THE EFFECT OF THE PRE-FERMENTATIVE SKIN CONTACT ON THE COLOUR CHARACTERISTICS AND TOTAL PHENOLS OF WHITE WINES

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Abstract

Skin contact for aromatic grapes at low temperatures is essential for the quality of the resulted wines, Sometimes, even non-aromatic grapes can benefit from skin contact so that the wines obtained achieve the desired mouthfeel and aroma. In this study we have evaluated the effect of the pre-fermentative skin contact on a blend of white grapes consisting of 80% of a non-aromatic Romanian variety, Feteasca alba, and 20% of the aromatic variety Muscat Ottonel. The macerations were conducted at controlled temperature for 6 hours (T6) and 12 hours (T12), while for control, no skin contact was allowed (T0). The effects of maceration on the CIELab parameters and total polyphenols (TPI) of resulted wines were evaluated. The wines with 12 hours of maceration (T12) were significantly different from the samples with no maceration (T0) and samples with short time skin contact (T6). The colour differences can be easily perceived by an inexperienced observer, as long as the total colour differences AE values (T12-T0) = 3.90 ± 0.98 and, respectively, (T12-T6) = 2.44 ± 0.97 . The TPI results suggest that the skin contact period, favours more polyphenol extraction, but also promotes oxidation of polyphenols and then their precipitation.

Key words: CIELab, pre-fermentative maceration, total polyphenols, white wine.

INTRODUCTION

The pre-fermentative skin contact on white grapes is occasionally performed in order to extract certain primary aroma compounds, along with some phenolic compounds important for wine texture. However, when extracting more polyphenols, later on, they should be protected from oxidation (Jones et al., 2008; Bueno et al., 2010; González-Barreiro et al., 2015; Esti & Tamborra, 2006). Most importantly, for white winemaking the well-balanced phenolic compound extraction and harmonious preservation is decisive for the wine quality modern consumers expect. With or without maceration, white wines are preferred with supple tannins, with one notable exception represented by orange wines (Schneider & Chichua, 2021), for which the long maceration on skins leads to a higher extraction and oxidation. Moreover, lack of temperature control during skin contact will change dramatically the rate of the extraction of volatile and phenolic compounds. For an adequate management of skin contact, most authors recommend keeping the temperature around 10-15°C or even lower, to limit the extraction of phenolic compounds, while enhancing the extraction of aroma precursors or beneficial volatile compounds (Ramey et al., 1986). The pre-fermentative maceration at temperatures lower than 15°C limited the extraction of both excessive tannins and proteins, lowering the browning capacity and the required dose of bentonite necessary to achieve the commercial heat stability of young wines (Ramey et al., 1986). In the case of the aromatic grape varieties, the scope of maceration is mainly the extraction of aroma compounds. The varieties from the Muscat family, as it is the case of Muscat Ottonel which was used in our blend with the nonaromatic Feteasca alba (20% and 80% respectively), the characteristic varietal aroma is determined by over 50 monoterpene alcohols and derivatives identified in the berries (Mateo & Jiménez 2000). These terpene alcohols exist either in free forms or as glycosides (Versini et al., 1994; Carrau et al., 2008), the latter being released by enzymic hydrolysis in the presence of β -glycosidase or by chemical hydrolysis at low pH (Williams et al., 1992; Skouroumounis & Sefton, 2000; Boido et al., 2002; Swiegers et al., 2005). Nevertheless, yeast can also have influence on the aroma, including on the terpenic aroma, a recent study showing that certain yeast strains of Saccharomyces cerevisiae can produce monoterpene alcohols in a simple chemically defined medium, even in the absence of precursors such as the terpenic glycoconjugates (Carrau et al., 2005). Irrespective of the aroma compounds found in grapes, their free or precursor concentrations are increased by pellicular maceration, as compared to the case of directly pressing musts, as Peyrot des Gachons (2002) showed in their study on Sauvignon blanc. The extraction is potentiated by the maceration temperature, higher concentrations of the skin located compounds being obtained at 18°C as compared with 10°C (Pevrot des Gachons, 2002).

In modern winemaking, however, keeping the temperature at higher values is not always desirable, as this is also accompanied, during pre-fermentative phase, by higher polyphenol extraction and by the growth of unwanted microorganisms and certain enzymatic reactions (Gómez-Míguez et al., 2007; Marais, 1998; Salinas et al., 2005). Conducting the skin maceration at lower temperatures is thus preferred in modern winemaking and it comes

also with the advantage of reducing the concentrations of sulphur dioxide during this phase. Whenever possible, during prefermentative phase, the effect of oxygen, which is more soluble at lower temperatures, may be reduced by adding carbonic ice (Carillo et al., 2011; Roussis et al., 2007). Other effects observed as a result of the skin contact is an increased extraction of potassium ions, leading later on to more potassium bitartrate precipitation, thus, to lower final titratable acidity and higher pH (Ough, 1969; Boulton, 1980; Sokolowsky et al., 2015), requiring sometimes other interventions for correction. As few studies regarding the effect of length of pre-fermentative skin contact have been conducted on Romanian grape varieties, this research was dedicated to the evaluation of the colour characteristics and total phenols of musts for white wines with maceration based on Feteasca alba as the main variety (Moroşanu et al., 2016; Moroșanu et al., 2018).

