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Comparison of Odor-Active Compounds in Sherry Wines Processed from Ecologically and Conventionally Grown Pedro Ximenez Grapes

LOURDES MOYANO,* LUIS ZEA, LAURA VILLAFUERTE, AND MANUEL MEDINA

Department of Agricultural Chemistry, Faculty of Sciences, Edificio Marie Curie, Campus de Rabanales, University of Cordoba, E-14014 Cordoba, Spain

The aroma of young and biologically aged sherry wines from Pedro Ximenez grape cultivated conventionally and ecologically has been studied. Fifty-five compounds were quantified by GC, and the odor activity values for the 19 odor-active compounds considered were grouped into 8 odorant series, the fruity and fatty series showing the highest OAVs. The OAVs of the eight series were subjected to a principal component analysis. PC1 separated the young wines from the aged wines, also distinguishing the traditional young wines from the ecological young ones, whereas PC2 was effective only in separating the traditional aged Fino wines from the ecologically aged ones. The ecological Fino wines showed lower values than traditional Fino wines for the OAVs of all the series, except for the balsamic and fatty series, the ecologically aged wines showing a sensorial profile similar to that of the traditional Fino but with a lower odor intensity.

KEYWORDS: OAV; odorant series; wine aroma; ecological wine; sherry wine

INTRODUCTION

Currently, there is a growing worry among consumers of developed countries for the protection of the environment, being substantially increased in the past few years the surface devoted to ecological agriculture and, as a result, the foods derived from it (1, 2). The intensive use of chemical fertilizers and pesticides in the past 50 years has led to the inevitable worsening of several agricultural ecosystems, causing a decrease in the natural quality of foods (3). This, along with the increased worry for health shown by consumers, has generated growth in the world demand for organic or ecological products (4-6). In reality, the so-called organic or ecological wines are wines obtained from ecological grapes, that is to say, from grapes cultivated with limitations in the use of chemical fertilizers, insecticides, and other pest control synthetic substances, but using sustainable agricultural practices such as cover crops and natural products such as manure or compost. In this way, the presence of any chemical residue in the wine is avoided, and therefore, Pomarici (7), Fotopoulos et al. (8), and Dani et al. (9) have observed an increase in products from ecological sources in the past 20 years, the most from countries with a major tradition in wine consumption.

Andalusia (southern Spain) has a long tradition in the production of sherry white wines. Particularly, in the Andalusian region of Montilla-Moriles the cv. Pedro Ximenez is the main variety of grape used to produce a type of sherry wine known as "Fino". This wine has a natural ethanol content of about 14.5% (v/v), and it is obtained by means of a long process (3-7)

years) of biological aging carried out by film yeasts growing in the wine surface ("flor"). The method traditionally used to obtain the Fino wine, named "criaderas and solera", essentially involves mixing less aged wines with more aged ones several times in a year (so-called "rocios"). This technique enables the production of a wine with similar sensory characteristics without dependence of a particular vintage, in this way achieving the desired homogeneity in the product. More detailed information about this traditional aging method can be found in the papers by Casas (10) and Domecq (11).

Aroma is an especially significant sensory attribute of foods and, particularly, of wines. In fact, the quality and specificity of each product are associated in most cases with a particular aroma. Changes in the content of aroma compounds during the biological aging of Fino sherry type wine are essentially of two different origins. On the one hand, it is a consequence of the activity of flor yeasts, which is a function of wine composition, the distribution of the population of the different flor yeast strains, and environmental conditions of temperature and moisture of the cellar, among other factors (11, 12). On the other hand, the compounds released by the wood of the casks used in the aging are a second important contribution to aroma of the wine. The type of wood, the ethanol content of the wine, and the temperature of the cellar are the main factors that influence the efficiency of extraction of these compounds in all types of wines (13, 14).

The main objective of the present work is the comparative study of the aroma profile of Fino type sherry wines, obtained from Pedro Ximenez grapes cultivated both conventionally and ecologically. In this respect, a more complete knowledge of the

^{*} Corresponding author (e-mail qe1mocal@uco.es; fax + 34957212146; telephone + 34957218636).

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aroma profile of these wines and their evolution during aging is essential to produce alternative organic Fino wine of a quality that can satisfy consumer demands for ecological products.

