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STUDIES REGARDING THE QUALITY OF CERTAIN FRUIT DISTILLATES IN CORRELATION WITH THE ANALYTICAL DATA AND SENSORIAL ASSESSMENT

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ABSTRACT - Out of the 20 samples under analysis only 14 meet the requirements for the award of a distinct denomination whereas the other six may be called just spirits. The fact that some drinks of the second category do not mention on the label the denomination of spirit is a crime. Total acidity and the volatile acidity have concordant values giving the opportunity to identify the products maturated as well as the neutralization or bonification treatments. The pH values allow the classification of the distillates/distilled drinks by their degree of naturalness and the possible treatments effectuated.The polyphenol content may indicate the existence or inexistence of the wooden (oak) storage areas and the possible time of contact with these spaces or the reduction of influence due to the diverse treatments. The ester content indicates for 11 samples the cause that leads to their classification into a superior quality class. The values of the extract content may also explain, even more than the ester content, the favorable impression and the superior gustative quality for the 10 samples in their respective order. Except for two samples that showed quality defects, the rest of the distillates and distilled drinks registered positive or very positive sensorial qualities (especially Vinia maturated cherry distillate raw material and Vinia maturated plum distillate raw material)

Key words : Fruit distillates; Analytical data; Sensorial characterization.

REZUMAT - Studii privind calitatea unor distilate din fructe în corelaţie cu datele analitice şi aprecierea senzorială. Din cele 20 de probe analizate, doar 14 îndeplinesc condiţiile acordării unei denumiri distincte, în timp ce restul de şase pot fi denumite doar băuturi spirtoase. Faptul că unele din cea de a doua categorie nu menţionează pe etichetă denumirea de băutură spirtoasă, constituie o contravenţie. Aciditatea totală şi aciditatea volatilă au valori concordante, dând posibilitatea identificării produselor maturate sau învechite, precum şi a tratamentelor de neutralizare sau bonificare. Valorile pH permit încadrarea distilatelor / băuturilor distilate în funcţie de gradul de naturaleţe şi eventuale tratamente efectuate. Conţinutul în polifenoli este de natură să indice

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existența sau inexistența spațiilor de depozitare din lemn (stejar), precum și durata posibilă a contactului cu aceste spații sau diminuarea influenței datorată diverselor tratamente. Conținutul în esteri indică, pentru 11 probe, cauza care determină clasificarea acestora într-o categorie superioară de calitate. Valorile conținutului în extract pot și ele să explice, chiar mai mult decât conținutul în esteri, impresia favorabilă și calitatea gustativă superioară, la primele 10 probe, în ordinea respectivă.
Cu excepția a două probe, care au manifestat defecte de calitate, restul distilatelor și băuturilor distilate au prezentat calități senzoriale pozitive sau foarte pozitive (în special distilatul învechit de cireşe - Vinia materie primă și distilatul de prune învechit - Vinia materie primă).

Cuvinte cheie : distilate din fructe; date analitice; caracterizare senzorială.

INTRODUCTION

The denominations of the distilled drinks existing in Romania have a different origin connected to their place of origin and the spreading direction of their production.

The word **rachiu** is of oriental origin. It comes from an Arabian word (*arak – al – tamr*) signifying the sweat (perspiration) of dates, so it refers to the condensation water forming inside the containers where these fruits were stored for a long period of time. Fermentations may have occurred sometimes due to the moisture resulted from perspiration and the temperature in the area was quite high. Many times, this condensation water is alcoholic. The term *arak* was taken over from the Turkish language *araki/raki*, and through Greek (*raki*) it entered the Romanian language as **rachiu**.

The word **palincă** is of Slavic origin. *Paliti* means "to burn", so it is about something burnt, passed through the fire (etymological synonym with *brandy*). It may have come from the Slavic peoples from the west of Europe (Slovaks or Czechs). **Șlibovița (**slivovice) is a Slav term meaning "plum distillate" (*sliva = plum*) which is traditional for Serbians and Croatians.

The word **țuică** is the most difficult to explain. Authors gave very diverse and contradictory explanations, and the most sincere ones said it is of "unknown origin". Some said it is of Dacian origin which is obviously an inadvertence if we take into account the one millennium gap between the Dacians' civilization and the first information regarding the alcohol distillation (Beceanu, 2000; Pomohaci *et al.,* 2002)

Țuica is a plum distilled drink specific to the regions of hill and mountains from Wallachia and Oltenia. Initially, it was obtained by simple distillation at 25-30 vol% alcohol, but nowadays there are more and more cases when the denomination has been extended for distillates having a higher alcoholic concentration. In the rest of the country, people use double distillation and obtain brandies (Ardeal brandy) from different fruits at 40-50 vol% alcohol. (Beceanu , Niculaua, 2009)

The industrial production of distillates use more advanced technologies, sometimes to the

detriment of quality but with superior productivity and efficiency. The plants may be discontinuous (blaise in battery, Charante installations etc) or continuous (columns of different types). It is not our intention to detail the phases of a classical technology that has been practiced for decades. We will focus on some very useful trends of distillation for the juices extracted from fruits and fermented. The advantages are multiple: space economy, superior quality of distillates, elimination of undesirable compounds that may appear by fermentation and keeping the marcs and reduction of the distillation period.

