STUDY OF VOLATILE COMPOUNDS IDENTIFIED BY HEAD-SPACE METHOD IN BĂBEASCĂ NEAGRĂ ROSE WINES OBTAINED BY DIFFERENT PREFERMENTATIVE MACERATION PERIODS

STUDII PRIVIND COMPUȘII VOLATILI IDENTIFICAȚI PRIN METODA HEAD-SPACE ÎN VINURILE ROZE DIN SOIUL BĂBEASCĂ NEAGRĂ OBȚINUTE PRIN DIFERITE PERIOADE DE MACERAȚIE PREFERMENTATIVĂ

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Abstract. *This study reveals the content in volatile compounds of rosé wines obtained by different prefermentative maceration periods of Băbească neagră (Vitis Vinifera L.) native grape varieties in Romania, using GC-MS SHIMADZU 2010 through Head-Space method. Prefermentative maceration process was conducted in eight styles of Băbească neagră grape variety; first one without maceration representing the control sample and the others was subjected to the maceration process for the following seven periods of time: 3 and a half hours, 7 hours, 10 and a half hours, 14 hours, 17 and a half hours, 21 hours and 24 and a half hours. Prefermentative maceration process exerts a significant influence on the amount of volatile compounds. We observed a decrease of volatile compounds content along with using longer prefermentative maceration periods. This study represents a beginning in the influence assessment of the prefermentative maceration process to the volatile compounds content in Băbească neagră rosé wine.*

Key words*: volatile compounds, prefermentative maceration, Băbească neagră, rose wine.*

Rezumat: *Studiul de față relevă conținutul în compuși volatili a vinurilor rose obținute prin diferite perioade de macerație prefermentativă din soiul tradițional românesc, Băbească neagră (Vitis Vinifera L.), utilizând GC-MS SHIMADZU 2010 prin metoda Head-Space. La soiul Băbească neagră s-au realizat opt variante de macerare prefermentativă, prima varianta reprezentând martorul, căreia nu i s-a aplicat procedeul de macerație prefermentativă, iar celelalte șapte variante au fost supuse acestui proces pentru următoarele perioade de timp: 3 ore și jumătate, 7 ore, 10 ore și jumătate, 14 ore, 17 ore și jumătate, 21 ore și 24 ore și jumătate. Procesul de maceratie prefermentativă exercită o influență semnificativă asupra cantității de compuși volatili. Se observă o diminuare a cantității de compuși volatili odată cu folosirea unor perioade mai mari de macerație prefermentativă. Acest studiu reprezintă un început în ceea ce privește evaluarea influenței procesului de macerație prefermentativă asupra conținutului în compuși volatili din vinurile roze de Băbească neagră.*

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***Cuvinte cheie**: compuși volatili, macerație prefermentativă, Băbească neagră, vin roze.*

INTRODUCTION

Băbească neagră is a Romanian local red variety of *Vitis silvestris*, which acquires its superior quality in the Moldavian vineyards where wines with a protected geographic origin are produced. This grape variety is very important for production of high-quality rosé and red wines.

The volatile profile of wines is determined by the combined effects of hundreds of chemical compounds (Cabaroglu, 1997; Cotea, 1985; Cotea, 1988). The formation of the aroma bouquet depends on many factors that are dependent on the cultural conditions of the vineyard but also on the production technologies, fermentation conditions and aging of the wine (Marais, 1988; Günata, 1993).

This study is focused especially on the firts part of the wine-making process – prefermentative maceration. The conditions of prefermentative maceration process to the grape varieties influence the content of volatile compounds, because the total concentration and composition of volatile compounds exerts significant influences to the senzorial profile of the wines.

MATERIAL AND METHOD

The experiments were done during September 2012 – November 2012, at the Oenology Laboratory of the University of Agricultural Studies and Veterinary Medicine "Ion Ionescu de la Brad" Iasi.

In view of the study has been used a quantity of 1200 kg of grapes from Băbească neagră (*Vitis vinifera* L.) autochthonous grape varieties, harvested on September 29, 2012 from Iaşi vineyard, Bucium wine center. After conducting qualitative and quantitative receipt of grapes, they were desteeming not crushing, and then the whole mass of the resulting mark was divided into eight experimental variants that are identical in terms of quantity and quality, without adding oenological extraction enzymes or sulfur dioxide.

Băbească neagră 0 h (BN-0 h). In this variant, the must was pulled from the mass of the mark through the gravitational drainage without pressing pulp, immediately after getting it. The must obtained was passed quantitatively in glass containers (demijohns 50 L) and it was added activators for fermentation Nutristart type at a measure of 30 g/hL, selected yeasts species Saccharomyces cerevisiae RX 60 from Laffort® at a measure of 25 g/hL according to the protocols prescribed by the manufacturer.

