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Insights on the role of acetaldehyde and other aldehydes in the odour and tactile nasal perception of red wine

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(*E*,*Z*)-2,6-nonadienal (PubChem CID: 643731)
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ABSTRACT

Wine models with or without a dearomatised and lyophilized red wine extract containing a young red aroma base (control) plus one vector with one or several aroma compounds (unsaturated-aldehydes, saturated-aldehydes, benzaldehyde, isoamyl-alcohol, methoxypyrazines and (*Z*)-1,5-octadien-3-one) were prepared. Models were spiked with increasing amounts of acetaldehyde whose headspace concentrations were controlled. Odour and nasal chemesthesic properties were assessed by a trained sensory panel.

Results confirm the contribution of the different players, notably isoamyl-alcohol, (Z)-1,5-octadien-3-one, benzaldehyde and methoxypyrazines, to wine aroma and tactile nasal characteristics and demonstrate that acetaldehyde levels play an outstanding role in their modulation. At low levels, it can play positive roles in some specific aromatic contexts, while at higher levels, enhance the negative effects associated to the generic presence of other aldehydes (saturated, unsaturated and Strecker aldehydes) by enhancing “green vegetable” notes and “itching” character and the “burning” effects linked to high levels of isoamyl alcohol.

1. Introduction

Acetaldehyde is a basic compound in the composition of wine. It originates principally in the fermentation process being that it is an intermediate in the production of ethanol and glycerol. Nevertheless, it can also be formed during the oxidation of ethanol in the presence of a catalyser. These oxidation–reduction reactions can happen during the whole wine production process (Ribéreau-Gayon et al., 2000). Numerous important factors condition the acetaldehyde concentration in wine and one of the most important is sulphur dioxide (SO_2) that quickly reacts with acetaldehyde. Thus, controlling the quantity of sulphur dioxide is very important since it reacts with free acetaldehyde forming odourless hydroxy sulfonate (Liu & Pilone, 2000). However, the strain of yeast, the nutrition during the fermentation or grape variety also influence the levels of acetaldehyde in wine (Jackowetz et al., 2011) and recent studies show that wines made from grapes harvested early facilitate the accumulation of acetaldehyde (Arias-Pérez et al., 2020).

In the literature (Ribéreau-Gayon et al., 2000) a range of acetaldehyde concentrations in wine can be found; concentrations range from 30 to 130 mg L^{-1}. This compound, in low levels can give the wine fruit notes, but at higher concentrations it is reminiscent of nuts (Waterhouse et al., 2016), and at still higher levels produces a green, grassy or apple-like off-flavour (Liu & Pilone, 2000). At these concentrations, the classical wine aroma terminology includes the term “acetaldehyde” with the

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general descriptor “oxidised” (Noble et al., 1987) or it is defined as the molecule responsible for the “flat character” in wine (Ribéreau-Gayon et al., 2000). The levels of acetaldehyde can be higher in fortified wines such as Sherry from Jerez which have concentrations between 220 and 380 mg L^{-1} and in some cases even up to 700 mg L^{-1} in Jura wines (Ribéreau-Gayon et al., 2000). These levels of acetaldehyde contribute a pungent quality which is characteristic of these wines; which are referred to with chemical descriptors such as varnish, nail polish and alcohol (Zea et al., 2015). Other studies mention that acetaldehyde can produce distinct sensorial perceptions apart from olfactory ones, such as stinging or irritating sensations when the pure compound is smelled (Miyake & Shibamoto, 1993). Coughing and a burning sensation in the nose, throat, and eyes can also be caused by acetaldehyde (World Health Organization, 1994). In fact, studies with mice have demonstrated how this sensory effect could be the result of the activation of nociceptors (Bang et al., 2007). Other longer chain carbonylic compounds, such as aldehydes and ketones which are present in alcoholic beverages like distillates, also produce a stinging sensation which has been denominated as the “trigeminal burn” (Kokkinidou & Peterson, 2016). Even though the sensorial perception threshold has been found to decrease exponentially with the chain length of the compound (Cometto-Muñiz & Cain, 1993), normal concentrations of acetaldehyde found in still wines have never been scientifically proven to cause these types of reactions. All of these trigeminal sensations belonging to chemesthesis modality, which was first defined in a study of irritation sensations produced by capsaicin (Green, 1990). However, this sensory modality includes a lot of perceptions such as warming, itching, stinging, and burning. These sensations can occur when pungent chemical compounds in foods stimulate the free nerve endings of the trigeminal, glossopharyngeal and vagus nerves (Green, 2016). Several chemicals such as vanilloids, isothiocyanates, alcohols, aldehydes or acids have been typically described as “trigeminal irritants” (Doty, 1975; Green, 2016; Komatsu et al., 2012). These compounds can interact with chemosensitive molecular receptors which are members of the family of thermosensitive transient receptor potential (TRP) ion channels (Alpizar et al., 2016). Even though these receptors can be found in distinct parts of the body, studies focused on chemesthesis have centred principally on the nose and mouth cavities (Green, 2016) where the orthonasal perception is the most important (Cometto-Muñiz & Cain, 1993; Doty, 1975). The first hypothesis of this research was formulated for two main reasons. First, due to the significant chemical role acetaldehyde plays in wine. Secondly, because some aldehydes in alcoholic beverages can trigger chemesthesic sensory activity which can be detected in the orthonasal pathway. Therefore, the hypothesis was formulated as follows: Acetaldehyde can induce an aromatic sensory and chemesthesic effect in the nose when added to matrixes similar to wine.

The sensorial perception of wine is not simply the result of the sensory activity of individual compounds, but the result of complex interactions between a great quantity of both volatile and non-volatile chemical compounds (Francis & Newton, 2005). Odour producing compounds can interact between themselves to produce additive or complementary effects which can become synergetic or antagonistic, enhancing or masking aromatic sensations (Francis & Newton, 2005) along with chemesthetic sensations (Cain & Murphy, 1980). The particular effect produced by acetaldehyde is highly dependent on the matrix in which it is found; this is due to the above stated and because it can react with many compounds of distinct nature, such as SO_2, polyphenols, and amino acids (Liu & Pilone, 2000; Miyake & Shibamoto, 1993; Ribéreau-Gayon et al., 2000). This reactivity is illustrated by the great variability of the sensory thresholds for acetaldehyde found in the literature with a range from 0.5 to 100 mg L^{-1} (Guth, 1997; Waterhouse et al., 2016). Thus, the second hypothesis of this research: other aldehydes or compounds present in the matrix can modulate the sensory changes initiated by acetaldehyde. To test this hypothesis, distinct wine model contexts were selected. These model contexts contained distinct aromatic vectors with the capacity to generate sensory interactions with acetaldehyde and suspected to elicit active chemesthesis. The selected aromatic vectors included carbonyl compounds which can influence chemesthesic perceptions (Doty, 1975; Kokkinidou & Peterson, 2016), such as unsaturated aldehydes (first vector) and saturated aldehydes (second vector). Both of which are derivatives of the oxidation of fatty acids that are sensory relevance in their unsaturated (Alegre et al., 2020) and saturated forms (Culleré et al., 2004). The third aromatic vector, benzaldehyde normally does not reach the olfactory sensory threshold but could have a synergetic effect noted in wine aroma (Gómez García-Carpintero et al., 2012). The fourth aromatic vector included a higher alcohol, such as isoamyl alcohol being that it has been demonstrated to suppress fruit and wood characteristics or amplify animal or spirit-like notes (De-la-Fuente-Blanco et al., 2016). The fifth vector included was alkylmethoxypyrazines represented principally by 3-isobutyl-2-methoxypyrazine (IBMP) and 3-isopropyl-2-methoxypyrazine (IPMP) which are active-compounds with strong green-pepper or earthy scents and their levels have been related to maturation problems in grapes. Even though acetaldehyde has been found to suppress the green pepper character generated by IPMP (Coetzee et al., 2016), there are no studies with IBMP. The sixth and last aromatic vector selected was (*Z*)-1,5-octadien-3-one, a ketone related to strong metallic sensations or geranium leaf aromas which have been correlated with vineyard diseases (Pons et al., 2018), yet that could play a relevant part in the perception of vegetable notes (Alegre et al., 2020).

In this respect, the main objectives of this research were 1) to assess the sensory importance of acetaldehyde in wine aromatic and chemesthesic sensations in the nose and 2) to evaluate its potential sensory interaction with other groups of sensory-active volatile compounds (unsaturated-aldehydes, saturated-aldehydes, benzaldehyde, isoamyl alcohol, methoxypyrazines and (*Z*)-1,5-octadien-3-one).

