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Drying of Pedro Ximenez Grapes in Chamber at Controlled Temperature and with Dipping Pretreatments. Changes in the Color Fraction

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The drying of Pedro Ximenez grapes in chamber at a controlled temperature of 40 or 50 °C is studied. Compared to traditional sun-drying, the chamber-drying shortened the drying time by about 40% at 50 °C. In color terms, the musts obtained from grapes dried at 50 °C were closer in CIELab coordinates to those obtained by sun-dried grapes, with similar h_{ab} values and slightly lower L^* and C_{ab}^*. To shorten further the drying times at 50 °C, the grapes were dipped in olive oil or ethyl oleate emulsions containing potassium carbonate. The ethyl oleate pretreatment shortened additionally the drying time by about 25%, providing musts with chroma, lightness, and hue similar to those without grape pretreatment. In general, except for the phenolic compounds corresponding to the drying with ethyl oleate pretreatment, most of these compounds in the remainding conditions studied increased to a lesser extent than expected because of water losses of the grapes during drying, revealing degradation reactions.

KEYWORDS: Grape drying; grape browning; CIELab; phenolic compounds

INTRODUCTION

Grapes can be dehydrated by drying in the sun or shade or with more recent mechanical methods (*1*). Sun-drying is the most traditional, inexpensive, and widely used grape-drying method (*2*) to obtain raisins ready-to-eat or used in winemaking. Raisins are not directly used in winemaking, but their must, color, sweetness, flavor, and output of must are important to the production of sweet wines. The valuable textural aspects of raisins ready-to-eat are not considered in winemaking. Although sun-drying requires virtually no equipment, its labor costs are substantial, increasing with time because of the need to turn grapes periodically to ensure uniform drying. Drying times typically range from 5 to 10 days in southern Spain, but can be even longer depending on the particular climatic conditions of the year. Insect attack, intense solar radiation, occasional rain, and fungi-producing toxins, such as ochratoxin A (OTA), can deteriorate sun-dried grapes. Particularly, the presence of OTA is negative because of the molecular stability of this compound, which can be incorporated into wines at concentrations >2 μg/L, the maximum allowed by the European Commission (*3*). Some authors have reported OTA at levels higher than the above-mentioned in sweet wines obtained from Pedro Ximenez (the cultivar studied in this work) sun-dried raisins (*4, 5*). Grape deterioration by the factors above-commented has encouraged the development in recent years of drying methods involving grape protection and/or indirect exposure of grapes to the sun (*6, 7*). These techniques can be used jointly with sun-drying to combine the advantages of both methods (*1*). A method based on microwave vacuum-drying has been reported in the literarure (*8*) to obtain puffy dried grapes (*9*).

Methods based on chamber-drying with controlled temperature are reliable, fast, and easy to use, but require high efficiency to be profitable. Because the energy needed to operate these drying methods is not free, drying times should be as short as possible, favoring the loss of grape water. Grape skin comprises both epidermal cells and a variable number of layers of small thick-walled cells dependent on the particular grape cultivar (*10, 11*). The outer skin of grapes is covered by a nonpermanent coating of lenticels, wax, and collenchymatous hypodermal cells (*12*). By effect of the hydrophobic properties of its wax coating, grape skin acts as a protective barrier against pathogenic fungi. In addition, the coating reduces moisture losses by transpiration, protects grapes from UV light and physical damage, and controls the exchange of gases (*13*). The epicuticular wax coating consists largely (60%) of oleanolic acid, a triterpenic acid (*14*), ensuring by its structure a low rate of moisture evaporation during grape-drying (*15*).

A number of dipping pretreatments for grapes have been tested in recent years with a view to increasing grape skin permeability and facilitating moisture removal to expedite drying. The effects of such chemical pretreatments on grape are widely documented (*6, 16*−*22*), the composition of the particular chemical agents used, their concentration, pH, and

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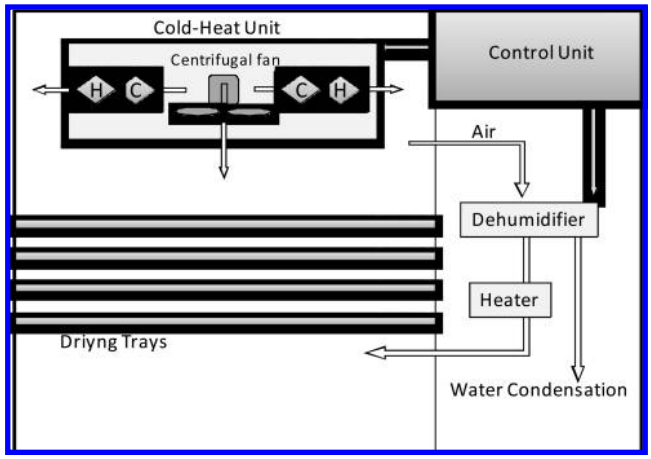

Figure 1. Schematic diagram of the chamber-drying.

temperature, and the dipping time being the main factors governing the alteration of the skin microstructure (*9*).

The most common pretreatments involve the use of an oil emulsion or diluted alkaline solution to accelerate the grape-drying by reducing the resistance to moisture transfer from the skin surface (*23*), improving the moisture diffusion coefficient (*24*). Each emulsion component can interact with others in the emulsion and/or in grape skin, lenticels, and the underlying layers (*25*). Authors such as Vazquez et al. (*26*) report microfissures in the grape skin by using potassium carbonate solution and suggest that this solution has three major effects: removing wax and fat, causing cell collapse in dry skin, and partially breaking ester bonds in pectins. Previously, the grape treatment with this solution was found to neutralize free fatty acids and surface charges, thereby boosting moisture removal (*27*). Sodium hydroxide has also been found to cause visible cracking in grape skin (*26, 28*). One other chemical used in this context, ethyl oleate, can expedite grape drying at an early stage by causing the formation of surface micropores in skin and also at late stage by increasing internal diffusion of water (*16, 24, 29*−*32*). Some authors (*20*) have reported that dipping treatments not only shorten drying times (with economic advantage) but also improve raisin quality in relation to their color, texture, and flavor.

