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An Assessment of the Role Played by Some Oxidation-Related Aldehydes in Wine Aroma

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The levels of important oxidation-related aldehydes, such as methional, phenylacetaldehyde, (*E*)-2-hexenal, (*E*)-2-heptenal, (*E*)-2-octenal, (*E*)-2-nonenal, methylpropanal, 2-methylbutanal, and 3-methylbutanal, were determined in 41 different wines belonging to different types (young whites and reds, natural sparkling wines, oxidized young whites and reds, Sherry, aged red wines, Port wines). Except (*E*)-2-hexenal and (*E*)-2-heptenal, all of them could be found at levels above threshold. Different compositional patterns were identified: Sherry wines have large amounts of branched aldehydes but not of (*E*)-2-alkenals, wines exposed to oxygen can have large amounts of (*E*)-2-alkenals but not of branched aldehydes, while aged wine and Port have relatively large amounts of both classes of compounds. Different sensory tests confirmed the active sensory role of these compounds and revealed the existence of interactions (additive or synergic) between them and with other wine volatiles. (*E*)-2-Alkenals are related to flavor deterioration, while branched aldehydes enhance dried fruit notes and mask the negative role of (*E*)-2-alkenals.

KEYWORDS: Wine; aroma; flavor; oxidation; aging; aldehydes; carbonyls; (*E*)-2-alkenals; off-flavors

INTRODUCTION

Many volatile aldehydes have remarkable odor properties (*1*), and, as this kind of compound can be formed from alcohols and other precursors by oxidation processes, the changes in aroma properties linked to oxidation are very often related to the formation of aldehydes (*2*). In the case of wine, the importance of these compounds in flavor development and deterioration was suggested a long time ago (*3*). However, and although a large number of aldehydes have been reported to be normal constituents of the volatile fraction of wines (*4*), the exact role of aldehydes in wine aroma is not known, mainly because of the lack of analytical data and because of the absence of systematic sensory studies. Classically, most of the aroma changes due to oxygen were attributed to the formation of acetaldehyde and of its acetals (*5*, *6*). Although this may be partly true in the case of Sherry wines aged under the Solera system (*7*, *8*), this is not the case of regular table wines (*9*). Gas chromatographic-olfactometric (GC-O) studies carried out on wines undergoing oxidation revealed the presence of strong-smelling aldehydes, particularly methional (*10*) and phenylacetaldehyde (*11*). The sensory role of methional in the development of characteristic oxidation notes of white wine was further demonstrated (*12*, *13*), while different studies confirmed that phenylacetaldehyde can be present at concentrations above threshold and that it is correlated with oxidation-related sensory notes (*13*−*15*). Other studies have suggested the presence of some (*E*)-2-alkenals in oxidized wine (*16*−*18*), but their origin and sensory role are not clear yet. One of these compounds, (*E*)-2-nonenal, has been identified as the cause of a "sawdust-like" off-flavor in wines aged in green oak (*19*). Finally, although the large amounts of isobutanol, 2-methylbutanol, and isoamylalcohol naturally occurring in the wine would suggest that the corresponding aldehydes should be easily found in oxidized wine, there are no conclusive studies about their presence or sensory significance.

The main goal of the present work is to determine the levels of some aldehydes with potential sensory significance of wine, and to evaluate their sensory role by means of different sensory tests.

MATERIALS AND METHODS

Reagents, Samples, and Standards. Methylpropanal 99%, 2-methylbutanal 95%, 3-methylbutanal 97%, (*E*)-2-hexenal 98%, (*E*)-2-octenal 94%, (*E*)-2-nonenal 97%, methional (3-methylpropanal) 99%, and phenylacetaldehyde 90% were purchased from Aldrich-España (Madrid, Spain). (*E*)-2-Heptenal 98%, 2-octanol, used as internal standard, and *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) (≥99%) were purchased from Fluka-España (Madrid, Spain).

