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THE INFLUENCE OF MACERATION TECHNIQUES ON THE POLYPHENOLIC CONTENT OF THE WINES FROM NEGRU AROMAT GRAPE VARIETY

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Abstract

The aim of the present study was to establish the influence of maceration techniques on the polyphenol and aroma compounds of wines obtained from Negru aromat grapes, a variety created at the Research and Development Institute for Viticulture and Enology Valea Calugareasca, Romania. Three maceration techniques were applied as follows: submerged cap, pump-over (must recirculation) and delestage (several rack and return processes). Wines were evaluated and compared by chemical and sensory analyses, in order to determine which one is most suitable for this grape variety and can lead to well-balanced wines. With higher amounts of anthocyanins (377 mg/L), total polyphenols (3478 mg/L) and a more intense aroma of fresh fruits (cherries, bitter cherries, black currants, grapefruit), the wines obtained through pump-over technique applied during the phase of maceration-fermentation were identified as being of optimal quality. Thus, must pump-over is recommended for the production of Negru aromat wines, but more studies are warranted to optimize the winemaking process.

Key words*: Negru aromat, wine, polyphenols, anthocyanins, maceration-fermentation techniques*

INTRODUCTION

In wines, in addition to clarity, other important parameters for quality evaluation are represented by colour and aroma. These two characteristics are especially important for the wines obtained from Negru aromat, which is a red aromatic variety. To enhance both of these parameters, in wine technology a process of skin maceration is applied, in order to extract the main colour and aroma compounds. For this reason, red wines, as well as aromatic wines are produced with maceration and researchers have always tried to improve these processes (Puertas et al., 2008; Şener and Yıldırım, 2013; Cojocaru and Antoce, 2017; Tartian et al., 2017, Cerbu et al. 2021). The maceration process is one of the most important factors influencing the quality of red wines, as it contributes not only to the colour but also to the structure through the extracted tannin levels (Yacco et al., 2016). Certain technological steps and treatments applied during winemaking can influence the content of phenolic compounds extracted from grapes, with direct effect on colour and taste (Vrhovsek et al., 2002; Cojocaru et Antoce, 2017). The skins and seeds have a significant role in red grape vinification because they are the main source of phenolic compounds which are extracted into wine during the maceration-fermentation process of grape marc (Cejudo-Bastante et al., 2011; Zamfir et al., 2008; Zamfir et al., 2012). Phenolic compounds (anthocyanins, phenolic acids, procyanidins, etc.) accumulate in the solid parts of the grapes (bunches, peel, seeds), and their content is variable depending on the variety, the level of grape ripeness, the climatic conditions and, last but not least, the winemaking technology applied (Baiano et al., 2016; Rodríguez-Delgado, 2002).

MATERIALS AND METHODS

The current study was carried out at the Research and Development Institute for Viticulture and Enology Valea Calugareasca, Dealu Mare vineyard, during 2020-2021, by

using grapes of the Negru aromat variety as raw-material.

A quantity of 150 kg of grapes were harvested in September 2020, at phenolic maturity.

The harvested grapes were divided in three batches for micro vinification experiments with the purpose to identify whether the application of a specific maceration-fermentation technique leads to statistically significant differences in wine composition and/or organoleptically observable treats.

The experimental variants, which differ only in the maceration-fermentation method, were coded as follows:

V1 - submerged cap (classical technology) is the control variant, where the cap is periodically crushed and mixed with the must, to facilitate the tannins extraction from the seeds;

V2 - pump-over (must recirculation) is the variant with recirculation, in which the must from under the cap is periodically pumped above the cap to facilitate the tannins extraction;

V3 - delestage (several rack and return processes) is the variant in which the must is completely separated from the cap and the cap is crushed for oxygenation.

The submerged cap technique was applied three times per day (morning, noon, evening), the pump-over was twice per day (morning, evening), and the Dele stage was performed in the first and last day of the process.

Each experimental variant consisted of 47 L of grape mash resulted after crushing and destemming of grapes. The crushed grapes in each variant were inoculated with selected yeasts *Saccharomyces cerevisiae* Viniferm TTA (Agrovin, Spain) in a concentration of 9 g/variant and treated with proteolytic enzymes Lafase fruit (Laffort, France) in a concentration of 1.5 g/variant in order to facilitate the extraction of red wine colour.

The maceration-fermentation process of the must was carried out at temperatures between 23-28^{o}C, for 6 days, and when density reached 1000 g/cm^3, the batches were pressed using a Hydropress TH 40 L (Inderst, Italy).

