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Comparative study of virgin olive oil sensory defects

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Abstract

The main sensory defects found in virgin olive oil (winey–vinegary, mustiness–humidity, fusty and rancid) were studied by dynamic headspace high-resolution gas chromatography with flame ionisation and mass spectrometry detection and dynamic headspace high-resolution gas chromatography–olfactometry to determine the most prominent volatile compounds responsible for them. A comparative study between defective and high quality virgin olive oils showed qualitative and quantitative differences in the volatile profiles, explained by the presence of enzymatic activities before the oil extraction process or by alteration during olive oil storage. The highest sensory significance, evaluated by odour activity values, corresponded to 1-octen-3-ol for mustiness–humidity, ethyl butanoate, propanoic and butanoic acids for fusty sensory defect, acetic acid, 3-methyl butanol and ethyl acetate for winey–vinegary and several saturated and unsaturated aldehydes and acids for rancid sensory defect.

Keywords: Virgin olive oil; Sensory defects; Off-flavours; Volatiles; Mustiness–humidity; Fusty; Winey–vinegary; Rancid

1. Introduction

Virgin olive oil flavour is usually characterised by pleasant sensory notes that are much appreciated by consumers (Aparicio, Morales, & Alonso, 1996; Aparicio, Morales, & Alonso, 1997). These sensory characteristics, together with nutritional aspects, are the main reasons for the increment of virgin olive oil consumption in recent years (IOOC, 2003). High quality olive oils have a profile of volatile compounds – mainly constituted of aldehydes, esters, alcohols and ketones – that generates a balanced flavour of green and fruity sensory characteristics (Aparicio & Morales, 1998). Some of these compounds are generated by biosynthetic pathways, e.g. lipoxygenase (LOX) cascade. Several processes, however, can alter the initial pleasant flavour, giving rise to unpleasant sensory notes, the virgin olive oil off-flavours. The current olive oil official regulations (EC, 1997; IOOC, 1996) classify the most frequent off-flavours into four groups: fusty, mustiness–humidity, winey–vinegary, and rancid. Fusty is the characteristic flavour of oils obtained from olives in an advanced stage of fermentation. Mustiness–humidity is the characteristic flavour of oils obtained from olives piled under humid conditions for several days with the consequence of the development of various kinds of fungi. Winey–vinegary is a sensory note due to the high concentration of acetic acid, ethyl acetate and ethanol. Rancid is a common sensory characteristic of all oils and fats that have undergone a process of auto-oxidation caused by a prolonged contact with air. The first three defects are due to inadequate fruit preservation before olive oil processing while the last is produced during olive oil storage.

All these defects are currently considered in the Organoleptic Assessment of Virgin Olive Oil (IOOC,

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1996), whose purpose is to determine the criteria needed to assess the flavour characteristics of virgin olive oil. The method is applicable to the classification of the virgin olive oils as a function of the intensity of the defects, according to the judgement of a group of selected and trained assessors working as a panel (EC, 1997). The acceptability of the oils depends on the defect intensities.

Under optimal extraction conditions, using healthy and mature olive fruits, extra-virgin olive oil is always produced, whichever the olive variety processed. Only the olives attacked by pests, or fallen to the ground before harvesting, produce off-flavours; the other defective sensory notes in the olive oils are due to inadequate harvesting or processing or olive oil preservation (Alba, 2001).

Lipolysis and oxidation are the processes leading to the most serious deterioration of olive oil. Lipolysis usually starts while the oil is still in the fruit, while oxidation begins after the oil is obtained from the fruit and proceeds mainly during storage (Morales, Rios, & Aparicio, 1997); both processes affect the composition and the sensory characteristics of the oil (Kochhar, 1993).

One of the main causes of sensory defects in virgin olive oil is the storage of olive fruits in piles before oil extraction; olives transpire during storage so that the temperature of the pile increases, which favours the attack of microorganisms. The storage of olives in piles, under high humidity conditions, for a long time favours the appearance of fungi and yeasts, and the microflora produce changes in the chemical composition of the volatiles.

Although microorganisms have been used since ancient times for the production of particular foods, due to their ability to use different kind of substrates, that ability can also have a negative effect since they may degrade products that are useful for consumers. Microorganisms produce a range of chemicals that alter the quality attributes of food, including flavour (Schnürer, Olsson, & Börjesson, 1999). In this way, when foodstuffs are stored under inadequate conditions, they suffer biodegradation or biospoilage by microorganisms that inevitably give rise to lower quality products, ultimately rendering the product inedible (Springett, 1993).

