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Analysis of virgin olive oil volatile compounds by headspace solid-phase microextraction coupled to gas chromatography with mass spectrometric and flame ionization detection

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Abstract

The efficiency of headspace solid-phase microextraction (SPME) was evaluated for the qualitative and semi-quantitative analysis of virgin olive oil volatile compounds. The behaviour of four fibre coatings was compared for sensitivity, repeatability and linearity of response. A divinylbenzene–Carboxen–polydimethylsiloxane fibre coating was found to be the most suitable for the analysis of virgin olive oil volatiles. Sampling and chromatographic conditions were examined and the SPME method, coupled to GC with MS and flame ionization detection, was applied to virgin olive oil samples. More than 100 compounds were isolated and characterised. The presence of some of these compounds in virgin olive oil has not previously been reported. The main volatile compounds present in the oil samples were determined quantitatively.

Keywords: Olive oil; Solid-phase microextraction; Headspace analysis; Food analysis; Volatile organic compounds

1. Introduction

Sensory characteristics are used to define virgin olive oil quality. This oil has a characteristic flavour that distinguishes it from other edible vegetal oils. After its extraction from the fruit of *Olea Europea* L., extra virgin olive oil can be consumed without refining and it preserves its typical aroma. European Union (EU) regulations establish the organoleptic quality of virgin olive oil by means of a panel test evaluating positive and negative descriptors [1].

In the last few years, the need for analytical procedures to evaluate virgin olive oil sensory characteristics has led to several studies of its volatile fraction. The use of dynamic headspace techniques fostered the analysis and identification of the large number of components that contribute to the aroma of olive oil. These techniques relate the

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composition of the olive oil headspace to sensory attributes [2–5] as well as to the volatile fraction composition with off-flavours or ''defects'' such as rancidness [6,7], the influence of *Dacus Oleae* infestation [8] and mustiness [9].

Recently, the solid-phase microextraction (SPME) technique was introduced as an alternative to the dynamic headspace technique as a sample preconcentration method prior to chromatographic analysis. SPME is a rapid, sensitive and solvent-free sampling technique developed by Arthur and Pawliszyn [10] for the analysis of pollutants in water. In recent years, SPME has extended its applications to numerous other fields, in particular food flavour analysis.

The volatile compounds in some vegetal oils have been identified and characterised by means of this SPME sampling method. In the case of refined vegetal oils, volatile compounds formed during oxidation reactions have been isolated by SPME and characterised by GC–MS [11,12]. Only a few studies have been carried out on the virgin olive oil volatile fraction by means of headspace SPME. The first qualitative analysis data of virgin olive oil aroma by SPME were reported recently [13–16].

In the present study, SPME was evaluated for the qualitative and semi-quantitative analysis of virgin olive oil aroma. The behaviour of four fibre coatings [polydimethylsiloxane (PDMS), Carboxen–polydimethylsiloxane (CAR–PDMS), polydimethylsiloxane–divinylbenzene (PDMS–DVB) and divinylbenzene–Carboxen–polydimethylsiloxane (DVB–CAR–PDMS)] was tested and compared for sensitivity, repeatability and linearity of response. The experiments involved the analysis of the extraction curves and response factors of 28 standard compounds represented by various aldehydes, alcohols, esters, ketones, terpenes and carboxylic acids reported in the literature as characteristic of the volatile fraction of olive oil. Sampling and chromatographic conditions were examined, and the developed method was applied to real samples of virgin olive oil. Characterisation of olive oil volatile compounds was carried out by means of the SPME method coupled to GC–MS and GC–flame ionization detection (FID). This involved chromatographic separation on two capillary columns with distinct polarity, and the main volatile compounds present in the oil samples were determined quantitatively.

2. Materials and methods

2.1. Reagents

Isovaleraldehyde, ethyl propanoate, pentanal, 1-penten-3-one, hexanal, 4-methyl-2-pentanol, heptanal, limonene, 2-methylbutan-1-ol, (*E*)-2-hexenal, hexyl acetate, octanal, hexenyl acetate, 1-hexanol, (*E*)-3-hexen-1-ol, (*Z*)-3-hexen-1-ol, nonanal, (*E*)-2-hexen-1-ol, (*Z*)-2-hexen-1-ol, methyl nonanoate, decanal, (*E*)-2-nonenal, 1-octanol, methyl decanoate, nonanol, α-terpineol, hexanoic acid and heptanoic acid were purchased from Sigma–Aldrich (St. Louis, MO, USA). The SPME fibres tested were PDMS 100 μm, CAR–PDMS 75 μm, PDMS–DVB 65 μm and DVB–CAR–PDMS 50 and 30 μm, 2 cm long, all from Supelco (Bellefonte, PA, USA).

2.2. GC–FID and GC–MS analysis

GC analyses were performed on two Hewlett-Packard 5890 series II gas chromatographs, one equipped with a FID system and one coupled to a Hewlett-Packard 5971A quadrupole mass-selective spectrometer. Both were provided with a split-splitless injection port. Helium was the carrier gas at a linear velocity of 23 and 17 cm/s for GC–FID and GC–MS, respectively.

Separation of compounds was performed on two columns with distinct polarity: Supelcowax-10 and SPB-1 (both 30 m×0.25 mm I.D., 0.25 μm film thickness), both purchased from Supelco. The column temperature was held at 40 °C for 10 min and increased to 200 °C at 3 °C/min. The FID temperature was set at 280 °C, and the temperatures of the ion source and the transfer line were 175 and 280 °C, respectively. Electron impact mass spectra were recorded at 70 eV ionization energy in the 15–250 u mass range, two scans/s.

The injector temperature was 260 °C for PDMS, PDMS–DVB and DVB–CAR–PDMS fibres and 280 °C for CAR–PDMS. Several desorption times of the fibres into the injection port (5, 2, 1 and 0.5 min) were tested and the desorption time was fixed at 1 min.

2.3. SPME sampling conditions

A solution was prepared containing all the stan-

dard compounds in deodorised olive oil at a concentration of 10 μg/g. Solutions at various concentrations were then obtained by further dilutions with deodorised olive oil. No solvents were employed to avoid interference.

To determine the optimal exposure time of the fibres to the sample headspace, each fibre was held for several time periods in the headspace of the standard mixture at a concentration of 1 μg/g. 1.5 g of standard mixture was placed in a 10 mL vial fitted with a silicone septum which was then placed in a water bath at 40 °C under magnetic stirring. After 2 min sample conditioning, each fibre was exposed for time periods of 10, 20, 30 and 40 min, and immediately desorbed in the gas chromatograph injector. Each extraction was repeated three times. A sampling time of 30 min was chosen to perform the analysis.

2.4. Response factors

Standard mixtures with concentrations in the range 0.1–5 μg/g (0.1, 0.25, 0.5, 1, 1.5, 2.5 and 5 μg/g) were analysed under the conditions described above by means of PDMS–DVB, DVB–CAR–PDMS and CAR–PDMS fibres. The absolute response factors of the standard compounds were calculated as the slopes of the linear regressions obtained from the ratio of total peak area as a function of concentration. Relative response factors were obtained as the ratio of the absolute response factor of each standard compound to that of the internal standard calculated at the concentration in olive oil samples.

2.5. Olive oil samples

The SPME method was applied to seven samples of virgin olive oil from Italy. The virgin olive oil samples chosen for analysis were from various olive cultivars, harvesting years and states of preservation, so that the analytical method was applied to a heterogeneous group of virgin olive oils. Table 1 shows the cultivar, production year, acidity and peroxide value of the samples.

SPME sampling of the oils was carried out as described for standard solutions. Immediately before sampling, the olive oil samples were spiked with internal standard to a concentration of 1.5 μg/g.

