

## Off-Vine Grape Drying Effect on Volatile Compounds and Aromatic Series in Must from Pedro Ximénez Grape Variety

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Changes in 36 volatile compounds of must from ripe grapes dried by direct exposure to sun and must from ripe grapes were studied. Compounds not dependent on sampling site in both musts were selected, and their concentration/Brix degree ratio values, were subjected to variance analysis. Only butan-1-ol and isoamyl alcohols showed no differences, while (*E*)-hex-3-en-1-ol, (*Z*)-hex-3-en-1-ol, (*E*)-hex-2-en-1-ol, (*E*)-hex-2-enal, hexanoic acid, isobutanol, benzyl alcohol, 2-phenylethanol,  $\gamma$ -butyrolactone,  $\gamma$ -hexalactone, and 5-methylfurfural, showed significant differences between the two must types, which may be ascribed to the drying process. An approach to describe must odor has been carried out by grouping volatile compounds in aromatic series, increasing their values in the fruity, solvent, sweet, and roasted series and diminishing the herbaceous as a consequence of the drying process.

**KEYWORDS:** Volatiles; aroma; musts; off-vine grape drying; Pedro Ximénez

### INTRODUCTION

High quality dessert wines are obtained by means of special vinification techniques using grapes with special characteristics as raw material. As a result, their production is very limited. In this way, ice-wines are obtained in Ontario (Canada), Maine-Franken, Mosela and Rhin (Germany), and in Neusiedlersee (Austria) from frozen grapes and Sauternes and Tokay wines from grapes affected by noble-rot in France and Hungary. Sweet wines of great quality are also obtained using grapes of Muscat variety in different grape-growing areas worldwide.

Some Mediterranean countries (viz., Spain, Greece, Cyprus, Italy, and Turkey) make special sweet wines using dried grapes by direct exposition to sun. This process is feasible only in some warm or semi-arid regions of these countries, such as Montilla-Moriles, Málaga, and Jerez grape growing areas in Spain, which make a special dessert wine from dried grapes of Pedro Ximénez variety. The Montilla-Moriles region, in particular, can be included in the V climatic zone of Winkler classification (1), showing a heliothermic index above 2597 °C (considered as the sum of the temperatures higher than 10 °C) and maximum temperature above 40 °C during grape ripening (2). Grapes can be harvested within first 15 days of August and they can be subjected to the off-vine drying for the remainder of the summer.

Off-vine drying process is performed on esparto mats where the grape bunches are turned over on a regular basis and covered at night to avoid the adverse effects of high air moisture (3). Grapes reaching sugar levels above 300 g/L are crushed and

pressed by means of vertical presses. The must yield is very low (0.24–0.32 L/kg dried grapes), exhibiting a dark-brown color, a high viscosity, and a characteristic “raisiny” aroma. The must is fortified with ethanol during winemaking to ensure that the aged wine will contain at least 15–18% alcohol. Montedoro and Bertuccioli (4) show a simplified scheme for the elaboration of Pedro Ximénez wines.

The off-vine grape drying process is in many ways similar to the natural on-vine drying process established by twisting each bunch stalk. Physically, berries gradually shrink, deteriorating their skin as consequence of the loss of water. According to Ribéreau-Gayon et al. (5) the drying process has a concentration effect on sugars and a lesser effect on acids (it even decreases their contents); however, the effect of this process on the volatile fraction of the grapes has not been studied. It is also known that freshly cut grapes show an anaerobic metabolism (6), which is reflected in the production of ethanol, CO<sub>2</sub>, and fermentation byproducts (7) affecting the composition in volatile compounds of the grapes.

The odor of one volatile compound is described in terms of one or several descriptors agreed upon by experts (8–12). In addition, several authors have used odorant series to describe the aroma of wine (13–14). Grouping the volatile aroma compounds with similar descriptors in odorant series, an organoleptic profile of the must or wine can be established, and the contribution of each compound to each series can be determined. This procedure allows one to relate quantitative information derived by chemical analysis to sensory perceptions with a view to obtaining an aroma profile for the must and wine,

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which is simpler and based on more objective criteria than existing alternatives (15).