When oils reach high intensities of sensory defects they are classified as lampante olive oils and must undergo refining before being consumed. Perhaps this fact is responsible for the scarce attempts carried out to study the volatile compounds responsible for virgin olive oil sensory defects. From an economic point of view, it is important to detect the presence of off-flavours, since classification of an olive oil as lampante means low incomes for farmers. The aim of this paper is to determine the main volatile compounds responsible for virgin olive oil sensory defects from a chemical and sensory point of view.

2. Materials and methods

2.1. Reagents

Octane, pentanal, hexanal, heptanal, octanal, nonanal, decanal, E-2-pentenal, E-2-hexenal, E-2-heptenal, E-2-octenal, E-2-decenal, E,E-2,4-heptadienal, E,E-2,4-nonadienal, E,E-2,4-decadienal, ethanol, butan-2-ol, pentan-1-ol, 3-penten-2-ol, 2-methyl-butan-1-ol, 3-methyl-butan-1-ol, E-2-hexen-1-ol, heptan-2-ol, octan-2-ol, 1-octen-3-ol, 6-methyl-5-hepten-3-ol, nonanol, guaiacol, butan-2-one, heptan-2-one, octan-2-one, 1-octen-3-one, 6-methyl-5-hepten-2-one, acetic acid, propanoic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, ethyl acetate, ethyl propanoate, butyl acetate, ethyl butanoate, propyl butanoate, and 2-methyl-propyl butanoate were purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.2. Samples

The International Olive Oil Council (IOOC) supplied one sample of each of four standard oils used in the training process for assessors to detect sensory defects. Each standard oil was characterised by one of the following attributes: rancid, winey–vinegary, mustiness–humidity and fusty.

Information from a database, previously built with a sample bank of 91 virgin olive oil samples, was used to establish the mean, minimum and maximum content of volatile compounds in extra-virgin olive oils of different varieties and geographical origins (Italy, Greece and Spain). This set of samples represents the most produced and consumed European virgin olive oils.

2.3. Dynamic headspace

Volatile compounds of virgin olive oil samples were analysed by a dynamic headspace gas chromatography (DHS-GC) technique previously reported (Morales, Aparicio, & Rios, 1994; Morales, Luna, & Aparicio, 2000). Samples of 0.5 g were used in the case of extra-virgin, winey–vinegary, mustiness–humidity and fusty standard oils. However, only 0.25 g was used when rancid standard oil was analysed due to its high concentration of volatile compounds. Samples were heated at 40 °C and swept with N_2 (200 ml/min) for 15 min and the volatiles adsorbed on a Tenax TA trap (Chrompack, Middleburg, The Netherlands) at room temperature. A Chrompack thermal desorption cold trap injector (TCT, Chrompack, Middleburg, The Netherlands) was employed to carry out the thermal desorption of the trapped volatiles by heating at 220 °C for 5 min. Volatiles were then condensed on a fused silica trap cooled at −110 °C with liquid nitrogen for 5 min, just before injection, that was carried out by flash heating of the

cold trap at 170 °C, where it was held for 5 min. The volatiles were transferred to a fused silica J &W (Folsom, CA) DB-WAX column (60 m × 0.25 mm i.d., 0.25 μm film thickness). The oven temperature was held at 40 °C for 6 min and programmed to rise at 2 °C/min to a final temperature of 200 °C where it was held for 10 min. A Hewlett–Packard 5890 (Palo Alto, CA) series II chromatograph with a FID detector was employed. Quantification was carried out using isobutyl acetate as internal standard (Morales & Aparicio, 1993). All samples were analysed in duplicate.

The identification of volatile compounds was achieved using standards. Mass spectrometry was applied using the above mentioned GC conditions. A Fisons Mass Detector MD800 coupled to a GC 8000 series was employed. Masslab v 1.3 was the software used. Sample components were verified by comparison of mass spectral data and retention times with those of authentic reference compounds.

2.4. High resolution gas chromatography–olfactometry

To assess the aroma notes corresponding to olive oil volatile compounds, a high resolution gas chromatography (HRGC)-olfactometry technique was applied to virgin olive oil samples (Morales et al., 1994). The effluent of the GC column was split, 1–10, to the detector and the sniffing port, respectively. Four assessors, full-trained assessors for virgin olive oil (EC, 1997), carried out the evaluation. The descriptions of the odour-active regions of the eluate were noted on a form with a pre-printed time scale; assessors did not see the chromatogram; they basically agreed on the odours of volatiles, although different semantic terms were used to describe some of them. A consensus-building discussion was held with assessors to decide the final sensory descriptors.

