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INFLUENCE OF MACERATION DURATION ON VIORICA WINES QUALITY

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Abstract. The subject of the research refers to experimental wines obtained from local selection grape variety Viorica, which were macerated for 4, 8 or 12 hours at 10, 15 and 20 °C. The maceration duration had a positive influence on the general characteristics of the studied wines. The analysis of terpenic compounds by spectro-photometric method showed that increasing the contact time of the must with the solid phase from 4 to 8 hours increases by about 20 % the amount of free terpenes, while decreasing the amount of bound terpenes by 15 %. Once the duration is increased, the concentration of the non-reducing extract is also increased. Considering the increase in the intensity of the color and the REDOX potential with the duration of maceration, the macerated wines for 8 and 12 hours were defined as having oxidation notes with decrease of the sensory quality. Therefore, the maceration regimes for optimal extraction of terpenic compounds were concluded to be at the temperature of 15 °C for 4 hours, thereby increasing the aromatic potential of the local selection grape variety Viorica.

Keywords: *aroma, flavor, local selection variety, maceration, terpenes, wine.*

Introduction

The content of free and glycoside terpenes evidence obvious dynamic changes during the evolution of grapes berries. Knowledge about the bound and free volatile terpenes PVT/FVT ratio is very important for choosing the optimal regime for contact between the solid and liquid phases in order to improve the aromatic quality of wines [1].

High values of bound terpene content in juice and solid fraction are characteristic for several grape varieties, but, considering that they are hydrophilic, they do not essentially contribute to the aroma of the wine.

Therefore, the winemakers are interested in hydrolyzing these potential precursors for the release of volatile terpenes with floral aromas and enhancing the varietal aroma [2]. Depending on the content of free terpenes in the solid fraction, any extraction step during the winemaking process is beneficial in order to obtain a better quality of the wine's aroma.

Materials and methods

In order to carry out this study, the grapes of local selection grape variety *Viorica* were manually harvested from the plantations of the Scientific-Practical Institute of

Horticulture and Food Technologies from Chisinau and processed under micro-vinification conditions at the Technical University of Moldova.

In order to obtain information regarding the influence of the maceration duration and temperature on the content of terpenic compounds, the free and glycozidic monoterpenes were determined by the spectro-photometric method in nine experimental wine variants, by varying the maceration temperature and duration. All the variants were subject of sulfur dioxide addition in a concentration of 75-100 mg/dm^3 applied on marc when macerating, gravitational racking and sulphitation after the completion of alcoholic fermentation. The principle of the spectro-photometric determination method consists in separating the aromas by water vapor (distillation) and colorimetric determination of free volatile terpenic aromas (FVT) in neutral medium and bound as precursors (PVT) in acidic environment by colour reaction with sulfuric vanillin [3].

Shortly before the analysis, the grape berries were crushed and homogenized in 200 cm^3 phosphate buffer solution (pH 7,0) saturated with NaCl and stored at 4 °C. Subsequently the extracts were filtered and adjusted to pH 7,0 with 20% sodium hydroxide solution.

In order to determine the distribution of volatile monoterpenes in the solid and liquid fractions, the skin, pulp and seeds were manually removed. The pulp was homogenized and filtered to obtain the juice. The skins and the pulp residues were weighed and separately homogenized each in 200 cm^3 saturated phosphate buffer solution (pH 7,0) and stored for 3 and 6 days at 4 °C. Subsequently the extracts were filtered and adjusted to pH 7,0 with 20% sodium hydroxide solution. In steam distillation flask there was added 50 cm^3 of the sample, the pH of which was previously adjusted to 7,0 with 20% sodium hydroxide solution. The distillate was collected in a stoppered test tube, which was placed in an ice container. The distillation was stopped when collecting the volume 20 cm^3 of distillate containing FVT. Without being stopped vapor flow, the test tube was replaced with another stoppered test tube of the same volume. In the distillation flask was added 2.5 cm^3 of 20% orthophosphoric acid solution. The distillation was stopped upon accumulation of 20 cm^3 of distillate, which contained PVT.

In two stoppered test tubes (10 cm^3), there were taken 5 cm^3 of the first and the second distillates. The absorbances of the samples were related to the calibration curve and were established the concentrations in terpenic aromas expressed in mg/cm^3.

