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THE INFLUENCE OF DIFFERENT MACERATION TECHNIQUES ON THE PHENOLIC COMPOUNDS AND COLOR PARAMETERS OF RED GRAPES *FETEASCĂ NEAGRĂ* VARIETY

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Abstract

The investigation of various technological parameters affecting the extraction of the valuable compounds from the *Feteasca neagră* variety of red grapes was performed. In particular, the impact of various maceration techniques on phenolic composition, color indicators, and biological potential expressed as antioxidant activity was evaluated. The grapes were manually processed and then subjected to different types of processing: low temperature maceration at 4°C (V1), conventional maceration at 25°C (V2), thermomaceration at 70°C (V3), and ultrasound-assisted maceration at different temperature values, such as: 5-10°C (V41), 30°C (V42) and 60-65°C (V43) with the same duration of 30 minutes. The evolution of the physico-chemical parameters of the samples was monitored at different time intervals of 2, 4, and 6 days, depending on the maceration type. The results revealed the higher impact of the temperature on polyphenolic compounds extraction from grape skins in the must, as well as for the compounds related to color of red wines.

Keywords: red grapes, cold maceration, anthocyanins, antioxidant activity

Introduction

Recent studies revealed the actual concerns of the world wine industry and of international oenological research focused on some significative directions. The most important directions which affect the red wines quality are briefly presented below. New unconventional maceration procedures and techniques are applied to the crushed red grapes with the purpose of technological efficiency and optimization of

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the sensory and sanogenic properties of the resulting red wines (Morata *et al*., 2017). The intrinsic and extrinsic factors affect the extraction of polyphenolic compounds during maceration (Setford *et al.*, 2017), as well as the distribution of these compounds into the red grapes (Pinelo *et al.*, 2006). The measures to ensure the durability and stability of the red wines color order to meet the growing expectations and demands of consumers (Quaglieri *et al.*, 2017) and monitoring the quality of red grape harvests and especially their polyphenolic composition under the conditions of new methods of scaling current climate changes (Neethling *et al.*, 2019 Gutierrez-Gamboa *et al.*, 2021) are as well of high interest. An increasing concern for the in-depth knowledge of polyphenols in wines (Garido *and* Borges, 2013), especially of stilbenes (Surguladze and Bezhuashvili, 2017; Benbouguerra *et al*., 2021) together with other bioactive compounds (Fernández-Mar *et al*., 2012) with positive influence on human health was noticed. Moreover, diversifying the sensory profiles of red wines by using natural yeast derivatives (Rigou *et al.*, 2021) and the permanent attention of the factors that influence the maturation of wines in oak barrels (Garde-Cerdan and Ancın-Azpilicueta, 2006) are among the priorities of the world wine industry.

Among the directions mentioned above, specific non-conventional procedures and techniques for maceration of red grapes (cold maceration, hot maceration or thermo maceration, ultrasound treatment assisted maceration) depending on the main technological parameters (thermal regime and maceration duration) were never compared with each other as experimental maceration variants, nor with conventional maceration considered as a control variant.

Considering this aspect, this complex comparative study aimed to establish the influence of the above-specified maceration variants, applied to the marc from the *Fetească Neagră* grapes variety, on their phenolic composition, color indicators and the value of their antioxidant activity as an expression of active biologic potential, with beneficial therapeutic implications of some of the analyzed phenolic compounds.

Materials and methods

The grapes (*Vitis vinifera* subsp. *vinifera*, var. *Fetească neagră*) were purchased from a producer in the Terasele Dunării county.

The 2,2-diphenyl-1-(2,4,6-trinitrophenyl)-hydrazinyl (DPPH); Folin-Ciocâlteu reagent; Na_2CO_3; $NaNO_2$; $AlCl_3$; NaOH; KCl, CH_3COONa, methanol HPLC purity were provided by Sigma Aldrich Steinheim (Darmstadt, Germany).

Preparation of the grapes and obtaining the marc

To carry out the maceration operations, the grapes were thawed and manually destemmed, and the collected berries were selected, so that only whole berries that were not mechanically or biologically affected were processed. They were weighed and subjected to manual crushing in order not to allow the uncontrolled release of some components from the seeds. The must samples resulted from the separation of liquid fraction by free draining.

Afterward, the marc consisting of the mixture between the liquid part (must) and the solid parts (skin, pulp, and seeds) was subjected to several experimental maceration variants, briefly presented below.

Experimental maceration variants

The low-temperature maceration (V1) was carried out on a sample of 100 g of marc which was treated at a low temperature of 4 °C for 2 days, 4 days and 6 days, respectively.

The conventional maceration (V2) was performed subjecting the marc sample (100g) to maceration at 25 °C for 2 days and 4 days, respectively.

The thermomaceration (V3) involved heating the marc sample (100 g) at a temperature of 70°C for 30 minutes in a digital heater (Stuart, United Kingdom). An aliquot sample was collected to assess the specific effects of this treatment (V3`). Afterwards, the sample was subjected to a conventional maceration, similar to sample V2, for 2 days, 4 days and 6 days, respectively.

In case of the ultrasound's treatment assisted maceration, different experimental conditions were tested. In this respect, three experimental variants were achieved, the marc samples being identically treated with ultrasounds (40 kHz for 30 minutes) in a ultrasonic bath (Smart sonic MRC. LTD, Israel), at different temperatures: 5-10°C (V41), 30°C (V42) and 60-65°C (V43).

Determination of the content of monomeric anthocyanins

The content of monomeric anthocyanins was assessed according to the protocol proposed by the AOAC method (2005.02), as follows: 200 µL were taken from each sample of must and were mixed with 800 µL of KCl 0.025 M solution (pH = 1.0), respectively with 800 µL of 0.4 M CH_3COONa solution (pH = 4.0). Following a 15-minute rest period, the absorbance was assessed using a spectrophotometer (Libra S22, United Kingdom) at wavelengths of 520 nm and 700 nm. The total monomeric anthocyanin content was quantified as mg of cyanidin-3-glucoside equivalents per mL of product (mg CGE/L).

