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Combined Effects of Prefermentative Skin Maceration and Oxygen Addition of Must on Color-Related Phenolics, Volatile Composition, and Sensory Characteristics of Airén White Wine

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ABSTRACT: The effects of the joint prefermentative maceration and hyperoxygenation of Airén white must and wine on the phenolic content, chromatic characteristics, volatile composition, and sensory characteristics, not previously described in combination, have been evaluated. A total of 20 phenolic and 149 volatile compounds have been identified and quantified for that purpose. As a consequence of the oxygen addition, the concentrations of hydroxycinnamic acid derivatives and flavan-3-ols decreased (above all *t*-GRP and (+)-catechin), leading to color stabilization, but also the concentrations of several volatile compounds with a great importance for quality aroma decreased. Prefermentative skin maceration, previously applied to the hyperoxygenation of Airén musts, provided the aforementioned color stabilization in the respective wine but also increased the content of short-chain fatty acid esters and terpenes and decreased the concentration of C_6 alcohols. That combination of prefermentative treatments (skin maceration followed by must hyperoxygenation) produced an improvement of the global impression of the final wine based on significantly better scores of tropical fruit, body, and herbaceous notes.

KEYWORDS: color, hyperoxygenation, Airén, polyphenols, prefermentative skin maceration, volatile compounds, sensory analysis

INTRODUCTION

The content of almost all phenolic compounds decreases due to oxygen addition, and the hydroxycinnamic acid derivatives present in white wines are the most susceptible polyphenolic compounds (particularly the major caftaric acid and *p*-coutaric acids).[1] As a consequence, the susceptibility of browning of the final white wines decreases in a treatment called hyperoxygenation. As well as hydroxycinnamic acid derivatives, sulfur compounds also play an important role in browning. On the one hand, the browning of must could be avoided by the formation of grape reaction production (GRP) (2-*S*-glutathionylcaftaric acid),[2,3] which derived from the reaction between glutathione and the *o*-quinone formed from caftaric or coutaric acid by means of grape polyphenol oxidase (PPO) and the presence of oxygen. That is, while glutathione is available, the susceptibility to browning decreases by trapping caftaric acid quinones in the form of stable GRP because this compound is no longer a substrate for further oxidation of PPO. On the other hand, the presence of an excess of glutathione permits the laccase action from *Botrytis cinerea* to give rise to 2,5-di-*S*-glutathionylcaftaric acid. This prevents the participation of *o*-quinones in coupled reactions leading to pigment formation and, subsequently, browning. Due to the importance of the behavior of glutathione toward enzymatic oxidation of must polyphenols, several authors have studied the addition of glutathione and other thiol-containing compounds, such as cysteine, to fresh must as prefermentative practice to prevent browning.[4]

With regard to the effect of must hyperoxygenation on the volatile composition, it greatly depends on the grape variety. For instance, the aroma profile improved in Chardonnay, Muscat de Alejandría, Macabeo, Muscat, and Parrellada white wines as a consequence of the oxygen addition,[5−7] due to an increase in the amounts of alcohols, fatty acids and their esters, and terpenes, whereas the aroma intensity decreased in Semillon, Chardonnay, Chenin blanc, French Colombard, and Muscadelle wines derived from hyperoxygenated musts.[8,9]

The skin contact provoked an improvement of wine quality due to the extraction of several phenolic and volatile compounds. According to several authors, higher maceration times provoked an increase of the content of terpenes and monoterpenic alcohols[10,12] and phenolic compounds,[13] increasing the astringency and bitterness in the wines.[8]

The joint use of hyperoxygenation and prefermentative skin maceration techniques could be advantageous, taking into account the positive aspects of each treatment. On the one hand, the hyperoxygenation involves the oxidation of phenolic compounds of musts due to the oxygen addition.[14] This provoked the diminution of the concentration of those phenolic compounds, the final wines being less susceptible to oxidation and subsequent browning. On the other hand, the aroma quality of the final wines

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improved as a consequence of the skin maceration. As a consequence, the detrimental effects of the length of contact with the solid parts, such as higher browning susceptibility,[6] off-odors, and higher astringency and bitterness,[8] were avoided with the hyperoxygenation treatment, providing as well the varietal character of the skins.[15] Several authors have studied the effect on phenolic compounds of the both treatments, such as procyanidins and some individual and global hydroxycinnamic acid derivatives and flavan-3-ols.[6,8,11] However, no scientific study dealing with the combined effects of maceration and hyperoxygenation treatments on a large number of phenolic and volatile compounds has been yet carried out.

From a sensory point of view, the effect of hyperoxygenation on the organoleptic characteristics deeply depends on the grape variety. Whereas aromatic quality increased in Chardonnay, Muscat, and Faberrebe white wines[5,7,16] due to the higher concentration of long-chain acetates, fatty acids and their esters, and terpenes, several French white wines suffered losses of aromatic intensity and varietal character, due to the concentration decrease of long-chain alcohols and increase of the content of medium- and long-chain acetates and aldehydes characterized by vegetal aroma.[17,18] An increase of lemon notes and a diminution of apricot odor were reported in Riesling white wines by Schneider[19] as a consequence of the oxygen addition. Moreover, an increase in banana notes and a decrease in herbaceous and flowery notes were found in wines derived from Chardonnay hyperoxygenated must.[20] However, only a few scientific works on the effect of the joint application of skin maceration and hyperoxygenation on sensory analysis have been found, resulting in the treated wines being less fruity and having a lower quality aroma than the untreated wines.[6,8]

The aim of this research study was based on the hyperoxygenation effects and their joint application with the prefermentative maceration on color, phenolic compounds, volatile composition, and sensory analysis. The study was performed on Airén white musts and wines, and our interest was focused on several perspectives not previously considered in conjunction. Moreover, a detailed study about the effect of the joint maceration and hyperoxygenation treatment on a large number of phenolic and volatile compounds, not previously reported, has been developed.

MATERIALS AND METHODS

Winemaking. Grapes from *Vitis vinifera* cv. Airén cultivated in Ciudad Real (region of Castilla-La Mancha, Spain) were harvested at their optimal ripening stage and in good sanitary conditions. After the grapes were destemmed and crushed in a bladder press, the must was homogenized in a stainless steel tank of 2000 L capacity and quickly distributed in six stainless steel tanks of 250 L, which were destined to the elaboration of the following wines: two tanks for untreated control wine; two tanks for wine from hyperoxygenated must; and the two final tanks for wine from must that was first submitted to prefermentative skin maceration and, subsequently, to hyperoxygenation.

Control tanks were treated with SO_2 (100 mg/L, as $K_2S_2O_7$) for avoiding possible must oxidation during cold settling. Prefermentative skin maceration was developed by adding the corresponding proportional amount of grape solids (separated after pressing of the crushed and destemmed grapes) and maintaining this homogenized mixture at 8−10 °C for 24 h under N_2 atmosphere. Then, the macerated must was drained for the next treatment. Hyperoxygenation of nonmacerated must was made immediately after its obtaining, whereas the treatment of macerated must was delayed for 24 h (maceration time). For the hyperoxygenation treatment, a silicon diffuser was connected to an oxygen cylinder (purity > 99.9%) and introduced into the musts, and then oxygen was pumped from the bottom to the top of the tank. After 4.5 h, the oxygen concentration reached 50 mg/L, measured by an oxymeter for flow control (Laffort, Spain). Later, musts were cold-settled at 4 °C for 48 h, and clean fractions were racked and treated with SO_2 (100 mg/L, as $K_2S_2O_7$) for avoiding further oxidation. All of the musts (control, hyperoxygenated, and macerated−hyperoxygenated) were inoculated with *Saccharomyces cerevisiae* selected yeasts (UCLM S377, Found-Springer, France) for promoting alcoholic fermentation, which was conducted at a temperature of 18 °C. The development of fermentation was controlled by monitoring of density and enzymatic measurement of residual sugar (Boehring Mannheim, Germany). Once alcoholic fermentation ended, all of the wines were racked and, after filtration, were supplied with 60 mg/L of SO_2 to prevent malolactic fermentation. All fermentations were performed in the experimental winery of Castilla-La Mancha University (Ciudad Real, Spain) and were carried out in duplicate. Samples were collected and analyzed from each tank at the start of the alcoholic fermentation (control, hyperoxygenated, and macerated−hyperoxygenated musts; CM, HM, and MHM, respectively) and at the end of alcoholic fermentation (control, hyperoxygenated, and macerated−hyperoxygenated wines; CW, HW, and MHW, respectively).

