JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

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Anthocyanin Evolution and Color Changes in Red Grapes During Their Chamber Drying

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ABSTRACT: In this work, the effects of chamber drying under controlled temperature and moisture conditions on three varieties of red grapes (Merlot, Tempranillo, and Syrah) cultivated in warm areas in southern Spain were studied. This drying was made with a view to their use in the production of sweet red wines. Analyses included color parameters, browning index, and anthocyanin concentrations measured by HPLC-DAD/MS. Based on the results, drying increases color and the concentration of these phenolic compounds by the effect of dehydration of the berries and diffusion of the colored compounds from the skin to the pulp due to the structural alterations in their skin. In addition, drying increased the browning index (OD 420), although less markedly than OD 520, as well as decreased the hue (OD 420/OD 520). The musts exhibited the typical color of red wines and a marked darkness by the effect of their low lightness ($L^* < 20$ CIELAB units). Although the sugar content of the musts obtained at 24 h of drying was less, these musts were better to use in the vinification process, even without the maceration step as a result of their higher anthocyanin content, less browning, and darker color. To increase the content of the high-molecular weight compounds and anthocyanin derivatives, more raisining time could be required.

KEYWORDS: *red grapes, chamber drying, anthocyanins, color, HPLC-DAD/MS*

INTRODUCTION

Sweet wines, which are highly appreciated as dessert wines, contain a high concentration of sugars. This is a result of stopping fermentation before the yeasts have consumed all available sugar (e.g., in Porto wines) or by raising the sugar content of the grapes prior to winemaking. The latter is the method used with some wines produced in southern Spain and southern Italy, where the grapes are dried before pressing in order to increase their sugar content. Sun drying is the most common natural method to dehydrate grapes in the Mediterranean region. Grapes, however, can also be dried by mechanical methods in closed environments with or without control systems of temperature, relative humidity, and airflow.

The end-product obtained after drying depends on a number of factors including the drying conditions. Different authors have studied the kinetics of grape drying[1,2] and some berry properties such as size, content in reducing sugars, degree of ripeness, and skin thickness.[3] These drying processes affect some of their properties such as color, texture, and density.[4] Air drying is used with a number of fruits and causes substantial color changes during the process.[5] Some authors have used mathematical models to assess the influence of the drying conditions.[6,7]Others have shown the microstructural changes of the grapes,[8] whereas biochemical changes caused by the endogenous metabolism of grapes influence the quality of the resulting wine.[9] In this sense, each drying method alters the composition of grapes in a different manner. Thus, changes in the phenol[10,11] and aromatic fractions[12] have been studied during the sun drying of Pedro Ximenez grapes or under controlled temperature and moisture conditions.

Some regions in southern Spain use a traditional procedure to obtain sweet wines from white grapes of the Pedro Ximenez variety. This type of wine, which is highly appreciated nationally and internationally, has a strong ebony color as a result of browning reactions in its components.[10] In recent years, these Spanish regions have started to market sweet red wines from sun-dried grapes. Sun drying induces enzymatic and non-enzymatic browning reactions, thereby altering the color of the grapes and the resulting musts.[13] Unlike traditional Pedro Ximenez white wines, the new wines should support the typical red color. However, the sun-dried grapes cause the formation of brown hues that conceal it. Chamber drying under controlled conditions might be an effective alternative method to preserve the typical color of red grapes while shortening the long drying time of the traditional method.

The aim of this work was established on the basis of the results obtained in a previous work by Marquez et al.,[14] who studied the winemaking of sweet red wines from chamber-dried raisins in order to optimize the maceration step with grape skins. The authors found that an optimum time of 24 h of maceration was required to obtain a wine with the maximum color and anthocyanin concentration from musts obtained with raisins. However, they observed that most of the anthocyanins were extracted from the skin to the pulp during the chamber drying of the grapes, and only a residual color was due to the maceration step. So, the purpose of this work was to optimize the drying time in order to obtain the minimum browning and maximum red color in the musts from Merlot, Tempranillo, and Syrah grape varieties cultivated in the Montilla−Moriles region (southern of Spain). Changes in color and phenolic

Received: May 24, 2013
Revised: September 12, 2013
Accepted: September 19, 2013
Published: September 19, 2013

dx.doi.org/10.1021/jf402263f | J. Agric. Food Chem. 2013, 61, 9908−9914

compounds during drying under controlled conditions were studied.