The total monomeric anthocyanin concentration was determined applying the following equation (1).

$$\text{Anthocyanin content (mg/L)} = \frac{A*M*F*10^3}{\varepsilon*L} \quad (1)$$

where:

$A = (A520nm - A700nm)_{pH=1.0} - (A520nm - A700nm)_{pH=4.5}$; M = molecular mass of cyanidin-3-glucoside (449.2 g/mol); F = dilution factor; ε = molar absorptivity of cyanidin 3-glucoside in methanol (26900 $L \cdot mol^{-1}$ cm^{-1}); L = optical path length (1 cm).

Determination of the total content of flavonoids

The total flavonoid content was assessed utilizing a method proposed by Bajčan *et al.*, 2017, incorporating changes derived from the aluminum chloride technique, which provides an optimum estimation of total flavonoid content. For this purpose, 250 µL of must were taken, over which a volume of 1.25 mL of distilled water and

0.075 mL of 5% $NaNO_2$ solution were added. The mixture was allowed to settle for 5 minutes, after which 0.15 mL of a 10% $AlCl_3$ solution was incorporated. The mixture was again allowed to rest for 6 min, after which 0.5 mL of 1M NaOH and 0.775 mL of distilled water were added. The absorbance at a wavelength of 510 nm was read for the resulting mixture using a spectrophotometer (Libra S22, United Kingdom). In parallel, a blank test was carried out. The total flavonoid content was determined using the standard curve for the catechin, the results being expressed in mg catechin equivalents/L of must (mg CE/L).

Determination of total polyphenols content

To determine the total polyphenols content, the colorimetric Folin-Ciocâlteu (OIV-MA-AS2-10) method was used: a volume of 200 µL of must was mixed with 15.8 mL distilled water and 1 mL of Folin-Ciocâlteu reagent; the mixture was vigorously stirred and set for reacting for 10 minutes. Subsequently, 3 mL of a 20% Na_2CO_3 solution was added, and the resultant mixture was placed in the dark for 60 minutes at room temperature. The absorbance of the supernatant was read spectrophotometrically (Libra S22, United Kingdom) at a wavelength of 765 nm. Gallic acid served as a standard for the calibration curve, and the results were reported as mg of gallic acid per L of product (mg GA/L).

Determination of chromatic indicators

The chromatic indicators (yellow, red, and purple components) and the total polyphenols indicator were determined using the method described by Delsart *et al.* (2012). The absorbance of the samples was recorded using a spectrophotometer (Libra S22, United Kingdom) at several wavelengths: 420 nm – yellow color component; 520 nm – red color component, and 620 nm – violet color component. Afterwards, the chromatic parameters (color intensity and hue) were calculated using equations (2) and (3).

$$Color\ intensity = A_{420} + A_{520} + A_{620} \quad (2)$$

$$Hue = \frac{A_{420}}{A_{520}} \quad (3)$$

The percentages corresponding to each color component (% yellow, % red, and % violet) were also calculated.

Determination of antioxidant activity

The DPPH Radical Scavenging Activity (DPPH RSA) method was applied to determine the antioxidant activity. A mixture consisting of 3.9 mL of DPPH solution and 100 µL of must was homogenized and allowed to settle in the dark for one and a half hours. Subsequently, the absorbance of the mixture at wavelength of 515 nm was measured relative to a control sample, which consisted of 3.9 mL of DPPH solution combined with 100 µL of distilled water.

The antioxidant activity represents the antiradical activity on DPPH, being expressed as a percentage inhibition, according to the equation (4).

$$Inhibition\ \% = \frac{A_{CS} - A_{AS}}{A_{CS}} \cdot 100 \quad (4)$$

where A_{CS} = the absorbance of the control sample; A_{AS} = the absorbance of the analyzed sample.

Statistical analysis

The results reported in this study are the average values of the duplicate analyses ± of the standard deviation. The significance of the difference between samples was analyzed using one way ANOVA and Tukey's test ($p < 0.05$) (MINITAB Version 17, Minitab, USA).

Results and discussion

Phytochemical characterization of macerated red grapes variants

The polyphenolic parameters of grapes subjected to the experimental maceration variants V1, V2, and V3 are presented in Table 1.

Table 1. The influence of the duration and the maceration technique on some polyphenolic constituents of the *Fetească neagră* variety (V1 - low temperature maceration, V2 – conventional maceration, V3 – thermomaceration, V3`- sample at time 0 after thermomaceration).

Sample	Total polyphenols, mg GA/L	Flavonoids, mg CE/L	Anthocyanins, mg CGE/L	Inhibition, %
Values obtained after 2 days of maceration				
V1	468.5 ± 0.87^{c}	130.4 ± 0.73^{c}	293.1 ± 0.10^{c}	78.70 ± 0.36^{b}
V2	682.2 ± 2.54^{b}	190.4 ± 0.12^{b}	623.0 ± 0.35^{b}	82.47 ± 0.90^{ab}
V3	809.6 ± 1.58^{a}	224.2 ± 0.02^{a}	760.3 ± 0.31^{a}	84.62 ± 1.56^{a}
V3`	482.4 ± 0.58^{c}	102.5 ± 0.42^{d}	324.1 ± 0.50^{c}	81.46 ± 2.53^{ab}
Values obtained after 4 days of maceration				
V1	502.4 ± 0.83^{c}	132.4 ± 0.15^{c}	561.5 ± 0.16^{b}	86.68 ± 0.03^{a}
V2	685.1 ± 1.54^{b}	169.6 ± 0.32^{b}	344.2 ± 0.11^{c}	83.61 ± 0.89^{b}
V3	742.8 ± 1.46^{a}	200.5 ± 0.02^{a}	665.1 ± 0.33^{a}	85.95 ± 0.82^{a}
Values obtained after 6 days of maceration				
V1	491.5 ± 1.12^{b}	124.5 ± 0.44^{b}	321.0 ± 0.25^{b}	81.01± 0.04^{b}
V3	673.4 ± 0.46^{a}	164.8 ± 0.42^{a}	558.2 ± 0.24^{a}	86.21 ± 0.71^{a}

For a specific maceration time, different letters in the same column indicate significant differences between samples ($p<0.05$)

Cold maceration

Differences regarding the polyphenolic parameters have been registered for the must obtained by pressing and low-temperature maceration. Thus, the total polyphenols content was 468.5±0.87 mg GA/ L after 2 days of maceration, revealing a slight increase to the value of 502.4±0.83 mg GA/L after 4 days of maceration.