2. Material and methods

2.1. Reagents, materials, solvents and standards

Dichloromethane, ethanol, hexane, diethyl ether and methanol for gas chromatography analyses were supplied by Fisher Scientific (Loughborough, UK) and Merck (Darmstadt, Germany). LiChrolut EN resins were supplied by Merck (Darmstadt, Germany). Pure water was obtained from a Milli-Q purification system (Millipore, USA). Semi-automated solid-phase extraction was carried out with a Vac Elut 20 station from Varian (Walnut Creek, USA). SPME fibers, polydimethylsiloxane/divinylbenzene (PDMS/DVB) 65 μm film thickness, were purchased from Supelco-Spain (Madrid, Spain). Standards and reagents were supplied by Merck (Darmstadt, Germany), Sigma Aldrich (St. Louis, MO, USA), ChemService (West Chester, PA, USA), Poly-Science (Niles, IL), Lancaster (Eastgate, UK), Alfa Aesar (Karlsruhe, Germany), Panreac (Barcelona, Spain), Firmenich (Geneva, Switzerland), AromaLab (Planegg, Germany), Toronto Research Chemical (Toronto, Canada), Waters (Milford, MA, USA) and Oxford Chemicals (Hartlepool, UK), as indicated in Table A.3 of Supplementary material.

2.2. Preparation of wine models

2.2.1. Isolation and purification of compounds

Isoamyl alcohol and β-phenylethanol standards were isolated and purified as described in the literature (De-la-Fuente-Blanco et al., 2016) and the purification of esters was carried out following the procedure described in a previous publication (De-la-Fuente-Blanco et al., 2020).

2.2.2. Wine model (WM) preparation

Two WMs, differing in non-volatile fractions, were used. The first one was a reconstituted lyophilised wine (RLW) generated to mimic a young red wine. The RLW was prepared by mixing a pool of volatile and non-volatile compounds of red wines. Non-volatile fraction was obtained by the lyophilisation of a dearomatised red wine. Therefore, a neutral (in terms of aroma and in-mouth properties) commercial young red wine made from Tempranillo (Valdepeñas region, Spain) of 2018 vintage was used (ethanol = 12.32% (v/v), pH = 3.5, total polyphenol index (TPI) measured as absorbance at 280 nm = 46.51 a.u., reducing sugars = 2.3 g L^{-1}, total acidity (TA) = 5.02 g L^{-1} expressed in tartaric acid, volatile acidity (VA) = 0.30 g L^{-1} and malic acid = 0.2 g L^{-1}). To begin, several 500-mL-flasks containing 200 mL of wine were firstly dealcoholized by evaporation under vacuum (8 mbar, 28 °C, 30 min) with a rotary evaporator (KNF, Freiburg,Germany) and then they were freeze-dried (LyoQuest85, Telstar, Tarrasa, Spain) at −80° C and 0.025 bar pressure. The resulting residue was stored at 5 °C until sensory analysis. Proportionate amounts of the non-volatile residue were redissolved in a hydroalcoholic solution based on MilliQ water to obtain samples with similar concentration of the non-volatile fraction as the original wine. The concentration of volatile compounds (Table 1) corresponds to the average concentration of aroma compounds found in a previous work (Table A.3. Supplementary Material). Single ethanol solutions of these compounds were mixed in a concentrate ethanol solution pool, which was later added to the different wines to achieve the target concentrations. Final ethanol concentration was adjusted to 12% (v/v) and pH to 3.5 was checked. The second WM was a synthetic wine (SW) which was prepared with ultrapure water, 5 g L^{-1} of tartaric acid, 12% ethanol (v/v), 10 g L^{-1} glycerol, 1.5% 1,2-propanediol with a pH of 3.5 adjusted with NaOH and the same pool of volatile compounds as for RLW (Table 1).

The two base wines (RLW and SW) were further spiked with one of the aroma vectors to generate 7 different contexts: control (CT), unsaturated aldehydes (UA), saturated aldehydes (SA), benzaldehyde (B), isoamyl alcohol (IA), methoxypyrazines (MPz) and (*Z*)-1,5-octadien-3-one (ZO). The effect of acetaldehyde on each of these 7 contexts was studied by adding different levels of acetaldehyde to the two WMs studied

The concentrations of the volatile compounds in different contexts are shown in Table 1. They correspond to concentrations of aromatic compounds found in red wines (for more detailed information regarding samples concentration see Table A.3 of Supplementary material). Preliminary bench top tastings were carried out with the aim of selecting concentrations of volatile compounds which provided distinct sensory properties for WMs.

All contexts were studied in both WM. Six acetaldehyde concentrations were spiked in the seven series/contexts prepared with RLW (0, 5, 10, 20, 50 and 100 mg L^{-1}), and two were evaluated in SW, corresponding to the lowest (0 mg L^{-1}) and highest levels of free acetaldehyde found in RLW matrix (approximately 50 mg L^{-1}). The highest and lowest concentrations were added to SW to verify that the results obtained in the RLW matrix were due to the acetaldehyde and other compounds present in the lyophilised wine matrix.

RLW samples were prepared 8 h before the sensory analysis, in order to allow free acetaldehyde to reach equilibrium, while SWs were prepared ten minutes before each session. The selection of the preparation protocol of the samples was based on a study evaluating the time needed for the free acetaldehyde concentration to reach equilibrium in the headspace. Therefore, free acetaldehyde was measured at consecutive time points in the two matrices. The RLW was spiked with 25 mg L^{-1} of acetaldehyde in a closed flask at room temperature. The free acetaldehyde was measured at 0, 3, 8, 24, 47 and 72 h. An acetaldehyde concentration of 50 mg L^{-1} was added to the SW. The free acetaldehyde was measured at 0, 0.5, 1 and 2 h. The analysis method employed is described in section 2.4.2.

Table 1
Aroma contexts and composition of wine models used in the study (micrograms per litre).

	Compounds	Concentration	Odour threshold[a]
Pool of compounds conforming the common aroma base	acetic acid	150,000	300000[1]
	ethyl acetate	50,000	12300[2]
	diacetyl	400	100[1]
	isoamyl acetate	1000	30[1]
	isoamyl alcohol	180,000	30000[1]
	β-phenylethanol	30,000	14000[3]
	ethyl vanillate	250	990[4]
	vanillin	70	995[2]
	γ-nonalactone	20	25[5]
	guaiacol	10	9.5[3]
	β-damascenone	4	0.05[1]
	β-ionone	0.3	0.09[3]
	linalool	7	25[3]
	geraniol	13	20[2]
	3(2H)-furanone (furaneol)	30	5[4]
	hexanoic acid	2000	420[3]
	isovaleric acid	300	33[3]
	ethyl hexanoate	1000	62[2]
	ethyl 2-methylbutyrate	120	18[3]
	ethyl cinnamate	0.43	1.1[3]
Saturated aldehydes context	hexanal	30	4.5[5]
	heptanal	5	15–3[5]
	octanal	25	15[2]
	nonanal	5	15[2]
	decanal	5	10[2]
Unsaturated aldehydes context	(*E*/*Z*)-2,6-nonadienal	0.05	0.01[5]
	(*E*/*E*)-2,4-decadienal	0.05	0.07[5]
	(*E*)-2-hexenal	5	4[2]
	(*E*)-2-heptenal	5	4.6[2]
	(*E*)-2-octenal	5	3[2]
	(*E*)-2-nonenal	0.2	0.6[2]
	(*E*)-2-decenal	0.5	0.3[5]
	(*E*)-2-undecenal	5	n.a.[b]
Benzaldehyde context	benzaldehyde	150	2000[6]
Isoamyl alcohol context	isoamyl alcohol	500,000	30000[1]
Methoxypyrazine context	2-isopropyl-3-methoxypyrazine	0.0037	0.001[7]
	2-isobutyl-3-methoxypyrazine	0.012	0.015[7]
(*Z*)-1,5-octadien-3-one context	(*Z*)-1,5-octadien-3-one	0.005	0.0012[8]
Acetaldehyde	acetaldehyde	0–100000	500 [1]

[a] Reference in which the odour threshold value has been calculated is given in table A.3 of supplementary material. The matrix in which the odour threshold value has been calculated is given in brackets: In [1], threshold was calculated in a 10% water/ethanol mixture; in [2] the matrix was a 10% water/ethanol solution containing 5 g/L tartaric acid and pH 3.2; in [3] the mixture was 11% water/ethanol, pH = 3.4, 7 g/L glycerol and 5 g/L tartaric acid; in [4] the matrix was a synthetic wine containing 11% ethanol (v/v), pH = 3.4, 7 g/L glycerol and 5 g/L tartaric acid; in [5] the thresholds were calculated in water; in [6] threshold was calculated in a 10% water/ethanol mixture adjusted to pH 3.5 with tartaric acid; in [7] the thresholds were calculated in red wine; and [8] the matrix was a synthetic wine. [b] Threshold is not available.

