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# Changes in Color and Odorant Compounds during Oxidative Aging of Pedro Ximenez Sweet Wines

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Pedro Ximenez sweet wines obtained following the typical criaderas and solera method for sherry wines and subjected to oxidative aging for 0, 1.3, 4.2, 7.0, or 11.5 years were studied in terms of color and aroma fraction by using the CIELab method and gas chromatography, respectively. The parameters defining the CIELab color space ($a^*$, $b^*$, and $L^*$) were subjected to a multiple-range test ($p < 0.05$) that allowed discrimination of the five wine aging levels studied into five uniform groups according to aging time. The aroma fraction was found to include 15 active odorant compounds with OAV > 1 that enriched the wines with fruity, fatty, floral, and balsamic notes during the aging process. The changes in color parameters and active odorants were not linearly related to aging time, being especially marked during the first 1.3 years and then less substantial up to the 7 years, the oldest wines exhibiting sensorial properties markedly departing from all others. For the wines aged over 1.3 years (minimum aging), 2,3-butanedione, linalool, and decanal can be used as reliable fingerprints of the older wines' quality.

**KEYWORDS: Oxidative aging; sweet wine; color; active odorants**

## INTRODUCTION

Some Spanish sweet wines are produced by raisining of the grapes on esparto mats to allow them to dry in the sun for 5−10 days depending on the particular weather conditions. In Spain, this practice is feasible only in warm or semiarid zones such as those in the southern regions of Malaga, Jerez, and Montilla-Moriles. Specifically, Montilla-Moriles grapes are harvested in the second half of August and easily reach a maximum temperature over 40 °C while exposed to sunlight (*1*), cv. Pedro Ximenez being the only white grape variety used to obtain sweet wines of the same name. Their pressing gives a highly sweet must (containing >400 g/L sugars) that is dark and viscous and possesses a very typical aroma.

Grape berries must be dried homogeneously to a moderate extent because the pressing of grapes with low water contents is extremely difficult. Therefore, the raisins obtained after drying usually contain roughly twice the amount of sugars of freshly harvested grapes. Further information about the production of Pedro Ximenez sweet wines can be found in Montedoro and Bertuccioli (*2*).

The high concentration of sugars in raisin musts allows yeasts to ferment only a small fraction and provide alcohol contents below 5% (v/v) as a result. After fermentation, the wines are fortified to an ethanol content of 9% (v/v), allowing them to stand for several months to facilitate their clarification by decantation. Then, the wines are again fortified to about 13.5% (v/v) alcohol and subjected to oxidative aging in a "criaderas" and "solera" system over long periods exceeding 10 years in some cases. During the aging the wines increase their aromatic sensations described as muscat, raisin, and fatty with buttery notes. This traditional aging system, typical of sherry wines, essentially involves mixing the older wine with younger wine at least once a year to homogenize wine composition at each aging stage irrespective of the particular composition of each raisin vintage. A more detailed description of this system can be found in refs *3*−*5*.

Color and aroma are two especially significant sensory attributes of foods (particularly wines). In fact, the quality and specificity of each food product are associated with a particular color and aroma. Wines obtained from white grapes become darker through browning as their oxidative aging develops, likewise changing their aroma fraction to an extent that increases with aging (*6*−*11*). There is also abundant literature on the contribution of the color and/or the aroma fraction to the typical characteristics of other types of wines also obtained by oxidative aging from white grapes: Porto wines (*12*−*15*), fortified French sweet white wines (*16*), Madeira wines (*17*, *18*), and young wines from Zalema in the county of Huelva, Spain (*19*).

The high qualitative and quantitative complexity of the aroma fraction of wine (*18*, *20*) makes it seems reasonable to assume that the compounds with the highest odor activity values (OAV, defined as the number of times a given compound exceeds its perception threshold concentration) should be those most strongly contributing to the aroma profile of wine. In this way, the aroma fraction can be studied not only in analytical terms

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but also by taking into account the sensorial contribution of each compound. This method has been applied to several types of wines (*21*−*29*); however, no studies of this type have been carried out on Pedro Ximenez sweet wines.

In this work, changes in color and some odorant compounds (with OAV > 1) in Pedro Ximenez sweet wines during their industrial oxidative aging are studied. The main objective was to relate the parameters and compounds best defining the degree of wine aging with the time needed to obtain them.