This paper describes the changes in volatile compounds of must from Pedro Ximénez ripe grapes variety and must obtained as results of the off-vine grape drying process. A first approach to the contribution of volatile compounds to must aroma was established grouping the quantified compounds in aromatic series.

## MATERIAL AND METHODS

**Musts.** Two types of must from the Pedro Ximénez grape variety were studied. One type was obtained from grapes harvested at industrial ripeness in the Montilla-Moriles grape-growing area (Córdoba, Spain) and the other from ripe grapes dried off-vine by direct exposure to the sun, which is the drying method traditionally used in this area. Musts from ripe grapes were obtained by means of horizontal presses in three local cellars and those from off-vine-dried grapes by using vertical presses in three local wineries specializing in the production of these musts. Three samples per each cellar and three for each winery from the same pressing, site, and day were used for analysis.

All musts were sterilized prior to analysis by passage through Supra EK filters from Seitz (Bad Kreuznach, Germany) of 0.45- $\mu$ m pore size. The filtered musts thus obtained were immediately subjected to routine and volatile compound analyses.

**Analyses.** Total soluble solids ( $^{\circ}$ Brix) were determined with a refractometer; the volumic mass was quantified using the aerometric method, and the pH and titratable and volatile acidities were determined using the European Community Official Analytical Methods (16).

Volatile compounds were determined by capillary-column gas chromatography–mass spectrometry following continuous extraction of 100 mL of must sample with 100 mL of Freon-11 for 24 h according to the method described by Rapp et al. (17). Must was adjusted to pH 3.5 and 5 mL of a 30-mg/L solution of 2-octanol was added as internal standard. The Freon extract containing the volatile compounds was concentrated to 0.2 mL in a Kuderna-Danish microconcentrator, and 1.5  $\mu$ L was injected into a Hewlett-Packard HP-6890 gas chromatograph equipped with an HP MS 5972A mass detector (Agilent Technologies, Palo Alto, CA). An HP-Innovax fused silica capillary column (60-m  $\times$  0.32-mm ID, 0.25- $\mu$ m film thickness) was used. The temperature program was as follows: initial temperature 40  $^{\circ}$ C, held for 10 min, 1  $^{\circ}$ C/min ramp to 180  $^{\circ}$ C, and held for 35 min. Helium at a constant flow rate of 0.9 mL/min was used as carrier gas, and a 30:1 split ratio was employed at the injection port. The mass detector was used with a voltage of 1612 V in the scan mode to cover a mass range from 39 to 300 amu.

Retention times and spectral library, supplied by Wiley, and pure chemicals obtained from Merck, Sigma-Aldrich, Riedel de Haën and Fluka were used to identify and confirm the volatile compounds studied and to prepare their standard solutions. Each compound was quantified from its response factor, which was obtained by using standard solutions of known concentration subjected to the same treatment as the samples and using the target ions and qualifier ions selected for each compound by a Hewlett-Packard Chemstation. (Palo Alto, CA).

**Odor Perception Threshold Determination.** The odor perception threshold is defined as the lowest concentration capable of producing a sensation. That sensation has to be detected by at least 50% of the judges in the taste panel (18, 19). Different solutions of ascending concentrations of each compound were used. Starting from the lowest concentration solution, the judges have to indicate the solution whose stimulus was different to that perceived in the control. The control consisted of a solution of 1/10 ethanol/water without compound. The judges trained but not selected for the test consisted of 30 people of both sexes and between 20 and 55 years old. On the other hand, the judges gave odor descriptor of the studied compounds.

**Statistical Analysis.** Statgraphics Plus v. 2 software package (STSC, Inc., Rockville, MD) was used to perform statistical analysis. In this way, a homogeneous groups analysis of means was performed using Fischer's LSD procedure at the 95% confidence level to establish the dependence of each compound due to the sampling site for each must

**Table 1.** Mean and Standard Deviation for pH, Titratable Acidity, Brix Degrees and Volumic Mass in Musts from Ripe and Off-Vine-Dried Pedro Ximénez Grapes<sup>a</sup>

	ripe grapes	homogeneous groups <sup>b</sup>	off-vine dried grapes	homogeneous groups <sup>b</sup>
pH	4.1 $\pm$ 0.1	AAA	4.5 $\pm$ 0.2	AAA
titratable acidity (g tartaric acid/L)	2.4 $\pm$ 0.1	AAA	2.5 $\pm$ 0.5	AAB
Brix degree	24.5 $\pm$ 0.5	AAA	46 $\pm$ 2	AAA
volumic mass (g/mL)	1.18 $\pm$ 0.01	AAA	1.27 $\pm$ 0.01	AAA

<sup>a</sup> Values are obtained by analysis of nine samples from must type (three samples from each cellar or winery). Degrees of freedom 2/6. Homogeneous groups for sampling site were obtained at the 95% confidence level using LSD procedure.