Wine conventional analytical data were obtained using OIV Official Methods.[21]

Analysis of Must and Wine Polyphenolic Compounds and Color Parameters. Total polyphenolic compounds, hydroxycinnamic acid derivatives, and flavonol[22] and flavan-3-ol families[23] were measured by spectrophotometry, using a Hewlett-Packard 8452A apparatus. Also, the CIELAB chromatic coordinates (illuminant D65 and 10 degree observer) (L^*, C^*_{ab}, h_{ab}, a^*, and b^*) were calculated.[24]

Prior to the HPLC method, phenolic compound extracts were obtained by solid-phase extraction (SPE) on reverse-phase cartridges (Sep-Pak, 500 mg of adsorbent; Waters) according to the method developed by Cejudo-Bastante et al.[25] After conditioning of the cartridge with 4 mL of methanol and water, 2 mL of sample was passed through the C18 cartridges. Ten milliliters of methanol was used for the elution of the phenolic compounds of musts and wines. The eluate was dried in a rotatory evaporator (40 °C) and resolved in 2 mL of the phase A (87% distillate water, 3% acetonitrile, 10% formic acid) used in the HPLC separation.

HPLC separation, identification, and quantification of phenolic compounds were performed on an Agilent 1100 series system (Agilent, Waldbronn, Germany), equipped with a DAD photodiode detector (G1315B) and a LC/MSD Trap VL (G2445C VL) electrospray ionization mass spectrometry (ESI/MS^n) system, both coupled to an Agilent Chem Station (version B.01.03) for data processing. The samples, after filtration (0.20 μm, polyester membrane, Chromafil PET 20/25, Machery-Nagel, Düren, Germany), were injected (50 μL) in duplicate on a reversed-phase column Zorbax Eclipse XDB-C18 (4.6 × 250 mm; 5 μm particle; Agilent), thermostated at 40 °C. We used the chromatographic method developed by Castillo-Muñoz et al.,[26] as follows: the solvents were water/acetonitrile/formic acid (87:3:10, solvent A; 40:50:10, solvent B), with a flow rate of 0.63 mL/min.

Quantification was made using the DAD chromatograms obtained at 320 nm for the hydroxycinnamic acid derivatives, at 280 nm for the flavan-3-ols compounds and benzoic acids, and at 360 nm for flavonols. For identification, the ESI-MS^n was used in positive mode for flavan-3-ols, whereas both positive and negative modes were used for flavonols, benzoic acids, and hydroxycinnamic acid derivatives.[26,27]

Analysis of Must and Wine Volatile Compounds. After centrifugation for 30 min at 12000 rpm and 4 °C, samples were passed through glass wool, spiked with 2-pentanol as internal standard (1 g/L),

Table 1. Mean Values of Concentration (Milligrams per Liter) and Standard Deviations ($n = 2$) of Several Types of Polyphenolic Compounds Belonging to Different Chemical Families (Hydroxycinnamic Acid Derivatives (HCAD), Benzoic Acids, Flavan-3-ols, and Flavonols) Identified by HPLC-MS^n, Global Types of Phenolic Families, and Chromatic Characteristics by Spectrophotometric Measurements, in Control (C), Hyperoxygenated (H), and Macerated−Hyperoxygenated (MH) Airén White Musts (M) and Wines (W)[a]

	CM	HM	MHM	CW	HW	MHW
HCAD						
t-GRP	19.4 c ± 0.20	8.24 b ± 0.51	9.01 b ± 0.19	14.3 ± 4.09	8.50 ± 0.55	9.61 ± 0.05
t-caftaric acid	2.01 ± 0.26	1.77 ± 0.01	2.40 ± 0.23	4.56 ± 1.40	2.06 ± 0.04	3.48 ± 1.26
c-GRP	8.75 c ± 0.51	4.31 b ± 0.31	4.34 b ± 0.09	8.54 ± 1.18	7.64 ± 0.10	7.81 ± 0.05
t-coutaric acid	1.45 d ± 0.28	0.09 b ± 0.03	0.62 c ± 0.01	2.53 c ± 0.52	nd b	nd b
c-coutaric acid	0.87 c ± 0.00	0.31 b ± 0.10	1.37 c ± 0.28	1.84 bc ± 0.12	0.05 b ± 0.01	3.50 c ± 1.31
t-fertaric acid	3.76 ± 0.20	1.99 ± 0.75	2.86 ± 0.75	3.69 ± 0.09	3.14 ± 0.29	3.58 ± 0.63
c-fertaric acid	1.45 ± 0.01	0.97 ± 0.34	0.56 ± 0.19	1.27 ± 0.37	1.47 ± 0.11	1.33 ± 0.07
p-coumaric acid	nd	nd	nd	0.06 ± 0.02	0.03 ± 0.00	0.08 ± 0.02
benzoic acids						
gallic acid	3.18 ± 0.13	2.41 ± 0.61	4.36 ± 1.03	1.24 ± 0.26	1.01 ± 0.12	1.06 ± 0.13
flavan-3-ols						
(+)-catechin	9.75 c ± 0.50	3.06 b ± 1.01	4.32 b ± 0.08	4.95 c ± 1.26	0.95 b ± 0.08	0.48 b ± 0.15
(−)-epicatechin	3.35 c ± 0.07	nd b	nd b	10.23 ± 2.39	10.2 ± 0.16	10.3 ± 1.02
(−)-epicatechin gallate ester	nq	nq	nq	nq	nq	nq
flavonols						
quercetin-3-glucuronide	1.85 b ± 0.07	1.14 b ± 0.33	8.77 c ± 0.62	0.92 b ± 0.30	0.95 b ± 0.00	8.65 c ± 0.12
quercetin-3-glucoside	1.19 c ± 0.06	0.41 b ± 0.14	3.12 d ± 0.09	0.65 b ± 0.19	0.27 b ± 0.00	3.06 c ± 0.35
kaempferol-3-galactoside	0.14 b ± 0.01	0.09 b ± 0.03	0.61 c ± 0.01	0.23 c ± 0.06	0.11 b ± 0.00	0.99 d ± 0.00
kaempferol-3-glucuronide	nd b	nd b	0.42 c ± 0.02	nd b	nd b	0.36 c ± 0.01
kaempferol-3-glucoside	0.25 b ± 0.02	0.19 b ± 0.07	1.40 c ± 0.00	nd b	nd b	0.72 c ± 0.03
isorhamnetin-3-glucoside	0.04 ± 0.01	0.04 ± 0.00	0.10 ± 0.01	nd b	nd b	0.09 c ± 0.00
quercetin	0.74 c ± 0.13	0.05 b ± 0.01	0.09 b ± 0.00	1.23 c ± 0.32	0.44 b ± 0.17	2.37 d ± 0.05
kaempferol	0.02 c ± 0.00	nd b	0.03 d ± 0.00	nd b	nd b	0.55 c ± 0.06
global families						
total polyphenols	172 b ± 14.8	152 b ± 11.2	297 c ± 0.40	174 c ± 10.6	143 b ± 2.58	175 c ± 4.04
HCAD	55.9 c ± 5.53	38.2 b ± 3.70	92.9 d ± 0.07	55.2 c ± 3.65	36.2 b ± 0.46	59.9 c ± 0.94
flavonols	42.9 b ± 5.48	39.5 b ± 3.67	101 c ± 0.13	43.6 b ± 3.84	36.4 b ± 1.02	51.9 c ± 0.69
flavan-3-ols	22.6 ± 2.67	22.3 ± 2.68	25.6 ± 1.45	15.9 ± 1.09	11.8 ± 0.37	13.8 ± 1.38
chromatic characteristics						
L^*	81.1 ± 2.93	74.5 ± 2.62	47.3 ± 13.5	98.5 ± 0.18	99.0 ± 0.04	98.4 ± 0.39
C^*_{ab}	20.8 b ± 0.34	35.3 c ± 1.12	51.3 d ± 6.82	5.20 ± 0.04	5.10 ± 0.48	6.52 ± 0.86
h_{ab}	86.4 c ± 0.57	82.6 c ± 0.55	75.1 b ± 3.57	91.8 b ± 1.39	95.8 c ± 0.04	94.6 c ± 0.01
a^*	1.31 b ± 0.23	4.53 c ± 0.48	12.9 d ± 1.34	−0.17 ± 0.13	−0.52 ± 0.05	−0.53 ± 0.07
b^*	20.8 b ± 0.32	35.1 c ± 1.07	49.6 d ± 7.40	5.19 ± 0.04	5.07 ± 0.48	6.49 ± 0.86

[a] Different letters in the same row denote significant differences according to Student−Newman−Keuls test ($p < 0.05$) separately applied to musts and wines. *t*, *trans*; *c*, *cis*; GRP, grape reaction product (2-*S*-glutathionyl caftaric acid); nd, not detected; nq, not quantifiable.

and directly injected (in split mode) in a Hewlett-Packard 5890 series II gas chromatograph coupled to a flame ionization detector for the determination of major volatile compounds.