The content of FVT and PVT was calculated according to the Eq.(1):

$$\text{FVT or PVT} = a \times b/c \times d, \text{ (mg/dm}^3\text{)} \quad (1)$$

where: a - the concentration of linalool read on the calibration curve, mg/dm^3;

b - volume of distillate collected by distillation of samples, dm^3;

c - volume of must used for distillation, dm^3;

d - volume of aliquot used for spectro-photometric measurements, dm^3.

The sensory analysis was carried out with the participation of seven tasters, which were offered for tasting the wines obtained from the grapes fermented with three local selection yeast strains. Sensory evaluation was performed according to a 100 points scale (ISO 4121:2003) and a specially designed form to highlight aromatic characteristics of wines [4]. Tasters rated the wines with points after what an average score was obtained for each sample, including flavor descriptors. Sensory quality assessment based on the calculation of weighted average scores was performed according to Eq.(2).

$$S_{wa} = S_{unwa} \times f_w \quad (2)$$

where: S_{unwa} – unweighted average scores (the arithmetic mean of the results);

f_w – weighting factor.

The summation of the weighted average scores to obtain the total average score served to establish the organoleptic quality of the product [5].

Results and discussion

The content of free and bound monoterpenes reveals obvious dynamic changes during the evolution of grape berries. In the case of grape varieties for winemaking, the knowledge about the distribution in juice and skin, as well as the content of FVT and PVT, are very valuable for the application of contact treatments between the solid and liquid phase in order to optimize the aromatic quality of the wines [6].

Analyzing Figure 1, we see that the FVT and PVT contents in the Viorica variety averaged 0,02 and 0,37 mg/kg respectively. The distribution of FVT and PVT in juice, pulp and skin varies differently depending on the contact duration.

From Figure 1 we can observe important differences between the scores given for each characteristic, depending on the yeast strain used for fermentation.

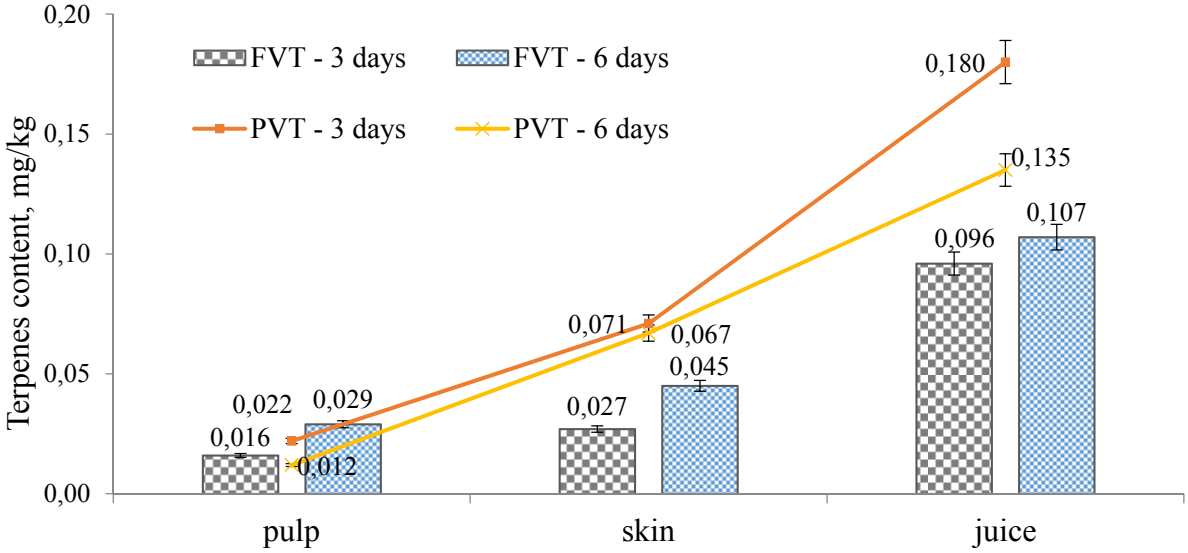


Figure 1. Distribution of FVT and PVT in different parts of Viorica variety grapes.

Also, from Figure 1, we observe a greater difference of the ratio PVT/FVT in the skin, both in the case of maintaining fractions for 3 days (2,63) and for 6 days (1,49), compared to the juice (1,88 – 3 days and 1,26 – 6 days) and pulp (1,07 – 3 days and 0, 41 – 6 days). From the presented data, we observe that there is a general tendency of increasing the content of free terpenes with the increase of the contact time for all three fractions, which denotes an inevitable hydrolysis of the glycosidic precursors in the grapes. Thus, the hydrolysis of bound terpenes and the subsequent release of free terpenes allows improving the quality of the varietal aroma of wines from the local grape variety Viorica.