The following analyses were performed during the maceration process: sugar content (refractometric method, OIV 2021a); total acidity (titrimetric method, OIV 2021b); pH (potentiometric method, OIV 2011); anthocyanins and total polyphenols (OIV, 2021c; Cayla and Renard, 2008) colour intensity and hue (spectrophotometric method, OIV 2021c).

Three types of wines were obtained and used to compare the influence of maceration technique on phenolic composition. The resulted wines were treated with 65 mg/L of sulphur dioxide for antioxidant protection and left for maturation in 25 L glass demijohns.

Wine samples were analysed after 6 months, determining the following parameters: determination of anthocyanins by the Ribéreau–Gayon-Stonestreet method was calculated with the formula Anthocyanins (mg/L)=875*Δd (Ribéreau-Gayon et Stonestreet, 1965); total polyphenols index by the Folin Ciocâlteu method was calculated with the formula Polyphenols (mg GAE/L)= Dilution*(A750-b)/a (OIV, 2021d); tannins were calculated with the formula Tannins (g/L) = Dilution*(0.0025+0.3647*DO550) using the leucoanthocyanidin method (Ribéreau-Gayon et Stonestreet, 1966). The colour analyses of the wines were performed using the CIELab method (Ribéreau-Gayon et al., 2006; OIV, 2021e).

The organoleptic profile of the wines was evaluated by a panel of wine experts by using specially designed tasting sheets (Antoce and Năməloşanu, 2007).

RESULTS AND DISCUSSIONS

At harvest, the grapes of Negru aromat had good maturation parameters, such as sugar content of 236.4 g/L, total acidity of 3 g/L tartaric acid (39.4 milliequivalents/L), a gluco-acidmetric index of 78.8. The 100 berries weighted 144.89 g and the level of grape spoilage was under 5%. The berry composition index, that is the ratio of the liquid and solid fraction of berries, reached a value of 5.29.

Evolution of phenolic composition during the maceration-fermentation process

Throughout the maceration-fermentation process the anthocyanins and total polyphenols registered a continuous increase until the moment when the wine was separated from the pomace.

The highest amount of anthocyanins was recorded in the variant produced with must pump-over (V2), reaching 426 mg/L on the sixth

day of maceration (Figure 1). Regarding the total polyphenols content, from Figure 2 it can be observed that the must pump-over variant (V2) registered values close to the control wine (4256 mg/L versus 4145 mg/L), while for the delestage variant (V3), a much smaller amount of polyphenols (2367 mg/L) was extracted.

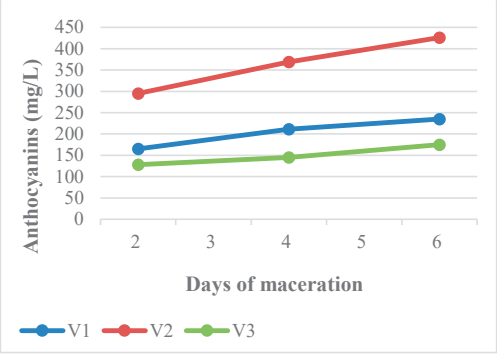

Figure 1. Evolution of anthocyanins during the maceration-fermentation process

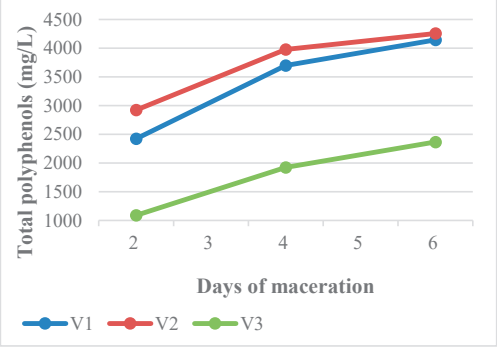

Figure 2. Evolution of total polyphenols in during the maceration-fermentation process

Colour intensity and hue showed a continuous increase during the maceration-fermentation process in all experimental variants (data not included for brevity).

The colour intensity values are quite close in all variants, but the wines obtained by pump-over (V2) had the highest colour intensity, and the wines obtained by delestage (V3) had the lowest colour intensity. Regarding the hue of the Negru aromat wines, the highest value was registered by the delestage variant (0.49), and the lowest value was registered by the submerged cap variant (0.439), showing that oxidation effect was higher in the delestage procedure.

Evaluation of wine quality

Red wines were evaluated and compared by chemical and sensory analyses after 6 months.

The alcohol content of the wines, irrespective of the maceration technology, was around 14.5% v./v., a concentration specific for the region and determined by the high amount of sugar in grapes at harvest.