Băbească neagră - the other seven variants (BN-3½ h; BN-7 h; BN-10½ h; BN-14 h; BN-17½ h; BN-21 h and BN-24½ h). All these seven variants run a prefermentative maceration process for the following periods of time: 3 and a half hours, 7 hours, 10 and a half hours, 14 hours, 17 and a half hours, 21 hours and 24 and a half hours, each time interval corresponding to a variant. The must was subsequently subjected to the same technological wine-making methods that were applied to variant 1 (BN-0.0 h).

To each variant, the mark was been vigorously homogenized for five minutes every hour throughout the prefermentative maceration process. After the finished of the alcoholic fermentation wines were pulled from yeast deposit, were not sulphited only filtered with 0.45 μm sterile membrane filters and bottled in 0.75 L wine glass bottle. The prefermentative maceration process and alcoholic fermentation took place at 10°C temperature in a room with controlled temperature. Wine bottles were stored in a cellar at a 12°C constant temperature.

After the alcoholic fermentation wines were analyzed in terms of physico-chemical characteristics: alcoholic strenght (% vol.), relative density at 20°C, pH, χ (mS/cm), total acidity (g/L $C_4H_6O_6$), reducing sugars (g/L), non reducing extract (g/L), total dry extract (g/L).

After two weeks, in November the volatile compounds were determined with a Shimadzu GC-MS QP 2010Plus using HeadSpace method. 1000 μL extract are injected into a Supelco SLB 5 ms GC column, of 15 m length, column oven temperature 30 °C, in splitless mode, initial temperature 30 °C for 5.75 minute, then it grows at a rate of 6°C until 80 °C where it stays for 0,5 minutes; then it grows at a rate of 10 °C until 200 °C where it stays for 0,2 minutes; then it grows at a rate of 14 °C until 245 °C where it stays for 1 minute. The program lasts for 31 minutes.

RESULTS AND DISCUSSIONS

After GC–MS analyses were identified the following volatile compounds (Fig.1):

- 2 methyl 1 propanol (isobutanol) is produced in wine during alcoholic fermentation ((CH3) $_2CHCH_2OH$) and gives wines their specific character;

- 3-methyl-1butanol (isoamilic alcohol – $C_5H_{12}O$) is a clear liquid, colorless and appears during the alcoholic fermentation;

- 3-methyl-1-butanol acetate (isoamyl acetate – $C_7H_{14}O_2$) is an ester, very inflammable and insoluble in water. It is produced in wine during alcoholic fermentation and it gives fermentation bouquet to the young wines. It gradually disappears during the aging period of wine;

- butanoic acid is produced during the alcoholic fermentation and, sometimes, under the action of microorganisms from *Acetobacter sp.;*

- **butiric acid** ($C_6H_{12}O_2$) is un oily liquid, colorless, slightly soluble in water, ethanol, ether. The smell of this acid is similar to rancid butter. (Cotea, 2009);

- **hexanoic acid** ($CH_3(CH_2)_3CH(C_2H_5)CO_2H$), is produced during the alcoholic fermentation;

- **octanoic acid** is produced during the alcoholic fermentation, is slightly soluble in water, with a smell and taste unpleasant of rancid;

- decanoic acid is produced during the alcoholic fermentation. It has a wax-like smell;

- propanoic acid ($C_5H_{10}O_2$) is a clear liquid, colorless, with a sweetish smell. It's soluble in water and alcohol; melts at -21°C, boils at 141° C. It has a acid fruits-like taste;

- **hydroxyacetic acid** hase a signal with a high area at variant 3 (B.N. 7.0 h) witch suggests its presence in the highest amount compared to other options. Hydroxyacetic acid is colorless and odorless;

- ethyl propionate ($C_2H_5(C_2H_5COO)$) is the ethylic ester of propionic acid. It has a pineapple-like aroma;

- **formic acid** (HCOOH or HCO_2H) called as metanoic acid, is the most simple carboxylic acid. In wine is formed by non-enzymatic oxidation of glyoxylic acid (HOOC-CHO). Bottled wines revealed a higher content of formic acid. It has a pungent odor. Participation of formic acid in volatile acidity of wine is poor, only 59% of existing formic acid in the wine is driven by distilled water vapors (Țârdea, 2007). Formic acid is a colorless liquid with a penetrating smell, very pungent at room temperature. It is miscible in water and polar organic solvents and is somewhat soluble in hydrocarbons;

- **heptane-2, 3-dione** (valeryle acetyl – $C_7H_{12}O_2$) is a clear liquid with a buttery smell, of fatty cheese;

- **izobutil acetate** is un ester of the acetic acid. It is produced following the esterfication of acetic acid and isobutanol. Like other esters it has a floral or fruit-like smell. In high concentrations isobutyl acetate has an unpleasant odor and can be harmful to health;

- **aspartic acid** is an amino acid ($HOOCCH(NH_2)CH_2COOH$). Aspartic acid plays a key role in the metabolism of other amino acids and biochemicals in the citric acid cycle. Among the biochemicals that are synthesized by aspartic acid are asparagine, arginine, lysine, methionine, threonine, isoleucine, and more. Aspartic acid also plays a vital role in energy production. Aspartic acid is similar to the taste of lemon. Figure 1 present the overlay of chromatograms of volatile compounds profile detected in Băbească neagră rosé wine.

