

## Analytical characterization of three distilled drinks

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**Abstract:** The aim of this research is to characterize three distilled drinks commercially available on the market (Courvoisier cognac, Vinars Miorita and alcoholic drink Alexandrion). In this purpose it was determined the alcoholic concentration, the total acidity, the extract content and other specific parameters. The concentrations of esters, aldehydes and superior alcohols have been determined by simple analytical methods based on spectrometric UV-VIS method, respectively titrimetric method (Schoorl) for saccharose. Furfural compound was identified by reaction with fresh aniline.

The analytical characterization was offered a promising approach for the classification of these three drinks by the content in distilled wines. This study shows that the Vinars Miorita (old distilled wine) and Courvoisier cognac (young distilled wine) can be discriminated from the alcoholic drink Alexandrion (a mixture obtained from a distilled wine with ethylic alcohol, water, sugar, aroma and dyestuff) using the differences between the obtained results for these distilled drinks. Moreover, the lack of furfural in alcoholic drink Alexandrion goes to the conclusion that the rate of distilled wine used to obtain this drink is very low.

**Keywords:** distilled drinks, spectrometric methods, esters, aldehydes, superior alcohols, saccharose

### 1. Introduction

Aroma substances (alcohols, aldehydes, esters and acids) are important in beverages as they make a major contribution to the quality of the distilled wines. Most of them appear during fermentation process as main volatile compounds and their concentrations vary over a wide range [1].

The name „vinars” is generally attributed to many strong drinks and officially the term denotes the drink obtained from the distilled wines at open fire, in Charente installations, followed by natural aging in 500 l oak barrels that give finesse, elegance and nobility.

Courvoisier is a brand of cognac is extra old having been aged 20-35 years. Courvoisier tasted like caramel, chocolate, nuts, oak, and orange.

Alexandrion is a distilled drink which keep the same characteristics but which is different through the higher alcoholic concentration.

Several analytical methods have been published for characterization of distilled drinks, such as liquid chromatography coupled with mass spectrometry followed by NMR spectroscopy [2], gas chromatography coupled with mass spectrometry [3] and capillary electrophoresis [4].

Analyses of the aroma fraction could perform by high reverse gas chromatography coupled either

with flame induction detector or mass spectrometry, with direct injection in gas chromatograph of full proof distillates [5].

Another technique used in this purpose is high performance liquid chromatography (HPLC). For example ethyl carbamate derivatization with 9-xanthidrol in an acidic medium allows its quantitation by fluorescence detection after separation by HPLC [6].

Also, UV-VIS spectrometric methods were used for characterization of distilled drinks [7]. Furthermore fluorescence spectroscopy offers a promising approach for the characterization of distillates [8].

In this study, the attention has been principally focused on identification of furfural (a compound which is formed in the distillation period) and quantification of esters, aldehydes, superior alcohols and saccharose from three distilled drinks (Courvoisier cognac, Vinars Miorita and alcoholic drink Alexandrion).

### 2. Experimental

All used reagents were of analytical reagent grade and were purchased from Merck.

### 2.1. Sampling

The studies were performed on 3 distilled drinks (Courvoisier cognac, Vinars Miorita and alcoholic drink Alexandrion) samples purchased from the local supermarkets.

The alcoholic drink Alexandrion was produced by S.C.Alexandrion Group România. Vinars Miorita was produced by S.C. Vincon Vrancea S.A Romania and Courvoisier cognac was produced in France.

Samples were stored in a dark at room temperature until the day of analysis.

### 2.2. Analysis of sample

The extract of the samples was obtained by evaporation of 50 mL sample and drying the residues at 100 °C for 2h and 30 min, followed by weighing.

Furfural compound was identified by reaction with fresh aniline: in a glass test tube was introduced 10 mL sample, a drop of Complexan III 0.1 N, 3 drops of HCl and a drop of fresh distilled aniline. The appearance of a pink-red coloration indicates the presence of furfural.

