ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/8420040

Effect of the Maceration Technique on the Relationships between Anthocyanin Composition and Objective Color of Syrah Wines

ARTICLE *in* JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY · SEPTEMBER 2004

Impact Factor: 2.91 · DOI: 10.1021/jf049570z · Source: PubMed

CITATIONS
36

READS
37

2 AUTHORS, INCLUDING:

Francisco J. Heredia
Universidad de Sevilla

190 PUBLICATIONS **3,313** CITATIONS

SEE PROFILE

Available from: Francisco J. Heredia
Retrieved on: 04 February 2016

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

J. Agric. Food Chem. **2004,** *52,* 5117−5123 **5117**

Effect of the Maceration Technique on the Relationships between Anthocyanin Composition and Objective Color of Syrah Wines

MANUELA GÓMEZ-MÍGUEZ AND FRANCISCO J. HEREDIA*

Laboratory of Nutrition and Food Science, Faculty of Pharmacy, University of Seville, 41012 Seville, Spain

The effects of two different vinification techniques, traditional fermentation and carbonic maceration, on the anthocyanin composition and color of young red wines, made with Syrah grapes grown in a warm climate, were compared. Tristimulus colorimetry was applied to study the color of wines during the vinification, and a high-performance liquid chromatography (HPLC) procedure was used for the analysis of anthocyanins. Carbonic maceration led to wines with lower anthocyanin content, mainly monoglucosides, and total phenols. This was related to lighter wines, less saturated, but more colorful (higher chroma C^*_{ab} values), and hues h_{ab} similar to those of the Syrah wines made by traditional vinification. Thus, the lightness L^* had much more influence on the saturation s^*_{uv} of the wines obtained by carbonic maceration than the chroma ($s^*_{uv} = C^*_{uv}/L^*$). From a study of the color−composition relationships using linear and multiple regression, better relationships were found for the wines from traditional vinification, where the chromatic parameters L^*, h_{ab}, and s^*_{uv} could be predicted from the 3-monoglucosides of delphinidin, petunidin, peonidin, and malvidin concentrations ($R > 0.9$). However, a good prediction of the chroma C^*_{ab} from the anthocyanin composition was not possible. On the contrary, C^*_{ab} was the best predicted parameter from the anthocyanins monoglucosides ($R > 0.9$) in the carbonic maceration wines.

KEYWORDS: Color; anthocyanins; winemaking; carbonic maceration; HPLC; red wine

INTRODUCTION

Anthocyanins extracted from red grape skins during maceration are the principal components responsible for red wine color. The grape variety and the vinification technique affect the concentration and composition of wine anthocyanins, so these factors affect the wine color, too (*1*).

The most commonly used vinification technique is the traditional vinification with stem contact, but the use of carbonic maceration is important, too, mainly to obtain very young fruity red wines with a certain astringency. It is well-known that the color and phenolic composition of the wines obtained by these two techniques are different. This difference is due to the anaerobic fermentation during the carbonic maceration (*2*). Rizzon et al. (*3*) evaluated the effects of conventional vinification, thermovinification, and carbonic maceration on the chemical composition and quality of Cabernet Franc wines. The sensory evaluation showed that carbonic maceration produced lighter wines with lower color intensity and with worse body and lower quality in both taste and aroma.

In addition, carbonic maceration leads to wines with a different concentration and composition of phenolics from that in wines produced by traditional methods. In this way, carbonic maceration produces wines containing a lower average content of total phenolics, anthocyanins (*4*, *5*), and resveratrol (*6*) but higher amounts of catechins and oligomeric and polymeric proanthocyanidins (*7*).

In both vinification processes, temperature and length of maceration are two of the factors that affect the color characteristics and composition of the final red wine. Lörincz et al. (*8*, *9*) studied the effect of these factors on the phenolic composition of red wines produced by carbonic maceration. They found that the longer carbonic maceration time (14−21 days) greatly increased the amount of phenolic constituents (anthocyanins, catechins, leucoanthocyanins) and improved the color stability of the wines. Besides, wines obtained by cold carbonic maceration (16−18 °C) contained less phenolics than the warm wines (30−32 °C). Therefore, prolonged maceration at higher temperature is important for grapes with low levels of anthocyanins. Lörincz also saw that an additional skin fermentation process, which followed the carbonic maceration, resulted in a higher amount of phenolic substances.

In this study, two vinification techniques (traditional on-skin fermentation and carbonic maceration) were tested with Syrah grapes grown in a warm climate. The evolution of the color characteristics and phenolic composition, mainly anthocyanins, was studied to compare the effects of the two processing

* Author to whom correspondence should be addressed (telephone ++34 954556761; fax ++34 95455 7017; e-mail heredia@us.es).

10.1021/jf049570z CCC: $27.50 © 2004 American Chemical Society
Published on Web 07/17/2004

conditions. Possible color−anthocyanin composition relationships were studied by using multivariate statistical analysis.

MATERIALS AND METHODS

Vineyards. Grapes from *Vitis vinifera* var. Syrah were grown in an experimental vineyard located in "Condado de Huelva" Designation of Origin, in southwestern Spain, with the typical climatological conditions of warm climate regions.

Vinification Protocol. Grapes were harvested in 2000 at 12 °Bé (1.091 g/mL) and transported to the winery. Then, two different standardized vinification procedures were carried out on a pilot scale: carbonic maceration and a conventional on-skin fermentation.

Traditional Maceration (TM). Four hundred kilograms of Syrah grapes was crushed and destemmed, and the must was pumped into a 600 L stainless steel tank. Potassium metabisulfite was added (80 mg of SO_2/L), and the pH was adjusted to 3.70 prior to the on-skin fermentation at controlled temperatures (25−27 °C) of the must. Fermentation caps were punched down twice daily during the skin maceration period, which was 9 days. Then, when alcoholic fermentation was finished, the mash was pressed and the free-run and press wines were both combined in another 600 L tank and left to mature at 20 °C for 21 days.