2.5. Odour threshold of volatile compounds

A fully refined and deodourised olive oil was the matrix for the assessment of the odour threshold values; the absence of volatile compounds in the matrix was checked by the DHS-GC procedure described above. The sensory evaluation was carried out in the test room used for evaluating virgin olive oil sensory characteristics (IOOC, 1996). The same assessors who carried out the HRGC-olfactometry were in charge of the detection of the volatile thresholds. Three samples were presented to the assessors following the triangle test, the results of which were statistically analysed. 15 ml of each sample were kept in standardised glasses at 29 ± 2 °C for 15 min and then tested.

The odour activity values (OAVs) (ratio of the concentration to the odour threshold) (Aparicio & Morales, 1998; Buettner & Schieberle, 2000; Rothe & Thomas, 1963) of volatile compounds were calculated to determine their sensory significance. Thus, the concentration of each volatile found in the oil samples was divided by its corresponding odour threshold value, previously determined as described above.

3. Results and discussion

Main volatile compounds usually found in high sensory quality virgin olive oil are produced through biogenic pathways of the olive fruit, such as the LOX cascade, and fatty acid or amino acid metabolism (Morales & Tsimidou, 2000). These processes give rise to the wide variety of volatile compounds that constitute the profile of high quality virgin olive oils. The presence of sensory defects is detected due to the great concentrations of some volatiles versus the profile of high quality oils. However, each one of the defective olive oils has its own profile (Figs. 1 and 2), which allows their characterisation.

Fig. 1(a) shows the profile of the standard of the mustiness–humidity virgin olive oil supplied by IOOC. Although some volatiles of the virgin olive oil remain, they are in low concentration, so indicating a ''flattening'' of the oil flavour. In olive fruits stored in piles, under high humidity conditions, (Angerosa, Lanza, & Marsilio, 1996; Rodriguez de la Borbolla, 1958) the presence of several species of genus *Aspergillus*, together with ascomycetes, *Penicillium notatum*, have been reported as being among the most abundant deuteromycetes. These microorganisms have the ability to oxidise free fatty acids, producing volatile compounds such as methyl ketones (2-heptanone, 2-nonanone). Other fungi (*Alternaria*, *Fusarium*, *Rhizopus*) have also been detected although they are less abundant. Yeasts, on the other hand, are able to reduce carbonyls and partially esterify alkyl moieities, and some species of the genera *Candida*, *Pichia* and *Saccharomyces* have been detected under the described conditions. The result is an olive oil characterised by the sensory note mustiness–humidity (IOOC, 1996).

Table 1 shows the most characteristic volatile compounds identified in this standard oil, their concentrations and sensory characterisation. It is interesting to underline the presence of volatile compounds that do not appear in extra-virgin olive oils, such as C_8 volatile compounds or short chain fatty acids. Also interesting is the low concentration of E-2-hexenal (0.17 mg/kg) in contrast to the high concentration of hexanal (2.10 mg/kg), far different from the usual concentrations of these compounds in extra-virgin olive oils (0.57–11.60 and 0.01–1.10 mg/kg, respectively). This fact could be explained by the action of the fungal enzymes in the LOX pathway of olives (Schnürer et al., 1999). The activity of the microorganisms present in olives can also explain the high concentration of 1-octen-3-ol, 3-methyl-

