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Characterization of volatile compounds of French and Spanish virgin olive oils by HS-SPME: Identification of quality-freshness markers

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Abstract

Headspace-Solid Phase Microextraction (HS-SPME) was applied to the analysis of volatile compounds of virgin olive oils from southern France (Alpes–Maritimes) and Spain (Reus). Forty one compounds were isolated and characterized by GC–RI and GC–MS, representing 85.3–92.8% of the total amount. (E)-Hex-2-enal, the main compound extracted by SPME, characterized the olive oil headspace for all samples. The other compounds identified were mainly hexanal, (Z)-hex-3-enol, (E)-hex-2-enol and hexanol. Changes in the chemical composition of the olive oil headspace were also monitored during storage. The content of (E)-hex-2-enal decreased over several months, and that of the C_6 alcohols and C_5 ketones increased. These compounds can be used as markers for the evaluation of olive oil quality.

Keywords: Headspace-solid phase microextraction; GC–FID; GC–MS; Olive oil composition; Lipoxygenase pathway

1. Introduction

Olive oils are complex mixtures consisting of two main groups of substances: (a) saponifiable substances which represent nearly 98% of the chemical composition, such as triglycerides, partial glycerides, esters of fatty acids or free non-esterified fatty acids; and (b) unsaponifiable substances, with many different chemical structures, which represent only 2% of all olive oil composition, such as sterols, hydrocarbons, pigments, phenols, flavonoids or volatile compounds (Aparicio & Aparicio-Ruíz, 2000).

These volatile compounds are mainly responsible for the flavor of olive oil, which is of prime importance in the food industry because it plays a significant role in consumer choice. C_6 and C_5 volatile components are mainly responsible for the ''green'' odour notes of olive oil aroma, and they are characteristics of the good quality of virgin olive oils required by consumers (Angerosa, 2002).

Many analytical procedures have been used to identify and quantify the volatile components that characterize olive oil aroma (Angerosa, 2002). Among these extraction techniques, Solid Phase Micro Extraction (SPME) is a solvent-free sample preparation technique for the extraction of volatile and non-volatile compounds, and is also a simple and fast technique to implement. This method, developed by Arthur and Pawliszyn in 1990 (Arthur & Pawliszyn, 1990; Zhang & Pawliszyn, 1993), has been used in many applications: the analysis of pollutants in water (Abalos, Bayona, & Pawliszyn, 2000; Arthur & Pawliszyn, 1990), headspace analysis of aromatic and medicinal plants (Bicchi, Drigo, & Rubiolo, 2000) or in food flavor analysis (Kataoka, Lord, & Pawliszyn, 2000; Yang & Peppard, 1994). In just a few years, SPME has considerably extended its

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applications to many fields (Baltussen, Cramers, & Sandra, 2002; Lord & Pawliszyn, 2000). Several studies have been published on the analysis of olive oil volatile compounds using SPME, and many components have been identified (Bentivenga, D'Auria, De Luca, De Bona, & Mauriello, 2001; Flamini, Cioni, & Morelli, 2003; Jeleń, Obuchowska, Zawirska-Wojtasiak, & Wasowicz, 2000; Vichi et al., 2003).

Finally, all volatile components can be used to check the quality of an olive oil (Angerosa, 2002), to detect an adulteration (Lorenzo, Pavón, Laespada, Pinto, & Cordero, 2002), to detect a possible rancidity (off-flavors) (Morales, Ríos, & Aparicio, 1997) or to determine the variety of olive used (Lorenzo et al., 2002).

The aim of this study was to compare different French (Cailletier and Blanquettier varieties, studied for the first time by SPME) and Spanish (Arbequines variety) olive oil samples by the characterization of their volatile compounds. The headspace composition was studied by solid phase microextraction. Eight virgin olive oils from southern France (Alpes–Maritimes) and one virgin olive oil from Spain (Reus) were used in this study. The results obtained by SPME were then compared. Changes in the chemical composition of the olive oil headspace were also monitored during the storage of three samples after conservation in ambient temperature in darkness.

2. Materials and methods

2.1. SPME–GC/FID and SPME–GC/MS analysis

A manual SPME device and fiber were obtained from the Supelco Company (Bellefonte, PA). The fiber used for the extraction of the volatile components was divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 50/30 μm.