MATERIALS AND METHODS

Wines. Ecological and traditional white wines obtained from cv. Pedro Ximenez ripe grapes growing in the Montilla-Moriles region (southern Spain) were used in the present study. Conventional and organic grapes were cultivated by means of agricultural technologies based on the Regulations of the European Union (15, 16). Both grapes were treated with the fungicides S powder and copper oxychloride, although the doses used for organic grapes were low and according to European regulation for organic agriculture (15). Ecological management used cover crops of native wild species with spontaneous selection and regular addition of organic matter (manure and compost). In addition, neither insecticides nor synthetic fertilizers were used in organic agriculture during the crop. Conversely, conventional agriculture used organophosphate insecticides (clorpyriphos and malathion) to fight against different plagues (*Ocnogyna baetica* Ram and *Empoasca vitis*).

Three samples of both traditional and organic wines were collected after alcoholic fermentation (young wine, unaged) and from casks containing wine biologically aged for 3 years (Fino). These last samples were obtained by mixing the wine extracted from 20 casks. For both traditional and organic wines, biological aging was spontaneously carried out by flor veil yeasts, mainly contributed by *Saccharomyces cerevisiae capensis* race (17-19).

Analytical Methods. *Enological Variable Analysis.* Ethanol was quantified according to the Crowell and Ough (20) method. Reducing sugars, volatile and titratable acidity, pH, and SO₂ were determined in accordance with the Official Report of the European Community (21).

Identification and Quantification of Volatile Compounds. Each of the 55 compounds analyzed was identified in our laboratory following the chromatographic procedure below described for its quantification. The identification was made by comparison of its retention time with a standard solution of commercial product (Sigma-Aldrich, Munich, Germany) and by coelution with the standard and confirmed by mass spectrometry (Hewlett-Packard 5972 MSD), also by comparison with the data of a standard. 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 R-Biopharm (Darmstadt, Germany). For the remaining volatile compounds, samples of 100 mL of wine were adjusted to pH 3.5, 150 μ g of 2-octanol was added as an internal standard and then extracted with 100 mL of freon-11 (Sigma-Aldrich Quimica, S.A., Madrid, Spain) in a continuous extractor for 24 h (liquid-liquid extractor for use with solvents with higher density than sample). These compounds were quantified by GC (Hewlett-Packard 5890 series II) in a HP-INNOWax column of 60 m \times 0.32 mm \times 0.25 μ m thickness (Agilent Technology, Palo Alto, CA) 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 FID detector. The oven temperature program was as follows: 5 min at 45 °C, 1 °C/min 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 (Munich, Germany).

Perception Threshold Determination and Odor Activity Value (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. For all of the compounds analyzed five solutions of ascending concentration of each in a 14% v/v ethanol/water matrix were subjected to a sensorial analysis in our laboratory (22, 23). Starting from the lowest concentration solution, the judges indicated an odor sensation different from that 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.

Table 1. Mean and Standard Deviations (n = 3) of the Enological Variables in Traditional and Ecological Young and Fino Wines

	young wines		Fino wines	
enological variable	traditional	ecological	traditional	ecological
ethanol (% v/v) reducing sugars (g/L) volatile acidity (mequiv/L) titratable acidity (mequiv/L) pH SO ₂ total (mg/L)	$\begin{array}{c} 15.5\pm0.1\\ 1.3\pm0.1\\ 4.8\pm0.1\\ 76\pm1\\ 3.3\pm0.1\\ 103\pm3 \end{array}$	$\begin{array}{c} 15.3\pm0.4\\ 1.4\pm0.1\\ 4.5\pm0.1\\ 75\pm1\\ 3.1\pm0.1\\ 95\pm1 \end{array}$	$\begin{array}{c} 15.0\pm0.2\\ 1.0\pm0.1\\ 4.7\pm0.1\\ 67\pm1\\ 3.2\pm0.1\\ 147\pm3 \end{array}$	$\begin{array}{c} 15.1 \pm 0.5 \\ 1.1 \pm 0.1 \\ 4.6 \pm 0.4 \\ 64 \pm 1 \\ 3.3 \pm 0.1 \\ 82 \pm 2 \end{array}$

The OAV for each compound is defined and was calculated as the ratio between the concentration of a compound and its perception threshold (24)

Statistical Procedures. Analysis of variance (ANOVA) and principal component analyses (PCA) were performed on the replicated samples by using the Statgraphics 5.0 computer program (STSC Inc., Rockville, MD).

RESULTS AND DISCUSSION

Table 1 shows the winemaking variables in young wines (unaged) and Fino wines (biologically aged for 3 years), both traditional and ecological. The ethanol, reducing sugars, volatile and tritratable acidity, and pH do not exhibit great differences between the wines studied. As can be expected, sulfur dioxide showed a lower content in young and Fino ecological wines than in the traditional ones.

Table 2 lists the concentrations of volatile compounds in the wines studied and their perception thresholds, grouped in the following chemical families: acetaldehyde and its derivatives, alcohols, esters, acids, aldehydes, lactones, and volatile phenols.