## MATERIALS AND METHODS

**Wines.** Sweet Pedro Ximenez wines obtained from the grape cultivar of the same name and subjected in aerobic conditions to oxidative aging in American oak casks were used. For better precision the aging times were calculated following commercial criteria (by considering the age and volume of the mixed wines in the solera and criaderas system), resulting in times of 0 (without aging), 1.3, 4.2, 7.0, and 11.5 years. The wines were elaborated by means of the typical criaderas and solera system in the D.O. Montilla-Moriles (southern Spain). For each aging time samples of three different solera and criaderas systems were taken. Each sample was obtained by mixing the wine extracted from 20 casks. The content in reducing sugars of the wines was 421 ± 21.7 g/L and 13.5 ± 0.18% (v/v) in ethanol.

**Experimental Analyses.** *Browning and Color Evaluation.* Browning of the samples was measured as absorbance at 420 nm. Color was determined according to the recommendations of the International Commission on Illumination (*30*), with the illuminant $D_{65}$ (daylight source) and 10° standard observer (perception of a human observer). The parameters calculated were *a** (red/green values), *b** (yellow/blue values), and *L** (lightness). From the CIELab space other psychophysical parameters were calculated, such as *C** (chroma or saturation) and *h** (hue angle). All spectrophotometric measurements were obtained, after the centrifugation of the wine samples for 15 min at 3000 rpm, in a Beckman DU-640 spectrophotometer provided with quartz cells of 1 mm path length. The $A_{280}$ values were determined prior to 1:25 dilution. All of the measurements were carried out in triplicate.

*Identification and Quantification of Aroma Compounds.* Each of the 44 aroma compounds analyzed was identified in previous laboratory works by means of its retention time, coeluted with a standard solution of commercial product (Sigma Aldrich), and confirmed by mass spectrometry (Hewlett-Packard 5972 MSD). The conditions of MS were scan mode at a voltage of 1612 V and mass range from 39 to 300 amu.

Acetaldehyde was quantified by using the enzymatic test from Boehringer-Mannheim. For the quantification of the remaining aroma compounds, samples of 100 mL of wine were adjusted to pH 3.5, 150 μg of 2-octanol was added as an internal standard, and then the samples were extracted with 100 mL of freon-11 in a continuous extractor for 24 h. These compounds were quantified by GC (Hewlett-Packard 5890 series II) in a HP-INNOWax column of 60 m × 0.32 mm × 0.25 μm thickness (Hewlett-Packard) after concentration of the freon extracts to 0.2 mL in a micro-Kuderna−Danish concentrator. Three microliters was injected into the chromatograph equipped with a split/splitless injector and a flame ionization detector. The oven temperature program was as follows: 5 min at 45 °C, 1 °C/min up to 185 °C, and 30 min at 185 °C. Injector and detector temperatures were 275 and 300 °C, respectively. The carrier gas was helium at 70 kPa and split 1:100. The quantification was made by using chromatographic correction factors, calculated for each compound in relation to the internal standard, in standard solutions of commercial products supplied by Sigma Aldrich.

**Perception Threshold Determination and OAV Calculation.** The odor perception threshold is defined as the lowest concentration capable of producing a sensation. This sensation must be detected by at least 50% of the judges in a taste panel. Five solutions of ascending concentration of each compound (supplied by Sigma Aldrich) were used. Starting from the lowest concentration solution, the judges indicated that with an odorant sensation different from the one perceived in the control (14% v/v ethanol/water). Likewise, the judges were asked for the aroma descriptors, and these were fixed by comparison with bibliography. The taste panel consisted of 20 judges of both sexes (between 20 and 55 years old), trained but not selected. The OAVs were calculated as the ratio between the concentration of a compound and its perception threshold.

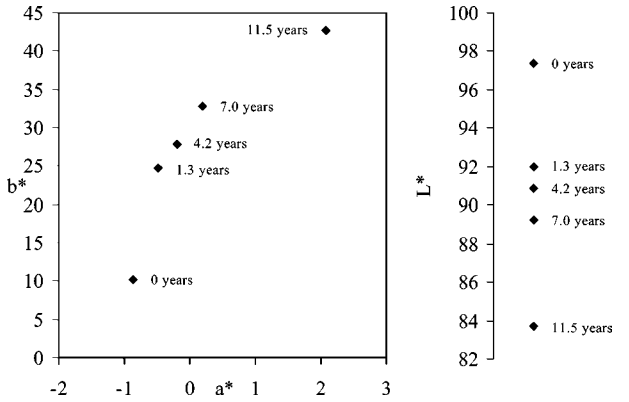


**Figure 1.** Plot of the Pedro Ximenez sweet wines in the CIELab space.

**Statistical Procedures.** The analysis of variance (ANOVA), the regression analyses, and the principal component analysis (PCA) were carried out by using the Statgraphics 5.0 computer program (STSC Inc., Rockville, MD).