At the moment of distillation, the authenticity and specific qualities also depend on the level of alcohol concentration. By rectification (redistillation), flavours, tastes and the primary value of a distillate obtained after a simple distillation are partially lost. Maturation may eliminate (sometimes completely) these qualities replacing them with other components depending on the maturation vessel and the length of this process. (Beceanu, Anghel, 2006).

For this reason, some distillates are used in their earlier stage in the preparation of the distilled drinks and for some species it is not recommended to store the distillates in wooden vessels for a long time since this may influence quality (e.g. cherries).

Maturation is more and more diminished economically since it blocks useful spaces for the new harvest or the new distilled assortments. These products have triggered numerous studies that are still in process. More and more frequently consumers may not tell an original maturated product from an imitation made from cheap raw materials and by rapid methods. The only criterion allowing for the identification of the authentic quality is the cost price.

According to Stănciulescu *et al.*, 1975, during the maturation period, the extract increases its volume. The titrating acidity increases to the detriment of the volatile acidity. There occur basic changes in the products kept in oak vessels through the extraction of certain components from the staves, followed by their evolution in relation with the oxygen and the primary components (including the volatile ones) of distillates. By evaporation in time, some components get concentrated.

There might be a correlation between the increase of total acidity and the improvement of the quality of maturated distillates attributed to the increased reactivity in contact with the wood and the facilitation of hydrolysis/esterification and other similar reactions. The non-volatile component of acidity gets completed and increases by the extraction of the uronic acids from oak, the tannins having an acid character etc. and the pH may decrease to values inferior to 4. Acids favor hydrolysis of hemicelluloses and the increase of distillates' content in the resulting

components with repercussions on taste and bouquet.

Esters positively influence the gustative harmony being in a direct relation with acidity and the existing extract. The higher the acidity, the more intense is the formation of esters.

In most cases, the effects of increasing or decreasing acidity and the tanning substances are due to the quantity of acetic acid resulted from the oxidization of alcohol or the uronic acids extracted from wood as well as from the simultaneous decomposition of the acetic acid by decarboxylation.

During the maturation of distillates, one may notice an increase of the dry extract, the fixed acidity and the tanning substances which are proportional to the dissolving of the wooden extract. At the same time, there appears a small content of sugar coming from the hydrolysis of the wood hemicelluloses. One may also notice a concentration in esters and superior alcohols. The vanillin content increases as distillates get older, especially for the distillates from smaller vessels that are partially full. This is due to the favorable conditions for lignin extraction from wood which helps to the formation of vanillin.

According to the European laws, the fruit brandy must contain at least 200 g/hL alcohol 100% in volatile substances. They insist a lot on the correctness of denominations as well as the origin/authenticity of distillates (Cantagrel, 1992)

According to Tanner and Brunner,1982, many European countries have elaborated acceptability norms in terms of the content in basic components.

Germany published (*Table 1*) the ultimate in values mg/100mL a.p for the following components:

Switzerland has established (*Table 2*) the following ultimate values in mg/100mL a.p:

Table 1

Drink	Acetic aldehyde mg/100 ml pure alcohol	Total esters mg/100 ml pure alcohol	Superior alcohols mg/100 ml pure alcohol	Total acidity mg/100 ml pure alcohol
Pomace marc distillate	Max. 80	100 (40-500)	150	8- 100
Pomace brandy	50	100	150	100
William pear brandy	50	150	150	100
Kirsch (cherry brandy)	50	250	150	100
Plum brandy	50	200	150	100

Table 2

Drink	Acetic aldehyde	Total acidity (acetic acid)	Esters	Acrolein
Pomace marc distillate	Max. 160	Max. 100	Max. 100	Max. 0.2
Pomace brandy	100	100	50	0.4
William pear brandy	160	150	100-500	0.2
Kirsch (cherry brandy)	80	150	150-700	0.2
Plum brandy	80	100	200-700	0.2

MATERIAL AND METHOD

In 2007 we purchased and studied a number of 20 alcoholic drinks distilled from fruits (*Table 3*) from the supermarkets of Iaşi.