Before use, fiber was conditioned as recommended by the manufacturer. The olive oil (20 g) was placed in a 40 mL amber vial closed by a PTFE/silicone septa (Supelco). Before extraction, stabilization of the headspace in the vial was obtained by equilibration for 60 min at 25 °C. The extraction was carried out at 25 °C (room temperature) with magnetic stirring (900 trs/min).

To determine the optimal adsorption time of the fiber to the sample headspace, the fiber DVB/CAR/PDMS was exposed for time periods of 10, 30, 60, 90 and 120 min. A sampling time of 90 min was chosen to perform the analysis (Cavalli, Fernandez, Lizzani-Cuvelier, & Loiseau, 2003).

After exposure, the fiber was thermally desorbed into a GC and left in the injection port (equipped with a 0.75 mm i.d. inlet liner) for 4 min. The injector was set at 250 °C and operated in the splitless mode for 4 min unless otherwise stated. GC analyzes were carried out using two Hewlett-Packard 5890 Series II Gas Chromatographs, one equipped with a FID and one coupled to a Hewlett-Packard 5971A Mass Selective Detector (quadrupole). Both were equipped with fused-silica capillary columns HP-1 (polydimethylsiloxane, 50 m × 0.2 mm i.d., film thickness: 0.33 μm for GC–FID and 0.5 μm for GC–MS). The carrier gas was nitrogen for GC–FID and helium for GC–MS (both column head pressures: 25 psi); oven temperature programmed from 60 to 250 °C at 2 °C/min and then held isothermal (20 min). The FID temperature was set at 250 °C and the temperatures of the ion source and the transfer line were 170 and 280 °C; energy ionization, 70 eV; electron ionization mass spectra were acquired over the mass range 35–350 atomic mass units (amu). Before sampling, the fiber was reconditioned for 5 min in the GC injection port at 250 °C, and blank runs were carried out periodically during the study.

2.2. Component Identification

Identification of the components in each olive oil was based on: (a) their GC retention indices (RI) on apolar column, determined relative to the retention times of a series of *n*-alkanes (C-5 to C-28; retention times determined for SPME experiment: 20 s at 50 °C; the other sampling conditions were the same as described above) with linear interpolation with those of authentic compounds or literature data (BACIS, 1999); (b) computer matching with the reference mass spectra of the Wiley 6 library and comparison of spectra with those of the laboratory library. To make analytical data comparable, the peak areas of each identified compound in olive oil samples were percent normalized.

2.3. Olive oil samples

Nine virgin olive oil samples (200 mL per sample), extracted from olives of the Cailletier and Blanquettier varieties (both cultivated in France), and Arbequines variety (cultivated in Spain) were used for the investi-

Table 1
Sample letter, origin, variety and harvesting year of the nine virgin olive oils

Sample	Origin	Variety	Year
A	Castagniers (France)	Cailletier	01-2002
B	Grasse (France)	Cailletier	12-2002
C	Grasse (France)	Cailletier	01-2003
D	Gattières (France)	Cailletier	01-2003
E	Valbonne (France)	Cailletier	01-2003
F	Le Rouret (France)	Cailletier	01-2003
G	Ville Vieille (France)	Cailletier	02-2003
H	Cap Antibes (France)	Blanquettier	12-2002
I	Reus (Espagne)	Arbequines	12-2002

gation in this study. All samples were certified as natural and monovarietal by producers. The fruits were harvested in January and December 2002, January and February 2003. The olive oils were stored at ambient temperature between each analysis in darkness. Table 1 describes the characteristics of the nine samples of virgin olive oil which were used in this study.