The fermentation process went well in parallel with the maceration, most of the sugar being transformed in ethanol. Some differences were however observed, the control wine (V1) ending up as a dry wine with a 3.56 g/L of sugar, while the other variants remaining as semi-dry wines with 4.81 g/L (V2) and 7.93 g/L (V3) sugar, respectively.

The titratable acidity and pH affect the wines and other beverages stability and colour (Meng et al., 2012; Ju et al., 2021). The titratable acidity of the wine samples varied in the normal range for red wines, from 3.75 g/L to 4.35 g/L. The wine obtained by submerged cap (V1) had the highest titratable acidity content, reaching 4.35 g/L, followed by the wine obtained by must pump-over (V2) with 4.20 g/L.

As regards the pH, considering that recent studies recommend values between 3.0 and 4.0 for most wines to ensure balanced sensory properties and good stability (Forino et al., 2020), it was observed that Negru aromat placed at the upper end or higher of the optimum range. The pH values of the Negru aromat wines were 3.99 (V3), 4.06 (V1) and 4.16 (V2), respectively.

The results presented in Figure 3 show the influence of the extraction methods on the final content of total polyphenols, anthocyanins and tannins in Negru aromat wines. It can be seen that, the maceration done by must pump-over (V2) favoured an increase of anthocyanins content with 58.63% and a total polyphenol increase with 17.52% compared to control wines (V1), while the delestage method lead to lower values compared to both other technologies. The level of tannins in grapes and wines is influenced by the maceration-fermentation technique used (Figure 3), being higher in the wines obtained by delestage (1608 mg/L), compared to the other two variants (1152 mg/L

for the submerged cap, respectively 1403 mg/L for the must pump-over).

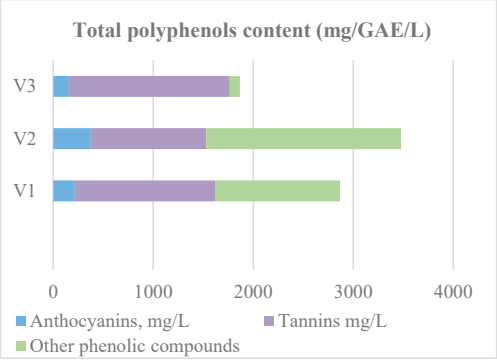

Figure 3. The influence of the maceration-fermentation method on the content of total polyphenols, anthocyanins and tannins in wines

The results regarding the colour of Negru aromat wines were obtained with the CIElab system. In this system, the colour can be decomposed into three independent orthogonal parameters L*, a*, and b*. Parameter L* indicates the lightness (or darkness) of the colour, while parameters a* and b* indicate the components of the hue (OIV, 2021). By analyzing these CIElab parameters we can numerically describe the colour characteristics of wines (Li et al., 2017; Ju et al., 2021).
Among the analyzed samples (Table 1), the colour of the wine obtained by delestage was the brightest, having the highest L* value (23.66), and the wine obtained by must pump-over was the darkest, having the lowest L* value (20.09). With these L values it is evident that the wine sample clarification process was not completed at the date of measurement.

Table 1. The CIELab colour parameters of the wine samples produced with various maceration technologies

Variants	Colour parametres				
	L^*	a^*	b^*	H^*	ΔE^*
V1	20.39	46.65	36.56	38.09	14.39
V2	20.09	46.80	37.71	38.86	14.46
V3	23.66	49.15	32.87	33.78	14.54

Parameter a* represents the position in the colour space between the red and green colour components, with values under 0 for green and over 0 for red, and parameter b* represents the position in the colour space between the blue and yellow components of colour, with values under 0 for blue and over 0 for yellow (Ju et al., 2021). Therefore, it can be observed that in the space a* and b* we have only positive values (Figure 4), meaning that the wines have a colour composed of a mixture of red (parameter a*) and yellow (parameter b*). Wines obtained by submerged cap and must pump-over are very similar in colour, while wines obtained by delestage show a slight shift towards more red and less yellow, which may indicate that due to a higher level of tannins there is a higher polymerisation of polyphenols and stabilisation of anthocyanins for the later winemaking method.

