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Volatile Compounds, Profiles of Virgin Olive Oils Produced In the Eastern Morocco: Oxidative Stability and Sensory Defects

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Abstract

Studies on flavor profiles of virgin olive oil (VOO) are becoming more and more numerous. The VOO aromas are determined by a mixture of chemicals in olive oil, which influence its quality. Various studies around the world have shown that the volatile compounds in VOO depend on the climate, cultivation and process.

The present work is a first approach to compare volatile profiles of VOO largely produced in eastern of Morocco after 6 months of storage at ambient temperature in darkness. Oxidative stability measured by Rancimat method at 101°C was also determined. VOO volatile profiles were examined using the solid-phase micro extraction fibre method (SPME) in conjunction with gas chromatography/mass spectrometer (GC/ MS). 84 volatile compounds were identified; they belong to various chemical classes, such as aldehydes, alcohols, esters, ketones, carboxylic acids and hydrocarbons. The main volatile compounds present in olive oil samples were compounds with 6 carbon atoms (C6) such as Hexanal, (E)-hex-2-enal, Z-3-Hexen-1-ol and 1-Hexanol. Ethanol and Z-3, 7-dimethyl-1, 3, 6-octatriene, methyl acetate and ethyl acetate were also found. In general, these compounds have been identified in all VOO analyzed samples. The chemical compositions of the analyzed virgin olive oil headspaces evidenced that the most representative compounds In Isly and Kenine were carboxylic acids accounted for 59.24%-49.7% respectively, whereas the volatile fraction of the oil from Achajara almoubaraka showed significantly higher amounts of the alcohols (46%). Concerning oxidative stability, Isly and Kenine OO, have lower stability values compared to Achajara almoubaraka. Their potential oxidative susceptibility is therefore much higher than Achajara almoubaraka.

Keywords: virgin olive oil, volatile compounds, SPME, GC/MS, oxidative stability

1. Introduction

Olive oil is a fundamental ingredient in the Mediterranean diet. Besides the cardiovascular protective properties, this product is especially appreciated for its taste and special aromas.

The unique and delicate flavor of the VOO is attributed to the presence of the volatile compounds, which are mainly produced by oxidation of fatty acids through a chain of enzymatic reactions known as the lipoxygenase (LOX) pathways (Angerosa & Basti, 2001; Kalua et al., 2007). The (LOX) involves a series of enzymes that oxidize (lipoxygenase) and cleave (hydroperoxide lyase) polyunsaturated fatty acids to produce aldehydes. These latter are reduced to alcohols (by alcohol dehydrogenase) and afterward esterified to yield esters (by alcohol acyl transferase) (Kalua et al., 2007). During the extraction of the VOO, the lipoxygenase pathway is initiated by the

crushing and continues during malaxation. The volatile compounds formed during these operations result from the activity of enzymes of all lipoxygenase pathways and contribute to the final flavor of the VOO. Levels can be modified by the conditions of crushing and malaxation used and depend on the level and the activity of enzymes involved in the various pathways (Angerosa, 2002; Angerosa & Basti, 2001; Angerosa, Basti, & Vito, 1999). Yet, other factors that influence the evolution of volatile compounds, responsible for aromas, are fruit maturity, irrigation, extraction methods, storage and condition of the fruit at harvest, cultivar and geographic region (Aparicio & Morales, 1998; Ben Temime Campeol, Cioni, Daoud, & Zarrouk, 2006; Diego, Gonzalez, & Aparicio, 2010; Garcia-Gonzalez, Aparicio-Ruiz, & Aparicio, 2009; Gomez-Rico, Salvador, La Greca, & Fregapane, 2006; Haddada et al., 2007; Inarejos-Garcia, Gómez-Rico, Salvador, & Fregapane, 2010a; Koprivnjak, Procida, & Zelinotti, 2000; Venkateshwarlu, Meyer, & Jacobsen, 2004). The levels of major volatile components decreased in the course of ripening but were higher in irrigated olive trees (Gomez-Rico et al., 2006).