3. Results and discussion

3.1. Headspace composition by SPME

Headspace-solid phase microextraction was used to characterize the volatile compounds present in the nine virgin olive oils. Forty one volatile compounds were

Table 2
Compounds extracted by HS-SPME in the nine virgin olive oils

Compounds[a]	RI[b]	A(%)[c]	B(%)	C(%)	D(%)	E(%)	F(%)	G(%)	H(%)	I(%)
Ethanol	<500	1.6	9.0	1.1	1.3	1.0	4.8	1.0	1.6	25.4
Propan-2-one	<500	0.6	9.5	0.4	0.2	0.3	2.2	0.6	nd[d]	nd
Pent-2-ene[f]	503	1.4	nd	0.4	1.1	1.0	1.6	1.8	0.5	2.5
Acetic acid	561	2.9	nd	0.3	nd	0.1	nd	0.8	0.4	0.2
Pentan-2-one	659	2.7	1.3	1.0	0.5	0.6	0.5	2.5	1.1	0.8
Pentan-3-one	671	4.3	1.5	0.4	0.2	0.2	0.7	2.3	1.1	0.5
Heptane	700	1.0	nd	0.2	nd	nd	nd	0.5	nd	nd
3-Methylbutanol	715	nd	0.4	0.5	0.5	0.3	0.4	0.2	0.4	0.8
Pent-2-enal[f]	718	0.8	nd	nd	nd	nd	0.4	0.1	nd	1.0
(Z)-Pent-2-enol	748	1.0	nd	nd	nd	0.2	nd	0.4	nd	nd
Toluene	753	1.1	0.3	0.4	0.6	0.3	0.1	0.8	0.6	0.3
Hex-3-enal[f]	771	nd	nd	0.3	0.5	0.3	nd	nd	nd	nd
Hexanal	774	5.2	2.1	6.6	4.7	4.0	3.9	7.4	3.1	1.7
Octane	800	1.2	0.3	0.7	1.0	0.8	0.6	1.2	0.4	0.4
(E)-Hex-2-enal	827	39.4	37.3	52.5	62.0	64.0	51.8	60.4	51.8	28.3
(Z)-Hex-3-enol	835	4.6	2.9	3.4	3.5	3.4	3.7	nd	4.3	4.3
(E)-Hex-2-enol	845	6.6	4.0	9.0	4.9	3.7	5.8	2.7	4.5	2.8
Hexanol	848	7.8	5.0	6.8	4.5	3.6	7.4	4.6	5.4	4.9
p-Xylene	856	2.9	1.0	1.3	2.4	0.7	1.2	2.6	1.5	0.9
Hexa-2,4-dienal[f]	875	nd	nd	0.1	0.1	0.1	0.2	tr[e]	0.3	nd
o-Xylene	878	0.2	nd	nd	nd	nd	nd	nd	nd	nd
3,4-Diethylhexa-1,5-diene[f]	895	0.2	nd	0.1	nd	0.1	nd	0.1	nd	nd
3,4-Diethylhexa-1,5-diene[f]	900	0.2	nd	0.1	0.1	0.1	nd	0.1	nd	nd
Benzaldehyde	927	nd	1.0	0.1	0.1	0.2	nd	0.1	0.4	nd
α-Pinene	929	nd	1.0	2.4	0.4	3.2	1.2	nd	0.4	0.2
3-Ethylocta-1,5-diene[f]	932	1.1	nd	nd	nd	nd	nd	0.5	nd	nd
3-Ethylocta-1,5-diene[f]	939	0.8	0.3	0.4	0.2	0.4	nd	0.3	0.3	0.2
Octanal	977	0.2	0.4	0.1	0.2	0.1	0.6	nd	nd	nd
(Z)-Hex-3-enyl acetate	979	0.2	nd	0.2	0.1	0.3	nd	nd	0.6	6.3
Deca-3,7-diene[f]	982	0.3	0.5	0.2	0.1	0.1	0.3	tr	0.2	nd
Deca-3,7-diene[f]	985	0.4	0.8	0.2	0.1	0.3	0.1	0.1	0.3	nd
Deca-3,7-diene[f]	987	0.3	0.5	0.3	0.1	0.5	0.5	0.2	0.3	nd
Hexyl acetate	988	nd	nd	nd	nd	nd	nd	nd	nd	3.6
δ-3-Carene	990	nd	nd	0.4	nd	0.2	nd	nd	nd	nd
α-Terpinene	1003	0.1	nd	0.3	0.4	0.4	0.3	nd	nd	nd
Limonene	1017	0.1	nd	nd	0.3	nd	nd	nd	nd	nd
β-Ocimene[f]	1032	0.1	1.0	0.4	0.3	0.9	1.0	0.1	6.9	1.1
γ-Terpinene	1043	nd	0.2	nd	0.4	0.2	nd	nd	nd	nd
Nonanal	1075	0.1	0.3	0.5	0.4	0.8	1.4	0.1	1.8	1.1
(Z)-4,8-Dimethylnona-1,3,7-triene	1098	nd	4.5	0.1	nd	0.2	0.3	nd	0.5	0.4
Sesquiterpene	1364	nd	nd	nd	0.1	0.1	nd	nd	nd	nd
Farnesene[f]	1473	tr	0.2	0.1	0.1	0.1	1.0	nd	0.2	1.4
Total		89.4	85.3	91.3	91.4	92.8	92.0	91.5	88.9	89.1