Dichloromethane HPLC-quality was from Fisher Chemical (Leicester, UK), methanol HPLC-grade was from Merck (Darmstadt, Germany), pentane for GC ≥99% was from Fluka, ethanol absolute, tartaric acid, and sodium hydrogen carbonate all ARG quality were from Panreac (Barcelona, Spain), and sulfuric acid (95−97%, synthesis grade) was from Scharlau (Barcelona, Spain). Pure water was obtained from a Milli-Q purification system (Millipore, Bedford, USA). LiChrolut EN resins (styrene-vinylbenzene, divinylbenzene polymer) prepacked in 200 mg cartridges (3 mL total volume) were obtained from Merck.

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Table 1. Sample Types, Codes, and Some Characteristics of the Samples Considered in the Study

type-trademark	code	origin	grape[a]	aging
Young Red				
Valdemadera	R1	Cariñena	G	none
Veranza	R2	T. Cinca	CS	none
Castillo Paniza	R3	Cariñena	G–CS	none
Domaine de Camparnaud	R4	Côtes de Provence	C	none
Red, Short Aging				
Viñas Vero	AR1	Somontano	T–CS	3–12 m in oak, 1 year bottle
Serra	AR2	R. Duero	T	3–12 m in oak, 1 year bottle
Viña Salceda	AR3	Rioja	T–G	3–12 m in oak, 1 year bottle
Borsao	AR4	Borja	G–CS	3–12 m in oak, 1 year bottle
Viñas Vero	AR5	Somontano	CS	3–12 m in oak, 1 year bottle
T. Pesquera	AR6	R. Duero	T	3–12 m in oak, 1 year bottle
Red, Long Aging				
Muga	GR1	Rioja	T–G	>24 m in oak, >2 years bottle
Viña Salceda	GR2	Rioja	T–G	>24 m in oak, >2 years bottle
Viñamayor	GR3	R. Duero	T	>24 m in oak, >2 years bottle
Red Port Wines				
Pousada-Tawny	P1	Oporto	na	>3 years in oak casks
Pousada-Ruby	P2	Oporto	na	>3 years in oak casks
Ramos-Pinto-Tawny	P3	Oporto	na	>3 years in oak casks
Oxidized Young Reds				
Veranza	OR1	T. Cinca	CS	4 days under air
Castillo Paniza	OR2	Cariñena	G	30 days under air
Valdemadera	OR3	Cariñena	G, T	30 days under air
Domaine de Camparnaud	OR4	Côtes de Provence	C	30 days under air
Pirineos	OR5	Somontano	CS	30 days under air
Young White				
Viñas Mar	W1	Penedés	X–P	none
Veranza	W2	T.Cinca	M	none
Viñas Vero	W3	Somontano	M–Ch	none
Viñas Vero	W4	Somontano	Ch	none
Oxidized Young Whites				
Veranza	OW1	T.Cinca	M	4 days under air
Viñas Mar	OW2	Penedés	X–P	4 days under air
Aura	OW3	Rueda	V	30 days under air
Pirineos	OW4	Somontano	Ch	30 days under air
Viñas Vero	OW5	Somontano	Ch	30 days under air
Natural Sparkling				
Rondel	C1	Cava	X–M–P	>9 months with yeast in bottle
Non Plus Ultra	C2	Cava	X–M–P	>21 months with yeast in bottle
Anna Codorniu	C3	Cava	X–M–P	>21 months with yeast in bottle
Jaume Serra	C4	Cava	X–M–P	>21 months with yeast in bottle
Vernier	C5	Champagne	PN	>21 months with yeast in bottle
Mum	C6	Champagne	PN	>21 months with yeast in bottle
Sherry, Fino Type				
La Ina	S1	Jerez	Pa	>3 years under yeast flor in cask (Solera)
Tio Pepe	S2	Jerez	Pa	>3 years under yeast flor in cask
Quintana	S3	Jerez	Pa	>3 years under yeast flor in cask
La Guita	S4	Jerez	Pa	>3 years under yeast flor in cask
Solear	S5	Jerez	Pa	>3 years under yeast flor in cask

[a] G, Garnacha; CS, Cabernet Sauvignon; C, Carignan; T, Tempranillo; X, Xarel-lo; P, Parellada; M, Macabeo; Ch, Chardonnay; V, Verdejo; PN, Pinot Noir; Pa, Palomino; na, not available.