Table 1
Description of the virgin olive oil samples

Sample code	Cultivar	Year	Acidity (%)	Peroxide value (mequiv. O_2/kg)
1	Bianchera	2000–2001	0.52	10.8
2	Casaliva	2000–2001	0.70	30.4
3	Maurino	2000–2001	0.39	8.7
4	Leccino	2000–2001	0.33	15.8
5	Leccino	1999–2000	0.23	13.3
6	Frantoio	1999–2000	0.35	12.0
7	Radar	1996–1997	0.83	49.2

4-Methyl-2-pentanol was chosen as the internal standard because it is normally not present in the volatile fraction of olive oil. Moreover, the chromatographic retention time of 4-methyl-2-pentanol does not correspond to that of other compounds in olive oil aroma.

2.5.1. Acidity degree and peroxide value

Quality parameters such as free acidity and peroxide value were obtained as established by EU regulations [1].

2.6. Qualitative and quantitative analysis

Compounds were identified by comparison of their mass spectra and retention times with those of standard compounds, or by comparison of the mass spectrum with those of the mass spectrum library Wiley 6. Moreover, Kováts' retention indexes were determined on two chromatographic capillary columns with distinct polarities and compared with retention indexes of the compounds available in the literature.

Quantitative determination was carried out by the method of internal standards. For standard compounds for which a calibration curve was available, the relative response factors were calculated. These factors were the ratio between the absolute response factor of the single standard compounds and the absolute response factor of the internal standard at the concentration used (1.5 μg/g). For the other compounds identified in olive oil headspace, the relative response factor was assumed to be 1.

3. Results and discussion

3.1. Desorption time

After sampling of the standard mixture, various desorption times (5, 2, 1 and 0.5 min) were evaluated. By decreasing the time of desorption, chromatographic resolution was improved, while avoiding overlapping of some of the peaks that occurred at longer periods of desorption. Within 5 and 1 min, the uptake of most of the compounds presented no relevant differences, while peak areas slightly decreased at shorter desorption times (only for the less-volatile compounds). At times shorter than 1 min, the uptake of most of the compounds was reduced. On this basis, the time of desorption yielding the best chromatographic resolution without relevant decreases in the peak areas of most of the compounds was considered to be 1 min.

3.2. Evaluation of fibres

3.2.1. Extraction time

To identify the most suitable sampling time, the behaviour of each fibre was evaluated at several extraction times (10, 20, 30 and 40 min) by analysing a standard mixture (1 μg/g). Fig. 1 shows the uptake of 4-methyl-2-pentanol as representative of the majority of the analysed compounds. It can be seen that the PDMS and PDMS–DVB fibres appear to reach saturation at 10 and 30 min, respectively, whereas for the DVB–CAR–PDMS and CAR–PDMS fibres equilibrium is not attained within 40 min.

The sampling time was fixed at 30 min, when most of the compounds have attained maximum uptake in the case of the PDMS and PDMS–DVB fibres. For the DVB–CAR–PDMS and CAR–PDMS fibres, this is the minimal period of exposure needed to detect all the standard compounds with a relative standard deviation generally lower than 10% (Table 2).

We compared the peak areas (mean of three repetitions) obtained at a sampling time of 30 min using the four fibres (Fig. 2). The greatest responses for the majority of compounds were obtained with DVB–CAR–PDMS and CAR–PDMS fibres. However, the latter seems to be more selective for some of the most volatile compounds. At the same time, it is not as sensitive as DVB–CAR–PDMS for the other compounds. PDMS–DVB also allows detection of all the compounds of the standard mixture, although with lower responses and slightly lower repeatability. The lowest responses and repeatability

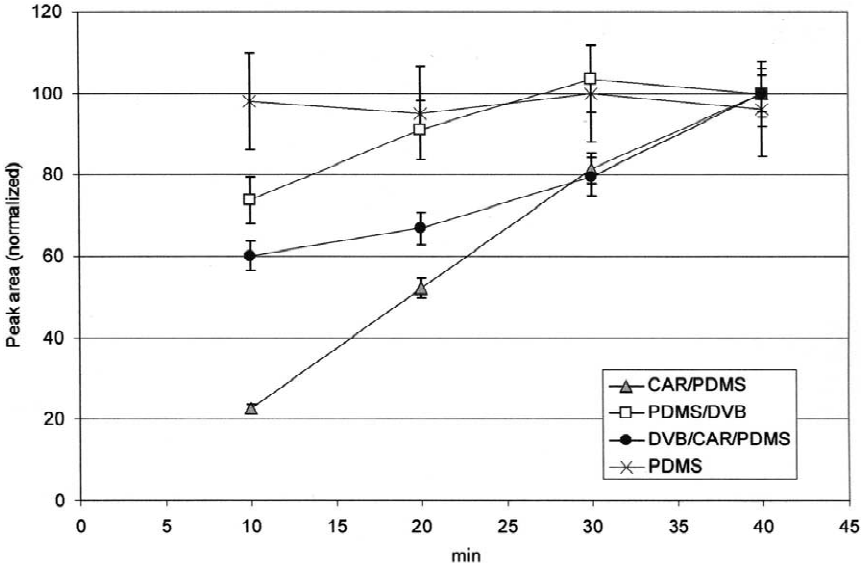

Fig. 1. Uptake of 4-methyl-2-pentanol by four types of fibre coating at different sampling times. Data obtained by GC–FID analysis.

Table 2
Relative standard deviations obtained with four fibre coatings by means of SPME–GC–FID analysis

		RSD (%)			
		CAR–PDMS	PDMS–DVB	DVB–CAR–PDMS	PDMS
1	Isovaleraldehyde	7.3	7.8	3.4	27.8
2	Ethyl propanoate	15.0	10.9	6.9	26.2
3	Pentanal	6.9	4.2	2.0	25.0
4	1-Penten-3-one	17.2	11.6	10.0	32.8
5	Hexanal	0.7	0.1	1.3	27.6
6	4-Methyl-2-pentanol	4.4	8.6	6.1	12.8
7	Heptanal	2.2	0.9	7.2	12.0
8	Limonene	1.8	7.1	2.9	5.9
9	2-Methylbutan-1-ol	4.5	6.0	3.4	9.7
10	(*E*)-2-Hexenal	4.8	5.0	4.8	6.7
11	Hexyl acetate	3.0	3.1	3.4	2.6
12	Octanal	0.4	1.8	0.1	4.7
13	Hexenyl acetate	3.2	3.4	3.2	1.8
14	1-Hexanol	3.2	4.3	4.6	3.3
15	(*E*)-3-Hexen-1-ol	3.3	4.6	5.1	3.4
16	(*Z*)-3-Hexen-1-ol	3.0	4.6	4.3	4.1
17	Nonanal	2.8	1.1	7.9	13.8
18	(*E*)-2-Hexen-1-ol	2.6	4.9	4.2	4.2
19	(Z)-2-Hexen-1-ol	1.6	4.6	3.7	2.8
20	Methyl nonanoate	1.5	2.7	2.7	4.3
21	Decanal	0.0	13.4	0.4	24.6
22	(*E*)-2-Nonenal	3.8	9.3	5.2	5.4
23	1-Octanol	0.1	9.0	2.6	0.8
24	Methyl decanoate	6.0	10.1	2.6	2.1
25	Nonanol	4.1	4.7	10.2	1.4
26	α-Terpineol	1.0	8.6	2.6	1.1
27	Hexanoic acid	0.4	8.4	3.1	15.2
28	Heptanoic acid	2.9	7.4	3.0	15.4

(Table 2) were observed for the PDMS fibre, which was ruled out of further analyses.