A–**G**: Cailletier variety; **H**: Blanquettier variety; **I**: Arbequines variety. Unknowns [number (%)]: **A**: 33 (10.6); **B**: 21 (14.7); **C**: 41 (8.7); **D**: 39 (8.6); **E**: 32 (7.2); **F**: 14 (8.0); **G**: 23 (8.5); **H**: 23 (11.1); **I**: 20 (10.9).

[a] Order of elution and percentages of components are given on apolar column (HP-1).

[b] Retention indices as determined on HP-1 column using the homologous series of *n*-alkanes.

[c] Peak area % (percent normalized areas) determined by HS-SPME–GC/FID analysis.

[d] Compound not detected.

[e] Trace (<0.1%).

[f] Correct isomer not characterized.

isolated and characterized by GC–RI and GC–MS analysis (Table 2).

In the seven French Cailletier olive oils (samples **A**–**G**) the isolated and identified compounds are mainly aldehydes with 41.1% to 69.5% of the total peak area percentage such as (E)-hex-2-enal (37.3–64.0%), hexanal (2.1–7.4%) or nonanal (0.1–1.4%), alcohols (8.9–22.1%) such as (E)-hex-2-enol (2.7–9.0%), hexanol (3.6–7.8%) or (Z)-hex-3-enol (2.9–4.6%) as well as monoterpenes (α-pinene or β-ocimene) and sesquiterpene (farnesene). Seven isomeric unsaturated hydrocarbons (3,4-diethyl-hexa-1,5-diene, 3-ethylocta-1,5-diene and deca-3,7-diene, known as pentene dimers) were identified in the volatile fraction of the seven virgin olive oils by