All of the wines used in the study were purchased from a local retailer. A total of 41 wines classified in the categories detailed in **Table 1** were analyzed. Oxidized samples were prepared by pouring 500 mL of wine in a 750 mL sterile bottle and keeping it for 4 or 30 days in contact with air. Samples oxidized with this procedure had the typical odors of oxygen-spoiled wines.

Semiautomated solid-phase extraction was carried out with a VAC ELUT 20 station from Varian (Walnut Creek, USA).

Analytical Method. Aldehydes were analyzed following the method optimized and validated in refs *20* and *21*. According to that method, 10 mL of wine was loaded onto a 200 mg LiChrolut-EN solid phase-extraction cartridge (previously conditioned with 4 mL of dichloromethane, 4 mL of methanol, and 4 mL of a 13% ethanol (v/v) aqueous solution). Acetaldehyde and some other major carbonyls were removed by cleanup with 10 mL of an aqueous solution containing 1% $NaHCO_3$. Carbonyls retained in the cartridge were directly derivatized by passing through 2 mL of an aqueous solution of PFBHA (5 mg mL^{-1}), and letting the cartridge be imbibed with the reagent 15 min at room temperature (25 °C). Excess of reagent was removed with 10 mL of a 0.05 M sulfuric acid solution. Derivatized analytes were finally eluted with 2 mL of dichloromethane. Forty microliters of the chromatographic internal standard solution (2-octanol 46.4 mg L^{-1} in dichloromethane) was added to the extract. Forty microliters of this extract was then injected in the GC−MS system. The ion peak areas corresponding to the *m*/*z* fragments chosen are normalized to that of 2-octanol. These relative peak areas were interpolated in the calibration graphs built as

Table 2. Average Levels of Aldehydes Found in the Nine Different Groups of Wines Studied[a]

compound[b]	young red	young white	sparkling	oxidized red	oxidized white	red, short aging	Port	red, long aging	Sherry
methylpropanal***	4.96 (3.3) a	1.93 (1.4) a	3.97 (0.6) a	5.45 (2.8) a	3.25 (2.6) a	11.8 (2.8) a	33.2 (7.8) b	44.2 (14) b	76.7 (35) c
2-methylbutanal***	16.4 (7.6) a	9.16 (1.4) a	15.6 (5.2) a	7.11 (2.9) a	16.4 (15) a	18.8 (7.3) a	75.7 (20) bc	90.2 (15) bc	51.2 (28) b
3-methylbutanal***	6.52 (2.9) a	3.37 (1.3) a	8.43 (1.2) a	2.90 (2.1) a	5.56 (3.7) a	12.2 (12) a	27.7 (4.1) b	31.3 (6.1) bc	37.4 (9.6) c
(*E*)-2-hexenal***	0.08 (0.01) a	0.06 (0.02) a	0.08 (0.04) a	0.20 (0.2) a	0.55 (0.4) b	0.37 (0.4) ab	1.45 (0.2) c	0.63 (0.1) b	0.09 (0.01) a
(*E*)-2-heptenal	0.08 (0.05)	0.05 (0.02)	0.08 (0.02)	0.09 (0.1)	0.09 (0.05)	0.08 (0.03)	0.06 (0.04)	0.14 (0.1)	0.06 (0.03)
(*E*)-2-octenal	0.29 (0.18)	0.12 (0.07)	0.18 (0.07)	1.17 (1.7)	1.11 (1.1)	0.42 (0.2)	0.57 (0.1)	0.76 (0.2)	0.63 (0.3)
(*E*)-2-nonenal**	0.19 (0.07) a	0.14 (0.04) a	0.22 (0.03) a	0.99 (0.5) a	0.49 (0.3) a	0.53 (0.3) a	1.02 (0.2) a	2.08 (0.8) b	0.72 (0.2) a
methional***	2.14 (0.9) a	1.08 (0.39) a	2.99 (2.1) a	10.9 (6.6) b	4.16 (4.0) ab	9.82 (6.2) b	17.3 (8.0) c	24.4 (2.6) d	10.3 (2.2) b
phenylacetaldehyde***	11.0 (7.7) ab	4.63 (1.7) a	14.9 (2.6) ab	69.2 (41) cde	53.5 (34) cd	17.5 (12) ab	78.7 (18) de	91.2 (22) e	39.1 (5.5) bc

