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Concentrations of Aroma Compounds and Odor Activity Values of Odorant Series in Different Olive Cultivars and Their Oils

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ABSTRACT: Olives from Picual, Arbequina, Manzanilla de Sevilla, and *Local* cultivars together with their corresponding oils were analyzed in terms of odor activity values (OAVs) to establish the relationship between the aromatic profile of both olives and oils. The OAVs for the different compounds were classified in nine odorant series: grass, leaf, wood, bitter, sweet, pungent, olive fruit, apple, and banana. The total intensities for every aromatic series were calculated as the sum of the OAVs of each compound associated with this series. As a result, olives had characteristic profiles. Picual cultivar had not a clear sensory characterization from the volatile compounds. Arbequina cultivar was mainly characterized by apple and bitter odorant series; Manzanilla de Sevilla by apple, bitter, and grass odorant series; and *Local* variety by banana and olive fruit. However, in the oils obtained from those olives, these differences disappeared, and all oils showed the same profile with pungent, bitter, and wood odorant series most strongly contributing.

KEYWORDS: *olives, olive oil, odor activity value (OAV), odorant series, lipoxygenase (LOX) pathway*

■ INTRODUCTION

Extra virgin olive oil (EVOO) is the highest quality and most flavorful olive oil category. In chemical terms it is described as having a free acidity, expressed as oleic acid, of not more than 0.8 g per 100 g and a peroxide value of less than 20 mequiv per kg of oil. It must be produced entirely by mechanical means without the use of any solvents, and under temperatures that will not degrade the oil. In order for an oil to qualify as "extra virgin", the oil must also pass both an official chemical test in a laboratory and a sensory evaluation by a trained tasting panel recognized by the International Olive Council (IOC).[1] The olive oil must be free from defects while exhibiting some fruitiness. The positive attributes are described by olive oil tasters according to IOC glossary:[2]

- Fruity: set of olfactory sensations characteristic of the oil that depends on the variety and comes from sound, fresh olives, either ripe or unripe. It is perceived directly and/or through the back of the nose.
- Bitter: characteristic primary taste of oil obtained from green olives or olives turning color. It is perceived in the circumvallate papillae on the "V" region of the tongue.
- Pungent: biting tactile sensation characteristic of oils produced at the start of the crop year, primarily from olives that are still unripe. It can be perceived throughout the whole of the mouth cavity, particularly in the throat.

Ripe fruit yields oils that are milder, aromatic, buttery, and floral. Green fruit yields oils that are grassy, herbaceous, bitter, and pungent. Fruitiness also varies with the variety of olives. The oil's green and fruity attributes depend on many volatile compounds derived from the degradation of polyunsaturated fatty acids through a chain of enzymatic reactions known as the lipoxygenase (LOX) pathway taking place during the oil extraction process.[3−5] Aliphatic C_6 and C_5 compounds—aldehydes, alcohols, and their corresponding esters from the LOX pathway—represent the most important fraction (80%) of volatile compounds of high-quality virgin olive oils from a quantitative point of view.[6] The presence of other minor volatile compounds gives information about authentication of olive oils[7] and/or ecocontaminants.[8] Chemical oxidation and exogenous enzymes, usually from microbial activity, are associated with sensory defects.[9] In this sense, it is of paramount importance to prevent off-flavors by different contamination processes.[10,11]

The odor activity value (OAV) allows estimation of the contribution of each odorant to the olive oil aroma. OAVs are calculated by dividing the concentrations of the odorants in the oil sample by their odor threshold values. The odor of a compound can be described by one or several descriptors. Thus, on grouping the OAVs of the aroma compounds with similar descriptors into aromatic series, estimation of the organoleptic profile of the oil can be established. This procedure, applied until now only to wine studies,[12−15] makes it possible to relate quantitative information obtained by chemical analysis to sensory perception, providing a tentative aroma profile.

The main objective of this study was the search for a relationship between aroma profiles of olives and their corresponding oils, both estimated by the use of OAV data, to evaluate whether a link between both profiles could be established with the purpose to predict the sensory characteristics of EVOOs prior to processing the olives.

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■ MATERIALS AND METHODS

Olive Samples. For this study, four olive cultivars growing in Galicia (NW Spain) were selected: Picual, Arbequina, Manzanilla de Sevilla, and *Local*. From each cultivar five independent lots of olive fruits (approximately 3 kg each) were collected in December 2010 and immediately transported to the laboratory under refrigerated conditions. Once in the laboratory, the samples were stored at −80 °C until analysis.

Fingerprinting based on simple sequence repeat (SSR) markers was employed for characterizing the studied cultivars. Approximately 1 kg of olives from each cultivar was sent to the Pomology Group at the Department of Agronomy at the University of Cordoba (Spain) to develop molecular studies. Nine microsatellite primers (DCA01, DCA04, DCA09, DCA18, UDO15, UDO17, GAPU59, GAPU71B, and GAPU89) were used for the analysis following the protocol described by Belaj et al.[16] Correctly identified varieties included in the database of World Olive Germplasm Bank (WOGB) of Cordoba-Spain, which represents the main repository of olive genotypes in Spain, were employed as reference samples. One of the samples (called by the authors *"Local"* variety) did not match with any variety included in the database. Additionally, this cultivar was characterized using biometrical parameters of the fruit and endocarp.[17]

Extra Virgin Olive Oil Samples. EVOO from olives above-described were produced in December 2010. All the samples were extracted in two identical local oil mills equipped with an olive washing machine, a hammer crusher, a kneader, and a two-phase horizontal decanter; the olive paste was kneaded at 27 ± 3 °C during 30 min.