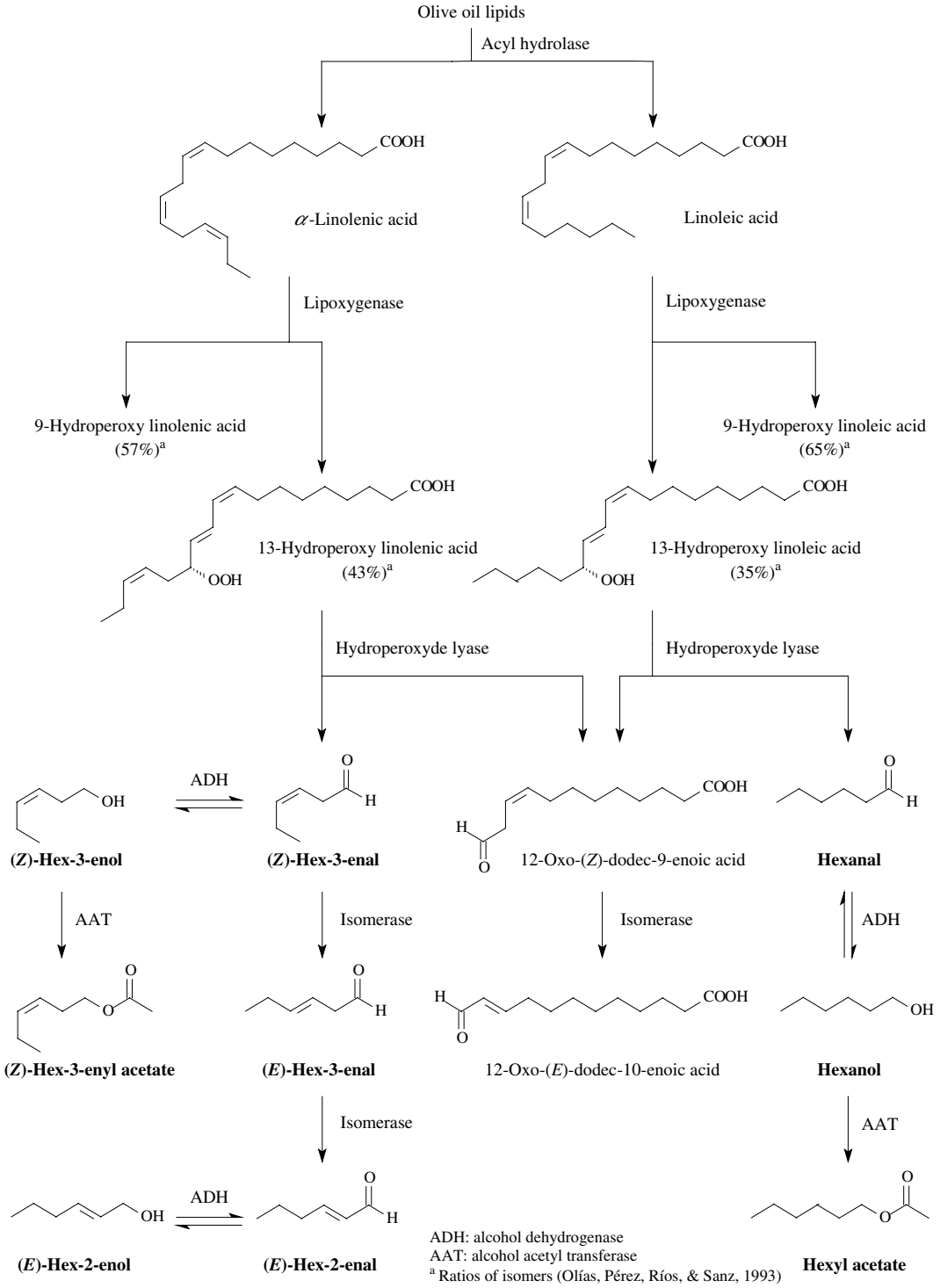

Fig. 1. The "Lipoxygenase Pathway" involved in the production of volatile compounds responsible for virgin olive oil aroma.

comparison of mass spectra and order of elution according to Angerosa, Camera, Alessandro, and Mellerio (1998). These seven compounds derive from the enzymatic transformation of the fatty acids (Angerosa et al., 1998). (E)-Hex-2-enal was the principal compound extracted by HS-SPME in the seven French olive oils of the Cailletier variety, and the majority of the identified components were previously reported in the literature as constituents of olive oil aroma (Vichi et al., 2003).