MATERIALS AND METHODS

Reagents. Malvidin-3-*O*-glucoside chloride was obtained from Extrasynthese (Genay, France). Methanol, formic acid, hydrochloric acid, and acetonitrile were purchased from Merck (Madrid, Spain).

Grape Drying and Must Extraction. The grapes used were *Vitis vinifera* L. cv. Merlot (M), Syrah (S), and Tempranillo (T) berries from the 2009 harvest in the Montilla−Moriles region (southern of Spain). A small amount of grapes were pressed to obtain the initial musts.

Then, an amount of about 30 kg of grapes was uniformly distributed in a single layer in several trays (11−19 kg/m^2 depending on the variety) and dried *off-vine* in a Frisol Climatronic chamber at a constant temperature of 40 °C and an initial relative humidity of 20%. During the drying process, samples of each variety were daily collected, and the weight loss and reducing sugar concentration of the grapes were measured using a refractometer model Atago Master. The grapes collected each day were pressed, obtaining the corresponding musts.

The drying process was finished when the reducing sugar content reached approximately 31.4 °Brix. Whole bunches of raisins were pressed on a vertical press similar to industrial models, obtaining the final musts. The maximum pressure reached in each two pressing cycle was 300 bar. The musts were centrifuged at 3000 rpm, filtered, and analyzed in triplicate.

Moisture Determination. The moisture contents (kg water/kg dry matter) at any time of drying (M_t) were registered. The moisture ratio (MR) and drying rate (DR) of grapes during experiments were calculated using the following equations:

$$\mathrm{MR} = \frac{M_t}{M_0} \qquad \mathrm{DR} = \frac{M_{t+\Delta t} - M_t}{\Delta t}$$

where M_t, M_0, and $M_{t+\Delta t}$ are the moisture content at any time of drying, initial moisture content, and moisture content at $t+\Delta t$, respectively, and t is time (hours).

Spectrophotometric Determination. Spectrophotometric measurements were made on a PerkinElmer (Waltham, MA) Lambda 25 spectrophotometer, using quartz cells of 1 mm light path. Samples were previously passed through Millipore (Billerica, MA) HA filters of 0.45 μm pore size. All measurements were corrected for a path length of 1 cm.

Optical densities at 420, 520, and 620 nm were measured. Color intensity (CI) represents the amount of color and was calculated as the sum of the optical densities at 420, 520, and 620 nm. Hue indicates the proportion between orange and red colors, and OD 420 and OD 520 nm relation were calculated. CIELAB parameters were carried out following CIE recommendations[15] and using the visible spectrum obtained from 380 to 780 nm. In this work, the following CIELAB uniform space colorimetric parameters have been considered: rectangular coordinates L^* (black-white component, lightness), a^* and b^* (chromatic coordinates representing red-green and yellow-blue axes, respectively). These parameters were measured using as references the CIE 1964 Standard Observer (10° visual field) and the CIE standard illuminant D65.

Polymeric pigment color (PPC) was obtained as the absorbance at 520 nm of 5 mL of sample previously supplied with 15 mg of $NaHSO_3$ and allowed to stand at 25 °C for 45 min. Anthocyanin monomers were immediately decolorized by the excess $NaHSO_3$ added, so the residual color was due to the polymeric forms of the pigments.

Total polyphenols index (TPI) was determined by diluting 1 mL of sample 10 times with 1 M HCl and measuring its absorbance at 520 nm after 45 min at 25 °C.

Extraction of Anthocyanins. Two milliliters of must was passed through a Sep-Pak C18 cartridge packed with 900 mg of material (Long Body Sep-Pak Plus, Waters Corporation, Milford, MA) previously activated with methanol and washed with aqueous 0.01% (v/v) HCl. The cartridge was successively washed with 0.01% aqueous HCl and ethyl acetate, and the anthocyanins were recovered with 5 mL of methanol acidified to pH 2 with HCl. Anthocyanin samples were concentrated on a vacuum centrifuge thermostatted at 35 °C and passed through a filter of 0.45 μm pore size for injection into a P4000 HPLC instrument from Spectra-Physics (San Jose, CA).