The major volatile compounds responsible for VOO aromatic notes are the C6 and the C5 volatile compounds (Angerosa, 2002; Kiritsakis, Nanos, Polymenoupoulos, Thomai, & Sfakiotakis, 1998) formed from C18 unsaturated fatty acids (oleic, linoleic and linolenic acids) through a chain of enzymatic reactions of the lipoxygenase (LOX) pathway (Angerosa, 2002; Kalua et al., 2007; Kiritsakis et al., 1998). The aroma of olive oil is attributed to a large number of chemical compounds of different chemical classes, aldehydes, alcohols, esters, hydrocarbons, ketones, furans and, probably, other as yet unidentified volatile compounds (Kalua et al., 2007; Kiritsakis et al., 1998; Vichi, Pizzale, Conte, Buxaderas, & Lopez-Tamames, 2003a). Furthermore, it is well established that aliphatic C6 compounds (aldehydes, alcohols and their corresponding esters) are the most abundant compounds of virgin olive oil (VOO) aroma (Angerosa et al., 1999; Angerosa, Mostallino, Basti, & Vito, 2000). They mainly contribute to its green odour notes (Dhifi et al., 2005; Guth & Grosh, 1991; Morales, Calvente, & Aparicio, 1996).

It is generally agreed that endogenous plant enzymes, through the lipoxygenase pathway (LOX) are responsible for the positive aroma perceptions in VOO. Whereas, chemical oxidation and exogenous enzymes, usually from microbial activity, are responsible for the off-flavor referred to as oxidative rancidity (Angerosa & Basti, 2001; Kalua et al., 2007; Morales, Rios, & Aparicio, 1997). This disagreeable sensory note is especially perceptible in oils that are strongly oxidized due to incorrect or excessively long storage and cause the consumers to reject such products (Bendini, Cerretani, Salvador, Fregapane, & Lercker, 2010; Villière & Genot, 2006). The absence of the C6 aldehydes, alcohols and esters from the lipoxygenase pathway and the presence of many saturated and unsaturated aldehydes from chemical oxidation, including hexanal, C5 branched aldehydes and alcohols and some C8 ketones, in relatively high concentrations, in the aroma of virgin olive oil, is associated with unpleasant notes (Angerosa, 2000; Gomes da Silva, Costa Freitas, Cabrita, & Garcia, 2012; Ha, Nihei, & Kubo, 2004; Kalua et al., 2007). Chemical oxidation is responsible for the formation of off- flavor compounds, such as pent-2-enal and hept-2-enal. The off- flavor compounds associated with unpleasant sensory notes can be assembled in five classes- fusty, moistness- humidity, winey- vinegary, metallic and rancid (Angerosa, 2002; Escuderos, Uceda, Sánchez, & Jiménez, 2007; Faria, Cárdenas, G-Mesa, Hernández, & Valcárcel, 2007; Kalua et al., 2007; Morales et al., 1997; Morales, Luna, & Aparicio, 2005).

Solinas, Angerosa & Cucurachi (1987) found that the concentrations of the aldehydes *E*-2-pentenal, hexanal and *E*-2-heptenal, nonanal, 2-heptenal and 2-decenal, increase considerably in the oxidized oils. The authors suggested using *E*-2-heptenal as a marker for oxidation rather than *E*-2-pentenal and hexanal, since these two compounds are already present in the aroma of extra virgin olive oils (Bendini et al., 2010). On the other hand Kalua, Bedgood, Bishop and Prenzler (2006) demonstrated that all volatile compounds found in fresh oil decreased during storage in the light in the presence of oxygen, particularly *E*-2-hexenal. The major compounds indicated by different researchers as markers of virgin olive oil oxidation, their sensory characteristics and odor thresholds are reported in (Table 1).