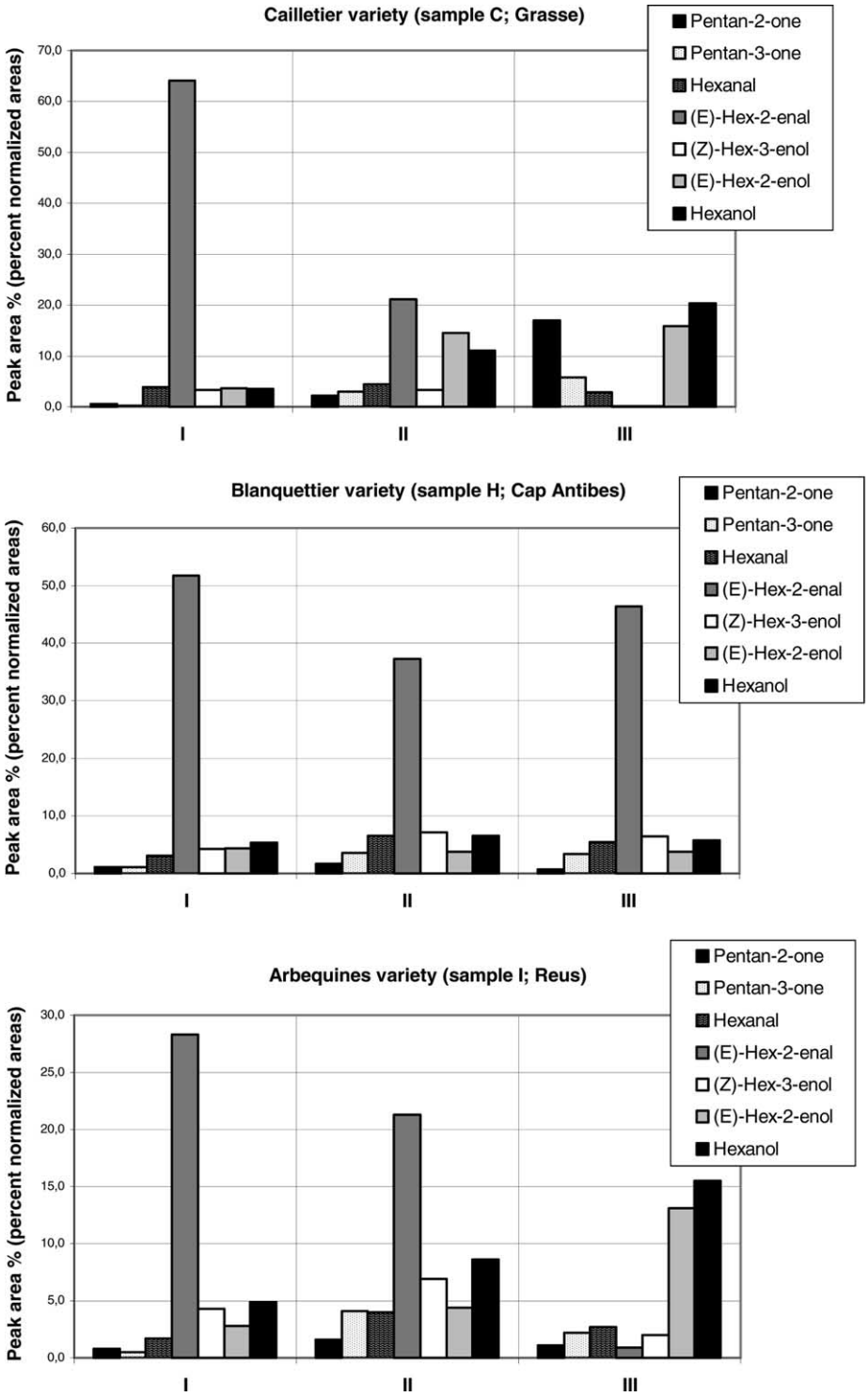

Fig. 2. Variation of volatile compounds with storage time for three olive oils produced from Cailletier, Blanquettier and Arbequines varieties (**I**: January 2003; **II**: March 2003; **III**: September 2003).

The analysis of sample **H** (Blanquettier variety) shows the same composition as the seven Cailletier olive oils (Table 2). There are weak qualitative and quantitative variations. Indeed, the major constituents that characterize the olive oil headspace were always: (E)-hex-2-enal (51.8%), hexanol (5.4%), (E)-hex-2-enol (4.5%) and (Z)-hex-3-enol (4.3%). However, the content of β-ocimene (6.9%) is the most significant of the nine samples (0.1–1.1%). Four pentene dimers were also identified in olive oil **H**.

Finally, the chemical composition of the Arbequines olive oil headspace (sample **I**) was characterized by the pre-eminence of two compounds: (E)-hex-2-enal (28.3%) and ethanol (25.4%) (see Table 2). This high level of ethanol can be explained by the transport of olives from Spain towards France (Brague mill, Opio, France), and is mainly due to fermentation before olive oil extraction. Other main compounds are C_6 alcohols such as hexanol (4.9%), (Z)-hex-3-enol (4.3%) and (E)-hex-2-enol (2.8%). The ester fraction also represents nearly 10% of the headspace chemical composition compared to the other samples (up to 0.6%) with two compounds: (Z)-hex-3-enyl acetate (6.3%) and hexyl acetate (3.6%).

