DETERMINIG THE OPTIMAL METHODES OF DETECTING COUNTERFEIT WINES BY ADDING SUGAR AND SYNTHESIS SWEETENERS

STABILIREA METODELOR OPTIME DE DEPISTARE A VINURILOR FALSIFICATE PRIN ADAOS DE ZAHAR ŞI ÎNDULCITORI SINTETICI

RANCA Aurora[1], ARTEM Victoria[1], AISEL Galip[1]
SAVIN C.[2], VASILE Ancuța[2], PASA Rodica[2]
[1]Station for Research and Development for Viticulture and Vinification of Murfatlar,
[2]Station for Research and Development for Viticulture and Vinification of Iaşi

Abstract. *Experiments were made on witness wines, representative for each vineyard Murfatlar and Iaşi and wines purchased from the internal market for the detection of counterfeits (the addition of sugar in grape must and the addition of synthetic sweeteners). For the detection of added sugar beyond the limits permitted by law were used several processes: establishment of the alcohol /nonreduced extract report, establishment of the glycerol /alcohol, determining the polarimetric deviation, detection of natural sweeteners by chromatographic methods and detection of chaptalisation by isotopic analysis. Oenological reports alcohol /extract and glycerol /alcohol can indicate if the wine was made from must with added sugar or wine was fortified. The thin-layer chromatography method detects the natural sweeteners used, but it is difficult to assess the quantity and their origin. The* $^{13}C/^{12}C$ *isotope ratio gives useful indications for tracing the origin of ethanol in wine depending on the type and amount of sugar that has undergone fermentation. The thin-layer chromatography can detect exactly if the wine was treated with synthetic sweeteners.*

Key words: chaptalisation, synthetic sweeteners, chromatography

Rezumat. *Experimentele au fost făcute pe vinuri martor reprezentative pentru podgoriile Murfatlar şi Iaşi şi vinuri achiziționate de pe piața internă pentru depistarea falsurilor (adaos de zahăr în must şi adaosul de îndulcitori sintetici). Pentru depistarea adaosului de zahăr în must s-au folosit mai multe procedee: stabilirea raportului alcool/extract nereducător, stabilirea raportului glicerol/alcool, determinarea deviației polarimetrice, depistarea îndulcitorilor naturali prin metode cromatografice şi detectarea şaptalizării prin analize izotopice. Rapoartele oenologice alcool/extract şi glicerol/alcool ne pot indica dacă vinul a fost obținut din must cu adaos de zahăr sau vinul a fost alcoolizat. Metoda cromatografică în strat subțire depistează îndulcitorii naturali utilizați, dar este dificil de apreciat cantitatea şi originea acestora. Raportul izotopic* $^{13}C/^{12}C$ *dă indicații utile pentru depistarea originii etanolului din vin în funcție de tipul şi cantitatea de zahăr care a fost supusă fermentării. Prin cromatografia în strat subțire se poate detecta cu exactitate dacă vinul a fost tratat cu îndulcitori sintetici.*

Cuvinte cheie: şaptalizare, îndulcitori sintetici, cromatografie

INTRODUCTION

Wine is a beverage resulting exclusively from complete or partial alcoholic fermentation of fresh grapes or of grape must. The main attributes of quality wines are

their naturalness and authenticity. The addition of sugar to grape must is to increase the alcoholic concentration of wine operation known as chaptalisation. According to the regulations of Vine and Wine Law, by sugar addition in must aim to raise the alcoholic degree of wines equivalent of more than 2% alcohol. Authentic wines are characterized by a harmony of their chemical composition, naturally, any intervention which would alter the natural intrinsic composition of the wine is not allowed.