Additionally, a reduction in this content was reported up to 491.5±1.12 mg GA/L after 6 days of maceration.

The cold maceration process ensured a total flavonoids content of 130.4 mg CE/L after 2 days, with no significant increase after 4 days of maceration (132.4±0.15 mg CE/L). Anyway, extending the maceration step up to 6 days resulted in a slight decrease of the flavonoids (124.5±0.44 mg CE/L) extracted in the must.

The highest content of anthocyanins was noticed after 4 days of cold maceration (561.5±0.16 mg CGE/L). Further increase of the cold maceration period to 6 days resulted in the significant decrease of anthocyanins content (321.0 ± 0.25 mg CGE/L).

These results are in agreement with those reported by similar studies available in the literature. Thus, in a study performed by Gómez-Míguez *et al*. (2007) it was demonstrated that the cold maceration of marc (from the Syrah variety to temperature of 15 °C instead of 4 °C as in our study, with a duration of 7 days instead of 6 days as in our study), allowed the increase of the contents of total polyphenols and anthocyanin compounds. A separate investigation of Frangipane and De Santis (2010) performed on red grapes demonstrated a more rapid elevation of the anthocyanin concentration relative to other phenolic components, a finding corroborated by the current study. The authors attributed their findings to the enhanced stability of anthocyanins at reduced temperatures and the protracted extraction of other components, such as proanthocyanidins, which tend to associate with anthocyanins, resulting in pigments of higher molecular mass (Frangipane and De Santis, 2010). The results also confirm the findings of Aleixandre-Tudo and Du Toit (2018), according to which most of the polyphenolic constituents found in the skins of the grape seeds diffused rapidly in the first days of the maceration process, excluding the tannins derived from the skins and particularly from the grape seeds, as well as, in certain instances, the anthocyanins.

The dynamics of flavonoid content evolution, consisting of the increase in the first two days, followed by a quasi-stationary phase over the subsequent four days, are in line with other studies (Cheynier *et al*., 2010). It can be attributed to the localization of flavonoids in the grape skins and pulp, facilitating their immediate release during maceration and resulting in enhanced accumulation in the must (Casassa and Harbertson, 2014).

The observed reduction in anthocyanin content after six days of maceration aligns with findings in the scientific literature (Aleixandre-Tudo and Du Toit, 2018). Studies on red grape varieties, such as Cabernet Sauvignon and Carignan, indicate a comparable trend during low-temperature maceration (Panprivech *et al*., 2015).

Polymerization reactions were initially considered a principal factor contributing to the reduction of anthocyanin content; however, they were subsequently partially dismissed as the polymer fraction remained constant in certain studies (Panprivech *et al*., 2015). In contrast, other factors, such as adsorption phenomena (Sacchi *et al*., 2005), continue to attract the interest of researchers.

Conventional maceration

The traditional maceration ensured significantly higher amounts of the total polyphenol content of 682.2 ± 2.54 mg GA/L after 2 days of maceration, compared to the cold maceration method. This finding demonstrate that temperature is a critical factor in the diffusion dynamics of phenolic compounds. At the end of the 4-day maceration interval, an increase in the content of total polyphenols was reported up to the value of 685.1 ± 1.54 mg GA/L (Table 1).

The increase of the maceration time from 2 to 4 days resulted in the decrease of the total flavonoids and anthocyanins contents from 190.4 ± 0.12 mg CE/L to 169.6 ± 0.32 mg CE/L and from 623.0 ± 0.35 mg CGE/L to 344.2 ± 0.11 mg CGE/L, respectively. It should be noted that after 2 days of conventional maceration, the concentration of monomeric anthocyanins was double compared to the cold maceration process (Table 1).

This increased concentration of monomeric anthocyanins in V2 compared to the V1 variant can be primarily attributed to the effects of elevated thermal conditions. Conversely, during four days of maceration, a variation in the anthocyanin content was reached, with an increase in the V1 variant (561.5±0.16 mg CGE/L) and a decrease in the V2 variant (344.2±0.11 mg CGE/L). The substantial reduction in anthocyanin compounds in the V2 variant can be attributed to the diminished stability of anthocyanins at elevated temperatures (25°C versus 4°C), potential interactions between anthocyanins and other phenolic compounds, the influence of endogenous enzymes and microorganisms from the grape's epiphytic microbiota, and co-pigmentation phenomena (Aleixandre-Tudo and Du Toit, 2018; Garrido and Borges, 2013). In the same context, Aleixandre-Tudo and Du Toit, (2018) reported a general instability of the phenolic compounds, especially of the anthocyanins, if the alcoholic fermentation does not begin simultaneously or almost simultaneously in the case of macerations at a low temperature of marcs applied for longer time intervals. They justified this finding by the increased solubility of anthocyanins in alcoholic solutions. The reactions of anthocyanins with other compounds, such as tannins or acetaldehyde, can increase their stability, as well as the presence of different compounds added in the winemaking process such as sulfurous anhydride (Aleixandre-Tudo and du Toit, 2018).

