ABSTARCT

By knowing the fact that on an international level Romanian red wines enjoy a considerable attention, this study was initiated in order to know the possibilities of obtaining in Iaşi vineyard quality red wines from Fetească neagră, Merlot and Cabernet Sauvignon grape varieties, according to the variety potential and the phenolic compound extraction technique from grape skins.

As the ecological and climate conditions directly influence the quality of raw matter, research on grapes was conducted, by tracing the evolution of sugars' content, acids, anthocyans, polyphenolic index and anthocyans profile during maturation, thus establishing the moment of technological maturity, harvest date and also the characteristics of raw matter used in wine production.

At harvest, grapes contained 195 – 225 g/L sugars, 8,2 – 10,9 g/L $C_4H_6O_6$ total acidity and a normal glucose-acidic index (20,7 – 25). The total anthocyan quantity varies according to variety between 35 – 45 mg/g skins; among those, free anthocyans (malvidin, delfinidin, petunidin, peonidin and cyanidin) represent 88 – 89% of the total quantity, while the acetylated forms of malvidin and peonidin only 11 – 12%, as these are formed mainly during alcoholic fermentation.

Red quality wines production depends on the composition of the raw matter and also on the extraction process of these components by the applied technology in the processing of grape and musts. For this purpose, methods of skin maceration- fermentation (classical and in rotating tanks), were experimented, and also other techniques like microwave maceration, thermomaceration, cryomaceration and ultrasound maceration. For every grape processing technique used on the three grape varieties used (Fetească neagră, Merlot and Cabernet Sauvignon), certain observations and research were conducted that refer to fundamental theoretical problems, to technological aspects and qualitative compositional characteristics of obtained wines.

Although the raw matter was homogenous, the quality and the wine composition were different, due to the used techniques. In order to register the obtained wines in different quality categories for every grape variety, harvest year and applied technology, the Wine and Vine Law no 244/2002, republished in 2007 in M.O. no. 633 of 14.08 was consulted. Through this law, the

distinct category of "wines with controlled origin denomination" (DOC) was maintained and, in regard to the maturation degree of the grapes at harvest, wines can be:

- wines with recognized geographical indication, also known as "superior wines" (VS) with a minimum of 10,5% vol. alcohol, 19 g/L non-reductive dry extract and a minimum of 4,5 g/L $C_4H_6O_6$ total acidity;
- wines with controlled origin denomination, obtained from grapes harvested at full maturity (DOC-CMD) with a minimum of 11% vol. alcohol, 23 g/L non-reductive dry extract and a minimum of 4,5 g/L $C_4H_6O_6$ total acidity;
- wines with controlled origin denomination obtained from grapes harvested late (DOC-CT) with a minimum of 11,5% alcohol, 23 g/L non-reductive dry extract and a minimum of 4,5 g/L $C_4H_6O_6$ total acidity (Axente D. ş. a., 2004).

For red wines, the coloring elements have the same degree of importance that determines the wine quality category, as well as the ones described above.

The obtained results have shown that in the years with less favorable climatic conditions for grape ripening, from Fetească neagră variety, wines can be obtained that can be registered in the DOC category only in the case of skin maceration-fermentation (F.N.-V1 and F.N.-V2) due to the normal content in extract, alcohol and acids; the other obtained wines contain less than 23 g/L non-reductive dry extract. In years with normal climatic conditions, the extract exceeds 23 g/L.

Even in the years with less favorable climatic conditions, from the Merlot grapes, quality wines were obtained, that meet the rules and regulations of the Vine and Wine Law no. 244/2002, excepting the wine samples processed through microwave maceration (M.-V3) and ultrasound maceration (M.-V6), that only have 21 – 22 g/L non-reductive dry extract; regarding the alcohol content, all experimental samples reached an alcoholic concentration of 11% and more. Due to the fact that the grapes had at harvest a total acidity of 8,2 g/L $C_4H_6O_6$ favorable conditions for the malolactic fermentation were created, conducted right after the end of the alcoholic fermentation, thus obtaining wines with a proper acidity. The total SO_2 varies between 68 and 106 mg/L, out of which 15 – 27 mg/L is found in free form, fact that confirms the statement that one can obtain superior quality red wines with low SO_2, content by applying an adequate technique. The wines obtained from Merlot grape variety are rich in glycerol (8 – 9 g/L), fact that favorably influences the organoleptical characteristics.