In this work, the influences in chamber-drying of temperature and two dipping treatments on the drying rate of Pedro Ximenez grapes are studied, as well as their impact on color and phenol contents in the resulting raisins, which are largely used to produce sweet wines of the same name. The main objective of the work was to search for alternatives to sun-drying in order to avoid the problems related with this traditional grape-drying method.

MATERIALS AND METHODS

Drying Experiments. Pedro Ximenez grapes were harvested in the Montilla-Moriles region (southern Spain). In a first experiment, two batches of grapes of 6 kg each were distributed uniformly (14 kg/m^2) in a single layer and dried in chamber at air temperatures of 40 and 50 °C, respectively. A schematic diagram of the chamber-drying is given in **Figure 1**. For each temperature the experiment was carried out in triplicate.

In a second experiment (also in triplicate), grapes were dipped in pretreatment solutions and dried afterward at 50 °C in the same distribution conditions above-mentioned. Pretreatment solutions and dipping time were the following: D0, untreated grapes; D1, dipping of grapes in alkaline emulsion of olive oil (7% of K_2CO_3 + 0.4% of commercial olive oil) for 1 min at ambient temperature; and D2, dipping of grapes in alkaline emulsion of ethyl oleate (2.5% of K_2CO_3 + 2% of ethyl oleate) for 10 s at ambient temperature.

In the two experiments, samples were periodically collected, and the weight loss of the grapes was measured. The reducing sugar content (measured as °Brix) was used as tracking criterion of the grape dehydration process. The drying was concluded when the sugar concentration was around 450 g/L.

In the laboratory, the raisins were crushed and subsequently pressed in a vertical press similar to those used at the industrial level. The highest pressure reached in each pressing cycle was 300 bar, and each raisin batch was pressed in three cycles. The musts thus obtained were centrifuged at 3000 rpm and subjected to the different determinations.

UV−**Visible Spectra and Color Measurements.** All spectrophotometric measurements were obtained after filtration of the samples through a filter of HA-0.45 μm pore size (Millipore) and on a 10 mm path length. The absorbances at 280 nm (after dilution 1:10) and at 420 nm were measured by using a Perkin-Elmer Lambda 25 spectrophotometer. This last absorbance was considered to be the browning index. Color analyses were carried out following CIE recommendations (*33*) 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), and the cylindrical coordinates C_{ab}^* (chroma) and h_{ab} (hue angle). These parameters were measured using as references the CIE 1964 Standard Observer (10° visual field) and the CIE standard illuminant D65.

Dialysis. Musts were dialyzed using cellulose dialysis tubing (Sigma-Aldrich) that retained the molecules of a size ≥12000 Da. About 15 mL of must was put into the dialysis tubing, and it was placed in a vessel with 1 L of water. This solution was maintained at 4 °C with stirring for 12 h, followed by a replacement of the water surrounding the dialysis tubing. This procedure was repeated six times. The dialyzed fraction was obtained by dilution to 25 mL with distilled water of the volume of must that remained in the dialysis tubing.

Extraction of Phenolic Compounds. A volume of 25 mL of must was adjusted to pH 7 with 0.1 M NaOH. The sample was passed through a Sep-Pak C18 cartridge, with 900 mg of filling (Long Body Sep-Pak Plus; Waters Associates, Milford, MA) that was previously activated with 8 mL of methanol and washed with distilled water, which was adjusted to pH 7 with NaOH (*34*). The cartridge was eluted with 8 mL of water at pH 7. This volume in addition to the volume obtained as a result of the sample run-through prior to the elution was used for the determination of the phenolic acids fraction. After preconditioning of the cartridge with 2 mL of water at pH 2, the flavan-3-ol fraction was eluted with 8 mL of 16% acetonitrile in water at pH 2 (*35*). These two collected fractions were concentrated and passed through a filter of 0.45 μm pore size for injection into a Spectra-Physics (San Jose, CA) P4000 HPLC instrument.

Identification and HPLC Analysis. The identification of the phenolic compounds was achieved by comparison with the retention times of the standards, UV spectra obtained by HPLC diode array (Spectra-Physics UV6000LP), and calculation of UV absorbance ratios after co-injection of samples and standards (*36*). The identification of compounds was confirmed by HPLC/ESI-MS analysis (TermoQuest Finnigan AQA quadrupole mass spectrometer). The instrument was operated in both the negative ion and positive ion modes. The ion spray voltage was −4 kV and the orifice voltage, −60 V. Mass data were acquired in two different ways, namely, in the scan mode (by scanning the m/z range 150−1066 at 1.2 intervals) and in the multiple ion mode (by using mass ranges around specific m/z values). Commercial standards were purchased from Sigma-Aldrich Chemical Co. (Madrid, Spain) and Extrasynthese Co. (Genay, France). Caftaric and coutaric acids were isolated according to the method described by Singleton et al. (*37*). The standards purity was 95−99%. Each compound was quantified by comparison with a calibration curve obtained with the corresponding standard, except the caftaric, coutaric, and feftaric acid that were quantified as caffeic, *p*-coumaric, and ferulic acid, respectively, and procyanidins that were quantified as catechin.