MATERIALS AND METHODS

This study was carried out on a blend consisting of 80% Fetească alba and 20% Muscat Ottonel grapes, harvested on September 10th, 2018 from a vineyard located in Dealu Mare - Boldesti Scaeni DOC (Denomination of Controlled Origin). The experimental variants were done in triplicate and the pre-fermentative technological conducted steps (I-VII) accordingly to Table 1.

Pre-fermentative technological steps	Must variants depending on the duration of skin maceration			
and parameters	TO	T6	T12	
I. Grape mash (crushed grapes)	5 kg	5 kg	5 kg	
II. Treatment with SO ₂ on grape mas	50 mg/kg	50 mg/kg	50 mg/kg	
III. Skin contact	0 hours	6 hours	12 hours	
IV. Temperature during skin contact	8-10°C	8-10°C	8-10°C	
V. Reserved grape must after press	3 litres	3 litres	3 litres	
VI. Clarification time by settling at 10°C	3 hours	3 hours	3 hours	
VII. Reserved clarified grape must for fermentation	2 litres	2 litres	2 litres	

After maceration, the separated and clarified musts were allowed to ferment with their natural yeasts, at temperatures between 15 and 20°C. The resulted wines were racked off the lees and stored for two months at cellar temperatures before they were analysed. The classical analyses conducted on musts and wines were in accordance to the OIV recommended methods (OIV, 2018). The CIELab parameters and Total Polyphenolic Index were determined with a UV-VIS Specord 250 spectrophotometer from Analytik Jena AG (Germany) equipped with Chroma software Ver. 2.0. The CIELab parameters were

measured in glass cuvettes of 10 mm path length (OIV, 2018), while the Total Polyphenol Index (TPI) was measured in a quartz cuvette of 10 mm optical thickness at a wavelength of 280 nm on 10% diluted samples. The TPI results were multiplied with 10.

RESULTS AND DISCUSSIONS

The physico-chemical parameters determined on two different stages of winemaking (Table 2) showed a tendency for pH increase and a total acidity decrease in direct relation to the length of skin contact time. These changes in titratable acidity and pH are well explained by the higher extraction of potassium cations from the skins with the longer maceration times.

The results presented in Table 2 are in agreement with other previous studies (Ough, 1969; Boulton, 1980; Sokolowsky *et al.*, 2015). The pH and total titratable acidity values are also affected by some potassium bitartrate precipitation and to a certain degree by microorganism metabolism.

Table 2. Physico-chemical analyses of musts and wines obtained with maceration

Winemaking phase	Variants	Physico-chemical parameters*			
		Sugars, g/l	Total acidity, g/l tartaric acid	pH	
Grape must after settling	Т0	$205\pm2.35^{\rm a}$	$5.39\pm0.15^{\rm a}$	$3.10\pm0.02^{\text{b}}$	
	T6	$215\pm4.10^{\rm a}$	$4.67\pm0.06^{\rm b}$	$3.34\pm0.05^{\rm a}$	
	T12	$208\pm5.56^{\rm a}$	4.76 ± 0.42^{ab}	$3.41\pm0.11^{\rm a}$	
Wine after cold treatment	T0	$0.84\pm0.69^{\rm a}$	$5.73\pm0.21^{\rm a}$	3.23 ± 0.03^{b}	
	T6	$0.57\pm0.19^{\rm a}$	$5.17\pm0.70^{\rm a}$	$3.33\pm0.02^{\rm a}$	
	T12	$0.76\pm0.15^{\rm a}$	$5.16\pm0.61^{\mathrm{a}}$	3.32 ± 0.05^{ab}	

*Average values ± Standard Deviations. Different letters indicate significant differences at p<0.05 determined by One-Way ANOVA and Tukey HSD test.

That is why the wine titratable acidity is not anymore correlated with the maceration time, the samples stabilizing all around a similar value. The values of acidity in our wines are not significantly different than in the case of the correspondent musts, due to several conditions during fermentation.

Generally, the titratable acidity decreases after alcoholic fermentation as a result of ethanol accumulation and storage at low temperature, which both affect the solubility of potassium bitartrate leading to crystallization and precipitation.