## RESULTS AND DISCUSSION

**Figure 1** shows the location of the studied wine samples in the CIELab space. Their data were subjected to a multiple-range test (ANOVA, $p < 0.05$) that discriminated five homogeneous groups corresponding to the aging levels studied. As can be seen, the oldest wines (11.5 years) exhibited the highest *a** (positive toward red and negative toward green) and *b** values (positive toward yellow and negative toward blue). In contrast, the wines without aging exhibited the lowest *a** and *b** values, showing the wines aged for 1.3, 4.2, and 7.0 years values closer to one another and intermediates between those for the oldest wines and the youngest. With regard to lightness *L**, the wines behaved very similarly as they did in relation to *a** and *b**, albeit in the opposite direction. Thus, the nonaged wines had the highest *L** values and the oldest wines the lowest, the other wines lying between these two extremes and their values being closer to one another.

Parameters *C** (color saturation) and *h** (hue), which were calculated from *a** and *b** using the equations $C^* = (a^{*2} + b^{*2})^{1/2}$ and $h^* = \arctan(b^*/a^*)$, respectively, are related to psychophysical attributes of color (*31*), some authors such as Recamales et al. (*19*) pointing out a chroma increase and a hue decrease during wine storage. A multiple-range test at $p < 0.05$ on the *C** and *h** values also classified the wines into five homogeneous groups, *C** exhibiting an increase during the aging process (**Figure 2**), as a result of the development of browning reactions with the formation of reddish brown polymers in the wines. On the other hand, *h** decreased during aging, so red hues increased more markedly than did yellow hues in the wines. The greatest changes in chroma and hue were observed during the first 1.3 years of aging, where Δ*C**/year and Δ*h**/year were 5−10 times higher than in any other period. Nevertheless, both parameters continued to increase, albeit more moderately, throughout the aging period and peaked in the oldest wine (11.5 years).

The absorbance at 280 nm is frequently used as a measure of total of phenolic compounds in wine. As can be seen from **Figure 2**, $A_{280}$ increased throughout the aging period, albeit proportionally more markedly (3−7 times) during the first 1.3

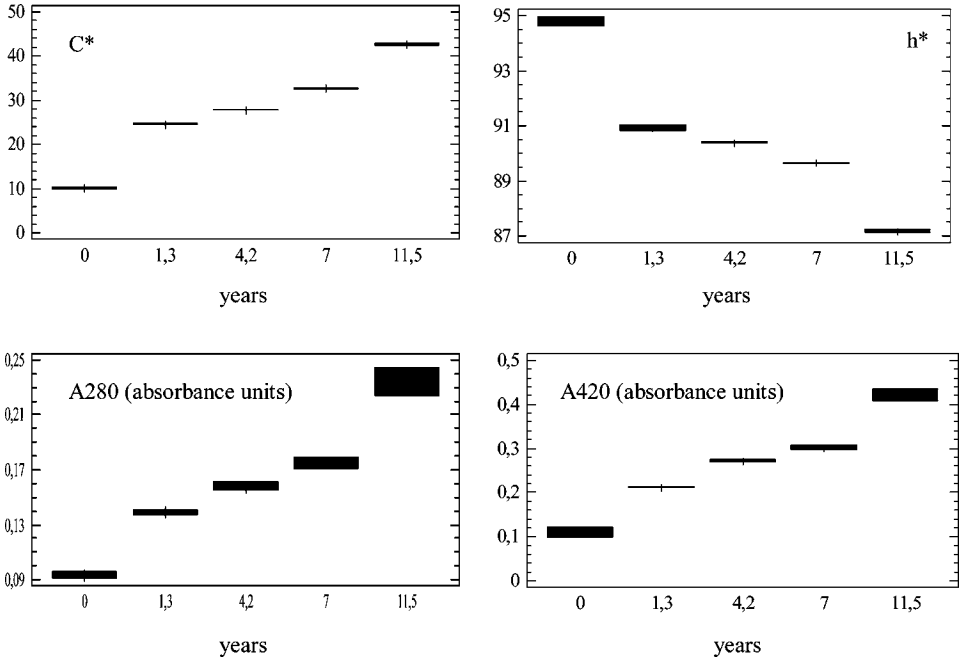


**Figure 2.** Changes in the chroma (*C**), hue (*h**), and absorbances at 280 and 420 nm of the Pedro Ximenez sweet wines during oxidative aging.

years. This general increase can be ascribed to the wine being enriched with phenolic compounds from cask wood, particularly intense during the first aging period. In addition, the possibility of an increase in the absorption coefficients of brown polymers in relation to those of the precursor monomers should be also considered.