[a] Values in parentheses correspond to the standard deviation for the group. Different letters indicate the existence of a significant difference. All data are given in μg L^{-1}. [b] Significance of the factor "wine type" according to one-way ANOVA: *** indicates significance with $\alpha < 0.001$, and ** with $\alpha < 0.01$.

follows: A known mass of analyte was dissolved in 10 mL of red or white wine. This volume was then loaded onto a 200 mg LiChrolut-EN cartridge. The oximes were formed, eluted, and analyzed as in the standard procedure.

Gas Chromatography−Mass Spectrometry. Gas chromatographic analysis was performed with a CP-3800 chromatograph coupled to a Saturn 2200 ion trap mass-spectrometric detection system from Varian (Sunnyvale, CA). A DB-WAXETR capillary column (J&W Scientific, Folsom, CA) (60 m × 0.25 mm i.d., film thickness 0.5 μm) preceded by a 3 m × 0.25 mm uncoated (deactivated, intermediate polarity) precolumn from Supelco (Bellefonte, USA) was used. Helium was used as carrier gas at a flow rate of 1 mL min^{-1}. The oven temperature program was 10 min at 40 °C, 10 °C/min up to 220 °C, and finally held at this temperature for 20 min. The injector was a programmed temperature vaporization (PTV) injector. The glass insert was filled with 50 mg of silanized glass wood. The initial injector temperature was 40 °C, and, after 0.5 min, it was raised at 200 °C/min to 250 °C. The split flow was 100 mL min^{-1}; the split valve was open during injection and was closed at 0.6 min. It was opened again at 3.5 min. During the splitless period, the carrier gas flow was set at 3 mL min^{-1} to ensure a complete transfer of analytes. The MS-parameters were both MS transfer line and ionization chamber temperature 200 °C, and trap emission current 80 μA.

Statistical Analysis. One-way analysis of variance (ANOVA) was carried out to determine the influence of the factor "wine type" on the levels of each aldehyde. This analysis was run with SPSS vs. 11.5 from SPSS Inc. (Chicago, IL). Principal component analysis was carried out using Unscramble vs. 9.5 from Camo (Norway).

Sensory Analysis. The sensory panel was formed by nine judges aged 23−35. All of the judges had previous experience in sensory analysis and were trained during five sessions by ranking solutions containing increasing amounts of odorants and by means of discriminative tests (triangle tests). The tastings were carried out in a conditioned tasting room. In all cases, samples (20 mL) were served presented in black tulip-shaped wine coded glasses covered with a Petri-dish top after an equilibration time of 30 min at 21 °C. The determination of odor thresholds was carried out according to the Spanish Norm (AENOR 87-006-92) by means of triangle tests, presenting to the panelists solutions containing the tested odorant or group of odorants progressively diluted (dilution factor was 1:2). The solutions were hydroethanolic solutions (10%, v/v) containing aroma components, tartaric acid at 5 g L^{-1}, and pH adjusted to 3.2. Each panelist made two evaluations at each concentration level.

"Addition" tests were carried out also by means of triangle tests. In this kind of test, a red or white wine showing a neutral aromatic character (not very intense, not smelling of anything particular, and free from any off-odor) was spiked with a known amount of odorant or group of odorants to assess whether the addition brought about a perceptible change in their sensory characteristics. Judges were asked to identify which of the samples was different and to describe the reasons why it was different. The neutral wine samples selected for the study were those showing minima levels of the studied compounds (samples W2 and R2).