For these assortments we effectuated the following determinations:

- Determination of the relative density and alcoholic concentration by means of Anton Paar DMA 5000 electronic densimeter ;

- Determination of total acidity and volatile acidity according to STAS 184/5-70 by the potentiometric method**;**

- pH determination according to STAS 6182/14-72;

- Total polyphenol index (TPI) or D_{280} index by means of UV-VIS spectrophotometer;

- Ester determination – according to STAS 184/6-70 by titration with sodium hydroxide;

- Extract determination **-** according to STAS 184/3-70;

- Determination of the organoleptic characteristics.

Table 3 - Data related to the origin of distillates

No	Denomination	Manufacturer	Alcohol % vol.	Packing
1	Brandy, Zalău	APPPN Sălaj	50.0	PET bottle
2	Brandy, Bocşiţa	APPPN Sălaj	50.0	PET bottle
3	Maramureş brandy	Valco S.A. Baia Mare	40.0	glass bottle
4	Maramureş plum brandy	Valco S.A. Baia Mare	38.0	glass bottle
5	Tomeşti plum distillate (raw material)	S.C.Vinia S.A. Iaşi	36.0	sample
6	Brandy, Tomeşti Iaşi matured for 14 years	S.C. Vinia S.A. Iaşi	42.0	glass bottle
7	Bucium plum distillate (raw material)	S.C.A. Bucium S.A	40.0	sample
8	Vinia matured plum distillate (raw material)	S.C.A. Bucium S.A	38.0	sample
9	Vlad, extra fine brandy Cluj Napoca	Prodvinalco S.A. Cluj-Napoca	45.0	glass canteen
10	Hanul ars Câlnău Buzău	S.C. Euroavipo S.A. Câlnău	38.0	glass bottle

No	Denomination	Manufacturer	Alcohol % vol.	Packing
11	Rameros Bucium Iaşi	S.C.A. Bucium S.A.	42.0	glass canteen
12	Apple brandy, Borşa	Valco S.A. Baia Mare	48.0	glass bottle
13	Apple brandy, Moisei	Valco S.A. Baia Mare	49.0	glass bottle
14	Bucium sour cheery brandy	S.C.A. Bucium S.A.	40.0	glass bottle
15	Cherry brandy, Tomeşti	S.C.Vinia S.A. Iaşi	42.0	glass bottle
16	Con Senso cheery brandy, Italy	Italy	42.0	glass bottle
17	Vinia matured cherry distillate (raw material)	S.C.Vinia S.A. Iaşi	38.0	sample
18	Cheery brandy, Cotnari	S.C.Vinia S.A. Iaşi	39.0	glass bottle
19	Vinia quince brandy	S.C.Vinia S.A. Iaşi	42.0	glass bottle
20	Vinia pear brandy	S.C.Vinia S.A. Iaşi	42.0	glass bottle

RESULTS AND DISCUSSION

The alcoholic concentration of the analysed products (*Table 4*) show values superior to 37.5 vol. % alcohol in 14 cases ranging from 39.13 vol% to 50.15 vol%, allowing for the their classification in the superior category where they have the right to bear a distinct origin denomination. Six assortments do not enter this category, but most of them registered small differences as compared to the minimum limit. Thus, four assortments have the alcoholic concentration over 37 vol%, but below 37.5 vol%, and the other two have lower alcoholic concentrations (35.12 vol% and 36.82 vol%).

We mention that four of the distillates under analysis that do not have a superior alcoholic concentration represent old products and are raw materials for the preparation of distilled drinks. Only two of the samples (Hanul ars and Maramureş Plum brandy) were bottled without mentioning that they are spirits having an alcoholic concentration below 37.5 vol.%.

The acidity of the raw material is transmitted in proportion up to 1/5 into the distillate acidity. It consists in characteristic organic acids and fast reaction esters and other acid compounds. In the process of discontinuous distillation, the fraction of distillate last drops cumulates an obvious acidity. By redistillation, acids accumulate both in the first and the last drops of distillate. In Romania, they do not frequently make the acidity correction of the raw material before fermentation with phosphoric or sulphuric acid (Gomez – Cordoves C. *et al.*, 1992).

According to Stănciulescu Gh. *et al.*, 1975, in the maturation period, titrating acidity may increase on the basis of and to the detriment of the volatile acidity.

To prepare the distilled drinks, excessive acidity may be corrected by mixings, dilutions (of the consumption concentration) or neutralizations (frequently by means of the calcium carbonate). (Câmpeanu *et al*. 1992).

