Influence of cold-maceration on colour and anthocyanin composition of Syrah wines

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ABSTRACT

Prefermentative cold-maceration of Syrah musts conducted with different maceration times (11, 13 and 15 days) was studied. Colour and phenolic composition, mainly anthocyanins, of the wines were studied until the end of the alcoholic fermentation period and compared with a wine produced by traditional vinification. The results showed that cold macerated wines were a bit lighter, with higher h_{ab} and C^*_{ab} values, and with higher anthocyanin content. However, the saturation values were very similar to those the traditional vinification wines. Besides, it has been possible to predict the wine colour from the anthocyanin content by using multiple linear regression analysis.

1. INTRODUCTION

During red wine vinification, the length and temperature of skin contact are two of the factors that affect the extraction of phenolic compounds into the must, and so the final wine colour[1]. In recent years "cold-maceration" (*cryo-maceration*), that is, low maceration temperatures (10º-15ºC) prior to fermentation, is being used to improve the extraction of pigments, tannins and aromas from the grape skins to the wine. However, the knowledge of the influence of this technique on the final wine composition and sensory quality, specially on its colour, has not been well researched yet so only a few data can be found in the literature[2,3]. Therefore, the purpose of this work is to study more deeply the effects of cold-maceration (10-15 ºC) on colour and phenolic composition of Syrah wines made in southwestern Spain.

2. METHODS

Winemaking protocol. Four vinification methods were carried out by using Syrah grapes from the "Condado de Huelva" Designation of Origin, in southwestern Spain: a traditional on-skin fermentation (TV) at controlled temperature (23º C) with 7 days of maceration, and three other vinifications that consisted of prefermentative macerations carried out at low temperature (15 ºC) with 11 days (CM-1), 13 days (CM-2) and 15 days (CM-3) of cold maceration, respectively. Each vinification procedure was carried out in duplicate. Must and wine samples were taken periodically until the end of the alcoholic fermentation period.

Colorimetric measurements. Colour measurements were made by transmission with an UV-vis HP 8452 Spectrophotometer, using 0.2 cm path length glass cells. The whole visible spectrum (380-770 nm) was recorded ($\Delta\lambda$ = 2 nm), and Illuminant D_{65} and 10º Observer were considered as references. The CIELAB parameters (L^*, a^*, b^*, C^*_{ab}, h_{ab}) and saturation s^*_{uv} by CIELUV were determined by using the software CromaLab[4], following the recommendations of the Commission Internationale de L'Eclariage[5].

HPLC analysis of anthocyanins. Anthocyanins were analysed by direct injection of the samples in a Hewlett-Packard 1100 chromatographic system, using a Zorbax-SB C_{18} column. The solvents used were water/acetonitrile/formic acid (3:10:87) as solvent A and water/acetonitrile/formic acid (50:10:40) as solvent B. The elution profile was 0 min, 94% A, 6% B; 10 min, 80% A, 20% B; 20 min, 60% A, 40% B; 30 min, 50% A, 50% B; 35 min, 94% A, 6% B. The flow-rate was at 0.8 mL/min and the injection volume was 50 μL. UV-vis spectra were recorded from 250 to 780 nm with a bandwith of 2.4 nm, and the detection wavelength was 525 nm. Quantitation was made by means of a calibration curve obtained with standard solutions of malvidin-3-monoglucoside.

Besides, the total phenol contents of the samples were determined by using the Folin-Ciocalteu method[6], which expresses the results as milligrams of gallic acid per liter.

Statistical Analysis. Correlations between colour parameters and anthocyanin content were studied by forward stepwise multiple linear regression. Statistica v. 6.0. software was used[7].

3. RESULTS

Colour. When the evolution of wine colour was studied, it was observed that the most significant colour changes were produced during the maceration period, and all the colorimetric parameters became stable during fermentation. Therefore, the progressive degradation of anthocyanins and the formation of new pigments during the fermentation period seem not to affect a lot the colorimetric changes that take place during this stage. Besides, all the four wines underwent a decrease of L*, a*, b*, C^*_{ab} and h_{ab}, although the fall in L* was more marked, and an increase of s^*_{uv}. Therefore, at the end of the test, the wines were darker, with a more bluish-red colour, more saturated (s^*_{uv}), but with lesser values of chroma than at the beginning of the maceration. These data suggest that the low values of lightness of these wines influences the saturation ($s^*_{uv} = C^*_{uv}/L^*$) more than the chroma does.

Table 1 shows the colour characteristics of the four Syrah wines at the end of the fermentation period. It can be seen that cold macerated wines (CM-1, CM-2 and CM-3) were a bit lighter, with a more red-orange colour, but with higher C^*_{ab} values. However, the saturation values were very similar to those the traditional vinification wines (TV). These observations were more appreciated in the CM-1 wine, so the length of the maceration period was a factor influencing the wine colour. Specifically, the wines produced with less days of cold-maceration had a lighter colour, but above all, a more vivid colour (higher values of chroma).

Table 1: Colour parameters of the wines at the end of the alcoholic fermentation period.