2.3. Sensory analysis

2.3.1. Participants

Eight laboratory staff participants, experienced in wine aroma description, carried out the sensory tasks. These participants (5 men and 3 women, ranging in age from 22 to 51, $\bar{x} = 34$ years old) were selected from a panel of 12 trained panellists that had previously participated in an independent project focused on conventional descriptive analysis. These eight participants presented the best performance in terms of repeatability, reproducibility and consistency of the panel. They were not informed about the aim of the study.

2.3.2. Generation of sensory descriptors and panel training

Participants attended a total of 20 training sessions held on distinct days throughout a four-week period. The training sessions consisted of three main steps: 1) general training, 2) generation of sensory descriptors, and 3) specific training.

General training consisted of six, 15-min, sessions to familiarise participants with overall aroma and chemesthesic sensations present in red wines. The participants were provided 45 reference standards prepared at LAAE (Laboratorio de Análisis del Aroma y Enología). Reference standards belonged to a wide range of aroma and chemesthesic categories including: fruit (dried, black, red, tropical, citrus, white, yellow or candied), vegetable (green and cooked vegetables, herbs, fresh and dried grass), floral, spicy, roasted, woody, animal, undergrowth, along with chemesthesic sensations (burning, freshness and itching) and others. Participants were qualified when they were able to correctly identify at least 80% of the reference standards presented.

The second step was devoted to generating distinct aroma descriptors among the samples. It consisted of seven sessions, one for each of the contexts studied. Therefore, participants were presented simultaneously with the six wines belonging to each context (differing exclusively in acetaldehyde levels) and were asked to cite the aroma and/or chemesthesic descriptors that differed among the samples. They were provided with a list of 121 aroma and chemesthesic descriptors compiled from other projects (Green & Shaffer, 1993; Noble et al., 1987) as an aid for descriptor generation. The participants cited a maximum of five descriptors from the list or their own experience. The descriptors generated by the panel were grouped according to semantic similarities by three experienced researchers using a triangulation task (Abric, 2005). Descriptors cited by at least 2 participants were considered in the analysis. The final list of descriptors for each context (between 6 and 8 per context), along with the reference standards used to train the panel in the specific training sessions are detailed in Table A.1 of the Supplementary material.

The third part consisted of seven specific 90-min training sessions, one for each context, held in different days. These specific training sessions were carried out the same day as sessions devoted to describe the wine models object of study (section 2.3.3). They aimed to train participants in the specific descriptors (Table A.1 of the Supplementary material) selected in the previous step and to familiarise them with the type of matrix to be evaluated in the study. Therefore, each session consisted of two parts, in the first one the panellists were presented with reference standards illustrating the specific aroma and chemesthesic descriptors selected for each context. Participants should be able to identify all of them correctly to qualify. In the second part, they were taught and trained in the use of the 10 cm-structured scale (labelled in the extremes with 0 = "absence" and 10 = "very intense"). For this, four commercial wines with characteristic aroma and chemesthesic descriptors similar to those of the final study were used to familiarise panellist with the sensory space of each wine context. Participants had to describe wine samples in duplicate by rating the intensity of all the descriptors selected for each of the seven specific contexts (between 6 and 8 descriptors: Table A.1 of the Supplementary material) using the scale described. After the description the results were discussed until achieving consensus.

2.3.3. Evaluation of sample sets

A total of 21 sessions were carried out to describe the samples. Fourteen sessions were devoted to evaluating the series of seven contexts in duplicate prepared in RLW. They were held in seven different days, one for each context, with two sessions per day separated at least 2 h. In the same day, duplicated sessions were carried out in order to evaluate repeatability. In each session six wine models were presented (differing exclusively in acetaldehyde concentration). In the other seven sessions the samples in synthetic wine (SW) were evaluated. Each session was devoted to one of the seven contexts. In each session, two SW (non-spiked and spiked with 50 mg L^{-1} of acetaldehyde) were presented in duplicate.

In each session, participants were asked to carry out an orthonasal evaluation and rate the intensity of aroma and chemesthesic descriptors on a 10-cm structured scale (anchored at each end with the labels "absence" and "very intense"). To avoid bias due to order of presentation, the descriptors appeared on the list in a distinct, randomised order for each panellist. Smelling water during 30 s, taking a sip of water and then smelling water again for 30 s between each sample was imposed in order to avoid fatigue of the panellists.

Eight-mL samples (20 ± 1 °C) were served in dark ISO approved wine glasses covered with plastic Petri dishes. The samples were labelled with three-digit random codes and arranged in a distinct random order for each participant. Sample wines were served 5 min before the beginning of the sensory task and evaluated in a ventilated, air-conditioned, tasting room under ambient light in individual booths.

2.3.4. Data analysis

Panel performance: For each of the 7 wine contexts and for each attribute, intensity scores of duplicated wines were submitted to three-way analysis of variance (ANOVA) involving samples (S), judge (J) and replicate (R) as fixed factors and all first-order interactions were calculated. None of the S*J, J*R or S*R effects were significant ($p < 0.1$ in all cases) and thus panel repeatability (measured by J*R and S*R) and consistency (S*J) could be confirmed.

Wine description: For each context (control, unsaturated aldehydes, saturated aldehydes, benzaldehyde, isoamyl alcohol, methoxypyrazines and (*Z*)-1,5-octadien-3-one) and wine matrix (RLW and SW) a two-way ANOVA (panellists as random and acetaldehyde level as fixed factors) was calculated with the scores of aroma and chemesthesic descriptors. Then, for significant effects pair-wise comparison test (Fisher test) was applied (5% risk). All statistical analyses were performed using XLSTAT (2018).

Correlation studies and Student's *t*-test were carried out with Excel 2016 (Microsoft, Washington, USA). Two correlation studies were carried out. In the first one, quantitative data of aldehydes and the mean scores of sensory descriptors were correlated. In the second study correlations between sensory descriptors were calculated.

2.4. Chemical analysis

2.4.1. Oenological parameters

Ethanol content (%, v/v), pH, total acidity (TA), volatile acidity (VA), total polyphenol index (TPI), free and total sulphur dioxide, reducing sugars, and malic acid concentrations were determined according the methodology stipulated by *Office International de la Vigne et du Vin* (OIV, 2018).

2.4.2. Quantitative analysis of free acetaldehyde

Free acetaldehyde was determined by headspace gas chromatography mass spectrometry (HS-GC–MS) using a variation of the method described in the literature (Carrascon et al., 2017). GC–MS analysis was carried out on a GC Varian CP-3800 equipped with a Saturn 2000 mass spectrometer with a VF-35 (20 m × 0.15 mm i.d. × 0.15 μm) capillary column from J&W Scientific (Agilent Technologies, Santa Clara, CA, USA). For the analysis, 5 mL of each sample were transferred into a 10 mL headspace vial, after which were spiked with 20 μL of methyl 2-methylbutyrate (1100 mg L^{-1} in ethanol) as an internal standard. Vials were then closed and incubated at 40 °C for 5 min. After this, 100 μL of the headspace were injected in a PTV injector, working in split mode (1:50 split ratio) at 200 °C with a pulse of pressure of 310 kPa. A CombiPAL autosampler with a static headspace unit from CTC Analytics (Zwingen, Switzerland) was employed. The one mL gas-tight syringe was heated 10 °C above incubation temperature. After the injection the hot syringe was cleaned by purging with pure nitrogen for 5 min. The temperature program for the method started at 35 °C for 4 min and then raised to 50 °C min^{-1} then to 220 °C for 5 min. Helium at 55.7 cm s^{-1} was carrier gas employed. The mass spectrometer acquisition was performed in SCAN mode from 40 to 110 m/z. The m/z used for quantification were 43 + 44 for acetaldehyde and 88 for internal standard (methyl 2-methylbutyrate).