Once in the laboratory, the samples were kept at a constant temperature of 15 ± 2 °C in amber bottles without headspace. The samples were allowed to settle for about 2 months, and later were racked, following the procedure of local olive oil producers before the oil marketing.

Aroma Determination in Olives and Oils. *Preparation of Volatile Standard Solutions.* Volatile compounds tested in olives and their corresponding oils were purchased from Sigma-Aldrich (St. Louis, MO, USA). Individual standard solutions for the volatile compounds were prepared in EtOH (about 20,000 μg/mL). Secondary standard solutions were prepared by dilution in hexane of each individual standard solution. Working solutions, containing target analytes, were prepared by mixing and diluting different amounts of secondary standard solutions in hexane. In the same manner was prepared a solution contained the internal standard (IS), 2-octanol. Stripped oil, used as matrix for calibration, was prepared by vacuum pumping commercial refined sunflower oil purchased by Aceites Abril S.L. (Galicia, Spain). Calibration standard solutions (12 levels ranging from 10 to 10,000 ng/mL) were prepared by spiking appropriate working solutions (5, 50, and 200 μg/mL in hexane) in the stripped refined sunflower oil.

Extraction of Volatile Compounds from Olives and Oils. Volatile compounds were extracted from the samples by dynamic headspace (DHS) with an automatic sampler device, the Master DHS (DANI Instruments S.p.A., Cologno Monzene, Milan, Italy), following our previous works.[18,19] In the case of olives, temperature of extraction was diminished from 60 to 40 °C to avoid excessive water evaporation because olives contain a high proportion of water.[20]

To evaluate the aroma compounds from olives, 2 g of the crushed material was placed into a 20 mL vial with the internal standard (2-octanol). The vial was maintained at 25 °C and 15 min to develop LOX pathway compounds, and then 2 mL of $CaCl_2$ saturated solution as an enzymatic inhibitor was added, following the protocol by Servili et al.[21] To evaluate the aroma compounds from oils, 8 g of oil was placed into a 20 mL vial with the internal standard (2-octanol).[18]

Identification and Quantification of Volatiles by GC-ITMS. Aroma compounds were separated and identified on a TRACE GC gas chromatograph with a Polaris Q ion trap mass selective detector and interfaced to a computer running the software Xcalibur 1.4, from Thermo Finnigan (Rodano, Italy). Chromatographic separations were done with a ZB-WAX fused-silica capillary column (60 m × 0.32 mm i.d., 0.50 μm film thickness) (Phenomenex, Torrance, CA, USA). The carrier gas, helium, was circulated at 1 mL/min in the constant flow mode. A split/splitless injector in the split mode was used (split ratio: 10). The injector temperature was 200 °C. The oven temperature program was as follows: 40 °C for 5 min; 2 °C/min ramp to 125 °C; 10 °C/min ramp to 250 °C and holding for 5 min. The transfer line temperature was 250 °C, and the ion trap manifold temperature 200 °C. The ion energy for electron impact (EI) was set constantly at 70 eV. Identification of the aroma compounds was performed by comparing the GC retention times and mass spectra over the mass range 35−300 amu for the samples with those for pure standards analyzed under the same conditions. Mass detection was performed in the selected ion recording (SIR) mode for quantification. The ions (m/z) selected are shown in Table 1.

Table 1. Quantification Fragments (m/z) and Relative Intensities (%) for Volatile Compounds Analyzed by GC−ITMS

volatile compound	m/z (rel abundance, %)
	Aldehydes
trans-2-hexen-1-al	55 (96.2) + 69 (63.9) + 83 (84.9)
trans-2-pentenal	55 (48.4) + 83 (99.9)
hexanal	41 (99.9) + 67 (39.3)
pentanal	43 (9.0) + 58 (65.1)
	Alcohols
trans-2-hexen-1-ol	57 (33.6) + 67 (99.9)
cis-2-hexen-1-ol	67 (99.9) + 82 (28.5)
trans-3-hexen-1-ol	67 (99.9) + 82 (17.9)
cis-3-hexen-1-ol	67 (99.9) + 82 (15.4)
1-penten-3-ol	57 (99.9) + 67 (12.3)
1-hexanol	41 (99.9) + 69 (33.0)
1-pentanol	41 (81.9) + 55 (99.9)
trans-2-penten-1ol	57 (99.9) + 67 (39.5)
cis-2-penten-1-ol	57 (99.9) + 67 (86.2)
	Esters
cis-3-hexenyl acetate	67 (99.9)
trans-2-hexenyl acetate	67 (99.9) + 82 (42.4) + 100 (23.5)
hexyl acetate	56 (49.3) + 119 (30.0)
	Ketones
3-pentanone	56 (62.7) + 57 (99.9)
1-penten-3-one	55 (99.9) + 83 (61.0)

Odor Activity Values (OAVs). To evaluate the actual contribution of a volatile compound to the aroma of olives and oils the odor activity value (OAV) was determined.[22,23] Nine odorant series were established: grass, leaf, wood, bitter, sweet, pungent, olive fruit, apple, and banana. The OAV was calculated by dividing the concentration of each compound by its odor threshold concentration. The total intensities for every odorant series were calculated as a sum of the OAV of each compound assigned to this series.