The absorbance at 420 nm is a measurement of yellow-brown color in wine, it being used by many authors and winemaking industries as an index of browning. The changes in this color parameter during the aging of the studied wines fitted well a simple regression model based on the root square of time ($R^2$ = 0.96). Consequently, it is reasonable to use the increase in yellow-brown color as a measure of oxidative aging progress in these wines, and $A_{420}$ as reference to examine changes in odorant compounds during the process.

**Table 1** lists the odor activity values (OAVs) and perception thresholds for the 44 aroma compounds analyzed in the sweet wines. As can be seen, the compounds exhibiting the highest odorant activity after 11.5 years of aging were ethyl octanoate, 2,3-butanedione, linalool, and 1,1-diethoxyethane, with average OAVs of 47.2, 41.5, 38.9, and 32.8, respectively. The esters isoamyl acetate, ethyl butanoate, and ethyl hexanoate, as well as acetaldehyde, also proved to be potent odorants, with average OAVs between 10 and 30. Ethyl acetate (8.05) and eugenol (6.78) also exhibited substantial odorant activity, whereas decanal, acetoin, 2,3-pentanedione, and diethyl succinate contributed with OAVs of about 3, ethyl decanoate showing no odorant activity in the oldest wines, although it did in those aged for 1.3−7.0 years. All other compounds exhibited average OAVs of <1, so they contributed little to the aroma profile of the wines, in any case depending on potential synergic effects enhancing specific odor sensations (*32*−*34*).

**Table 2** lists the aroma descriptors for the 15 active odorants (OAVs > 1 in at least one aging level), which were grouped into 6 aroma series (fruity, chemical, balsamic, fatty, floral, and spicy) by adapting the terms of Noble et al. (*35*) to the peculiar aroma of sherry wines, according to criteria adopted in previous works (*24*, *28*). The OAVs of the series, which were calculated by combining those for the individual compounds in each, can be used to establish objective features of the aroma fraction for

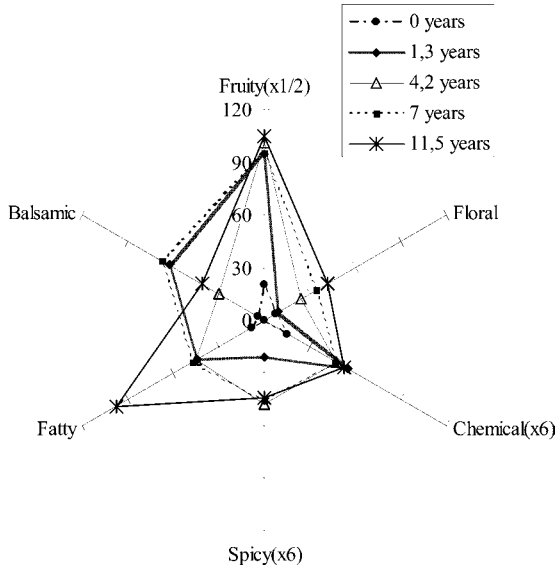


**Figure 3.** Aroma profiles of the Pedro Ximenez sweet wines during oxidative aging.

the wines in relation to aging time and, therefore, to compare the different wines studied in terms of aroma profile. The compounds included in each series were as follows: fruity (acetaldehyde, ethyl acetate, 1,1-diethoxyethane, ethyl butanoate, isoamyl acetate, ethyl hexanoate, ethyl octanoate, decanal, linalool, and diethyl succinate); chemical (ethyl acetate and ethyl decanoate); balsamic (ethyl acetate and 1,1-diethoxyethane); fatty (2,3-butanedione, 2,3-pentanedione, acetoin, ethyl octanoate, decanal, and ethyl decanoate); floral (linalool and diethyl succinate); and only eugenol in the spicy. As can be seen in **Figure 3**, the fruity series was the most important by far, with OAVs of about 200 after 1.3 years of wine aging. It was followed in quantitative terms by the balsamic series, with average OAVs of 30−60 also after 1.3 years, and the fatty series, with OAVs of about 45 in the wines that were 1.3−7.0 years old and then increasing to 100 in the oldest ones (11.5 years). The OAVs for the floral series increased from about 7 in the nonaged wines to 42 in the oldest wines. On the other hand,