The total acidity was determined by titration with NaOH in presence of phenolphthaleine after the moving off the CO<sub>2</sub>.

The alcoholic concentration was measured using the picnometre method and the calculation of alcoholic concentration was based on relative density determination and reading from tables of the alcoholic concentration values at 20°C, expressed in % vol. function relative density of obtained distillate.

The quantification of saccharose in studied samples was realized using a titrimetric method (Schoorl method). In a 500 mL volumetric flask was introduced 5 mL sample and then was filled up to the mark with distilled water. 50 mL from this solution with 25 mL distilled water and 2 mL HCl was transferred in a Berzelius glass. Then the mixture was heated at 70°C and maintained the temperature for 5 min. After the cooling, the mixture was neutralized with NaOH in presence of phenolphthaleine. Aliquots of 20 mL from this mixture was transferred in an Erlenmayer glass, then was added 10 mL Fehling I solution, 10 mL Fehling II solution, 25 mL distilled water and then boiled for 2 min. After cooling, were added 10 mL

KI 30% and 15 mL H<sub>2</sub>SO<sub>4</sub> 20%. Finally the iodine was titrated with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 0.1N in presence of starch. In parallel was made a reference sample.

The concentrations of esters, aldehydes and superior alcohols have been determined by simple analytical methods based on spectrometric UV-VIS method.

The esters react quantitatively with hydroxylamine chloride in alkaline medium and it's formed the hydroxamic acids which react with ferric ions in acid medium and finally a complex is formed. The absorption measurement of the formed complex was made at 525 nm. A calibration curve was obtained with ethyl acetate solutions (concentration range 0–30mg/100mL ethylic alcohol) as standard.

To obtain the maximum and stable absorbance the optimal sequence of reagents addition was: 2 mL of hydroxylamine chloride 2M, 2 mL NaOH, then the mixture was homogenized, was warm up to 20 °C for 15 min and then was added 2 mL HCl 4M and 2 mL FeCl<sub>3</sub> 0.37M. At the end the absorbance of the final solution was measured at 525 nm.

In order to measure the aldehydes concentration in analyzed samples a calibration curve was obtained and results were expressed as acetic aldehyde equivalents (mg/100mL ethylic alcohol). Into a series of 25 mL standard volumetric flasks were transferred different aliquots of acetic aldehyde stock solution and 2.5 mL pinkaniline sulphite prepared in acid medium and fill up to the mark with distilled water. The mixture was keep under the room temperature for the color stabilization (20 min) and then the absorbance of the complex was measured at 560 nm.

For the determination of superior alcohols concentrations in distilled drinks was necessary a pretreatment of sample. So, in a distillation balloon flash of 250 mL were introduced 100 mL sample, then was added 1 g of methaphenilendiamine, a few grains of pumice stone and the mixture was boiled for an hour and finally the distillate was captured in 100 mL volumetric flask and fill up to the mark with distilled water. Then 2 mL of distillate was introduced in a glass test tube and shake continuously under ice. After that was added 1 mL of methaphenilendiamine, after 3 min was added 10 mL H<sub>2</sub>SO<sub>4</sub> and keep under ice for another 3 min. Then the glass test tube was introduced in warmer

water for 20 min. At the end the mixture was transferred into 25 mL volumetric flask and fill up to the mark with distilled water.

The calibration curve was obtained with a mixture of isoamylic and isobutylic alcohol as standard at a concentration range from 10 to 100mg/100mL ethylic alcohol. The calibration curve was plotted using ten standard solutions diluted from the stock solution.

### 3. Results and discussions

The goal of the study was to characterize three distilled drinks and compare these drinks in the context of ageing process. In this purpose was identified the furfural compound and determined the values of extract, total acidity, alcoholic concentration, saccharose, esters, aldehydes, and superior alcohols in the analyzed samples. The results were presented in tables 1-8.