Table 1. Changes in CIELab Parameters for the Musts during Grape-Drying at 40 and 50 °C

		40 °C				50 °C		
	initial	24 h	48 h	96 h	120 h	24 h	48 h	96 h
L^*	92.0 ± 0.150	92.4 ± 0.070	94.9 ± 0.062	92.0 ± 0.232	91.4 ± 0.001	91.3 ± 0.296	89.9 ± 0.121	83.1 ± 0.435
C^*_{ab}	18.7 ± 0.057	17.2 ± 0.116	15.3 ± 0.058	19.2 ± 0.173	23.5 ± 0.057	21.9 ± 0.252	24.4 ± 0.057	35.9 ± 0.152
h_{ab}	87.0 ± 0.054	90.5 ± 0.062	93.3 ± 0.062	91.9 ± 0.320	90.4 ± 0.070	86.4 ± 0.094	85.8 ± 0.062	83.5 ± 0.153

Table 2. Changes in Phenolic Compound Contents (Milligrams per Liter) for the Musts during Grape-Drying at 40 and 50 °C[a]

		40 °C				50 °C		
compd	initial	24 h	48 h	96 h	120 h	24 h	48 h	96 h
gallic acid	2.33 ± 0.111	2.85 ± 0.101	4.07 ± 0.151	6.37 ± 0.427	7.24 ± 0.283	2.99 ± 0.234	3.59 ± 0.237	10.2 ± 0.051
c-caftaric acid	nd	nd	nd	nd	nd	1.73 ± 0.053	1.55 ± 0.084	1.84 ± 0.103
t-caftaric acid	1.94 ± 0.123	1.98 ± 0.101	2.00 ± 0.055	2.01 ± 0.195	2.33 ± 0.211	1.96 ± 0.055	1.90 ± 0.095	2.24 ± 0.059
cis-coutaric acid	nd	nd	nd	nd	nd	nd	0.733 ± 0.039	1.38 ± 0.021
trans-coutaric acid	nd	nd	0.916 ± 0.061	0.822 ± 0.040	1.50 ± 0.135	nd	0.748 ± 0.039	0.932 ± 0.060
cis-feftaric acid	0.962 ± 0.084	0.983 ± 0.075	0.994 ± 0.095	1.04 ± 0.044	1.08 ± 0.156	1.15 ± 0.055	0.953 ± 0.024	0.978 ± 0.010
trans-feftaric acid	1.12 ± 0.087	1.12 ± 0.086	1.14 ± 0.081	1.05 ± 0.082	1.21 ± 0.099	1.24 ± 0.092	1.02 ± 0.040	0.898 ± 0.081
(+)-catechin	17.7 ± 1.40	19.2 ± 1.23	22.1 ± 1.82	18.8 ± 0.751	30.1 ± 2.63	20.4 ± 0.917	19.0 ± 0.153	14.4 ± 0.751
(−)-epicatechin	10.3 ± 0.153	12.5 ± 0.123	17.9 ± 1.60	17.0 ± 1.56	19.4 ± 1.90	12.3 ± 0.666	16.9 ± 1.46	14.4 ± 0.335
procyanidin B1	4.02 ± 0.322	4.82 ± 0.125	4.93 ± 0.035	5.91 ± 0.551	6.56 ± 0.187	1.68 ± 0.040	4.05 ± 0.282	6.67 ± 0.374
procyanidin B3	0.284 ± 0.036	0.345 ± 0.035	0.657 ± 0.018	0.692 ± 0.011	0,698 ± 0,001	0.647 ± 0.006	0.940 ± 0.062	1.30 ± 0.042

[a] nd, not detected.

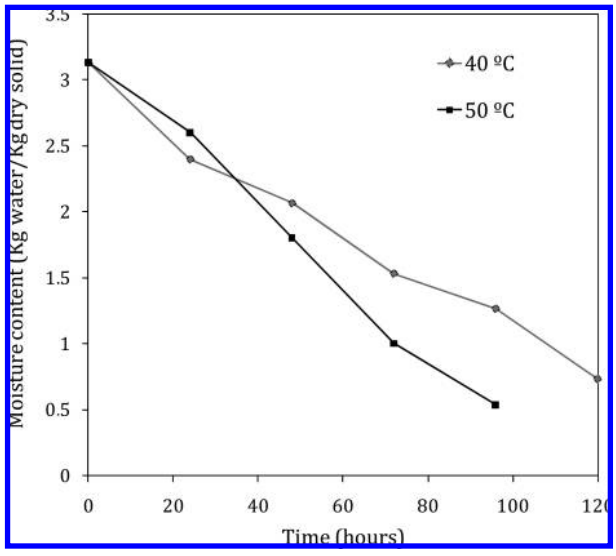

Figure 2. Drying curves of grapes dried at 40 and 50 °C.

Analyses were carried out on a LiChrospher 100 RP-18 column (250 mm × 4.6 mm, 5 μm particle size) by using 2% aqueous formic acid and acetonitrile as mobile phases at a flow rate of 1 mL/min and detection at 280 nm (phenolic acids and flavan-3-ol fractions) and 315 nm (esters of hydroxycinnamic acid).

The elution phases were as follows: gradient elution from 5 to 10% CH_3CN in 25 min, gradient elution to 20% CH_3CN in 10 min, gradient elution to 30% CH_3CN in 10 min, gradient elution up t100% CH_3CN in 15 min, and isocratic elution for 10 min.

RESULTS AND DISCUSSION

Influence of Temperature on Grape-Drying. Figure 2 shows the grape-drying curves obtained at 40 and 50 °C by plotting moisture contents (kg of water/kg of dry solid) versus drying time. As expected, the drying rate was higher at the higher temperature, which shortened the process by slightly over 20% judging by the final moisture contents of the grapes (0.73 kg of water/kg of dry solid at 40 °C and 0.53 of water/kg of dry solid at 50 °C). At that point, the contents in reducing sugars were 420 and 435.3 g/L at 40 and 50 °C, respectively, increasing by a factor of 2.1 at the former temperature and by a 2.3 at the latter from 190 g/L at the start of the drying process. Certainly, during drying at the temperatures studied small amounts of reducing sugars can be consumed through caramelization and mainly Maillard reactions; nevertheless, when the high final contents of these compounds are taken into account, it is reasonable to attribute most of these increases to water evaporation from the grapes. Therefore, the increases in sugars can be used as references of the concentration effect on other parameters during drying.