External calibration curves in model wine (5 g L^{-1} tartaric acid, 12% ethanol, 1.5% propane-1,2-diol, 10 g L^{-1} glycerine, pH 3.5) containing known amounts of acetaldehyde were prepared.

2.4.3. Quantitative analysis of Strecker aldehydes

The determination of free and bound forms of Strecker aldehydes in wine are described in the method proposed by Bueno et al. (2014). Wines were spiked with internal and surrogate standards and let to equilibrate for at least 12 h in an oxygen-free chamber. Aldehydes in the headspace were preconcentrated on a PDMS/DVB fibre and were further analysed on a GC–MS equipped with a quadrupole in SIM mode.

3. Results and discussion

3.1. Quantitative chemical study of free acetaldehyde levels

Due to the high volatility and reactivity of acetaldehyde (Liu & Pilone, 2000), the concentration of free acetaldehyde in the headspace during the sensory analysis was analytically controlled. Equilibration experiments were carried out in samples of both wine models. The samples of RLW models (12% (v/v) of ethanol, 3.5 of pH, contained 12 mg L^{-1} of free SO_2 and 42 mg L^{-1} of total SO_2 and other different components of the lyophilised wine) were spiked with 25 mg L^{-1} of total acetaldehyde. Results (expressed as average ± standard deviation) revealed that acetaldehyde levels in the headspace decreased dramatically. Immediately after the addition, measured levels of free acetaldehyde in the headspace were only 18.44 ± 1.26 mg L^{-1}. Three hours later, levels had fallen to 11.35 ± 0.25 mg L^{-1} and after 8 h, levels had reached a plateau at 8.61 ± 0.12 mg L^{-1}, remaining fairly constant for at least the following 16 h (levels at 9.25 ± 0.01 mg L^{-1} 24 h after the addition). Afterwards, levels begin to increase, so that after 72 h the concentration of free acetaldehyde had increased to 16.41 ± 0.08 mg L^{-1}. Since the non-volatile fraction used to prepare the RLW model contained free and total SO_2, this initial decrease is likely due to the formation of adducts between acetaldehyde with polyphenols and also with SO_2. This underlines that monitoring these compounds is very important in aldehyde trials, because free aldehydes are the ones that will really have a sensory impact. If we focus on total aldehydes, we could underestimate their sensory perception. The ulterior increase should be most likely attributed to the cleavage of the previously formed acetaldehyde-bisulphite adducts. The cleavage would be the indirect consequence of the oxidation and evaporation of free SO_2 and maybe also to the oxidation of ethanol (De Azevedo et al., 2007; Liu & Pilone, 2000). In accordance with this result, samples for the present study were prepared at least 8 h in advance to the beginning of the sensory analysis to ensure that the level of sensory-active acetaldehyde (i.e., free acetaldehyde) reaches the equilibrium.

The samples used in the experiment were therefore prepared by spiking reconstituted lyophilised wine (RLW) with 0, 5, 10, 20, 50 and 100 mg L^{-1} of acetaldehyde and letting them to equilibrate for 8 h. After this time, the headspaces of the samples contained 0.00 ± 0.14 mg L^{-1}, 0.18 ± 0.09 mg L^{-1}, 0.71 ± 0.18 mg L^{-1}, 2.74 ± 1.15 mg L^{-1}, 17.5 ± 2.9 mg L^{-1} and 56.2 ± 2.4 mg L^{-1} of free acetaldehyde respectively, levels which remained stable during the remaining four hours in which the sensory analyses took place. In the experiments, synthetic wine matrix (SW) was also used. In this matrix, there is no need for equilibrating because it is simpler and it does not contain polyphenols or SO_2, but the evaporation of acetaldehyde causes an inevitably and steady drop in its concentration. A synthetic wine (SW) was spiked with 50 mg L^{-1} and the free acetaldehyde levels dropped steadily from initial measured values of 47.05 mg L^{-1} to 45.28 mg L^{-1}, after 0.5 h; 44.08 mg L^{-1}, after 1 h, and 41.49 mg L^{-1} after 2 h. Only two different levels of acetaldehyde were used in this matrix, 0 and 56.2 mg L^{-1}, matching the minima and maxima concentrations of the other experiment. Experimentally, it could be determined that levels contained in the 0 mg L^{-1} SW samples were below 0.34 ± 0.04 mg L^{-1} and that those contained in the 56.2 mg L^{-1} SW were above 48.67 ± 0.07 mg L^{-1} during the sensory experiments.

3.2. The different aromatic contexts: influence of selected aroma chemicals on sensory profiles

In addition to a control aromatic context, which fits the aroma profile of a neutral young red wine, 6 additional aromatic contexts were prepared by adding to the basic aroma composition (that of the control), one or several aroma chemicals with suspected chemesthesic action or with aroma properties. The compositions of the 6 aromatic contexts are given in Table 1. The first context included the five major saturated aldehydes (C6-C10), which were spiked at levels potentially found in wine. Only two of them, hexanal and octanal, were above odour detection threshold levels. The second context was formed by a complex mixture of 8 unsaturated aldehydes, common components of grapes and many other vegetables. In this case, (*E*,*Z*)-2,6-nonadienal was clearly above threshold, but most of the others were at levels slightly above or below the corresponding thresholds. The third context contained benzaldehyde, a single aroma chemical compound at levels well below threshold. This is a common constituent of the grape aroma precursor fraction, but its concentration is always under-threshold levels. The fourth context contained isoamyl alcohol, a common wine aroma constituent, which levels contained in this context go to the upper limit at which this compound can be found in wines. The fifth level was formed by two methoxypyrazines, one of them at levels above threshold and the other at levels slightly below threshold. Finally, the last aroma contest contained (*Z*)-1,5-octadien-3-one at levels just four times above threshold.

The sensory work carried out in the present study specifically aimed at understanding the effects of acetaldehyde and its interaction within the different aromatic contexts on the sensory properties of wine models. Notwithstanding, it is also possible to derive some observations about the sensory differences on the basic aroma profile introduced by the different aromatic contexts. A summary of the descriptors and scores of the seven contexts is given in Table 2.

The last rows in the table are just numerals counting 1) the number of descriptors used by the sensory panel in each context (total), 2) the number of descriptors used in the control not present in the other contexts (lack), 3) the number of additional descriptors used to describe the contexts (additional), and 4) the number of descriptors differing from the control (difference). As can be seen, the two aromatic contexts introducing maxima differences with respect to the control (7 different descriptors) are those containing isoamyl alcohol and (*Z*)-1,5-octadien-3-one, closely followed by that containing benzaldehyde (6 different descriptors). The strong effects played by isoamyl alcohol have been previously described (De-la-Fuente-Blanco et al., 2016) and were expected, but the powerful effects apparently played by just 5 ng L^{-1} of (*Z*)-1,5-octadien-3-one or, more strikingly, by levels below 10% of the threshold of benzaldehyde, are very remarkable and warrant further research. The (*Z*)-1,5-octadien-3-one is a strongly odorant compound, with geranium odour (Pons et al., 2018), that plays a role in the perception of vegetable notes and it can be involved in syrup and alcoholic character (Alegre et al., 2020). Although benzaldehyde does not exceed the olfaction threshold in wines, its sensory effect was proved to be related to chemesthesic perceptions (Doty, 1975; Kokkinidou & Peterson, 2016) and some studies suggest the possibility of a synergistic effect of this compound on the fruity and floral aroma notes of wine (Gómez García-Carpintero et al., 2012). It is also noticeable that the three contexts include relatively high scores of the chemesthesic attribute "burning", which seems to replace the chemesthesic attribute "itching", present in the control, in the cases of benzaldehyde and (*Z*)-1,5-octadien-3-one and reinforced in the case of isoamyl alcohol context. The differences between these two chemesthesic perceptions are defined by Green and Shaffer (1993); "itching" was described as *"the sensation associated with the desire to scratch"*, while "burning" as *"the sensation produced by extreme temperatures or chemical irritants, which may or may*

Table 2

Descriptors and scores of the seven aromatic contexts built on reconstituted red wine (RLW) containing no acetaldehyde. Data are mean scores with the standard error of the mean (calculated as $S/N^{1/2}$: (s) standard deviation; (n) number of panellists). No statistical tests were performed between contexts since scores are not directly comparable because of the nature of the sensory work carried out.