Although the co-pigmentation reactions, occurring especially between anthocyanins and proanthocyanidins (catechin, epicatechin, etc.), are more frequent in the conventional maceration variant (V2) compared to that at low temperature (V1), the probability of their development is lower in the case of macerations carried out in the absence of ethyl alcohol, considering that proanthocyanidins have a low solubility in aqueous media. Therefore, there is the possibility of inducing the co-pigmentation phenomenon by combining anthocyanins with other phenolic compounds such as tannins. The significant reduction in anthocyanin component levels during pre-fermentative macerations was predominantly attributed to resorption processes (Aleixandre-Tudo and du Toit, 2018).

A significant factor contributing to the reduction of phenolic compound content during pre-fermentative macerations, such as the V1 and V2 variants, is the activity

of enzymes released from the grapes, as well as those produced by the epiphytic microbiota, particularly hydrolases and oxidases. On the other hand, an example in this regard is the action of β-glycosidases on anthocyanins in glycosylated form with the release of anthocyanins that, in free form, are no longer as stable or soluble in aqueous solutions (Khoo *et al.*, 2017).

The slight increase in the content of total polyphenols simultaneously with the decrease in the content of flavonoids and monomeric anthocyanins also observed in the pre-fermentative maceration variants V1 and V2, can be explained by the diffusion of proanthocyanidins in the must from the skins of the grape seeds, on the one hand, but also from their seeds. When applying maceration procedures with longer duration and greater intensity under the action of temperature, microwaves or ultrasound, enzymatic extraction preparations, ethylic alcohol, SO_2 or ascorbic acid (Ghanem *et al.*, 2014), the extraction of tannins from the seeds begins, contributing to the increase in the concentration of total polyphenols (Aleixandre-Tudo and du Toit, 2018; Garrido and Borges, 2013).

Thermomaceration

For the thermomaceration experimental variant, the sample collected immediately after heating at 70 °C for 30 minutes (V3') was characterized, and the results were associated with the moment t_0 (Table 1). Subsequently, the marc was conventionally macerated for 2, 4, and 6 days, respectively. After 2 days of maceration from the moment t_0, the content of total polyphenols reached a maximum value of 809.6 ± 1.58 mg GA/L, and further decreased with increasing the time (Table 1).

In a similar manner, after 2 days of maceration the flavonoids content reached the maximum of 224.2 ± 0.02 mg CE/L, significantly higher compared to experimental variants V1 and V2 (Table 1). Moreover, the concentration of monomeric anthocyanins decreased from 760.5 to 558.2 mg CGE/L with increasing the maceration time from 2 to 6 days.

The initial thermal treatment, applied in case of the variant V3 immediately after pressing the destemmed grapes, ensured the rapid release of the phenolic components. The thermal degradation of the grape berry tissues (especially those specific to the skins and seeds) ensured the destruction of the integrity of the cells and, implicitly, of the vacuoles, in which the main analyzed phenolic compounds are found (Aleixandre-Tudo and du Toit, 2018).

The notable aspect concerning the V3 variant is the high content of phenolic compounds found even after the 30 minutes of thermal treatment at 70 °C (482.4 ± 0.58 mg GA/L; 324.1 ± 0.50 mg CGE/L) comparable to the content obtained after 2 and, respectively, 4 days of maceration by variant V1 at 4 °C (468.5 ± 0.87 GA/L and respectively 502.4 ± 0.83 mg GA/L) or variant V2 (682.2 ± 2.54 mg GA/L and respectively 685.1 ± 1.54 mg GA/L). The extraction ensured reaching its peak around the 2nd day of maceration, with content of phenolic compounds significantly higher than the samples belonging to the other processes, V1 and V2 (Table 1).

The antiradical activity was influenced by the temperature, the lowest inhibition values being noticed in case of V1 (78.70 ± 0.36 %) followed by variants V2 (82.47 ± 0.90 %) and V3 (84.62 ± 1.56 %).

These results are correlated with the previously determined total polyphenol content, which was the main factor responsible for the reduced activity of the samples. The evolution of the antioxidant activity after four days of maceration can be explained by the changes in phenolic content. In the case of sample V1 an increase of the inhibition values (from 78.70 ± 0.36 to 86.68 ± 0.03 %) was determined. This evolution is explained by the accumulation of phenolic compounds in sample V1 from 468.5 ± 0.87 after 2 days of maceration to 502.4 ± 0.83 mg GA/L after 4 days of maceration and especially the conditions of temperature that led to their better stability, in contrast to samples V2 and V3 where stagnation and especially decreases in the analyzed phenolic compounds are observed.

In the case of the V2 variant, the changes are not major, with a slight increase in inhibition (Table 1). This variant, under optimal temperature conditions (25 °C for epiphytic microorganisms and enzymes in the must, without prior heat treatment as in variant V3), is most likely to promote various chemical and biochemical reactions that may lead to spontaneous fermentations, resulting in predominantly uncontrolled maceration. The changes in the parameter's indicative of the antiradical activity of the V2 variant after 2 and 4 days of maceration can be partially associated with the values of the examined phenolic compounds. The total polyphenol content remained relatively stable, fluctuating imperceptibly from 682.2 ± 2.54 to 685.1 ± 1.54 mg GA/L. In contrast, the concentration of monomeric anthocyanins significantly diminished from 623.0 ± 0.35 to 344.2 ± 0.11 mg CGE/L, while the flavonoid content experienced a less marked decline from 190.4 ± 0.12 to 169.6 ± 0.32 mg CE/L.

At the same time, following the thermal treatment, the inactivation of the plant tissue's own enzymes and the reduction of the epiphyte microflora (especially yeasts and bacteria) took place, thus preventing the occurrence of spontaneous fermentations and the release of enzymes specific to these microorganisms.