Minor volatile compounds of wines were extracted in duplicate by SPE technique, according to the method proposed by Sánchez-Palomo et al.[28] Forty microliters of 4-nonanol as internal standard (1 g/L) to 100 mL of wine was added. The SPE was carried out using 500 mg of styrene divinylbenzene cartridges (Lichrolut EN Merck, KGaA, Darmstadt, Germany). The cartridges were previously conditioned by passing, first, 10 mL of dichloromethane, then 5 mL of methanol, and finally 10 mL of 10% (v/v) aqueous ethanol. Nonvolatile hydrophilic compounds were washed out of the cartridges, by means of 50 mL of bidistilled Milli-Q plus water, and minor volatiles were eluted with 10 mL of dichloromethane. Extracts were concentrated to 200 μL under a gentle stream of nitrogen and were stored in a freezer (−20 °C) until chromatographic analysis in scan rate. A volume of 1 μL of extracts was injected in splitless mode into an Agilent Technology 6890 N Network GC System equipped with an Agilent Technology 5973 *inert* mass selective detector, in a BP-21 capillary column (60 m × 0.32 mm i.d.; 0.25 μm film thickness). Operation conditions were as follows: oven temperature program, 70 °C (5 min), raised at 1 °C/min to 95 °C, which was held for 10 min, and then raised at 2 °C/min to 190 °C and held for 40 min. Injector and transfer line temperatures were 250 and 280 °C, respectively. Mass detector conditions were electronic impact (EI) at 70 eV; source temperature, 178 °C; scanning rate, 1 scan/s; mass acquisition, 40−450 amu. Chromatographic conditions were followed according to the method proposed by Sánchez-Palomo et al.[29]

The identification was based on comparison of the mass spectra with those provided for authentic standards and by the NBS75K and Wiley A libraries. The response factor of each volatile compound was calculated by injection of commercial standard. For compounds for which commercial standards were not available, the response factors of compounds with similar chemical structures were used. All samples were injected in duplicate.

Descriptive Sensory Analysis. A panel of expert assessors (between 12 and 15) with experience in sensory analysis evaluated Airén control wines, wines derived from hyperoxygenated musts, and wines derived from macerated−hyperoxygenated musts. Discriminative tests allowed that assessors were trained in descriptive sensory analysis during 15 sessions, using reference standards for the descriptors evaluation. Assessment took place in a standard sensory-analysis chamber,[30] equipped with separate booths and wine-testing glasses[31] covered with a watch-glass to minimize the escape of volatile compounds. After wines had been sniffed and tasted, judges generated sensory terms individually. Finally, six olfactive attributes (fresh, citrus, herbaceous, fruity, tropical fruit, and banana) and seven gustative attributes (herbaceous, fruity, tropical fruit, acidity, body, and intensity and quality of persistence) were selected by consensus. Also, global impression was valued for each tester.

The panelists used a 10 cm unstructured scale to rate the intensity of each attribute. The left extreme of the scale indicated a null intensity of the descriptor and the right extreme the maximum value. All wine samples were evaluated in duplicate.

Statistical Analysis. Statistical analyses were carried out by using the SPSS version 15.0 for Windows statistical package. The Student−Newman−Keuls test was applied to discriminate among the means of chemical and sensory data. Furthermore, a principal component analysis (PCA) was carried out with the aim of highlighting the main contributors to the variance among samples.

RESULTS AND DISCUSSION

General Parameters. The general composition of Airén wines, control (CW) and derived from hyperoxygenated musts (HW) and macerated−hyperoxygenated musts (MHW), was analyzed (pH, volatile acidity, alcoholic content, glucose, and fructose). Alcoholic fermentation developed correctly as indicated by the low values of fructose and glucose, thus being considered dry white wines (<5 g/L), and the values of the alcoholic content (11.0−11.5 (v/v)). For all wines, the pH and volatile acidity values were optimal (pH, 3.25−3.26; volatile acidity, 0.22−0.29), and the latter value, although significantly higher in MHW, was below the limit established by CEE[32] (1.08 g/L). According to the Student−Newman−Keuls test, significant differences between the three wines were practically nonexistent.

Effects of Prefermentative Maceration and Must Hyperoxygenation on the Phenolic Composition and Color Characteristics of Airén Wines. Several polyphenolic compounds have been identified in Airén white wines, belonging to different chemical families: hydroxycinnamic acid derivatives, benzoic acids, flavan-3-ols, and flavonols (Table 1). The benzoic acids and flavan-3-ols identified were the expected, well-known, compounds usually present in white musts and wines. Among the hydroxycinnamic acid derivatives, the two isomers (*trans* and *cis*) of coutaric acid and fertaric acid, as well as the reaction product of glutathione with oxidized caftaric acid, 2-*S*-glutathionylcaftaric acid (also known as grape reaction product (GRP)) were identified, together with *trans*-caftaric acid and *p*-coumaric acid. With regard to flavonols, the main glycosylated flavonols present in Airén musts and wines were the quercetin derivatives (3-glucuronide and 3-glucoside), together with the free aglycone quercetin in white wines. Also, the complete series of glycosylated kaempferol was identified (3-galactoside, 3-glucuronide, and 3-glucoside), together with the 3-glucoside of isorhamnetin and the free aglycone kaempferol.

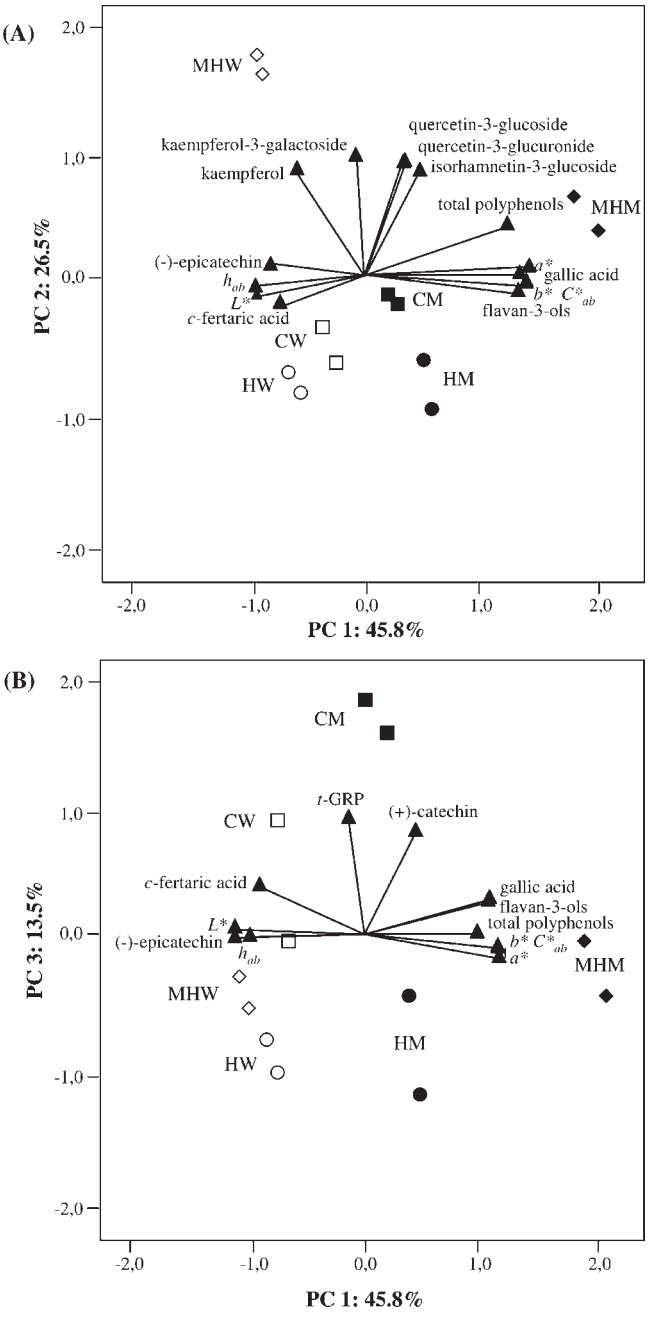

Figure 1. Plot of Airén white wine samples in the space defined by principal components PC1 versus PC2 (A) and PC1 versus PC3 (B): control (C), hyperoxygenated (H), and macerated−hyperoxygenated (MH) musts (M), control wines (CW) and wines from hyperoxygenated (HW) and macerated−hyperoxygenated (MHW) musts, with regard to polyphenolic compounds and color parameters.

With the aim of establishing statistical differences as a consequence of the hyperoxygenation and maceration technique prefermentative treatments, PCA was applied to the set of phenolic compounds and color characteristics data corresponding to control (C), hyperoxygenated (H), and macerated−hyperoxygenated

(MH) musts (M) and wines (W). The first three principal components (PCs) explained nearly the total accumulated variance (Figure 1). PC1 mainly allowed the distinction between musts and wines, regardless of the hyperoxygenation treatment and prefermentative maceration technique (Figure 1A). Airén musts (CM, HM, and MHM) were situated in the positive side of PC1 and had a higher yellow-brown tonality (higher values of the red and, especially, the yellow component of the color, a^* and b^*) and a lower luminosity (L^*) (Table 1). As well, the value of the chroma (C^*_{ab}) was high, especially after skin maceration (Table 1), according to the results obtained by Ricardo-da-Silva et al.[11] for Grenache blanc grapes. With regard to the phenolic compounds, Airén musts had higher contents of the global families of total polyphenols and flavan-3-ols and lesser contents of (−)-epicatechin and *cis*-fertaric acid (Figure 1A).