3.2.2. Response factors

The linearity of the response of the tested fibres as a function of concentration was evaluated by means of *r* values of linear regressions relative to the response of each standard compound and concentration. The absolute response factors were considered as the slopes of the linear regressions calculated within the range of concentration in which the absolute response factor was already constant. This range was considered to be 0.1–2.5 μg/g for all the compounds tested by the three fibre coatings. Table 3 shows the absolute response factors and *r* values.

Nevertheless, when the concentration was increased to 5 μg/g, the absolute response factor decreased (around 12 and 14% with PDMS–DVB and DVB–CAR–PDMS fibres, respectively), in particular for CAR–PDMS fibres (around 30%).

In summary, CAR–PDMS and, especially, DVB–CAR–PDMS fibres yielded higher responses, while DVB–CAR–PDMS and PDMS–DVB fibres resulted in a greater linearity within a wider interval of concentrations (1–5 μg/g), the repeatability being comparable for the three fibres.

3.2.3. Analysis of virgin olive oil headspace

Virgin olive oil was sampled using the three fibres previously tested with the standard mixture.

The effect of sample composition on internal standard uptake using the three fibres was then evaluated. For each fibre, the mean of the internal standard peak areas for the seven samples was

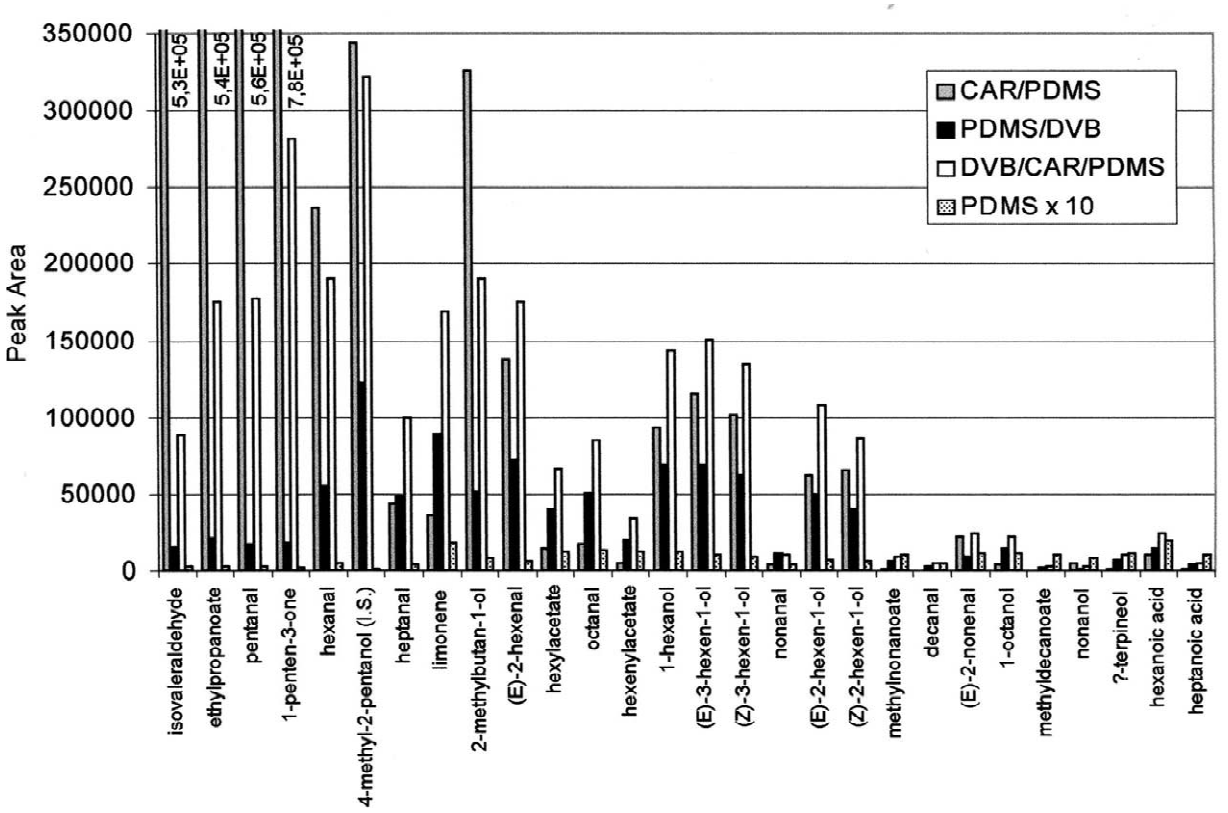

Fig. 2. Uptake of the standard compounds tested using four fibre coatings at a sampling time of 30 min. Data are expressed as peak areas obtained by GC–FID analysis.

calculated and considered to be 100 (Fig. 3). Greater variations of internal standard uptake were observed using DVB–CAR–PDMS and PDMS–DVB. By comparison with the relative standard deviation of 4-methyl-2-pentanol due to experimental errors of the method (reported in Table 2 and represented in the figure by error bars), the greater variability observed for DVB–CAR–PDMS and PDMS–DVB can be attributed to the influence of sample composition on the equilibrium reached by 4-methyl-2-pentanol. This effect is especially evident for sample 7, which possesses a high concentration of oxidation compounds that compete in the equilibrium. The variability of uptake obtained by CAR–PDMS was comparable to that calculated for the method, revealing a minimal effect of sample composition on the uptake of 4-methyl-2-pentanol. Therefore, for the quantitative analysis of virgin olive oil samples, the CAR–PDMS fibre seems to be more suitable than DVB–CAR–PDMS, even if the latter exhibits better linearity.

However, the CAR–PDMS fibre gave a lower resolution of the chromatographic peaks, probably due to the slower desorption of compounds in the injection port, even if the temperature of desorption in this case was higher than in the case of the other fibres. Given the lower chromatographic resolution, a number of peaks cannot be determined and therefore the CAR–PDMS fibre does not allow the qualitative or quantitative analysis of all the compounds present in a complex volatile fraction such as that of virgin olive oil.

With regard to the other fibres tested, as expected the largest number of compounds detected was given by DVB–CAR–PDMS, while the lower response factors observed for PDMS–DVB led to fewer peaks, with areas not always sufficient to distinguish the mass spectra.

Table 3
Absolute response factors (AbsRF) and *r* values of the relative linear regressions of standard compounds determined by SPME–GC–FID analysis by means of three fiber coatings within the concentration range 0.1–2.5 μg/g