HPLC Analysis of Anthocyanins. The identification of the phenolic compounds was achieved by comparison of the retention times of the standards, UV spectra obtained by diode array HPLC (Spectra-Physics UV6000LP), and calculation of UV absorbance ratios after co-injection of samples and standards one at a time. Peak-height comparison was based on the results of samples with and without the standard. The identification of compounds was confirmed by HPLC/ESI-MS analysis (TermoQuest Finnigan AQA quadrupole mass spectrometer). The instrument was operated in both negative and positive ion modes. The ion spray voltage was −4 kV, and the orifice voltage was −60 V. Mass data were acquired in two different ways: scan mode (by scanning the m/z range of 150−1066 at 1.2 intervals) and multiple ion mode (by using mass ranges around specific m/z values). Each compound was quantified by comparison with a calibration curve obtained with malvidin-3-*O*-glucoside.

The column used in the analyses was a 250 mm × 4.6 mm inside diameter, 5 μm, LiChrospher 100 RP-18, using 10% aqueous formic acid (A) and acetonitrile/formic acid/H_2O (45:45:10) (B) as mobile phases at a flow rate of 1 mL/min. The mobile phase gradient was as following: gradient elution from 15 to 30% B in 17 min, gradient elution up to 73% B in 28 min, gradient elution up to 100% B in 3 min, and isocratic elution for 3 min, using absorbance at 520 nm to quantify.

Statistical Procedures. The results for all samples were subjected to analysis of variance (ANOVA) in triplicate and principal component analysis (PCA), using the Statgraphics computer package version 5.0 from Statistical Graphics Corp.

RESULTS AND DISCUSSION

Merlot (M), Syrah (S), and Tempranillo (T) grapes were dried in a chamber at a controlled temperature of 40 °C in order to raise their residual sugar content. The initial concentration in the berries increased to 312 g/L in Tempranillo (after 72 h), 323 g/L in Syrah (36 h), and 336 g/L in Merlot (48 h). These increases caused the concentration to increase by 1.5, 1.6, and 2.3 times in Syrah, Merlot, and Tempranillo, respectively, due to the loss of water by evaporation and the resulting decrease of berry weight. Therefore, the above-mentioned increases in sugars can be used as a reference of the concentration effect on all compounds during drying.

As can be seen in Table 1, the Tempranillo variety had a higher initial moisture content (M_0) (4.46 kg water/kg drying matter versus 2.76 and 2.66) by the effect of its higher water content and lower content in dry matter. According to Serratosa et al.,[16] Tempranillo grapes show the greatest mean berry weight and size and the lowest relative proportion of skin mass. As a result, the drying rate (DR) of Tempranillo grapes was much higher than those of the other two varieties. The differences in drying kinetics were assessed by using the Henderson–Pabis mode,[17] which is widely used in most organic and biological materials.[18] The equations corresponding to this model for the three grape varieties are shown in Table 1. As can be seen from the coefficients of determination (R^2) listed, the experimental data were adjusted to the chosen exponential model.

Table 1. Initial and Final Reducing Sugar Concentrations, Moisture Contents, and Drying Rates of Merlot, Syrah, and Tempranillo Grapes in the Raisining Process

		M	S	T
sugar concentration (g/L)				
0 h		206	215	193
24 h		275	261	249
48 h		336	312	285
72 h				323
dry matter (kg)		0.532	0.546	0.366
M_0 (kg water/kg drying matter)		2.76	2.66	4.46
M_t (kg water/kg drying matter)		1.37	1.42	1.40
Δt (hours)		48	36	72
DR (kg water/kg drying matter h)		0.029	0.034	0.043
MR = $a\cdot\exp(-kt)$	a	0.911	0.894	0.949
	k	0.013	0.014	0.019
	R^2	0.999	0.991	0.995

Figure 1 shows the changes of the optical densities at 420, 520, and 620 nm (yellow-orange, red, and blue pigments, respectively) and the color intensity (CI) of the musts during the grape drying process. As can be seen, Tempranillo grapes initially exhibited a higher CI value than Merlot and Syrah grapes (1.89 au versus 1.26 and 1.09 au, respectively). The drying process clearly raised CI, especially during the first 24 h, being this increment over 6 times in Merlot and Syrah (6.2 and 6.8, respectively), and 5.1 times in Tempranillo. The CI peaked at 36 h in Syrah and 48 h in Merlot and Tempranillo. The high increases found during the drying may have resulted from the diffusion of colored compounds from the berry skin to the pulp by the effect of the damage caused to skin cells by dehydration. Thus, the musts from dried grapes exhibited an increase in red color (OD 520) of up to 10.6 times in the Syrah variety and a smaller increase in the other two.