MATERIAL AND METHOD

Experiments were made on witness wines, representative for Murfatlar and Iasi vineyards and existing wines on the internal market for the detection of counterfeits (the addition of sugar in grape must and the addition of synthetic sweeteners. Wines were analyzed in terms of physico-chemical and organoleptic, using international analytical methods (OIV) and the existing STAS. For detection of added sugar in the must were used several processes: establishment of the alcohol /nonreduced extract report, establishment of the glycerol /alcohol, determining the polarimetric deviation. The detection of natural sweeteners was made by chromatographic methods and the detection of chaptalisation by isotopic analysis. The $^{13}C/^{12}C$ isotope ratio was determined at the National Institute of Research and Development for Cryogenics and Isotopic Technologies Ramnicu-Valcea.

RESULTS AND DISCUSSIONS

Witness wines have a normal composition, representative for each vineyard it comes from. Samples purchased in commerce, are table wines bottled in PET of 2 litres, bulk and DOC wines, bottled in 0.75 litre bottles. Samples of witness wine and those purchased from the market were analyzed in terms of physico-chemical and sensory, analytical results are presented in tables 1 and 2. The analyses showed that wines of DOC category fit into the physico-chemical characteristics of natural wines. Samples of bulk or bottled table wine, despite having the chemical parameters characteristic to natural wines, were disqualified at tasting receiving weak notations because mostly were thin, oxidized, stained and with odour defect, without typical.

The influence of chaptalisation on wine composition is manifested in particular by raising the alcoholic degree, slight decrease of total acidity, a slight increase of glycerol and of non-reduced extract. For the control of added sugar in the grape must were used the following methods:

Determination the report of total alcohol / non-reduced extract

The addition of sugar before fermentation produces an increase of this report, which is never proportional to the increase in alcoholic strength. Sugar gives with alcohol glycerol, succinic acid and other extractive materials that come to increase the wine extract. The report total alcohol/nonreduced extract increases even at the addition of alcohol in wine. Values of this report for the white wine purchased from the internal market ranges between 4,64 (white table wine, semidry, bottle 1,5 l) and 5,99 (table wine, semidry, PET 2 l). The average value of this report, subject to an alcohol concentration between 8,5-15% volume for natural wines is 4,3 for white wines and 3,6 for red wines**,** with the upper limit 6,5, 4,6 respectively. Maximum values or higher of these limits indicate the addition of sugar or alcohol in wine.

Table 1

Compositional characteristics of witness wines and those existing on the internal market - SCDVV MURFATLAR

Wine type	Alcohol vol. %	Total alcohol vol. %	Total acidity g/L H_2SO_4	Volatile acidity g/L H_2SO_4	Fix acidity g/L H_2SO_4	Density g/ml	Nonreduced extract g/L	Reduced sugar g/L	Ash g/L	Glycerol g/L	SO_2 total mg/L	SO_2 free mg/L	Tasting mark	Alcohol/ EN	Glycerol/EN
Pinot gris DOC-witness	12,4	12,54	3,84	0,39	3,45	0,9921	23,1	2,4	2,02	7,6	29,2	156,0	Very good	4,30	7,63
Table wine semidry white PET 2 L,	12,1	12,73	3,33	0,60	2,73	0,9931	17,0	10,8	1,69	7,1	98,4	24,6	Good	5,99	7,33
Table wine semisweet white, PET 2L	9,1	9,82	2,56	0,69	1,87	0,9971	16,2	12,3	1,48	6,3	113,6	31,9	Mediocre	4,84	8,65
Table wine semidry white, PET 2L	10,5	12,06	3,53	0,56	2,97	1,0014	17,3	26,6	1,60	7,9	93,4	22,1	Stained, mediocre	5,57	9,40
Table wine semidry white aromatic, PET 2L	9,8	10,97	3,33	0,82	2,51	1,0005	19,3	19,9	1,64	5,7	132,8	29,5	Stained, no aroma, mediocre	4,54	7,22
Table wine semisweet, red PET 2L	10,6	11,67	3,79	0,80	2,99	1,0028	22,8	18,3	1,79	7,1	120,5	39,3	Poor, colored, mediocre	4,09	8,37
Table wine semidry white	11,5	12,14	3,74	0,39	3,35	0,9947	18,7	11,0	1,71	7,8	125,4	24,6	Acceptable	5,19	8,47
Table wine semidry white, 1,5 L bottle	11,3	11,9	3,87	0,56	3,31	0,9953	20,5	10,2	1,9	6,7	119,2	17,2	Satisfactory	4,64	7,41