■ RESULTS AND DISCUSSION

Aroma Profile of Olives. *C6 Content in Olives.* C6 saturated and unsaturated volatile compounds, responsible for the positive green sensory perceptions in olive oil, are mainly produced by endogenous olive enzymes through the LOX pathway (from linoleic acid (LA) and linolenic acid (LnA)), and they are later incorporated into the oily phase. Table 2 shows the results obtained when C6 compounds were determined in four olive cultivars (Picual, Arbequina, Manzanilla de Sevilla, and *Local*) grown in Galicia. According to Ridolfi et al.[24] work there seems to be a relationship between the quantity of C6 compounds and LOX activity. The fruits of *Local* and Manzanilla de Sevilla varieties presented the highest C6 content, consequently a higher enzymatic activity would be

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Table 2. Concentration of Volatile Compounds in Olives (ng/g of Olive) and Their Corresponding Oils (ng/g of Oil)

	concentration ± SD (ng/g, n = 5)							
	olives				oils			
compound	Picual	Arbequina	Manzanilla de Sevilla	*Local*	Picual	Arbequina	Manzanilla de Sevilla	*Local*
aldehydes								
trans-2-hexen-1-al (LnA)	465 ± 49	3206 ± 332	3067 ± 257	416 ± 47	2125 ± 364	3479 ± 318	4450 ± 363	1253 ± 200
trans-2-pentenal (LnA)	<LOQ (4.9)	<LOQ (4.9)	<LOQ (4.9)	<LOQ (4.9)	5.1 ± 1.7	19.5 ± 4.8	11.0 ± 1.2	<LOQ (4.9)
hexanal (LA)	218 ± 24	312 ± 33	412 ± 74	410 ± 57	137 ± 18	769 ± 109	396 ± 114	197 ± 31
pentanal (LA)	45.4 ± 9.3	<LOQ (18.2)	227 ± 26	116 ± 5	3775 ± 631	6974 ± 1262	14142 ± 2127	2761 ± 766
∑aldehydes	**728**	**3518**	**3706**	**942**	**6042**	**11241**	**18999**	**4212**
alcohols								
trans-2-hexen-1-ol (LnA)	117 ± 9	11.6 ± 2.7	160 ± 17	26.2 ± 2.6	2946 ± 388	2573 ± 134	3439 ± 167	922 ± 51
cis-2-hexen-1-ol (LnA)	nd	<LOQ (10.0)	<LOQ (10.0)	nd	11.7 ± 2.2	11.6 ± 0.7	nd	nd
trans-3-hexen-1-ol (LnA)	<LOQ (5.4)	nd	<LOQ (5.4)	22.2 ± 5.0	14.4 ± 2.7	16.6 ± 1.4	21.0 ± 1.7	16.9 ± 0.9
cis-3-hexen-1-ol (LnA)	284 ± 35	42.7 ± 3.7	642 ± 51	2493 ± 271	1218 ± 178	181 ± 17	967 ± 83	1084 ± 60
1-penten-3-ol (LnA)	<LOQ (9.5)	<LOQ (9.5)	<LOQ (9.5)	<LOQ (9.5)	861 ± 140	1986 ± 319	763 ± 132	496 ± 61
1-hexanol (LA)	384 ± 35	55.9 ± 8.0	279 ± 35	1625 ± 167	53.4 ± 12.7	1748 ± 127	197 ± 30	172 ± 3
1-pentanol (LA)	<LOQ (10.0)	<LOQ (10.0)	52 ± 8	61.6 ± 8.2	16.8 ± 2.7	44.8 ± 6.1	44.6 ± 11.6	16.0 ± 6.1
trans-2-penten-1ol (LnA)	<LOQ (8.3)	nd	nd	32.3 ± 7.2	30.4 ± 5.6	39.2 ± 5.9	42.1 ± 1.7	18.8 ± 2.0
cis-2-penten-1-ol (LnA)	<LOQ (7.4)	<LOQ (7.4)	<LOQ (7.4)	nd	128 ± 23	206 ± 26	179 ± 12	86.5 ± 20.8
∑alcohols	**786**	**110**	**1133**	**4260**	**5280**	**6806**	**5653**	**2812**
esters								
cis-3-hexenyl acetate (LnA)	47.5 ± 4.9	31.4 ± 3.1	499 ± 45	566 ± 52	51.2 ± 6.0	10.7 ± 1.4	668 ± 52	670 ± 29
trans-2-hexenyl acetate (LnA)	nd	nd	nd	nd	nd	7.8 ± 1.0	8.7 ± 0.6	nd
hexyl acetate (LA)	<LOQ (20.0)	32.5 ± 3.0	256 ± 26	89.7 ± 6.8	46.7 ± 7.4	19.8 ± 2.5	163 ± 23	100 ± 10
∑esters	**47.5**	**63.9**	**755**	**656**	**97.9**	**38.3**	**840**	**770**
ketones								
3-pentanone (LA)	<LOQ (9.5)	<LOQ (9.5)	41.6 ± 8.1	110 ± 8	1100 ± 208	944 ± 233	3523 ± 344	1555 ± 424
1-penten-3-one (LnA)	<LOQ (2.9)	<LOQ (2.9)	<LOQ (2.9)	<LOQ (2.9)	27.7 ± 6.4	95.5 ± 18.6	30.6 ± 2.1	22.7 ± 2.4
∑ketones			**41.6**	**110**	**1128**	**1039**	**3554**	**1578**
∑total compounds	**1561**	**3692**	**5636**	**5968**	**12548**	**19124**	**29046**	**9372**