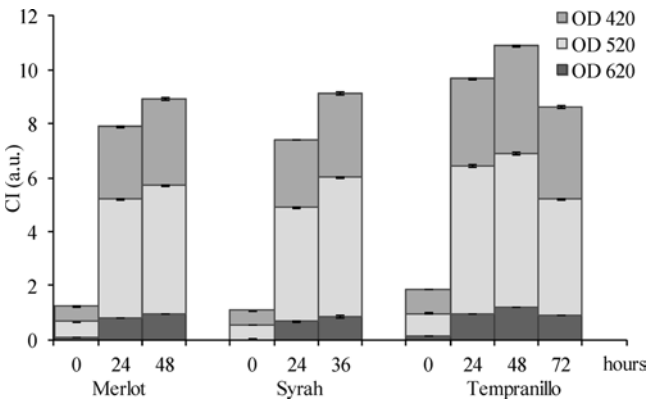

Figure 1. Changes in the absorbances at 420, 520, and 620 nm in the musts from Merlot, Syrah, and Tempranillo grapes during the chamber drying.

The browning index (OD 420) also increased during the drying process. This suggests that, in addition to the concentrating effect of the loss of water by evaporation, drying caused the extraction and/or production of brown-colored pigments. These pigments can be formed in various reactions such as nonenzymatic browning (Maillard reaction and/or auto-oxidation) and enzymatic browning catalyzed by polyphenol oxidases (PPOs), involving phenolic compounds (particularly hydroxycinnamic acids). In this study, the Maillard reaction products should not be formed because the drying temperature was lower than 50 °C, a temperature above which the reaction occurs preferentially.[19] Also, dehydration alters the structure of the skin berry, which loses elasticity and is prone to breaking as a result. These changes can damage PPO-containing cells and facilitate a contact of the enzymes with their substrates, thereby favoring enzymatic browning reactions. However, drying at a constant temperature of 40 °C resulted in a continuous evaporation of water, which may have blocked a continuous incorporation of oxygen. Sun drying in very hot areas in southern Spain occurs at extreme temperatures that favor browning. However, the temperature in such areas usually falls dramatically during the night and allows berries to saturate with oxygen. It is therefore reasonable to believe that chamber drying results in less browning than does sun drying.

The initial hue values (OD 420/OD 520) were near unity, indicating that the contribution of orange and red pigments was similar (Table 2). These values decreased throughout the drying process in all musts, being the minimum values at 24 h. A decrease in hue suggests that the red color (OD 520) increased to a greater extent than did the brown color (OD 420) in all cases. Consequently, the musts exhibited a strongly red color typical of red wines and very similar to that obtained by maceration in the presence of grape skins.[14] Browning did not mask the red color resulting from diffusion of colored compounds from grape skins.

In addition, drying caused a marked decrease in lightness (L^*), with small values below 20 CIELAB units, so the darkest musts were obtained at 24 h in all grape varieties. With a practice point of view, it is useful to calculate the Euclidean distance ΔE_{ab}^* between two samples, indicating the color differences perceived by the human eye. The Euclidean distance formula is as follows:

$$\Delta E_{ab}^* = \sqrt{\Delta a^2 + \Delta b^2 + \Delta L^2}$$

According to some authors,[20,21] two different red musts can be distinguished by the human eye when ΔE_{ab}^* exceeds a value of 3. Euclidean distances between the three grape varities have been calculated. In initial musts, the colors were distinguishable by the human eye (7.13 Merlot versus Syrah, 15.9 Merlot versus Tempranillo, 19.8 Syrah versus Tempranillo). However, the differences in this respect decreased by the effect of grape drying, and the final musts exhibited shorter Euclidean distances as a result (5.07 Merlot versus Syrah, 3.12 Merlot versus Tempranillo, 2.15 Syrah versus Tempranillo). Overall,