Table 2

Composition characteristics of wines purchased from the market SCDVV IAŞI

Wine type	Alcohol vol. %	Total acidity g/L H_2SO_4	Volatile acidity g/L H_2SO_4	Nonreduced extract g/L	Sugar g/L	SO_2 free mg/L	SO_2 total, mg/L	Glycerol, g/L	Ash g/L	Politeness, g/L	Dry matters, g/L	Colour	Density	Tasting mark
White wine DOC-CMD- Fetească albă semisweet 11,0 % vol.	12,6	3,6	0,44	23,2	21,0	20	160	11,0	1,56	0,117	43,0	0,099	1,0073	Very good
White wine DOC-CMD- Muscat Ottonel semisweet11,5 % vol.	11,4	4,2	0,45	23,9	11,8	22	128	8,3	2,18	0,237	34,4	0,191	0,9975	Very good
White wine DOC-CMD- Muscat Ottonel semisweet 12,0 % vol.	12,0	3,8	0,48	24,6	31,5	16	130	7,47	2,11	0,165	54,9	0,107	1,0041	Good
White wine DOC-CMD- Grasă de Cotnari 12,0 % vol.	11,3	3,5	0,54	21,8	40,0	14	146	7,70	1,92	0,277	59,8	0,203	1,0073	Very good
White wine, bulk, semisweet	9,5	3,4	0,71	22,8	31,3	-	56	7,36	1,92	0,177	49,2	0,108	1,0062	Mediocre
White wine, bulk, semisweet	9,4	3,4	0,42	19,6	9,8	27	129	5,75	1,70	0,449	25,1	0,228	0,9910	Good
Red wine, bulk, semisweet	11,1	3,2	0,72	22,2	19,4	7	46	6,44	2,11	0,834	38,44	1,350	0,994	Mediocre
White wine semisweet 9,0 vol.	9,0	2,4	0,57	20,8	9,8	30	76	7,13	1,63	0,086	30,34	0,053	0,9982	Acceptable

Analyzing the report of total alcohol / nonreduced extract at the studied samples we note that their values exceed the permissible average. The distinction between added sugar and fortification is generally difficult to establish with this report especially if the wine contains no sugar. To determine if there is added sugar no alcohol we determined and the ratio glycerol / alcohol.

Establishment the report of glycerol / alcohol

Between glycerol content and alcoholic degree of wines there is a linear correlation: glycerol content increases with increasing alcohol. The report of glycerol / alcohol for wines which have suffered the addition of sugar is always higher than 7. Ratio values for the studied wines are between 7,22-9,40, these values indicate a presumption of sugar addition in the grape must and ratio values around the figure 6 shows the addition of alcohol in wine. The influence of chaptalisation is easily found when the chemical composition of wine is known and difficult for an unknown wine, because sometimes the values of the chemical constants of falsified wine are very close to those of natural wine.

Determination of wines polarimetric deviation

Natural wine, with no added sugar, always presents a negative value of polarimetric deviation due to fructose. Use of this report is based on the fact that in the grape must, the glucose and fructose content is almost equal (G / F approximately 1), which corresponds to a P / α, of -5,1 at 20 ° C. During alcoholic fermentation yeast consumes priority sugar and therefore at the end of fermentation P / α report will be smaller. The addition of sugar during fermentation does not change too much the value of the report and can not be detected by calculating of this report when the wine is dry. Analyzing the data in table no. 3 we note that there are not very large deviations of the P / α report thereof we are unable to draw a clear conclusion on the intervention of sugar to obtain these wines. The report of P/α can be considered as an aid in determining a wine naturalness with other determinations but can not be regarded as an absolutely safe way to detect an unsupported intervention with sugar.