		CAR–PDMS		PDMS–DVB		DVB–CAR–PDMS	
		AbsRF	*r*	AbsRF	*r*	AbsRF	*r*
1	Isovaleraldehyde	497 303	0.9984	12 190	0.9918	47 981	0.9607
2	Ethyl propanoate	520 414	0.9997	14 136	0.9930	105 757	0.9623
3	Pentanal	499 449	0.9996	7919	0.9932	85 232	0.9584
4	1-Penten-3-one	768 194	0.9989	13 743	0.9968	235 074	0.9970
5	Hexanal	200 691	0.9986	9334	0.9898	96 269	0.9934
6	4-Methyl-2-pentanol	263 665	0.9995	49 301	0.9780	195 671	0.9938
7	Heptanal	53 650	0.9970	40 103	0.9982	106 919	0.9970
8	Limonene	43 448	0.9983	78 655	0.9992	178 197	0.9938
9	2-Methylbutan-1-ol	288 130	0.9987	30 623	0.9797	122 106	0.9772
10	(*E*)-2-Hexenal	161 820	0.9977	52 970	0.9941	184 517	0.9966
11	Hexyl acetate	17 616	0.9976	37 695	0.9996	76 229	0.9919
12	Octanal	22 174	0.9967	47 781	0.9995	99 124	0.9909
13	Hexenyl acetate	21 070	0.9978	38 567	0.9996	78 831	0.9904
14	1-Hexanol	104 999	0.9990	56 469	0.9977	150 102	0.9968
15	(*E*)-3-Hexen-1-ol	130 490	0.9990	55 037	0.9964	156 250	0.9971
16	(*Z*)-3-Hexen-1-ol	116 892	0.9989	49 531	0.9963	140 591	0.9968
17	Nonanal	6502	0.9774	10 895	0.9979	14 814	0.9529
18	(*E*)-2-Hexen-1-ol	72 318	0.9989	43 473	0.9983	116 255	0.9947
19	(*Z*)-2-Hexen-1-ol	64 624	0.9984	34 564	0.9980	85 939	0.9989
20	Methyl nonanoate	785	0.9954	6083	0.9994	10 988	0.9829
21	Decanal	475	0.9872	3836	0.9977	6126	0.9908
22	(*E*)-2-Nonenal	1341	0.7912	5737	0.9833	10 027	0.9448
23	1-Octanol	4880	0.9970	13 794	0.9996	27 254	0.9868
24	Methyl decanoate	833	0.9864	2086	0.9996	3066	0.9874
25	Nonanol	4162	0.9923	1095	0.9965	3027	0.9980
26	α-Terpineol	1872	0.9977	7031	0.9996	13 301	0.9825
27	Hexanoic acid	7413	0.9977	7811	0.9975	7324	0.9768
28	Heptanoic acid	1423	0.9978	3019	0.9983	1631	0.9827

We thus used DVB–CAR–PDMS to characterise the aroma of olive oil and confirmed the suitability of this fibre to analyse the olive oil sample headspace quantitatively.

3.3. Qualitative and quantitative analysis of virgin olive oil samples

3.3.1. Characterisation of the volatile fraction

The volatile fraction was identified by matching the mass spectra of the compounds with the reference mass spectra of the Wiley 6 library, supported by comparing the retention indexes calculated on two capillary columns of distinct polarity with those reported in the literature (Table 4)). In some cases, identification was based on a comparison with standard compounds.

Fig. 4 shows the chromatographic profile of one of the analysed samples, obtained by separation on Supelcowax-10. Identification of the chromatographic peaks according to Table 4 is shown.

The majority of the 102 compounds isolated and characterised by this SPME–GC–MS method are those reported in the literature as constituents of virgin olive oil aroma and mainly determined by means of dynamic headspace techniques.

A number of compounds were detected and tentatively identified, the presence of which in virgin olive oil aroma has not been previously reported in the literature. This is the case for some hydrocarbons such as 2- and 3-methylpentane, 1-acetylcyclohexene, 1-methyl-3-(hydroxyethyl)propadiene and (*E*)-4,8-dimethyl-1,3,7-nonatriene, which gave chromatographic peaks of considerable area and were detected

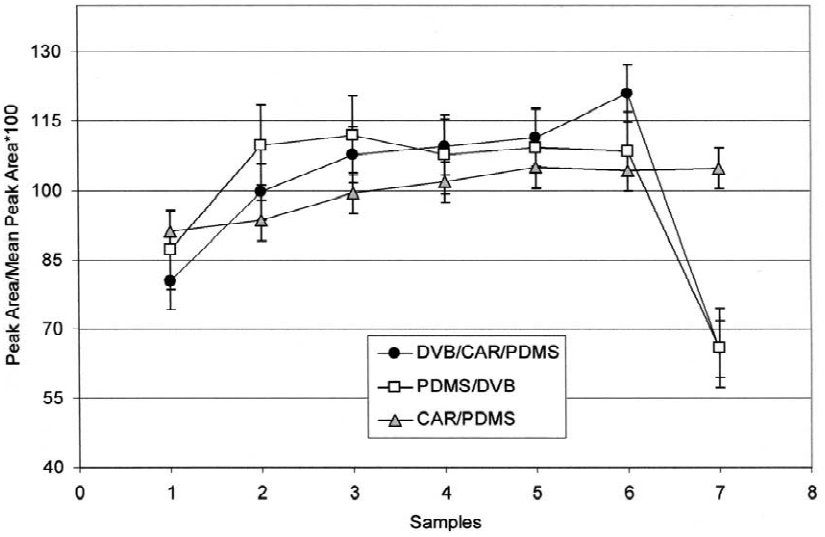

Fig. 3. Internal standard uptake for the seven samples tested, expressed by normalisation of the peak areas obtained from GC–FID analysis.

in all the samples analysed. Carboxylic acids with various molecular structures, e.g. formic acid and (*E*)-2-hexenoic acid, were also tentatively identified in the majority of samples. Moreover, traces of compounds tentatively identified as trichloroethene, benzyl alcohol, methoxyhexane, hexyl formate and methyl benzoate were detected.

The compounds not previously reported as constituents of olive oil headspace were tentatively identified using the mass spectra library, since standards or chromatographic retention indexes were not available. The mass spectra of these compounds were related to the reference mass spectra of the library with a probability of certainty of $>80\%$. Identifications giving a lower probability of certainty were not taken into consideration, as is the case of an unidentified compound detected in all the analysed samples (compound 47, Table 4). The mass spectrum was characterised by fragment ions m/z 41, 43, 55, 57, 69, 83, 97, 111 and 126, and probably corresponded to a hydrocarbon.

Seven of the detected peaks showing the same mass spectrum, not identified by the available libraries, were attributed to the structure of pentene dimers, in agreement with the characterisation proposed by Angerosa et al. for seven isomeric hydrocarbons found in virgin olive oil aroma [17]. Typical fragment ions of the mass spectra coincided with those found by these authors and were the same for the seven hydrocarbons (m/z 39, 41, 53, 67, 68, 69, 95, 109 and 138). The molecular structures of the isomers elucidated in the above-mentioned paper by chiral chromatography were attributed in this report to the seven compounds according to their sequence of elution on the same polar chromatographic column used by those authors. Nevertheless, the retention indexes calculated for the apolar chromatographic column for the peaks with a pentene dimer spectrum could not be attributed to each specific isomer structure.

Some compounds giving small peak areas were detected only by using the polar or the apolar column, probably because the retention time using one of the capillary columns coincided with that of other compounds, and their retention index could not be calculated for both columns, as shown in Table 4.

After chromatographic separation on the apolar column, four components were found with the same mass spectrum, while only one peak with the same spectrum was detected for the polar capillary column. Typical fragment ions were m/z 77, 91, 105 and 120, and they may be characteristic of the mass spectrum of trimethylbenzene isomers or ethyltoluene isomers (M_r 120). Some trimethylbenzene isomers have been reported in the literature as constituents of virgin olive oil aroma (Table 4),