Carbonic Maceration (CM). Forty kilograms of another 400 kg lot of Syrah grape clusters was crushed and destemmed, collected in a 600 L stainless steel tank, and treated with sulfur dioxide (80 mg/L). Then, the remaining 360 kg of the grape clusters was emptied into the same tank. The material was stored at 22−25 °C under a CO_2 atmosphere for 6 days. Then, the free-run juice was drawn off and the grapes were crushed, destemmed, and pressed. The free-run and press juices were both combined in the tank and stored at 25 °C to undergo extracellular fermentation. After 2 days, when alcoholic fermentation was finished, the wine was transferred to another 600 L tank and left to mature at 20 °C for 19 days.

In both vinification processes, temperature and must density were monitored periodically during the fermentation periods, which were carried out with indigenous yeasts. Must and wine samples (250 mL) were collected daily during the maceration period and after pressing every other day for 21 days. Aditional samples (100 mL) were frozen for subsequent anthocyanin analysis by HPLC.

Colorimetric Measurements. Color measurements were made with a Hewlett-Packard UV−vis HP 8452A spectrophotometer (Palo Alto, CA), 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 10° Observer were considered as references. The CIELAB parameters (L^*, a^*, b^*, C^*_{ab}, h_{ab}) and a CIELUV parameter (s^*_{uv}) were determined by using the original software PCROM (*10*), following the recommendations of the Commission Internationale de L'Eclairage (*11*). The samples were centrifuged at 3500 rpm, and the supernatants were filtered through Millipore-AP20 filters (Bedford, MA), prior to the spectrophotometric analysis.

Sample Preparation before Chromatographic Analysis. After different solid-phase extraction (SPE) methods had been tested (*12*−*14*), the one providing results most closely corresponding to the results obtained by direct injection of the sample was used. Therefore, anthocyanins were isolated directly from the musts and wines by passing 1 mL of wine sample through a C_{18} Sep-Pak cartridge (Waters Corp.) previously conditioned to pH 7 with water and methanol. Sugars and phenolic acids were removed using water. Anthocyanins were eluted with 1% HCl in methanol. The collected methanolic fraction was then evaporated to 1 mL in a rotary evaporator and filtered through a 0.45 μm nylon membrane (Millipore, Bedford, MA) before injection into the chromatographic system.

Chromatographic Analysis. Anthocyanin analysis was carried out using a Waters HPLC system (Milford, MA) consisting of a Waters 600E pump, a Rheodyne 7161 manual injector furnished with a 50 μL loop, a Waters 996 photodiode array detector, and a Millenium^{32} workstation. Anthocyanins were separated on a Spherisorb C_{18} column (250 × 4.6 mm, 5 μm particle size) with a Spherisorb C_{18} guard column (10 × 4 mm) (Waters). Both were maintained at 38 °C. 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 as follows: 0 min, 94% A, 6% B; 10 min, 70% A, 30% B; 15 min, 60% A, 40% B; 25 min, 55% A, 45% B; 35 min, 50% A, 50% B; 45 min, 40% A, 60% B; 55 min, 94% A, 62% B. The system was equilibrated using the starting conditions for 10 min prior to injection of the next sample. 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. The detection wavelength was 525 nm. All analyses were made in triplicate.

Table 1. Major Individual and Total Anthocyanin Contents (Milligrams per Liter) and Total Polyphenols (Milligrams per Liter) in the Two Syrah Wines, at the End of the Test (Values Are the Mean ± SD of Three Replicates)

		vinification technique[a]	
peak	compound	TM	CM
1	delphinidin-3-monoglucoside	3.05 ± 0.09	1.08 ± 0.05
2	cyanidin-3-monoglucoside	nd	nd
3	petunidin-3-monoglucoside	11.05 ± 0.76	4.07 ± 1.17
4	peonidin-3-monoglucoside	10.59 ± 1.02	3.93 ± 0.05
5	malvidin-3-monoglucoside	139.75 ± 5.76	69.14 ± 3.30
6	petunidin-3-monoglucoside-acetate	2.60 ± 0.01	1.02 ± 0.11
7	peonidin-3-monoglucoside-acetate	3.41 ± 0.23	1.64 ± 0.17
8	malvidin-3-monoglucoside-acetate	21.64 ± 0.19	14.34 ± 1.50
9	petunidin-3-monoglucoside-*p*-coumarate	3.04 ± 0.13	0.95 ± 0.02
10	peonidin-3-monoglucoside-*p*-coumarate	5.98 ± 0.25	1.53 ± 0.06
11	malvidin-3-monoglucoside-*p*-coumarate	22.88 ± 1.13	10.53 ± 0.32
	sum of all individual anthocyanins	229.16 ± 6.22	112.18 ± 5.85
	total anthocyanins[b]	524.83 ± 13.37	289.96 ± 7.72
	total polyphenols[c]	2219.50 ± 29.16	978.30 ± 19.63

[a] TM, traditional maceration; CM, carbonic maceration; nd, not detected. [b] Quantified by the Somers and Evans method. [c] Quantified by the Folin–Ciocalteu method.

Quantitation and Identification of Anthocyanins. The different anthocyanin compounds were identified, at 525 nm, by comparing their retention times and spectral characteristics with data given in the literature (*15*−*17*). Quantitation was made by means of a calibration curve obtained with standard solutions of malvidin-3-monoglucoside chloride, purchased from Extrasynthese (Genay, France).

Total anthocyanins (TA), ionized anthocyanins (IA), polymeric pigment index (PPI), and total phenolics (TP) were calculated according to the method of Somers and Evans (*18*, *19*). Total phenolics were also calculated using the Folin−Ciocalteu method (*20*), which expresses the results as milligrams per liter of gallic acid.