The extract values for Vinars Miorita and Courvoisier cognac were very close (table 1) because these two distilled drinks are natural drinks obtained from wine by distillation process and deposited in oak casks. The higher content of extract in Alexandrion drink appeared due to the addition of the sugar which is specified on the label of this product. The addition of the sugar it's forbidden by the French law [9].

The presence of furfural in distilled drinks (table 2) is the result of pentose dehydration during the distillation process under the heat.

**Table 1.** The values of extract in analyzed samples

Distilled drinks	Extract (g /100 mL sample)
Alcoholic drink Alexandrion	1.79
Vinars MIORITA	0.78
Courvoisier cognac	0.86

This compound has a better contribution to the bouquet of drink when it's present in small concentrations (under to 2 mg/100 ml ethylic alcohol) [b] and a negative contribution when it's present in higher concentrations [10].

The furfural compound was identified in natural distilled drinks (a pink coloration in Courvoisier cognac and a pink-yellow coloration in

Vinars Miorita). The absence of furfural in Alexandrion drink goes to the supposition that this drink contain the lowest quantity of distilled wine.

**Table 2.** The identification of furfural in analyzed samples

Distilled drinks	Furfural
Alcoholic drink Alexandrion	missing
Vinars MIORITA	present
Courvoisier cognac	present

From Table 3 was observed that the lowest value of total acidity was registered for Alexandrion drink. This fact can be explained by the small proportion of old distilled wine in composition of Alexandrion drink.

**Table 3.** The values of total acidity in analyzed samples

Distilled drinks	Total acidity (mg acetic acid /100 ml ethylic alcohol anhydrous)
Alcoholic drink Alexandrion	22
Vinars MIORITA	158
Courvoisier cognac	68

It's known that the distillate loses water by evaporation and an aliquot of ethylic alcohol in the period of ageing process. So, the value of total acidity increases because the same quantity of acids is found in a small volume of distillate and its report to a smaller quantity of ethylic alcohol. In this way was explained the higher value of total acidity in Vinars Miorita sample in comparison with younger Courvoisier cognac.

In the literature was reported that in the first 3 years of ageing process, the value of total acidity increases, for the next six month decreases and then increases again [10].

Vinars Miorita has a higher alcoholic concentration than other two analyzed distilled drinks with approximately 2% vol. (table 4).

The value of alcoholic concentration for this distilled wine (42.05% vol.) ranged in the limits imposed by the Law of vineyard and wine [11] for

the Romanian distilled wine (minimum 36% vol.) and by SR 13442 [12].

**Table 4.** The values of alcoholic concentration in analyzed samples

Distilled drinks	Alcoholic concentration (% vol.)
Alcoholic drink Alexandrion	40.07
Vinars MIORIȚA	42.05
Courvoisier cognac	40.10

Also, the Courvoisier cognac and alcoholic drink Alexandrion respect the French normative which stipulate that the cognac has a minimum alcoholic concentration of 40% vol. when it's sold on the market [9].

During the ageing process the saccharose content increases initial and then (after 5-6 years) the concentration decreases due to the complex transformation produced in this period. Table 5 showed that the saccharose concentration in Vinars Miorita was zero and this is a clue that this distillate drink had initial a small concentration of saccharose.

**Table 5.** The values of saccharose concentrations in analyzed samples

Distilled drinks	Saccharose (g /100 ml sample)
Alcoholic drink Alexandrion	1.425
Vinars MIORIȚA	0.000
Courvoisier cognac	3.135

Also, this result may be interpreted like a missing of adding sugar in the technologic process of Vinars Miorita drink.

The high saccharose concentration obtained for Alexandrion drink was explained by the adding sugar in the technological process (specified on the label). The highest saccharose concentration was found in Courvoisier cognac, but it didn't knew the causes of this (are necessary further more investigations in this purpose).