Table 4
Identification of compounds by means of GC–MS analysis

Compound	*I*		*I* Ref.		ID Ref.
	SW	SPB-1	SW	SPB-1	
1 2-Methylpentane*	n.d.[d]	584			[b]
2 3-Methylpentane*	n.d.	589			[b]
3 Hexane	600	600			[a,b] [7][e,f]
4 Heptane	700	700			[a,b]
5 Octane	800	800			[a,b] [21][e], [9][e], [24][e,g]
6 (*E*)-2-Octene	n.d.	809	880 [25]	811 [25]	[b] [7][e], [2][e]
7 2-Propanone	820	n.d.			[b] [14][e]
8 Methyl acetate	828	566	813 [25]	513 [25]	[b] [7][e], [2][e]
9 2-Propenal	854	n.d.			[b]
10 Ethyl acetate	892	n.d.	872 [25], 822 [26]	595 [25], 587 [26]	[b] [7][e], [20][e], [3][e], [2][e], [21][e], [9][e]
11 2-Methylbutanal	915	631	1001 [26]	639 [26]	[b] [20][e], [21][e], [9][e]
12 Isovaleraldehyde	916	626	937 [25], 910 [26]	649 [25], 641 [26]	[a,b] [7][e], [20][e], [2][e], [21][e]
13 Ethanol	932	551	900 [25], 929 [26]	500 [25], 651 [26]	[a,b] [14][e], [15][e], [20][e], [21][e], [9][e], [24][e,g]
14 1-Methoxyhexane*	941	816			[b]
15 1,5-Hexadiene, 3,4-diethyl (*R*,*S*+*S*,*R*)	952	n.d.			[c] [17][e]
16 *meso*-1,5-Hexadiene, 3,4-diethyl	955	n.d.			[c] [17][e]
17 Ethyl propanoate	952	695	944 [25], 925 [26]	691 [25], 686 [26]	[a,b] [7][e], [2][e]
18 Pentanal	977	666	1002 [25], 935 [26]	694 [25], 791 [26]	[a,b] [7][f], [18][e,f], [3][e], [23][e,f]
19 3-Pentanone	979	669	984 [26]	619 [26]	[b] [7][e], [3][e], [2][e]
20 Trichloroethene*	993	680			[b]
21 1,5-Octadiene, 3-ethyl (*E* or *Z*)	1012	n.d.			[c] [17][e]
22 1-Penten-3-one	1016	654	973 [26]	680 [26]	[a,b] [7][e], [15][e], [20][e], [2][e], [21][e], [9][e], [24][e]
23 1,5-Octadiene, 3-ethyl (*E* or *Z*)	1018	n.d.			[c] [17][e]
24 Toluene	1030	741	1042 [26]	756 [26]	[b] [7][e,f], [3][e], [2][e]
25 (*E*)-2-Butenal*	1035	n.d.			[b] [23][f], [24][e,g]
26 3,7-Decadiene (*EE* or *ZZ* or *EZ*)	1069				[c] [17][e]
27 Hexanal	1074	769	1084 [25], 1024 [26]	780 [25], 772 [26]	[a,b] [2][e], [7][e,f], [15][e], [18][e,f], [19][e], [20][e], [21][e], [22][e], [9][e], [23][e,f], [24][e,g]
28 3,7-Decadiene (*EE* or *ZZ* or *EZ*)	1077	n.d.			[c] [17][e]
29 3,7-Decadiene (*EE* or *ZZ* or *EZ*)	1079	n.d.			[c] [17][e]
30 Isobutylalcohol*	1097	n.d.			[b] [18][e], [21][e], [24][e,g]
31 Ethylbenzene*	1119	n.d.			[b] [2][e], [3][e], [7][e]
32 Isoamylacetate	1120	n.d.	1110 [25]	860 [25]	[b] [15][e]
33 (*E*)-2-Pentenal	1127	743	1131 [26]	766 [26]	[b] [2][e], [7][e], [18][e,f], [20][e], [21][e], [9][e], [23][e,f]
34 *m*- or *p*-Xylene	1133	849	1147 [26], 1140 [25]	863 [26], 860 [25]	[b]
35 (*Z*)-3-Hexenal	1137	n.d.	1072 [26]	795 [26]	[b] [2][e], [7][e], [22][e]
36 1-Penten-3-ol	1164	n.d.	1130 [25], 1157 [26]	673 [25], 792[26]	[b] [2][e], [7][e,f], [20][e], [21][e], [9][e], [24][e]
37 4-Methyl-2-pentanol (I.S.)	1172	737	1124 [26]	758 [26]	[a,b]
38 *o*-Xylene	1174	871	1191 [25], 1183 [26]	884 [25], 818 [26]	[b]
39 2-Heptanone	1181	867	1170 [26]	872 [26]	[b] [2][e], [7][e]
40 Heptanal	1184	877	1186 [25], 1174 [26]	883 [25], 885 [26]	[a,b] [7][f], [18][e,f]
41 3-Octen-2-one	n.d.	1013	1285 [26]	1023 [26]	[b]
42 Limonene	1190	1015	1206 [25], 1178 [26]	1030 [25], 1022 [26]	[a,b] [14][e], [3][e], [9][e,h]
43 1-Methyl-3-(hydroxy-ethyl)propadiene*	1193	819			[b]

Table 4. Continued

	Compound	*I*		*I* Ref.		ID	Ref.
		SW	SPB-1	SW	SPB-1		
44	3-Methylbutanol	1211	717	1205 [26]	736 [26]	[a,b]	[2][e], [7][e], [20][e], [3][e], [22][e], [9][e]
45	2-Methylbutanol	1211	719	1208 [26]	843 [26]	[a,b]	[2][e], [7][e], [20][e]
46	(*E*)-2-Hexenal	1216	824	1207 [25], 1220 [26]	832 [25], 826 [26]	[a,b]	[2][e], [14][e], [15][e], [18][e,f], [19][e], [20][e], [3][e], [7][e,f], [21][e], [22][e], [9][e]
47	n.i.[d] (hydrocarbon)	1242	1203				
48	β-Ocimene	1250	1038	1250 [25], 1242 [26]	1038 [25], 1043 [26]	[b]	[14][e], [15][e]
49	1-Pentanol	1250	748	1255 [26]	747 [26]	[b]	[2][e], [7][e], [20][e], [9][e]
50	1-Acetylcyclohexene*	1255	931			[b]	
51	Methyl benzoate	n.d.	1064	1600 [25], 1600 [26]	1078 [25], 1064 [26]	[b]	
52	Styrene*	1065	n.d.			[b]	[2][e], [7][e]
53	Hexyl acetate	1274	997	1307 [25]	1012 [25]	[a,b]	[2][e], [7][e], [19][e], [19][e], [9][e]
54	1,2,4-Trimethylbenzene*	1274	974			[b]	[7][e]
55	Octanal	1288	981	1278 [25], 1280 [26]	985 [25], 982 [26]	[a,b]	[7][f], [18][e,f]
56	Ethyl hexanoate	n.d.	985	1223 [25], 1229 [26]	983 [25], 983 [26]	[b]	
57	(*E*)-4,8-Dimethyl-1,3,7-nonatriene*	1306	1105			[b]	
58	(*Z*)-3-Hexenyl acetate	1316	989	1300 [25], 1338 [26]	987 [25], 988 [26]	[a,b]	[2][e], [7][e], [15][e], [19][e], [20][e], [22][e], [9][e], [24][e]
59	(*E*)-2-Heptenal	1320	929	1243 [26]	954 [26]	[b]	[7][f], [18][e,f], [23][f]
60	α-Pinene	n.d.	913	1039 [25], 1032 [26]	942 [26], 920 [26]	[b]	[3][e]
61	Hexyl formate	n.d.	912	1258 [25]	994 [25]	[b]	
62	(*Z*)-2-Pentenol*	1320	n.d.			[b]	[2][e], [7][e], [20][e], [21][e], [9][e], [24][e]
63	*m*-Ethyltoluene*	n.d.	944			[b]	
64	*o*-Ethyltoluene*	n.d.	945			[b]	
65	1,3,5-Trimethylbenzene*	n.d.	952			[b]	
66	2-Octanone	n.d.	972	1304 [25], 1285 [26]	991 [25], 982 [26]	[b]	[2][e], [7][e]
67	6-Methyl-5-hepten-2-one	1337	965	1335 [25], 1336 [26]	968 [25], 965 [26]	[a,b]	[2][e], [7][e]
68	1-Hexanol	1357	858	1316 [25], 1360 [26]	858 [25], 858 [26]	[a,b]	[2][e], [7][e,f], [14][e], [15][e], [19][e], [20][e], [21][e], [9][e], [24][e,g]
69	(*E*)-3-Hexen-1-ol	1366	836			[a,b]	[2][e], [7][e,f]
70	(*Z*)-3-Hexen-1-ol	1385	838	1351 [25], 1391 [26]	847 [25], 844 [26]	[a,b]	[2][e], [7][e], [14][e], [15][e], [19][e], [20][e], [21][e], [22][e], [9][e]
71	Nonanal	1396	1082	1382 [25], 1385 [26]	1087 [25], 1079 [26]	[a,b]	[7][f], [18][e,f], [3][e], [23][f]
72	2,4-Hexadienal 1*	1397	899			[b]	[2][e], [7][e]
73	2,4-Hexadienal 2*	1402	879			[b]	
74	(*E*)-2-Hexen-1-ol	1408	853	1368 [25], 1377 [26]	854 [25], 870 [26]	[a,b]	[2][e], [7][e], [14][e], [20][e], [21][e], [3][e], [9][e], [24][e,g]
75	(*Z*)-2-Hexen-1-ol	1417	855			[a,b]	[7][e]
76	(*E*)-2-Octenal	1425	1032	1427 [25], 1345 [26]	1045 [25], 1031 [26]	[b]	[7][e,f], [23][f], [18][f]
77	Acetic acid	1448	617	1450 [26]	710 [26]	[b]	[2][e], [7][e,f], [15][e], [20][e], [3][e], [21][e], [22][e], [9][e], [24][e,g]
78	(*E*)-1-Octen-3-ol	1455	970	1420 [25], 1394 [26]	968 [25], 969 [26]	[b]	[9][h], [7][f]
79	2,4-Heptadienal 1	1463	968	1373 [26]	1000 [26]	[b]	[7][f]
80	α-Copaene	1481	1367	1519 [25], 1488 [28]	1398 [25], 1380 [28]	[b]	[14][e], [20][e]
81	2,4-Heptadienal 2*	1487	n.d.			[b]	[7][f]
82	Methyl nonanoate	1491	1207	1479 [25], 1572 [26]	1207 [25], 1207 [26]		[7][e]
83	Decanal	1497	1182	1485 [25], 1484 [26]	1188 [25], 1186 [26]	[a,b]	[3][e], [7][f]