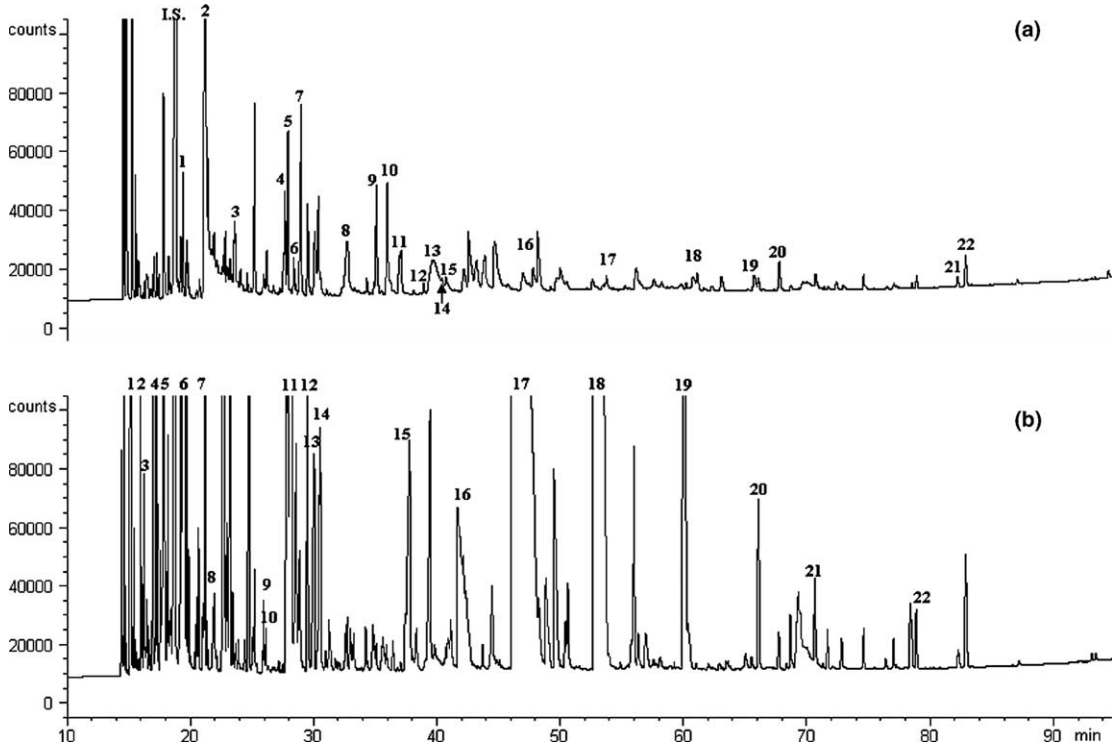

Fig. 1. (a) Chromatogram of mustiness–humidity virgin olive oil standard. Codes are described in Table 1. (b) Chromatogram of fusty virgin olive oil standard. Codes are described in Table 2. I.S.: internal standard.

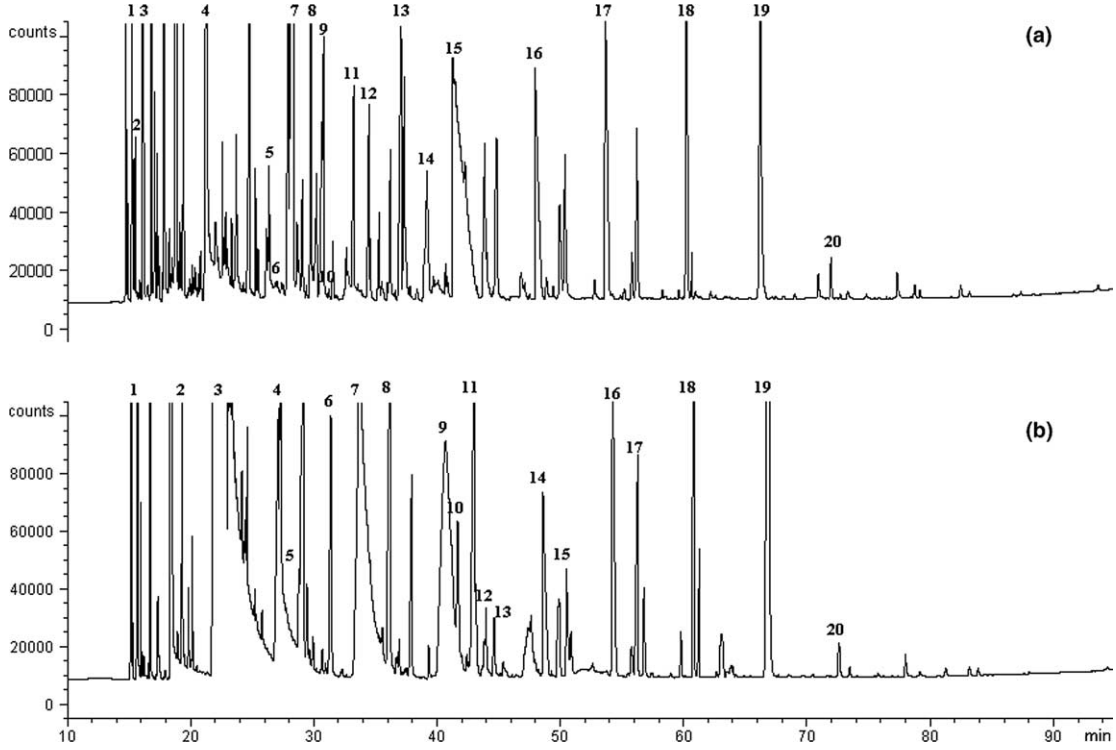

Fig. 2. (a) Chromatogram of winey–vinegary virgin olive oil standard. Codes are described in Table 3. (b) Chromatogram of rancid virgin olive oil standard; sample size is half of the other defective standard oils. Codes are described in Table 4.