The total contents in acetaldehyde and its derivatives showed differences between the traditional and ecological wines, as a result of not only the values of acetaldehyde but also those corresponding to acetoin, 1,1-diethoxyethane showing similar levels. Acetaldehyde and derivatives are compounds synthesized by yeasts during alcoholic fermentation, and their contents depend on different factors, such as the conditions of yeast growth in aerobic stress and the composition of the must (17, 25-28). Flor yeasts also synthesize these compounds during biological aging, although their expected increases in Fino wines were greater in traditional than in ecological wines. Several authors consider the acetaldehyde and 1,1-diethoxyethane as good fingerprints of the aging degree of Fino wines (12, 18, 22, 29). According to this consideration, the aging of ecological wines was developed more slowly than in the traditional wines, which indicates a lower activity of veil yeasts and/or a different distribution in the species and races of them.

As can be seen in **Table 2**, the alcohols and esters were the major chemical families from qualitative and quantitative points of view. Both ecological young and Fino wines showed lower total concentrations in alcohols and esters than those obtained from conventional grape. These results are according to the findings of Shinohara (30) and Valcarcel et al. (31), which point out an increase in the production of these compounds by the yeasts in the presence of increased concentrations of SO₂.

During biological aging the total acids content remained virtually constant in ecological wines. In contrast, it increased in traditional ones, the main contributors being the isobutanoic and hexanoic acids. Aldehydes were detected in only Fino wines, the total content in ecological wines being slightly lower than that of the traditional ones. The contribution of lactones to wine aroma has received special attention from some researchers, particularly in relation to sherry wines (18, 32-35). Z-Oak

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Table 2. Mean and Standard Deviation (n = 3) of the Concentrations for the Compounds Determined in Traditional and Ecological Young and Fino Wines and Their Odor Thresholds