Statistical Analysis. Correlations between color parameters and anthocyanin content were studied by both linear and multiple regression. Statistica v. 6.0. software was used (*21*).

RESULTS AND DISCUSSION

Changes in Anthocyanin Composition. Qualitatively, the two Syrah wines showed the same chromatographic profile, independently of the vinification protocol, where 11 peaks could be identified on the basis of the retention times and UV−vis spectra, as **Table 1** shows. In the two Syrah wines, malvidin derivatives were the major components, mainly malvidin-3-monoglucoside (representing the 60% of all individual anthocyanins).

In the course of the traditional fermentation, the pigments responsible for the red wine color, which are mainly individual anthocyanins, are being extracted due to the contact with the skins. In the carbonic maceration, anthocyanins are transferred from the skin to the pulp during the intracellular fermentation/maceration, and when most of the grapes have burst, the anthocyanins diffuse to the must-wine. **Figure 1** shows the evolution of the different anthocyanin fractions during the two vinification protocols. The highest concentrations belong to nonacylated anthocyanins in the two techniques. In the tradi-

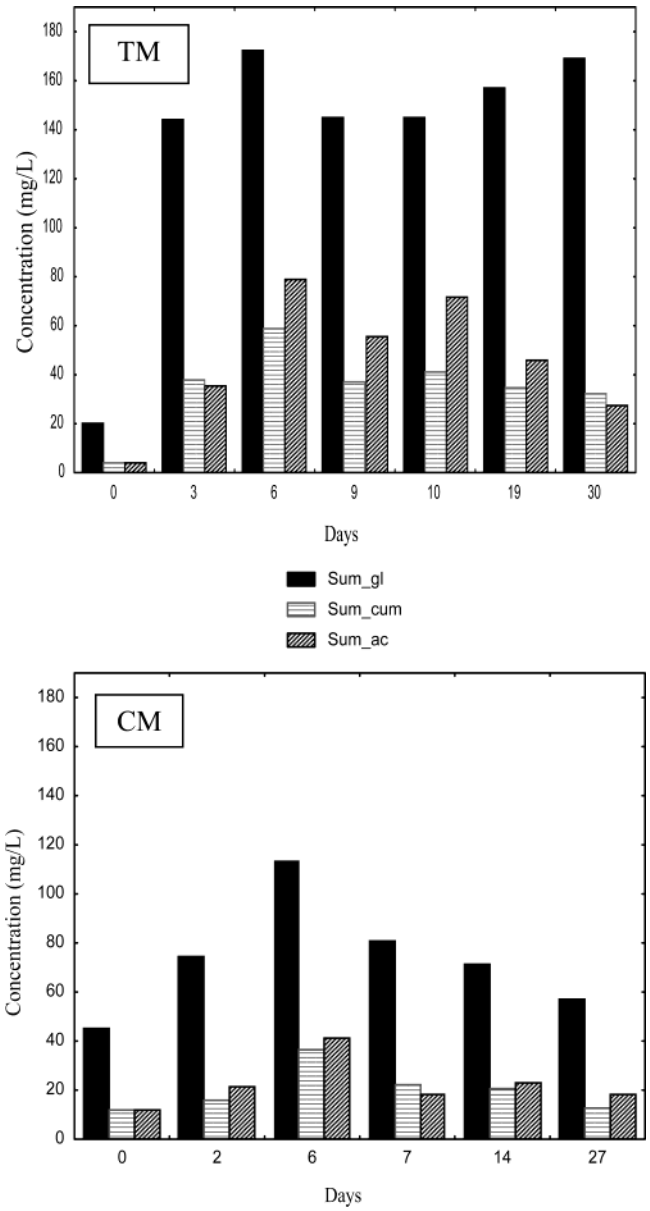

Figure 1. Evolution of the anthocyanin fractions (mg/L) during the two vinification processes. TM, traditional maceration, day of pressing = day 9; CM, carbonic maceration, day of pressing = day 6; Sum_gl, sum of nonacylated anthocyanins; Sum_ac, sum of acetates; Sum_cm, sum of coumarates.

tional vinification, it can be observed that the maximum of all fractions was reached on the sixth day of fermentation (total monoglucosides = 172.53 mg/L; total coumarylglucosides = 58.49 mg/L; total acetylglucosides = 78.82 mg/L), and after that, a slight decrease in the fractions was produced until the pressing. This shows that the pigment extraction from the grape skins is not constant during the whole maceration period, and parallel to the extraction the anthocyanins are slowly linked to other compounds, thus decreasing the concentration of free anthocyanins in dissolution. In fact, a constant increase in the polymeric pigment index is observed from the first day of maceration (**Figure 4**).

On the other hand, a constant increase in all anthocyanin fractions during the whole maceration period was observed in the carbonic maceration, reaching its maximum just before the pressing (total monoglucosides = 113.36 mg/L; total coumarylglucosides = 36.51 mg/L; total acetylglucosides = 40.76 mg/L). After pressing, a marked decrease of individual anthocyanins was produced. This fact could be due to, among other factors, the fact that after the pressing of very whole grapes, typical of carbonic maceration, there is practically the same amount of anthocyanins, but now they are dissolved in a much higher volume of must-wine than before pressing.

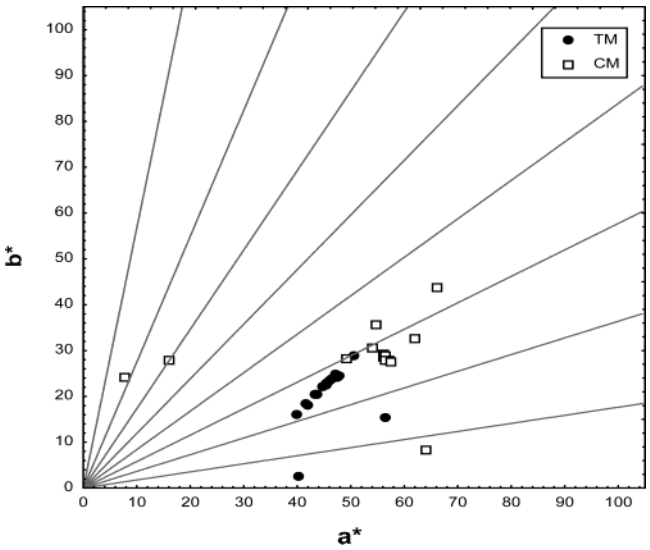

Figure 2. Representation of the musts and wines in the *a**,*b** plane. TM, traditional maceration; CM, carbonic maceration.