The kinetics of the extraction of phenolic compounds in variant V3 is similar to the other two processes analyzed (V1 and V2), especially that of conventional maceration (V2). The main difference attributed to the V3 variant consisted of increased diffusion of polyphenols and other phenolic components, especially in the first part of the maceration, as well as in a slightly higher stability of these compounds.

The reduction in the concentration of monomeric anthocyanins and total flavonoids in the thermo-maceration variant (V3), similar to the conventional maceration variant (V2), can be ascribed to certain probable physical and, particularly, chemical phenomena occurring in the marc during maceration. The decrease of the content of flavonoids with lower molecular mass can be attributed to their participation to chemical reactions, because of their increased reactivity. Among flavonoids, the flavan-3-ols and flavan-3,4-diols are considered to be the most prone to participate in non-enzymatic reactions such as cleavage ones (Cheynier *et al*., 2010). In turn,

catechins can be degraded into compounds with lower molecular mass, a phenomenon favored by several factors such as the increase in the temperature of the marc or the presence of acids. In addition, flavonoids can participate in condensation reactions with other compounds, such as vanillin, which can also contribute to color changes (Garrido and Borges, 2013).

The reduction in the content of monomeric anthocyanins in the pre-fermentative maceration stage, which also corresponds to the variants V1, V2 and V3, several authors attribute this reduction to the influence of some treatments carried out in the absence of ethylic alcohol, as well as to resorption phenomena (Panprivech *et al*., 2015; Aleixandre-Tudo and du Toit, 2018), with results that attribute a major role to the degree of degradation of grape skins and, implicitly, of cell membranes under the mechanical action of technological processing or under the action of various SO_2 treatments, acids or enzyme preparations (Sacchi *et al.*, 2005; Watrelot *et al*., 2013; Liu *et al*., 2021). Certain authors (Álvarez *et al.*, 2006; Gil-Muñoz *et al.*, 2009; González-Neves *et al.*, 2010) attributed the reduction of anthocyanin content during maceration to polymerization reactions, whereas others (Aleixandre-Tudo *et al.*, 2013; Panprivech *et al.*, 2015) found no alteration in the polymer fraction at this stage of red winemaking.

The efficacy of extracting phenolic compounds specific to the V3 variant might enhance the process's applicability in the wine industry, facilitating a reduction in the maceration period and improving cost efficiency and logistical considerations. Consequently, it has become the preferred method among major wine-producing companies, as indicated by Ghanem *et al*. (2014).

In a previous study (Ghanem *et al*., 2014) carried out in France in the Beaujolais wine region, several pre-fermentative thermal processes were applied at a temperature of 70°C with durations between 8 and 16 h, which demonstrated an increase of up to 40% in the coloring intensity and up to 55% in the tannin content compared to the values of the same parameters in wines made by the traditional process, accompanied by an intensification of the aroma, especially the notes of red fruits. Some authors who studied the issue of thermomaceration in red grapes from Pinot noir, Lemberger and Cabernet Franc varieties, revealed an increase in the contents of anthocyanin compounds, flavonols (especially quercetin-glucosides) and total flavan-3-ols (with a significant percentage from the seeds), while the contents of monomers (catechins and epicatechins) and dimers (proanthocyanidins B_1 and B_2) of flavan-3-ols were similar to those of the control samples (Netzel *et al*., 2003). Comparable results were obtained by other authors (Borazan and Bozan, 2013). Alternative methods of thermal maceration utilizing high-temperature heat treatment (> 95°C) resulted in a 50% increase in total polyphenol content relative to control samples (Souquet *et al*., 2000) and demonstrated elevated levels of anthocyanins, catechins, and proanthocyanidins, alongside an augmented presence of tannins in the seeds, potentially facilitating the formation of anthocyanin-tannin adducts and altering the tannin-anthocyanin ratio (Morel-Salmi *et al*., 2006).

Ultrasound-assisted maceration

The results showing the influence of the temperature on the phytochemical profile of marc obtained from *Fetească Neagră* grape variety subjected to ultrasound-assisted maceration (V41, V42, V43) are presented in Table 2.

Table 2. The influence of thermic regime on ultrasound-assisted maceration of marc on some polyphenolic compounds for *Fetească Neagră* variety.

Sample	Total polyphenols, mg GA/L	Flavonoids, mg CE/L	Anthocyanins, mg cyanidin-3-glucozid/L	Inhibition, %
V_{41}	419.7 ± 0.29^{c}	142.6 ± 0.76^{c}	93.0 ± 0.54^{c}	66.82 ± 0.31^{c}
V_{42}	676.3 ± 0.79^{b}	200.7 ± 0.17^{b}	600.1 ± 0.08^{b}	85.35 ± 0.36^{b}
V_{43}	1056.5 ± 0.46^{a}	306.5 ± 0.07^{a}	985.8 ± 0.10^{a}	83.60 ± 0.75^{a}

Different letters in the same column indicate significant difference among mean values ($p<0.05$)

Analysing the results presented in Table 2 one can observe that the total content of total polyphenols increased with the temperature ensured during the ultrasound treatment from 419.7 ± 0.29 mg GA/L in the V41 variant to 1056.5 ± 0.46 mg GA/L in variant V43. A similar trend was observed in case of the total flavonoid and monomeric anthocyanins contents (Table 2). In particular, ten times increase of the monomeric anthocyanins content (from 93.0 ± 0.54 mg CGE/L in the V41 variant, to 985.8 ± 0.10 mg CGE/L in the V43 variant) was observed when raising the temperature from 5-10 to 60-65^{o}C.

Comparing the results regarding the phytochemical profile obtained for the musts treated through ultrasounds (V41, V42 and V43) with those obtained thorough V1, V2 and V3 maceration variants, one can observe a variety of similarities among samples (676.3 ± 0.79 mg GA/L for sample V42 vs. 685.1 ± 1.54 mg GA/L for sample V2 after 4 days of maceration; 600.1 ± 0.08 mg CGE/L for sample V42 versus 623.0 ± 0.35 mg CGE/L for sample V2 after 2 days of maceration), while in most cases they were clearly superior (for example, the value of 1056.5 ± 0.46 mg GA/L in the V43 variant compared to any of the other samples from the previous maceration variants or the value of 306.5 ± 0.07 mg CE/L specific to the V43 variant as well compared to any of the other analyzed samples of the previous maceration variants).