	young wines		Fino	wines	
compound	traditional	ecological	traditional	ecological	odor threshold (mg/L)
acetaldehyde	59 ± 6	94 ± 4	195 ± 2	171 ± 10	10 ^a
1,1-diethoxyethane	1.11 ± 0.01	1.5 ± 0.2	10.5 ± 0.6	9.57 ± 0.01	1 ^{<i>a</i>}
acetoin	4.93 ± 0.07	$\textbf{6.73} \pm \textbf{0.01}$	39.3 ± 0.7	$\textbf{32.5} \pm \textbf{0.4}$	30 ^a
total acetaldehyde and derivatives	65 ± 6	102 ± 4	245 ± 2	213 ± 11	
methanol	100 ± 7	57 ± 3	43 ± 2	64 ± 5	668 ^a
1-propanol	39 ± 2	26 ± 2	40.8 ± 0.3	37 ± 3	830 ^a
isobutanol	34.2 ± 0.1	$\textbf{37.8} \pm \textbf{0.6}$	58.4 ± 0.1	44 ± 3	40 ^a
2-butanol	nd	nd	1.8 ± 0.1	1.14 ± 0.05	1000 ^a
1-butanol	3.5 ± 0.2	2.8 ± 0.2	4.2 ± 0.2	3.5 ± 0.2	830ª
A-methyl-1-pentanol	310 ± 12 0.04 + 0.01	313 ± 1 0.03 \pm 0.01	334 ± 1 0.08 \pm 0.01	295 ± 19 0.06 \pm 0.01	50 ^a
3-methyl-1-pentanol	0.04 ± 0.01 0.21 ± 0.01	0.00 ± 0.01 0.14 ± 0.03	0.16 ± 0.04	0.00 ± 0.01 0.19 ± 0.03	50 ^a
1-hexanol	0.79 ± 0.04	0.62 ± 0.03	0.85 ± 0.04	0.63 ± 0.01	8 ^a
1-octanol	nd	nd	3.1 ± 0.9	1.2 ± 0.2	10 ^a
furfuryl alcohol	4.2 ± 0.3	0.44 ± 0.05	29.1 ± 0.7	23.2 ± 1.9	15 ^a
benzyl alcohol	0.47 ± 0.01	0.07 ± 0.01	1.08 ± 0.06	0.4 ± 0.1	900 ^a
pnenetnyi alconol	26 ± 3	3 ± 1	56 ± 2	31 ± 2	10 ^a 50 ^a
methionol	0.23 ± 0.01 1.69 ± 0.06	0.17 ± 0.01 24 + 02	0.74 ± 0.05 17 + 01	0.57 ± 0.01 1 1 + 0 1	0 5 ^a
total alcohols	521 ± 23	476 ± 4	576 ± 4	503 ± 25	0.0
athul agatata	25 4	00 0	20.9 0.6	40 1 1	7 5 8
nronyl acetate	35 ± 4 0 15 \pm 0 05	22 ± 3 0.04 + 0.01	39.0 ± 0.0	40 ± 1	7.5 65 ^a
isoamvl acetate	1.6 ± 0.10	1.7 ± 0.2	2.8 ± 0.1	1.52 ± 0.08	0.03 ^a
phenethyl acetate	0.86 ± 0.06	0.61 ± 0.09	0.56 ± 0.08	0.14 ± 0.02	0.25 ^a
ethyl propanoate	$\textbf{0.46} \pm \textbf{0.01}$	0.8 ± 0.1	nd	nd	5 ^a
ethyl butanoate	0.82 ± 0.01	1.67 ± 0.09	1.4 ± 0.1	0.63 ± 0.09	0.02 ^a
ethyl hexanoate	0.15 ± 0.01	0.05 ± 0.01	0.06 ± 0.01	0.04 ± 0.01	0.005"
ethyl actanoate	103 ± 7 0.26 \pm 0.01	00 ± 1 0.39 \pm 0.01	307 ± 0 0.13 + 0.01	210 ± 7 0.15 \pm 0.02	0 002 ^a
isobutyl lactate	1.6 ± 0.2	0.00 ± 0.01 0.72 ± 0.04	0.10 ± 0.01	0.10 ± 0.02 0.83 ± 0.06	340 ^a
butyl lactate	nd	0.21 ± 0.02	0.63 ± 0.05	0.36 ± 0.09	10 ^b
ethyl 3-hydroxybutanoate	0.37 ± 0.05	$\textbf{0.15} \pm \textbf{0.02}$	3.7 ± 0.1	$\textbf{0.62}\pm\textbf{0.05}$	67 ^a
ethyl decanoate	3.3 ± 0.3	1.42 ± 0.09	3.5 ± 0.2	0.79 ± 0.04	0.51°
ethyl 2-turoate	0.4 ± 0.1	0.35 ± 0.01	2.2 ± 0.2	0.8 ± 0.1	1ª 100 <i>a</i>
diethyl malate	$1/\pm 1$	14.3 ± 0.3 0.06 \pm 0.01	11.5 ± 0.1 0.48 \pm 0.04	10.7 ± 0.5 2.0 \pm 0.4	100 760 ^a
phenethyl octanoate	0.03 ± 0.01	0.00 ± 0.01 0.03 ± 0.01	0.40 ± 0.04 0.15 ± 0.03	0.11 ± 0.02	10 ^a
monoethyl succinate	86 ± 4	83 ± 5	131 ± 5	102 ± 1	1000 ^a
total esters	250 ± 8	196 ± 5	565 ± 8	379 ± 7	
isobutanoic acid	0.9 ± 0.1	0.69 ± 0.01	1.82 ± 0.09	0.47 ± 0.07	20 ^a
butanoic acid	nd	$\textbf{0.35}\pm\textbf{0.04}$	$\textbf{0.34} \pm \textbf{0.03}$	0.11 ± 0.01	10 ^a
hexanoic acid	0.78 ± 0.01	0.83 ± 0.01	2.2 ± 0.2	2.05 ± 0.03	3 ^a
octanoic acid	0.07 ± 0.01	0.11 ± 0.01	0.07 ± 0.01	0.11 ± 0.01	8.8ª
lauric acid	100 + 0.01	10004 + 0.01	0.07 ± 0.01 0.36 ± 0.08	0.04 ± 0.01 0.19 + 0.01	10 ^a
total acids	1.8 ± 0.1	2.1 ± 0.1	4.8 ± 0.3	2.9 ± 0.1	10
octanal	nd	nd	0.02 ± 0.01	0.01 ± 0.01	0.61 ^a
furfural	nd	nd	1.24 ± 0.01	1.11 ± 0.02	15 ^a
decanal	nd	nd	0.22 ± 0.04	0.05 ± 0.01	1 ^b
benzaldehyde	nd	nd	$\textbf{0.66} \pm \textbf{0.02}$	$\textbf{0.19}\pm\textbf{0.04}$	5 ^a
5-methylfurfural	nd	nd	0.66 ± 0.03	0.62 ± 0.08	16 ^a
total aldehydes	nd	nd	2.8 ± 0.1	2.1 ± 0.1	
γ -butyrolactone	4.9 ± 0.9	2.7 ± 0.3	13±1	7.4 ± 0.3	100 ^a
(<i>E</i>)-oak lactone	nd	nd	0.07 ± 0.01	0.03 ± 0.01	0.122 ^b
(∠)-Oak lactone	na	nu 0.36 ⊥ 0.05	0.12 ± 0.01 13 \pm 2	U.U6 ± 0.01 2 1 ± 0 1	0.035° 500ª
ν -decalactone	nd	0.00 ± 0.00 nd	0.11 ± 0.03	2.1 ± 0.1 0.4 ± 0.1	1 ^a
total lactones	4.9 ± 0.9	3.1 ± 0.4	26 ± 3	10.1 ± 0.4	·
4-ethylguaiacol	nd	nd	0.24 ± 0.01	0.23 ± 0.04	0.046 ^a
4-ethylphenol	nd	nd	0.05 ± 0.01	0.01 ± 0.01	140 ^a
total volatile phenols	nd	nd	$\textit{0.29} \pm \textit{0.01}$	$\textit{0.24} \pm \textit{0.03}$	
farnesol	0.27 ± 0.05	0.37 ± 0.01	1.47 ± 0.08	0.34 ± 0.08	5 ^b
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^a From Moreno et al. (22). ^b From Chaves et al. (23). ^c nd, not detected.