RESULTS AND DISCUSSION

The main goal of this paper is to assess the role played by some aldehydes most likely formed during wine oxidation on wine aroma. The experimental work carried out to get an answer to such a question has involved the quantitative analysis of small sets of wines belonging to different types, a chemometric analysis, and a series of sensory tests to assess whether the measured concentration levels have some sensory significance. The nine types of wines studied can be seen in **Table 1**. Each type represents a group of wines with a particular kind of elaboration or aging and, therefore, with a characteristic relationship with oxygen. Two of the groups were made of young wines (reds or whites) for which contact with oxygen, supposedly, only took place during the pre-fermentative and fermentative periods. There are two groups of red wines that were aged in wood casks for a short (<12 months) or long (>24 months) period. Another group is made of three samples from red Port wine, which underwent a long aging in oak casks. There is also a group of sparkling wines, all of them made following the traditional champenoise method. These wines do not have an oxidative aging, but they suffer two fermentations and are stored quite a long time in contact with the lees of the second fermentation. Another group contains Sherry wines (Fino type), which were all aged a long period in the Solera system. Finally, there are two groups made up by samples of young wines oxidized in the laboratory, which may represent the accidental oxidation of wine.

Quantitative Data. Table 2 summarizes the analytical composition of the studied aldehydes in the nine sets of samples and also includes the results of the analysis of variance carried out on the data set. Data confirm, as expected, that the levels of most of the aldehydes are linked to the type of wine and, therefore, to the kind of aging it had. (*E*)-2-Heptenal and (*E*)-2-octenal seem to be an exception, although in this last case the levels of this aldehyde found in some of the samples oxidized in the laboratory were particularly high. In fact, if samples are regrouped into two broad categories (samples oxidized in the laboratory and commercial samples), the differences for this compound are significant ($\alpha < 0.05$). Leaving aside these two compounds, there are remarkable quantitative differences between the different wine types, and in all cases the ratio maximum/minimum for each compound is larger than 1 order of magnitude. The three branched aliphatic aldehydes analyzed in the study, methylpropanal, 2-methylbutanal, and 3-methylbutanal, were found at high levels in Port, reds with a long aging, and Sherry wines. In the cases of methylpropanal and 3-methylbutanal, Sherry wines had the highest levels, while in the case of 2-methylbutanal, the highest levels were found in Ports and in aged reds. For (*E*)-2-hexenal, the highest levels were again

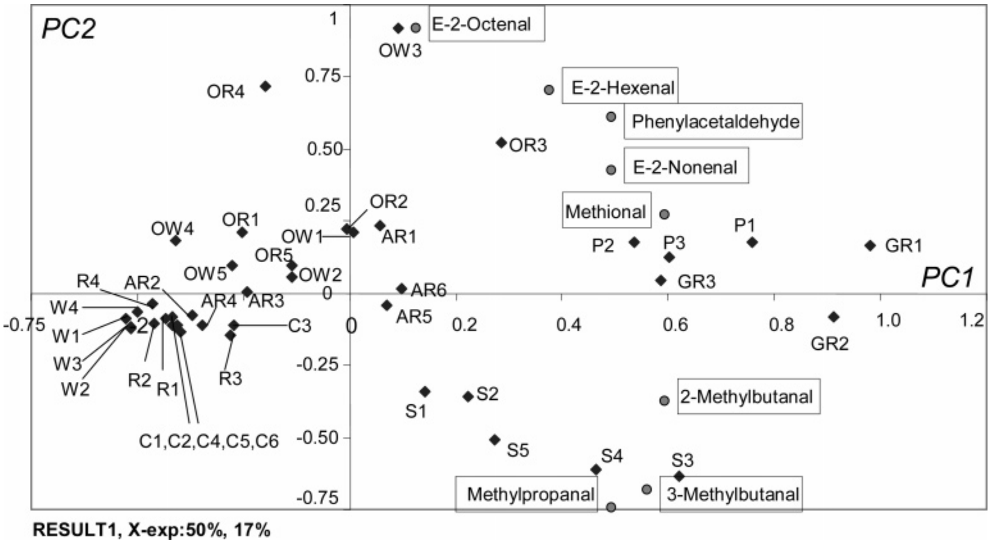

Figure 1. Representation of samples (sample scores) and variables (loadings) in the plane formed by the two first principal components. The first component retained 50% of the variance, and the second retained 17%. Sample codes can be seen in **Table 1**.

found in Port wines, followed by reds with a long aging, by the oxidized white wines, and by reds with a short aging. In the case of (*E*)-2-nonenal, differences were less clear, and only red wines with a long aging showed a significantly higher level of this compound. On the other hand, differences were more acute for methional and phenylacetaldehyde. Four different concentration levels were found for the former and five for the latter. In both cases, the highest levels were found in reds with a long aging, followed by Port wines. Sherries, reds with a short aging, and oxidized wines also had levels of these compounds significantly higher than those found in young wines or in cava wines, as can be seen in **Table 2**.