**Table 1.** Odorant Activity Values and Perception Thresholds of the Aroma Compounds Determined in Pedro Ximenez Sweet Wines during Oxidative Aging

| compound[a] | aging time | | | | | threshold (mg/L) |
|---|---|---|---|---|---|---|
| | 0 years | 1.3 years | 4.2 years | 7.0 years | 11.5 years | |
| acetaldehyde | 22.7 ± 3.46 | 23.8 ± 3.43 | 32.6 ± 0.350 | 24.8 ± 2.47 | 17.7 ± 4.99 | 10 |
| 1,1-diethoxyethane | 2.11 ± 0.930 | 55.4 ± 3.17 | 24.1 ± 7.10 | 61.6 ± 9.50 | 32.8 ± 4.80 | 1 |
| ethyl acetate | 2.23 ± 0.980 | 7.25 ± 0.410 | 6.34 ± 1.86 | 5.90 ± 0.910 | 8.05 ± 1.18 | 7.5 |
| methanol | 0.210 ± 0.040 | 0.220 ± 0.030 | 0.250 ± 0.030 | 0.200 ± 0.030 | 0.170 ± 0.010 | 668 |
| 2,3-butanedione | 4.74 ± 1.30 | 22.6 ± 2.84 | 27.2 ± 2.09 | 27.4 ± 1.18 | 41.5 ± 6.36 | 0.1 |
| methyl butanoate | 0.140 ± 0.010 | 0.270 ± 0.030 | 0.780 ± 0.020 | 0.540 ± 0.220 | 0.420 ± 0.090 | 1 |
| 1-propanol | nd[b] | 0.02 ± 0.001 | 0.01 ± 0.001 | 0.01 ± 0.001 | 0.01 ± 0.001 | 830 |
| ethyl butanoate | 4.31 ± 0.180 | 24.3 ± 2.53 | 25.0 ± 3.46 | 15.1 ± 1.42 | 17.7 ± 2.18 | 0.02 |
| 2,3-pentanedione | nd | nd | 0.11 ± 0.020 | 0.21 ± 0.060 | 2.27 ± 0.230 | 1 |
| isobutanol | 0.090 ± 0.020 | 0.190 ± 0.040 | 0.320 ± 0.050 | 0.330 ± 0.080 | 0.490 ± 0.120 | 40 |
| isoamyl acetate | 1.80 ± 0.600 | 47.4 ± 8.36 | 62.7 ± 5.05 | 16.7 ± 2.08 | 27.5 ± 9.81 | 0.03 |
| isoamyl alcohols | nd | 0.270 ± 0.060 | 0.220 ± 0.020 | 0.370 ± 0.070 | 0.460 ± 0.050 | 65 |
| ethyl hexanoate | nd | 7.57 ± 0.401 | 11.7 ± 3.25 | 15.6 ± 4.01 | 10.8 ± 0.820 | 0.005 |
| hexyl acetate | nd | nd | 0.03 ± 0.001 | 0.04 ± 0.012 | 0.05 ± 0.006 | 1 |
| acetoin | 3.09 ± 0.66 | 3.59 ± 0.620 | 3.27 ± 0.080 | 2.99 ± 0.030 | 2.83 ± 0.300 | 30 |
| ethyl lactate | 0.01 ± 0.001 | 0.160 ± 0.030 | 0.140 ± 0.010 | 0.230 ± 0.040 | 0.360 ± 0.010 | 100 |
| 1-hexanol | 0.04 ± 0.006 | 0.03 ± 0.006 | 0.02 ± 0.006 | 0.02 ± 0.006 | 0.02 ± 0.006 | 8 |
| ethyl octanoate | nd | 14.2 ± 2.19 | 11.1 ± 1.79 | 12.0 ± 0.850 | 47.2 ± 14.3 | 0.002 |
| 1-heptanol | 0.01 ± 0.001 | 0.01 ± 0.001 | 0.01 ± 0.001 | 0.01 ± 0.001 | nd | 2.5 |
| isobutyl lactate | nd | 0.04 ± 0.012 | 0.02 ± 0.001 | 0.03 ± 0.001 | 0.04 ± 0.001 | 340 |