Table 3. Mean and Standard Deviation (n = 3) of the Odor Activity Values and Odorant Series for the Odor-Active Compounds in Traditional and Ecological Young and Fino Wines

	young w	vine (OAV)	Fino wine (OAV)		
compound	nonorganic	organic	nonorganic	organic	odorant series
acetaldehyde	5.9 ± 0.6	9.4 ± 0.4	19.5 ± 0.2	17 ± 1	fruity
1,1-diethoxyethane	1.11 ± 0.01	1.5 ± 0.2	10.5 ± 0.6	9.57 ± 0.01	fruity, balsamic
acetoin	0.17 ± 0.01	0.22 ± 0.01	1.31 ± 0.02	1.08 ± 0.01	fatty
isobutanol	0.85 ± 0.02	0.95 ± 0.01	1.46 ± 0.01	1.10 ± 0.08	chemical
isoamyl alcohols	4.8 ± 0.2	4.82 ± 0.02	5.13 ± 0.02	4.5 ± 0.3	chemical
furfuryl alcohol	0.28 ± 0.02	0.030 ± 0.001	1.94 ± 0.05	1.5 ± 0.1	balsamic
phenethyl alcohol	2.6 ± 0.2	3.1 ± 0.1	5.6 ± 0.2	3.1 ± 0.2	floral
methionol	3.4 ± 0.1	4.8 ± 0.4	3.5 ± 0.2	2.3 ± 0.3	vegetal
ethyl acetate	4.6 ± 0.5	3.0 ± 0.5	5.30 ± 0.09	6.4 ± 0.1	fruity, balsamic, chemical
isoamyl acetate	52 ± 4	58 ± 7	94 ± 4	51 ± 3	fruity
phenethyl acetate	3.4 ± 0.2	2.4 ± 0.3	2.2 ± 0.4	0.6 ± 0.1	floral
ethyl butanoate	41.1 ± 0.6	84 ± 5	71 ± 6	32 ± 4	fruity
ethyl hexanoate	29 ± 2	10 ± 1	11 ± 1	8 ± 2	fruity
ethyl lactate	1.03 ± 0.07	0.68 ± 0.01	3.67 ± 0.06	2.10 ± 0.06	fruity, fatty
ethyl octanoate	131 ± 3	193 ± 7	67 ± 7	77 ± 9	fruity, fatty
ethyl decanoate	6.4 ± 0.6	2.8 ± 0.2	6.9 ± 0.4	1.56 ± 0.08	fatty, chemical
ethyl 2-furoate	0.40 ± 0.09	0.35 ± 0.01	2.2 ± 0.2	0.8 ± 0.1	chemical
(Z)-oak lactone	nd ^a	nd	3.5 ± 0.2	1.7 ± 0.2	fruity, empyreumatic, spicy
4-ethylguaiacol	nd	nd	5.19 ± 0.07	4.9 ± 0.8	empyreumatic, spicy

^a nd, not detected.



Figure 1. Aroma profile for traditional and ecological young wines drawn from the eight odorant series calculated by adding the OAVs of the odor-active compounds grouped in each one. The fruity and fatty series are drawn as the 10th part of their real values. Asterisks indicate significant differences at p < 0.05 between traditional and ecological wines.

lactone, also known as wood lactone and originating from precursors extracted by ethanol from the casks, was used in a recent study by Moreno et al. (22) as an analytical marker of the changes in Fino wine during its biological aging. Young and Fino ecological wines showed a lower total content in lactones than traditional ones. As can be seen, γ -butyrolactone and pantolactone were the lactones detected in young wines, the last only in ecological wines. After 3 years of biological aging, these lactones increased their contents, and small quantities of Z and E isomers of the oak lactone and γ -decalactone were also quantified in the Fino wines. The traditional wines showed the highest values for these lactones (except for γ -decalactone), suggesting a delay in the aging of organic wines compared to traditional ones. The quantified volatile phenols in the Fino wines were 4-ethylguaiacol and 4-ethylphenol, showing a similar concentration of the former in both ecological and traditional wines and a higher concentration of the latter in traditional wines. Finally, farnesol was the only terpene identified, also reaching the highest concentration in the traditional Fino wines.