Table 3

The report of P/α at studied wines

No	Type of wine	Report of P/α
1	Pinot gris DOC-witness	-1,70
2	Table wine, white, semidry alb , PET 2 L,	-2,14
3	Table wine, white ,semisweet, PET 2L	-2,28
4	Table wine, white ,semisweet , PET 2L	-2,72
5	Table wine, white ,semisweet, flavoured, PET 2L	-2,67
6	Table wine, red ,semisweet, PET 2L	-2,81
7	Table wine, white ,semidry	-3,05
8	Table wine, white ,semidry, bottle1,5 L	-3,81

Detection of chaptalised wine through isotopic analyses

Deuterium atoms contained in the sugar from the grape must, will be redistributed after the alcoholic fermentation, in the alcohol molecules of wine. By the addition of exogenous sugar in the grape must, the deuterium content increases, which affect the redistribution of deuterium in the alcohol molecules which are formed in wine. Based on the deuterium content and the isotope ratio D/H we can determine the

nature of alcohol in wine. Sugar addition in the grape must leads to a displacement of the value $^{13}C/^{12}C$ of the isotopic report of ethanol resulted by his fermentation. Degree of differentiation depends on the amount of added sugar, but also the source of sugar used. Parallel use of ratio D/H of ethanol allows a more reliable identification of chaptalisation. Both D and ^{18}O are measured by mass spectrometric method from the water remaining after the distillation of wine. ^{13}C is measured from the ethanol obtained by distilling the wine after it is subjected to the process of combustion in excess of oxygen to get CO_2, on which is determinate the ^{13}C by mass spectrometry compared to a standard report. In the process of photosynthesis, the CO_2 assimilation by plants occurs through two metabolic processes: metabolism C_3 (Calvin cycle) and C_4 metabolism (Hatch and Slach cycle). These two types of metabolism produce different carbon isotopic fractionations of the CO_2 used by plants in the process of photosynthesis. Products resulting from the metabolism of C_4, such as sugars and alcohol derived from fermentation, have higher concentrations of ^{13}C than similar products resulting from plants with C_3 metabolism. Data obtained from the ^{13}C measurement of ethanol in wine permit to detect the addition of sugar diverged from C_3 plants (sugar beet).

Table 4

Values of isotopic ratios in the witness wine and purchased from the market

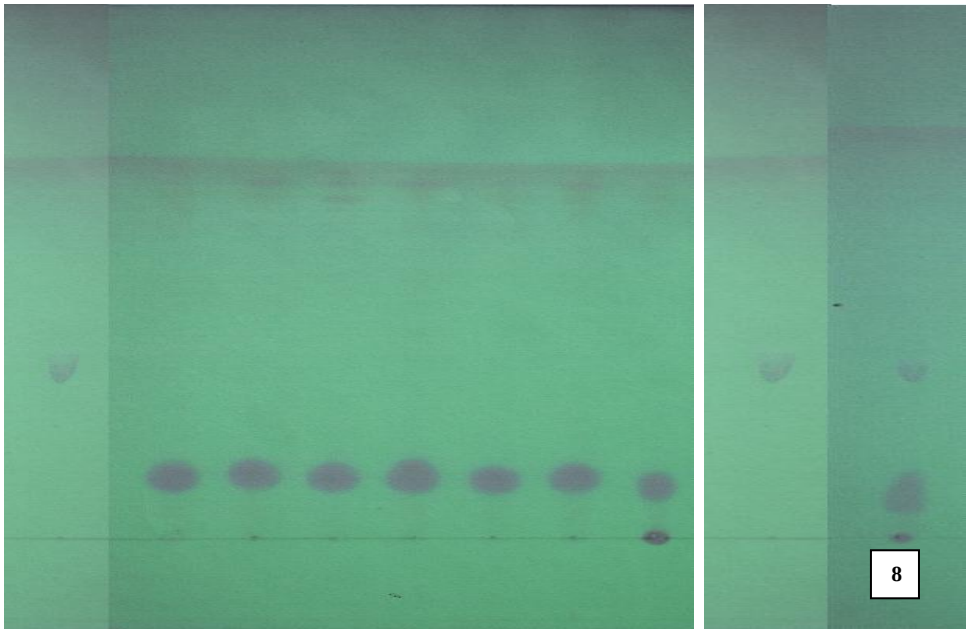
No.	Name of the sample	Concentration (D/H) of water extracted from wine (PPm)	$\delta^{18}O/^{16}O$ vs. SMOW of water extracted from wine (‰)	$\delta^{13}C/^{12}C$ vs. PDB of alcohol extracted from wine (‰)
1.	White wine DOC witness	154	1,05	- 23,52
2.	White wine PET 2 L	146	- 8,67	-24,36
3.	Water	141	- 9,98	-
4.	Absolute ethanol	-	-	- 24