Table 1
Main volatile compounds identified in mustiness–humidity standard virgin olive oil

Code	Volatile compound	Concentration (mg/kg)	Odour threshold in oil (mg/kg)	HRGC-Olfactometry
1	3-Penten-2-ol	0.15	0.40	Perfumey, woody
2	Hexanal	2.10	0.08	Green apple, grassy
3	1-Octen-3-one	0.13	0.01	Mushroom, mould, pungent
4	E-2-Hexenal	0.17	0.42	Bitter almonds, green
5	Ocimene[a]	0.25	–	Warm, mouldy
6	2-Methyl-butan-1-ol	0.06	0.48	Winey, spicy
7	3-Methyl-butan-1-ol	0.38	0.10	Woody, sweet
8	E-2-Heptenal	0.34	0.001	Pungent, soapy
9	6-Methyl-5-hepten-2-one	0.22	1.00	Herbaceous, pungent
10	Piranone[a]	0.35	–	Burnt candle
11	Heptan-2-ol	0.13	0.01	Earthy, sweety
12	Octan-2-ol	0.02	0.10	Earthy, fatty
13	1-Octen-3-ol	0.25	0.001	Mould, earthy
14	2,4-Heptadienal	0.05	0.36	Fatty, nutty
15	6-Methyl-5-hepten-3-ol	0.06	2.00	Perfumey, nutty
16	Propanoic acid	0.11	0.72	Pungent, sour, mould
17	Butanoic acid	0.09	0.65	Rancid, cheese, sweat
18	Pentanoic acid	0.06	0.60	Unpleasant, pungent
19	Hexanoic acid	0.06	0.70	Sour, sharp
20	Guaiacol	0.07	0.02	Woody, smoky, spicy
21	Octanoic acid	0.02	3.00	Oily, fatty
22	3,4-Xylenol[a]	0.07	–	Dry odour

[a] Tentatively identified by MS.

butan-1-ol and 6-methyl-5-hepten-2-one detected in this standard olive oil. The sensory characterisation of many of the volatile compounds described in Table 1 – with mouldy, woody, earthy and nutty sensory notes – can explain the mustiness–humidity sensory attribute. In fact, the odour thresholds of the volatile compounds indicate that 1-octen-3-ol is the volatile compound having the highest sensory significance (OAV = 250). E-2-heptenal, 1-octen-3-one and hexanal (OAVs = 68, 13 and 26, respectively) also show high contributions to the sensory profile. 3-methyl-butan-1-ol, 6-methyl-5-hepten-2-one, guaiacol, heptan-2-ol and octan-2-ol have OAVs > 1, and their sensory descriptions also indicate that they contribute to the mustiness–humidity sensory defect.

Fig. 1(b) displays the volatile profile of the standard olive oil characterised as fusty by IOOC. The microorganisms found in the olives that produce olive oils characterised by the fusty sensory note depend on the length of storage. The enterobacteriaceae genera *Aerobacter* and *Escherichia* were found at the beginning of storage, while the genera *Pseudomonas*, *Clostridium* and *Serratia* were the most significant after a long time of storage (Angerosa et al., 1996; Rodriguez de la Borbolla, 1958).

The activity of these microorganisms results in the presence of volatile compounds other than usual. Table 2 shows the main volatile compounds identified in the standard of fusty olive oil. The concentrations of the usual biosynthetic volatiles are low in comparison with the great amounts of new compounds, the amount of total volatiles being high (Fig. 1(b)). Noticeable is the high concentration of esters which are characteristic of olive oils obtained from over-ripe olives as well as due to the enzymatic activity of the cited microorganisms. Thus, the presence of ethyl butanoate (3.70 mg/kg) has been detected, while the concentrations of ethyl propanoate and butyl acetate, 0.67 and 2.22 mg/kg, respectively, are higher than in extra-virgin olive oils (0.21 and 0.64 mg/kg, respectively). The concentrations of other compounds, such as octane (2.05 mg/kg) and 3-methyl butan-1-ol (0.48 mg/kg) are also higher than in extra-virgin olive oils (0.35 and 0.14 mg/kg, respectively). In contrast, the concentrations of the volatile compounds produced through the LOX pathway, hexanal (0.32 mg/kg) and E-2-hexenal (1.70 mg/kg), are low, although they are within the range of virgin olive oils (0.01–1.10 and 0.57–11.6 mg/kg, respectively). The high concentration of 6-methyl-5-hepten-2-one (0.55 mg/kg versus the range of tr-0.17 mg/kg in extra-virgin olive oils) can be explained by the presence of *Pseudomonas*, that are liable to degrade terpenic alcohols (Berger, 1995), geraniol and other related terpenols very abundant in olive oil. The high concentrations of butanoic acid (11.5 mg/kg) and propanoic acid (15.6 mg/kg) in this standard oil, in comparison to their trace levels in extra-virgin olive oils, could also be explained by processes induced by some species of *Clostridium* (Angerosa et al., 1996) and *Propionibacterium*, while the presence of carbonyl compounds and alcohols indicates fatty acid oxidation by microorganisms (Springett, 1993).