On the other hand, the must hyperoxygenation provoked changes in the phenolic composition and chromatic characteristics, which were much more marked in musts submitted to both treatments, maceration and hyperoxygenation (Figure 1B). This fact is in agreement with Romero-Cascales et al.[33] in Monastrell samples. PC3 permitted the separation of the musts and wines submitted to hyperoxygenation treatment from the untreated ones, regardless of the maceration technique, *trans*-GRP and (+)-catechin being the phenolic components most affected, with lower concentrations after the oxygen addition (Table 1). The space distribution of the musts and wines highlighted that the differences between control and hyperoxygenated samples were more significant in musts than in wines (Figure 1B). According to the Student−Newman−Keuls test (Table 1), the significantly higher concentrations of (−)-epicatechin, *cis*-GRP, and *trans*-coutaric acid of control musts also distinguished the nontreated musts (CM) from the musts with oxygen addition (HM and MHM), as well as in wines for the latter phenolic compound.

The prefermentative maceration technique previously applied to the hyperoxygenation provoked notable changes in the evolution of the hyperoxygenated musts. The maceration effect on the hyperoxygenated musts and wines resulted in a higher concentration of virtually all flavonols present in the grape skins, according to PC2 (Figure 1A). The Student−Newman−Keuls test also revealed significant differences of the macerated−hyperoxygenated musts and wines with regard to the global and individual flavonol contents (Table 1). Whereas the hyperoxygenated musts (HM) had a slight lower content of virtually all flavonols glycosides (Figure 1A; Table 1) and much more lower contents of *trans*-GRP and (+)-catechin (Figure 1B) in comparison with their respective control musts, macerated−hyperoxygenated musts (MHM) had a higher content of flavonols glycosides (extracted from the grape skins during the maceration, according to Ricardo-da-Silva et al.[11]), maintaining also the lower content of *trans*-GRP and (+)-catechin, in comparison with CM. This fact also is maintained in the respective wines.

Therefore, not only was the maceration effect predominant over hyperoxygenation technique, above all in musts, but also it had a synergic effect on the pursued effects with the oxygen addition. On the one hand, Airén wines derived from hyperoxygenated musts (HW) were similar to the untreated wines (CW), according to the variables more correlated with PC1 and PC2 (Figure 1A) (the former wines had only a slightly clearer color and a lower yellow color intensity). However, HW had a significantly lower content of (+)-catechin (PC3, Figure 1B), which permitted differentiation of the musts and wines submitted to hyperoxygenation, regardless to the maceration application (Table 1), being more resistant to browning. On the other hand, the joint application of prefermentative maceration and must hyperoxygenation permitted wines with even higher contents of glycosylated flavonols to be obtained, in agreement with Darias-Martín et al.[15] for the Listán Blanco variety elaborated with skin contact, being a positive fact from an antioxidant point of view.

Effects of Prefermentative Maceration and Must Hyperoxygenation on the Volatile Profile of Airén Wines. A total of 149 volatile compounds have been identified in Airén white musts and wines, belonging to different chemical families. Among the varietal volatile fractions, C_6 alcohols, terpenes, C_{13}-norisoprenoids, and benzenic compounds (including volatile phenols, aromatic alcohols, aldehydes, and shikimic acid derivatives) have been identified in Airén musts and wines. In addition, several volatile compounds formed as a consequence of alcoholic fermentation were also identified: fatty acids, lactones, and alcohols, as well as a large extent of ethyl esters of fatty acids and acetates (short-, medium-, and long-chain ethyl esters). To elucidate significant differences between them, Student−Newman−Keuls tests ($p < 0.05$) were applied to the set of data.

With regard to Airén musts, the most relevant hyperoxygenation effect was the significant increase in the concentration of virtually all volatile compounds (Table 2). In agreement with the results obtained by Cejudo-Bastante et al.[20] for Chardonnay musts, the content of the majority esters, alcohols, and acids increased as a consequence of oxygen addition, which can be very important for these musts' quality aroma (Table 2). The concentration of C_6 alcohols and aldehydes, such as 1-hexanol and hexenal, increases due to the oxidation conditions, which provoke the formation of these compounds from their precursors linoleic and linolenic acids.[34] Other alcohols (i.e., 2-phenylethanol), the synthesis of which is favored by the presence of oxygen,[35] showed the same behavior. The amount of terpenes did not greatly change as a consequence of the hyperoxygenation treatment; only a significant increase in the concentration of linalool was observed, contrary to the behavior of hotrienol.

Moreover, the maceration applied on Airén hyperoxygenated musts provoked a significant increase in the concentration of virtually all volatile compounds (above all, esters, alcohols, acids, and terpenes), in comparison to the application of only the hyperoxygenation treatment. This fact was in agreement with the results obtained by Marais et al.[10] and Salinas et al.[36] in macerated juices and wines. However, the content of compounds responsible for the herbaceous character, C_6 alcohols and aldehydes such as 1-hexanol, both isomers of 2-hexen-1-ol, and their respective aldehydes, and other compounds with great importance in the aroma quality (2-phenylethyl acetate, benzoic acid, and vanillin) decreased as a consequence of the prefermentative maceration[37] (Table 2). In addition, in comparison with CM, the contents of almost all volatile compounds were significantly higher after maceration of HM. This fact could provide an improvement of the varietal character, due to the higher content of the varietal compounds (C_6 alcohols, terpenes, and benzenic compounds).[20] The amount of isoamyl acetate and ethyl decanoate increased with the maceration of HM, significantly even more than the values found in CM. This fact was in agreement with Piñeiro et al.[37] and Álvarez et al.[38] in Palomino negro and Monastrell wines, respectively.

Table 2. Mean Values of Concentration (Micrograms per Liter) and Standard Deviations (n = 2) of Several Types of Volatile Compounds Belonging to Different Chemical Families (Esters, Alcohols, C_6 Alcohols, Acids, Terpenes, Benzenic Compounds, C_{13}-Norisoprenoids, and Aldehydes) Identified by GC-MS, in Control (C), Hyperoxygenated (H), and Macerated−Hyperoxygenated (MH) Airén White Musts (M)[a]

	CM	HM	MHM
esters			
isoamyl acetate	3.06 c ± 0.37	1.63 b ± 0.06	4.04 c ± 0.66
ethyl hexanoate	2.38 b ± 0.02	2.77 b ± 0.35	4.54 c ± 0.39
hexyl acetate	1.14 b ± 0.09	4.60 c ± 0.04	7.10 d ± 1.00
ethyl octanoate	8.02 ± 1.85	12.1 ± 0.52	12.3 ± 0.02
ethyl decanoate	2.81 c ± 0.05	2.07 b ± 0.35	4.58 d ± 0.07
diethyl succinate	1.07 ± 0.06	1.05 ± 0.03	1.27 ± 0.76
ethyl 9-decanoate	1.26 b ± 0.10	1.10 b ± 0.09	1.83 c ± 0.01
3,7-dimethyl-2,6-octadien-1-ol acetate	nd b	nd b	31.3 c ± 0.35
2-phenylethyl acetate	1.83 b ± 0.17	5.15 c ± 0.24	2.43 b ± 0.12
alcohols			
2-methyl-1-propanol	nd b	7.48 c ± 1.33	17.2 d ± 1.24
1-penten-3-ol	0.93 b ± 0.06	1.10 b ± 0.28	3.38 c ± 0.21
3-penten-2-ol	2.45 b ± 0.36	2.07 b ± 0.68	4.07 c ± 0.25
3-methyl-3-buten-1-ol	nd b	0.77 c ± 0.01	0.96 c ± 0.36
3-ethyl-2-pentanol	nd b	nd b	0.76 c ± 0.16
4-heptanol	0.75 ± 0.04	0.70 ± 0.03	0.82 ± 0.03
1,2-butanediol	nd b	nd b	4.55 c ± 0.40
2-hexadecanol	nd b	nd b	0.77 c ± 0.08
(*Z*)-2-penten-1-ol	1.93 b ± 0.05	2.20 b ± 0.14	4.78 c ± 0.56
2,3-butanediol	nd b	1.13 c ± 0.07	2.14 d ± 0.11
3-ethyl-2-heptanol	nd b	nd b	3.31 c ± 0.92
3-octanol	1.61 ± 0.43	1.51 ± 0.42	0.75 ± 0.02
1-octen-3-ol	0.39 bc ± 0.00	0.21 b ± 0.05	0.61 c ± 0.11
1-heptanol	0.30 b ± 0.02	0.52 b ± 0.02	0.88 c ± 0.15
3-hepten-1-ol	nd b	nd b	0.74 c ± 0.13
2-methoxy-1-butanol	nd b	nd b	2.13 c ± 0.49
2-methylthioethanol	nd	0.08 ± 0.04	0.15 ± 0.03
2-ethyl-1-hexanol	0.64 ± 0.17	0.69 ± 0.03	0.74 ± 0.18
3-methylthiopropanol	nd b	1.12 c ± 0.02	1.09 c ± 0.02
C_6 alcohols			
2-hexanol	2.51 b ± 0.23	2.33 b ± 0.05	3.20 c ± 0.02
1-hexanol	252 b ± 1.94	556 d ± 12.9	527 c ± 6.98
(*E*)-3-hexen-1-ol	1.29 b ± 0.21	2.33 c ± 0.20	4.98 d ± 0.53
(*Z*)-3-hexen1-ol	19.4 b ± 0.46	25.1 c ± 0.25	36.0 d ± 2.91
(*E*)-2-hexen-1-ol	60.0 d ± 6.86	31.3 c ± 0.62	13.4 b ± 0.79
(*Z*)-2-hexen-1-ol	0.78 b ± 0.06	3.70 d ± 0.10	1.70 c ± 0.04
acids			
isobutanoic acid	0.14 b ± 0.02	1.18 c ± 0.05	1.05 c ± 0.13
butanoic acid	0.09 b ± 0.02	0.19 b ± 0.01	0.50 c ± 0.12
isovaleric acid	0.45 b ± 0.01	1.85 b ± 0.10	3.76 c ± 0.84
hexanoic acid	11.3 b ± 1.60	27.0 c ± 0.79	29.1 c ± 0.47
2-ethylhexanoic acid	0.99 ± 0.03	1.69 ± 0.00	1.36 ± 0.40
(*E*)-3-hexenoic acid	3.94 ± 0.16	6.01 ± 0.63	5.71 ± 1.41
(*E*)-2-hexenoic acid	8.38 b ± 0.49	7.96 b ± 0.28	14.5 c ± 0.36
octanoic acid	8.40 b ± 2.82	18.3 b ± 0.88	36.7 c ± 7.54
nonanoic acid	8.18 c ± 0.71	6.21 b ± 0.23	7.66 c ± 0.23
decanoic acid	12.4 b ± 2.11	27.7 c ± 1.45	27.5 c ± 0.88
dodecanoic acid	0.99 b ± 0.03	6.37 c ± 0.65	8.55 c ± 2.19
mono-oxygenated terpenes			
linalool	0.84 c ± 0.12	1.97 d ± 0.20	tr b