	Control	Unsaturated aldehydes	Saturatedaldehydes	Benzaldehyde	Isoamyl alcohol	Methoxy pirazines	(*Z*)-1.5-octadien-3-one
Red fruit	4.73 ± 0.60	–	–	6.55 ± 0.83	–	–	3.55 ± 0.58
Freshness	2.66 ± 0.56	2.95 ± 0.47	2.52 ± 0.85	–	–	–	–
Cooked vegetables	4.26 ± 0.82	2.87 ± 0.65	2.75 ± 0.58	2.42 ± 0.80	3.08 ± 0.75	2.44 ± 0.80	3.88 ± 0.93
Itching	4.03 ± 0.86	3.58 ± 0.85	4.72 ± 0.67	–	3.68 ± 0.79	5.23 ± 0.91	–
Green vegetables	2.30 ± 0.99	2.63 ± 0.72	2.83 ± 0.67	2.40 ± 0.64	1.94 ± 0.53	5.95 ± 0.82	2.55 ± 0.85
Dried Fruit	4.53 ± 0.86	3.60 ± 0.82	4.31 ± 0.89	4.74 ± 0.81	3.24 ± 0.59	3.52 ± 0.68	3.61 ± 0.54
Alcoholic	4.63 ± 0.79	–	5.14 ± 0.67	–	–	4.26 ± 0.82	–
Humidity	–	3.80 ± 0.70	–	2.76 ± 0.82	–	–	3.54 ± 0.98
Undergrowth	–	–	2.88 ± 0.87	–	–	3.85 ± 0.83	–
Burning	–	–	–	5.31 ± 0.92	5.01 ± 0.78	–	5.86 ± 0.93
Animal	–	–	1.96 ± 0.56	2.04 ± 0.77	1.54 ± 0.42	–	–
Solvent	–	–	–	–	4.41 ± 0.56	–	2.91 ± 0.56
Wood	–	–	–	–	3.32 ± 0.63	–	–
Geranium	–	–	–	–	–	–	3.08 ± 0.87
TOTAL[a]	7	6	8	7	8	6	8
Lack[a]		2	1	3	3	3	3
Additional[a]		1	2	3	4	1	4
Difference[a] (lack + additional)		3	3	6	7	4	7

[a] The last rows in the table are just numerals counting: Total: the number of descriptors used by the sensory panel in each context. Lack: the number of descriptors used in the control not present in the other contexts. Additional: the number of additional descriptors used to describe the contexts. Difference: the number of descriptors differing from the control (lack + additional).

not be associated with a thermal sensation". The three contexts also lack the attribute "freshness" present in the control. Apart from this, the context containing isoamyl alcohol is specifically different because of its "solvent" notes, and the (*Z*)-1,5-octadien-3-one context due to its "humidity" and "geranium" odour notes. Differently, benzaldehyde context does not contain specifically different descriptors with high intensity, but presents the maxima scores in "red fruit". The fourth most different context seems to be that containing low levels of the two methoxypyrazines (with 4 different descriptors from control), displaying, not surprisingly, maxima scores in "green vegetables" note, in the "itching" descriptor and having a noticeable "undergrowth" odour note. The two last aromatic contexts showed only three descriptors different from the control. The unsaturated aldehydes just seem to introduce some "humidity" notes, while saturated aldehydes a relatively low "undergrowth" and "animal" odour notes.

Results therefore suggest that some of the contexts were effectively introducing remarkable differences on the sensory nuances, particularly on the chemesthesic notes of the basic red wine aroma profile. This implies that common concentrations of these compounds in wine may be responsible for chemoesthetic and non-aromatic sensations as often described for industry and consumers.

3.3. Influence of acetaldehyde concentration on the sensory descriptors

As can be seen in Table 2 (the complete data set in Supplementary material Table A.2), fourteen different descriptors were quantified in the experiment. Only the terms "cooked vegetables", "dried fruit" and "green vegetables" differed among wine samples with different acetaldehyde levels regardless the context and the term "itching" varied in five out of the seven contexts. Then, six descriptors appeared to vary depending on the level of acetaldehyde in three contexts ("red fruit", "freshness", "alcohol", "humidity", "burning" and "animal"), the descriptors "undergrowth" and "solvent" only in two, and the "geranium" note, only in one. The results of the ANOVA study (detailed together with measurements of intensity in the Supplemental material in Table A.2) make it possible to state that acetaldehyde levels exert deep (and complex) effects on the sensory profiles, significantly affecting to nearly all sensory descriptors. In fact, only the descriptors "alcohol", "animal" and "solvent" were not significantly affected by addition of acetaldehyde in RLW matrix. Some effects were rather general, but some other were dose- and/or context-dependent. Effects will be split into two main categories attending to the amount of acetaldehyde in the headspace: low (below 1 mg L^{-1} or sub ppm levels) or high (above 1 mg L^{-1}). These levels of acetaldehyde would correspond to wines with different levels of oxidation.

3.3.1. Effects of low levels of acetaldehyde

The presence of low levels of acetaldehyde (below 1 mg L^{-1}) in the headspace of the wine-like samples significantly affects to 6 different aromatic notes in 4 (out of the 7) aromatic contexts. On the basis of results summarised in the Table 3, the addition of very low levels of acetaldehyde exerts a major effect on the "red fruit" note, inducing strong changes in the scores measured in two of the three aroma contexts in which it was measured (benzaldehyde and (*Z*)-1,5-octadien-3-one), and close to significance changes in the third (control). Changes are, at first sight, apparently contradictory but they may be congruent. In the control there is a close to significance increase in the score of "red fruit". At higher levels of addition of acetaldehyde (Table A.2 Supplementary

Table 3

Summary of the main significant changes introduced by the presence of sub-ppm levels of acetaldehyde in the headspace of wine models containing different aromatic contexts (control-CT, benzaldehyde-B, methoxypyrazines-MPs and (*Z*)-1,5-octadien-3-one context -ZO) expressed as the average ± standard error (calculated as $S/N^{1/2}$: (s) standard deviation; (n) number of panellists).

Attribute	Context	Free acetaldehyde concentration		
		0.00 ppm	0.18 ppm	0.71 ppm
Red fruit	CT	4.73 ± 0.60 ab	6.05 ± 0.89 a	5.81 ± 0.63 a
	ZO	3.55 ± 0.58 bc	2.94 ± 0.71c	4.33 ± 0.89 ab
	B	6.55 ± 0.83 a	5.43 ± 0.77 ab	4.49 ± 0.76 bc
Freshness	CT	2.66 ± 0.56c	4.84 ± 0.78 a	4.73 ± 0.51 a
Humidity	ZO	3.54 ± 0.99 a	2.00 ± 0.59b	1.49 ± 0.44b
Geranium	ZO	3.08 ± 0.88 a	3.11 ± 0.80 a	1.61 ± 0.46b
Green vegetables	MPs	5.95 ± 0.82 a	6.03 ± 0.97 a	3.66 ± 0.81b
Undergrowth	MPs	3.85 ± 0.84 a	3.22 ± 0.65 ab	2.04 ± 0.60 bc

Different letters indicate significant differences ($p < 0.05$ according to pairwise Fisher test) among the six concentrations of free acetaldehyde (0.00 mg L^{-1}, 0.18 mg L^{-1}, 0.71 mg L^{-1}, 2.74 mg L^{-1}, 17.5 mg L^{-1} and 56.2 mg L^{-1} of free acetaldehyde).

material) the scores show a consistently and significantly decrease (see Fig. 1a), suggesting that little amounts of acetaldehyde are beneficial for the sensory note, but higher levels are not (Coetzee et al., 2016). This is also partly seen in the (*Z*)-1,5-octadien-3-one aromatic context, for which the score in this fruity note significantly increases at acetaldehyde levels in the headspace of 0.71 mg L^{-1}. In the benzaldehyde context, however, the addition of little amounts of acetaldehyde causes a significant and relevant decrease on the "red fruit" odour nuance. It should be observed, however, that the score for the "red fruit" odour nuance in the benzaldehyde context containing no acetaldehyde is the highest score registered for this descriptor. This suggests that the small amount of benzaldehyde added to the control context to form the benzaldehyde context is responsible for such score, playing a role similar to that observed for acetaldehyde in the control, so that the presence of additional levels of the aldehyde (even in low concentrations) brings the scores of "red fruit" down, with the consequent possible loss of wine quality.