Table 4. Continued

	Compound	*I*		*I* Ref.		ID	Ref.
		SW	SPB-1	SW	SPB-1		
84	Formic acid*	1521	563			[b]	
85	3,5-Octadien-2-one*	1521	1043			[b]	[7][f]
86	(*E*)-2-Nonenal	1525	1132	1540 [25], 1502 [26]	1146 [25], 1137 [26]	[a,b]	[22][e], [7][f]
87	Ethyl nonanoate	n.d.	1282	1523 [25]	1280 [25]		
88	Propanoic acid*	1528	n.d.			[b]	[7][e], [20][e]
89	1-Octanol	1562	1070	1519 [25], 1553 [26]	1061 [25], 1071 [26]	[a,b]	[21][e], [9][h], [7][f]
90	Isobutylic acid*	1565	n.d.			[b]	[9][h]
91	Methyl decanoate	1596	1306	1581 [25], 1591 [26]	1307 [25], 1307 [26]	[a,b]	[2][e], [7][e]
92	Butanoic acid	1626	802	1634 [26]	681 [25]	[b]	[27][e]
93	(*E*)-2-Decenal	1641	1235	1842 [25], 1590 [26]	1449 [25], 1234 [26]	[b]	[7][f]
94	2,4-Decadienal	n.d.	1285	1710 [26]	1283 [26]	[b]	[22][f], [7][f]
95	1-Nonanol	1665	n.d.	1624 [25]	1161 [25]	[a,b]	[7][f]
96	Pentanoic acid*	1667	n.d.			[b]	[27][e]
97	(*E*,*E*)-α-Farnesene	1750	1493	1751 [28]	1515 [28]	[b]	[14][e], [7][f]
98	Hexanoic acid	1841	n.d.	1850 [26]	890 [26]	[a,b]	[7][f]
99	Benzyl alcohol	1883	n.d.	1822 [25], 1865 [26]	1033 [25], 1117 [26]	[b]	
100	Phenylethyl alcohol	1919	n.d.	1859 [25]	1104 [25]	[b]	[22][e]
101	Heptanoic acid	1962	n.d.			[a,b]	[7][f], [27][e]
102	(*E*)-2-Hexenoic acid*	1970	837			[b]	

I, Kováts' retention index; SW, polar capillary column (Supelcowax-10); SPB, apolar capillary column (SPB-1); ID, identification method.

*Tentatively identified.

[a] Identified by comparison with standard compounds.

[b] Identified by Wiley 6 mass spectra library search.

[c] Identified by comparison of mass spectra and order of elution according to Angerosa et al. [17].

[d] n.d., not determined; n.i., not identified.

[e] Detected in extraVirgin olive oil.

[f] Detected in virgin olive oil with ''rancid'' defect.

[g] Detected in virgin olive oil with ''fusty'' defect.

[h] Detected in virgin olive oil with ''mustiness'' defect.

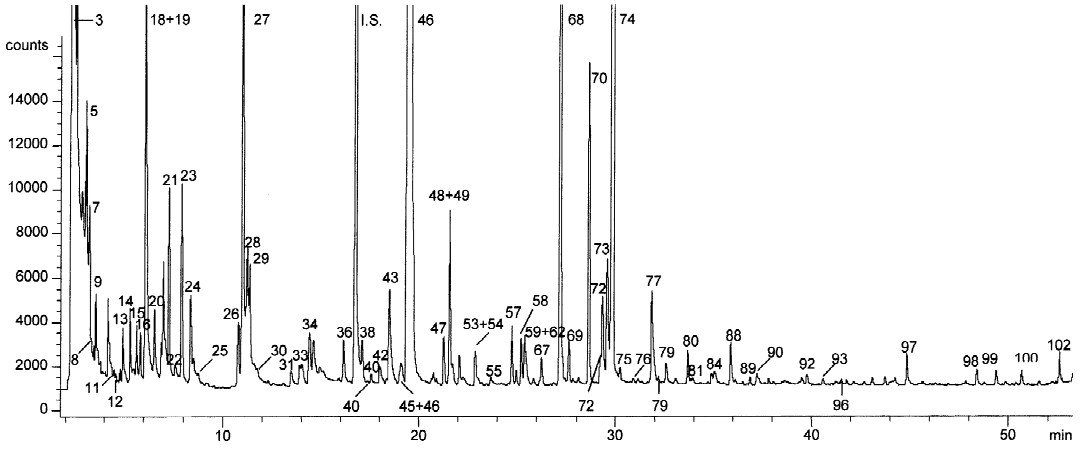

Fig. 4. HS-SPME–GC–FID chromatogram of sample 3, sampling being performed by DVB–CAR–PDMS and chromatographic separation being carried out on a Supelcowax-10 capillary column. Identification numbers correspond to those reported in Table 4.