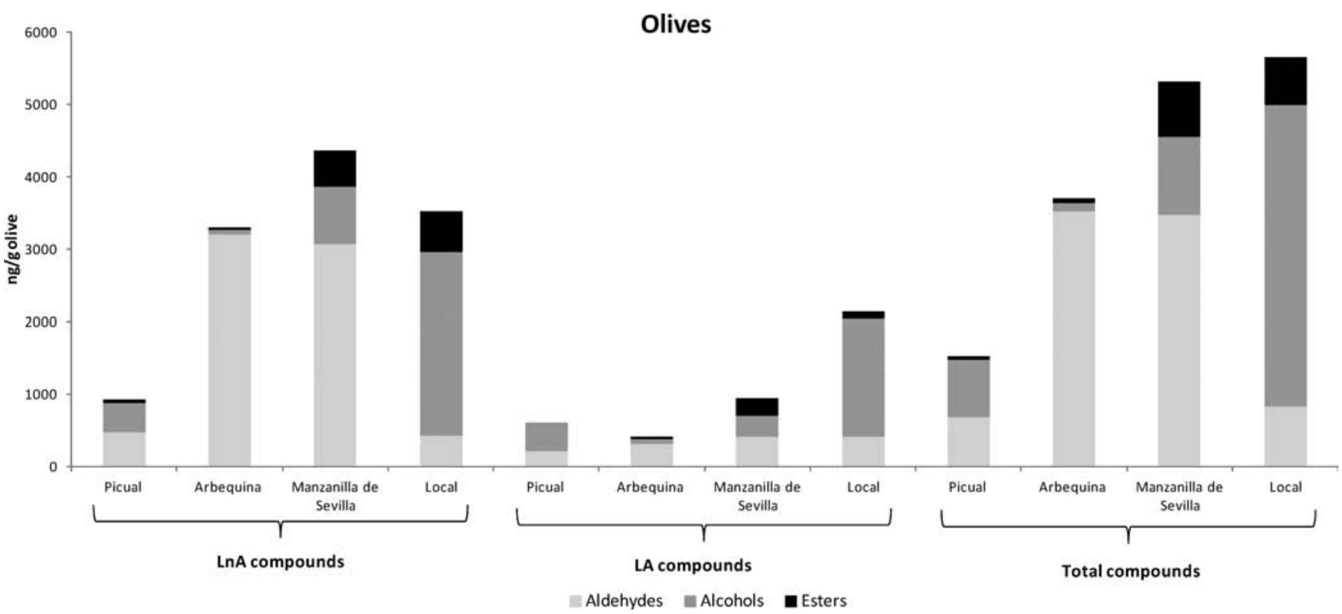

Figure 1. Sum of C6 volatile compounds derived by LOX action in Galician olive fruits. Volatile content of C6/LnA aldehydes is *trans*-2-hexen-1-al. Volatile contents of C6/LnA alcohols are the sum of *cis*-2-hexen-1-ol, *trans*-2-hexen-1-ol, *cis*-3-hexen-1-ol, and *trans*-3-hexen-1-ol. Volatile contents of C6/LnA esters are the sum of *cis*-3-hexenyl acetate and *trans*-2-hexenyl acetate. Volatile content of C6/LA aldehydes is hexanal. Volatile content of C6/LA alcohols is hexanol. Volatile content of C6/LA esters is hexyl acetate.

expected. Nevertheless, the Picual variety showed the lowest C6 content, probably due to a lower enzymatic activity.

As can be seen in Figure 1, *Local* variety had the highest concentration of alcohols and mean contents of aldehydes and

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esters. It was characterized by high concentrations of *cis*-3-hexen-1-ol (2493 ng/g) and 1-hexanol (1625 ng/g). The aldehydes, *trans*-2-hexenal and hexanal, were present at the same order (ca. 400 ng/g). *cis*-3-Hexenyl acetate content (566 ng/g) was higher than that of hexenyl acetate (89.7 ng/g). Manzanilla de Sevilla variety was characterized by the highest concentration of aldehydes and a mean content of alcohols and esters. It was characterized by a high concentration of *trans*-2-hexenal (3067 ng/g) and a lower content of hexanal (412 ng/g). *cis*-3-Hexenyl acetate (499 ng/g) and hexenyl acetate (256 ng/g) were the main esters identified. Arbequina variety, like Manzanilla de Sevilla, showed a high content of aldehydes. It was characterized by a high concentration of *trans*-2-hexenal (3206 ng/g). However, alcohols and esters coming from LnA and LA were present at low levels (110 and 63.9 ng/g, respectively, for each group). Finally, Picual variety had low contents of aldehydes and alcohols; moreover substantially no esters were quantified (47.5 ng/g).

Description of the Aroma Profile of Olives. The odor descriptors of the C6 and C5 compounds that contribute most positively to the sensory properties of EVOOs were taken from the literature[3,25,26] and grouped in 9 different odorant series: grass, leaf, wood, bitter, sweet, pungent, olive fruit, apple, and banana. Some compounds were included in two or more odorant series based on the similarity of odor descriptor (Table 3). The total intensities for every odorant series were calculated as sum of the OAV of each compound assigned to this series.