Figure 3 shows the changes in the absorbance at 280 nm (mean and standard deviation) for the musts obtained from grapes dried at 40 and 50 °C, and those for their high molecular weight fractions (HMW). As can be seen, A_{280} increased with increasing drying time in both types of must (from 6 to 12.5 au at 40 °C and to 16.5 au at 50 °C). Some authors (*38*) have studied traditional drying (sun-drying for 7 days in a typical year with zero rainfall in August) in grapes of the same variety with an initial sugar content of 204.8 g/L. Starting from an initial A_{280} value of 5.74 au, which was similar to ours, these authors obtained absorbances between the previous two values (14.9 au after 7 days), even though the concentration effect due to water losses was greater (the final sugar concentration in sun-dried grapes was 494 g/L and that in chamber-dried grapes at 50 °C was 435 g/L). In relative terms, drying at 40 °C increased A_{280} 2.1 times, which is the same value as the increase in reducing sugars at the same temperature, indicating that the increase in A_{280} at this temperature can be mainly ascribed to the concentration effect resulting from water evaporation of the grapes. However, the A_{280} values obtained at 50 °C exceeded those found in sun-dried grapes, and their absorbances increased 2.8 times, whereas their sugar contents rose by a factor of only 2.3. Therefore, the higher temperature must not only facilitate moisture evaporation and its consequent concentration effect but also favor chemical reactions leading to increased levels of compounds absorbing at this wavelength and/or transformation of some into others with higher molar extinction coefficients. This assumption is supported by the fact that such reactions were more markedly favored by chamber-drying at 50 °C than by sun-drying, even though the previous authors pointed out

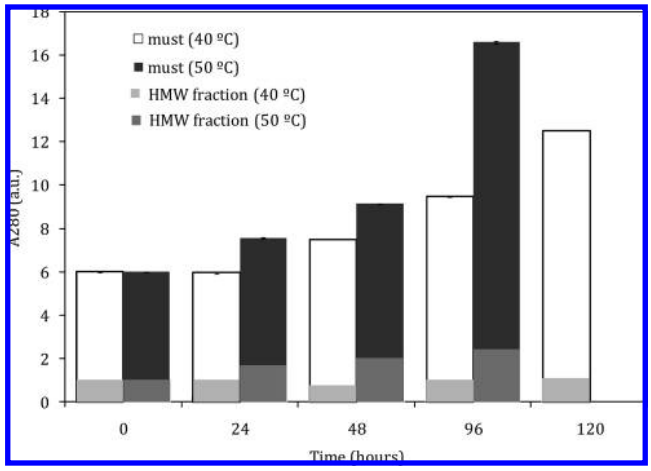

Figure 3. Changes in the absorbance at 280 nm for the musts and their dialyzed fractions during grape-drying at 40 and 50 °C.

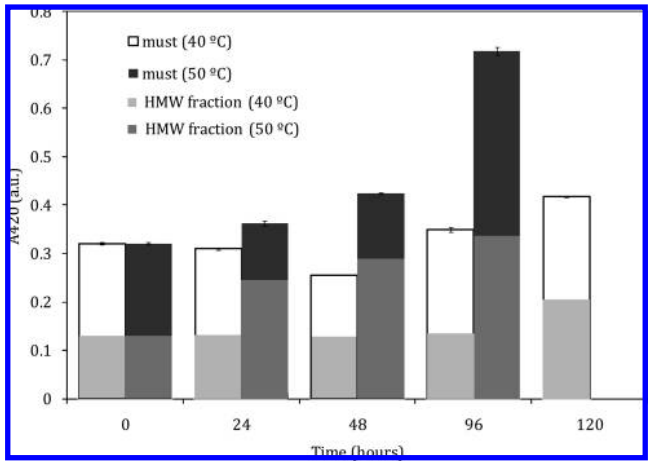

Figure 4. Changes in the absorbance at 420 nm for the musts and their dialyzed fractions during grape-drying at 40 and 50 °C.

that diurnal temperatures during the sun-drying were close to 50 °C. However, although the temperature during sun-drying declines in its nocturnal period, chamber-drying maintains a constant temperature throughout the day, thereby favoring these types of reactions in a more sustained manner.

The dialyzed fraction (HMW) includes high molecular weight brown polymers, such as possible melanoidins, caramelization products, and high molecular weight phenolic compounds and their browning products. As can be seen, this fraction exhibited low A_{280} values relative to the musts at both 40 and 50 °C, which indicates that absorption at 280 nm was due mostly to low molecular weight compounds. In addition, A_{280} increased little during the drying process and only at the higher studied temperature.