From the point of view of the extraction efficiency of the analyzed polyphenolic compounds, judging by the antioxidant activity, the V42 variant (40 kHz; 30 °C) seems to present the best results. Thus, the antioxidant activity induced by variant V42 (85.35 ± 0.36 %) after 30 min of ultrasonication at 30 °C is comparable to that of samples V1, V2 and V3 after 4 days of maceration (Table 1). These results indicate the superior efficiency of the ultrasound-assisted extractions. The reduction of the time required for the maceration operation presenting not only economic benefits, but also technological and sensory benefits, as a result of the advanced extraction of phenolic compounds with antioxidant activity. Reducing the duration

of maceration appears to directly affect the stability of phenolic compounds, as numerous studies indicate that, in instances where maceration occurs prior to alcoholic fermentation, although enhanced extraction of these compounds may be achieved in certain scenarios, findings also suggest a heightened instability not only during the maceration phase but throughout the entire winemaking process (Álvarez *et al*., 2006; Gil-Muñoz *et al*., 2009; Frangipane and de Santis, 2010; Borazan and Bozan, 2013; Ghanem *et al*., 2014; Aleixandre-Tudo and du Toit, 2018).

A detailed examination of the experimental variants V43 (60 – 65 °C) and V42 (30 °C) facilitated the classification of these as combined ultrasound maceration variants with thermal treatment. This categorization aligns the V43 variant more closely with the V3 variant (subjected to heat treatment at 70 °C) and the V42 variant with the V2 variant (subjected to heat treatment at 25 °C). However, both variants are distinctly differentiated from the preceding V1 maceration variant, due to their short duration of action, limited to only 30 minutes, in contrast to the 2, 4, or 6 days of action observed in the latter. The results obtained in case of the V41, V42 and V43 variants are comparable and sometimes superior to those obtained by applying most of the techniques currently used or tested, but with the advantage of reducing the time required for their implementation (Ghanem *et al.*, 2014). Other benefits are as well observed, as follows: improvement of the phenolic compounds stability, which, being extracted in a short time, no longer participate in the chemical, physical and biochemical reactions that induce a decrease in their concentration (Garrido and Borges, 2013; Aleixandre-Tudo and Du Toit, 2018); the increase in color intensity following the increased extraction of anthocyanin compounds, some flavonoids and proanthocyanidins; favorable olfactory and gustatory changes as a result of the extraction of tannins and flavor compounds, as well as a higher content of polysaccharides (Ghanem *et al*., 2014; Martínez Lapuente *et al*., 2021).

The ultrasound treatment's effects result from cavitation, which degrades cell walls and their structure, facilitating the quick and effective release of chemicals predominantly located in grape berry skins (Martínez Lapuente *et al*., 2021).

Evaluation of color parameters as a function of the proposed technological variants

The results obtained for color intensity and hue after 2 and 4 days of maceration, for V1, V2 and V3 variants are presented in figure 1a and 1b.

Generally, the evolution of the chromatic indicators follows the trend of accumulation or reducing of the phenolic compounds, which are responsible for the color evolution (total polyphenols, total flavonoids and monomeric anthocyanins).

In the case of sample V1, the increase in the total content of polyphenols from 2 to 4 days is also reflected in the increase of the total polyphenols index from the value of 4.72 to the value of 4.85 (Figure 1). Also, with the accumulation of monomeric anthocyanins, there is also an increase in the color intensity from 6.79 to 6.98. This research concludes that after 2 and 4 days of maceration, there was an increase of anthocyanin compounds responsible for the red hue (attributed to the AH^+) (Garrido and Borges, 2013).

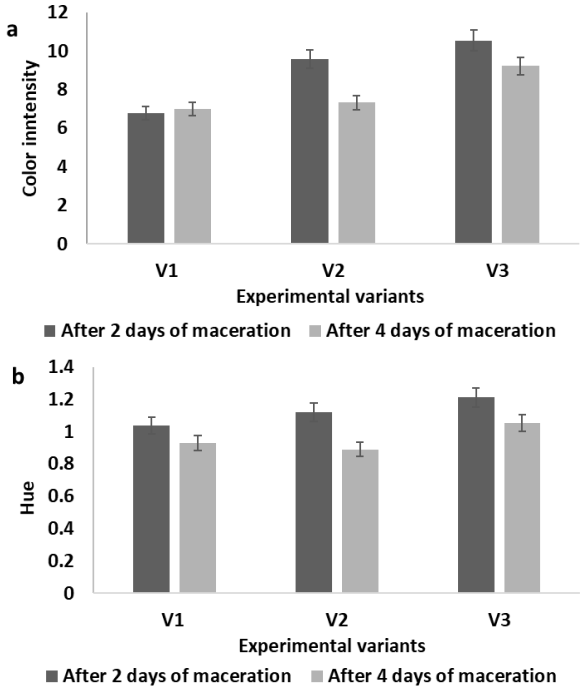

Figure 1. Values of the color intensity (a) and hue (b) for V1, V2 and V3 experimental variants.

In sample V2, the decrease in color intensity from 9.572 to 7.322 is correlated with the decrease in the content of monomeric anthocyanins from 622.9 ± 0.35 mg to 344.0 ± 0.11 mg CGE/L, as well as with that of total flavonoids from 190.4 ± 0.12 to 169.6 ± 0.32 mg CE/L. An explanation for this evolution may be the enhanced stability of the compounds responsible for the red coloration in the specific environment of maceration, attributable to pH conditions, the absence of ethyl alcohol and acetaldehyde, or the presence of SO_2 (Aleixandre-Tudo and du Toit, 2018).