<sup>b</sup> Different letters indicate significant differences at 95% confidence level, due to sampling site.

type. Compounds not dependent on sampling site were subjected to one-way analysis of variance (ANOVA) to identify those compounds exhibiting significant differences between the two musts obtained from ripe and dried grapes.

## RESULTS AND DISCUSSION

**Changes in Winemaking Variables.** The Montilla-Moriles grape-growing region is located in Andalusia (southern Spain); it exhibits high temperatures above 40  $^{\circ}$ C and low rainfall during the grape ripening season. These two features make it highly suitable for the production of special sweet wines from off-vine-dried grapes.

The Pedro Ximénez variety is used extensively in areas of Montilla-Moriles, Jerez, and Málaga. In Málaga, however, winemakers also use the Muscat variety. The enological variables of Pedro Ximénez musts from ripe grapes shown in **Table 1** are in agreement with López et al., (2).

Grapes subjected to off-vine sun exposure showed a loss of water, shrinkage, and darkening of berries, and a concentration effect of its chemical components by a factor of 1.76 to 2.0, as derived from the Brix values for dried and ripe grapes. As a result, dried grapes crushed on vertical presses produced a low volume of must (0.24–0.32 L/kg).

The most relevant characteristics of the dried grape musts are summarized in **Table 1**. All variables showed the absence of significant differences due to the sampling site in ripe grape musts. On the other hand, only titratable acidity showed significant differences due to the sampling site in dried grape musts.

Total soluble solids in off-vine-dried grape must are 46  $\pm$  2  $^{\circ}$ Bx, increasing the major components (largely sugars) with respect to ripe grape must by a factor of 1.88 through the drying process. Acids behave differently, showing titratable acidity comparable values in two must types. Apparently, no significant change was observed in acid contents; however, an increase should be produced as a result of the loss of water in the grapes. In addition, volatile acidity showed undetectable values in both must types; and pH values increased in must from dried grapes as a result of its decreased free acids contents.

Values obtained for the titratable acidity/total soluble solids ratio (0.1 g tartaric/L $^{\circ}$ Bx) in ripe grape musts and dried grape musts (0.05 g tartaric/L $^{\circ}$ Bx) show the real decrease in acid content as a result of off-vine drying. This ratio avoids the concentration effect on each compound resulting from the loss of water and clearly exposes the involvement of other factors, especially prominent among which is the anaerobic metabolism of the grapes.

**Table 2.** Concentrations ( $\mu\text{g/L}$ ), Standard Deviation, and Homogeneous Group in Volatile Compounds of Musts from Ripe and Off-Vine-Dried Pedro Ximénez Grapes<sup>a</sup>