The highest concentration of esters was determined in Vinars Miorita, a distilled drink obtained in a 12 years of ageing process. In case of younger distillates like Courvoisier cognac (obtained in a 2 years of ageing process) it's

registered a smaller concentration of esters (table 6).

**Table 6.** The values of esters concentrations in analyzed samples

Distilled drinks	Esters (mg ethyl acetate /100 ml ethylic alcohol anhydrous)
Alcoholic drink Alexandrion	16.22
Vinars MIORIȚA	224.03
Courvoisier cognac	72.6

Also, it's have to considered that in case of younger distillates was added a higher quantity of aroma waters because it suffered lower decreases of ethylic alcohol concentration. In this way the content of esters is lower.

In Alexandrion drink was determined the lowest concentration of esters due to the composition of this distilled drink (a small proportion of old distilled wine in comparison with water and alcohol, saccharose, aroma, dyes).

On the other hand the esters content of distilled drinks depends on the distillation installation. For example the concentrations of esters increases when distillation was accomplished in discontinuous flow installations. In this case was observed that the reciprocal action of acids and alcohols was strong, there were higher contact times and higher temperatures.

The predominant aldehyde in freshly distilled drinks is acetaldehyde and it's contribution to organoleptic quality has been investigated intensively [13]. Among acetaldehyde, the main aldehydes identified were: acrolein (which is known to given an unpleasant pungent odor), 2,3-butanedione with a buttery aroma and also furfural. According to the literature aldehydes showed low concentrations in distilled drinks and this can be observed also from table 7. Nevertheless, due to their low content in distillates, they can produce an important olfactive impact [14].

Aldehydes were found in distillation fraction called "head" which comprehend almost of the volatile substances. Another part of the present aldehyde in the distilled drinks was formed during the ageing process. During this process the lignin from the oak wood was soluble in the alcoholic

medium, but in acid medium this compound was decomposed in some compounds which by oxidation leads to the formation of aldehydes.

**Table 7.** The values of aldehydes concentrations in analyzed samples

Distilled drinks	Aldehydes (mg acetic aldehyde/100 ml ethylic alcohol anhydrous)
Alcoholic drink Alexandrion	3.3
Vinars MIORIȚA	7.2
Courvoisier cognac	4.6

So, the higher content present in Vinars Miorita can be explained by the ageing process during the 12 years. Courvoisier cognac is a younger distillate, with an ageing period about 2 years and Alexandrion drink is a mixture of distillate, water and alcohol. Because of this the aldehyde concentration in this two samples are lower.

Higher superior alcohols concentrations were detected for the two natural distilled drinks: Vinars Miorita and Courvoisier cognac (see table 8).

**Table 8.** The values of superior alcohols concentrations in analyzed samples

Distilled drinks	Superior alcohols (mg /100 ml ethylic alcohol anhydrous)
Alcoholic drink Alexandrion	321.4
Vinars MIORIȚA	646.8
Courvoisier cognac	701.6

Cognac is a younger distillate but the higher content of superior alcohols may be due to more adding of aroma waters in the correction process of alcoholic concentration.

#### 4. Conclusions

The goal of the study was to characterize three distilled drinks: Vinars Miorita (old distilled wine), Courvoisier cognac (young distilled wine) and alcoholic drink Alexandrion (a mixture obtained from a distilled wine with ethylic alcohol, water, sugar, aroma and dyestuff) in the context of ageing process.

The analytical characterization was offered a promising approach for the classification of these three drinks by the content in distilled wines. This study shows that the Vinars Miorita and Courvoisier cognac can be discriminated from the alcoholic drink Alexandrion using the differences between the obtained results for these distilled drinks. Also, the lack of furfural in alcoholic drink Alexandrion goes to the conclusion that the rate of distilled wine used to obtain this drink is very low. This hypothesis is maintained by the lowest value of total acidity registered for Alexandrion drink. Moreover, for the two natural distilled drinks were detected higher concentrations of esters, aldehydes, superior alcohols.

#### 5. References

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