The odour threshold of the quantified compounds (Table 2) indicates the influence that the volatiles have

Table 2
Main volatile compounds identified in fusty standard virgin olive oil

Code	Volatile compound	Concentration (mg/kg)	Odour threshold in oil (mg/kg)	HRGC-Olfactometry
1	Octane	2.05	0.94	Sweety, alkane
2	Ethyl acetate	0.48	0.94	Sticky, sweet
3	Butan-2-one	0.18	40.0	Ethereal, fruity
4	Ethyl propanoate	0.67	0.10	Fruit, strong
5	Butyl acetate	2.22	0.30	Green, fruity, pungent
6	Ethyl butanoate	3.70	0.03	Sweet, fruity
7	Hexanal	0.32	0.08	Green apple, grassy
8	Propyl butanoate	0.20	0.15	Pineapple, sharp
9	2-Methylpropyl butanoate	0.10	0.10	Unpleasant, winey, fusty
10	Butan-2-ol	0.11	0.10	Winey
11	E-2-Hexenal	1.70	0.42	Bitter almonds, green
12	2-Methyl butan-1-ol	0.36	0.48	Spicy, winey
13	3-Methyl butan-1-ol	0.48	0.10	Woody, sweet, whiskey
14	Pentan-1-ol	0.43	3.00	Sticky, balsamic, strong
15	6-Methyl-5-hepten-2-one	0.55	1.00	Pungent, green
16	Acetic acid	1.06	0.50	Sour, vinegary
17	Propanoic acid	15.6	0.72	Pungent, sour
18	Butanoic acid	11.5	0.65	Fusty, strong, cheese
19	Pentanoic acid	2.48	0.60	Putrid, pungent
20	Hexanoic acid	0.33	0.70	Sharp, rancid
21	Heptanoic acid	0.22	0.10	Rancid, fatty
22	Octanoic acid	0.09	3.00	Rancid, fatty

in the final sensory perception of the fusty sensory note. Fifteen out of all the identified volatile compounds show OAVs > 1, and hence contribute to the sensory perception fusty. Esters and acids are, from a sensory point of view, the two main groups of volatiles. Ethyl butanoate (OAV = 123) is the volatile with the highest sensory significance, and butyl acetate, ethyl propanoate, propyl butanoate, and 2-methylpropyl butanoate (OAVs = 7.4, 6.7, 1.3 and 1.00, respectively) are other esters also responsible for this sensory perception. Among the acids, propanoic and butanoic (OAVs = 21.6 and 17.8, respectively) are the most relevant compounds from a sensory point of view. Acetic, pentanoic and heptanoic acids (OAVs = 2.12, 4.13 and 2.2, respectively) also contribute. The sweet, sour, and putrid perceptions, typical of this attribute, can be explained by both groups of volatiles and are also modulated by octane, butan-2-ol and 3-methyl butan-1-ol with OAVs in the range of 5–1. Hexanal and E-2-hexenal also contribute to the sensory perception as they have OAVs = 4.

Fig. 2(a) shows the profile of the standard of the winey–vinegary olive oil. The main reason for the appearance of this defect is the production of off-flavours associated with a fermentative process due to microbial contamination of the olives. Lactic acid (*Lactobacillus*) and acetic acid bacteria have been detected on olives later used to obtain olive oils (Angerosa et al., 1996; Rodriguez de la Borbolla, 1958). This kind of microorganism induced a fermentative process in the olives, so giving rise to the production of ethanol, ethyl acetate and acetic acid that are the principal volatiles responsible for the described sensory note. Table 3 shows the main peaks identified and quantified. Notable are the high concentration of octane (1.13 mg/kg), although less than in the studies of fusty defect, and the presence of some new volatile compounds at high concentrations, ethanol (2.41 mg/kg), 1,3-butanediol (0.88 mg/kg) and acids from 2 to 7 carbon atoms. Two compounds that are usually at very low concentration in virgin oils, ethyl acetate and acetic acid, were found at very high concentrations (3.53 and 6.21 mg/kg, respectively). Acetic acid, ethyl acetate, pentan-1-ol (0.62 mg/kg) and butan-2-ol (0.31 mg/kg) have good correlations with samples at different intensities of this defect (Morales et al., 2000). The volatile compounds with higher OAVs were acetic acid (12.4), 3-methyl butanol (7.10) and ethyl acetate (3.76), as expected for this defect. Ethanol did not show sensory significance, due to its high odour threshold value. Other compounds that contribute to the defect with less intensity were octane (1.20), 2-methyl butanol (1.31), octan-2-one (1.16), and propanoic, butanoic, pentanoic, hexanoic and heptanoic acids, with OAVs in the range of 1.20–2.01. Although the sample showed a very winey–vinegary profile from a sensory viewpoint, hexanal and E-2-hexenal showed high contributions to the aroma of the sample with OAVs of 23.9 and 7.93, respectively.