Table 2. Continued

	CM	HM	MHM
hotrienol	0.31 d ± 0.04	tr b	0.18 c ± 0.03
α-terpineol	0.14 b ± 0.09	tr b	0.86 c ± 0.15
citronellol	0.28 b ± 0.19	nd b	1.46 c ± 0.24
nerol	nd b	tr b	1.28 c ± 0.42
geraniol	1.14 b ± 0.02	3.00 b ± 0.08	8.71 c ± 1.45
geranic acid	nd b	nd b	9.82 c ± 1.94
polyoxygenated terpenes			
cis-linalool oxide	nd b	tr b	0.11 c ± 0.02
2,6-dimethyl-3,7-octadiene-2,6-diol	1.72 ± 0.27	2.50 ± 0.84	2.20 ± 0.16
3,7-dimethyl-1,7-octadiene-3,6-diol	2.58 b ± 0.64	2.74 b ± 0.64	11.3 c ± 2.38
3,7-dimethyl-1,6-octadien-3-ol	nd b	nd b	0.37 c ± 0.09
epoxylinalool	0.48 b ± 0.27	0.87 bc ± 0.24	1.39 c ± 0.00
benzenic compounds			
benzaldehyde	3.28 ± 0.16	3.57 ± 0.36	4.01 ± 0.59
2-phenylacetaldehyde	tr b	0.45 b ± 0.45	2.91 c ± 0.17
ethyl benzaldehyde	1.14 ± 0.50	nd	1.08 ± 0.63
benzyl alcohol	34.3 ± 1.73	40.9 ± 0.58	51.3 ± 7.48
2-phenylethanol	43.7 b ± 3.99	153 c ± 16.0	214 d ± 25.9
4-vinylguaiacol	3.41 ± 0.73	4.71 ± 0.56	5.69 ± 0.75
isoeugenol	nd b	nd b	9.75 c ± 0.73
benzoic acid	63.5 c ± 6.34	49.7 c ± 3.05	23.1 b ± 4.02
4-hydroxy-3-methoxybenzoic acid	nd b	nd b	191 c ± 1.62
vanillin	8.26 b ± 1.17	41.2 d ± 0.74	27.3 c ± 2.76
acetovanillone	nd b	nd b	16.2 c ± 0.62
zingerone	nd	nd	0.12 ± 0.01
methyl vanillyl ether	nd b	nd b	4.25 c ± 0.22
C_{13}-norisoprenoids			
β-damascenone	nd b	nd b	0.12 c ± 0.01
3-oxo-α-ionol	nd b	nd b	1.75 c ± 0.37
aldehydes			
hexanal	0.42 c ± 0.01	3.30 d ± 0.19	tr b
2-hexenal	5.51 c ± 0.94	4.88 c ± 0.05	3.63 b ± 0.95

[a] Different letters in the same row denote significant differences according to Student−Newman−Keuls test ($p < 0.05$). nd, not detected; tr, traces.

Contrarily to the musts, the effect of the must hyperoxygenation on Airén wines had no clear tendency, deeply depending on each individual volatile compound (Table 3). This fact is in agreement with Baumes et al.[39] and Sánchez-Palomo et al.,[40] who affirmed that no direct relationship is possible to establish between the must and wine composition. However, in general, the concentration of short-chain fatty acid esters (such as ethyl butanoate and ethyl hexanoate) significantly decreased as a consequence of the oxygen addition, characterized by present fresh and fruity aromas. As well, the amount of long-chain fatty acid esters (ethyl glutarate and diethyl monosuccinate) tended to be equal or even also decreased. Again, a diminution was observed in several acids and benzenic compounds with great impact on wine flavor, such as butanoic acid, hexanoic acid, benzyl alcohol, and guaiacol. However, the content of the majority of alcohols increased in HW, in agreement with the results obtained by Artajona[7] and Schneider[16] in Parrellada, Muscat, Chardonnay, and Faberrebe wines derived from hyperoxygenated musts. This fact could be possibly due to the activation of yeast metabolism as a consequence of the initial oxygen addition. The evolution of C_6 alcohols, terpenes, furans, and lactones greatly depended on each individual volatile compound (Table 3).

The maceration applied to the Airén HM provoked positive effects on the concentration of several volatile compounds of the respective white wines. In general, the amount of short-chain fatty acid esters and mono- and polyoxygenated terpenes increased as a consequence of the skin maceration, in agreement with Esti et al.[41] for Italian wines, and even with a higher concentration in comparison with the values obtained in control wines (Table 3). That is the case of hexyl acetate, hotrienol, and citronellol due to the already higher content in the MHM. This fact could be of great importance in the fruity and floral aroma of the wines, which could reinforce the varietal character of the Airén wines.[20] In the same way, the content of the ethyl esters of lactic acid and succinic acid increased as a consequence of the prefermentative maceration, in agreement with the study carried out by Piñeiro et al.[37] in monovarietal wines. According to other authors,[36] the amount of another important flavor compound, 2-phenylethanol, significantly decreased in macerated wines, despite the increase observed when hyperoxygenated musts were macerated. However, the content of acids and C_6 alcohols decreased in MHW, in agreement with Piñeiro et al.,[37] with a lower content than is present in untreated wines. This fact could positively influence the acidity and herbaceous character of the

Table 3. Mean Values of Concentration (Micrograms per Liter) and Standard Deviations ($n = 2$) of Several Types of Volatile Compounds Belonging to Different Chemical Families (Esters, Alcohols, C_6 Alcohols, Acids, Terpenes, Benzenic Compounds, Furans, and Lactones) Identified by GC-MS, in Control (C), Hyperoxygenated (H), and Macerated−Hyperoxygenated (MH) Airén White Wines (W)[a]