In Figure 2a, comparison of the aromatic profiles for the studied olive cultivars is presented. It can be observed that the greatest difference was registered in apple, bitter, banana, and olive fruit odorant series. The numerical value of these differences was established by subtracting the highest and the lowest OAV values of each odorant series, as can be seen in the text accompanying the figure.

In apple odorant series, the highest value corresponded to Manzanilla de Sevilla olives (OAV = 12.5) and the lowest value to Picual olives (OAV = 4). For bitter odorant series, Manzanilla de Sevilla presented the highest value (OAV = 8.2), meanwhile *Local* and Picual had the lowest ones (OAV = 1.3 and 1.5, respectively). On the other hand, *Local* olives showed the greatest potential in the banana odorant series (OAV = 7) in contrast to Arbequina olives (OAV = 0.3). In olive fruit and grass odorant series, *Local* and Manzanilla de Sevilla had the highest value (both OAV = 5, respectively), whereas Picual and Arbequina olives had the lowest OAVs (1 and 0.2, respectively).

As a conclusion, Picual cultivar had not a clear sensory characterization from the volatile compounds. Arbequina cultivar was mainly characterized by apple and bitter odorant series; Manzanilla de Sevilla by apple, bitter, and grass odorant series; and *Local* variety by other odorant series different from those described above, namely, banana and olive fruit.

Aroma Profile of Olive Oils. *C6 and C5 Content in Olive Oils.* C6 compounds derived by LOX action were also determined in the oil samples obtained from the previous olive samples. As can be seen in Table 2, the same 19 compounds were determined; nevertheless, there was a significant quantitative and qualitative difference in the volatile compounds in the fruit compared to the oil. As a difference of the behavior observed for the C6 compounds in olives, Manzanilla de Sevilla oil showed the highest C6 content; meanwhile *Local* oil showed the lowest C6 content. For all oils tested, the final concentrations found were higher than those determined in olives. This fact is due to the continuity of the LOX pathway, initiated by the release of enzymes when olive fruit tissues are disrupted during all stages of oil processing (see C6 contents in Table 2).

Table 3. Odorant Series, Chemical Compounds, and Odor Threshold (ng/g) Used

odorant series	chemical compound	odor threshold (ng/g)
grass	hexanal	300[23]
	trans-2-hexenal	1125[32]
	hexyl acetate	1040[32]
	cis-3-hexenylacetate	750[32]
	trans-2-hexen-1-ol	8000[33]
	1-penten-3-one	50[32]
	3-pentanone	70000[34]
	1-penten-3-ol	400[34]
leaf	*cis*-3-hexen-1-ol	1100[23]
	trans-2-hexen-1-ol	5000[9]
	1-penten-3-one	50[32]
wood	pentanal	240[9]
olive fruit	hexyl acetate	1040[32]
	cis-3-hexenylacetate	750[32]
	1-hexanol	400[32]
	3-pentanone	70000[34]
	1-penten-3-ol	400[34]
	1-pentanol	470[32]
	cis-2-penten-1-ol	250[34]
apple	hexanal	80[9]
	trans-2-hexenal	424[23]
	cis-3-hexen-1-ol	1100[23]
	trans-2-pentenal	300[9]
banana	*cis*-3-hexenylacetate	200[23]
	1-hexanol	400[33]
	cis-2-penten-1-ol	250[34]
bitter	*trans*-2-hexenal	420[9]
	trans-3-hexen-1-ol	1500[33]
	pentanal	240[9]
	1-penten-3-one	0.73[23]
	trans-2-pentenal	300[32]
sweet	hexanal	75[32]
	hexyl acetate	1040[32]
	3-pentanone	70000[34]
	cis-2-penten-1-ol	250[34]
pungent	1-penten-3-one	0.73[23]
	1-penten-3-ol	400[34]
	1-pentanol	3000[9]

Local oil presented mean contents of alcohols and aldehydes and a lower concentration of esters (Figure 3). It was characterized by *trans*-2-hexen-1-ol (922 ng/g) and *cis*-3-hexen-1-ol (1084 ng/g) within the group of alcohols. The aldehyde *trans*-2-hexenal showed the highest value (1253 ng/g). *cis*-3-Hexenyl acetate concentration (670 ng/g) was higher than that of hexyl acetate (100 ng/g). On the other hand, Manzanilla de Sevilla oil presented elevated contents of alcohols and aldehydes and lower ester concentrations. It was characterized by a high concentration of *trans*-2-hexenal (4450 ng/g) and a lower concentration of hexanal (396 ng/g). The *trans*-2-hexen-1-ol content (3439 ng/g) was higher than *cis*-3-hexen-1-ol content (967 ng/g). *cis*-3-Hexenyl acetate (668 ng/g) and hexyl acetate (163 ng/g) were the main esters identified. Arbequina oil had lower content of esters in comparison with *Local* or Manzanilla de Sevilla oil. It was characterized by a high