Rancid off-flavour is one of the most important problems in food spoilage and it is undoubtedly the most studied sensory defect. It is involved in a great number of fat-containing foods due to the fact that it is produced from fatty acid oxidation. In the case of rancid virgin olive oil, the number and concentration of volatile compounds depend on the kind and intensity of the oil

Table 3
Main volatile compounds determined in standard winey–vinegary virgin olive oil

Code	Volatile compound	Concentration (mg/kg)	Odour threshold in oil (mg/kg)	HRGC-Olfactometry
1	Octane	1.13	0.94	Sweety, alcane
2	Ethanol	2.41	30.0	Alcohol
3	Ethyl acetate	3.53	0.94	Sticky, sweet
4	Hexanal	1.91	0.08	Green apple, grassy
5	Butan-2-ol	0.31	0.15	Winey
6	2-Pentenal	0.05	0.30	Green, apple
7	Heptan-2-one	0.04	0.30	Sweet, fruity
8	E-2-Hexenal	3.33	0.42	Bitter almonds, green
9	2-Methyl butan-1-ol	0.63	0.48	Winey, spicy
10	3-Methyl butan-1-ol	0.71	0.10	Woody, whiskey, sweet
11	Pentan-1-ol	0.62	3.00	Strong, sticky, balsamic
12	Octan-2-one	0.59	0.51	Mould, green
13	1,3-Butanediol[a]	0.88	–	Pungent
14	E-2-hexen-1-ol	0.58	5.00	Green grass, leaves
15	Acetic acid	6.21	0.50	Sour, vinegary
16	Propanoic acid	1.45	0.72	Pungent, sour
17	Butanoic acid	1.37	0.65	Rancid, cheese
18	Pentanoic acid	1.01	0.60	Unpleasant, pungent
19	Hexanoic acid	1.27	0.70	Pungent, rancid
20	Heptanoic acid	0.12	0.10	Rancid, fatty

[a] Tentatively identified by MS.

Table 4
Main volatile compounds determined in standard rancid virgin olive oil

Code	Volatile compound	Concentration (mg/kg)	Odour threshold in oil (mg/kg)	HRGC-Olfactometry
1	Octane	3.83	0.94	Sweet, alcane
2	Pentanal	2.63	0.24	Woody, bitter, oily
3	Hexanal	33.8	0.32	Fatty, strong, green
4	Heptanal	3.76	0.50	Oily, fatty, woody
5	E-2-Hexenal	0.85	0.42	Bitter almonds, green
6	E-2-Heptenal	1.18	0.005	Oxidised, tallowy, pungent
7	Octanal	8.44	0.32	Fatty, sharp
8	6-Methyl-5-hepten-2-one	2.54	1.00	Oily, pungent
9	Nonanal	7.12	0.15	Fatty, waxy, pungent
10	E-2-Octenal	1.10	0.004	Herbaceous, spicy
11	Acetic acid	3.20	0.50	Pungent, sour
12	2,4-Heptadienal	0.68	3.62	Fatty, rancid
13	Decanal	0.58	0.65	Penetrating, sweet, waxy
14	E-2-Decenal	1.54	0.01	Painty, fishy, fatty
15	Nonanol	0.76	0.28	Fatty
16	Butanoic acid	1.86	0.14	Rancid
17	2,4-Nonadienal	1.17	2.50	Soapy, penetrating
18	2,4-Decadienal	1.72	2.15	Strong, fatty
19	Hexanoic acid	6.47	0.70	Rancid, pungent
20	Heptanoic acid	0.22	0.10	Rancid

alteration (Morales et al., 1997). Fig. 2(b) shows the profile of volatiles of the standard rancid olive oil and Table 4 shows the predominance of compounds produced by auto-oxidation against volatiles produced by fruit biogenesis. The high concentrations of aldehydes are mostly produced by oxidation of the unsaturated fatty acids, while the presence of acids is due to the oxidation of the aldehydes previously formed. The presence of acids indicates a high level of alteration of the oil sample as these compounds appear at the end of the oxidative process (Kochhar, 1993).