compounds	ripe grapes	homogeneous groups <sup>b</sup>	off-vine dried grapes	homogeneous groups <sup>b</sup>
isobutanol	188 ± 58	AAA	913 ± 372	AAA
butan-1-ol	43 ± 5	AAA	107 ± 41	AAA
butan-2-ol	22 ± 10	ABC	42 ± 14	AAA
isoamyl alcohols	1112 ± 153	AAA	1930 ± 433	AAA
benzyl alcohol	31 ± 3	AAA	160 ± 26	AAA
2-phenylethanol	170 ± 46	AAA	790 ± 225	AAA
hexan-1-ol	1016 ± 409	ABC	194 ± 72	ABB
(E)-hex-3-en-1-ol	16 ± 8	ABA	nd <sup>c</sup>	AAA
(Z)-hex-3-en-1-ol	79 ± 44	ABC	nd	AAA
(E)-hex-2-en-1-ol	358 ± 263	ABC	nd	AAA
hexanal	195 ± 201	AAB	88 ± 57	ABC
(E)-hex-2-enal	297 ± 346	AAB	nd	AAA
benzaldehyde	4 ± 3	ABB	12 ± 9	AAB
butane-2,3-dione	181 ± 91	ABC	568 ± 225	ABC
pentane-2,3-dione	119 ± 118	ABB	249 ± 267	ABB
acetoin	17 479 ± 13 844	ABC	77 412 ± 22 248	AAA
1,1-diethoxyethane	100 ± 55	ABC	679 ± 295	AAB
furfural	4 ± 3	ABC	12 ± 4	ABA
5-methylfurfural	nd	AAA	2.4 ± 0.9	ABC
isobutanoic acid	1 ± 2	ABB	18 ± 5	AAA
butanoic acid	23 ± 14	ABB	10 ± 5	ABB
2 & 3-methylbutanoic acids	3 ± 1	ABB	9 ± 3	AAA
hexanoic acid	43 ± 14	AAA	40 ± 14	AAA
octanoic acid	2 ± 2	ABB	2 ± 1	AAB
ethyl acetate	2772 ± 1822	AAB	4567 ± 1021	AAA
hexyl acetate	101 ± 140	ABB	133 ± 168	ABB
2-phenylethyl acetate	0.3 ± 0.5	ABB	2.7 ± 1.0	AAB
ethyl lactate	4 ± 4	AAB	7 ± 11	ABB
isoamyl butanoate	12 ± 15	ABB	15 ± 9	ABC
$\gamma$ -butyrolactone	828 ± 476	AAA	5606 ± 992	AAA
$\gamma$ -hexalactone	2.5 ± 0.9	AAA	23 ± 9	AAA
$\gamma$ -heptalactone	0.3 ± 0.5	ABB	1.8 ± 0.4	ABB
$\gamma$ -decalactone	1.0 ± 0.0	ABC	1.1 ± 0.3	AAA
terpinen-4-ol	1.0 ± 1.5	ABB	2 ± 1	AAA
$\alpha$ -terpineol	4 ± 6	ABB	6 ± 1	AAA
farnesol	80 ± 115	ABB	36 ± 17	AAB

<sup>a</sup> Values are obtained by analysis of nine samples from must type (three samples from each cellar or winery). Degrees of freedom 2/6. Homogeneous groups for sampling site were obtained at the 95% confidence level using LSD procedure. <sup>b</sup> Different letters indicate significant differences at 95% confidence level, due to sampling site. <sup>c</sup> nd, not detected.

It is known that high temperatures during grape ripening results in slow acid contents of the grapes. In this sense, malic acid rarely exceeds 1 g/L in ripe grapes growing in the studied area (2). According to Flanzly (7), from 50 to 35% of malic acid content is catabolized at 35 °C within 8 days; no lactic acid is produced, but ethanol, carbon dioxide, and succinic acid are produced in small concentrations. In contrast, tartaric acid seems not to be related with this anaerobic metabolism.

**Changes in Volatile Compounds.** Table 2 shows the concentrations of 36 volatile compounds identified in two must types, as well as the homogeneous groups they formed. Only 9 compounds show no significant differences among sampling sites for musts obtained from ripe grapes and 20 compounds for dried grape musts. In general, the analyzed compounds increase their concentrations during the drying process, and this effect can be explained partially by the loss of water from the grapes. Only 6-carbon alcohols and aldehydes decreased in concentration to no detectable values.

Acetoin, ethyl acetate, isoamyl alcohols, and hexanol-1, with concentrations above 1000  $\mu\text{g/L}$ , and  $\gamma$ -butyrolactone (828  $\mu\text{g/L}$ ) were the major volatile compounds in must from ripe grapes. By contrast, acetoin,  $\gamma$ -butyrolactone, ethyl acetate, isoamyl alcohols, isobutanol, and 2-phenylethanol, in this sequence, were the major volatile compounds in must from dried grapes. Except for farnesol and C<sub>6</sub> alcohols and aldehydes, whose concentrations decreased from ripe to dried grape-musts, and octanoic

acid, hexanoic acid, and  $\gamma$ -decalactone, whose concentrations remained constant, all other volatile compounds showed higher concentrations (from 1.2 times for isoamyl butanoate to 18.0 times for isobutanoic acid) in the musts obtained from dried grapes than in those from ripe grapes.