Additionally, and as can be seen in Table 3, small levels of acetaldehyde induce a significant increase in "freshness" in the control, and significant and relevant decreases in four different odour notes ("humidity", "geranium", "green vegetable" and "undergrowth") in two specific contexts (methoxypyrazines and (*Z*)-1,5-octadien-3-one). The score in "freshness" reached by the control spiked with 0.18 mg L^{-1} of acetaldehyde is the maximum score for this descriptor in the whole data set (also with 17.5 mg L^{-1} of acetaldehyde). The same happens to the scores reached by "geranium", "green vegetables" and "undergrowth", in this case in the corresponding unspiked contexts. The equivalent score for "humidity" is the second most intense. This suggests, that leaving aside the benzaldehyde context, the effects of the addition of under mg/L amounts of acetaldehyde seem to be highly positive from the sensory point of view, strongly reducing the intensity of rather hedonically-negative scores, such as "humidity", "geranium", "green vegetables" and "undergrowth", and/or increasing the intensity of "red fruit". The fact that the three positively affected aromatic contexts (control, methoxypyrazines and (*Z*)-1,5-octadien-3-one) did not contain any aldehyde or increased amounts of isoamyl alcohol can lead to think that the positive effect is counteracted by any other aldehyde or by isoamyl alcohol.

3.3.2. *Effects of high levels of acetaldehyde*

The addition of relatively high levels of acetaldehyde to RLW brings about, in general, relevant increases in the three sensory descriptors common to the seven aromatic contexts studied ("cooked vegetables", "dried fruit" and "green vegetables") and also to "itching", which was present in 5 out of the 7 aromatic contexts.

3.3.2.1. Descriptors "cooked vegetables" and "dried fruit". Increases were particularly relevant and general for "dried fruit" and "cooked vegetables" in practically all the contexts (Table A.2 Supplementary material). The effects can be seen for the particular case of the control in Fig. 1b and 1c, respectively. It is most remarkable, however, that such increases were not observed when the addition was carried out in similar aromatic contexts prepared in synthetic wines (SW), not containing wine lyophilisate. This strongly suggests that the sensory effects are not caused by acetaldehyde itself, but by other aldehydes, mostly Strecker aldehydes, released from their bisulphite combinations by acetaldehyde. The formation constants of the acetaldehyde-bisulphite adduct (1-hydroxyethyl sulfonate) are higher than those of the Strecker aldehyde-bisulphite adducts (Bueno et al., 2018; De Azevedo et al., 2007), so that acetaldehyde displaces the other aldehydes, releasing them. This is demonstrated by the determination of free and total levels of the five Strecker aldehydes in the samples from the control context containing the different amounts of acetaldehyde. While the total concentration of Strecker aldehydes (expressed as average ± standard deviation) hardly varied when the concentration of acetaldehyde increased

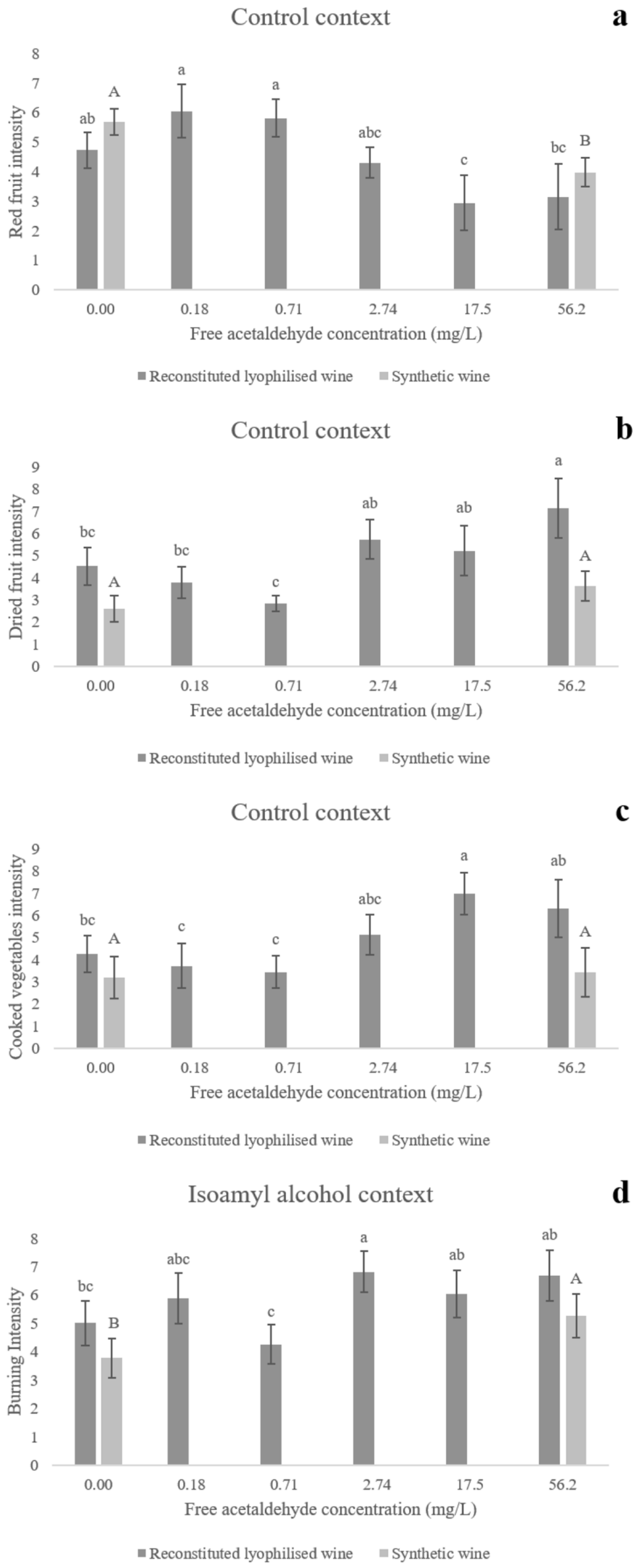

Fig. 1. Average scores (for eight panellists in duplicate; error bars calculated as $S/N^{1/2}$: (s) standard deviation; (n) number of panellists) at different acetaldehyde amounts for: a) "red fruit" in control context in reconstituted lyophilised wine and synthetic wine, b) "dried fruit" and c) "cooked vegetables" in control context in two different matrixes (reconstituted lyophilised wine and synthetic wine), d) "burning" in isoamyl alcohol context in reconstituted lyophilised wine and synthetic wine. Different letters (indicate significant differences for the acetaldehyde content in each model (lowercase for RLW and uppercase for SW) (Fisher posthoc test, $p < 0.05$).

(isobutyraldehyde: 26.47 ± 0.34 μg L^{-1}; 2-methylbutanal: 6.98 ± 0.11 μg L^{-1}; isovaleraldehyde: 100.3 ± 3.1 μg L^{-1}; methional: 5.69 ± 0.37 μg L^{-1} and phenylacetaldehyde: 20.67 ± 0.65 μg L^{-1}), free levels of those aldehydes (Strecker) significantly (R = 0,87, p = 0,02) increased when the free acetaldehyde raised from 0 mg L^{-1} to 56.2 mg L^{-1} (isobutyraldehyde: 3.98 ± 3.21 μg L^{-1} to 21.40 ± 0.89 μg L^{-1}; 2-methylbutanal: 0.70 ± 0.23 μg L^{-1} to 4.00 ± 0.16 μg L^{-1}; isovaleraldehyde: 18.06 ± 0.63 μg L^{-1} to 90.40 ± 3.46 μg L^{-1}; methional: 1.76 ± 0.17 μg L^{-1} to 2.60 ± 0.08 μg L^{-1} and phenylacetaldehyde: 7.65 ± 0.34 μg L^{-1} to 16.00 ± 0.75 μg L^{-1}). Complete data are presented in Fig. A.1 of Supplementary material. The sensory implication of Strecker aldehydes on the "dried fruit" and "cooked vegetables" notes was showed (Culleré et al., 2007; Escudero et al., 2000) and it is corroborated in the correlation studies of this work (data not included). It is remarkable that increases in the "dried fruit" note in contexts containing benzaldehyde and saturated aldehydes were not significant, which reveals the existence of a strong perceptual interaction between these aldehydes and Strecker aldehydes. This was not observed, however, in the "cooked vegetables" note.