| furfural | nd | 0.05 ± 0.001 | 0.03 ± 0.005 | 0.1 ± 0.017 | 0.07 ± 0.006 | 15 |
| decanal | 0.10 ± 0.010 | 2.00 ± 0.290 | 1.66 ± 0.040 | 2.80 ± 0.500 | 3.20 ± 0.040 | 1 |
| butyl lactate | nd | nd | 0.007 ± 0.005 | 0.01 ± 0.001 | 0.03 ± 0.001 | 10 |
| ethyl 3-hydroxybutanoate | nd | 0.01 ± 0.001 | 0.007 ± 0.003 | 0.003 ± 0.001 | 0.007 ± 0.003 | 67 |
| linalool | 4.36 ± 0.180 | 7.22 ± 0.530 | 21.0 ± 3.16 | 31.0 ± 5.22 | 38.9 ± 1.76 | 0.015 |
| 5-methylfurfural | nd | 0.02 ± 0.001 | 0.02 ± 0.005 | 0.03 ± 0.012 | 0.03 ± 0.01 | 16 |
| ethyl decanoate | 0.330 ± 0.030 | 1.87 ± 0.280 | 1.67 ± 0.340 | 1.94 ± 0.510 | 0.760 ± 0.080 | 0.51 |
| $\gamma$-butyrolactone | 0.03 ± 0.001 | 0.05 ± 0.001 | 0.03 ± 0.006 | 0.04 ± 0.010 | 0.03 ± 0.012 | 100 |
| ethyl 2-furoate | nd | 0.07 ± 0.010 | 0.04 ± 0.011 | 0.06 ± 0.013 | nd | 1 |
| ethyl benzoate | 0.01 ± 0.001 | 0.03 ± 0.001 | 0.08 ± 0.01 | 0.05 ± 0.01 | 0.04 ± 0.001 | 5 |
| 3-methylbutanoic acid | 0.03 ± 0.001 | 0.05 ± 0.001 | 0.17 ± 0.02 | 0.11 ± 0.015 | 0.07 ± 0.015 | 3 |
| furfurylic alcohol | nd | 0.150 ± 0.010 | 0.200 ± 0.010 | 0.250 ± 0.050 | 0.370 ± 0.030 | 15 |
| diethyl succinate | 2.54 ± 0.160 | 2.35 ± 0.460 | 3.06 ± 0.620 | 3.25 ± 0.550 | 2.93 ± 0.010 | 100 |
| phenethyl acetate | nd | 0.540 ± 0.120 | 0.640 ± 0.080 | 0.860 ± 0.190 | 0.810 ± 0.060 | 0.25 |
| hexanoic acid | nd | 0.05 ± 0.005 | nd | 0.033 ± 0.006 | 0.050 ± 0.010 | 3 |
| *E*-oak lactone | nd | nd | 0.217 ± 0.020 | 0.200 ± 0.020 | 0.300 ± 0.070 | 0.122 |
| phenethyl alcohol | 0.120 ± 0.030 | 0.360 ± 0.080 | 0.370 ± 0.050 | 0.540 ± 0.130 | 0.500 ± 0.060 | 10 |
| *Z*-oak lactone | nd | nd | 1.13 ± 0.410 | 0.940 ± 0.160 | 0.610 ± 0.150 | 0.035 |
| pantolactone | nd | 0.003 ± 0.001 | 0.007 ± 0.002 | 0.007 ± 0.015 | nd | 500 |
| octanoic acid | 0.006 ± 0.001 | 0.013 ± 0.002 | 0.020 ± 0.005 | 0.02 ± 0.004 | 0.02 ± 0.003 | 8.8 |
| eugenol | nd | 3.52 ± 1.82 | 6.87 ± 0.870 | 6.70 ± 1.80 | 6.78 ± 0.332 | 0.005 |
| decanoic acid | nd | nd | 0.013 ± 0.003 | 0.003 ± 0.001 | 0.003 ± 0.001 | 15 |
| farnesol | nd | 0.01 ± 0.001 | 0.023 ± 0.004 | 0.023 ± 0.007 | 0.033 ± 0.009 | 5 |
| phenethyl octanoate | nd | 0.003 ± 0.001 | 0.007 ± 0.002 | 0.007 ± 0.001 | 0.01 ± 0.002 | 10 |