C_6 aldehydes and alcohols and their corresponding esters are the most abundant volatile compounds, and are produced enzymatically from polyunsaturated fatty acids through the "Lipoxygenase Pathway" (Angerosa, 2002; Angerosa, Basti, & Vito, 1999; Benincasa et al., 2003; Olías, Pérez, Ríos, & Sanz, 1993). Lipoxygenase action on the linolenic and linoleic acids produces 13-hydroperoxides, which are the substrate for further enzymatic reactions (see Fig. 1). Indeed, 13-hydroperoxide of linolenic acid is cleaved by hydroperoxide lyase (HPL) producing (Z)-hex-3-enal. This compound is quickly enzymatically reduced to (Z)-hex-3-enol by alcohol dehydrogenase (ADH) or isomerized to (E)-hex-2-enal (isomerase) and then reduced to (E)-hex-2-enol by ADH. The metabolism of 13-hydroperoxide of linoleic acid is simpler. 13-Hydroperoxide is cleaved by HPL producing hexanal, which is reduced to hexanol by ADH. Finally, (Z)-hex-3-enol and hexanol are subsequently transformed into their corresponding ester: (Z)-hex-3-enyl acetate and hexyl acetate respectively by alcohol acetyl transferase (AAT).

Moreover, the high level of (E)-hex-2-enal in olive oils shows the pre-eminence of the (E)-hex-2-enal/(E)-hex-2-enol pathway compared to the hexanal/hexanol pathway in all the varieties considered (Fig. 1). The low level of esters in the Cailletier and Blanquettier varieties also indicates a lower content of AAT in these olive oils compared with the Arbequines variety (Angerosa et al., 1999).

3.2. Changes in flavor profiles during storage

Changes in the chemical composition of the olive oil headspace were also monitored during the storage of three samples after conservation in ambient temperature in darkness. The olive oils were analyzed in January (**I**), in March (**II**) and in September 2003 (**III**) (Fig. 2). For samples **C** and **I** we noted, on the one hand, that the content of (E)-hex-2-enal decreases quickly over a few months (up to 0.1% in September) and on the other hand, that the content of C_6 alcohols ((E)-hex-2-enol and hexanol) slowly increases. However, the reduction in the amount of (E)-hex-2-enal in sample **H** (Blanquettier variety) is very weak compared to that in the other two samples. Moreover, we also observed an increase in the (Z)-hex-3-enol content of olive oils in March followed by a decrease in September. All of these changes are linked to enzymatic activities through the lipoxygenase pathway previously described.

The content of C_5 ketones (pentan-2-one and pentan-3-one) also increases over several months especially for sample **C**, and in a smaller proportion in the other oils. These compounds do not result from the lipoxygenase pathway by enzymatic actions, but from homolytic cleavage of 13-hydroperoxides (Angerosa, 2002) to the detriment of C_6 aldehyde and alcohol formation.

The chemical composition of olive oils depends on their enzyme content and on their activities (Angerosa, 2002). These two parameters are linked to genetic characteristics, to the ripeness stage of fruits, and to the extraction conditions of olive oils. All of these factors contribute to the aroma of the olive oils and to its evolution in time. C_6 aldehydes and alcohols are the most abundant compounds, and contribute significantly to flavor of virgin olive oil. Moreover, a low amount of C_5 ketones, pentene dimers or monoterpenes also affects the aroma.

4. Conclusion

Analysis of the nine French and Spanish virgin olive oils by SPME enabled us to identify 41 compounds, representing 85.3 to 92.8% of the chemical composition. (E)-Hex-2-enal, the principal compound extracted by SPME, characterized the olive oil headspace for all samples. The other compounds identified were mainly hexanal, (Z)-hex-3-enol, (E)-hex-2-enol and hexanol.

The differences between varieties (Cailletier, Blanquettier and Arbequines) were mainly quantitative, because most compounds were present in all olive oils analyzed. A comparison with literature data on the chemical composition of olive oils is difficult because of the great variability of the volatile compositions, which depends on several parameters such as ripeness stage, extraction technique or analytical method (Flamini et al., 2003; Vichi et al., 2003).

The study of the evolution of olive oils during storage showed a reduction in the amount of (E)-hex-2-enal depending on the samples studied, and an increase in the

C_6 alcohol and C_5 ketone content. These compounds can be used as quality-freshness markers of virgin olive oils.

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