Regarding the V3sample, a decrease in the color intensity can be observed from 10.54 to 9.21, as well correlated with the decrease in the content of monomeric anthocyanins and that of total flavonoids. As in the previous case, the tendency to decrease the percentages of yellow color (from 42.79% to 42.06%) and violet (from 21.84% to 17.98%) was noted, similarly with the increasing of the percentage of red color (from 35.37% to 39.96%). In the case of sample V3, a higher polyphenolic richness compared to V1 and V2 was found, which can contribute to optimal chromatic characteristics and increased color stability, probably as a result of the more intense heat treatment, which led to a decrease in the biochemical reactions generating hue instability (Ghanem *et al.*, 2014).

Following the first two days of maceration, the hue values diminish in the sequence V3 > V2 > V1, a pattern that persists after four days of maceration. Conversely, the hue variation between the second and fourth days of maceration is marginally positive in the V1 variant (an increase of 2.8%), significantly declines in the V2 variant (a decrease of 23.5%), and experiences a smaller reduction in V3 (a decrease of 12.6%). In addition, the hue value after 4 days of maceration for the V3 variant (9.214) is comparable to the hue value after only 2 days of maceration for the V2 variant (9.572).

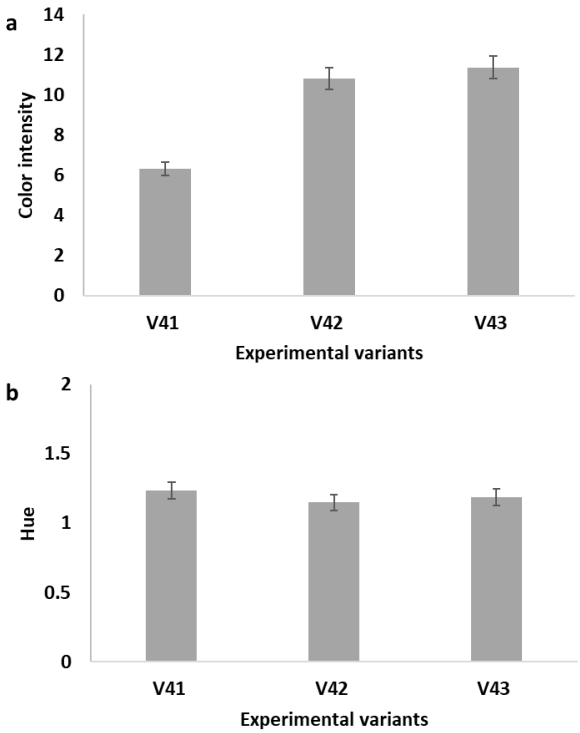

Figure 2. Values of the color intensity (a) and hue (b) for the ultrasounds assisted experimental variants – V41, V42 and V43.

After the first 2 days of maceration, the value of the hue decreases in the order V3 > V2 > V1, while, after the 4 days of maceration, the hue evolution was V3 > V1 > V2. In turn, the difference in hue value between the 2nd and 4th day of maceration is decreasing in all variants, being lower in the V1 variant (10.14%), higher in variant V2 (20.48 %) and intermediate to variant V3 (12.98 %).

The results for color parameters after the ultrasound treatment for the variants V41, V42 and V43 are shown in Figure 2a and 2b.

Comparative evaluation of the red, yellow and purple colors percentage for all the experimental variants

The red color decreased in the order V2 (4 days) > V1 (4 days) > V1 (2 days) > V3 (4 days) > V2 (2 days) > V41 > V42 > V3 (2 days) > V43. It was observed that the extraction of the red components in the pre-fermentative stage was not significantly influenced by the ultrasound treatment associated with heat treatment (variants V41, V42 and V43) and in this situation the time of action had a higher influence than temperature applied (in the case of variants V1, V2 and V3) (Figure 3a and d).

It was noticed that for V1, V2 and V3 variants, the yellow color decreased over the maturation time of 4 days, being less dependent on the temperature evolution, while for variants V41, V42 and V43 this percentage decreases with the temperature increase (Figure 3b and d).

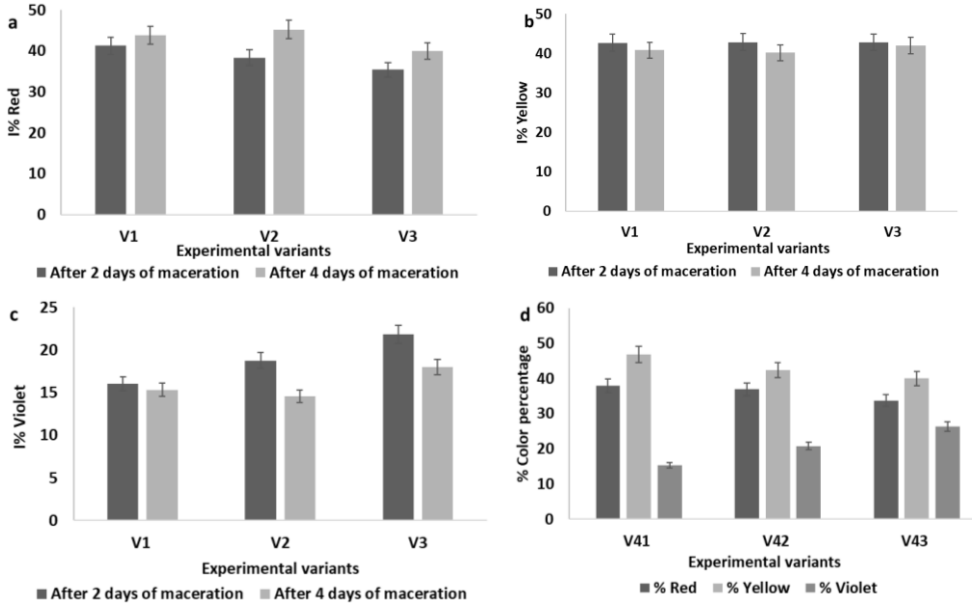

Figure 3. The red (a), yellow (b) and violet (c) colours percentage evolution for V1, V2 V3 and V4 (d) experimental variants.

