear and plum brandies were registrated. For apple brandy, a positive correlation was noticed between methanol and ethanol, which can be related to higher concentration of methoxylated apple pectins and their degradation to methanol.

Tab. 9. A comparison between the mean values obtained in this study and other reported researches

Major volatile compound	Type of fruit distillate	Mean values obtained in the present study	Values obtained in other reported study
		mg/100 ml anh. alc.	
Acetaldehyde	Plum brandy	14.49±6.62	2.6-38.5 (Winterová *et al.*, 2008); 12.4-24.6 (Satora and Tuszyński, 2010)
	Apple brandy	14.93±2.63	3.0-26.0 (Winterová *et al.*, 2008)
	Pear brandy	19.92±8.43	1.3-56.2 (Winterová *et al.*, 2008)
Ethyl Acetate	Plum brandy	285.29 ±157.61	56.3-235.9 (Winterová *et al.*, 2008); 27.7-192.5 (Satora and Tuszyński, 2010)
	Apple brandy	246.04 ±169.62	12.5-233.4 (Winterová *et al.*, 2008); 17-128 (Versini et al., 2009)
	Pear brandy	312.62 ±175.63	7.6-293.7 (Winterová *et al.*, 2008)
Methanol	Plum brandy	955.17±221.23	287.7-1141.4 (Winterová *et al.*, 2008); 755-974.4 (Satora and Tuszyński, 2010)
	Apple brandy	904.70±256.62	179.4-916.8 (Winterová *et al.*, 2008); 540-1140 (Versini *et al.*, 2009)
	Pear brandy	990.68±209.54	93.2-1080.9 (Winterová *et al.*, 2008)
Furfural	Plum brandy	3.09±2.52	
	Apple brandy	3.66±2.19	0.23-6.23 (Versini *et al.*, 2009)
	Pear brandy	2.68±1.41	
1-Propanol	Plum brandy	89.50±46.58	35.6-308.4 (Winterová *et al.*,2008)
	Apple brandy	51.09±56.75	12.1-229.0 (Winterová *et al.*, 2008); 15.0-73 (Versini *et al.*, 2009)
	Pear brandy	116.90±84.07	14.1-706.8 (Winterová *et al.*, 2008)
1-Butanol	Plum brandy	11.04±8.76	2.1-12.6 (Winterová *et al.*, 2008)
	Apple brandy	8.13±4.83	8.0-20.5 (Winterová *et al.*, 2008), 6.3-116 (Versini *et al.*, 2009)
	Pear brandy	11.95±3.88	1.6-22.8 (Winterová *et al.*, 2008)
2-Butanol	Plum brandy	8.33±11.78	1.3-19.5 (Winterová *et al.*, 2008)
	Apple brandy	1.36±2.01	0.8–32.3 (Winterová *et al.*, 2008)
	Pear brandy	61.09±36.93	0.6-73.3 (Winterová *et al.*, 2008)

For acetaldehyde, ethyl acetate, methanol and all superior alcohols pear brandy samples registered significantly higher values than plum or apple; only furfural had the lowest value for pears, apple brandy being the richest in furfural (Tab. 5-7).

Methanol represents the most important volatile component, which, as described before was released during processing, and it is characteristic to fruit brandies, significantly higher than in cereal distillates, due to methoxylated pectin degradations. Therefore, this molecule can be considered not only a parameter of distillate safety but also may indicate, indirectly, the natural origin and the fermentation technology used in traditional processing.

Anyway, in all 26 samples of fruit brandies the values of methanol concentrations were below the maximum admissible values (1200 mg/100 ml anh.alc) established by European Commission.

Conclusions

Using GC-FID analysis three different types of brandies (apple, pear and plum) originating from Transylvania region, Romania, were compared. The volatiles identified and quantified using GC-FID analysis were: acetaldehyde, ethyl acetate, methanol, 2-butanol, 1-propanol, *iso*-butilic alcohol, 3-pentanol (internal standard), 1-butanol, amyl active alcohol, *iso*-amylic alcohol and furfural. Their average values were in concordance with other reported data from other European countries (Czech Republic, Slovenia, Serbia, Italy, Greece, and Turkey). Acetaldehyde, ethyl acetate and amyl alcohols are the main responsible for the flavor of distilled beverages, and the quality of these drinks depends on their concentration. Calculations were performed on the correlation coefficients for each type of brandy considering the relations between the methanol release, ethanol and furfural, as a marker of carbohydrate thermal degradation. Positive but no significant correlations between methanol and furfural concentrations in plum brandy and apple brandy were also noticed.

To evaluate the differences in composition regarding the geographical origin of plum brandies and to compare the composition of plum, apple and pear brandies, it has been compared the mean values (MVP, MVA and MVPe) obtained for each volatile.

For plum brandies, it has been observed differences among the mean values (MVP) of each volatile, in plum brandies originating from 3 counties, Cluj, Bistrița-Năsăud and Maramureş, Further investigations will be focused more on authenticity parameters for these three types of Romanian traditional brandies from Transylvania.

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