In favorable climatic conditions of grape ripening in 2009, the wines from Cabernet Sauvignon grapes were registered as dry, with an alcoholic concentration of 13 – 13,4%, rich in extract (25 – 28 g/L) and glycerol (8,7 – 10,2 g/L). Although the grapes had a high acidity (10,9 g/L $C_4H_6O_6$), the wines, after a malolactic fermentation and detartration, reached a proper

and pleasant acidity (6 – 6,5 g/L $C_4H_6O_6$). The volatile acidity was between 0,25 and 0,63 g/L CH_3COOH, indifferent of the grape variety. This characteristic indicates the health state of the wine and the possibility of a normal evolution. In order to use a as small as possible quantity of SO_2, the capacity of each wine of bounding sulphurous anhydride was determined, thus reaching 65 – 67 mg/L SO_2 total, out of which 20 – 25 mg/L free SO_2.

The dry extract is a criterion for appreciating the wines' authenticity and specificity. At Cabernet Sauvignon wines, it had values of 24,8 – 28,2 g/L; the most extractive wines were obtained through cryomaceration (28,2 g/L) and thermomaceration (27,8 g/L), followed by variants processed through skin maceration-fermentation (C.S.-V1 and C.S.-V2), that contain 26,6 g/L, respectively 27,3 g/L extract. For the other two studied grape varieties, the wines obtained by using these four techniques were remarkable due to their rich extract content. By creating conditions for the glycerol synthesis, wines with 8,5 – 10,2 g/L glycerol were obtained, component that has an important role in wines as it imprints a certain velvety finish, succeeding in diminishing the astringency that certain phenolic compounds have.

Besides the current analyses, certain specific analyses to red wines were conducted, that are of the same importance for establishing their authenticity and their registration in different quality levels; wine polyphenols are represented mainly by anthocyans and tannins with an important influence on the overall phenolic characteristics. The total polyphenolic value varies in regard to the maceration technology applied: at Fetească neagră, between 18,6 and 47,4, at Merlot between 17,8 and 45,6 and at Cabernet Sauvignon between 19,7 and 44,2. By using skin maceration fermentation techniques (V1 and V2) the most balanced values for this index were obtained. The total polyphenolic content expressed in g/L, has values between 2,18 – 2,75 g/L for Fetească neagră, 1,97 – 2,86 g/L for Merlot and 2,2 – 2,29 g/L for Cabernet Sauvignon when the wines have been obtained by maceration-fermentation (V1 and V2) and thermomaceration (V4). Ultrasound maceration did not favor the phenolic compound concentration from grape skins and the obtained wines have poor anthocyans and tannins concentration (0,94 – 1,1 g/L); these quantities are not sufficient to imprint wines with the specific characteristics of the variety.

The anthocyan content is different according to grape variety, harvest year and maceration technique used. The obtained results vary in a wide array between 112 mg/L (Fetească neagră), when the maceration process involved the use of ultrasounds, and 455 mg/L (Cabernet Sauvignon), when the wines were obtained through thermomaceration. V1 and V2 samples were characterized by normal values in the case of Fetească neagră (211 – 238 mg/L) and Merlot (301 mg/L), in the conditions of a less favorable climatic year. At Cabernet Sauvignon, the values for this parameter varied between 358 – 372 mg/L, thus insuring a variety and vineyard specific color to the wine. Good results were also obtained through microwave