The concentrations of major individual anthocyanins, total anthocyanins, and total polyphenols in the two wines at the end of the test are shown in **Table 1**. It can be again seen that in our test conditions the anthocyanin content is dependent on the winemaking technology. As expected, the final carbonic maceration wine contained the lowest amounts of all individual anthocyanins, mainly nonacylated anthocyanins, so the maceration with intracellular fermentation did not favor the extraction or stabilization of monoglucoside anthocyanins, which was greater when on-skin fermentation took place. Besides, the total polyphenol content was lower, too, in the carbonic maceration wine (978.30 versus 2219.50 mg/L in traditional vinification). This fact seems to show that the degree of skin tissue degradation was insufficient.

Some authors have found that the smaller quantity of individual anthocyanins in the wine produced by carbonic maceration is related to a higher quantity of polymeric pigments (*7*). However, in our winemaking conditions, the polymeric pigment index was constantly higher in the traditional vinification, reaching 1.88 units by the end of the test, whereas in the carbonic maceration it reached only 1.07 units (**Figure 4**). In addition to this, after pressing, the polymeric pigment formation rate was higher in the traditional wine, so not only has the extraction of phenolic compounds, including anthocyanins, been greater in the traditional fermentation but also the polymerization of these compounds, which increase the chromatic stabilization of the wine, was greater. Perhaps, if the maceration time tested in the carbonic maceration had been longer, a higher liberation of catechins and proanthocyanidins would have occurred. In fact, the amount of total polyphenols in the wine obtained by carbonic maceration was smaller, too.

Changes in Wine Color. The evolution of the samples during the winemaking processes in the *a**,*b** plane (by CIELAB space) is shown in **Figure 2**. The samples found at a greater distance from the others in both cases belonged to the first days of maceration. After that, all of the samples formed a group of around 20 units of *b** and 45 units of *a**, in the traditional

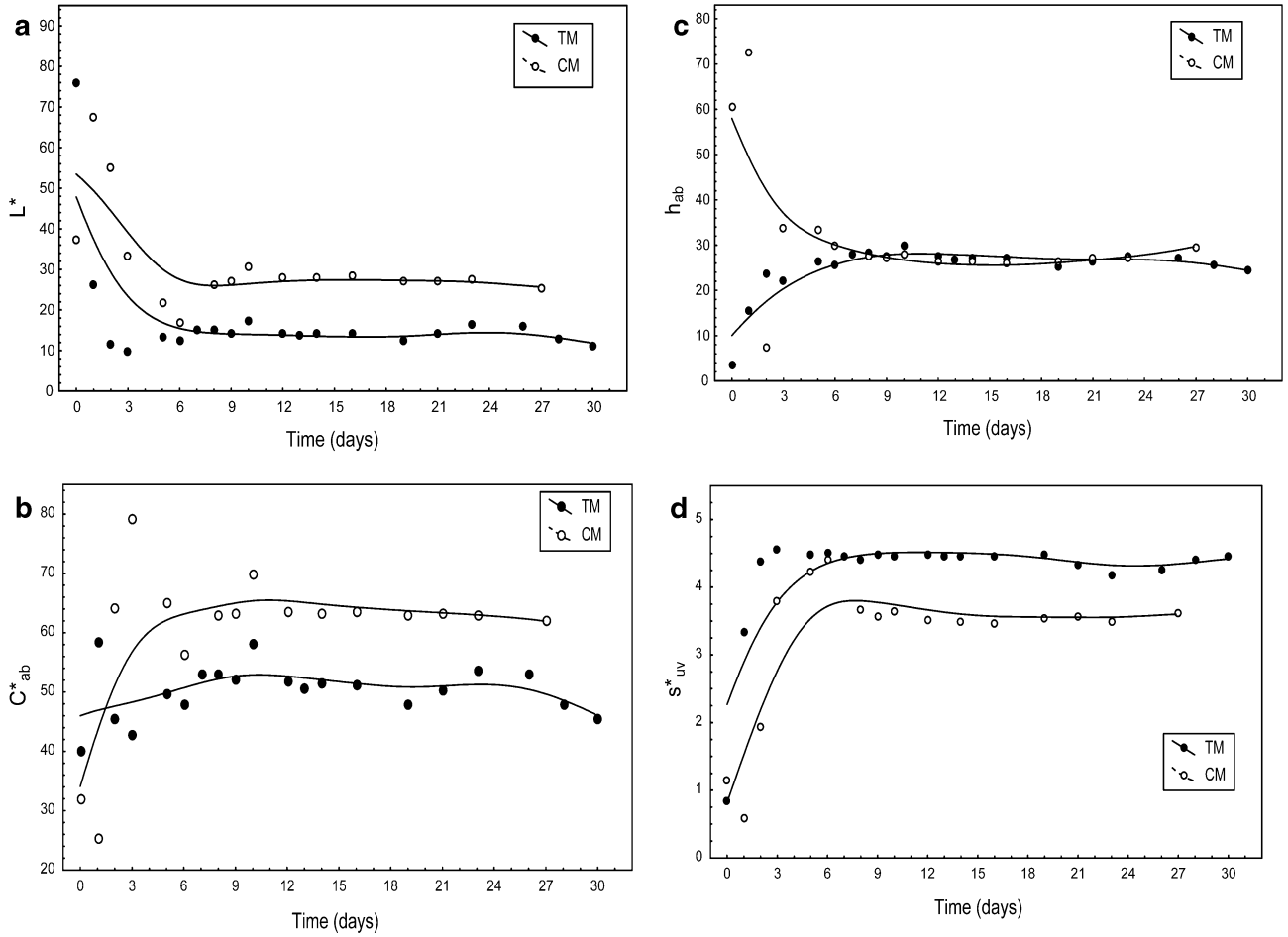

Figure 3. Evolution of L^* (lightness) (**a**), C^*_{ab} (chroma) (**b**), h_{ab} (hue angle) (**c**), and s^*_{uv} (saturation) (**d**) during the two vinification techniques. TM, traditional maceration; CM, carbonic maceration.