Table 1. Compounds indicated as markers of off-flavor of virgin olive oil oxidation, their sensory properties, odor thresholds and related references

Compounds	Sensory caracteristics	Odor threshold (mg/kg)	References
Octane	sweet	0.94	Morales et al., 2005
hexanal	Fatty, powerful, oily, grassy	0.32	Kochhar, 1993; Meijboom, 1964
Octanal	Fatty, soapy, sharp, citrus	0.32	Morales et al., 2005
			Kochhar, 1993; Meijboom, 1964
Nonanal	Fatty, Waxy, paint, soapy, citrus	0.15	Guth & Grosh, 1991
			Morales et al., 2005
		13.5	Kochhar, 1993; Meijboom, 1964
E-2-pentenal	Paint, apple	0.3	Servili et al., 2001
			Morales et al., 2005
E-2-heptenal	Oxydized, tallowy, pungent	0.05	Morales et al., 2005
			Kochhar, 1993; Meijboom, 1964
E-2-decenal	Paint, fishy, fatty	0.01	Morales et al., 2005
			Kochhar, 1993; Meijboom, 1964
Pentanal	Woody, bitter, oily	0.24	Kochhar, 1993; Meijboom, 1964
2,4-heptadienal	Fatty, nutty, rancid, cinnamon	3.62	Ullrich & Grosh, 1988
			Morales et al., 2005
			Kochhar, 1993; Meijboom, 1964
Undecenal	Fatty, tallowy	n.d.	Kochhar, 1993; Meijboom, 1964
Heptanal	Oily, fatty, heavy, woody, penetrating, nutty	3.2	Kochhar, 1993; Meijboom, 1964
Decanal	Penetrating, sweet, waxy, painty	6.7	Kochhar, 1993; Meijboom, 1964
E,E-2,4-decadienal	Fatty, deep-fried, citrus	0.18	Reiners & Grosh, 1998
		2.15	Kochhar, 1993; Meijboom, 1964
2-ethylfuran	Sweet, rancid	n.d.	Morales et al., 1997
Hexanoic acid	Sweaty, rancid	0.7	Morales et al., 1997

2. Materials and Methods

2.1 Olive Oil Samples

The study focused on fresh virgin olive oil (crop season, 2010) produced in three different geographical areas in eastern Of Morocco, VOO samples are from olive growers' cooperatives Kenin (Rislane-Tafoughalt), Achajara almoubaraka (Tanacharfi El Aioun) and from Isly (EIG terroir of Oriental, Oujda "Economic Interest Group").

Analysis of volatile compounds was performed in the laboratory of Industrial Biological Chemistry, Faculty of Agricultural Sciences Gembloux, Belgium and oxidative stability analysis was conducted at the same university within the Unit of General and Organic Chemistry. Analysis protocols were provided by the two laboratories.

2.2 Characterization of Volatile Compounds

2.2.1 Solid-phase Microextraction (SPME)

Volatile compounds were analyzed using a solid phase microextraction - gas chromatography (SPME-GC) technique. The sample (10 ml) was placed in a glass vial equipped with a silicon septum and allowed to equilibrate for 30 min at 30°C. After the equilibration time, SPME fiber (DVB/CAR/PDMS, Supelco) was inserted through the septum and exposed to the headspace of the sample for 30 min at 30°C. After extraction, the fiber was transferred to be desorbed into a GC/MS system. Once sampling was finished, the fiber was reconditioned for 30 min at the injection port at 250°C to re-use.

2.2.2 Analysis GC/MS

Solid phase microextraction - gas chromatography – mass spectrometry (SPME-GC-MS) was used to qualitatively analyze volatile compounds using a capillary column HP-5 (0.25mm * 30m * 0.25um), model Agilent 19091J-433. The thermal desorption was done in splitless mode. The oven temperature was held at 35°C for 5 min, increasing to 85°C at a rate of 15°C/min to a final temperature of 300 °C where it was held for 10 min.

2.2.3 Identification of Volatile Compounds

The volatile compounds were identified by comparing their mass spectra with those of the mass spectra library. The retention index (RI) was calculated and compared with RI available in the literature. The RI was determined by injecting a mixture of hydrocarbons containing the homologous series of alkanes (C7-C18) under the same conditions described above.