However, it is not uncommon to observe a rise in total titratable acidity of wines due to various yeast fermentations under certain conditions during alcoholic fermentation (temperature, nutrient, oxygen, etc.) or presence of strains which promote succinic acid and/or lactic acid production, as normal fermentation by-products (Thoukis *et al.*, 1965; Vilela, 2019; Mendes-Ferreira & Mendes-Faia, 2020; Sainz *et al.*, 2022). Another cause of titratable acidity increase may be the volatile acidity production by unwanted microorganisms and uncontrolled winemaking process (Zoecklein *et al.*, 2012; Chidi *et al.*, 2018), but this is not our case. Sugar concentration of the resulted musts showed small variations between the variants, with average of around 5 g/l (Table 2).

After wine cold stabilization and racking the colour and TPI index were measured, to determine the relationship between maceration and the wine quality. The results (Table 3) showed a statistically significant decrease of TPI in macerated wines as compared to control wine. This was surprising at first, as many studies show that polyphenols tend to increase in white musts and wines produced with prefermentative skin contact, the effect being more evident as the time and temperature of maceration increase (Cheynier *et al.*, 1989; Marais, 1998; Darias-Martin *et' al.*, 2004; Gomez-Miguez *et al.*, 2007).

Table 3. Total polyphenol index and CIELab parameters of wines after cold stabilization

Variants	TPI*,	Colour parameters*				
	UA	Clarity (L)	Parameter a	Parameter b	Chroma (C)	hab°
TO	$7.28\pm0.14^{\rm a}$	$98.69\pm0.04^{\rm a}$	-0.156 ± 0.06^{b}	$5.23\pm0.09^{\circ}$	$5.23\pm0.09^{\rm c}$	$91.72\pm0.65^{\mathrm{b}}$
T6	$6.13\pm0.59^{\text{b}}$	$98.22\pm0.05^{\rm a}$	$\textbf{-0.384} \pm 0.03^{a}$	$6.88\pm0.08^{\rm b}$	$6.89\pm0.08^{\text{b}}$	$93.19\pm0.18^{\rm a}$
T12	6.52 ± 0.39^{b}	96.41 ± 0.50^{b}	$0.133\pm0.05^{\rm c}$	$8.38\pm0.90^{\rm a}$	$8.39\pm0.90^{\rm a}$	$89.11\pm0.28^{\rm c}$

*Average values ± Standard Deviations. Different letters indicate significant differences at p<0.05 determined by One-Way ANOVA and Tukey HSD test.

The decrease we have observed could be due to a natural process of stabilization, where the phenolic-protein interaction under cellar temperature conditions caused the precipitation of these aggregates, especially because the wines were not treated with bentonite to remove unstable proteins.

It is well known that the pH, alcohol content and the concentration of polyphenols and proteins in the wine may affect colloidal stability and therefore cause spontaneous precipitation (Siebert & Lynn, 2003; Charlton et al. 2002; Adamczyk et al., 2012). Moreover, phenolic compounds are demonstrated to be among the factors involved in protein haze formation, as they were found, for example, in the natural proteinaceous precipitate in a Sauvignon blanc wine (Esteruelas et al., 2011). The colour CIELab parameters are also included in Table 3. Clarity or lightness parameter (L) is very good for all wines, with a tendency to slightly decrease with skin contact, but a significant difference is observed only in the case of 12 hours skin contact. In the same time, with the decrease in lightness, the chromaticity of the samples increases.



Figure 1. Placement of wines in the CIELab space described by parameters Clarity and Chroma

In Figure 1, an inverse direct relationship can be observed between the lightness parameter (L) and chroma (C), with the increase in the skin contact time. The experimental white wines resulted from long time skin contact had deeper colour, with enhanced colour saturation. The colour saturation itself (Chroma in Table 2) significantly increased with the maceration time (T) for all the experimental variants, the chromaticity being extremely well correlated to the time of skin contact (C=5.256+0.263*T; R^2 =0.999). Even though the lightness was affected to a lesser extent than chroma (L=98.91-0.19*T; R^2 =0.896), both parameters contribute to total colour difference (ΔE), a practical parameter for interpretation of the overall colour. The values of parameter a (showing the position of the sample colour between red and green) showed statistically significant differences among the samples, indicating that the colour loses some of its green component with the time of maceration, at 12 h maceration even a slight red component being present (Table 3 and Figure 2).



Figure 2. Placement of wines in the CIELab space described by parameters a and b

On the other hand, the parameter b (showing the position of the sample colour between yellow and blue) was also significantly different for all the experimental samples, the values increasing linearly with the skin contact time, indicating an increase of yellowness in macerated wines (Table 3 and Figure 2). Nevertheless, in white wines, the parameter b is generally more important than parameter a, having the most influence on the colour saturation (C), from which it does not differ much (Table 3).