A decrease of the violet percentage was observed in the order V43 > V3 (2 days) > V42 > V2 (2 days) > V3 (4 days) > V1 (2 days), so it can be stated that the ultrasound process associated with higher heat treatment favored the extraction of the compounds responsible for the violet color in the pre-fermentative stage, after a short interval of action (only 30 min) compared to the V3 variant (which needed an interval of action of 2 days and a temperature of 70 °C to insignificantly exceed the specific value of the variant V42 with a temperature of only 30 °C and a duration of action of only 30 min) and especially compared to the variants V3 (after 4 days) (Figure 3 c and d).

An intensification of the red color percentage was induced, to the detriment of the yellow and purple color was generally observed that during maceration. These findings can be correlated with several factors such as: the environmental conditions (pH, presence or absence of some compounds), an insufficient degradation of the plant material at the cellular level, able to facilitate the complete release of the phenolic compounds (Pinelo *et al*., 2006), certain agro-biological characteristics specific to the variety (Surguladze and Bezhuashvili, 2017).

However, it can be seen that with the application of higher temperatures (V2 - 25°C; V3 - 70°C) or the application of the cavitation phenomenon together with the increase in temperature (V42 – 40kHz, 30°C; V43 – 40kHz , 60-65°C) more advanced polyphenolic extractions were obtained, which leads to the possibility that pre-fermentative thermal treatments, especially those carried out at low temperatures, do not demonstrate increased efficiency in releasing the compounds responsible for color (anthocyanin compounds) in the case of the *Feteasc*ă *Neagra* variety. In order to elucidate this important aspect, it is necessary to continue the studies with the inclusion of the technological stage of alcoholic and malolactic fermentations and even the maturation stage, with the parallel achievement of some samples obtained by conventional maceration-fermentation.

Generally, with the exception of pre-fermentative thermal treatments at higher temperatures (> 60 °C), there are no unanimously accepted opinions regarding the technological efficiency of macerations carried out separately from the fermentation stage, especially in the case of maceration carried out at low temperature (cold maceration). The research on low-temperature macerations is inconclusive, as some studies indicate enhanced efficiency for some grape varietals (Aleixandre *et al.*, 2013; Coletta *et al.*, 2013; Puertas *et al*., 2013) as well as sufficient studies that obtained variable or contradictory results in the case of experiments on various grape varieties (Casassa and Sari, 2015; González-Neves *et al.*, 2015; González-Neves *et al*, 2016). The primary aspect in the identified issue appears to be the grape variety utilized in winemaking and its morphological traits from the outset (Álvarez *et al*., 2006; Morel-Salmi *et al.*, 2006; Frangipane *et al*., 2010; González-Neves, 2010; Borazan and Bozan, 2013; Watrelot *et al.*, 2013; Casassa and Harbertson, 2014; Panprivech *et al*., 2015; Aleixandre-Tudo and du Toit, 2018).

Conclusions

The study was dedicated to grapes from the local *Feteasc*ă *neagr*ă variety, with an old winemaking tradition, which has remained a relatively little analyzed variety regarding the degree to which it lends itself to new winemaking techniques, although the favorable sensory assessments of its wines have exceeded the national framework.

Based on the obtained results, it can be stated that the low-temperature maceration process V1 does not seem to lend itself to the vinification of *Feteasc*ă *neagr*ă grapes, as no extractions of phenolic compounds comparable to the other processes, V2 and V3, are obtained, regardless of the total duration maceration applied, and one of the

causes refers to the morphological peculiarities of the *Fetească neagră* variety. Therefore, the possibility that the simple prolonged contact between the liquid fraction (must) and the solid fraction (skin and pulp, less the seeds which yield much more difficult to the phenolic compounds in the pre-fermentative stage) is not enough to release the phenolic compounds of interest found predominantly in the skins grape berries, being necessary either other technological interventions (treatment with enzymatic extraction preparations, administration of sulfur dioxide or ascorbic acid), or the combination of this process with another, such as maceration assisted by ultrasound or carbonic maceration. It was observed, however, that low temperature plays an important role in stabilizing the extracted phenolic compounds, as expected. The obtained results showed that by applying thermomaceration (variant V3), satisfactory extractions of phenolic compounds can be achieved, with the advantage of reducing the total duration of maceration, which ensures a high degree of applicability in the wine industry.

However, in both variants V1 and V3, as well as in the case of variant V2 of conventional maceration, a low share of the percentage of violet in the color composition was observed in relation to the percentages of yellow and red, which may indicate a certain inefficiency of these procedures in obtaining red wines with attractive and durable chromatic characteristics in the later stages of maturation and aging.

Ultrasound-assisted macerations combined with heat treatment yielded improved outcomes in short periods of time, enhancing the extraction of phenolic compounds, color development, and the reduction capacity of the musts. It is advisable to extend the research to encompass the technological phases of alcoholic and malolactic fermentations, as well as the maturation and conditioning processes (clarification, stabilization, filtering) followed by bottle aging, to monitor the long-term evolution of the examined parameters. This recommendation is necessary because it was observed that even in the case of some pre-fermentative extractions considered successful, the benefits regarding the optimal concentrations of phenolic compounds obtained were not maintained over time.

Having as an inspirational model the results obtained with the *Fetească neagră* grape variety, later the studies could be extended to other Romanian red varieties as the morphological characteristics of the grape seeds seem to be of major importance in the choice of the extraction procedures of the phenolic compounds useful in the expression of some chromatic characteristics and superior sensory, as well as a higher value of the antioxidant capacity with real health benefits.

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