[a] Compounds arranged by retention time. [b] Not detected.

the chemical and spicy series were the least contributors to the aroma profile of the wines, showing average OAVs below 10 that changed little for the former after first 1.3 years and for the latter after 4.2 years.

To more precisely evaluate differences in aroma profile among the wines, the results for the 15 active odorant compounds were subjected to PCA. The first two components obtained accounted for 71% of the total variance, the first component (PC1) contributing 47.3%. **Figure 4** shows the scores of the different wine samples in the plane defined by the two components. As can be seen in relation to PC1, the nonaged wines (zone I) placed far away from the other wines, which sorted according to aging time and close to one another (zone II). In addition, the oldest wines (11.5 years, zone III) placed separately from those aged for 1.3−7.0 years. This distribution was similar to that of chroma and hue parameters discussed above, which reveals that the greatest changes in aroma profile occurred within the first 1.3 years of aging, the subsequent changes up to 7 years being less marked and again moving away for the wines 11.5 years old. The compounds most strongly contributing to the first principal component were decanal, 2,3-butanedione, eugenol, ethyl hexanoate, ethyl acetate, and linalool, which belong to the fruity, fatty, chemical, balsamic,

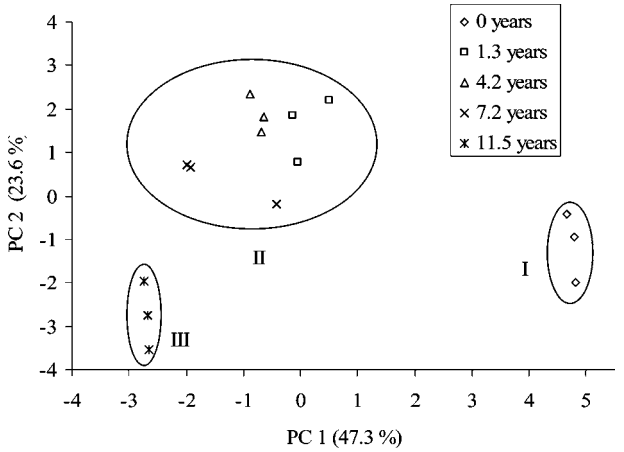


**Figure 4.** Principal component analysis of the active odorants determined in Pedro Ximenez sweet wines.

**Table 2.** Odor Descriptors, Odorant Series, and *p* Values of ANOVA Analysis (Obtained with the Data after 1.3 Years of Aging) for the Active Odorant Compounds in Pedro Ximenez Sweet Wines

| compound | odor descriptors | series | *p* |
|---|---|---|---|
| acetaldehyde | overripe apple | fruity | 0.0038 |
| ethyl acetate | pineapple, varnish, balsamic | fruity, chemical, balsamic | 0.2102 |
| 1,1-diethoxyethane | green fruit, licorice | fruity, balsamic | 0.0003 |
| 2,3-butanedione | buttery | fatty | 0.0010 |
| ethyl butanoate | banana, pineapple, strawberry | fruity | 0.0878 |
| 2,3-pentanedione | buttery, cream | fatty | 0.0000 |
| isoamyl acetate | banana | fruity | 0.0002 |
| ethyl hexanoate | banana, green apple | fruity | 0.0149 |
| acetoin | buttery, cream | fatty | 0.1038 |
| ethyl octanoate | pineapple, pear, soapy | fruity, fatty | 0.0010 |
| decanal | soapy, green lemon | fruity, fatty | 0.0007 |
| linalool | muscat, rose, lavender | fruity, floral | 0.0000 |
| ethyl decanoate | synthetic, rancid | chemical, fatty | 0.0093 |
| diethyl succinate | overripe fruit, lavender | fruity, floral | 0.1927 |
| eugenol | cinnamon, clove | spicy | 0.0001 |

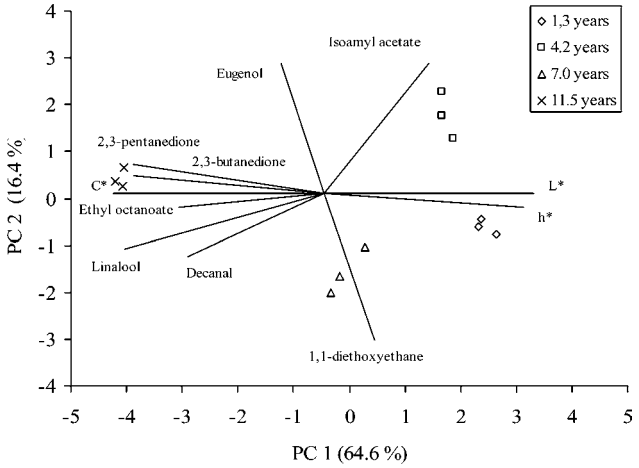


**Figure 5.** Principal component analysis of the color parameters *L**, *C**, and *h** and the active odorants that exhibited significant changes ($p < 0.001$) after 1.3 years of aging.

floral, and spicy series, respectively, and represent a large part of the aroma profile of these wines.