Figure 4 shows the changes in A_{420} for the musts obtained from grapes dried at the two studied temperatures, as well as the values for their HMW fractions. As can be seen, A_{420} increased in the musts from grapes dried at 40 and 50 °C (from 0.321 au at the beginning to 0.418 and 0.719 au, respectively, at the end). A_{420} increased little (1.3 times) during drying at 40 °C, which suggests that the reactions giving browning compounds developed to a very small extent at this temperature. Furthermore, some brown polymers may have been degraded, judging by the small increase observed relative to the effect of moisture evaporation alone (2.1 times). The final A_{420} values obtained at 50 °C were substantially higher (170%) than those obtained at 40 °C, mostly by effect of increased browning in the last 48 h of drying. Logically, the temperature played an undeniable role in this difference, but also it is known that in the foods drying an initial decrease from a high water activity to a determined value accelerates processes such as the Maillard reaction, which produces not only brown-colored polymers but also simple derivatives of furan that increase brown color. Taking into account that the grapes dried at 50 °C lost more water (and had lower a_w values as a result), temperature and a_w could act synergistically, increasing browning. In support of this hypothesis is the fact that the A_{420} values obtained at 50 °C were lower than those obtained by Serratosa et al. (*38*) for the sun-dried grapes (1.02 au), despite the previous comments about the constant temperature in the chamber. However, one should bear in mind that chamber-drying at 50 °C was stopped at a sugar content of grapes of 435 g/L, this value being lower than that obtained for the sun-dried grapes (494.2 g/L), leading to a lower water activity in the latter and resulting in stronger browning in their musts. Therefore, on the basis of the browning trend of the grapes dried at 50 °C, it is reasonable to assume that allowing the grapes to stand for a few more hours in the chamber would have led to A_{420} levels similar to those for the sun-dried grapes. However, the grapes dried at 40 °C would have required a much longer time in the chamber to reach similar A_{420} values.

With regard to the HMW fraction, A_{420} for the chamber-dried grapes at 40 °C increased very little within the first 96 h (from 0.130 to 0.137 au) and more markedly after 120 h, when it exhibited values of 0.205 au (1.57 times the initial levels), therefore increasing to a slightly greater extent than the brown polymers of low molecular weight. At 50 °C, however, A_{420} for the HMW fraction increased gradually from 0.130 to 0.337 au (2.6 times) at the end of the process, the HMW fraction showing at this temperature a more marked increase than the brown polymers of low molecular weight. In any case, HMW compounds contributed similarly to browning (49 and 46.9% in the grapes dried at 40 and 50 °C, respectively).

In dark white wines, not only is important browning but also the type of color of the brown compounds. In this respect, CIELab coordinates provide a useful tool for measuring color in these wines. **Table 1** lists the variation of L^*, C_{ab}^*, and h_{ab} for the musts during grape-drying at the two temperatures studied. The hue angle (h_{ab}) is a measure of redness at levels close to 0° and yellowness near 90°. As can be seen, h_{ab} decreased gradually to slightly lower values during drying at 50 °C, the musts showing an increasingly red hue. However, h_{ab} increased during chamber-drying at 40 °C, indicating an increase in the yellowish hues of the musts during the first 96 h and then a slight reddening at the end of the drying process, their final h_{ab} values, nevertheless, being higher than the initial values. Chromaticity (C_{ab}^*) increased in both chamber-drying processes, but particularly at 50 °C, with final values 1.92 times higher than the initial values, but only 1.26 times at 40 °C. Finally, lightness (L^*, which can range from 0 for black to 100 for white), remained virtually at its initial values in the must from grapes dried at 40 °C and decreased (from 92 to 83.1) in the must from grapes dried at 50 °C. Overall, chamber-drying at 50 °C led to redder, darker, and more strongly colored musts than did drying at 40 °C, when musts darkened little and exhibited a more yellowish hue.

Table 2 lists the changes in the contents of phenolic compounds during drying at 40 and 50 °C. In the absence of reactions, drying should increase the contents in phenolic compounds by effect of water evaporation from the grapes. However, some phenols can take part in different types of

Table 3. Changes in the CIELab Parameters for the Musts during Grape-Drying at 50 °C without Pretreatment (D0) and Pretreated (D1, D2)

		D0			D1			D2		
	initial	21 h	45 h	70 h	21 h	43 h	55 h	21 h	30 h	48 h
L^*	86.3 ± 0.456	78.1 ± 0.347	78.8 ± 0.174	64.9 ± 0.361	78.0 ± 0.265	71.0 ± 0.306	61.9 ± 0.608	70.3 ± 0.404	67.3 ± 0.436	64.2 ± 0.472
C^*_{ab}	31.2 ± 0.346	48.4 ± 0.907	49.3 ± 0.251	67.7 ± 0.155	47.8 ± 0.056	58.8 ± 0.058	61.4 ± 0.264	52.5 ± 0.153	61.0 ± 0.062	65.9 ± 0.175
h_{ab}	81.6 ± 0.150	78.3 ± 0.150	77.2 ± 0.062	72.1 ± 0.058	80.0 ± 0.062	74.5 ± 0.062	73.3 ± 0.153	75.6 ± 0.099	73.6 ± 0.049	72.7 ± 0.058

Table 4. Changes in the Phenolic Compound Contents (Milligrams per Liter) for the Musts during Grape-Drying at 50 °C without Pretreatment (D0) and Pretreated (D1, D2)[a]