The results obtained from this initial assessment of the volatile and potentially volatile terpenes content, as well as their distribution between the component parts of the grape berries of a local selection variety develop a particular interest for varietal white wine production in Republic of Moldova.

Considering the significant influence of the raw material characteristics for the final product, it is very important to determine the effects of maceration on the general

characteristics of the wine, which is expressed by: improving the extraction of the aroma precursors and the composition of the wines. In order to study how different factors such as temperature and maceration time are reflected on the physico-chemical and sensory composition of wines, the most important physico-chemical parameters have been determined (Table 1).

Analyzing the data in Table 1, it can be observed that maceration duration and temperature significantly influence some characteristic parameters of wines. First of all, there is a tendency to increase the total acidity of samples during the maceration due to the migration of the organic acids from the solid parts of the berries in the liquid phase, with the concomitant decrease of the pH. Some researchers believe that this is due to the extraction and solubilisation of tartrates from the berry skin [7].

Regarding the content of volatile acidity, it can be mentioned that it increases insignificantly with the increase of the maceration time. At the same time, with the increase of the maceration duration and temperature is observed the increase of the non-reducing dry extract concentration with up to 0,8 g/dm^3 compared to the initial version.

Table 1

Physico-chemical indices of *Viorica* variety dry white wines depending on the duration and temperature of maceration

Physico-chemical indices	V1	V2	V3	V4	V5	V6	V7	V8	V9
Alcohol, ± 0,1 % vol.	11,6	11,7	11,7	11,6	11,6	11,7	11,6	11,7	11,7
Titratable acidity, ± 0,08 g/dm^3	6,84	6,84	7,05	6,65	6,72	6,94	6,52	6,75	6,75
Volatile acidity, ± 0,04 g/dm^3	0,26	0,33	0,33	0,26	0,33	0,33	0,40	0,40	0,40
Non-reducing dry extract, ± 0,5 g/dm^3	17,1	17,3	17,4	17,4	17,6	17,7	17,6	17,7	17,9
pH , ± 0,01 units	3,08	3,02	2,95	3,16	3,11	3,07	3,18	3,15	3,09
REDOX potential, ± 10 mV	224	228	235	239	241	246	248	257	264
Organoleptic score, ± 0,1 points (out of 100)	76	77	80	79	81	81	80	79	78

Legend: V1 – t=10 °C and τ=4 h; **V2** – t=10 °C and τ=8 h; **V3** – t=10 °C and τ=12 h; **V4** – t=15 °C and τ=4 h; **V5** – t=15 °C and τ=8 h; **V6** – t=15 °C and τ=12 h; **V7** – t=20 °C and τ=4 h; **V8** – t=20 °C and τ=8 h; **V9** – t=20 °C and τ=12 h.

The REDOX potential has higher values (224–264 mV) as the contact time of the solid and liquid phase increases, but also in parallel with the increase of the maceration temperature. These results show that during the maceration takes place the extraction of polyphenolic compounds from the skin and pulp.

These results denote a larger polyphenol-oxidase enzymatic load of the *Viorica* variety, and the polyphenol compounds extracted during maceration show an increased

oxidation tendency. In this respect, researchers underline the action of polyphenol-oxidase on cinnamates (especially cinnamic tartrate), as the most important factor of browning [8].

These oscillations are due to the interaction of two interdependent phenomena: the extraction of polyphenols from the skin in the liquid phase (which leads to the tendency to browning) and the oxidation and polymerization reactions of these compounds (which, respectively, are manifested by their diminution). The preponderance of one mechanism or another depends largely on the concentration of oxygen dissolved in the must, the content of oxidase enzymes and temperature [9].

The influence of the maceration duration on the sensory analysis of the volatile aromatic complex of the studied wines is shown in Figure 2, from which we can observe greater values of the taste persistence, also of flavor and color intensity as the maceration duration increases. Thus, an increase of the taste persistence and color intensity is very important for all three maceration durations, which may be due to the increased accumulation of polyphenols and organic acids that takes place during this process.

Considering the increase of the color intensity and the REDOX potential with the maceration duration, the wines macerated for 8 and 12 hours were defined as having oxidation notes, the best results being obtained for 4 hours maceration.