Where, the standard used for both $^{13}O/^{12}O$ and $^{2}H/^{1}H$ is V-SMOW (Vienna - Standard Ocean Water), is provided by AIEA Vienna and characterized by isotope ratio of $^{2}H/^{1}H$ = 155,76 x10-6, respectively $^{18}O/^{16}O$ =2005,2 x 10^{-6}. The international standard for $^{13}C/^{12}C$ was defined by PDB ($^{13}C/^{12}C$ =11237,2 x 10^{-6}), a calcium carbonate from the Pee Dee Belmnite area (South Carolina, USA). Isotopic analysis of this sample confirms that the addition of sugar to the grape must led to a shift of the isotope ratio value $^{13}C/^{12}C$ of the ethanol resulted through its fermentation.

Detection of synthetic sweeteners

Synthetic sweeteners are food additives with a high sweetening power. These substances are used for fraudulent imitation of sweet wines and to mask a high acidity. In both cases, the action is a **forgery** and the identification of these substances is necessary. The Vine and Wine Law does not admit any such synthetic sweetener in wine. In most cases, when the synthetic sweetening substances are present in a relatively large proportion can be identified by tasting. Most used synthetic sweeteners are saccharin and sodium cyclamate. Chromatogram shows that the benzene extracts of the first 7 samples of wine in table no. 2 does not contain saccharin (fig. 1, a), sample no 8 show the synthetic sweetener saccharin (fig. 2, b). To achieve the goal of obtaining a semisweet wine, the forger probably used a dry wine to which added solution of

fructose and saccharin. In most cases the samples studied contained no synthetic sweeteners. With thin layer chromatography method can be accurately identified saccharine.



a. etalon 1 2 3 4 5 6 7 b. etalon 8

Fig. 1. a) The Chromatogram of benzene extracts obtained from samples of wine 1 - 7 compared with the saccharine etalon; **b)** The Chromatogram of benzene extracts obtained from sample of wine no 8 compared with the saccharine etalon

CONCLUSIONS

Oenological reports alcohol / extract and glycerol / alcohol can indicate if the wine was produced from must grape containing added sugar or the wine has been fortified.

The thin layer chromatography method detects natural sweeteners, but is difficult to assess the quantity and origin.

The $^{13}C/^{12}C$ isotope ratio gives useful information for tracing the origin of ethanol in wine depending on the type and quantity of sugar that has undergone fermentation.

REFERENCES

1. **Mihalca Al., Iancu Gh., 2002** - *Mustul şi vinul în legislație.* Editura Gutemberg, Arad;
2. **Ribereau-Gayon J., Peynaud E., Sudraud P., Ribereau-Gayon P., 1976 -** *Traité d'œnologie-Sciences et techniques du vin*. Vol 1, Editura Dunod, Bordas Paris.
3. **Țârdea C., 2007 -** *Chimia şi analiza vinului.* Editura Ion Ionescu de la Brad Iaşi.
4. **OIV, 2005**-*Recueil des methodes internationales d'analyse des vins et des mouts*, vol 1.