Table 3 lists the OAVs for the 19 odor-active compounds (OAV > 1 in at least one of the wines studied), as well as the aromatic series in which they can be grouped (fruity, balsamic, fatty, chemical, floral, vegetal, empyreumatic, and spicy), according to criteria used in previous works (*36, 37*).

To compare the aroma profiles of the different wines, the total OAVs for each odorant series were calculated by the addition of individual OAVs of the compounds grouped in this series. **Figures 1** and **2** show the aroma profiles of young and Fino wines, respectively. Those series that exhibited significant differences at p < 0.05 (ANOVA) between traditional and ecological types of wine are marked with an asterisk. As can be observed in **Figure 1**, for traditional and ecological young wines, only floral, spicy, and empyreumatic series were not different at this significance level. The fruity (OAVs close to 265 and 360, respectively) and fatty (OAVs close to 140 and 200, respectively) were the major series, representing about 60 and 32%, respectively, of the total aroma series of the wines. Both odorant series reached the highest OAVs in ecological wines, mainly due to the participation of ethyl octanoate, so



Figure 2. Aroma profile for traditional and ecological Fino wines drawn from the eight odorant series calculated by adding the OAVs of the odor-active compounds grouped in each one. The fruity and fatty series are drawn as the 10th part of their real values. Asterisks indicate significant differences at p < 0.05 between traditional and ecological wines.



Figure 3. Principal component analysis performed on the OAVs of the compounds grouped into eight odorant series for traditional and ecological wines.

this compound can be considered to be a very potent odorant responsible largely for the fruity and fatty aromas.

The vegetal aroma series, contributed by only the methionol, reached a slightly higher total OAV in the ecological wine than in the traditional one, contrary to the balsamic and chemical series that exhibited higher total OAVs for the traditional wines. Ethyl acetate, as the main contributor odorant for the balsamic series (approximately 71%), was mainly responsible for the differences found between both types of wines for this series. On the other hand, although isoamyl alcohols, ethyl acetate, and ethyl decanoate were mainly responsible for the chemical odors, the differences observed between the two types of young wines were mostly due to the two esters.

As can be seen in **Figure 2**, the fruity and fatty series were also the major series for Fino wines, representing about 64 and 25%, respectively, of their total aroma series. However, conversely to young wines, the fruity series showed a significantly lower total OAV for ecological wines than for traditional ones, mainly due to the lower individual values of the isoamyl acetate and ethyl butanoate (**Table 3**). The fatty and balsamic series not distinguished between the ecological and traditional Fino wines at p < 0.05; therefore, taking into account that these series were significantly different in unaged wines, it is reasonable to admit that both series were not evolved in the same way during the biological aging process of the wines studied. The remaining significantly different series (floral, chemical, vegetal, spicy, and empyreumatic) showed a contribution below 5%, the highest OAVs being reached in the traditional Fino wines.

To evaluate the influence of each series in the aging process, as well as in the differentiation between ecological and traditional wines, the OAVs of the eight series were subjected to a principal component analysis. The two first components obtained explained 93% of the overall variance, PC1 accumulating >59%. Figure 3 shows the position of the wine samples according to their values on the two principal components. As can be seen, PC1 separated the young wines from the aged wines, also distinguishing the traditional young wines from the ecological young ones, whereas PC2 was effective only in separating the traditional aged Fino wines from the ecological ones. The variables most contributing to the first component were the fatty, empyreumatic, and spicy series, whereas the floral and fruity series contributed most to the second component.

Overall, although the compounds most contributing to the aroma of ecological sherry wines were the same as those of traditional ones, the aroma profiles were different prior to the biological aging. After this process, the ecological wines showed lower values than traditional Fino wines for the OAVs of all the series except the balsamic and fatty series. These decreases in the series originated a wine with a sensorial profile similar to the traditional Fino but with a lower odor intensity (like the traditional wine aged for <3 years). It is difficult to attribute this delay in the aging of ecological sherry wines, and further research is required. On the one hand, it is well-known that small differences in the initial composition of the wine before aging, particularly in the nitrogen fraction, can lead to a lower synthesis of alcohols and esters by flor film yeasts. On the other hand, as pointed out above, the higher concentrations of SO₂ used in traditional aging of sherry also can favor the synthesis of these compounds, but a lower use of this food additive is inherent to the ecological character of the wine. Finally, small differences in the distribution of the species and races of flor film yeasts can also contribute to changes in the composition of wines subjected to a medium-term aging.