2.3 Determination of the Oxidative Stability

Oxidative stability was evaluated by the Rancimat method (Metrohm model 679, Herisau, Switzerland). Stability was expressed as the induction time (hours), using an oil sample of 2,5g heated to 101°C under an air flow of 15 l/h. The analytical determinations were carried out in duplicate.

3. Results and Discussion

3.1 Volatile Compounds

A simple chemical analysis is not sufficient to determine the quality of VOO. Indeed, the volatile compounds that develop during the fabrication then during storage are able to modify the odor and flavor of the oil (Kalua, 2007; Prenzler, Robards, & Bedgood, 2007). Although the sensory properties of virgin olive oil are well known (IOOC, 1996), not too much information about the sensory characteristics of oxidized olive oils is available. For this the identification of compounds responsible for the different sensory attributes would be of great interest in the field of quality control.

For evaluating the flavor profile of VOO after 6 month of storage, oil samples were analyzed using the SPME/GC/ MS technique. The results of the qualitative analysis of investigated samples are presented in (Table 2). A total of 84 compounds were detected: including 56 in samples for Kenine association, 31 for Achajara Almoubaraka and 46 in Isly OO. The principal classes of volatile compounds identified were, aldehydes, alcohol, esters, ketones, carboxylic acids and hydrocarbons.

Table 2. Volatile compounds identified in virgin olive oil aroma detected by GC-MS

Aldehydes
2-methyl butanal (2,3,4)
Hexanal (3,4,5, 6)
E-2-hexenal (all samples)
2-methyl-4-pentenal (3,4)
Nonanal (1,5, 6)
E-2-decenal (1, 6)
Undecenal (1,2)
E-2-undecenal (1)
E-2-tridecenal (5,6)

Alcohols
Ethanol (all samples)
1-pentanol (2,3)
2- methyl-1-butanol (3,4)
3-methyl-1-butanol (all samples)
Z-2-penten-1-ol (2,4)
Z-3-hexen-1-ol (all samples)
1-hexanol (all samples)
E-2- hexen-1-ol (3, 4,5, 6)
1-penten-3-ol (3, 4)
2-methyl-1-propanol (4,5)

Esters
Methyl acetate (all samples)
Ethyl acetate (all samples)
2-methyl hexanoate (5)
2-propenyl stearate (1, 5)
Methyl stearate (6)
Ethyl stearate (6)
Methyl 4-hydroxyoctadecanoate (1)
3-hydroxypropyl (9E)-9-octadecenoate (2)
13-tetradecenyl acetate (1)
Methyl palmitate (6)
Ethyl palmitate (6)
2-hydroxyethyl (Z)-9-octadecanoate (1, 5)
E,E-9-12-methyl stearate (6)
E-9- methyl stearate (6)
2,3-dihydroxypropyl-(Z)-9- octadecanoate (1)
Acetate-3-methyl-1-butanol (5)
Z-3-hexenyl acetate (5)

Ketones
2-propanone (1, 2)
3-methyl-2-pentanone (3,4)
2-pentanone(3,4)
3-pentanone (all samples)
2-methylcyclododecanone (1)

Carboxylic acids
Acetic acid (1, 2,5, 6)
Nonanoic acid (1)
tridecanoic acid (1)
hexadecanoic acid (1,2,5, 6)
E-9- hexadecanoic acid (6)
Z-9- octadecanoic acid (1,2,5, 6)
octadecanoic acid (1,2,5, 6)
E-9- octadecanoic acid (1,5, 6)
Z, Z-9,12- octadecanoic acid (1,2)
Eicosanoic acid (1)