Table 2. Changes in Hue Values (OD 420/OD 520) and CIELAB Parameters in the Musts from Merlot, Syrah, and Tempranillo Grapes during the Raisining

	time (h)	hue (OD 420/OD 520)	L^*	h_{ab}	C^*_{ab}
M	0	0.992 ± 0.007	72.1 ± 0.647	31.5 ± 0.468	35.4 ± 0.163
	24	0.617 ± 0.007	20.2 ± 0.419	32.5 ± 0.175	60.2 ± 0.831
	48	0.686 ± 0.007	16.4 ± 0.436	30.3 ± 0.278	54.4 ± 0.911
S	0	1.11 ± 0.013	76.7 ± 0.144	40.4 ± 0.691	34.4 ± 0.178
	24	0.600 ± 0.004	22.9 ± 0.337	33.8 ± 0.116	64.8 ± 0.694
	36	0.596 ± 0.008	18.5 ± 0.903	31.9 ± 0.537	58.7 ± 1.89
T	0	1.08 ± 0.010	62.1 ± 0.506	35.4 ± 0.476	47.4 ± 0.396
	24	0.589 ± 0.003	16.7 ± 0.156	30.2 ± 0.131	55.8 ± 0.253
	48	0.695 ± 0.001	13.0 ± 0.166	26.7 ± 0.181	49.3 ± 0.309
	72	0.807 ± 0.004	17.0 ± 1.30	31.6 ± 0.202	57.1 ± 0.547

chamber drying grapes of the three red varieties led to a greater color uniformity in the resulting musts.

Changes in the total polyphenol index (TPI) during the drying process (Figure 2) were similar for the musts from

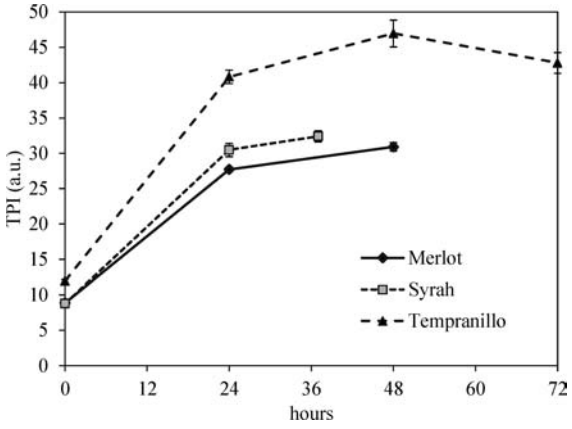

Figure 2. Changes in total polyphenols index (TPI) in the musts from Merlot, Syrah, and Tempranillo grapes during the chamber drying.

Merlot and Syrah (8.8 au) and somewhat higher (12.0 au) for that from Tempranillo. This index increased during the first 24 h in the three musts to levels from 30.9 au (Merlot must) to 42.8 au (Tempranillo must). These TPI values were lower than 50 au, so their corresponding wines could not be aged in wooden barrels. Therefore, the musts can be used to directly obtain young red wines, as well as being macerated with grape skins to extract greater amounts of phenolic compounds.

Changes in the anthocyanin composition during the drying time have been studied, and glucoside, acetylglucoside, coumaroylglucoside, and caffeoylglucoside derivatives were quantified, in addition to type B vitisins and anthocyanin-methylmethine-flavanol adducts. Figure 3 shows the changes in glucosides monomers of the anthocyanidins delphinidin, cyanidin, petunidin, peonidin, and malvidin in the musts. Initially, this anthocyanin family was the one that exhibited the highest concentrations, representing 54−61% of the overall monomeric anthocyanin content depending on the grape variety. Delphinidin-3-*O*-glucoside exhibited the lowest initial concentrations (2.14 mg/L, 2.15 mg/L, and 3.11 mg/L in Syrah, Tempranillo, and Merlot musts, respectively) and the glucoside derivative of malvidin the highest in the three types of must (from 9.26 mg/L in Syrah must to 23.5 mg/L in Merlot must), as is usually the case with *Vitis vinifera* L. varieties.

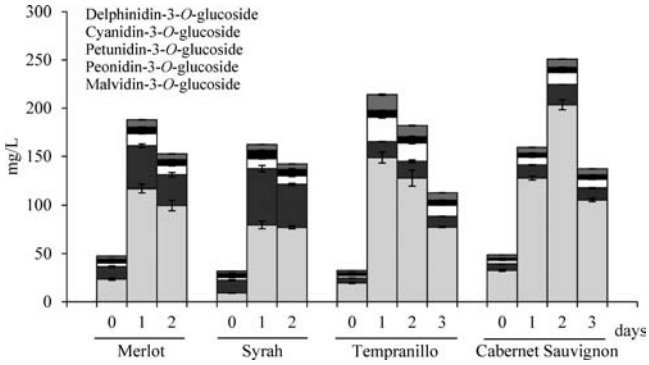

Figure 3. Changes in anthocyanin glucosides in the musts from Merlot, Syrah, and Tempranillo grapes during the chamber drying.