Table 4 - Relative density and alcoholic concentration of the analysed products

No.	Distillate sample	Alcoholic conc. % vol.	Relative density de^{20}
1	Brandy, Zalău	**50.15**	0.9340
2	Brandy, Bocşiţa	**49.40**	0.9336
3	Apple brandy, Moisei	**48.91**	0.9345
4	Apple brandy, Borşa	**47.63**	0.9368
5	Vlad, extra fine brandy Cluj Napoca	**44.50**	0.9398
6	Con Senso cheery brandy, Italy	**42.48**	0.9463
7	Cherry brandy, Tomeşti	**42.32**	0.9457
8	Brandy, Tomeşti Iaşi matured for 14 years	**42.23**	0.9445
9	Rameros	**42.09**	0.9469
10	Vinia pear brandy	**41.65**	0.9469
11	Vinia quince brandy	**41.12**	0.9491
12	Bucium sour cheery brandy	**39.99**	0.9503
13	Maramureş brandy	**39.80**	0.9477
14	Cheery brandy, Cotnari	**39.13**	0.9538
15	Vinia matured plum distillate (raw material)	37.43	0.9563
16	Hanul ars Câlnău Buzău*	37.41	0.9517
17	Maramureş plum brandy*	37.30	0.9514
18	*Vinia matured cherry distillate (raw material)*	*37.24*	0.9567
19	*Plum distillate, Bucium (raw material)*	*36.82*	0.9514
20	*Plum distillate, Tomeşti (raw material)*	*35.12*	0.9556
	Average	**41.636**	0.9470

* spirits (having less than 37.5 % vol. alcohol)

The total acidity determined (*Table 5*) ranged between 2.7 and 0.3 g/L $C_2H_4O_2$, the average of samples being almost 1.4 g/L $C_2H_4O_2$. We may say that the products coming from SC Vinia SA Iaşi or from Maramureş have an authentic acidity that could also be increased by maturation (for example, 14 years for Tomeşti plum brandy). The products coming from SC Agroindustriala Bucium SA Iaşi, besides other commercial products (Vlad, Hanu ars, Con Senso etc) have a low acidity or potentially diminished since they are distilled drinks obtained from non-maturated or corrected distillates.

As compared to the sample average (0.5 g/L $C_2H_4O_2$), for volatile acidity (*Table 6*) we may notice a certain parallelism with the situation of total acidity. The products from SC Agroindustriala Bucium SA, Transylvania brandies (Maramureş, Zalău) and the other assortments having a low acidity (Vlad, Hanul ars, Con Senso) are below the average. It is obvious that we speak of distillates obtained from raw materials produced immediately after fermentation that have not accumulated a volatile acidity. In case of the raw material plum distillate from Bucium, we may infer that the treatment for acidity reduction acted in both cases (total/volatile acidity).

Table 5 - Total acidity of the analysed products

No.	Distillate sample	Total acidity g/L $C_2H_4O_2$
1	Tomeşti Brandy, matured for 14 years	**2.69**
2	Vinia matured plum distillate (raw material)	**2.40**
3	Plum distillate, Tomeşti (raw material)	**2.39**
4	Vinia matured cherry distillate (raw material)	1.93
5	Vinia pear brandy	1.87
6	Cherry brandy, Tomeşti	1.84
7	Apple brandy, Moisei	1.71
8	Maramureş plum brandy	1.60
9	Brandy, Bocşiţa	1.57
10	Cheery brandy, Cotnari	1.53
11	Vinia quince brandy	1.45
12	Maramureş brandy	1.35
13	Brandy, Zalău	1.19
14	Apple brandy, Borşa	1.00
15	Rameros	0.85
16	Vlad, extra fine brandy Cluj Napoca	0.67
17	Hanul ars Câlnău Buzău	0.36
18	Plum distillate, Bucium (raw material)	0.35
19	Bucium cherry brandy	0.35
20	Con Senso cherry brandy, Italy	0.34
	Average	**1.372**

Table 6 - Volatile acidity of the analysed products

No.	Distillate sample	Volatile acidity g/L $C_2H_4O_2$
1	Tomeşti Brandy, matured for 14 years	**0.97**
2	Plum distillate, Tomeşti (raw material)	**0.87**
3	Cherry brandy, Tomeşti	**0.82**
4	Vinia pear brandy	0.76
5	Cheery brandy, Cotnari	0.71
6	Maramureş plum brandy	0.67
7	Vinia quince brandy	0.67
8	Maramureş brandy	0.63
9	Vinia matured plum distillate (raw material)	0.60
10	Vinia matured cherry distillate (raw material)	0.56
11	Apple brandy, Moisei	0.48
12	Brandy, Bocşiţa	0.44
13	Vlad, extra fine brandy Cluj Napoca	0.37
14	Apple brandy, Borşa	0.34
15	Brandy, Zalău	0.34
16	Bucium sour cherry brandy	0.22
17	Rameros	0.20
18	Hanul ars Câlnău Buzău	0.19
19	Agroindustriala Bucium plum distillate, (raw material)	0.19
20	Con Senso cherry brandy, Italy	0.19
	Average	**0.511**

The samples with a more significant volatile acidity come from SC Vinia SA Iaşi, including as raw material, besides two samples from Maramure. Here we may infer that the distillates were obtained from marcs processed after a period of keeping correlated with a slower manufacture rhythm.