		D0			D1			D2		
	initial	21 h	45 h	70 h	21 h	43 h	55 h	21 h	30 h	48 h
gallic acid	1.98 ± 0.012	2.84 ± 0.070	3.74 ± 0.107	4.36 ± 0.409	2.79 ± 0.050	2.44 ± 0.110	4.01 ± 0.101	2.09 ± 0.074	2.61 ± 0.217	4.31 ± 0.284
c-caftaric acid	1.43 ± 0.040	1.52 ± 0.121	1.66 ± 0.163	1.93 ± 0.151	1.61 ± 0.031	1.58 ± 0.072	2.97 ± 0.171	1.51 ± 0.072	1.57 ± 0.047	3.53 ± 0.146
trans-caftaric acid	1.35 ± 0.021	1.64 ± 0.104	1.58 ± 0.155	1.51 ± 0.058	1.55 ± 0.085	1.49 ± 0.093	3.08 ± 0.208	1.55 ± 0.086	1.67 ± 0.078	3.31 ± 0.075
cis-coutaric acid	nd	nd	nd	nd	nd	nd	nd	0.771 ± 0.030	0.760 ± 0.028	2.11 ± 0.035
trans-coutaric acid	nd	nd	nd	nd	nd	nd	nd	0.762 ± 0.062	0.748 ± 0.045	1.52 ± 0.012
cis-feftaric acid	0.944 ± 0.002	1.02 ± 0.053	0.905 ± 0.028	1.42 ± 0.064	0.835 ± 0.054	1.09 ± 0.091	1.99 ± 0.123	0.891 ± 0.004	0.945 ± 0.060	2.01 ± 0.172
trans-feftaric acid	0.969 ± 0.001	1.03 ± 0.015	0.914 ± 0.036	1.34 ± 0.036	0.892 ± 0.041	0.903 ± 0.004	2.03 ± 0.148	0.872 ± 0.010	1.09 ± 0.097	2.07 ± 0.082
(+)-catechin	15.8 ± 0.265	17.8 ± 0.208	14.3 ± 1.42	23.9 ± 1.70	11.3 ± 0.265	11.4 ± 0.603	18.5 ± 1.25	12.3 ± 0.252	15.1 ± 0.265	27.7 ± 0.781
(−)-epicatechin	10.8 ± 0.208	13.2 ± 1.13	8.71 ± 0.537	21.4 ± 1.40	10.9 ± 0.896	11.6 ± 0.200	12.6 ± 0.624	8.18 ± 0.312	9.04 ± 0.455	21.0 ± 0.500
procyanidin B1	2.23 ± 0.153	2.32 ± 0.006	2.25 ± 0.177	5.33 ± 0.302	2.85 ± 0.128	1.37 ± 0.110	3.34 ± 0.251	2.55 ± 0.135	3.15 ± 0.233	3.53 ± 0.230
procyanidin B3	0.757 ± 0.003	0.883 ± 0.003	2.14 ± 0.149	3.52 ± 0.075	1.73 ± 0.135	1.34 ± 0.114	1.14 ± 0.038	4.32 ± 0.378	3.54 ± 0.195	3.88 ± 0.095

[a] nd, not detected.

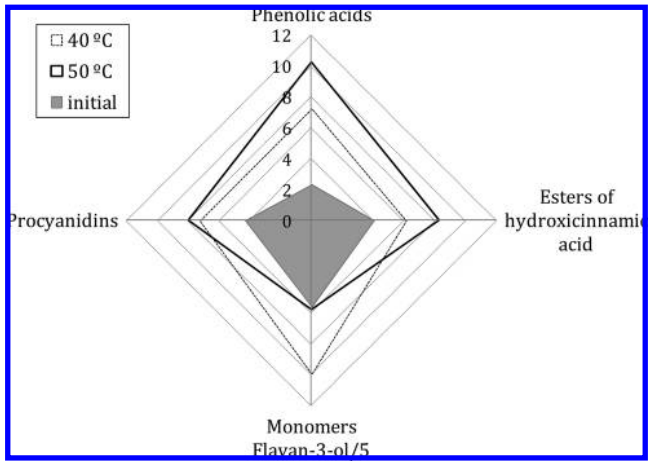

Figure 5. Contents in phenolic compounds of the initial must and those obtained at the end of the grape-drying at 40 and 50 °C.

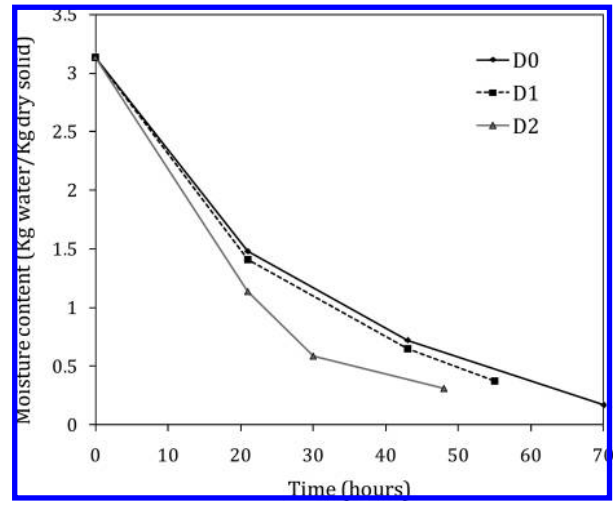

Figure 6. Drying curves of grapes dried at 50 °C without pretreatment (D0) and pretreated (D1, D2).

reactions including nonenzymatic browning and/or autoxidation and enzymatic oxidation reactions involving polyphenol oxidases or peroxidases (*39*), all of which reduce their concentrations. In addition, it is known that some flavan-3-ol high molecular weight derivatives can be hydrolyzed to phenolic compounds of lower molecular weights (*40*−*43*), increasing the contents in the latter. Therefore, the net outcome for some phenolic contents is a balance between concentration gains and losses. **Figure 5** shows the contents in phenolic compounds grouped in chemical families in the initial musts and those obtained at the end of the drying process. As can be seen, the contents in phenolic acids fraction (gallic acid) increased in both dryings, from 2.33 to 7.24 mg/L at 40 °C and to 10.2 mg/L at 50 °C, these increases being much greater than expected as a result of the effect of moisture evaporation from the grapes. Esters of hydroxycinnamic acids also increased (1.5 and 2.1 times at 40 and 50 °C, respectively), but in lower proportions than did reducing sugars, suggesting their involvement in some type of reactions leading to a reduction in their concentrations. The contents in flavan-3-ol monomers (catechin and epicatechin) increased from 28 mg/L in the initial musts to 49.5 and 28.8 mg/L at 40 and 50 °C, respectively, the former increase being much smaller than expected from the concentration effect and the latter virtually zero. This indicates that these compounds must have taken part in oxidation and condensation reactions during dehydration, these reactions obviously being more markedly favored at 50 °C than at the lower temperature. However, this difference between drying temperatures was not observed in flavan-3-ol oligomers, which increased to similar extents at both 40 and 50 °C (from 4.3 mg/L at the beginning to 7.25 and 7.97 mg/L, respectively, at the end). These increases were also smaller than expected because of a concentration effect, showing the involvement of these compounds in degradation reactions but not so strongly temperature-dependent as the previous ones, however.