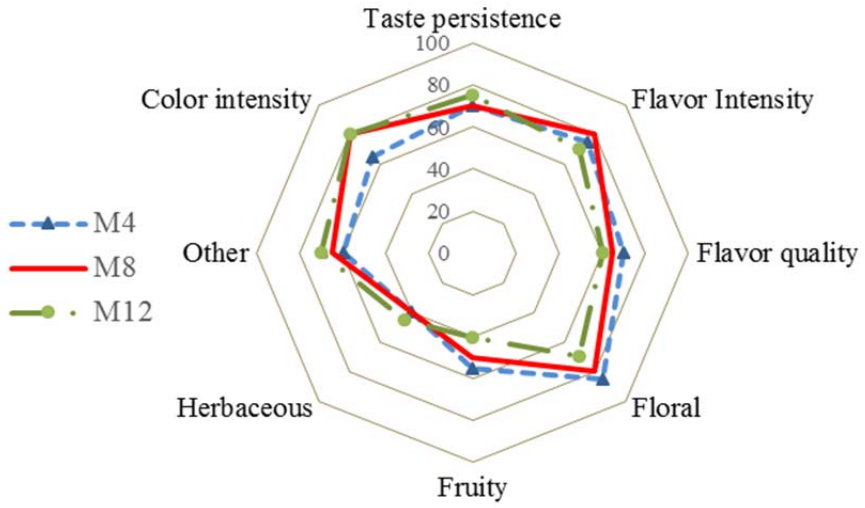


Figure 2. Sensory analysis of *Viorica* wines obtained through different maceration time (M4 – 4 hours; M8 – 8 hours; M12 – 12 hours) at the temperature of 15 °C.

Regarding the intensity and quality of the aroma, although there are clear differences in the aromas content depending on the maceration duration, the organoleptic assessment results showed significant differences, the 4 hours maceration reflecting higher values, also being characterized by notes of citrus, sage, basil, acacia and field flowers. In addition, the obtained wines are characterized by a balanced sensory profile with peaks oriented towards the class of floral aromas, which define the typicality of this variety [10].

The results obtained from the spectrophotometric analysis are indicated in Table 2, from which we can notice significant differences between the content of FVT and PVT depending on the maceration duration and temperature.

Table 2

Contents of free volatile terpene (FVT) and potentially volatile terpene (PVT) depending on the duration and temperature of maceration

Variants	**FVT**, μg/dm^3	**PVT**, μg/dm^3	**FVT/PVT**
V1	175,18	312,35	1,78
V2	191,62	310,42	1,62
V3	213,79	339,93	1,59
V4	203,45	346,68	1,15
V5	227,80	287,03	1,26
V6	209,58	346,85	1,66
V7	211,53	294,03	1,39
V8	294,28	338,42	1,24
V9	302,17	374,69	1,70

Legend: V1 – t=10 °C and τ=4 h; **V2** – t=10 °C and τ=8 h; **V3** – t=10 °C and τ=12 h; **V4** – t=15 °C and τ=4 h; **V5** – t=15 °C and τ=8 h; **V6** – t=15 °C and τ=12 h; **V7** – t=20 °C and τ=4 h; **V8** – t=20 °C and τ=8 h; **V9** – t=20 °C and τ=12 h.

This could be explained by the fact that the bound terpenes were hydrolyzed by the enzymes with β-glucosidase activity from the grapes and transformed into the free form.

From the results above we observe that increasing the contact time of must with the solid phase from 4 to 8 hours increases by about 20% the amount of free terpenes, while decreasing the amount of bound terpenes by 15%.

The lowest PVT/FVT ratio was recorded in the case of maceration at 15 °C for 4 hours – V4 (1,15) compared to the sample macerated 4 hours at 10 °C – V1 (1,78).

As well, we found that as the maceration temperature and duration increased, the amount of volatile terpenes increased and the content of precursors decreased.

However, in the case of maceration at 15 °C for 8 hours a decrease of the PVT/FVT ratio is observed by 25 % compared to the maceration for 4 hours, and when maceration took 12 hours there is a 31 % increase compared to the sample macerated for 8 hours, meaning that the optimal extraction duration of volatile terpenic compounds is 8 hours.

Considering that terpenic glycosides are a non-volatile form of terpenes, which are considered to be the aromatic potential from which, by enzymatic or acidic hydrolysis, volatile terpenic fractions are released, increasing the precursors form of the terpenes content is very important [11].

This could explain the fact that the wines obtained by must maceration have an extended duration of preservation of the organoleptic quality, especially maintaining the specific varietal aroma.