Such differences seem to indicate that there are more or less clear patterns of composition linked to the type of wine. This fact is more easily seen in the principal component plot shown in **Figure 1**. The plot reveals the existence of four different compositional patterns. Young wines (both reds and whites) and sparkling wines had in all cases the lowest levels of these compounds. This is the basic “pattern”. Within this trio of wine types, young white wines had in all cases the lowest levels of all compounds, although differences with young reds or cava were not significant. A second pattern is made of the wine samples oxidized in the laboratory, which are richer in (*E*)-2-alkenals (significant only for (*E*)-2-hexenal in oxidized whites) and in methional and phenylacetaldehyde than the corresponding young wines, but not in branched aliphatic aldehydes. On the contrary, Sherry wines are richer in branched aliphatic aldehydes, in methional, and in phenylacetaldehyde, but not in (*E*)-2-alkenals. The fourth pattern corresponds to Port wines and reds with a long aging, which have a composition characterized by large amounts of all of the studied compounds. Red wines with a short aging have a composition intermediate between those of young and aged red wines.

Sensory Significance. A first assessment of the sensory significance of the studied compounds was made by determination of the orthonasal odor thresholds in hydroalcoholic solution of the different aldehydes and further calculation of the corresponding odor activity values (OAVs). Results are summarized in **Table 3**. As can be seen, except (*E*)-2-hexenal and (*E*)-2-heptenal, most of the compounds can reach OAVs higher than the unity in the samples with highest levels. On the basis of their OAVs, methional and phenylacetaldehyde are the compounds that may have a stronger sensory impact. On the other hand, the OAVs in the samples with lowest levels of these compounds (young wines and natural sparkling wines) were below the unity, except in the cases of methional and phenylacetaldehyde, which had OAVs close to the unity. The sensory role of these two compounds has been previously studied and will not be further considered here (*12*−*15*). A second question that was addressed to estimate the potential sensory importance of these compounds was the calculation of the odor thresholds in hydroalcoholic solutions of different mixtures of the aldehydes. The purpose of these experiments was to check whether compounds with similar odors (and similar chemical structures and bio-chemical origins) could act together drawing on a sensory response quantitatively similar to, higher than, or smaller than that expected from the individual OAVs. These experiments were further complemented with addition tests, in which neutral wines were spiked with the different mixtures and with the determination of the thresholds of such additions.

Table 3. Odor Thresholds, Concentration Range, and Odor Activity Values (OAVs) of Each of the Studied Aldehydes

compound	odor threshold[a] (μg L^{-1})	concentration range[b] (μg L^{-1})	OAV range
methylpropanal	6.0	0.9–132	0.1–22
2-methylbutanal	16	3.3–105	0.2–6.6
3-methylbutanal	4.6	1–49	0.2–11
(*E*)-2-hexenal	4.0	0.02–1.6	<0.4
(*E*)-2-heptenal	4.6	<0.16	<0.03
(*E*)-2-octenal	3.0	0.04–4.1	<1.4
(*E*)-2-nonenal	0.6	0.1–3.7	0.2–6.1
methional	0.5[c]	0.5–29	1–58
phenylacetaldehyde	1.0	2.4–130	2.4–130

[a] Values calculated in a 10% water/ethanol solution containing tartaric acid at 5 g L^{-1} and pH adjusted to 3.2 with a panel composed of nine people (expected 95% confidence interval is $^1/_3$(th) – 3*x*(th)). [b] Concentration range found in wine. [c] Orthonasal odor threshold taken from ref *12*.