Most of the volatile compounds present in the rancid sample have low odour threshold values. Thus, the main contribution comes from aldehydes, the unsaturated ones being the most relevant as they have very high OAVs; 2-octenal (275), 2-heptenal (236) and 2-decenal (154) can be considered the main contributors to the rancid defect. Saturated aldehydes, such as hexanal (105.5), nonanal (47.5), octanal (26.4), pentanal (10.9) and heptanal (7.5) do clearly influence the final aroma. Butanoic (13.3), hexanoic (9.24) and acetic (6.4) acids also contribute to the sensory profile. Lower

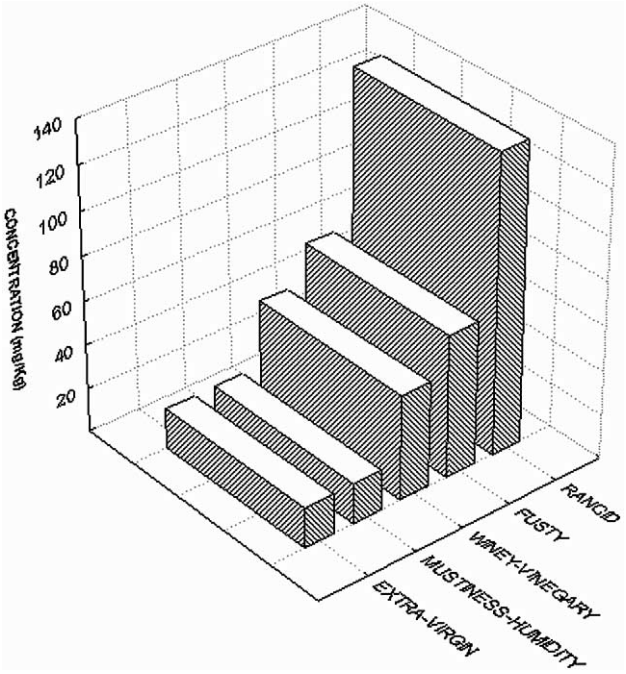

Fig. 3. Total content of volatile compounds corresponding to the mean value of 91 extra-virgin olive oil samples and the four samples with sensory defects.

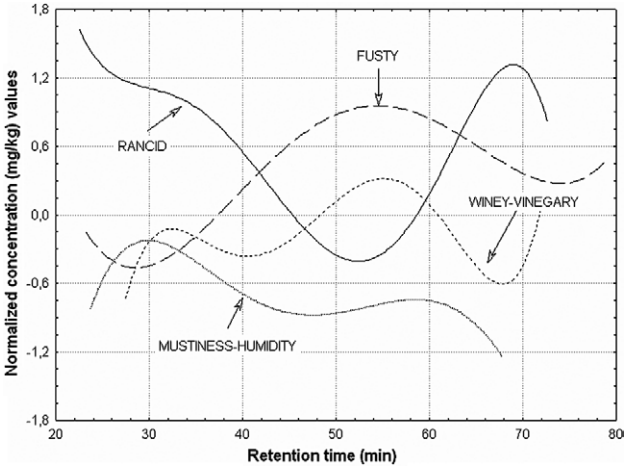

Fig. 4. Volatile profile of the olive oils characterised by the sensory defects.

contributions originate from heptanoic acid, octane, nonanol and 6-methyl-5-hepten-2-one, which have OAVs in the range of 2.2–4.0. Most of these compounds are characterised by sensory notes related to the perceptions rancid, oily and fatty, so justifying their importance in the development of the rancidity in olive oils.

Figs. 1 and 2 show that, not only the profile, but also the total volatile contents of defective virgin olive oil standards are very different. Fig. 3 shows that extra-virgin olive oil has a low content of total volatile compounds as well as the olive oil characterised by the mustiness–humidity sensory note although their profiles are different enough. Winey–vinegary and fusty defect oils have higher contents of total volatile compounds, these being approximately 2-fold in the case of winey–vinegary defect and 3-fold in the case of fusty defect with respect to extra-virgin olive oils. Rancid is the sensory defect that corresponds with the highest content of volatile compounds; the total concentration is approximately 8-fold higher than extra-virgin olive oils.

Finally, Fig. 4 shows the impact of the volatile compounds responsible for defective sensory notes over the retention time (20–80 min) of the chromatograms of the standard oils. The values of volatile compounds were previously normalised because they differ widely in terms of concentration. The chromatogram of the standard oil characterised by the mustiness–humidity defect shows higher amounts of compounds at the beginning of the chromatogram (25–35 min), the rest of the profile being very flat. Winey–vinegary standard defective oil has two impact zones, between 30 and 35 min, and 50 and 60 min, which correspond to compounds with high and low volatility. The chromatograms of olive oils characterised by fusty and rancid sensory notes show many volatiles throughout the chromatogram. The profile of the fusty olive oil shows the highest values in the middle of the chromatogram, due to short chain acids, while rancid olive oil shows two high zones; the first corresponds to aldehydes and the second to acid compounds.

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