	CW	HW	MHW
major volatile compounds			
acetaldehyde[b]	78.3 ± 5.08	76.0 ± 6.37	78.2 ± 14.5
ethyl acetate[b]	32.9 ± 3.90	32.3 ± 5.41	28.7 ± 3.93
methanol[b]	19.7 c ± 0.71	27.1 d ± 0.72	36.4 e ± 3.84
1-propanol[b]	16.7 ± 0.11	20.0 ± 0.81	16.9 ± 2.61
isobutanol[b]	30.4 d ± 0.04	25.3 cd ± 1.32	21.2 c ± 2.69
2-methyl-1-butanol[b]	63.0 ± 19.1	77.0 ± 2.86	67.7 ± 1.27
3-methyl-1-butanol[b]	152 d ± 1.60	141 d ± 3.96	114 c ± 7.50
minor volatile compounds			
esters			
ethyl butanoate	93.6 e ± 1.53	60.9 c ± 1.27	71.0 d ± 3.19
ethyl isovalerate	2.38 d ± 0.08	1.47 c ± 0.25	2.91 d ± 0.23
ethyl pentanoate	2.25 ± 0.59	2.01 ± 0.23	1.41 ± 0.20
isoamyl acetate[b]	1.33 d ± 0.27	0.62 c ± 0.12	0.55 c ± 0.13
ethyl hexanoate	768 e ± 1.24	587 d ± 19.4	545 c ± 0.28
hexyl acetate	71.6 c ± 0.52	90.4 cd ± 9.71	100 d ± 3.25
ethyl pyruvate	3.07 e ± 0.03	1.06 c ± 0.47	2.11 d ± 0.53
ethyl 3-hexanoate	3.87 ± 0.74	4.84 ± 0.46	4.10 ± 0.32
3-hexen-1-ol acetate	4.60 d ± 0.20	4.02 c ± 0.10	5.18 e ± 0.01
ethyl heptanoate	3.52 d ± 1.04	2.88 d ± 0.32	1.87 c ± 0.49
ethyl lactate	8.21 c ± 0.33	23.8 d ± 1.23	27.1 e ± 0.56
methyl octanoate	4.43 c ± 0.49	3.92 c ± 0.05	5.75 d ± 0.13
ethyl 2-hydroxy-3-methylbutanoate	0.89 ± 0.32	1.41 ± 0.62	0.87 ± 0.10
ethyl octanoate[b]	2.52 d ± 0.01	1.64 c ± 0.03	1.74 c ± 0.12
pentyl hexanoate	6.91 e ± 0.32	5.27 d ± 0.48	3.61 c ± 0.21
methyl 2-hydroxy-4-methylpentanoate	1.56 ± 0.09	1.18 ± 0.27	1.14 ± 0.15
ethyl nonanoate	3.64 e ± 0.02	2.51 c ± 0.12	3.21 d ± 0.00
ethyl 4-methyl-2-hydroxypentanoate	7.82 ± 0.91	8.94 ± 0.83	8.53 ± 0.33
1,2-petanediol diacetate	tr c	1.34 d ± 0.43	1.07 d ± 0.09
pentyl 2-hydroxypropanoate	3.37 c ± 2.52	20.1 d ± 0.79	20.6 d ± 1.24
methyl decanoate	1.48 ± 0.02	1.83 ± 0.24	2.56 ± 0.53
ethyl decanoate	851 d ± 29.1	644 c ± 30.8	807 d ± 3.50
ethyl methyl butanedioate	tr c	1.00 d ± 0.17	0.91 d ± 0.10
3-methylbutyl octanoate	16.4 ± 1.41	12.9 ± 2.06	13.0 ± 0.57
1,3-propanediol diacetate	9.71 ± 0.25	8.31 ± 2.01	6.26 ± 0.13
diethyl succinate	252 c ± 3.96	256 c ± 16.8	329 d ± 21.7
ethyl 9-decanoate	574 c ± 41.9	568 c ± 7.76	2560 d ± 47.9
methyl 4-methyloctanoate	1.81 ± 0.75	0.94 ± 0.18	1.09 ± 0.05
2-phyenylethyl acetate	715 e ± 25.1	493 d ± 6.02	437 c ± 3.41
ethyl laurate	31.3 ± 1.69	25.1 ± 2.82	26.9 ± 1.13
1,3-propanodiol acetate	36.1 c ± 3.99	36.7 c ± 1.46	53.5 d ± 1.26
ethyl 3-hydroxyhexanoate	21.5 d ± 0.01	20.6 d ± 2.67	15.6 c ± 0.77
diethyl malate	49.1 d ± 1.51	28.7 c ± 2.00	25.9 c ± 1.46
ethyl 3-hydroxydodecanoate	14.6 c ± 0.09	12.3 c ± 1.45	18.4 d ± 1.02
ethyl glutarate	42.9 d ± 1.55	45.1 d ± 2.17	31.6 c ± 0.96
diethyl monosuccinate[b]	3.13 d ± 0.21	2.49 c ± 0.03	2.75 cd ± 0.00
2-phenylethyl acetate	740 d ± 55.6	637 d ± 35.9	389 c ± 13.2
ethyl 3-methylthiopropanoate	0.23 ± 0.04	0.22 ± 0.05	0.26 ± 0.01
alcohols			
2-methyl-1-propanol	234 d ± 2.77	119 c ± 8.99	91.4 c ± 2.95
1-butanol	13.1 d ± 0.21	13.2 d ± 0.44	10.6 c ± 0.29

Table 3. Continued

	CW	HW	MHW
1-pentanol	3.42 c ± 0.08	3.50 c ± 0.38	7.34 d ± 0.43
3-methyl-3-buten-1-ol	1.33 d ± 0.02	1.22 d ± 0.07	1.00 c ± 0.06
1-hepten-4-ol	nd c	nd c	1.04 d ± 0.22
4-methyl-1-pentanol	2.65 c ± 0.22	12.8 e ± 0.20	11.9 d ± 0.30
(*Z*)-2-penten-1-ol	0.85 c ± 0.11	1.27 d ± 0.14	1.66 e ± 0.03
3-methyl-1-pentanol	47.9 d ± 0.36	47.9 d ± 0.64	31.5 c ± 0.38
3-ethoxy-1-propanol	1.30 c ± 0.37	2.12 d ± 0.07	1.20 c ± 0.03
3-octanol	0.97 ± 0.34	1.59 ± 0.09	1.75 ± 0.02
1-octen-3-ol	tr c	0.30 d ± 0.01	0.32 d ± 0.11
1-heptanol	7.61 d ± 0.51	8.15 d ± 0.90	1.61 c ± 0.10
butadienol	tr c	2.28 d ± 0.26	2.18 d ± 0.06
2-ethyl-1-hexanol	1.07 ± 0.36	1.18 ± 0.10	1.01 ± 0.01
1-octanol	4.19 d ± 0.01	1.64 c ± 0.91	3.02 cd ± 0.04
3-methylthiopropanol	15.1 ± 0.57	16.7 ± 4.04	17.4 ± 3.13
C_6 alcohols			
1-hexanol	233 c ± 11.4	382 d ± 7.84	383 d ± 2.34
(*E*)-3-hexen-1-ol	13.6 d ± 0.95	5.51 c ± 0.44	7.32 c ± 0.34
(*Z*)-3-hexen1-ol	62.6 d ± 0.55	24.2 c ± 0.49	23.4 c ± 1.71
(*Z*)-2-hexen-1-ol	1.02 c ± 0.18	2.77 e ± 0.01	1.48 d ± 0.01
acids			
isobutanoic acid	9.00 d ± 0.08	8.33 d ± 0.19	7.45 c ± 0.42
butanoic acid	9.68 d ± 0.15	9.01 cd ± 1.01	8.45 c ± 0.81
isovaleric acid	328 e ± 6.57	225 d ± 15.1	151 c ± 1.93
hexanoic acid	941 d ± 10.4	655 c ± 46.9	637 c ± 57.8
(*E*)-3-hexenoic acid	20.7 ± 0.95	21.9 ± 2.54	19.6 ± 0.46
(*E*)-2-hexenoic acid	10.4 c ± 2.15	20.9 d ± 1.03	10.0 c ± 1.32
octanoic acid[b]	2.61 e ± 0.00	1.49 d ± 0.00	1.43 c ± 0.00
decanoic acid[b]	1.08 d ± 0.00	0.73 c ± 0.00	0.72 c ± 0.00
dodecanoic acid	124 d ± 6.70	98.0 c ± 2.44	78.5 c ± 9.81
bis(2-ethylhexyl)hexanedioic acid	nd c	nd c	109 d ± 10.9
3-methylthiopropanoic acid	0.48 ± 0.20	0.49 ± 0.11	0.96 ± 0.03
mono-oxygenated terpenes			
linalool	4.84 ± 0.21	4.33 ± 0.73	3.43 ± 0.35
hotrienol	tr	1.00 ± 0.51	1.20 ± 0.23
α-terpineol	1.89 d ± 0.22	1.20 c ± 0.07	1.52 cd ± 0.02
citronellol	tr c	1.27 d ± 0.24	2.59 e ± 0.12
geranic acid	40.2 d ± 2.63	25.6 c ± 1.47	24.8 c ± 0.35
polyoxygenated terpenes			
cis-linalool oxide	tr	tr c	0.59 d ± 0.04
2,7-dimethyl-4,5-octanediol	5.99 d ± 0.22	5.08 c ± 0.15	9.06 e ± 0.21
2,6-dimethyl-3,7-octadiene-2,6-diol	9.09 c ± 0.42	15.8 ± 1.95	14.8 d ± 0.34
3,7-dimethyl-1-octene-3,7-diol	tr c	tr c	6.66 d ± 1.02
3,7-dimethyl-1,7-octadiene-3,6-diol	tr c	5.50 d ± 1.70	12.2 e ± 2.10
benzenic compounds			
1,4-dimethylbenzene	4.28 ± 1.70	2.46 ± 0.43	2.35 ± 0.23
benzaldehyde	2.43 c ± 0.35	2.46 c ± 0.34	8.98 d ± 0.25
acetophenone	6.52 d ± 0.05	0.87 c ± 0.67	1.45 c ± 0.37
ethyl phenylacetate	6.79 ± 0.37	4.02 ± 1.36	6.85 ± 0.24
guaiacol	7.67 d ± 0.54	4.07 c ± 0.32	3.68 c ± 0.25
benzyl alcohol	51.4 d ± 1.74	43.2 c ± 2.46	67.0 e ± 1.37
2-phenylethanol[b]	13.4 d ± 0.90	7.25 c ± 0.01	6.27 c ± 0.12
benzotiazol	66.8 e ± 1.05	41.0 d ± 1.01	23.6 c ± 2.11
ethyl 2-phenylbenzeneacetate	tr c	tr c	4.64 d ± 0.23
4-vinylguaiacol	138 d ± 10.8	45.8 c ± 0.50	42.7 c ± 1.43