Overall, compared to a sun-drying of 7 days with a final sugar content of 494.2 g/L (*38*), drying Pedro Ximenez grapes in a controlled-temperature chamber shortened drying times substantially by about 30% at 40 °C and 43% at 50 °C, with final sugar contents of 420 and 435.3 g/L, respectively. Because the total production of raisin is used to obtain Pedro Ximenez sweet wines, the color of the must is important. In our work, the musts

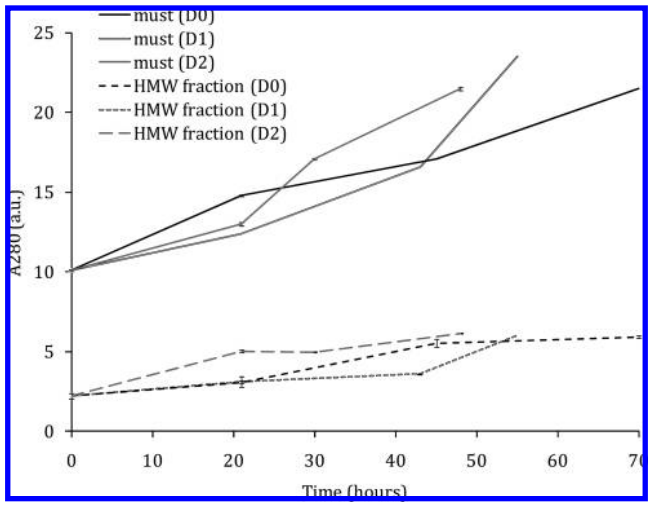

Figure 7. Changes in the absorbance at 280 nm for the musts and their dialyzed fractions during grape-drying at 50 °C without pretreatment (D0) and pretreated (D1, D2).

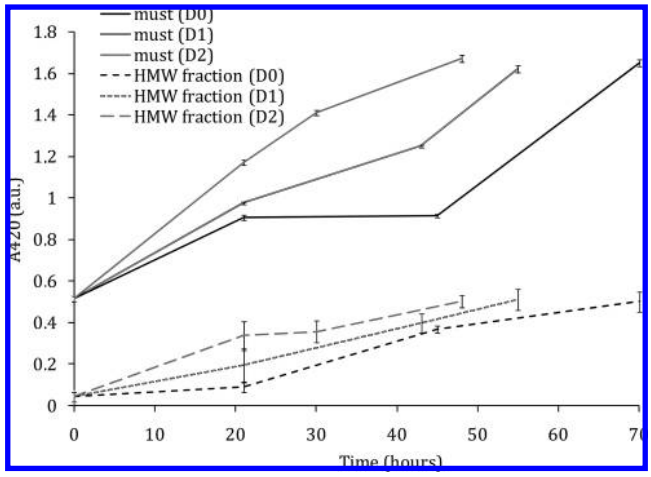

Figure 8. Changes in the absorbance at 420 nm for the musts and their dialyzed fractions during grape-drying at 50 °C without pretreatment (D0) and pretreated (D1, D2).

from chamber-dried grapes at 50 °C most closely resembled those from sun-dried grapes, with a slightly lower lightness and chroma and a similar hue. Chamber-dried grapes have the advantage that, unlike with sun-dried grapes, the outcome does not depend on the particular climatic conditions of the year, allowing an improved selection of grapes concerning their ripening and sanitary stage (mainly in relation to growth of toxin-producing fungi). Nevertheless, the energy costs of using drying chambers are obviously higher than those of the sun-drying process, although the latter involves high labor costs derived from the need to periodically turn the grapes to ensure a uniform drying. It would therefore be interesting to shorten chamber-drying times, without the need to increase the drying temperature, by pretreating chemically the grapes before putting them in the chamber to facilitate moisture release.

Influence of Pretreatments on Grape-Drying. Because the pretreatments were designed after the influence of temperature was studied, a second batch of Pedro Ximenez grapes was used for these experiments. On the other hand, because chamber-drying is not affected by the climatic conditions, the grapes used were of a higher ripening degree (initial sugar concentration in the must was 216.2 g/L); therefore, they required a shorter time of drying and consequently a higher effectiveness in energetic terms. However, grape ripeness cannot be exclusively estimated

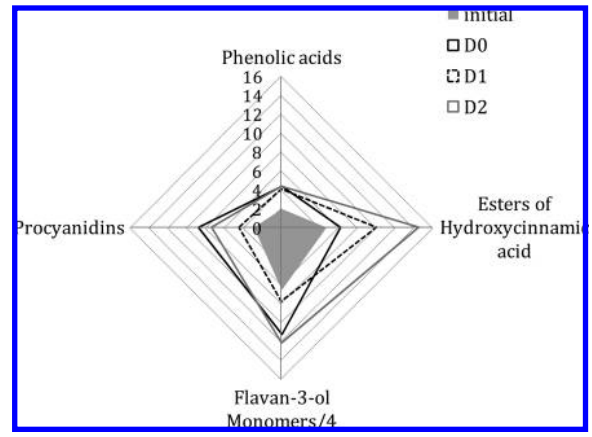

Figure 9. Contents in phenolic compounds of the initial must and those obtained at the end of the grape-drying at 50 °C without pretreatment (D0) and pretreated (D1, D2).

from sugar contents, so part of this second batch was chamber-dried without pretreatment, acting as reference.