According to Etievant (*36*), decanal is not a usual contributor to wine aroma. However, it exhibited average OAVs between 2 and more than 3 in all of the aging levels studied in this work, except the nonaged wines, suggesting that this compound forms mainly during oxidative aging of the wine. The increase in aldehyde levels during aging may be a result of the precursor alcohols' oxidation through a coupled pathway involving atmospheric oxygen (*37*).

2,3-Butanedione in wine appears by oxidation of acetoin, which in turn forms from acetaldehyde (*38*). Although it exhibited a relatively low odorant activity in the nonaged wines, it showed a notable contribution in the wines aged for more than 1.3 years, with OAVs >20 (**Table 1**).

Eugenol, the presence in wine of which is ascribed to extraction from cask wood (*36*, *39*, *40*), failed to reach its perception threshold in the nonaged wines, but was an active odorant in the wines aged for 1.3 years or longer.

The content in esters of aging wines is the result of their esterification/hydrolysis balance, the high concentrations in ethanol particularly favoring the esterification process of ethyl esters, such as ethyl acetate (*6*) and ethyl hexanoate (*41*). Both compounds showed a high odorant activity after 1.3 years, particularly the second.

Linalool is mainly of varietal origin, although some authors point out that the contents in some monoterpenols can be strongly altered by the effect of acid-catalyzed terpene interconversions during wine storage (*20*). Additionally, linalool can increase its concentration as a result of the hydrolysis of natural glycosides from grapes (*42*, *43*). As can be seen, this compound exhibited a large increase in odorant activity during the wine aging process and reached OAV values up to 9 times higher than the average level for the nonaged wines (4.36). In our case, the above-mentioned factors could start in the grape during the raisining process, subsequently progressing during the aging process. Taking into account that grapes lose about 50% of their weight as a result of raisining, leading to an effect of concentration in the grape compounds, it is reasonable to think that the concentration of terpene glycosides in raisin can be higher than in grape. As a hypothesis, this increased concentration could favor the formation of some single terpenes (depending on the interconversion among them) by hydrolysis during long aging (in our case 12 years). In any case, similar changes have been observed by Moreno (*44*) during the oxidative aging of sherry-type oloroso wines obtained from the same grape variety as the Pedro Ximenez sweet wines.

Because the greatest color and aroma differences occurred within the first 1.3 years (minimum aging), and to better observe the difference among older wines, the color and aroma changes during the aging process above 1.3 years were examined jointly. These data were subjected to PCA, using the color parameters *L**, *C**, and *h** and the eight active odorants that exhibited significant changes ($p < 0.001$) after 1.3 years of aging (**Table 2**). As shown in **Figure 5**, the first two principal components accounted for 81.0% of the total variance (64.6 and 16.4%, respectively), the samples sorting in groups according to aging time with respect to the first component.

As can also be seen from **Figure 5**, the variables most markedly influencing the first principal component were the color parameters *C**, *L**, and *h**, and the odorant compounds 2,3-pentanedione, 2,3-butanedione, linalool, decanal, and ethyl octanoate (higher statistical weights). The *C**, *L**, and *h** values fitted linearly well toward $A_{420}$ (with $R^2$ values of 0.97, 0.98, and 0.95, respectively). In addition, only 2,3-butanedione, linalool, and decanal exhibited a high linearity toward $A_{420}$ (with $R^2$ values of 0.92, 0.86, and 0.81, respectively), the $R^2$ values corresponding to 2,3-pentanedione and ethyl octanoate being markedly lower (0.65 and 0.46, respectively). Therefore, the first three compounds and/or parameters *C**, *L**, and *h** could be as useful, as is $A_{420}$, as indicators of the degree of development of oxidative aging in this type of wine.

In conclusion, both color and the active odorant compounds in the aroma fraction of Pedro Ximenez sweet wines allowed their discrimination in terms of aging time. In general, the wines lost lightness and became reddish and more saturated in color as they aged. Simultaneously, their aging resulted in a gradual enrichment in buttery, raisin, and muscat aroma notes according to the contribution of compounds included in the fruity, fatty, floral, and balsamic series. Nevertheless, neither color nor the contents in active odorants in these wines changed linearly with time. Thus, the major changes in these variables were observed during the minimum aging of 1.3 years and then became more gradual up to 7 years, the oldest wines departing from all others. Considering only the aging stage after 1.3 years, 2,3-butanedione, linalool, and decanal were the compounds more closely related to the changes in $A_{420}$, therefore allowing these compounds to be used as reliable fingerprints of the older wines' quality.

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