The first mixture studied was composed of the three branched aliphatic aldehydes at concentrations close to those found in an “average” Sherry, as is shown in **Table 4**. It was found that such a mixture had to be diluted 27 times to reach the threshold, which means that the odor activity value of such a mixture is 27. This value is quite close to that obtained by the summation of the individual OAVs of the three branched aldehydes in the mixture, which means that the sensory effect of these com-

Table 4. Odor Activity Values and Sensory Properties of Different Mixtures of Aldehydes on Different Media

	spiking level (μg L^{-1})	matrix	significance (α value)	OAV/sensory effect
		Branched Aliphatic Aldehydes		
mixture 1	[a]	synthetic		OAV (determined) = 27//OAV (calculated) = 24
	[a]	white		OAV (determined) = 9/sweet orange, fusel
mixture 1′	[b]	red	0.05	dried fruit, wet old wood, slightly papery
mixture 1″	[c]	red	0.02	dried fruit, wood, fusel, sweet
		(*E*)-2-Alkenals		
mixture 2	[d]	synthetic		OAV (determined) = 4//OAV (calculated) = 1.3
	[d]	white		OAV (determined) = 4/papery, wet old wood, moldy
mixture 3	[e]	synthetic		OAV (determined) = 6//OAV (calculated) = 3.6
	[e]	red		OAV (determined) = 9/dusty, rancid, decrease of aroma intensity
mixture 4	[f]	synthetic		OAV (determined) = 4//OAV (calculated) = 2.1
	[f]	red		OAV (determined) = 4/dirty, decrease of aroma intensity
(*E*)-2-octenal	4	red	0.04	closed room, pungent, less sweet
	1	red	0.05	closed room, earthy
	0.3	red	0.05	closed room, dirty
(*E*)-2-nonenal	9	red	0.001	oily, rancid oil, dusty, wet old wood
	3	red	0.05	earthy, rancid
	1	red	0.05	earthy, moldy, rancid
	0.30	red	0.04	brandy-like, maderized
		Branched Aliphatic Aldehydes + (*E*)-2-Alkenals		
mixtures 1′ + 3	*b*,*e*	red	0.02	dried fruit, sweet orange

[a] Mixture 1 = 76 μg L^{-1} methylpropanal + 56 μg L^{-1} 2-methylbutanal + 33 μg L^{-1} 3-methylbutanal [average conc. in Sherry]. [b] Mixture 1′ = 20 μg L^{-1} methylpropanal + 44 μg L^{-1} 2-methylbutanal + 21 μg L^{-1} 3-methylbutanal [minima conc. in aged reds]. [c] Mixture 1″ = 44 μg L^{-1} methylpropanal + 90 μg L^{-1} 2-methylbutanal + 51 μg L^{-1} 3-methylbutanal [average conc. in aged reds]. [d] Mixture 2 = 0.5 μg L^{-1} (*E*)-2-hexenal + 0.5 μg L^{-1} (*E*)-2-octenal + 0.6 μg L^{-1} (*E*)-2-nonenal. [e] Mixture 3 = 0.5 μg L^{-1} (*E*)-2-hexenal + 0.5 μg L^{-1} (*E*)-2-octenal + 2 μg L^{-1} (*E*)-2-nonenal. [f] Mixture 4 = 0.5 μg L^{-1} (*E*)-2-hexenal + 3 μg L^{-1} (*E*)-2-octenal + 0.6 μg L^{-1} (*E*)-2-nonenal.

pounds is additive. A further experiment was carried out by spiking a young neutral white wine with a solution containing the three branched aliphatic aldehydes so that the final level was increased by the concentrations indicated in mixture 1 (**Table 4**). The odor of the spiked sample was significantly different from that of the neutral wine, and the sensory effect caused by the addition was described by the judges as a decrease in fresh fruity notes and an increase in sweet, orange-like, and fusel nuances. The OAV for this mixture in wine was found to be 9. The difference between this value and that found in the synthetic mixture could be due to the effect of the small amounts of these aldehydes naturally present in the neutral wine. A second experiment was carried out by spiking a neutral young red wine with mixtures of these aldehydes (mixtures 1′ and 1″) so that their final levels would become close to the values found in aged reds or Ports. In both cases, the sensory effect was significant, bringing about an increase in the dried fruit, old wood, papery, sweet, or fusel notes of the wine. All this suggests that these compounds could be important contributors to some of the sensory properties of Sherrys, Port wines, or red wines with a long aging.