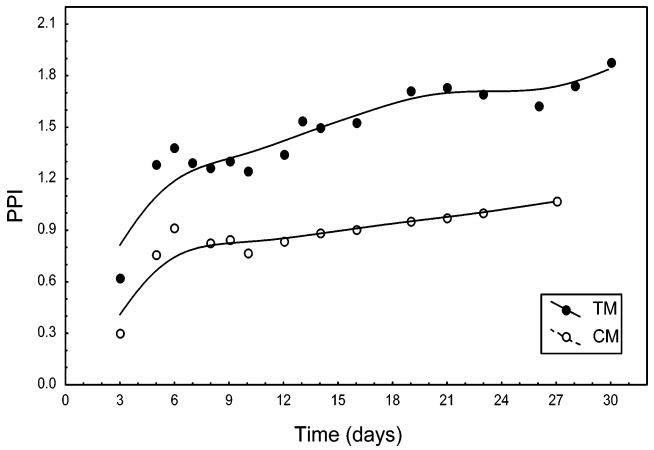

Figure 4. Evolution of the polymeric pigment index (PPI) during the two vinification techniques. TM, traditional maceration; CM, carbonic maceration.

vinification, and 30 and 55 units of b^* and a^*, respectively, in the carbonic maceration. Therefore, the wine made by carbonic maceration has a higher chroma value than the wine obtained by traditional vinification, but the two wines have very similar hues, located in the red region. Nevertheless, other authors have found that carbonic maceration produces less colorful and more red-orange wines (*7*). In the same way, none of the analyzed samples reached negative b^* values, that is, blue-violet hues, unlike those usually observed in young wines (*22, 23*).

The evolution of the colorimetric parameters in the course of the two winemaking techniques is shown in **Figure 3**. In the two wines, all of the colorimetric parameters, apart from the hue (h_{ab}), evolved in the same way. Besides, the most significant changes were produced during the maceration period, and all of the parameters became stable after pressing. Therefore, the extraction of compounds, mainly anthocyanins, that takes place in the course of the maceration seems to exert a higher influence on the colorimetric characteristics of the must-wines than the processes of precipitation, polymerization, and copigmentation, which are more important after pressing.

It was observed that L^* values (lightness) decreased while s^*_{uv} values, defined only in the CIELUV space, increased during the maceration period, due to the extraction of anthocyanins from the grape skins, which was less intense in the carbonic maceration, because lighter and less saturated wines were produced by this technique ($L^* = 25.35$ and $s^*_{uv} = 3.62$ versus 11.27 and 4.45 units, respectively, in the traditional vinification). These low values of L^* could explain why it was not possible to detect the bluish hue, which together with the red hue would give the wine a purple color.

Chroma (C^*_{ab}) modifications were more variable, showing a less defined tendency in the changes that the color quantity of the samples suffer, although in the maceration a slight increase was observed. The carbonic maceration wines had higher C^*_{ab} values despite being less saturated (62.07 versus 45.46 units in the traditional vinification). However, visually, this wine did not have a more vivid color. This fact can be due

Table 2. Pearson Correlation Coefficients in the Wines Produced by Two Vinification Techniques[a]

	vinification technique[b]											
	TM						CM					
	L^*	a^*	b^*	C^*_{ab}	h_{ab}	s^*_{uv}	L^*	a^*	b^*	C^*_{ab}	h_{ab}	s^*_{uv}
Sum_gl[c]	**–0.90**	0.09	**0.77**	0.34	**0.86**	**0.89**	**–0.55**	0.49	0.26	0.50	–0.42	**0.71**
Sum_ac[c]	–0.43	0.13	**0.54**	0.30	**0.53**	**0.51**	–0.39	0.22	0.12	0.22	–0.22	0.47
Sum_cm[c]	**–0.78**	0.02	**0.68**	0.25	**0.77**	**0.81**	–0.40	0.13	0.21	0.15	–0.09	0.48
DF[d]	**–0.46**	–0.04	0.07	–0.04	0.16	0.40	0.34	0.15	–0.07	0.19	–0.11	–0.10
PT[d]	**–0.85**	0.15	**0.79**	0.39	**0.85**	**0.87**	0.00	0.15	0.02	0.17	–0.13	0.19
PN[d]	**–0.69**	0.07	0.37	0.15	**0.46**	**0.66**	0.03	–0.06	0.06	–0.02	0.08	0.07
MV[d]	**–0.82**	0.11	**0.83**	0.38	**0.88**	**0.86**	**–0.59**	0.42	0.25	0.42	–0.32	**0.71**

[a] Boldfaced coefficients are significant at $p < 0.05$. [b] TM, traditional maceration; CM, carbonic maceration. [c] Sum_gl, sum of nonacylated anthocyanins; Sum_ac, sum of acetates; Sum_cm, sum of coumarates. [d] DF, PT, PN, MV, total delphinidins, petunidins, peonidins, and malvidins, respectively.