The positioning of the wine samples in the colour diagram described by the parameters a and b (Figure 2) reveals that control wines, resulted from direct pressing musts, have the least intense yellow component and a green component almost imperceptible for the naked eye, while the 6 hours macerated wine had a slight increase in yellow, but a noticeable increase in the green component. On the other hand, the 12 hours macerated wines showed a

higher increase in the yellow colour component, with a noticeable shift towards the red space of the diagram, thus suggesting an increased oxidation compared with the other experimental variants, due to the extraction of more oxidizable polyphenols.

To have an overall idea of the changes in colour induced by the maceration, the total

colour differences (ΔE) were calculated and included in Table 4, along with the differences of the main CIELab parameters. The total colour difference between control wines (T0) and wines with 6h maceration (T6) samples is $\Delta E = 1.73 \pm 0.14$, suggesting that, being higher than 1, but lower than 2, can only the noticeable for observers with trained eyes.

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Table 4. Colour	amerences	among in	e experimental	wine samples

	Colour differences				
Variant comparison	ΔL	Δa	Δb	Total colour difference ΔE^*	
T6-T0	-0.466 ± 0.05	0.228 ± 0.05	1.648 ± 0.15	1.73 ± 0.14^{b}	
T12-T0	-2.276 ± 0.54	0.289 ± 0.01	3.154 ± 0.81	3.90 ± 0.98^{a}	
T12-T6	-1.810 ± 0.53	0.517 ± 0.05	1.507 ± 0.95	$2.44 \pm \mathbf{0.97^{b}}$	

*Average values ± Standard Deviations. Different letters indicate significant differences at p<0.05 determined by One-Way ANOVA and Tukey HSD test.

The wine samples resulted through a longer maceration time (T12) compared to control wines (T0) had a total colour difference of $\Delta E = 3.90 \pm 0.98$, clearly noticeable by any observer, even inexperienced. Comparing the wines with different maceration times, T6 and T12, a colour difference of $\Delta E = 2.44 \pm 0.97$ is obtained, generally meaning that most inexperienced observers would be able to perceive it. Clearly, the difference of total colour is increasing with the time of skin contact.

CONCLUSIONS

The influence of skin contact time on the physico-chemical parameters of must and wine emphasizes that the longer the time of contact, the more noticeable increase is seen in pH and decrease in total acidity, even though the final values cannot be entirely predicted because of other influences such as yeast metabolism and potassium bitartrate precipitation during cold stabilization.

The influence of skin contact time on the polyphenol content evaluated by Total Polyphenol Index. The measurement of TPI showed a statistically significant decrease of polyphenol concentration in the macerated wines, as a result of wines stabilization through the precipitation of some phenolic compounds and proteins extracted through skin contact. As the musts and wines were not treated with bentonite for protein removal, a possible polyphenol-protein interaction and finally spontaneous precipitation could occur and

explain the decrease in the total polyphenolic index.

The influence of skin contact time on colour measured by CIELab parameters showed a higher Clarity (L, lightness) in non-macerated wines, while the skin contact time increased this parameter, meaning the samples with maceration were less transparent than the control. The decrease in lightness of 12 hours skin contact wines was statistically significant compared with the other experimental variants. The CIELab parameters a and b showed that the colour of controls with no skin contact (T0) is pale-yellow, while after a maceration of 6 hours (T6) a slightly more intense yellow-green colour resulted, which is desired by most winemakers because it suggests and is usually correlated with a higher mouthfeel. After a 12 hours maceration (T12), a higher value for the vellow component is obtained, with a perceivable pale reddish component. This deeper colour, with less green component than the other variants, suggests the possibly that the higher content of extracted polyphenols was also more prone to oxidation. These longmacerated wines, darker in colour and with enhanced colour saturation (C), are generally not desired by the winemakers, as this incipient oxidation can affect the general perception of wine quality.

The influence of skin contact time on total colour difference. The calculated ΔE clearly shows an influence of the maceration ΔE values on the colour of the resulted wines. There are differences of colour for both variants obtained with various times of maceration (T6, T12) as

compared with the control wines (T0). Especially in the case of wines with longer maceration (T12), the total colour difference $\Delta E = 3.90 \pm 0.98$ is easily recognized by any untrained wine consumer, which is not a good thing, as lighter coloured wines are preferred by most consumers. However, the differences in colour between the short-macerated wines (T6) compared to control wines are not so obvious for an inexperienced wine consumer, even though trained professionals would perceive the difference.

Considering the observed and discussed consequences of the skin contact time on the production of white wines, it can be concluded that a short maceration time of 6 hours is better for the wine quality as compared either with no maceration or with a longer maceration of 12 hours.

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