During fermentation, due to the giving off of the carbon dioxide, the more solid parts of the fruit marc come to the surface under the shape of a *hood* and there appears the danger of acetic fermentation in this area.

The distillates having a content of original acetic acid (resulted by distillation) may be encountered only in the first storage phase since, within a predictable time, the acetic acid will form esters with ethylic alcohol and the other existing alcohols. In a smaller quantity, the formation of esters is a desirable process giving flavour and balance. When in excess, the volatile acidity and esters give a stingy smell of a dissolvent and a contrasting acid taste.

In case of lower contents of volatile acidity, the distillates may be subjected to decantation with magnesium oxide or a basic magnesium carbonate (3-5 g/L), after having corrected it to the consumption concentration. Brandies must be perfectly homogenized with the administered product. After 6 hours, stirring it from time to time, it will separate from the deposit. This method is also useful because it eliminates the undesirable gustative compounds.

The pH values (*Table 7*) are concordant with the previous interpretation of data. Hanul ars product has a slightly basic pH besides the raw material plum distillate from Bucium. They were obviously subjected to a treatment for acidity neutralization.

The other assortments having a pH between 3 and 5.3 may be considered within the normal limits of some distillates/distilled drinks. The values superior to the average of about 4.4 may be correlated with less maturated products or with raw materials to which they applied a basic correction. The values lower than the average predominate (12 assortments) and they are maturated/old distillated as well as distilled drinks obtained fro such raw materials.

In the Western Europe (having a tradition in Schwartz wald – French-German-Swiss border area), where there is a real cult for the quality of fruit brandies, they are not maturated in wooden vessels so as not to denaturated the natural fruit flavour. For kirsch, they use large glass cork-less demijohns (bonbonnes) keeping the fineness, flavour and colorless nuance of these distillates. The plum brandies fro the same area (Mirabelle, Prune, Pruneaux etc) stand out by special gustatory nuances that may be lost when maturing in wooden vessels and replaced by other compounds extracted from staves (Brown, 1996; Delois, 1993; Dominé, 2008; Gasnier, 2005; Waltonand and Glover, 2006; Walton, 2007).

In case of the Romanian producers, the maturation of fruit brandies in small barrels, casks or oak wine-casks or from other wood essences represents a national specificity. For this reason, we analysed the impact of the contact distillate/oak stave on the composition of the assortments under study.

Table 7 - pH values of the analysed samples

No.	Distillate sample	pH
1	Hanul ars Câlnău Buzău	8.50
2	Bucium plum distillate, (raw material)	7.37
3	Bucium sour cherry brandy	5.32
4	Rameros	4.89
5	Brandy, Bocşiţa	4.59
6	Con Senso cherry brandy, Italy	4.53
7	Apple brandy, Borşa	4.48
8	Apple brandy, Moisei	4.41
9	Brandy, Zalău	4.30
10	Vlad, extra fine brandy Cluj Napoca	3.97
11	Maramureş plum brandy	3.91
12	Maramureş brandy	3.86
13	Plum distillate, Tomeşti (raw material)	3.81
14	Tomeşti Brandy, matured for 14 years	3.65
15	Vinia quince brandy	3.60
16	Cherry brandy, Tomeşti	3.50
17	Cherry brandy, Cotnari	3.40
18	Vinia pear brandy	3.25
19	Vinia matured cherry distillate (raw material)	3.08
20	Vinia matured plum distillate (raw material)	3.03
	Average	**4.3725**

We may notice that a series of products (*Table 8*) contain a very low quantity of polyphenols or at all (Hanul ars Câlnău Buzău). TPI value below 3 may be found in the apple brandy (Borşa, Moisei), sour cherry brandy (Bucium), cherry brandy (Con Senso), as well as other assortments that did not maturate in wooden vessels. Then we have the samples registering a relatively reduced polyphenol content that maturated in large vessels (wine-casks/large casks) with TPI from 3 to 4. The samples having TPI above 4 have an obvious polyphenol content (eight assortments) presenting the guarantee that they acquired this component naturally and not by chips addition.