Drying increased the concentrations of the five glucoside anthocyanins in the first 24 h. This may have resulted from the diffusion of anthocyanins from grape skins to the initially colorless pulp by the effect of the damages in the skin cells due to the high temperature. Based on this result, 24 h could be the optimum drying time to obtain the maximum concentration of this red compound. Subsequently, they decreased throughout the rest of the period, possibly as a result of their thermodegradation or cycloaddition and/or polymerization reactions. Thus, anthocyanins are known to take part in a number of condensation reactions with other anthocyanins or with tannins, as well as with flavanols via a methylmethine bridge or otherwise,[22] in addition to co-pigmentation reactions.[23] The dehydration of the grapes increased the content in malvidin-3-*O*-glucoside to a greater extent than the other glucoside anthocyanins. In fact, its final content in the Syrah, Merlot, and Tempranillo musts was 54.4, 65.3, and 68.6%, respectively.

Figure 4 shows the variation content in acetylglucoside derivatives. As can be seen, initially this compound family accounted for the values from 21% (Tempranillo) to 25% (Syrah) of all monomeric anthocyanins in the musts. The concentrations increased during the first day of drying and then decreased slightly as a result of the above-described reactions. Similar to the above-mentioned, with 24 h of dehydration, the maximum concentrations were obtained. During the drying process, the contents of delphinidin, cyanidin, and petunidin derivatives were very similar, but in contrast, those of peonidin-3-*O*-acetylglucoside and malvidin-3-*O*-acetylglucoside were different depending on the grape varieties. According to some authors,[24,25] the acetylglucoside composition of a must can be useful for varietal discrimination purposes.

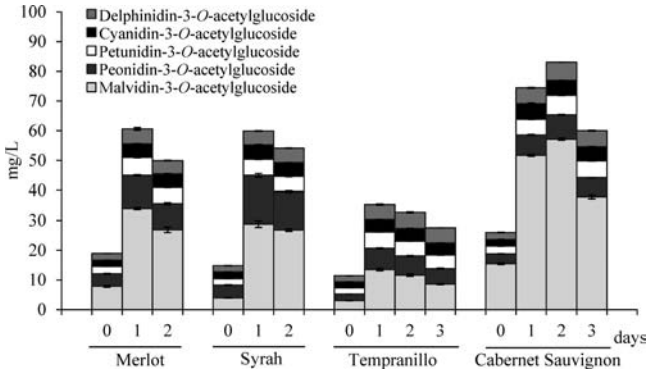

Figure 4. Changes in anthocyanin acetylglucosides in the musts from Merlot, Syrah, and Tempranillo grapes during the chamber drying.

Figure 5 shows the changes on the concentrations of the four coumaroylglucoside derivatives in the musts, in addition to that

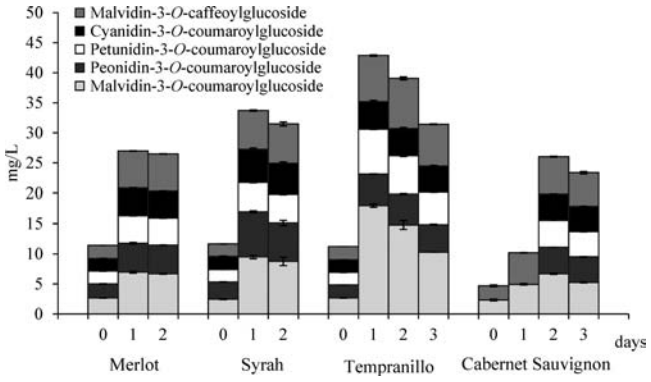

Figure 5. Changes in anthocyanins coumaroylglucosides and malvidine-3-*O*-caffeoylglucoside in the musts from Merlot, Syrah, and Tempranillo grapes during the chamber drying.

of malvidin-3-*O*-caffeoylglucoside, which was the sole member of this anthocyanin family present at detectable by chromatography. Coumarates contributed less markedly than the previous two compound families to the total content in monomeric anthocyanins. Thus, anthocyanin coumaroylglucosides were initially present at concentrations representing 12, 16, and 17% in the Merlot, Tempranillo, and Syrah musts respectively, but they decreased during grape drying.