The ratio calculated from °Brix of data in Table 1 reveal an increase by a factor of 1.76–2.0 in the concentration of total soluble solids as results of the drying process. Changes in winemaking variables and in volatile compounds out of this range may be ascribed to the presence of different processes to the concentration effect due to the water evaporation during off-vine grape drying. To identify the volatile aroma compounds whose concentrations changed by effect of other processes than the water evaporation, the concentration/°Bx ratios for the compounds not depending on sampling site were calculated, and an ANOVA was conducted. Also, this statistical analysis was made for the 6-carbon alcohols and aldehydes present at undetectable concentrations in the musts from dried grapes and for 5-methylfurfural, with no detectable concentrations in ripe grape musts.

Table 3 shows the mean ratio, standard deviation, and *p* values obtained for selected compounds. Only butan-1-ol and isoamyl alcohols showed no significant differences between the two musts, which indicates that they are only affected by the concentration effect. The other 11 compounds showed signifi-

**Table 3.** Volatile Compounds Not Dependent on Sampling Site in Musts from Ripe and Off-Vine-Dried Pedro Ximénez Grapes<sup>a</sup>

compound	ripe grapes	off-vine-dried grapes	<i>p</i> value <sup>b</sup>
isobutanol	7.64 ± 2.24	19.95 ± 8.17	***
butan-1-ol	1.74 ± 0.21	2.36 ± 0.97	ns
isoamyls alcohols	45.33 ± 5.65	41.89 ± 8.06	ns
benzyl alcohol	1.27 ± 0.12	3.50 ± 0.59	***
2-phenylethanol	6.97 ± 1.93	17.20 ± 4.62	***
( <i>E</i> )-hex-3-en-1-ol	0.65 ± 0.32	nd	***
( <i>Z</i> )-hex-3-en-1-ol	3.21 ± 1.79	nd	***
( <i>E</i> )-hex-2-en-1-ol	14.57 ± 10.78	nd	***
( <i>E</i> )-hex-2-enal	12.17 ± 14.18	nd	***
hexanoic acid	1.74 ± 0.56	0.89 ± 0.33	**
γ-butyrolactone	33.78 ± 19.50	122.04 ± 20.09	***
γ-hexalactone	0.10 ± 0.04	0.50 ± 0.19	***
5-methylfurfural	nd	0.06 ± 0.02	***

<sup>a</sup> Mean and standard deviations of concentrations-Brix degree ratio ( $\mu\text{g/L}^\circ\text{Bx}$ ), and *p* values obtained by ANOVA analysis. <sup>b</sup> *p*-values:  $p \leq 0.001$  (\*\*\*),  $p \leq 0.01$  (\*\*),  $p \leq 0.05$  (\*). Degrees of freedom 1/16. ns, no significant differences. nd, not detected.

cant differences at least with  $p \leq 0.01$  between the 2 types of must, which suggests the action of factors other than water evaporation.

The C<sub>6</sub> alcohols, (*E*)-hex-3-en-1-ol, (*Z*)-hex-3-en-1-ol, (*E*)-hex-2-en-1-ol, and the aldehyde (*E*)-hex-2-enal, exhibited undetectable contents in the musts from dried grapes. These compounds are always produced during the prefermentative operations used in winemaking. As a result of grape crushing,

the lipoxygenase enzymes liberated are put in contact with fatty acids in the presence of oxygen, leading to the formation of 6-carbon alcohols and aldehydes in must from ripe grapes (5, 19). The undetectable contents of these compounds in musts from dried grapes reveals a low lipoxygenase activity in the berry during off-vine drying and in the obtained must. In this respect, it is known that enzymes lose their biological activity by exposure to high temperatures, to which berries are indeed exposed while drying in the sun; also, berries do not break during this process, so the enzymes cannot be exposed to their substrates. Finally, must obtained from dried grapes is a liquid of high density and viscosity, showing a low water activity and low oxygen diffusion from the atmosphere, both factors have a negative effect on lipoxygenase activity. On the other hand, the concentrations in hexanoic acid showed significant differences ( $p \leq 0.01$ ) as a result of processes other than water evaporation from the grapes.