According to Stănciulescu Gh. *et al.*, 1975, in the group of tannins and colouring substances from the oak wood enter *quercitine,* a resin giving the wine distillate a special flavour, and *quercitrin* giving the distillate the yellow colour.

Table 8 - Total polyphenol index values for the analysed samples

No.	Distillate sample	TPI D_{280}
1	Vinia matured plum distillate (raw material)	**6.3**
2	Maramureş plum brandy	**5.8**
3	Vinia matured cherry distillate (raw material)	**5.8**
4	Maramureş brandy	**5.5**
5	Tomeşti Brandy, matured for 14 years	4.7
6	Cherry brandy, Tomeşti	4.3
7	Vinia quince brandy	4.3
8	Cherry brandy, Cotnari	4.1
9	Vinia pear brandy	3.9
10	Plum distillate, Tomeşti (raw material)	3.7
11	Brandy, Zalău	3.2
12	Brandy, Bocşiţa	3.2
13	Rameros	3.1
14	Vlad, extra fine brandy Cluj Napoca	2.3
15	Bucium sour cherry brandy	1.8
16	Apple brandy, Borşa	1.2
17	Plum distillate, Bucium (raw material)	1.0
18	Con Senso cherry brandy, Italy	0.5
19	Apple brandy, Moisei	0.4
20	Hanul ars Câlnău Buzău	0.0
	Average	**3.255**

The tanning substances inexistent at the beginning gradually increase as maturation progresses then their content decreases due to the reduction of the extracted quantities following the gradual spoliation of the inner layer of the oak wood and the partial oxidization. It has been noticed that the variation of the content in tanning substances leads to increases and decreases of the distillate's acidity (Beceanu, Anghel, 2006; Lavergne J. *et al*.,1992).

The tannin stimulates the oxidization of alcohol in acetaldehyde and contributes to the decomposition of the amino acids and pentose dehydration (Beceanu *et al.,* 2004).

The analysis of the ester content (*Table 9*) represents a test of authenticity and helps identifying the bonifications with ethylic alcohol of alimentary use. Thus, we may identify the product Hanul ars as being made on the basis of ethylic alcohol. The sour cherry brandy and the plum distillate from Bucium may be classified in the category of drinks bonified with exogenous ethylic alcohol. The rest of products having the ester content below 300 mg ethyl acetate / 100 mL anhydrous ethanol (Borşa Apple brandy, Zalău Brandy, Con Senso, Moisei Apple brandy, Bocşiţa brandy and Vlad extra fine brandy, Cluj Napoca) are products insufficiently maturated or which

have been bonified with exogenous ethylic alcohol.

The products having a significant ester content (between 370 and 480 mg ethyl acetate / 100 mL anhydrous ethanol) represent a category proving the existence of a maturation period that allowed the formation and accumulation of these compounds that give a superior quality. Despite all these, we must underline the counter productivity of maturation in the case of the cherry, quince or pear brandy which lost their natural quality through this process (five assortments).

***Table 9* - Total ester content of the analysed samples**

No.	Distillate sample	Total esters mg ethyl acetate / 100 mL anhydrous ethanol
1	Tomeşti Brandy, matured for 14 years	**479.5**
2	Vinia matured cherry distillate (raw material)	**478.1**
3	Plum distillate, Tomeşti (raw material)	**475.4**
4	Maramureş plum brandy	**447.0**
5	Vinia matured plum distillate (raw material)	**443.6**
6	Cherry brandy, Cotnari	**415.7**
7	Maramureş brandy	**401.7**
8	Rameros	389.0
9	Vinia quince brandy	379.9
10	Vinia pear brandy	376.6
11	Cherry brandy, Tomeşti	373.5
12	Vlad, extra fine brandy Cluj Napoca	283.3
13	Brandy, Bocşiţa	277.4
14	Apple brandy, Moisei	274.6
15	Con Senso cherry brandy, Italy	260.0
16	Brandy, Zalău	244.9
17	Apple brandy, Borşa	187.3
18	Plum distillate, Bucium (raw material)	67.4
19	Bucium sour cherry brandy	58.8
20	Hanul ars Câlnău Buzău	< 0.9
	Average	**332.3**

According to Tanner and Brunner, 1982, esters resulting after fermentation are of two kinds: acid esters and neutral esters. Acid esters are fixed and they form by the esterification of the ethylic alcohol with the acetic, propionic, butyric, lactic, succinic, malic, tartaric, citric acids etc.