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Table 3. Continued

	CW	HW	MHW
2,3-dihydrobenzofuran	122 d ± 33.5	nd c	73.1 d ± 18.2
benzoic acid	49.9 ± 4.79	53.8 ± 1.50	56.5 ± 2.93
ethyl benzenepropanoate	nd c	20.8 e ± 0.06	12.6 d ± 1.31
phenylacetic acid	32.2 e ± 2.66	25.4 d ± 0.50	20.3 c ± 0.58
vanillin	tr c	3.96 d ± 0.43	4.51 d ± 0.65
4-methoxyphenol[b]	6.05 d ± 0.01	1.17 c ± 0.01	1.48 c ± 0.21
zingerone	nd c	1.16 d ± 0.35	1.19 d ± 0.08
methyl vanillyl ether	nd c	7.51 d ± 0.63	29.5 e ± 1.67
furans			
furfural	3.09 d ± 0.09	1.44 c ± 0.39	1.86 c ± 0.14
5-ethoxymethylfurfural	19.2 c ± 1.55	36.8 d ± 2.40	35.7 d ± 1.35
ethyl furoate	3.00 d ± 0.58	2.47 d ± 0.03	1.14 c ± 0.12
lactones			
γ-butyrolactone	0.21 ± 0.00	0.22 ± 0.06	0.19 ± 0.02
γ-caprolactone	2.77 ± 0.74	1.65 ± 0.18	1.73 ± 0.00
γ-nonalactone	3.83 ± 0.90	5.51 ± 0.16	5.99 ± 0.26
pantolactone	6.62 c ± 1.82	10.3 cd ± 0.79	12.8 d ± 0.84
δ-decalactone	11.1 ± 1.09	18.0 ± 1.04	8.67 ± 0.17
γ-undecalactone	216 e ± 12.6	153 d ± 0.87	126 c ± 2.89
5-ethoxydihydro-2(3*H*)furanone	5.90 d ± 1.12	6.51 d ± 1.11	4.05 c ± 0.15
miscellaneous			
β-damascenone	11.2 ± 0.39	10.2 ± 0.92	12.5 ± 0.59
6-methyl-5-hepten-2-one	tr c	0.15 d ± 0.05	0.14 d ± 0.01
N-ethyl-*N*-phenylacetamide	tr c	13.0 d ± 5.34	12.5 d ± 0.48
2-methyldihydro-3(9*H*)-thiophenone	5.81 c ± 0.82	6.49 c ± 0.65	10.2 d ± 0.79
2-methyltetrahydrothiophen-3-one	6.73 d ± 0.20	5.80 c ± 0.15	5.54 c ± 0.33
2,5-bis(1,1-dimethylethyl)thiophene	4.83 e ± 0.43	3.17 d ± 0.03	2.09 c ± 0.16

[a] Different letters in the same row denote significant differences according to Student−Newman−Keuls test ($p < 0.05$). nd, not detected; tr, traces. [b] Milligrams per liter.

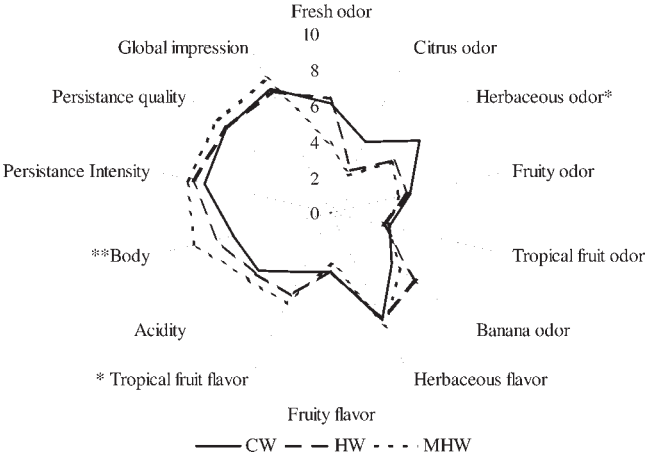

Figure 2. Olfactive and gustative attribute mean scores of Airén control wine (CW) and wine from hyperoxygenated must (HW) and from macerated and hyperoxygenated must (MHW). Significant differences according to the Student−Newman−Keuls test ($p < 0.05$) are indicated between CW and both HW and MHW (∗), on the one hand, and between MWH and both CW and HW (∗∗), on the other hand.

final wines. With regard to alcohols, benzenic compounds, furans, and lactones, each volatile compound behaved differently as a consequence of the skin maceration.

Descriptive Sensory Analyses of Airén White Wines. Figure 2 shows the attributes selected in descriptive sensory analysis to describe the samples, together with the mean scores for each one. With the aim of elucidating significant differences among control wines (CW), wines derived from hyperoxygenated (HW), and macerated−hyperoxygenated musts (MHW), not previously described in conjunction from a sensory point of view, the Student−Newman−Keuls test was applied to the set of data. On the one hand, with regard to the olfactory analysis, although without significant differences, oxygen addition provoked a decrease of herbaceous and fresh odor, after subsequent maceration technique, in agreement with Schneider[19] for oxygenated Riesling white wines. This fact could be probably due to the lower concentration of acids and C_6 alcohols present in these wines (Table 3).[26] In addition, the citrus attribute decreased in HW, which could be related to the lower amount of short-chain fatty acids esters and terpenes in these wines.[42] Despite the lower content of isoamyl acetate in oxygen-treated samples, no significant differences in banana aroma were found. According to Campo et al.,[43] the appreciation of any sensory attribute could change depending on the amount of other volatile compounds it is correlated with. These authors demonstrate that high amounts of linalool could mask the perception of isoamyl acetate. No significant differences were found as a consequence of oxygen addition with regard to the fruity and tropical fruit odor. The flavor of tropical fruit was significantly higher in MHW and could

be related to the higher content of short-chain fatty acid esters and mono- and polyoxygenated terpenes previously mentioned.

On the other hand, with regard to the gustatory analysis, significant and positive differences were found in tropical fruit flavor and body after oxygenation, even with high values taking into account the joint maceration technique. This could be due to the increase in the amount of the majority of fatty acid ethyl esters, acetates, and terpenes as a consequence of skin maceration, the content of which was even higher than those found in CW. Consequently, Airén HWs were positively valued, in agreement with the results obtained by Cheynier et al.[5] and Cejudo-Bastante et al.[20] for oxygen-treated Chardonnay wines, and even more with the joint use of prefermentative maceration.

In conclusion, the joint maceration and hyperoxygenation techniques provided Airén wines with several positive effects: the benefits of the hyperoxygenation technique (the lower content of the aforementioned polyphenolic compounds) and the advantages of the prefermentative maceration (such as the increase in the content of antioxidant flavonols, the higher content of short-chain fatty acid esters and terpenes, and the lower content of C_6 alcohols). Moreover, and closely connected to the aforementioned results, the global impression of Airén wines derived from macerated−hyperoxygenated musts was positively valued, with improved tropical fruit and herbaceous notes as well as body of the final wines.

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REFERENCES

(1) Castro, R.; García-Barroso, C. Behavior of a hyperoxidized must during biological ageing of Fino Sherry wine. *Am. J. Enol. Vitic.* **2000**, *51*, 98–102.

(2) Singleton, V. L.; Salgues, M.; Zaya, J.; Trousdale, E. Caftaric acid disappearance and conversion to products of enzymic oxidation in grape must and wine. *Am. J. Enol. Vitic.* **1985**, *36*, 50–56.

(3) Cheynier, V.; Trousdale, E. K.; Singleton, V. L.; Salgues, M. J.; Wylde, R. Characterization of 2-*S*-glutathionylcaftaric acid and its hydrolysis in relation to grape wines. *J. Agric. Food Chem.* **1986**, *34*, 217–221.

(4) Hosry, L. E.; Auezova, L.; Sakr, A.; Hajj-Moussa, E. Browning susceptibility of white wine and antioxidant effect of glutathione. *Int. J. Food Sci. Technol.* **2009**, *44*, 2459–2463.

(5) Cheynier, V.; Souquet, J. M.; Samson, A.; Moutounet, M. Hyperoxidation: influence of various oxygen supply levels on oxidation kinetics of phenolic compounds and wine quality. *Vitis* **1991**, *30*, 107–115.

(6) Cheynier, V.; Rigaud, J.; Souquet, J. M.; Barillere, J. M.; Moutounet, M. Effect of pomace contact and hiperoxidation on the phenolic composition and quality of Grenache and Chardonnay wines. *Am. J. Enol. Vitic.* **1989**, *40*, 36–42.