	TV	CM-1	CM-2	CM-3
L^*	5.55±0.08	9.54±0.35	6.37±0.72	5.71±0.12
a^*	32.99±0.22	40.27±0.45	34.96±1.65	33.40±0.32
b^*	9.57±0.13	16.41±0.60	10.97±1.24	9.83±0.20
C^*_{ab}	34.35±0.25	43.49±0.65	36.65±1.95	34.81±0.36
h_{ab}	16.17±0.11	22.16±0.51	17.37±1.07	16.41±0.17
s^*_{uv}	4.80±0.01	4.68±0.01	4.77±0.03	4.78±0.01

Anthocyanin composition. According to Singleton[8], during the maceration period, parallel to the extraction the anthocyanins are slowly linked to other compounds, thus decreasing the concentration of free anthocyanins in dissolution, as it has been observed in the TV wine. However, this decrease wasn't observed by using low temperatures during the skin contact period. Far from it, the pre-fermentative cold maceration technique has shown to favour the constant liberation of anthocyanins from skins to must, the maximum of total anthocyanin content being reached at pressing. Besides, after pressing and during the first days of fermentation, the content of individual anthocyanins carried on strangely increasing although the contact of the must with the skins has already finished. Probably, the appearance of ethanol in the medium and the increase of the must temperature produced a decrease of the stability of the copigmentation complexes previously formed with the subsequent liberation of flavilium ions[9-11].

Table 2 shows the anthocyanin contents of the wines at the end of the fermentation period. It can be seen that, quantitatively, glycosilated anthocyanins were predominant in all the Syrah wines (sum_gl=50-59%), followed by acetylated (sum_ac=23-27%) and coumarylated (sum_cm=13-18%), respectively. With respect to the influence of the maceration technique, TV wines had the highest content of sum_gl, but all the other fractions were higher in the CM wines, including the total anthocyanin content. Therefore, the use of low temperatures during the maceration period favoured the extraction of these compounds from skins to must. Besides, if the three cold-macerated wines are

compared, it can be seen that the longer the maceration duration (CM-3), the higher the content of anthocyanins. The total phenolic content was also higher in the CM-3 wines (3870 mg/L versus 3600 mg/L of the other wines).

Table 2: Anthocyanin composition of the wines (mg/L) at the end of the alcoholic fermentation period.

	TV	CM-1	CM-2	CM-3
Sum_gl	192.5±10.08	166.5±9.75	184.8±11.12	188.3±10.12
Sum_ac	96.8±5.22	93.9±6.45	101.8±9.48	103.7±9.21
Sum_cm	55.9±6.42	58.8±7.12	62.2±8.15	64.5±7.05
Ant_tot	367.5±17.06	339.4±12.11	373.6±15.32	377.3±14.02

Sum_gl: sum of non-acylated anthocyanins
Sum_ac: sum of acetates
Sum_cm: sum of coumarates
Ant_tot: total anthocyanin content

Colour-composition relationships. To evaluate the correlation between colour and anthocyanin composition of the wines, multiple linear regression analysis was made in forward stepwise manner to select suitable variables in the model. A value of $p<0.05$ was considered to be significant. The colorimetric parameters were considered as dependent variables, and the contents of anthocyanins, pH and SO_2 values were considered as independent variables, these latter parameters being also included in the analysis due to the fact that wine colour is highly dependent on them. The equations found for all the wines, with multiple correlation coefficients (R) higher than 0.80 are shown in Table 3. It can be seen that saturation s^*_{uv} and lightness L* were the best correlated parameters. Besides, TV and CM-1 were the vinification protocols that led to a greater number of valid equations. However, only saturation could significantly be predicted with longer maceration durations. It can also be observed that the coumarate derivatives are much more important to predict the colour of the cold-macerated wines than the colour of the traditional wines.

Table 3: Multiple linear regression equations and R values for the Syrah wines.

Vinification method		*R*
TV	$L^* = 0.22pH+0.72SO_2+0.42Sum\_gl-0.99Sum\_ac+0.38Sum\_cm$	0.98
	$a^* = 0.74pH+1.03Sum\_gl-1.27Sum\_ac$	0.80
	$C^*_{ab} = 0.70pH+1.14Sum\_gl-1.42Sum\_ac$	0.80
	$h_{ab} = -0.72SO_2+1.84Sum\_gl-3.03Sum\_ac$	0.87
	$s^*_{uv} = -0.97\ SO_2$	0.97
CM-1	$L^* = 0.62pH+0.24SO_2-0.30Sum\_gl-1.87Sum\_ac+2.07Sum\_cm$	0.97
	$a^* = 0.46pH-0.29SO_2-0.35Sum\_gl-3.06Sum\_ac+3.90Sum\_cm$	0.94
	$C^*_{ab} = 0.48pH-0.29SO_2-3.46Sum\_ac+3.98Sum\_cm$	0.92
	$s^*_{uv} = -0.62pH-0.47SO_2+0.26Sum\_gl$	0.93
CM-2	$L^* = 0.89SO_2-0.14Sum\_gl+0.39Sum\_ac-0.80Sum\_cm$	0.97
	$s^*_{uv} = -0.83SO_2+0.25Sum\_gl-0.47Sum\_ac+0.83Sum\_cm$	0.98
CM-3	$s^*_{uv} = -0.32SO_2+1.42Sum\_ac-0.80Sum\_cm$	0.92

4. CONCLUSIONS

The length and temperature of skin contact during the vinification of Syrah wines have shown to be two factors affecting the phenolic composition and colour of the wines. Specifically, the use of low temperatures during the maceration period (*cryo-maceration*) has favoured the extraction of phenolic compounds from skins to must, above all when longer maceration durations were tested. With respect to colour, cold macerated wines were a bit lighter, with a more red-orange colour and with higher chroma values. However, all the wines had very similar saturation values.

Multiple linear regression analysis has proved to be very useful to predict the wine colour from the anthocyanin composition, saturation and lightness being the best predicted parameters ($R>0.90$, $p<0.05$).

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