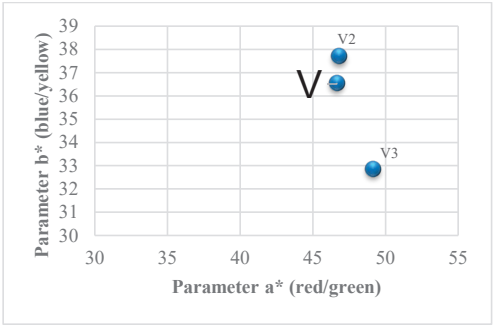

Figure 4. Variation of colour in Negru aromat wines obtained by three maceration techniques

The colour difference ΔE* is determined by the contribution of the three parameters L*, a* and b*, is calculated with the formula $\Delta E^* = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$ and characterizes the general colour difference between wine samples (Ju et al., 2021; Perez el al., 2007). As shown in Table 1, the colour difference (ΔE*) between the wine samples is relatively small.
It was observed that the maceration-fermentation techniques by submerged cap (V1) and must pump-over (V2) lead to wines with a lesser red colour component, while delestage (V3) considerably improved the redness of wine, fact that most likely makes this type of wine more appealing to the consumers.

Sensory evaluation of wines

The sensory evaluation of the wines consisted of the visual, olfactory and taste examination.
In the organoleptic profile resulted from the quantitative sensory analysis and depicted in figure 5, it can be observed that the wines obtained by the must pump-over (V2) and the ones resulted after using the submerged cap

technique (V1) are the most balanced in all aspects. These wines have less bitter and less astringent tannins compared to the wines obtained by delestage (V3), which are perceived as rough, even though are better structures, a fact also proven in the analytical analysis by the higher content of tannins. The wine obtained by delestage (V3), from a taste point of view, presented a polyphenolic imbalance.

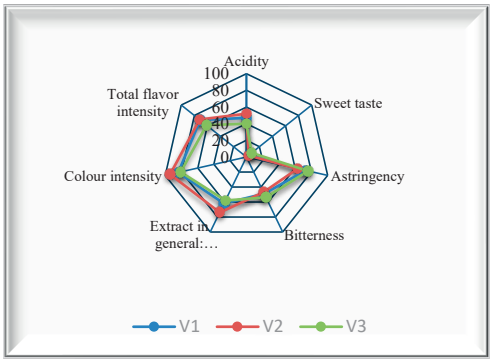

Figure 5. The influence of maceration-fermentation methods on the organoleptic profile of wines

As shown in figure 6, the wines obtained by the pump-over method (V2) differ from the other two wine samples by a more intense aroma of fresh fruit (cherries, bitter cherries, black currants and grapefruit). The control (V1) stands out with slight vegetal notes (fresh grass), and the wine obtained through delestage (V3) shows slight notes of spices (pepper, bitter chocolate) and especially vanilla.

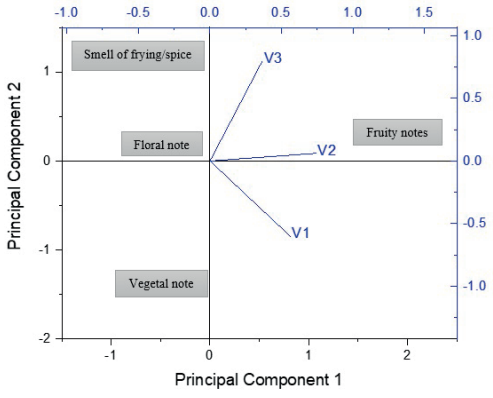

Figure 6. The influence of maceration-fermentation methods on the aromas of wines

CONCLUSIONS

This research confirms that the use of different maceration-fermentation techniques induces certain changes in the content of total polyphenols, anthocyanins, colour and on the sensory characteristics of red wines.

The anthocyanin and total polyphenols content in wine is clearly dependent on the maceration technique used. The results obtained for anthocyanins vary from 156 mg/L when the maceration was carried out by delestage (V3), to up to 377 mg/L when the maceration was carried out by must pump-over (V2).

The results show that the total polyphenols extraction ranged from 1867 mg/GAE/L when wine was obtained by delestage (V3), to 3478 mg/GAE/L when must pump-over method was applied (V2).

Regarding the content of tannins in the Negru aromat wines, it was observed that the use of delestage maceration technique (V3) was correlated with an increase in the level of this compound.

The analyses regarding the colour, it was found that the wines obtained by the submerged cap (V1) and the must pump-over (V2) had a very similar colour (red), while the wines obtained by delestage (V3) showed a slight shift towards a more red and less yellow.

The wines obtained through the maceration-fermentation technique by the must pump-over (V2) differ from the other two wine samples by a more intense aroma of fresh fruit (cherries, bitter cherries, black currants and grapefruit).

All things considered, the maceration by pump-over technique is recommended for the production of Negru aromat wines to be consumed within a few years from production, as it leads to well-balanced, full-bodied, intensely coloured and with specific fruity aroma, while delestage (V3) may be a better option for the case of wines meant for aging.

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