In addition to the previous monomeric anthocyanins, the musts contained other anthocyanin derivatives such as vitisins and adducts formed by the condensation of anthocyanins with (epi)catechin via a methylmethine bridge (Table 3). These compounds have been studied in depth on account of the color stability they introduce in red wines. In fact, they are more resistant to bleaching by sulfur dioxide than are other anthocyanins,[26] and they are also less prone to changes in hue produced by pH variations.[27] These anthocyanin derivatives were previously identified during the chamber drying of red grapes at a controlled temperature.[28,29] Their formation has invariably been ascribed to alcoholic fermentation because their synthesis requires the presence of pyruvic acid or acetaldehyde, two intermediates in the yeast-mediated conversion of sugars into ethanol. However, during chamber drying no alcoholic fermentation occurs, but both pyruvic acid and acetaldehyde were found in these musts. This has been ascribed to changes in cell membrane permeability by the effect of grape drying activating lipooxygenase enzyme (LOX).[30] This causes a switch from an aerobic metabolism to an anaerobic one, in addition to active alcohol dehydrogenase enzyme (ADH). The conditions prevailing under anaerobic metabolism may facilitate the activation of other enzymes capable of degrading sugars and/or malic acid in the grapes toward pyruvic acid and decarboxylates it to acetaldehyde, which would eventually be reduced to ethanol under the action of ADH.

The musts were found to contain two type B vitisins (a malvidin-3-*O*-glucoside derivative and a peonidin-3-*O*-acetylglucoside derivative) in addition to three malvidin-3-*O*-glucoside-methylmethine-(epi)catechin adducts, all at concentrations below 1.5 mg/L. Table 3 shows the variation of their concentrations during the drying process. As can be seen, the compounds were not quantified in the musts of all varieties. Thus, vitisin B was only detected in musts from Tempranillo dried grapes, whereas its peonidin-3-*O*-acetylglucoside derivative was present in Merlot musts from dried grapes. Finally, three adducts with a structure of malvidin-3-*O*-glucoside-methylmethine-(epi)catechin were detected in Syrah and Tempranillo musts and two of them in Merlot musts.

The color due to high-molecular weight compounds was quantified via polymeric pigment color (PPC), finding an increase substantially from the musts made with fresh grapes to those obtained from dried grapes (Figure 6). The increase was more marked than expected from the concentration effect due to the loss of water by evaporation. This suggests that some colored compounds undergo polymerization reactions during grape drying, most probably reactions of anthocyanins with tannins to form colored polymers contributing to color

Table 3. Changes in the Vitisins and Anthocyanin−Methylmethine−Flavanol Adduct Concentrations in the Musts from Merlot, Syrah, and Tempranillo Grapes during the Raisining

	time (h)	vitisin B	type B vitisin peonidin-3-acetylglc	malvidin-3-glc-methylmethine-(epi)catechin	malvidin-3-glc-methylmethine-(epi)catechin	malvidin-3-glc-methylmethine-(epi)catechin
M	0	nd	nd	nd	nd	nd
	24	nd	nd	0.772 ± 0.029	nd	0.353 ± 0.012
	48	nd	0.591 ± 0.087	0.447 ± 0.026	nd	0.265 ± 0.015
S	0	nd	nd	nd	nd	nd
	24	nd	nd	0.777 ± 0.031	nd	0.410 ± 0.024
	36	nd	nd	0.736 ± 0.082	0.390 ± 0.009	0.337 ± 0.014
T	0	nd	nd	nd	nd	nd
	24	0.628 ± 0.079	nd	0.519 ± 0.013	nd	0.399 ± 0.004
	48	1.01 ± 0.056	nd	0.310 ± 0.023	0.484 ± 0.071	0.372 ± 0.039
	72	1.18 ± 0.096	nd	0.370 ± 0.045	0.357 ± 0.033	0.327 ± 0.045

dx.doi.org/10.1021/jf402263f | J. Agric. Food Chem. 2013, 61, 9908−9914

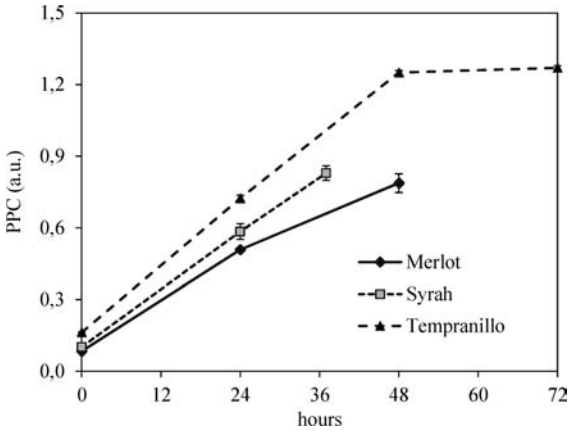

Figure 6. Changes in polymeric pigment color (PPC) in the musts from Merlot, Syrah, and Tempranillo grapes during the chamber drying.

stability.[31] Consequently, a higher drying time carried out a higher formation of polymeric compounds.