(7) Artajona, J.; Bobet, R.; Marco, J.; Sabat, F.; Torres, M. A. Expérience d'hyperoxygénation au Penedes. *Rev. Fr. Oenol.* **1990**, *124*, 65–67.

(8) Singleton, V. L.; Zaya, J.; Trousdale, E. White table wine quality and polyphenol composition as affected by must SO_2 content and pomace contact time. *Am. J. Enol. Vitic.* **1980**, *31*, 14–20.

(9) Dubourdieu, D.; Lavigne, V. Incidence de l'hyperoxygénation sur la composition chimique et les qualités organoleptiques des vins blancs secs du Bordelais. *Rev. Fr. Oenol.* **1990**, *124*, 58–61.

(10) Marais, J.; Rapp, A. Effect of skin-contact time and temperature on juice and wine quality. *S. Afr. J. Enol. Vitic.* **1988**, *9*, 22–30.

(11) Ricardo-da-Silva, J. M.; Cheynier, V.; Samsom, A.; Bourzeix, M. Effect of pomace contact, carbonic maceration, and hyperoxidation on the procyanidin composition of Grenache blanc wines. *Am. J. Enol. Vitic.* **1993**, *44*, 168–172.

(12) Radeka, S.; Herjavec, S.; Persuric, D.; Lukic, I.; Sladonja, B. Effect of different maceration treatments on free and bound varietal aroma compounds in wine of *Vitis vinifera* L. cv. Malvazija istarska bijela. *Food Technol. Biotechnol.* **2008**, *46*, 86–92.

(13) Hernanz, D.; Recamales, A. F.; González-Miret, M. L.; Gómez-Míguez, M. J.; Vicario, I. S.; Heredia, F. J. Phenolic composition of white wines with a prefermentative maceration at experimental and industrial scale. *J. Food Eng.* **2007**, *80*, 327–335.

(14) Guerzoni, M. E.; Zironi, R.; Intrieri, C.; Magnanini, E. Stabilization of white wine by early hyperoxidation of must. *Food Technol. Aust.* **1981**, *33*, 442–446.

(15) Darias-Martín, J. J.; Rodríguez, O.; Díaz, E.; Lamuela-Raventós, R. M. Effect of skin contact on the antioxidant phenolics in white wines. *Food Chem.* **2000**, *71*, 483–487.

(16) Schneider, V. Primäraroma. *Die Winzer-Zeitung* **1994**, *10*, 24–25.

(17) Guedes de Pinho, P.; Bertrand, A.; Guillou, I. Influence de l'hyperoxygénation des moûts sur la composition chimiques et sensorielle de vins blancs. *Rev. Fr. Oenol.* **1994**, *145*, 9–17.

(18) Cordonnier, R. E.; Bayonove, C. L. Etude de la phase préfermantaire de la vinification: extraction et formation de certains composés de l'arôme, cas des terpénols, des aldéhydes et des alcools en C6. *Connaiss. Vigne Vin* **1982**, *15*, 269–286.

(19) Schneider, V. Einfluß von maischestandzeit und mostoxidation auf die sensorik von Riesling. *Die Winzer-Zeitung* **1996**, *7*, 22–25.

(20) Cejudo-Bastante, M. J.; Hermosín-Gutiérrez, I.; Castro-Vázquez, L.; Pérez-Coello, M. S. Hyper-oxygenation and bottle storage of Chardonnay white wines: effects on color-related phenolics, volatile composition and sensory characteristics. *J. Agric. Food Chem.* **2011**, *59*, 4171–4182.

(21) OIV International Oenological Codex. *Recueil des Méthodes Internationales d'Analyse des Vins et des Moûts*; Office International de la Vigne et du Vin: Paris, France, 2006.

(22) Mazza, G.; Fukumoto, L.; Delaquis, P.; Girard, B.; Ewert, B. Anthocyanins, phenolics and color of Cabernet Franc, Merlot, and Pinot Noir wines from British Columbia. *J. Agric. Food Chem.* **1999**, *47*, 4009–4017.

(23) Amerine, M. A.; Ough, C. S. *Methods for Analysis of Musts and Wines*; Wiley: New York, 1980.

(24) Pérez-Caballero, V.; Ayala, F.; Echávarri, J. F.; Negueruela, A. I. Proposal for a new standard OIV method for determination of chromatic characteristics of wine. *Am. J. Enol. Vitic.* **2003**, *54*, 59–62.

(25) Cejudo Bastante, M. J.; Pérez Coello, M. S.; Hermosín Gutiérrez, I. Effect of wine micro-oxygenation treatment and storage period on color-related phenolic, volatile composition and sensory characteristics. *LWT−Food Sci. Technol.* **2011**, *44*, 866–874.

(26) Castillo-Muñoz, N.; Gómez-Alonso, S.; García-Romero, E.; Hermosín-Gutiérrez, I. Flavonol profiles of *Vitis vinifera* red grapes and their single-cultivar wines. *J. Agric. Food Chem.* **2007**, *55*, 992–1002.

(27) Castillo-Muñoz, N.; Gómez-Alonso, S.; García-Romero, E.; Gómez, M. V.; Velders, A. H.; Hermosín-Gutiérrez, I. Flavonol 3-*O*-glycosides series of *Vitis vinifera* cv. Petit Verdot red wine grapes. *J. Agric. Food Chem.* **2009**, *57*, 209–219.

(28) Sánchez-Paomo, E.; Alañón, E.; Díaz-Maroto, M. C.; González-Viñas, M. A.; Pérez-Coello, M. S. Comparison of extraction methods for volatile compounds of Muscat grape juice. *Talanta* **2009**, *79*, 871–876.

(29) Sánchez-Palomo, E.; González-Viñas, M. A.; Díaz-Maroto, M. C.; Soriano-Pérez, A.; Pérez-Coello, M. S. Aroma potential of Albillo wines and effect of skin-contact treatment. *Food Chem.* **2007**, *103*, 631–640.

(30) ISO Guide for the installation of a chamber for sensory analysis. ISO 8589-1998, Group E, 1998.

(31) ISO Sensory Analysis. Apparatus wine-tasting glass. ISO 3591-1997, Group B, 3 pp, 1997.

(32) Reglamento (CE) n° 606/2009 de la Comisión, de 10 de julio de 2009. *Diario Oficial* **2009**, *L 193*, 0001−0059.

(33) Romero-Cascales, I.; Fernández-Fernández, J. I.; López Roca, J. M.; Gómez-Plaza, E. The maceration process during winemaking extraction of anthocyanins from grape skin into wine. *Eur. Food Res. Technol.* **2005**, *221*, 163–167.

(34) Oliveira, J. M.; Faria, M.; Sá, F.; Barros, F.; Araújo, I. M. C_6-alcohols as varietal markers for assessment of wine origin. *Anal. Chim. Acta* **2006**, *563*, 300–309.

(35) Jackson, R. S. Chemical constituents of grapes and wine. In *Wine Science*; Charalambous, G., Ed.; Elsevier: Ontario, Canada, 2008; pp 270−331.

(36) Salinas, M. R.; Garijo, J.; Pardo, F.; Zalacaín, A.; Alonso, G. L. Influence of prefermentative maceration temperature on the colourcolor and the phenolic and volatile composition of rosé wines. *J. Sci. Food Agric.* **2005**, *85*, 1527–1536.

(37) Piñeiro, Z.; Natera, R.; Castro, R.; Palma, M.; Puertas, B.; Barroso, C. Characterisation of volatile fraction of monovarietal wines: influence of winemaking practices. *Anal. Chim. Acta* **2006**, *563*, 165–172.

(38) Álvarez, I.; Aleixandre, J. L.; García, M. J.; Lizama, V. Impact of prefermentative maceration on the phenolic and volatile compounds in Monastrell red wines. *Anal. Chim. Acta* **2006**, *563*, 109–115.

(39) Baumes, R.; Bayonove, C.; Cordonnier, R.; Torres, P.; Seguin, A. Incidence de la macération peliculaire sur la composante aromatique des vins doux naturels de Muscat. *Rev. Fr. Oenol.* **1989**, *116*, 6–11.

(40) Sánchez-Palomo, E.; Díaz-Maroto Hidalgo, M. C.; González-Viñas, M. A.; Pérez-Coello, M. S. Aroma enhancement in wines from different grape varieties using exogenous glycosidases. *Food Chem.* **2005**, *92*, 627–635.

(41) Esti, M.; Tamborra, P. Influence of winemaking techniques on aroma precursors. *Anal. Chim. Acta* **2006**, *563*, 173–179.

(42) Etiévant, P. X. Wine. In *Volatile Compounds of Food and Beverages*; Maarse, H., Ed.; Dekker: New York, 1991; pp 483−546.

(43) Campo, E. V.; Ferreiro, V.; Escudero, A.; Cacho, J. Prediction of the wine sensory properties related to grape variety from dynamic-headspace gas chromatography-olfactometry data. *J. Agric. Food Chem.* **2005**, *53*, 5682–5690.