A similar approach was followed to evaluate the effect of mixtures containing three (*E*)-2-alkenals. The odor thresholds in hydroalcoholic solutions of three different mixtures, resembling each one of them the average proportions of these compounds found in three different wine types, were determined. The first one (mixture 2 in **Table 4**) approximately imitates the composition found in the two slightly oxidized white wines (OW1 and OW2) in which the three compounds were at similar concentrations. Interestingly, the OAV of the mixture (measured as explained before) is 3 times higher than the summation of the individual OAVs, which indicates that these compounds interact in a synergic way and reveals the important effect of compounds below the threshold. The second model (mixture 3) more or less resembles the composition of an aged red wine, in which (*E*)-2-nonenal is more concentrated than the two others. In this case, the OAV of the mixture is 1.7 times higher than the summation of the individual OAVs. Finally, the third model (mixture 4) in which the concentration of (*E*)-2-octenal is maximum resembles the composition of the most different oxidized young wines (samples OR4 and OW3 in **Figure 1**). Again, a synergic interaction between the three components was evident.

Addition experiments carried out on neutral young wines confirmed the sensory importance of these compounds. Spiking a white wine with (*E*)-2-alkenals at the level of mixture 2 had as a consequence the apparition of papery, old-wood, and moldy notes (see **Table 4**). Spiking a young red with the levels of mixture 3 made the wine develop dusty and rancid notes, and a clear decrease of the overall aroma intensity. Finally, spiking a young red wine with the levels of mixture 4 brought about also a decrease on the overall aroma intensity, and the apparition of dirty, dusty, closed old room notes, as can be seen in **Table 4**. In all of these cases, the additions were significantly detected by the panel. Moreover, the OAVs of such additions were also determined and were found to be quite similar to those found with synthetic solutions, which suggests that the synergic effects previously described also apply to wine and confirms that these compounds can be detected at really low concentrations.

To better understand the role of these compounds, the sensory effect caused by the individual addition of increasing amounts of (*E*)-2-nonenal and (*E*)-2-octenal to a neutral young red wine was also investigated. The results of this experiment are also shown in **Table 4**. Surprisingly, the addition of under-threshold amounts of (*E*)-2-octenal or (*E*)-2-nonenal to such neutral red wine caused a significant sensory effect, which suggests the existence of synergic effects with other wine volatiles. The effect caused by the addition of (*E*)-2-octenal was in all cases negative, provoking the appearance of dirty, closed room, and earthy notes. In the case of (*E*)-2-nonenal, the addition of low levels of this compound was, however, not particularly negative; rather, such addition caused an “aging” effect with the apparition of brandy-like notes. The addition of higher amounts of this compound (above threshold), however, gave to the wine earthy, moldy, and rancid notes.

In any case, these results should indicate that all wines with a relatively large content of (*E*)-2-alkenals, such as oxidized wines, Ports, or red wines with a long aging, should show the nasty odor nuances linked to these compounds. However, this is true only in the case of oxidized wines: Ports and aged red wines can have relatively large amounts of (*E*)-2-alkenals and do not show necessarily rancid odors, as has been found in the present work. As the major difference between oxidized wines and Ports or reds with a long aging is that the latter two have also high amounts of branched aliphatic aldehydes, an experiment was carried out to check whether the presence of such compounds could mask the nasty odors linked to (*E*)-2-alkenals. Results of this experiment are shown in **Table 4** and confirm the previous hypothesis: the simultaneous addition of branched aliphatic aldehydes and of (*E*)-2-alkenals brings about an increase of sweet orange and dried fruits notes linked to the branched aldehydes, but not of the dusty, papery, rancid nuances linked to the presence of (*E*)-2-alkenals. These results suggest that the presence of aliphatic branched aldehydes in aged red wines is an essential part of their characteristics, not only because they contribute to some of the typical notes of these wines, but because they help to minimize the sensory effects of (*E*)-alkenals.

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