For an easier interpretation of the variables best defining the effects of the grape drying process, the results were subjected to principal component multivariate analysis (PCA). Figure 7

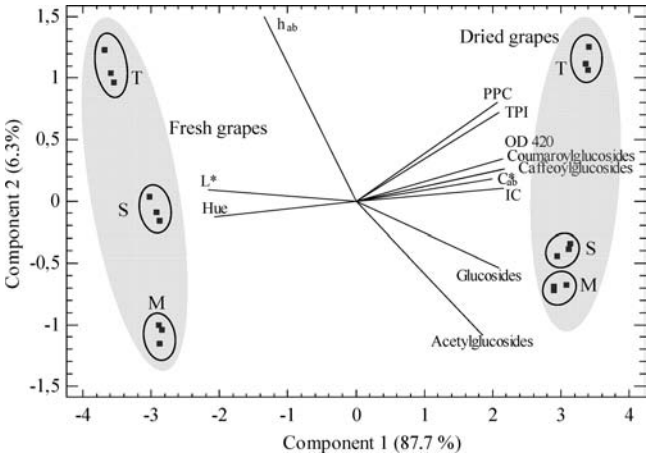

Figure 7. Principal component analysis: biplot representation of must samples and statistical variables.

shows the plane defined by the first two principal components (PCs), which jointly explained 94.0% of the total variance of the process. The plane contains the eigenvectors for each variable considered and their scores for each sample (must from fresh grapes and must from dried grapes). As can be seen, the three types of must were clearly discriminated by PC1. Based on the results, it is clear that drying increased the contents in all phenolic compounds, color intensity (CI), total polyphenol index (TPI), polymeric pigment color (PPC), browning index (OD 420), and chroma (C^*_{ab}) in all musts. By contrast, it decreased lightness (L^*) and hue (OD 420/OD 520), thereby rendering the musts darker and proportionally more redder than brown.

Grape chamber drying has some advantages over the sun-drying procedure traditionally used to obtain sweet wines in southern Spain. Thus, using a controlled temperature substantially shortens the time needed to obtain raisins of similar sweetness.[11] Besides, chamber conditions avoid the development of toxin-producing fungi such as *Aspergillus carbonarius* and arrest growth if the meteorological conditions have resulted in the contamination of the grapes during their ripening.[16] In relation to red grapes, the results have shown that the dehydration of the berries alters their skin, which loses some elasticity and tends to break more easily, thereby facilitating the diffusion of colored compounds to the pulp. This leads to very dark musts with the typical color of red wines owing to the extraction of anthocyanins despite the presence of browning. The formation of vitisin-type anthocyanin derivatives and condensation adducts between anthocyanins and (epi)-catechin via a methylmethine bridge make the resulting musts especially resistant to color degradation during their subsequent winemaking.

In conclusion, based on the foregoing, chamber drying can be an effective method for obtaining sweet red musts from the three grape varieties studied, with little differences between them. The darkest, less-browning musts with the highest values of glucosides, acetylglucosides, coumaroylglucosides, and caffeoylglucosides anthocyanin monomers were obtained at 24 h of chamber drying. However, in order to increase the high-molecular weight compounds and anthocyanin adducts more time could be required. Considering that the amount of reducing sugars in sweet wines is greater than 50 g/L, the musts obtained from dried grapes after 24 h were adequate to elaborate this type of sweet wine. Overall, the anthocyanic profile and the chromatic characteristic of the musts obtained in this way could be used to elaborate red wines without the skin maceration step, which is typical of red winemaking.

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Funding

The authors gratefully acknowledge financial support from the Spanish Government, Ministry of Education (FPU scholarship of Ana Marquez) for the realization of this work.

Notes

The authors declare no competing financial interest.

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