Table 5
Concentrations (expressed in μg/g) of the compounds detected in the headspace of the virgin olive oil samples, calculated from SPME–GC–FID data

Compound	Sample							Ref.
	1	2	3	4	5	6	7	
2-Methylpentane[a]	0.26	0.14	0.05	0.15	0.10	0.03	0.38	
3-Methylpentane[a]	0.41	0.22	0.57	0.20	0.18	0.04	0.49	
Hexane[a]	12.57	7.20	2.45	11.55	4.44	2.10	2.08	
Heptane[a]	0.12	0.11	0.15	0.54	0.07	0.07	1.59	
Octane[a]	0.26	0.35	0.03	0.36	0.20	0.14	2.38	
(*E*)-2-Octene[a]	0.03	0.04	0.01	0.02	0.02	0.01	0.11	
2-Propanone[b]	2.00	0.28	0.23	0.18	0.19	0.16	1.24	
Methyl acetate[b]	0.16	0.13	0.08	0.41	0.08	0.09	0.00	
2-Propenal[b]	0.22	0.22	0.12	0.13	0.12	0.14	1.05	
Ethyl acetate[b]	0.17	0.11	0.02	0.05	0.02	0.02	0.68	
2-Methylbutanal[b]	0.06	0.04	0.02	0.00	0.08	0.00	0.00	
Isovaleraldehyde[b,c]	0.41	0.21	0.07	0.00	0.62	0.00	0.00	62–106 μg/kg [29], 1.5–7.9 μg/g [21]
Ethanol[b]	3.67	1.26	0.10	0.31	0.56	0.28	5.42	
1-Methoxyhexane[b]	0.00	0.04	0.09	0.06	0.00	0.00	0.75	
1,5-Hexadien, 3,4-diethyl[b]	0.16	0.10	0.08	0.03	0.14	0.03	0.00	
meso-1,5-Hexadiene, 3,4-diethyl[b]	0.13	0.09	0.07	0.03	0.13	0.03	0.00	
Ethyl propanoate[a,c]	0.00	0.00	0.00	0.00	0.00	0.09	0.00	
Pentanal[b] + 3-pentanone[b,c]	1.21	1.54	0.55	1.69	1.13	0.59	4.64	62–409 μg/kg [29]
Trichloroethene[b]	0.10	0.00	0.15	0.00	0.00	0.00	0.00	
1,5-Octadiene, 3-ethyl (*E* or *Z*)[b]	0.20	0.29	0.27	0.08	0.40	0.10	0.04	
1-Penten-3-one[b,c]	0.30	0.19	0.04	0.05	0.21	0.04	0.16	26 μg/kg [29], 5.3–8.3 μg/g [21]
1,5-Octadiene, 3-ethyl (*E* or *Z*)[b]	0.31	0.31	0.26	0.10	0.53	0.07	0.08	
Toluene[b]	0.13	0.14	0.14	0.12	0.12	0.19	0.25	
(*E*)-2-Butenal[b]	0.07	0.14	0.06	0.07	0.05	0.12	0.11	
3,7-Decadiene (*EE* or *ZZ* or *EZ*)[b]	0.10	0.11	0.11	0.02	0.16	0.03	0.00	
Hexanal[b,c]	3.63	3.16	1.78	0.48	1.53	0.35	38.10	137–1770 μg/kg [29], 338–1274 μg/kg [22], 26.8–38 μg/g [21], 40–60 μg/L [30]
3,7-Decadiene (*EE* or *ZZ* or *EZ*)[b]	0.30	0.35	0.30	0.05	0.38	0.07	0.79	
3,7-Decadiene (*EE* or *ZZ* or *EZ*)[b]	0.43	0.27	0.24	0.09	0.34	0.05	0.73	
Isobutylalcohol[b]	0.11	0.14	0.08	0.21	0.05	0.01	1.05	
Ethylbenzene[b]	0.02	0.03	0.04	0.01	0.02	0.03	0.10	
Isoamylacetate[b]	0.02	0.03	0.00	0.05	0.01	0.01	0.16	
(*E*)-2-Pentenal[b]	0.15	0.22	0.03	0.03	0.17	0.03	2.17	
m- or *p*-Xylene[b]	0.06	0.10	0.12	0.06	0.06	0.07	0.43	
(*Z*)-3-Hexenal[b]	0.20	0.11	0.14	0.00	0.22	0.03	0.00	
1-Penten-3-ol[b]	0.21	0.22	0.09	0.04	0.21	0.08	0.72	
4-Methyl-2-pentanol[a,b]	I.S.	I.S.	I.S.	I.S.	I.S.	I.S.	I.S.	
o-Xylene[b]	0.07	0.09	0.09	0.06	0.06	0.06	0.17	
2-Heptanone[b]	0.01	0.03	0.01	0.01	0.02	0.01	0.32	
Heptanal[b,c]	0.07	0.14	0.04	0.02	0.12	0.02	0.80	
3-Octen-2-one[a]	0.04	0.04	0.02	0.02	0.02	0.02	0.00	
Limonene[b,c]	0.08	0.12	0.05	0.08	0.12	0.04	1.30	
1-Methyl-3-(hydroxyethyl)propad[b]	0.42	0.19	0.22	0.02	0.40	0.03	1.08	
3-Methylbutanol[a]	0.14	0.09	0.03	1.36	0.05	0.10	0.00	
2-Methylbutanol[a,c]	0.69	0.33	0.18	1.59	0.23	0.12	10.26	
(*E*)-2-Hexenal[b,c]	31.62	10.85	16.75	0.95	29.17	2.03	1.50	6770 μg/kg [29], 365–4296 μg/kg [22], 121–438.5 μg/g [21], 560–1600 μg/L [30]