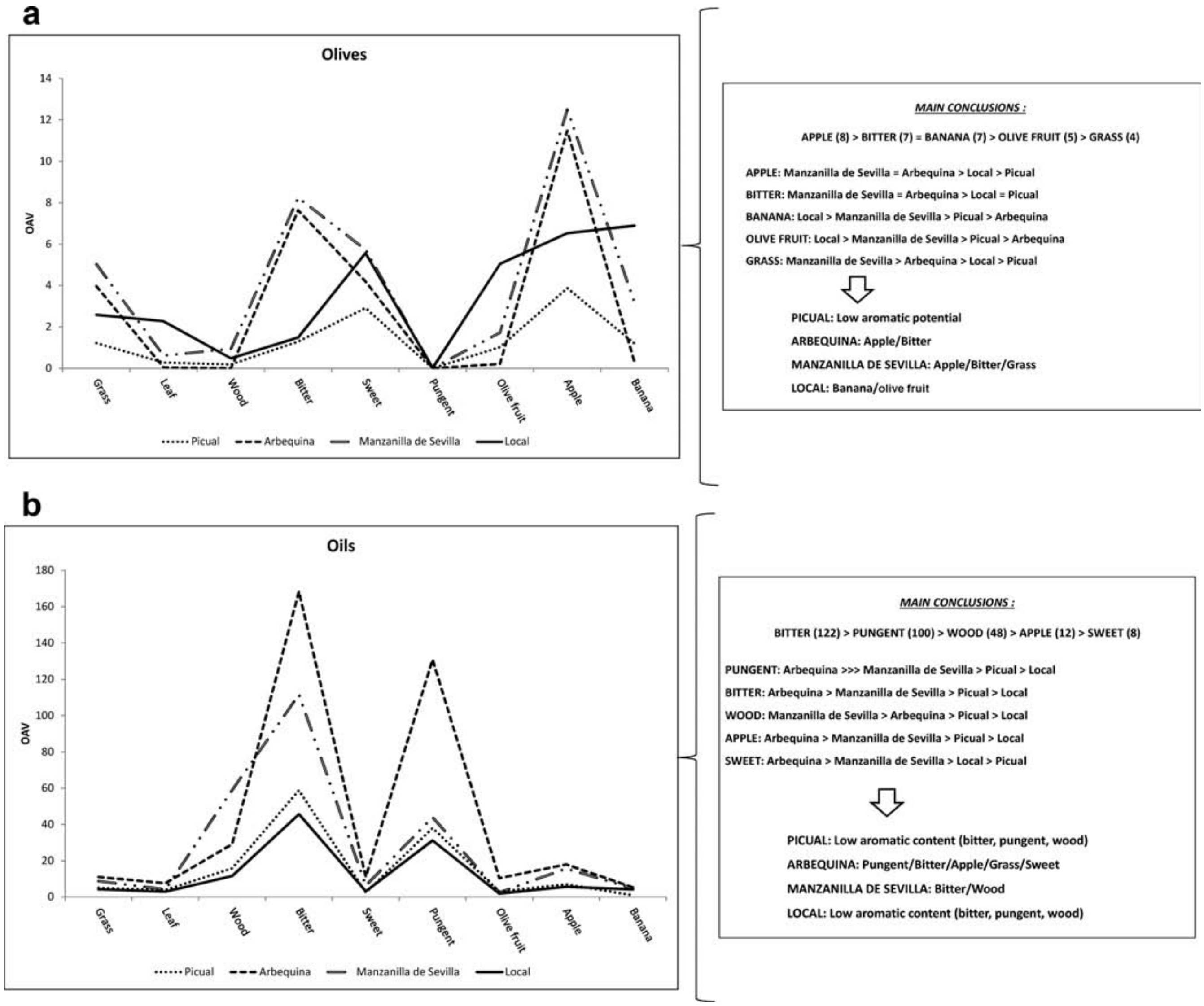

Figure 2. Comparation of OAVs in olives growing in Galicia (a) and their corresponding extra virgin olive oils (b).

concentration of *trans*-2-hexenal (3479 ng/g). The two main alcohols identified were *trans*-2-hexen-1-ol (2573 ng/g) and 1-hexanol (1748 ng/g). This variety had a lower content of esters: *cis*-3-hexenyl acetate (10.7 ng/g), *trans*-2-hexenyl acetate (7.8 ng/g), and hexyl acetate (19.8 ng/g). Finally, Picual oil was characterized by a high concentration of *trans*-2-hexen-1-ol (2946 ng/g) and *cis*-3-hexen-1-ol (1218 ng/g). The concentration of *trans*-2-hexenal (2125 ng/g) was higher than hexanal concentration (137 ng/g). *cis*-3-Hexenyl acetate and hexyl acetate had very similar values (51.2 and 46.7 ng/g, respectively). These results are in agreement with those found by Sanchez-Ortiz et al.[27]

On the other hand, C5 compounds were also important in oils but not in olives. These compounds would be generated through an additional branch of the LOX pathway that would involve the production of a 13-alkoxyl radical by LOX. This radical would undergo subsequent nonenzymatic β-scission to form a 1,3-pentene allylic radical that could be chemically dimerized to form pentene dimers or react with a hydroxyl radical to form pentenols. These pentenols would be the origin of C5 carbonyl compounds present in the aroma of olive oil through an enzymatic oxidation by alcohol dehydrogenase (ADH)[28] (see C5 contents in Table 2). The three compounds pentanal, 1-penten-3-ol, and 3-pentanone were the main volatile compounds identified in the four olive oils studied.

Manzanilla de Sevilla oil was characterized by the highest C5 content, meanwhile *Local* oil by the lowest one (Figure 4). This fact matched with the C6 content, and it could be also due to the continuity of LOX pathway such as for C6 compounds.