3.3.2.2. Descriptor "Green vegetable". The third general sensory descriptor, "green vegetables" increases parallel to levels of acetaldehyde in all the aromatic contexts, except for methoxypyrazines (Fig. 2a). Increases are also observed in this case in the synthetic wines (Fig. 2b), which confirms that they are the result of the direct action of acetaldehyde on the "green vegetables" note. Increases are strongly context-dependent, as can be seen in the figure. Maxima increases are observed for the contexts containing saturated aldehydes, followed by those containing unsaturated aldehydes and benzaldehyde. The control context and those containing isoamyl alcohol and (*Z*)-1,5-octadien-3-one have rather more modest increases. Interestingly, the effects on the methoxypyrazine context were exactly the opposite; the scores for green vegetables were maxima in the samples containing none or very little amounts of acetaldehyde, and increasing acetaldehyde levels from 0.18 to 0.71 mg L^{-1} bring about a dramatic decrease in the intensity of the

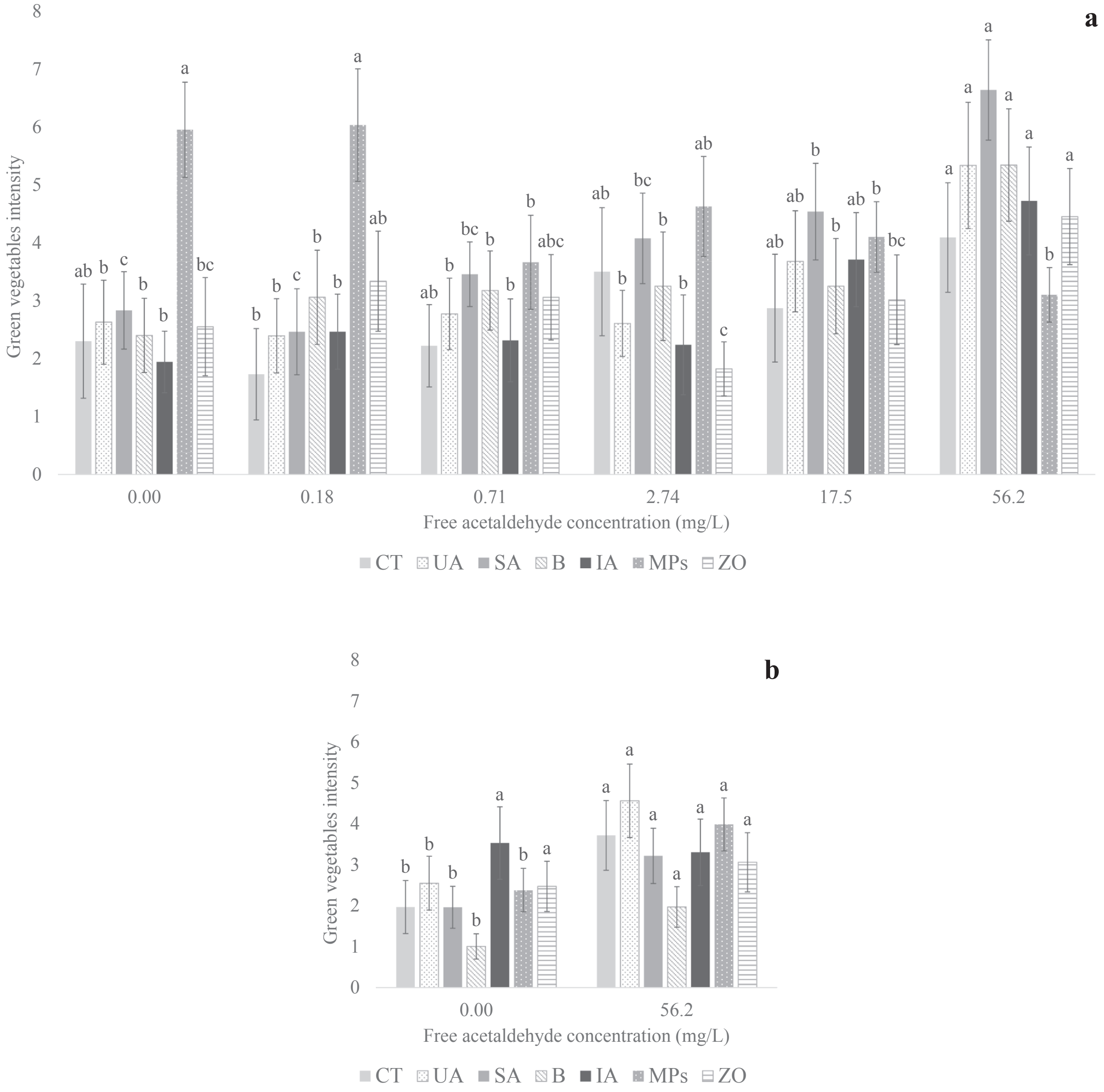

Fig. 2. Average scores (for eight panellists in duplicate; error bars calculated as $S/N^{1/2}$: (s) standard deviation; (n) number of panellists) for "green vegetable" evaluated in different contexts (control-CT, unsaturated aldehydes-UA, saturated aldehydes-SA, benzaldehyde-B, isoamyl alcohol-IA, methoxypyrazines-MPs and (*Z*)-1,5-octadien-3-one context -ZO) at different acetaldehyde levels: a) in reconstituted lyophilised wine, b) in synthetic wine. Different letters indicate significant differences for the acetaldehyde content in each context (Fisher posthoc test, $p < 0.05$).

descriptor which did not recover at higher levels of acetaldehyde. These results strongly suggest that there are at least two completely different origins for the "green vegetable" note. The first one would be directly caused by nearly every type of aldehydes, and the second one would be caused by methoxypyrazines, as widely described in the scientific literature (Coetzee et al., 2016; Francis & Newton, 2005). It can be hypothesised that the "green vegetables" notes given by methoxypyrazines or aldehydes are likely conceptually different, which suggests the need for addressing further sensory studies about their exact definition.

Regarding the role of aldehydes, results demonstrate that unsaturated, saturated and even Strecker aldehydes, support and enhance the role of acetaldehyde in the formation of the "green vegetable" note following a quite complex pattern of perceptual interactions. The effects of Strecker aldehydes can be seen by comparing the scores of the SW models with those of the RLW models in the Fig. 2a-2b. In the cases of saturated aldehydes and of benzaldehyde, the triple interaction is particularly outstanding, as can be seen in Fig. 2. The intensity of the "green vegetable" note in the SW models containing acetaldehyde (Fig. 2b) is much smaller than that measured in the equivalent RLW models (Fig. 2a). The practical implications of these observations could be potentially very high and could be behind some of the frustrating results obtained in the research of the chemicals responsible for green vegetable and herbaceous notes (Arias-Pérez et al., 2020; Sáenz-Navajas et al., 2018). It should be noted that unsaturated aldehydes (such as (*E*/*Z*)-2.6-nonadienal, (*E*/*E*)-2.4-decadienal, (*E*)-2-nonenal, (*E*/*E*)-2.4-nonadienal, (*Z*)-3-hexenal and (*Z*)-2-nonenal), saturated aldehydes (such as octanal, nonanal and/or decanal), and of course benzaldehyde and Strecker aldehydes, are common and relatively ubiquitous aroma compounds, present at very low concentrations in grapes (Alegre et al., 2020) and wines (Bueno et al., 2018; Culleré et al., 2007). Results in the present paper demonstrate that the concerted action of this complex pool of at least 15 aroma chemicals, none of them present at remarkably high levels, can induce relatively large scores in the "green vegetables" note in the presence of acetaldehyde.