Table 5. Continued

Compound	Sample							Ref.
	1	2	3	4	5	6	7	
n.i. (hydrocarbon)[b]	0.08	0.28	0.07	0.01	0.03	0.01	0.05	
β-Ocimene[a]	0.15	0.05	0.12	0.03	0.09	0.02	0.08	
1-Pentanol[a]	0.01	0.06	0.01	0.13	0.24	0.58	1.18	
1-Acetylcyclohexene[a]	0.12	0.19	0.05	0.07	0.02	0.12	0.68	
Methyl benzoate[a]	0.04	0.03	0.01	0.01	0.01	0.01	0.02	
Styrene[b]	0.04	0.05	0.04	0.04	0.03	0.00	0.19	
Hexyl acetate[a,c]	0.26	0.49	0.04	0.17	0.09	0.03	0.87	
1,2,4-Trimethylbenzene[a]	0.07	0.05	0.04	0.03	0.04	0.03	0.37	
Octanal[b,c]	0.10	0.16	0.05	0.02	0.18	0.05	1.57	99–382 μg/kg [29]
Ethyl hexanoate[a]	0.00	0.00	0.00	0.02	0.00	0.00	0.29	
(*E*)-4,8-Dimethyl-1,3,7-nonatriene[b]	0.13	0.13	0.08	0.08	0.14	0.14	0.09	
(*Z*)-3-Hexenyl acetate[b,c]	0.15	1.32	0.19	0.01	0.06	0.01	0.55	2250 μg/kg [29], 3212–3383 μg/kg [22]
(*E*)-2-Heptenal[a]	0.15	0.18	0.02	0.00	0.12	0.00	4.61	
α-Pinene[a]	0.06	0.05	0.00	0.02	0.02	0.02	0.05	
Hexyl formate[a]	0.01	0.00	0.00	0.00	0.00	0.00	0.29	
(*Z*)-2-Pentenol[a]	0.70	0.05	0.03	0.34	0.26	0.27	0.58	
m-Ethyltoluene[a]	0.05	0.04	0.03	0.02	0.03	0.02	0.10	
o-Ethyltoluene[a]	0.02	0.02	0.02	0.01	0.01	0.01	0.06	
1,3,5-Trimethylbenzene[a]	0.02	0.01	0.01	0.01	0.01	0.01	0.08	
2-Octanone[a]	0.02	0.03	0.00	0.01	0.01	0.02	0.00	
6-Methyl-5-hepten-2-one[b]	0.05	0.13	0.05	0.03	0.04	0.05	0.44	
1-Hexanol[b,c]	1.98	1.11	2.39	10.26	0.68	6.05	6.76	10–48.8 μg/g [21], 100–440 μg/L [30]
(*E*)-3-Hexen-1-ol[b,c]	0.09	0.08	0.10	0.08	0.06	0.13	0.16	
(*Z*)-3-Hexen-1-ol[b,c]	0.69	0.87	0.72	0.65	0.46	0.59	0.76	684 μg/kg [29], 662–796 μg/kg [22], 4.7–77.5 μg/g [21], 130–200 μg/L [30]
Nonanal[a,c]	3.74	1.99	1.02	0.93	1.39	0.85	14.98	
2,4-Hexadienal 1[b]	0.35	0.17	0.21	0.02	0.26	0.02	0.05	
2,4-Hexadienal 2[b]	0.45	0.18	0.23	0.03	0.34	0.04	0.10	
(*E*)-2-Hexen-1-ol[b,c]	6.83	2.23	9.27	1.24	2.26	10.40	8.79	26.6–48 μg/g [21], 310–880 μg/L [30]
(*Z*)-2-Hexen-1-ol[b,c]	0.11	0.06	0.14	0.08	0.09	1.12	0.17	
(*E*)-2-Octenal[b]	0.02	0.03	0.02	0.01	0.02	0.01	1.70	
Acetic acid[b]	1.33	1.58	0.26	0.72	0.44	0.07	3.84	
(*E*)-1-Octen-3-ol[b]	0.03	0.04	0.02	0.03	0.02	0.03	0.71	
2,4-Heptadienal 1[b]	0.08	0.17	0.05	0.03	0.03	0.02	0.45	
α-Copaene[b]	0.05	0.04	0.05	0.01	0.00	0.00	0.00	
2,4-Heptadienal 2[b]	0.02	0.04	0.02	0.01	0.01	0.01	0.29	
Methyl nonanoate[c]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Decanal[a,c]	0.19	0.10	0.06	0.21	0.14	0.10	3.44	
Formic acid[b]	0.15	0.45	0.08	0.33	0.07	0.00	2.65	
(*E*)-2-Nonenal[a,c]	0.45	0.22	0.08	0.07	0.21	0.09	2.98	24–91 μg/kg [29], 10–14 μg/kg [22]
Ethyl nonanoate[a]	0.01	0.00	0.00	0.00	0.00	0.00	0.00	
3,5-Octadien-2-one[a]	0.02	0.09	0.01	0.00	0.00	0.01	0.19	
Propanoic acid[b]	0.17	0.23	0.31	0.67	0.05	0.04	0.72	
1-Octanol[b,c]	0.13	0.22	0.10	0.14	0.10	0.18	1.07	3.6–5.6 μg/g [21]
Isobutylic acid[b]	0.06	0.03	0.02	0.37	0.03	0.01	0.05	

Table 5. Continued

Compound	Sample							Ref.
	1	2	3	4	5	6	7	
Methyl decanoate[c]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Butanoic acid[b]	0.06	0.07	0.02	0.05	0.02	0.01	0.17	
(*E*)-2-Decenal[b]	0.01	0.03	0.01	0.01	0.02	0.00	0.16	
(*E*,*E*)-2,4-Decadienal[a]	0.00	0.00	0.00	0.00	0.00	0.00	0.05	
1-Nonanol[c]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Pentanoic acid[b]	0.03	0.02	0.01	0.53	0.05	0.01	0.04	
(*E*,*E*)-α-Farnesene[b]	0.02	0.01	0.04	0.00	0.00	0.00	0.00	
Hexanoic acid[b,c]	0.97	1.17	0.31	4.77	0.78	0.10	20.19	
Benzyl alcohol[b]	0.03	0.02	0.02	0.03	0.02	0.01	0.05	
Phenylethyl alcohol[b]	0.05	0.03	0.02	0.07	0.03	0.01	0.10	
Heptanoic acid[b,c]	0.42	0.31	0.00	0.30	0.45	0.10	1.31	
(*E*)-2-Hexenoic acid[b]	0.08	0.04	0.04	0.35	0.04	0.02	0.11	

[a] Determined after separation on an apolar chromatographic column (SPB-1).

[b] Determined after separation on a polar chromatographic column (Supelcowax-10).

[c] Quantitatively determined by applying the calculated relative response factor. Where not specified the response factor was considered to be 1.

while no data on ethyltoluene isomers was found. As there are three possible trimethylbenzene isomers, the molecular structure of an ethyltoluene isomer can be attributed to at least one of the peaks detected with the same spectrum.

Another class of components was found showing a mass spectrum typical of xylene isomers and ethylbenzene (M_r 106), with characteristic fragment ions at m/z 39, 51, 65 and 77, and in greater amounts at m/z 91 and 106. Three peaks were detected on the polar column, but only two after separation on the apolar column. They were tentatively identified by comparison of their chromatographic retention indexes with those reported in the literature for xylene isomers (Table 4).

3.3.2. Quantitative analysis

Table 5 shows the concentration of each compound expressed in μg/g and the type of capillary column on which each compound was measured.

The compounds were determined on the column giving the better resolution of the chromatographic peaks. In particular, on the polar capillary column, a satisfactory separation of C_6 linear alcohols could be performed, while the retention indexes of these compounds on the apolar column are situated in a narrow interval that does not allow the resolution of their chromatographic peaks. The resolution of carboxylic acids on the apolar column was also unsatisfactory, since they gave broad peaks which could only be resolved on the polar column. On the other hand, alcohols such as 2- and 3-methylbutanol coelute on the latter column and they could only be separated on the apolar column.

Given the very similar chromatographic retention indexes of pentanal and 3-pentanone on polar and apolar columns, their quantification was not possible using the present method. Table 5 shows the sum of these compounds.

Data on the concentration of some virgin olive oil volatile compounds determined by other preconcentration methods are available in the literature and show a high variability depending on the sample analysed and the technique used for analysis (Table 5). However, the results obtained by the SPME method are comparable to the concentration ranges reported by some of these reference data. In general, these coincided with the results obtained by Reiners et al. [29] applying a dynamic headspace (HS) technique. The amounts of (*E*)-2-nonenal in all samples analysed by SPME were greater than those reported by other authors, while (*Z*)-3-hexenylacetate and 1-octanol were detected in smaller amounts by the present method.

In general, the compounds usually present in greater amounts in the samples were C_6 derivatives such as (*E*)-2-hexenal, (*E*)-2-hexen-1-ol, hexane, 1-hexanol, hexanal and hexanoic acid.

The uptake of some compounds seems to be related to the peroxide value, as is the case for octane, (*E*)-2-octene, 2-heptanone, limonene and aldehydes, in particular unsaturated aldehydes such as (*E*)-2-pentenal, (*E*)-2-heptenal, (*E*)-2-octenal, (*E*)-2-nonenal, (*E*)-2-decenal and (*E*,*E*)-2,4-heptadienal.

4. Conclusions

In conclusion, the HS-SPME method used may be a suitable tool for the quantitative and qualitative analysis of the volatile compounds in virgin olive oil. It is able to detect most of the compounds isolated and identified by other time-consuming pre-concentration techniques, such as dynamic headspace. Moreover, it has led to the identification of a number of compounds not previously detected in olive oil headspace when applied to a few olive oil samples.

This method provides a quantitative approach to the analysis of virgin olive oil aroma, within a specified range of concentrations and analytical conditions.

The results obtained in this study provide information on the performance of HS-SPME for the analysis of the volatile fraction of virgin olive oil and allow us to apply the developed method to further investigations.

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