Local oil showed mean contents of aldehydes and ketones and low values for alcohols. Pentanal had the highest concentration (2761 ng/g) followed by 3-pentanone (1555 ng/g). The most important alcohol was 1-penten-3-ol (496 ng/g). Manzanilla de Sevilla oil presented a high concentration of pentanal (14142 ng/g) and low of *trans*-2-pentenal (11.0 ng/g). 3-Pentanone was the main ketone identified (3523 ng/g). 1-Penten-3-ol content was the alcohol with the highest content (763 ng/g). Arbequina oil was characterized by a high concentration of pentanal (6974 ng/g). The two main alcohols identified were 1-penten-3-ol and *cis*-2-penten-1-ol (1986 and 206 ng/g, respectively). This variety had lower contents of 3-pentanone (944 ng/g) than Manzanilla de Sevilla. Finally, Picual oil was characterized by a high concentration of pentanal (3775 ng/g). The two main alcohols identified were 1-penten-

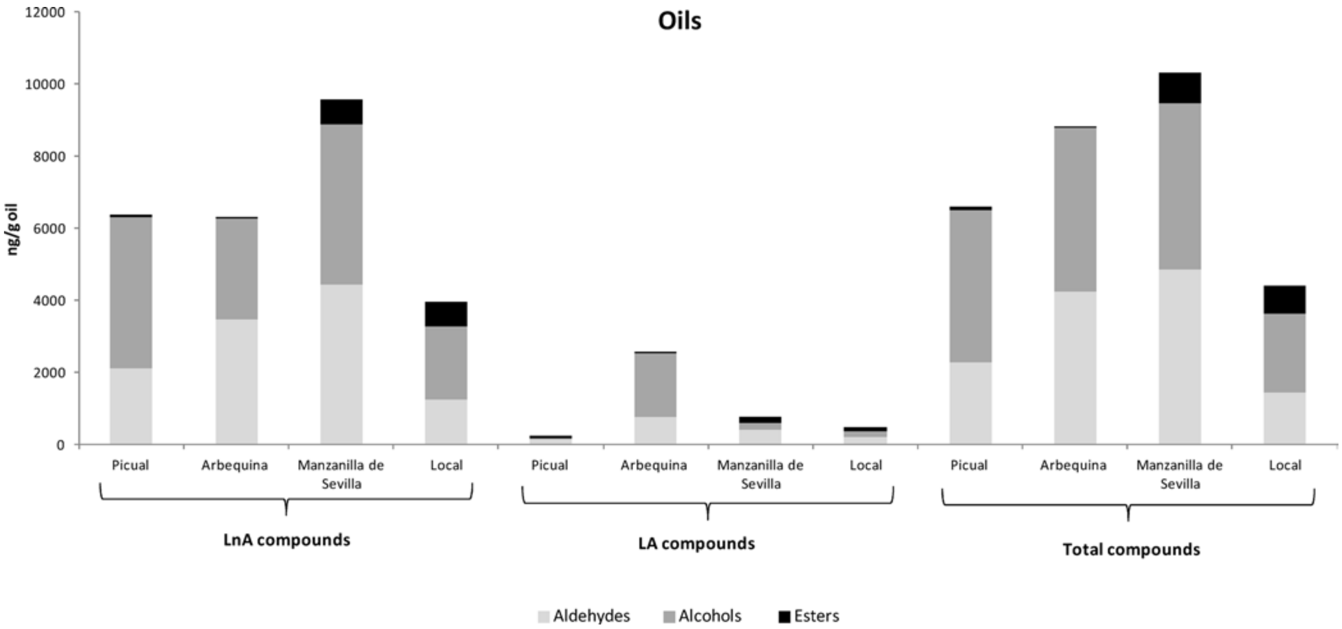

Figure 3. Sum of C6 volatile compounds derived by LOX action in Galician olive oils. Volatile content of C6/LnA aldehydes is *trans*-2-hexen-1-al. Volatile contents of C6/LnA alcohols are the sum of *cis*-2-hexen-1-ol, *trans*-2-hexen-1-ol, *cis*-3-hexen-1-ol, and *trans*-3-hexen-1-ol. Volatile contents of C6/LnA esters are the sum of *cis*-3-hexenyl acetate and *trans*-2-hexenyl acetate. Volatile content of C6/LA aldehydes is hexanal. Volatile content of C6/LA alcohols is hexanol. Volatile content of C6/LA esters is hexyl acetate.