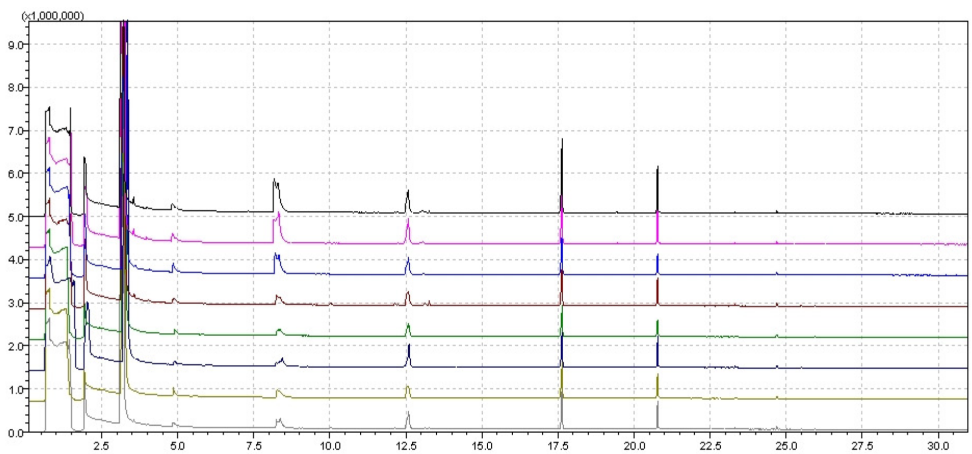

Fig. 1 - Chromatograms of volatile compounds profile detected in the studied wines.

It can be seen from table 1 a decrease in the content of volatile compounds on the extent of applying the prefermentative maceration operation. Therefore, isoamyl acetate, hexanoic acid, octanoic acid and decanoic acid are highest in the control sample, values that decrease with the prefermentative maceration application.

Table 1

Volatile compounds identified to all studied variants

Volatile compounds	BN 0.0 h		BN 3.5 h		BN 7.0 h		BN 10.5 h	
	Ret. time	Peak area	Ret. time	Peak area	Ret. time	Peak area	Ret. time	Peak area
2 methyl 1 propanol	1.95	11069	1.99	11720	1.92	15268	1.92	17904
3-methyl-1butanoll	3.20	51787	3.23	68756	3.28	57460	3.25	60712
3-methyl-1-butanol acetate	8.30	8001	8.32	5561	8.33	4024	8.25	1447
butanoic acid	4.81	2038	4.83	992	4.85	1231	4.88	677
hexanoic acid	12.58	4358	12.58	3572	12.58	2580	12.58	1422
octanoic acid	17.63	9191	17.63	5594	17.63	3376	17.63	3099
decanoic acid	20.77	3939	20.77	2222	20.78	1454	20.77	1440
	BN 14.0 h		**BN 17.5 h**		**BN 21.0 h**		**BN 24.5 h**	
	Ret. time	**Peak area**	**Ret. time**	**Peak area**	**Ret. time**	**Peak area**	**Ret. time**	**Peak area**
2 methyl 1 propanol	1.92	11282	2.03	22063	1.91	10171	1.94	6878
3-methyl-1butanoll	3.26	48458	3.35	74412	3.25	49706	3.21	57199
3-methyl-1-butanol acetate	8.37	1013	8.43	1002	8.26	1000	8.37	995
butanoic acid	4.89	630	4.90	443	4.85	832	4.88	343
hexanoic acid	12.55	973	12.60	921	12.57	899	12.59	867
octanoic acid	17.63	2486	17.64	2343	17.63	2180	17.63	1998
decanoic acid	20.77	1117	20.78	1090	20.78	1003	20.78	973

Ret. – retention time in minutes; Peak area – in thousands of mAU units.

CONCLUSIONS

1. This study is a step forward made in characterizing volatile profile of wines obtain from indigenous varieties of Babească neagră. Prefermentative maceration technology application and studying its effect on the volatile compounds of wines are new elements, both on the national and international plan.

2. The different technologies used to obtain this category if rose wines are able to provide assortment diversification and to ensuring constancy of quality.

3. Winemaking technology applied to obtain the 8 variants, has a influence on the major volatile compounds identified in the wines studied.

4. It is shown that Head-Space method, used in this study reveals less volatile componds than other methods used in gas chromatography.

5. Is observed a decrease in the content of volatile compounds by appling the prefermentative maceration treatment. Thus, most of the volatile compounds

found in wine present the highest values in the control sample, values that decrease with the prefermentative maceration application.

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