LITERATURE CITED

 Guthman, J. Raisin organic: an agro-ecological assessment of grower practices in California. <u>Agric. Hum. Values</u> 2000, 17, 257– 266.

- (2) Espinoza, J. A.; Mora, M.; Brugarolas, M. Vision actualizada del mercado de productos ecologicos en Europa. El mercado Español In *II Congreso Nacional de Ciencia y Tecnologia de los Alimentos*; University of Miguel Hernandez: Elche, Spain, 2003; pp 443– 446.
- (3) Bellapart, C. Agricultura Biologica en Equilibrio con la Agricultura Quimica: Fertilizacion Natural, la Agricultura del Futuro; Aedos: Barcelona, Spain, 1988.
- (4) Davis, A.; Titterington, A. J.; Cochrane, C. Who buys organic food? A profile of the purchase of organic food in N. Ireland. <u>Br.</u> <u>Food J.</u> 1995, 97, 17–23.
- (5) Zafrilla, P.; Morillas, J.; Mulero, J.; Cayuela, J. M.; Martinez-Cacha, A.; Pardo, F.; Lopez-Nicolas, J. Changes during storage in conventional and ecological wine: phenolic content and antioxidant activity. *J. Agric. Food Chem.* **2003**, *51*, 4694–4700.
- (6) Yildirim, H. K.; Li, A. A.; Akçay, Y. D.; Güvenç, U.; Sözmen, E. Y. Physical characteristics and antioxidant activities of organic grapes. *J. Food Biochem.* **2007**, *31*, 81–95.
- (7) Pomarici, E. Competitiveness of the Western European wine sector. In *The European Agro-Food System and the Challenge of Global Competition*; ISMEA: Rome, Italy, 1999; pp 157–186.
- (8) Fotopoulos, C.; Kristallis, A.; Ness, M. Wine produced by organic grapes in Greece: using means-end chains analysis to reveal organic buyers purchasing motives in comparison to the nonbuyers. *Food Oual. Pref.* 2003, 14, 549–566.
- (9) Dani, C.; Oliboni, L. S.; Vanderlinde, R.; Bonatto, D.; Salvador, M.; Henriques, J. A. P. Phenolic content and antioxidant activities of white and purple juices manufactured with organically- or conventionally-produced grapes. *Food Chem. Toxicol.* 2007, 45, 2754–2580.
- (10) Casas, J. F. Descripcion resumida de la tecnica enologica en los vinos de Jerez In *Proceedings of the III Jornadas Universitarias sobre el Jerez*; University of Cadiz: Cadiz, Spain, 1985; pp 333– 361.
- (11) Domecq, B. Sherry: state of art on a very special fermentation product In *Proceedings of the International Symposium on Yeasts*; University of Leuven: Leuven, Belgium, 1989; pp 15–35.
- (12) Garcia-Maiquez, E. Les levures de voile dans l'elaboration des vins de Xeres. In *Application a l'Oenologie des Progres Recents en Microbiologie et en Fermentation*; OIV: Paris, France, 1988; pp 341–351.
- (13) Singleton, V. Maturation of wines and spirits: comparisons, facts, and hypotheses. <u>Am. J. Enol. Vitic</u>, **1995**, 46, 98–115.
- (14) Arapitsas, P.; Antonopoulos, A.; Stefanou, E.; Dourtoglou, V. G. Artificial ageing of wines using oak chips. *Food Chem.* 2004, 86, 563–570.
- (15) Council Regulation (EC) 834/2007. Off. J. Eur. Union 2007, L-189/1.
- (16) Commission Regulation (EC) 423/2008. Off. J. Eur. Union 2008, L-127/13.
- (17) Martinez, P.; Valcarcel, M. J.; Perez, L.; Benitez, T. Metabolism of *Saccharomyces cerevisiae* flor yeasts during fermentation and biological ageing of Fino Sherry: by-products and aroma compounds. *Am. J. Enol. Vitic.* **1998**, *48*, 55–62.
- (18) Cortes, M. B.; Moreno, J.; Zea, L.; Moyano, L.; Medina, M. Changes in aroma compounds of Sherry wines during their biological ageing carried out by *Saccharomyces cerevisiae* races *bayanus* and *capensis*. *J. Agric. Food Chem.* **1998**, 46, 2389– 2394.
- (19) Peinado, R.; Mauricio, J. C. Biologically aged wines. In *Wine Chemistry and Biochemistry*; Springer: Berlin, Germany, 2008; ISBN 978-0-387-74116-1)(in press).
- (20) Crowell, E. A.; Ough, C. S. A modified procedure for alcohol determination by dichromate oxidation. <u>Am. J. Enol. Vitic</u>. 1979, 30, 61–63.