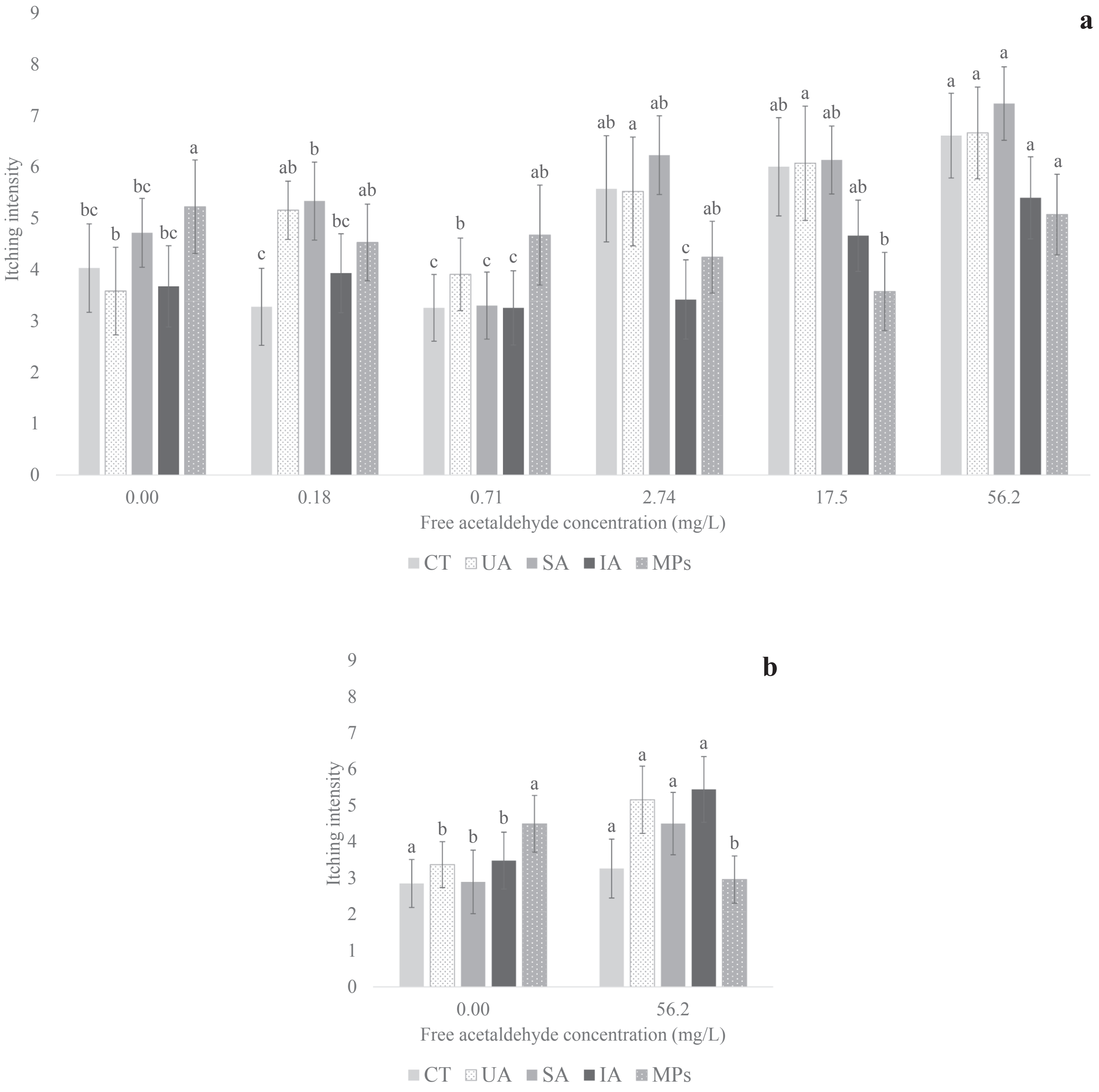

Fig. 3. Average scores (for eight panellists in duplicate; error bars calculated as $S/N^{1/2}$: (s) standard deviation; (n) number of panellists) for "itching" in different contexts (control, unsaturated aldehydes, saturated aldehydes, isoamyl alcohol and methoxypyrazines context) at different acetaldehyde levels: a) in reconstituted lyophilised wine, b) in synthetic wine. Different letters indicate significant differences for the acetaldehyde content in each context (Fisher posthoc test, $p < 0.05$).

3.3.2.3. Itchiness and burning effects. The increase in the concentrations of acetaldehyde produces an increase in the chemesthesic perception of “itching” in four out of the five aromatic contexts. Increases were, again, context dependent and were also different between RLW (Fig. 3a) and SW (Fig. 3b) samples. The plots in the figure reveal the existence of three markedly different patterns among the five contexts: the first one followed by unsaturated (UA) and saturated aldehydes (SA) and by isoamyl alcohol (IA), a second one followed by the control (CT), and a third completely different one followed by methoxypyrazines (MPs). In the first one, increases are evident both in RLW and SW models, although in the two contexts with aldehydes, increases were more evident in RLW models. In the control, increases in SW models were nearly null. Finally, in the MPs context, which had maxima levels for this descriptor, the increase of acetaldehyde brings about a decrease on its intensity, evident only in SW model (Fig. 3b). The lack of implication of acetaldehyde on “itchiness” in simple contexts, such as the control SW, at the levels tested in the present work, has been already shown by Muttray et. al (2009). At higher levels other authors reported time ago that acetaldehyde concentrations can produce the “itching” sensation (Miyake & Shibamoto, 1993), which would be consistent with the proven capacity of this molecule to interact with TRP receptors (Bang et al., 2007). Our results, paralleling those previously seen in the “green vegetable” note, suggest that this sensory note is the result of complex perceptual interactions between many different chemicals. Differences in the control and in the methoxypyrazine contexts between SW and RLW models evidence the potential implication of Strecker aldehydes. Differences in SW models between the control and the contexts containing other aldehydes and isoamyl alcohol evidence the active participation of saturated and unsaturated aldehydes and also of isoamyl alcohol. Finally, the decrease in “itchiness” noted with acetaldehyde in the SW model in the methoxypyrazine context, reveals a negative perceptual interaction between acetaldehyde and methoxypyrazines. It can be speculated that such negative perceptual interaction is counteracted by the enhancing effect exerted by Strecker aldehydes, which would explain why the decrease is not observed in the RLW model with methoxypyrazines. As saturated aldehydes at high concentrations are known elicitors of orthonasal (Abraham et al., 2007) and in mouth trigeminal effects (Kokkinidou & Peterson, 2016), and unsaturated aldehydes can stimulate TRPA1 receptors (Andrè et al., 2008), our results support a strong modulation effect of acetaldehyde on these chemesthesic effects.

Another relevant chemesthesic descriptor is “burning”, which was measured in three contexts (benzaldehyde, isoamyl alcohol and (*Z*)-1,5-octadien-3-one). In this case, effects of acetaldehyde were identified only in the context containing isoamyl alcohol, as seen in the Fig. 1d. Results indicate that the burning character of those models are modulated by acetaldehyde. It is remarkable that the minimum burning score is registered at low levels of acetaldehyde (0.71 mg/L), and that the addition of just 2 mg L^{-1} more induces a large increase in intensity of 2.55 points. This could explain some of the unexplained sensory changes experienced by wines after short periods of time, perhaps small increases in acetaldehyde levels due to poor storage can cause chemesthesic sensations in consumer.

4. Conclusions

Low-supra threshold levels of (Z)-1,5-octadien-3-one, far-under threshold levels of benzaldehyde or high levels of isoamyl alcohol induce “burning” character and limit the perception of “freshness” in the wine aroma profiles. The concentration of these compounds must be controlled in order to obtain aromatic quality wines.

The presence of levels below mg L^{-1} (sub ppm) of acetaldehyde enhances, in the absence of any other aldehyde, “red fruit” notes and wine “freshness”, and can also suppress effectively off-odours caused by (Z)-1,5-octadien-3-one (“humidity” and “geranium”) and by methoxypyrazines (“green vegetables” and “undergrowth”). Thus, low concentrations of acetaldehyde can even be positive for the aroma in non-oxidized wines. Such approaches have tentatively disclosed valuable information, that could be implemented in wine industry.

A side effect of the addition of higher amounts of acetaldehyde to wines is the release of Strecker aldehydes from their adducts with bisulphite, which provokes increases in “cooked vegetables” and “dried fruit” descriptors. Perceptual interactions with benzaldehyde and saturated aldehydes prevented increases in “dried fruit”.

Fifteen different aldehydes (unsaturated, saturated and Strecker aldehydes), none of them present at remarkably high levels, can induce a “green vegetable” note and an “itching” character in which acetaldehyde plays a strong enhancer role, contrarily to the “green vegetable” note and “itching” character caused by methoxypyrazines. This information might be useful to the wine industry in order to manage the green character of wines.

The “burning” character elicited by isoamyl alcohol is strongly affected by small changes in acetaldehyde levels.

This research shows the concourse of different players (aldehydes, isoamyl alcohol, (*Z*)-1,5-octadien-3-one and methoxypyrazines) on wine aroma and tactile nasal characteristics and demonstrates that acetaldehyde levels play an outstanding role in their modulation. At sub ppm levels, it can play positive roles in some specific aromatic contexts, while at higher levels, enhances the negative effects associated to the generic presence of other aldehydes by enhancing “green vegetable” notes and “itching” character and the “burning” effects linked to high levels of isoamyl alcohol.

CRediT authorship contribution statement

I. Arias-Pérez: Data curation, Formal analysis, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2021.130081.

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