The neutral esters of the ethylic alcohol or the superior alcohols with amino acids form during fermentation within the lees cells and their quantity depends on the lees species. Neutral esters are volatile and by distillation they go into the distillate giving it a pleasant smell. The most important ester if the *ethyl acetate*, which, in moderate quantities, contributes to the

formation of flavour, but in excess, has an unfavorable influence on the quality of the distillate. To avoid this situation, the marc/ the fermented juice to be distilled must not contain more than 200 mg/l ethyl acetate. The ethyl acetate goes into the distillate at the beginning of distillation. Other esters that are found in small quantities but which contribute to a large extent to the improvement of the distillate quality are the esters of the ethylic alcohol with caprylic, caprinic, lauric, palmitic, miristic acids etc. The largest quantity of esters is contained by the raw distillate, after redistillation, esters accumulate in the first and last drops of distillate. (Lemesle *et al*., 1992)

Esters are compounds coming from the reaction between alcohol and an acid, next to water. In the fruit brandies, ethyl acetate appears in large quantities. Esterifications are possible between all acids and alcohols. They are obtained regardless of the initial concentration of components, temperature and pH value. Esters generally have fruit favour and give distillates this nuance to the detriment of the acid and biting note appearing during maturation. But the esterification processes are reversible. The ethyl acetate may decompose reversibly in ethylic alcohol and acetic acid. This is a way allowing the reduction of the ester content.

According to Stănciulescu *et al.*,1975, the reason for a too high ester content is a must of grapes that might turn sour and for which they gave up neutralization before distillation. For this reason, an important quantity of acetic acid goes into the distillate what will partially lead to its combination with the ethylic alcohol. The treatment of the distillates with a too high volatile acidity consists in the esterification in an alkaline environment, in the presence of NaOH excess (reversible process). The ester formed shall return to the initial components and the acids resulted may be neutralized, afterwards they may make the distillation.

According to Tanner and Brunner, 1982, the cherry brandies have a too high content of esters and, for this reason, it is recommended a treatment process at 50-60vol%. For other distillates they shall proceed according to their specificity. Depending on the ester content, about 1/5 from the distillate having an ester excess is treated with NaOH up to a pH of 5.7± 0.1 then it is distilled separately and mixed with the rest of the quantity (4/5). They make a complete neutralization after each mixture, and sometimes they may need to add some more NaOH. Finally, ester hydrolysis takes place during heating for 2 hours at 75^0C. In the end, it is corrected by acidification to the initial pH (5.7± 0.1) after which it may be distilled using the usual method.

Table 10 - Extract values of the analysed samples

No.	Distillate sample	Extract mg/100 mL
1	Vinia matured plum distillate (raw material)	**1030**
2	Vinia matured cherry distillate (raw material)	**1030**
3	Vinia quince brandy	820
4	Rameros	790
5	Con Senso cherry brandy, Italy	770
6	Plum distillate, Bucium (raw material)	570
7	Bucium sour cherry brandy	570
8	Vinia pear brandy	550
9	Cherry brandy, Cotnari	480
10	Cherry brandy, Tomeşti	460
11	Tomeşti Brandy, matured for 14 years	140
12	Plum distilate, Tomeşti (raw material)	90
13	Brandy, Zalău	60
14	Hanul ars Câlnău Buzău	60
15	Apple brandy, Borşa	60
16	Brandy, Bocşiţa	10
17	Maramureş brandy	10
18	Maramureş plum brandy	10
19	Apple brandy, Moisei	10
20	Vlad, extra fine brandy Cluj Napoca	<5
	Average	**361**

The extract (mg/100mL) may indicate the lack of naturalness when it has too low values (*Table 10*), as the last 10 assortments analysed show (due to the bonifications with exogenous alcohol that distilled the original distillates). The existence of an extractive content may indicate two things: either the existence of a natural process of extraction from the stave followed by the hydrolysis of the extracted compounds (the case of the first two assortments – the raw material from Vinia), or an improver adding (as we suspect in Con Senso and the other distilled drinks).

The use of improvers in its broader sense consists in the adding of certain adjuvants to improve and round the gustatory, olfactory and colour qualities of the distilled drinks and, in the case of liquors, to define them in terms of assortment (Beceanu, Hobincu, 2006).

In the special distillations, there are strict limits for their use. (Beceanu *et al*., 1999).

Thus, in Sweden, for kirsch (cherry brandy), the plum brandies etc., they do not accept improvers When they accept them (alcoholic extracts from plants, sugar, caramel), the adding may not exceed 10g/L of distilled drink ready for consumption. Williams pear distillates may be adjusted with an adding of 6±2 g/L fructose. In Germany, they do not accept the colouring or adding of sugar to the fruit brandies.