Figure 6 shows the grape-drying curves (kg of water/kg of dry solid versus time) for grapes dried at 50 °C, both untreated (D0) and treated by dipping in potassium carbonate + olive oil (D1) or potassium carbonate + ethyl oleate (D2). As can be seen, the drying rates were very similar for both D1-treated and untreated (D0) grapes; however, it was substantially higher for D2-treated grapes, even though the dipping time was much shorter than in D1 (10 s versus 1 min). Because the treatments provided grapes with not exactly identical moisture contents, the moisture curves were fitted for each treatment to an exponential function with $p < 0.001$ to more precisely estimate the reduction in the drying time. As a result, to obtain the same moisture content as with D1 (0.377), treatment D2 needed a time estimate of 42.5 h, that is, 24% shorter than that in D1. Because the increased drying rates of the pretreated grapes are the result of chemical and/or physical changes in the skin wax layer (*9*), treatment D2 was more effective than D1, boosting moisture diffusion more markedly, which is consistent with previous results of other authors (*22*). Nevertheless, it must be considered that the specific efficiency of a pretreatment is largely dependent on the concentration of the dipping agent and the dipping time (*44*). In our case, when the above-commented large difference in dipping times is taken into account, the organic component of the dipping agent (ethyl oleate or natural glycerides in olive oil) was more influential than potassium carbonate.

Figure 7 shows the changes in the absorbance at 280 nm of the musts obtained from pretreated and untreated grapes, as well as those for their high molecular weight fractions (HMW). As can be seen, A_{280} increased from 10.1 au to similar levels with the three treatments (21.5 au for D0, 23.5 au for D1, and 21.5 for D2), the respective sugar concentrations amounting to 506, 468, and 472 g/L. The increases in A_{280} may have been the virtually exclusive result of moisture evaporation because they were of a similar order of magnitude as those of the reducing sugars. A_{280} also increased similarly for the HMW fractions, from 2.22 au (22.0% of the A_{280} value) to 5.93 au for D0, 6.02 au for D1, and 6.16 au for D2, which account for 27.6, 25.6, and 28.7% of the overall final values.

Figure 8 shows the changes in the absorbance at 420 nm for the musts and their HMW fractions. As can be seen, A_{420} increased gradually from 0.515 au to very similar levels for the three treatments at the end of the drying processes (1.65 au for D0, 1.62 au for D1, and 1.67 au for D2), the increase rate being

D2 > D1 > D0, and showing that dipping treatments had no influence on the final extent of browning. However, the marked difference between the final A_{420} value for the must from grapes of the first batch dried at 50 °C, which was used exclusively to examine the effect of the drying temperature, and that for the second batch without pretreatment (D0), which was employed as reference to observe the effect of the pretreatments, should be pointed out. Thus, A_{420} increased 224% for the first grape batch and 321% for the untreated portion of the second batch (D0). These results are difficult to interpret because, on the one hand, the initial A_{420} values were higher in the second grape batch than in the first, which could favor browning. On the other hand, the grapes of the second batch were harvested at a higher ripening degree (216 vs 190 g of sugars/L), therefore, with a lower water activity, which, as noted earlier, must have facilitated some reactions in the aqueous phase such as browning. However, only the formation of simple, low molecular weight browning compounds was favored because the HMW fraction in the first grape batch contributed 47% to the final A_{420} and only 30.4, 31.5, and 30.1% for the D0, D1, and D2 treatments, respectively.

Table 3 lists the changes in the CIELab coordinates for the musts during drying of pretreated (D1 and D2) and untreated grapes (D0). As can be seen, h_{ab} gradually decreased from 81.6 to 72.1 for D0, to73.3 for D1, and to 72.7 for D2, showing that the musts gradually reddened with time, without appreciable differences between treatments. In relation to C_{ab}* and L*, pretreatment D2 led to musts with values similar to those of D0 and slightly lower that those of D1.

Table 4 lists the changes in the contents of phenolic compounds during drying of pretreated (D1 and D2) and untreated grapes (D0). As above-commented, the outcome for each compound can be a balance of gains and losses resulting from a wide variety of factors ranging from concentration effect, because of moisture evaporation, to a group of chemical reactions not entirely known that can increase the contents in some cases and decrease them in others. Also, many polyphenols change their contents at the end of ripening in the grapes depending on the particular climatic conditions of the year. In addition, the treatments cause surface alkalinization and structural damage in grape skin, where a sizable fraction of polyphenols concentrates. Therefore, the combination of these factors makes difficult the observation of clear trends. Nevertheless, as can be seen in **Figure 9**, treatment D2 resulted in stronger concentration and/or less marked degradation of hydroxycinnamic esters and monomeric and dimeric derivatives of flavan-3-ol than did D1.

In conclusion, drying Pedro Ximenez grapes for the production of sweet wines in a chamber at controlled temperature shows some interesting advantages against the traditional sun-drying of grapes. On the one hand, the drying time is shortened and chamber-drying allows select grapes at a higher ripening degree and more independent of the particular climatic conditions of the year. Certainly, from low ripeness grapes can be obtained good-quality raisins if dehydrated artificially, due to instantly stopping cellular respiration, in comparison with sun-dried raisins (*45*). However, a higher ripening degree results in a drying time additionally shorter to obtain raisins of similar sweetness, as well as a higher output of must because lower water evaporation from the grapes is required to obtain a similar content in sugars, this last being important in winemaking. On the other hand, if grapes are dipped in a mixture of potassium carbonate and ethyl oleate prior to drying at 50 °C, the drying time is even shorter, obtaining musts with chroma, lightness, and hue similar to those without grape pretreatment. Finally, the chamber conditions and/or dipping should not favor the development of fungi-producing toxin. This subject, however, was not an objective of this work, and it requires further specific investigation taking into account the random growth of such fungi in relation to the climatic conditions prevailing during ripening of the grapes.

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