Table 3. Multiple Linear Regression Equations and *R* Values for the Syrah Wines Made with Traditional Maceration[a]

	R	*R* [b]
$L^* = -0.307$Sum_gl $- 0.284$Sum_cm $- 0.025$Sum_ac $+ 73.188$	**0.912**	0.550
$a^* = 0.046$Sum_gl $- 0.243$Sum_cm $+ 0.087$Sum_ac $+ 43.764$	0.289	0.201
$b^* = 0.130$Sum_gl $- 0.152$Sum_cm $+ 0.128$Sum_ac $+ 2.536$	0.823	0.575
$C^*_{ab} = 0.082$Sum_gl $- 0.296$Sum_cm $+ 0.131$Sum_ac $+ 43.458$	0.462	0.250
$h_{ab} = 0.136$Sum_gl $- 0.040$Sum_cm $+ 0.091$Sum_ac $+ 2.738$	0.890	0.570
$s^*_{uv} = 0.018$Sum_gl $+ 0.012$Sum_cm $+ 0.006$Sum_ac $+ 0.925$	**0.917**	0.598
$L^* = -5.412$DF $+ 1.002$PT $+ 0.581$PN $- 0.338$MV $+ 69.223$	0.898	0.456
$a^* = -1.626$DF $+ 1.039$PT $+ 0.284$PN $- 0.087$MV $+ 43.884$	0.319	0.191
$b^* = 0.086$DF $+ 0.679$PT $- 0.360$PN $+ 0.061$MV $+ 6.845$	0.857	0.544
$C^*_{ab} = -1.656$DF $+ 1.266$PT $+ 0.140$PN $- 0.069$MV $+ 45.086$	0.486	0.244
$h_{ab} = 1.045$DF $+ 0.191$PT $- 0.472$PN $+ 0.117$MV $+ 7.222$	**0.906**	0.592
$s^*_{uv} = 0.283$DF $- 0.043$PT $- 0.042$PN $+ 0.020$MV $+ 1.194$	**0.913**	0.595
$L^* = -2.947$Dpg $- 0.087$Ptg $- 0.276$Png $- 0.357$Mvg $+ 75.634$	**0.923**	0.602
$a^* = -2.408$Dpg $+ 1.851$Ptg $+ 0.368$Png $- 0.098$Mvg $+ 42.828$	0.385	0.224
$b^* = -0.288$Dpg $+ 1.583$Ptg $- 0.478$Png $+ 0.037$Mvg $+ 6.375$	0.851	0.411
$C^*_{ab} = -2.401$Dpg $+ 2.328$Ptg $+ 0.125$Png $- 0.088$Mvg $+ 44.247$	0.516	0.368
$h_{ab} = 0.612$Dpg $+ 0.909$Ptg $- 0.493$Png $+ 0.099$Mvg $+ 6.323$	**0.900**	0.577
$s^*_{uv} = 0.238$Dpg $+ 0.010$Ptg $- 0.033$Png $+ 0.021$Mvg $+ 1.052$	**0.909**	0.680

[a] Sum_gl, sum of nonacylated anthocyanins; Sum_ac, sum of acetates; Sum_cm, sum of coumarates; DF, PT, PN, MV, total delphinidins, petunidins, peonidins, and malvidins, respectively; Dpg, Ptg, Png, Mvg, 3-monoglucosides of delphinidin, petunidin, peonidin, and malvidin, respectively. [b] *R* values when pH and SO_2 are included in the equations as independent variables.

Table 4. Multiple Linear Regression Equations and *R* Values for the Syrah Wines Made with Carbonic Maceration[a]

	R	*R* [b]
$L^* = -0.519$Sum_gl $+ 1.028$Sum_cm $- 0.525$Sum_ac $+ 62.894$	0.600	0.487
$a^* = 1.185$Sum_gl $- 3.565$Sum_cm $+ 1.341$Sum_ac $+ 4.765$	0.828	0.505
$b^* = 0.079$Sum_gl $+ 0.165$Sum_cm $- 0.150$Sum_ac $+ 21.591$	0.278	0.155
$C^*_{ab} = 0.951$Sum_gl $- 2.789$Sum_cm $+ 1.030$Sum_ac $+ 21.894$	0.812	0.501
$h_{ab} = -1.023$Sum_gl $+ 3.411$Sum_cm $- 1.429$Sum_ac $+ 70.300$	0.797	0.436
$s^*_{uv} = 0.062$Sum_gl $- 0.129$Sum_cm $+ 0.059$Sum_ac $- 0.294$	0.799	0.490
$L^* = 0.507$DF $- 0.350$PT $+ 1.924$PN $- 0.354$MV $+ 51.010$	0.767	0.415
$a^* = 21.475$DF $+ 0.933$PT $- 7.268$PN $+ 0.649$MV $+ 10.605$	**0.934**	0.595
$b^* = 0.638$DF $- 0.561$PT $- 0.155$PN $+ 0.081$MV $+ 24.152$	0.285	0.129
$C^*_{ab} = 17.995$DF $+ 0.465$PT $- 5.707$PN $+ 0.522$MV $+ 26.218$	**0.920**	0.591
$h_{ab} = -16.974$DF $- 1.471$PT $+ 6.232$PN $- 0.528$MV $+ 65.510$	0.842	0.365
$s^*_{uv} = 0.583$DF $+ 0.091$PT $- 0.319$PN $+ 0.042$MV $+ 0.377$	**0.908**	0.556
$L^* = -12.262$Dpg $+ 11.891$Ptg $+ 1.879$Png $- 0.826$Mvg $+ 48.411$	0.781	0.489
$a^* = 32.868$Dpg $- 6.773$Ptg $- 10.354$Png $+ 0.816$Mvg $+ 18.382$	**0.917**	0.588
$b^* = 23.163$Dpg $- 22.338$Ptg $+ 0.247$Png $+ 0.805$Mvg $+ 29.477$	0.629	0.369
$C^*_{ab} = 35.845$Dpg $- 14.141$Ptg $- 8.011$Png $+ 0.929$Mvg $+ 34.585$	**0.928**	0.601
$h_{ab} = -8.809$Dpg $- 12.034$Ptg $+ 9.060$Png $- 0.112$Mvg $+ 63.174$	0.816	0.597
$s^*_{uv} = 2.058$Dpg $- 1.255$Ptg $- 0.370$Png $+ 0.088$Mvg $+ 0.848$	**0.923**	0.600