The conditions for optimizing the production of wines with a high content in terpenic compounds were statistically processed by a factorial analysis using the response surface method. The results that were obtained and detailed above revealed that the most relevant variables with direct effect on the FVT and PVT content in the wines were the temperature (X_1) and the maceration duration (X_2).

In order to determine the coeficients of regression equation it was used the partial least squares method [12].

The equation Eq.(3) describes the polynomial square with two factors model:

$$Y = a + b \cdot X_1 + c \cdot X_2 + d \cdot X_{12} + e \cdot X_{22} + f \cdot X_1 \cdot X_2 \quad (3)$$

The response surface model was created with the MathCad program, which used the Central Composite Design type: 2 factors, 2 levels (+1, -1), 1 central point, 1 block (one experiment series).

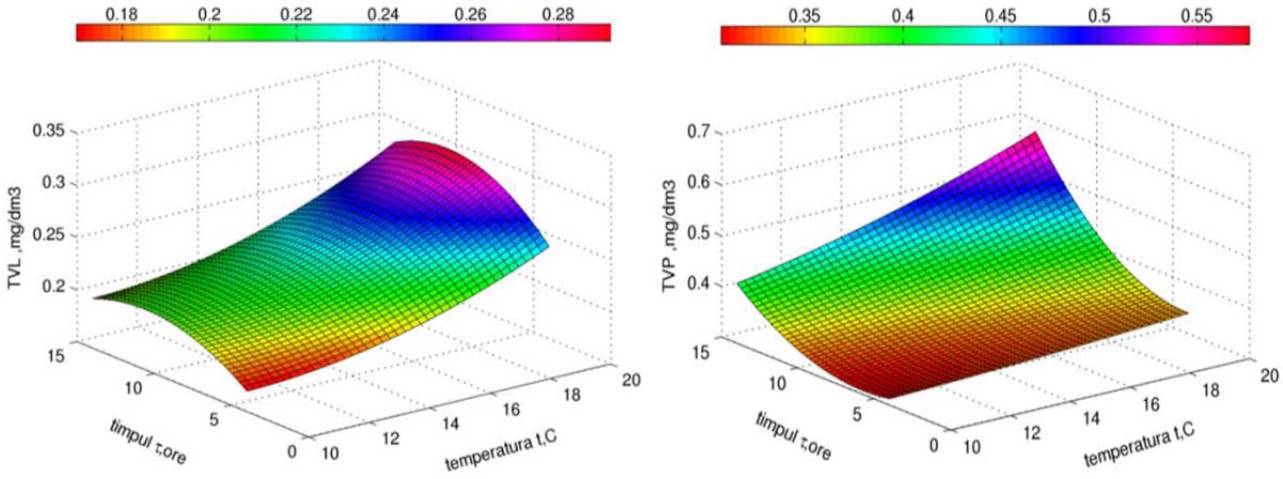
The mathematical models correspond to a second degree polynomial equation.

The graphs of tridimensional response surface (Figure 3 a,b) are the graphic representation of the interaction between the two selected factors (temperature and duration) in order to determine the optimal concentration and further to reach the maximum concentration of free or bound volatile terpenic aromas for the local selection grape variety *Viorica*.

From Figure 3(a) we can note that the maximum of free terpenes extraction is at 15 ^{o}C in the interval of 8 – 12 hours.

The comparison between the experimental content of terpenes and the content predicted by the regression model imply that it can be used for future prediction of the Y response values (free and bound terpenes content) corresponding to particular values of regression variables.

Thus, the estimated mathematical model is relevant and the data are significant and reproducible.



a) b)

Figure 3. Response surface describing the variation of FVT (a) and PVT (b) content for the *Viorica* variety wines depending on temperature and duration.

Conclusions

Following the study, it can be mentioned that the maceration has a positive influence on the general characteristics of the wines obtained from local selection grapes *Viorica*.

According to these results, the maceration with extended duration does not lead to obvious improvements, observing a diminution of the sensory quality with the increase of the maceration duration (8 and 12 hours), being recommended a short maceration for 4 hours.

When the maceration temperature rises from 10 °C to 15 °C there is an essential leap in the content of volatile terpenes by 58 % and by 53 % for bound form. It was established that increasing the contact time of the must with the solid phase from 4 to 8 hours increases by about 20 % the amount of free terpenes, while decreasing the amount of bound terpenes by 15 %.

The maceration regimes for optimal extraction of terpenic compounds were concluded to be at the temperature of 15 °C for 4 hours, thereby increasing the aromatic potential of local selection variety *Viorica*.

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