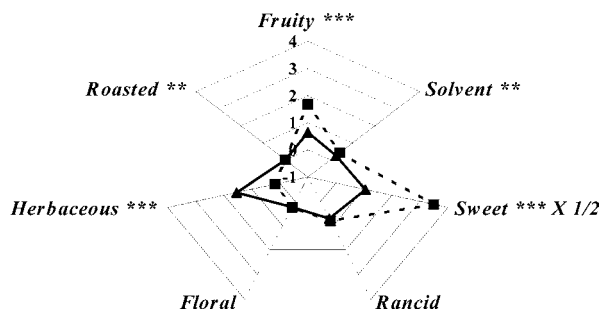
The high increase in concentration/°Brix ratio for some compounds should be related to the anaerobic metabolism of grapes detached from the vine. As can be seen in **Table 3**, isobutanol; benzyl alcohol; 2-phenylethanol; 5-methylfurfural; γ-butyrolactone, and γ-hexalactone concentrations showed significant differences ( $p \leq 0.001$ ) between the two types of must. These compounds are related with anaerobic metabolism of sugars and the presence of ethanol.

The presence of ethanol in on-vine ripe grapes has been reported (20) The synthesis of ethanol has also been described in off-vine grapes under typical oxygenation conditions at

**Table 4.** Perception Threshold (mg/L), Odor Descriptor, and Odorant Series Assigned to Volatile Compounds of Musts from Ripe and Off-Vine-Dried Grapes

compound	threshold <sup>a</sup>	descriptor	series <sup>b</sup>
isobutanol	75	alcohol, solvent	1
butan-1-ol	150	medicinal	1
butan-2-ol	50	medicinal, wine	1
isoamyl alcohols	60	solvent, sweet, cake	1, 2
benzyl alcohol	900	roasted, toasted	3
2-phenylethanol	200	rose, honey	4
hexan-1-ol	1.1	herbaceous, wood	5
( <i>E</i> )-hex-3-en-1-ol	1	herbaceous, green	5
( <i>Z</i> )-hex-3-en-1-ol	1	herbaceous, green	5
( <i>E</i> )-hex-2-en-1-ol	15	herbaceous, green	5
hexanal	0.35	fatty, herbaceous, green	5, 6
( <i>E</i> )-hex-2-enal	0.6	herbaceous	5
benzaldehyde	2	roasted, almond	3, 4
butane-2,3-dione	0.1	yogurt, sweet, cake	2
pentane-2,3-dione	0.9	butter, sweet, cake	2
acetoin	150	fatty	5
1,1-diethoxyethane	1	cake, fruity	2, 7
furfural	15	sweet, cake, burnt, almond	2, 3
5-methylfurfural	16	sweet, cake, caramel, burnt, almond	2, 3
isobutanoic acid	30	rancid, butter	6
butanoic acid	2.2	cheese, rancid	6
2 & 3-methylbutanoic acids	1.5	rancid	6
hexanoic acid	3	rancid, cheese, fatty	6
octanoic acid	10	rancid, cheese, fatty	6
ethyl acetate	12	pineapple, fruity, solvent	1, 7
hexyl acetate	0.67	apple, pear, floral	4, 7
2-phenylethyl acetate	0.25	fruity	7
ethyl lactate	150	fruity, butter	2, 7
isoamyl butanoate	1	banana, fruity	7
γ-butyrolactone	20	sweet, cake, caramel, fruity	2, 7
γ-hexalactone	359	sweet, cake, fruity, peach	2, 7
γ-heptalactone	1	fruity	7
γ-decalactone	0.01	peach, coconut	7
terpinen-4-ol	5	moldy	5
α-terpineol	5	lily, sweet, cake	2, 4
farnesol	1	floral	4

<sup>a</sup> As determined in a 1:10 alcohol/water mixture. <sup>b</sup> Odorant series: 1 solvent, 2 sweet, 3 roasted, 4 floral, 5 herbaceous, 6 rancid, 7 fruity.



**Figure 1.** Mean odor activity values (OAVs), in relative unities for the odorant series in musts from ripe and off-vine-dried grapes. Ripe grape must (▲). Dried grape must (■). Values obtained from the ANOVA: (\*\*\*) =  $p \leq 0.001$ ; (\*\*) =  $p \leq 0.01$ ; (\*) =  $p \leq 0.05$ . 1/2: Drawn values for the sweet series are one-half of the real values.