maceration (V3), due to the anthocyans' extraction from skins to must being a lot faster in comparison with tannin extraction and because of this particularity, even by short maceration time, one can obtain highly colored wines. Through thermomaceration (V4), the total anthocyans content of wines is 290 mg/L at Merlot, 356 mg/L at Fetească neagră and 455 mg/L at Cabernet Sauvignon, normal quantities for insuring the necessary color for quality wines. By following the working conditions, thermomaceration at 70 °C for 30 minutes is recommended in the less favorable for grape maturation, thus obtaining balanced wines, with no undesired taste and smell. By cryomaceration (V5), a smaller quantity of anthocyans was extracted in comparison to the previous mentioned techniques (V1 – V4); even in the case of Cabernet Sauvignon, the anthocyans content was only 252 mg/L, insufficient in regard to the variety potential. Although the wine is balanced, extract rich, with high contents of glycerol and alcohol and specific taste to the variety, because of the poor color, the wine cannot be registered in the class "wines with controlled origin denomination". Ultrasound maceration (V6) did not favor anthocyans extraction from grape skins and the obtained wines contained between 112 – 127 mg/L anthocyans, quantity specific to *rosé* wines.

In the case of this study, the anthocyan profile of the wine was analyzed, expressing the percentage of free and acylated anthocyans that compose color. As during the wine-making and maturation processes the acylated anthocyans are more stable and resilient to condensation, for establishing the anthocyans profile, the sum of acetylated and cumarilated anthocyans' percentages and their ratio was calculated. These data can lead to verify the vine's origin and also confirm the authenticity, tipicity and specificity. The analyses were conducted through high performance liquid chromatography (HPLC), when the relative proportions of the following anthocyans were identified and quantified: delphinidin-3-monoglicoside (Dp), cyanidin-3-monoglicoside (Ci), petunidin-3-monoglicoside (Pt), peonidin-3-monoglicoside (Po), malvidin-3-monoglicoside (Mv), peonidin-3-monoglicoide-acetilate (Po-a), malvidin-3-monoglicoide-acetilate (Mv-a), peonidin-3-monoglicoide-cumarilate (Po-c) and malvidin-3-monoglicoide-cumarilate (Mv-c).

In regard to grape variety and maceration method used, the free anthocyans are found in wines in different percentages, varying between 86 – 94% for Fetească neagră, 77 – 91% for Merlot and 71 – 75% for Cabernet Sauvignon. In all analyzed wines, malvidin is found in the highest percentage (40 – 80%), followed by peonidin, petunidin and delphinidin at Fetească neagră and Merlot; at Cabernet Sauvignon, after malvidin, that represents 48 – 55%, in descending order are found petunidin, delphinidin and then peonidin. Regardless of grape variety and maceration conditions, cyanidin is found in the lowest proportions (0,2 – 3%).

The percentage of acylated anthocyans (acetylated and cumarilated) vary depending on the grape variety and the maceration technique. By interpreting these data, one can know the anthocyan fingerprint of wines. Although the sum of acetylated and cumarilated anthocyans vary with the maceration technology used, the obtained values are specific to every variety regardless of the technological technique used. For the Fetească neagră grape variety, this sum has the lowest values between 5,6 – 13,5%; for Merlot these values are between 8,8 – 22,7%, and at Cabernet Sauvignon – between 25,2 and 28,6%. The ratio between the acetylated and cumarilated anthocyans has a subunitary value at Fetească neagră (0,17 – 0,88), low values for Merlot (1,1 – 2,8) and high values at Cabernet Sauvignon (5,1 – 6,8). By calculating this data, one can know the grape variety used to produce the red wine.

From the ANOVA statistical analysis applied to the anthocyans profile of Fetească neagră and Merlot wines obtained in 2008 the following conclusions appear:

- The participation percentages of the free anthocyans from the wine profile are statistically influenced by the maceration techniques used for at least 95% coverage probability thus the anthocyans percentages of delfinidine-3-monoglicoide, peonidine-3-monoglicoide and malvidine-3-monoglicoide are significantly influenced and the participation percentage of cyanidine-3-monoglicoide is distinct significantly influenced with a 99% trust level. On petunidine-3-monoglicoside, the different maceration technologies had a significant influence, from a statistical point of view with a 99,9% coverage probability;
- The participation percentages of acylated anthocyans are not significantly influenced by the applied maceration technologies, except malvidine-3-monoglicoside cumarilated, where a statistical significant influence of the technological variants on the compound's proportion in the anthocyan profile was found;
- The participation percentages of the acetylated and cumarilated forms of peonidine-3-monoglicoside are not statistically significant influenced either by the differences between the grape varieties or by the differences of the technological variants of maceration;
- The statistical analysis of the sum of acetylated and cumarilated anthocyans and their ratio confirmed the fact that these two values are dependent on the grape variety used for winemaking, representing an index of wine's authenticity and tipicity. Therefore, the ANOVA test showed that both the sum of the participation percentages of acetylated anthocyans as well as the ratio of these percentages are statistically significantly influenced by the differences between the grape varieties, with an at least 95% coverage probability. On the other hand, these two parameters were not statistically influenced by the maceration variants used.

The multivariable statistical analysis ANOVA proved to be a useful instrument both in the objective description of the maceration technologies influences on the anthocyan profile of red wine and also in the analyses of wine's authenticity and tipicity.

The analyses of chromatic characteristics and the computerized simulation of wine color allowed the objective visual differentiation of wines. Thus, by analyzing the absorption curves and the L, a, b, C and H wine chromatic parameters, these could be classified by means of color.

The values of the color intensity present a variation proportional to the variation of the absorbencies at the three relevant wavelengths (420, 520 and 620 nm), for all studied wines; the hue values vary inversely proportional. The most intensely colored wines were obtained by the first two experimental variants (classical maceration-fermentation and in rotating tanks) for all the three grape varieties studied. The wines obtained through thermo-maceration and microwave maceration present less intense color (with the exception of C.S.-V4) and the wines obtained through cryomaceration and ultrasound maceration are the least colored. The evaluations are similar in the case of the same harvest years. If a comparison is made between the wines obtained by the same maceration technology at different harvest years, the values present a higher variation, due to major differences between climatic conditions and the different varieties. From the color difference nomogram analysis, by using ΔE 1976 and ΔE 2000, it can be asserted that wines obtained through classical maceration fermentation (M.-V1) and thermomaceration (M.-V3) from Merlot grapes in 2008, and also the classical maceration-fermentation (C.S.-V1) and rotating tank maceration fermentation (C.S.-V2) wines from Cabernet Sauvignon grapes in 2009, have indistinguishable differences in regard to their color (ΔE 1976 and ΔE 2000 are subunitary); by using this method of calculation, all the other wines can be visually differentiated.

In conclusion, the lowest color differences between wines were registered among the same grape variety used but in some cases also among the wines obtained through the same maceration technique from different varieties and harvest years; this aspect creates the possibility of ensuring a constancy to wines obtained in different years from the same vineyard and through using the same maceration technology, regarding their color – a very much appreciated characteristic by the consumers.

The sensory appreciation of the obtained wines has a big importance, as it presents a determinant role on their differentiated register in quality categories. Two evaluation methods were used, considered being the most representative:

a) The evaluation method proposed by the International Oenological Union (UIO) that consists in giving bonus points to the sensory characteristics of wine during a "closed wine tasting". The jury is formed of 15 persons that marked every sample and the results were calculated

and graphically expressed in an evaluation graph. It was thus highlighted the contribution of every olfactory and taste characteristic in the general aromatic profile.

b) The "open tasting" method announces the variety, harvest year and the maceration technology used; the tasters evaluate the wine by describing its dominant characteristic, the overall harmony and its particularities, by using specific oenological terminology and grading.

Thus, for Fetească neagră wine, the variants V2 (rotating tank maceration) and V3 (microwave maceration), were distinguished and graded with "very good" and V1 (classical maceration) graded with "good". In the case of Merlot wines, the samples obtained by maceration-fermentation (V1 and V2) and V4 (thermomaceration) were graded as "very good" and with "good" – V3 wine sample (microwave maceration). The most appreciated wines were Cabernet Sauvignon, out of which V4 (thermomaceration) was evaluated as „excellent", and V1, V2 and V3 were graded with „very good". Through ultrasound maceration and cryomaceration techniques, low polyphenolic content is obtained, that cannot offer color, force, vigor to wines, imperative characteristics to quality red wines.