Following the sensorial assessment (*Table 11*), we notice that both the ester and extract content were the main factors determining the positive and significant assessment of quality. One single product had a smoky taste (Moisei Apple brandy) and Hanul ars Câlnău Buzău product was characterized as having an unpleasant taste (quite explicable since it was a counterfeited drink).

Table 11 - Sensorial analysis (assessment) of the analysed products

No.	Product under analysis	Assessment
1	Tomeşti Brandy, matured for 14 years (extract 140 mg/100mL)	clear, bright yellow colour, plum characteristic smell and pleasant taste due to **esters**
2	Vinia matured cherry distillate (raw material) (extract 1030 mg/100mL)	clear, bright olive-yellow colour, characteristic smell and smooth taste, discrete and very pleasant due to **extract** and **esters**
3	Plum distilate, Tomeşti (raw material) (extract 90 mg/100mL)	clear, bright olive colour, plum characteristic smell and pleasant taste due to **esters**
4	Maramureş plum brandy (extract 10 mg/100mL)	transparent, clear, bright yellow colour, partially pleasant taste and smell due to **esters**
5	Vinia matured plum distillate (raw material) (extract 1030 mg/100mL)	clear, bright olive colour, plum characteristic smell and very pleasant taste due to **extract** and **esters**
6	Cherry brandy, Cotnari (extract 480 mg/100mL)	clear, bright olive colour, characteristic smell and pleasant smooth discrete taste due to extract and **esters**
7	Maramureş brandy (extract 10 mg/100mL)	transparent, clear, white-greenish colour, almond smell and partially pleasant taste due to **esters**
8	Rameros (extract 790 mg/100mL)	clear, bright olive colour, characteristic smell and very pleasant taste due to **extract** and esters
9	Vinia quince brandy (extract 820 mg/100mL)	clear, bright olive colour, characteristic smell and pleasant smooth discrete taste due to **extract** and esters
10	Vinia pear brandy (extract 550 mg/100mL)	clear, bright olive colour, characteristic smell and pleasant smooth discrete taste due to **extract** and esters
11	Cherry brandy, Tomeşti (extract 460 mg/100mL)	clear, bright yellow colour, characteristic smell and very pleasant taste due to extract and **esters**
12	Vlad, extra fine brandy Cluj Napoca (extract 5 mg/100mL)	transparent, clear, colorless, plum characteristic smell and pleasant taste, moderate quality
13	Brandy, Bocşiţa (extract 10 mg/100mL)	transparent, clear, bright green colour, plum characteristic smell and pleasant taste, moderate quality
14	Apple brandy, Moisei (extract 10 mg/100mL)	colorless, discrete smoke smell, partially pleasant taste, modest quality
15	Con Senso cherry brandy, Italy (extract 770 mg/100mL)	colorless, special smell, harmonious smooth taste due to **extract**

No.	Product under analysis	Assessment
16	Brandy, Zalău (extract 60 mg/100mL)	transparent, clear, bright green colour, plum characteristic smell and pleasant taste, moderate quality
17	Apple brandy, Borşa (extract 60 mg/100mL)	clear, bright yellow colour, discrete smell and taste, modest quality
18	Plum distillate, Bucium (raw material) (extract 570 mg/100mL)	clear, bright yellow colour, pleasant smell and taste due to **extract**
19	Bucium sour cherry brandy (extract 570 mg/100mL)	clear, bright yellow colour, characteristic smell and very pleasant taste due to **extract**
20	Hanul ars Câlnău Buzău (extract 60 mg/100mL)	colorless, alcohol smell, unpleasant taste – the lowest ester content.

CONCLUSIONS

Out of the 20 analysed samples only 14 meet the requirements for the award of a distinct denomination whereas the other six may only be called spirits. The fact that some drinks of the second category do not mention on the label the denomination of spirit is a crime.

Total acidity and the volatile acidity have concordant values giving the opportunity to identify the products maturated as well as the neutralization or bonification treatments.

The pH values allow the classification of the distillates/distilled drinks by their degree of naturalness and the possible treatments effectuated.

The polyphenol content may indicate the existence or inexistence of the wooden (oak) storage areas and the possible time of contact with these spaces or the reduction of influence due to the diverse treatments.

The ester content indicates for 11 samples the cause that leads to their classification into a superior quality class.

The values of the extract content may also explain, even more than the ester content, the favorable impression and the superior gustative quality for the 10 samples in their respective order.

Except for two samples that showed quality defects, the rest of the distillates and distilled drinks registered positive or very positive sensorial qualities (especially Vinia maturated cherry distillate raw material and Vinia maturated plum distillate raw material)

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