35 °C (20). This fermentative metabolism was confirmed by Tesnière et al. (21), who encountered a high capacity for the synthesis of aldehyde dehydrogenase by the grape prior to harvesting, reporting a high activity of this enzyme, which is involved in the formation of ethanol. Respiration and ethanol production measurements in off-vine berries reveal the partial conversion of glucose and malic acid into ethanol and CO<sub>2</sub> via pyruvic acid (22, 23).

During ripening, grapes can change their metabolism from aerobic to anaerobic, which is reflected in the production of ethanol, CO<sub>2</sub>, and fermentation byproducts (19). Although these byproducts are the same ones as those obtained in the alcoholic fermentation carried out by yeast, their concentrations may change. Thus, grape musts under hypoxic conditions show high concentrations of  $\gamma$ -butyrolactone, acetoin, and cinnamic acid (24). In addition, the contents in C<sub>6</sub> alcohols and aldehydes decrease in relation to control samples (24, 25), and the contents of free and bound monoterpenols of Muscat grape musts increase, also showing a different distribution (26, 27).

In summary, the significant increase observed in the concentrations of the volatile compounds listed in **Table 3** can be ascribed to the anaerobic metabolism of Pedro Ximénez grapes during natural off-vine drying by direct exposure to the sun. In this sense, increases in alcohol dehydrogenase and glutamate oxalacetate transaminase activities caused by strong thermal shocks in post-harvest grapes have been described (28).

**Aromatic Series.** Finally, the contribution of each volatile compound to wine aroma can be evaluated qualitatively by means of its associate descriptor and quantitatively by means of its odor activity value (OAV), which is established as the concentration/perception threshold ratio. All the volatile compounds contribute to wine odor, and those that possess a higher OAV are those that will be responsible for the main odorant notes of musts or wines. By grouping volatile aroma compounds with similar descriptors, odorant series can be obtained, and the organoleptic profile of a must or wine can be established; one compound can be assigned to one or several odorant series, according its descriptors. In this respect, fruity, solvent, sweet, rancid, floral, herbaceous, and roasted odor series were chosen for the description of Pedro Ximénez must aroma, taking into account their extensive use by specialized tasters describing and distinguishing sweet wine aroma (29–31). **Table 4** shows the perception threshold, descriptors, and odor series assigned for each compound quantified. **Figure 1** shows the OAVs unities for the odorant series and must types, calculated by the addition of OAVs values for their components.

In the musts from ripe grapes, only butane-2,3-dione, hexan-1-ol, and (*E*)-hex-2-enal showed OAVs exceeding 50%

of their perception thresholds (1.8, 0.92, and 0.56, respectively), so these are the compounds most markedly contributing to their aroma, particularly the two last compounds with herbaceous odors. On the other hand, butane-2,3-dione, 1,1-diethoxyethane, and acetoin, with an OAV of 5.7, 0.68, and 0.52, respectively, are those accounting for most of the aroma of musts from dried grapes. These compounds have odor descriptors such as yogurt, cake, fruit, and sweets.

Only the floral and rancid series exhibited no significant differences between musts (**Figure 1**), showing the herbaceous series a lower OAV in the musts from dried grapes as a result of diminution in C<sub>6</sub> alcohols and aldehydes concentrations, which contribute the green (herbaceous) odor. By contrast, the roasted series showed a higher OAV in these musts, as a result of the increased contents in furfural and 5-methylfurfural (burnt and caramel odor), and so did the solvent series, which consists basically of higher alcohols. In any case, the series most markedly affected by off-vine drying of the grapes were the fruity and sweet ones, due to the increased concentrations of lactones in the former, and butane-2,3-dione in the latter.

Certainly, some aspects in the grouping of the compounds in aromatic series are subjected to criticism. Thus, the addition of the compounds' OAVs to calculate a series cannot be interpreted as an arithmetical addition of odorant sensations. In any case, the proposed method is valid for comparing must or wines, because the aromatic series always comprise the same compounds. On the other hand, the number of variables is greatly reduced, and the changes observed by the drying process can be discussed in terms of several aroma descriptor preserving their relative importance according to the OAVs of the compound assembled.

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