[a] Sum_gl, sum of nonacylated anthocyanins; Sum_ac, sum of acetates; Sum_cm, sum of coumarates; DF, PT, PN, MV, total delphinidins, petunidins, peonidins, and malvidins, respectively; Dpg, Ptg, Png, Mvg, 3-monoglucosides of delphinidin, petunidin, peonidin, and malvidin, respectively. [b] *R* values when pH and SO_2 are included in the equations as independent variables.

to the greater lightness that influences the saturation ($s^*_{uv} = C^*_{uv}/L^*$) more than the chroma does, making this wine less saturated and, so, preventing us from seeing the purer color (higher color intensity).

With reference to the hue, both wines evolved differently during the maceration: the hue decreased with the carbonic maceration, turning the must-wine samples from the orange-red region (60−75°) to the red region (25−30°), whereas in the traditional vinification h_{ab} values increased, reducing the blue component of the red color (evolution from 5 to 30°). However, after pressing, the values remained very close in both wines, ∼20−30°. Therefore, in our test conditions, the winemaking technique hardly influenced the hue of the final Syrah wine but did influence the other colorimetric parameters. In this way, carbonic maceration produced a lighter wine (double L^* value), less saturated but more vivid, with a C^*_{ab} value ∼20 units greater.

In the traditional vinification, it can be observed that a stabilization of all the colorimetric parameters studied was produced from the seventh day of maceration, that is, ∼2 days before pressing. Therefore, an improvement in the wine color was not observed by increasing the skin contact time. In our winemaking conditions and for this variety, 7 days of skin contact would have been enough.

On the other hand, this colorimetric stabilization before pressing was not observed in the carbonic maceration. Probably, on the sixth day of carbonic maceration, significant changes in the must-wine were still occurring because all of the grapes had not burst, so a constant liberation of must-wine was occurring. In that respect, the colorimetric changes in the carbonic maceration wine might have become stable before pressing with a longer maceration time.

Relationships between Wine Color and Content of Anthocyanins. To predict color from the anthocyanin composition of the wines, or vice versa, simple and multiple linear regression were explored.

Table 2 shows the Pearson correlation coefficients (r^*) obtained by means of simple linear regression. It can be observed that traditional vinification led to a greater number of significant linear correlations ($p < 0.05$), the saturation s^*_{uv} being the best correlated parameter. As expected, and according to the signs of the correlation coefficients, the higher the anthocyanin derivative content, the smaller the lightness of the two wines independent of the vinification technique. However,

chroma and saturation increase. On the contrary, a different behavior was observed in the hues, depending on the winemaking technology. In this way, when the amount of anthocyanin derivatives increased in the traditional wine, the hue angle increased, too (less bluish wine), whereas in the carbonic maceration wine the hue angle decreased (less orange wine).

When the individual anthocyanins were grouped by the presence or absence of acylation, the best correlations were found for L^* and s^*_{uv} versus Sum_gl in both vinification techniques ($r^* = -0.90$ and 0.89, respectively, in the traditional vinification, and $r^* = -0.55$ and 0.71, respectively, in the carbonic maceration). With reference to the acylated derivatives, the coumaryl derivatives were the ones that best correlated to L^* and s^*_{uv}, too, in the traditional vinification ($r^* = -0.78$ and 0.81, respectively). When the anthocyanins were grouped by the aglucona, the best correlation coefficients were found for petunidin and malvidin derivatives, the most abundant 3-monoglucoside anthocyanins, in the wine produced by traditional vinification. These anthocyanin derivatives were well correlated with L^*, s^*_{uv}, and h_{ab} ($r^* > 0.80$). In the carbonic maceration wine, very few good correlation coefficients were found, the best one being the one for the malvidin derivatives versus s^*_{uv} ($r^* = 0.71$).

To achieve a more accurate evaluation of the correlation between color and anthocyanin pigments, multiple linear regression was explored. The colorimetric parameters were considered as dependent variables, and the contents of anthocyanins were considered as independent variables. The best equations that allow the prediction of the colorimetric parameters in Syrah wines as a function of the content of anthocyanins and the multiple correlation coefficients (R) are both shown in **Tables 3** and **4**. It is well-known that the color of red wines is highly dependent on the pH and SO_2 values of the wine. In that respect, these parameters were also included in the equations as independent variables. However, an improvement of the relationships was not observed because lower values of R were obtained. This can be due to the fact that, in our test conditions, the pH and SO_2 values of the two wines were very constant over the course of the two winemaking processes. Specifically, the pH values were between 3.61 and 4.35 units in the traditional vinification wine and between 2.66 and 4.68 units in the carbonic maceration wine. The contents of SO_2 were very similar in the two wines with a mean value of ~50 mg/L. In **Tables 3** and **4** it can also be observed that with this statistical analysis, for the carbonic maceration the number of significant correlations increases with reference to the simple linear regression analysis. However, the best R values still belong to the traditional Syrah wine. The best R values ($R > 0.90$) are obtained for L^*, h_{ab}, and s^*_{uv} in the traditional vinification and for a^*, C^*_{ab}, and s^*_{uv} in the carbonic maceration.

A good prediction of C^*_{ab} and a^* was not possible in the traditional vinification; on the other hand, these parameters were the easiest to predict in the carbonic maceration wine, coinciding with the higher color intensity of these wines.