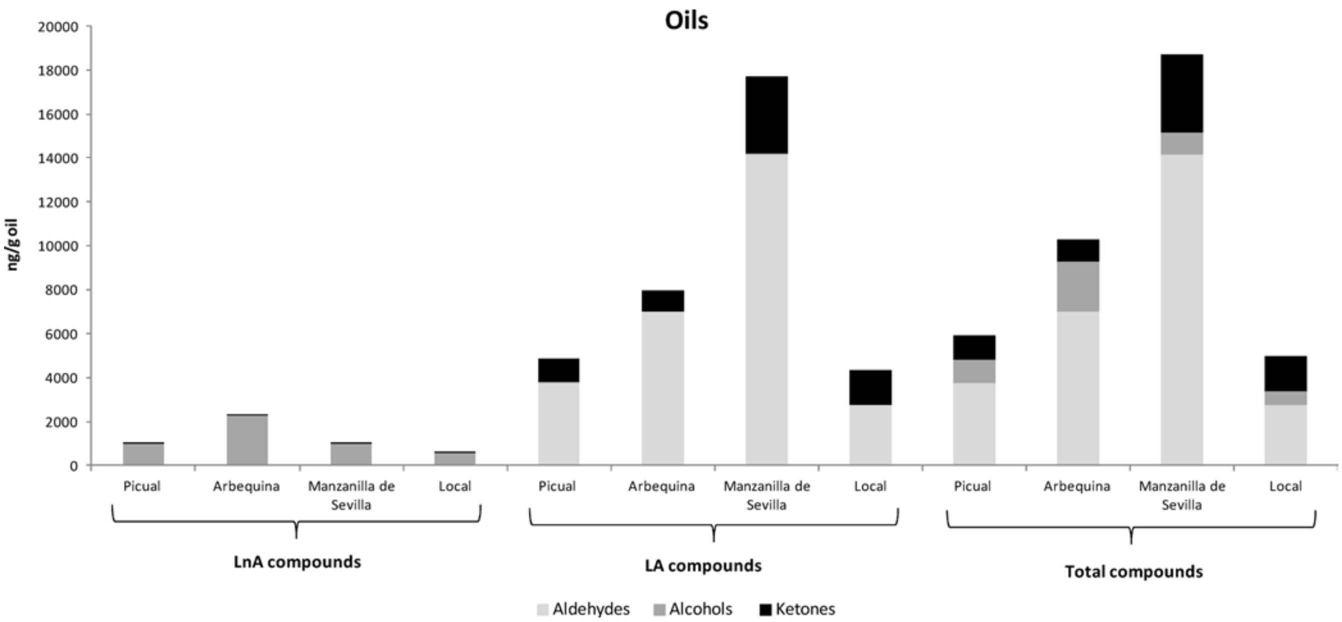

Figure 4. Sum of C5 volatile compounds derived by LOX action in Galician olive oils. Volatile content of C5/LnA aldehydes is *trans*-2-pentenal. Volatile contents of C5/LnA alcohols are the sum of 1-penten-3-ol, *cis*-2-penten-1-ol, and *trans*-2-penten-1-ol. A volatile content of C5/LnA ketones is 1-penten-3-one. Volatile content of C5/LA aldehydes is pentanal. Volatile content of C5/LA alcohols is 1-pentanol. Volatile content of C5/LA ketones is 3-pentanone.

3-ol and *cis*-2-penten-1-ol (861 and 128 ng/g, respectively). This variety had also a lower content of ketones than Manzanilla de Sevilla: 3-pentanone and 1-penten-3-one (1100 and 27.7 ng/g, respectively).

Description of the Aroma Profile of Olive Oils. As was described previously for olives, the specific contribution of each volatile compound on overall oil aroma was established by OAVs and the compounds were grouped in the same odorant series (see Table 3).

In Figure 2b, comparison of the aromatic profiles for the studied oils is presented. It can be observed that the greatest differences were registered in bitter, pungent, wood, apple, and sweet odorant series. As in Figure 2a for olives, the numerical value of these differences was established by subtracting the highest and lowest OAV values of each odorant series.

In bitter and pungent odorant series, the highest value corresponded to Arbequina oil (OAV = 168 and 131, respectively) and the lowest value to *Local* oil (OAV = 46 and 31, respectively). In wood odorant series, Manzanilla de

Sevilla oil showed the highest value (OAV = 59), and *Local* oil presented the lowest one (OAV = 12). For apple and sweet odorant series, Arbequina oil had the highest value (OAV = 18 and 11, respectively). The lowest values were registered in *Local* and Picual oils: for apple odorant series *Local* oil showed the lowest value (OAV = 6), and for sweet odorant series Picual oil had the lowest one (OAV = 3).

As a conclusion, the studied oils could be characterized by the following aroma profiles: Manzanilla de Sevilla oil by bitter and wood odorant series; Arbequina by pungent, bitter, apple, and grass. Picual and *Local* oils registered, in comparison, lower aroma content, characterized by bitter, pungent, and wood odorant series. From the aromatic point of view, Manzanilla de Sevilla and Arbequina oils are more suitable for monovarietal oils because of their aromatic intensity. However, *coupages* with other oils or fruit mixtures are recommended for Picual and *Local* oils to enrich their aromatic content.

A few sensorial studies on some of these oils showed a good agreement in connection with our findings: Manzanilla de Sevilla oils primarily provide a wealth of bitter herbal aromas;[29] Arbequina cultivar provides very aromatic oils with a clean, fresh, herbal olive flavor, often with apple, sweet almond, and artichoke undertones, and also with a light pungency and bitterness,[30] and the oils from Picual are fruity, with a hint of apple nuance, also having pungent and bitter notes that soften over time.[31]

Furthermore as can be seen in Figures 1 and 2a, olives showed characteristic and differentiated profiles, but in oils obtained from those olives this typification disappeared (Figure 2b). All the oils studied had the same profile; they were only modified by the intensity of the main odorant series (pungent, bitter, and wood). The aromatic composition of olives was, therefore, not determining for the aromatic potential of resulting oils.

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Notes

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ABBREVIATIONS USED

ADH, alcohol dehydrogenase; DHS, dynamic headspace; EI, electron impact; EVOO, extra virgin olive oil; GC, gas chromatograph; i.d., internal diameter; ITMS, ion trap mass spectrometer; LA, linoleic acid; LnA, linolenic acid; LOX, lipoxygenase; OAV, odor activity value; SIR, selected ion recording; SSR, simple sequence repeat; WGB, World Olive Germplasm Bank

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