- (21) European Commission Regulation 2676/90. *Off. J. Eur. Union* **1990**, *L*-272.
- (22) Moreno, J. A.; Zea, L.; Moyano, L.; Medina, M. Aroma compounds as markers of the changes in Sherry wines subjected to biological ageing. *Food Control* **2005**, *16*, 333–338.
- (23) Chaves, M.; Zea, L.; Moyano, L.; Medina, M. Changes in color and odorant compounds during oxidative ageing of Pedro Ximenez sweet wines. *J. Agric, Food Chem*, **2007**, *55*, 3592–3598.
- (24) Mayol, A. R.; Acree, T. E. Advances in gas chromatography– olfactometry. In *Gas Chromatography–Olfactometry. The State* of the Art; Leland, J. V., Schieberle, P., Buettner, A., Acree, T. E., Eds.; Washington, DC, 2001; pp 1–10.
- (25) Etievant, P. X. Wine In Volatile Compound in Foods and Beverages; Maarse, H., Ed.; Zeist, TNO-Civo. Food Analysis Institute: The Netherlands, 1991; pp 486–547.
- (26) Berlanga, T. M.; Peinado, R. A.; Millan, C.; Mauricio, J. C.; Ortega, J. M. Influence of blending on the content of different compounds in the biological ageing of Sherry dry wines. <u>J. Agric.</u> *Food Chem.* 2004, *52*, 2577–2581.
- (27) Berlanga, T. M.; Peinado, R. A.; Millan, C.; Ortega, J. M. Discriminant analysis of Sherry wine during biological ageing. *Am. J. Enol. Vitic.* 2004, 55, 407–411.
- (28) Muñoz, D.; Peinado, R. A.; Medina, M.; Moreno, J. Biological ageing of Sherry wines using pure cultures of two flor yeast strains under controlled microaeration. <u>J. Agric. Food Chem</u>. 2005, 53, 5258–5264.
- (29) Cortes, M. B.; Moreno, J. J.; Zea, L.; Moyano, L.; Medina, M. Response of the aroma fraction in Sherry wines subjected to accelerated biological ageing. <u>J. Agric. Food Chem</u>. **1999**, 47, 3297–3302.
- (30) Shinohara, T. Factors affecting the formation of volatile fatty acids during grape must fermentation. <u>Agric. Biol. Chem</u>. **1986**, 50, 3197–3199.
- (31) Valcarcel, M. J.; Perez, L.; Gonzalez, P.; Domecq, B. Efecto de las practicas enologicas en vendimia sobre las levaduras responsables de la fermentacion de mostos de Jerez, IV: Eestudio industrial. *Aliment., Equip. Tecnol.* **1990**, *3*, 171–174.
- (32) Fagan, G. L.; Kepner, R. E.; Webb, A. D. Additional volatile components of Palomino film sherry. <u>Am. J. Enol. Vitic</u>. 1982, 33, 47–50.
- (33) Williams, A. A. Post fermentative changes in wines with particular reference to the volatile flavour components of sherry and port. In Proceedings of the International Symposium on The Aroma Substances in Grapes and Wines; Scienza, A., Versini, G., Eds.; Instituto Agrario Provinciale: Trento, Italy; 1989; pp 201–222.
- (34) Maarse, H.; Visscher, C. A. Volatile Compounds in Alcoholic Beverages. Qualitative and Quantitative Data; Maarse, H., Ed.; Dekker: Zeist, The Netherlands, 1989.
- (35) Martin, B.; Etievant, P. X.; Le Quere, J. L.; Schlich, P. More clues about sensory impact of Sotolon in flor sherry wines. <u>J.</u> <u>Agric. Food Chem</u>. **1992**, 40, 475–478.
- (36) Moyano, L.; Zea, L.; Moreno, J.; Medina, M. Analytical study of aromatic series in Sherry wines subjected to biological ageing. <u>J.</u> <u>Agric. Food Chem.</u> 2002, 50, 7356–7361.
- (37) Zea, L.; Moyano, L.; Moreno, J. A.; Medina, M. Aroma series as fingerprints for biological ageing in fino sherry-type wines. <u>J. Sci.</u> <u>Food Agric</u>. 2007, 87, 2319–2326.

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