When the contents of anthocyanins were considered as dependent variables, valid equations were obtained for only the total anthocyanin content (ANT, mg/L). These equations are

traditional vinification

$$\mathrm{ANT} = -1.462(L^*) - 0.478(C^*_{ab}) + 5.732(h_{ab}) + 136.916 \qquad R = 0.892,\ p < 0.05$$

carbonic maceration

$$\mathrm{ANT} = 2.812(L^*) - 3.065(C^*_{ab}) - 0.566(h_{ab}) + 78.588(s^*_{uv}) - 10.988 \qquad R = 0.777,\ p < 0.05$$

LITERATURE CITED

(1) Auw, J. M.; Blanco, V.; O'Keefe, S. F.; Sims, C. A. Effect of processing on the phenolics and color of Cabernet Sauvignon: Chambourcin and Noble wines and juices. *Am. J. Enol. Vitic.* **1996**, *47*, 279−286.

(2) De Leo, F.; Massari, S. Phenolic component and antioxidant activity in red wines produced either through traditional fermentation on carbonic maceration. *J. Commodity Sci.* **2001**, *40* (4), 189−204.

(3) Rizzon, L. A.; Miele, A.; Meneguzzo, J.; Zanuz, M. C. Effect of three processes of vinification on chemical composition and quality of Cabernet Franc wine. *Pesquisa Agropecuaria Brasileira* **1999**, *34* (7), 1285−1293.

(4) Carnacini, A.; Zironi, R.; Potentini, G.; Antonelli, A.; Palotta, U.; Amati, A. Influence of the conservation conditions and aging on composition of wines obtained by carbonic maceration from grapes c.v. Montepulciano. *Vitic. Enol. Sci.* **1991**, *46*, 93−99.

(5) Pellegrini, N.; Simonetti, P.; Gardana, C.; Brenna, O.; Brighenti, F.; Pietta, P. Polyphenol content and total antioxidant activity of vini novelli (young red wines). *J. Agric. Food Chem.* **2000**, *48*, 732−735.

(6) Mattivi, F.; Nicolini, G. Influence of winemaking technique on the resveratrol content of wines. *L'Enotecnico* **1993**, *29* (7), 81−88.

(7) Sun, B. S.; Spranger, I.; Roque-do-Vale, F.; Leandro, C.; Belchior, P. Effect of different winemaking technologies on phenolic composition in Tinta Miuda red wines. *J. Agric. Food Chem.* **2001**, *49*, 5809−5816.

(8) Lörincz, G.; Pásti, G.; Kállay, M. Carbonic maceration: new experiments. *Magyar Szolo es Borgazdasag* **1997**, *7* (2), 24−28.

(9) Lörincz, G.; Kállay, M.; Pásti, G. Effect of carbonic maceration on phenolic composition of red wines. *Acta Aliment.* **1998**, *27* (*4*), 341−355.

(10) Álvarez, C.; Heredia, F. J. *PCROM®, cálculos colorimétricos*; Registro General de la Propiedad Intelectual 1994/41/18790: Madrid, Spain, 1994.

(11) CIE. *Colorimetry*, 2nd ed.; Publication 15.2; CIE: Vienna, Austria, 1986.

(12) Eder, R.; Wendelin, S.; Barna, J. *Mitt. Klosterneuburg* **1990**, *40*, 68.

(13) Hong, V.; Wrolstad, R. E. Use of HPLC separation-photodiode array detection for characterization of anthocyanins. *J. Agric. Food Chem.* **1990**, *38*, 708−715.

(14) Chandra, A.; Nair, M. G.; Lezzoni, A. Evaluation and characterization of the anthocyanin pigments in tart cherries (*Prunus ceraseus* L.). *J. Agric. Food Chem.* **1992**, *40*, 967−969.

(15) Hebrero, E.; Santos-Buelga, C.; Rivas-Gonzalo, J. C. High performance liquid chromatography-diode array spectroscopy identification of anthocyanins of *Vitis vinífera* variety Tempranillo. *Am. J. Enol. Vitic.* **1988**, *39* (3), 227−233.

(16) Revilla, E.; Ryan, J. M. Analysis of several phenolic compounds with potential antioxidant properties in grape extracts and wines by high-performance liquid chromatography-photodiode array detection without sample preparation. *J. Chromatogr. A* **2000**, *881*, 461−469.

(17) Vivar-Quintana, A. M.; Santos-Buelga, C.; Rivas-Gonzalo, J. C. Anthocyanin-derived pigments and colour of red wines. *Anal. Chim. Acta* **2002**, *458*, 147−155.

(18) Somers, T. C.; Evans, M. E. Wine quality: Correlations with colour density and anthocyanin equilibria in a group of young red wines. *J. Sci. Food Agric.* **1974**, *25*, 1369−1379.

(19) Somers, T. C.; Evans, M. E. Spectral evaluation of young red wines: Anthocyanin equilibria, total phenolics, free and molecular SO_2, chemical age. *J. Sci. Food Agric.* **1977**, *28*, 279−287.

(20) AOAC. *Official Methods of Analysis*, 15th ed.; Association of Official Analytical Chemists: Arlington, VA, 1990.
(21) StatSoft Inc. Statistica for Windows v. 6.0, data analysis software system; Tulsa, OK, 2001.
(22) Chicón, R. M.; Sánchez-Palomo, E.; Cabezudo, M. D. El color y la composición en polifenoles de los vinos tintos varietales de Castilla-La Mancha (España). *Afinidad* **2002**, *59* (500), *435*−*443*.
(23) Negueruela, A. I.; Echávarri, J. F.; Pérez, M. M. A study of correlation between enological colorimetric indexes and CIE colorimetric parameters in red wines. *Am. J. Enol. Vitic.* **1995**, *46* (3), 353−356.

Received for review March 16, 2004. Revised manuscript received May 28, 2004. Accepted June 13, 2004.

JF049570Z