Hydrocarbons
5-E-3-ethyl-1,5-octadiene (all samples)
Z-3,7-dimethyl-1, 3,6-octatriene (all samples)
E-4,8-dimethyl-1, 3,7-nonatriene (all samples)
Undecane (2,4)
Methyl-cyclodecane (all samples)
2-propenyl cyclopentane (2, 3, 4,5, 6)
E-8-heptadecene (1, 2, 5, 6)
1-nonadecene (1)
Pentane (3,4)
2,7-dimethyl-2,6-Octadiene (3,4,5)
2,6-dimethyl- Octane (4)
Octane (2,5, 6)
Decane (3,4)
Styrene (5)
4,8-dimethyl-1,7-nonadiene (5,4,6)
Tricosane (5, 6)
Hexadecane (5)
Pentacosane (5, 6)
Heneicosane (5)
Heptacosane (5, 6)
Octacosane (5)
Tétracosane (5)
Hexacosane (5)
1-ethyl-2-methyl-Benzene (3,4)

Terpenic compound
α-farnésène (2, 5, 6)
Squalene (1, 2,5, 6)
Farnesol (6)

Furanes
tetrahydro-3-methyl furan (2)

heterocyclic compound
Methoxy-phenyl-oxime (1, 5, 6)

sterols
gamma-sitosterol (1,2)
campesterol (6)
stigmasterol (6)
beta-sitosterol (6)

VOO reference number: VOO Isly: 1, 2; -VOO Achajara almoubaraka: 3, 4; -VOO Kenine: 5, 6.

In Isly (Samples 1 & 2) and Kenine (Samples 5 & 6) OO samples, the most representative compounds were carboxylic acids which accounted for 59.24% and 32.42% respectively (Figures 1 & 2). These volatile compounds are present only in Isly and Kenine OO. Moreover carboxylic acids are linked to sour and pungent sensations synonymous with sensory defects in olive oil (Kalua, 2007). Vichi et al. (2003b) and Velasco and Dobarganes (2002) reported that higher levels in carboxylic acids are associated with a high oxygen concentration, from storage of OO in contact with air or frequent opening of oil containers. Kalua et al. (2007) work showed that carboxylic acids with two or three carbon atoms are associated with microbial fermentation and other fruit handling defects, whereas the higher carboxylic acids are linked to oxidative rancidity. Moreover, carboxylic acids such as acetic, hexadecanoic, octadecanoic, Z-9-octadecanoic and E-9-octadecanoic acid were found in Isly and Kenine OO. The most representative carboxylic acid is acetic ranged between 10.04% and 20.73% respectively in Kenine and Isly OO. Baccouri et al. (2008) work showed that the level of this volatile compound increased considerably throughout the maturity process and in other studies reported that the presence of acetic acid in the headspaces of VOO might be the result of the process fermentation in the olives. This compound generates the off-flavor: "winey-vinegary" in VOO (Angerosa, 2000; IOOC, 1996; Morales et al., 2005).

In the volatile fraction of Achajara almoubaraka OO (Samples 3 & 4), the major compounds identified were alcohols (Figures 1 & 2), ranging around 45.99%. Ethanol is a major component, representing 20.77% of the total amount, which was related to the fermentation activity before olive oil extraction (Hansen & Hansen, 1996) and responsible of the sensory descriptor "Alcohol" (Morales et al., 2005). On the other hand, 1-pentanol, associated with the "fruity" aroma (Morales & Tsimidou, 2000; Aparicio & Luna, 2002; Morales et al., 2005) and Z-2-penten-1-ol, responsible for the "green" odor notes of VOO aroma (Morales & Tsimidou, 2000) were identified in the headspaces of Isly (0.33% for 1-pentanol and 0.21% for Z-2-penten-1-ol) and Achajara-almoubaraka (0.21% for 1-pentanol and 0.57% for Z-2-penten-1-ol) OO samples. On the other hand the volatile alcohol 2-methyl-1-propanol responsible for "green" sensory attributes (Morales&Tsimidou, 2000) was detected in Achajara-almoubaraka (3.67%) and Kenine OO (1.05%). C6 alcohols such as E-2-hexen-1-ol responsible for the sensory descriptor associated with the "ripe fruity, soft" and "green" aromatic sensory notes (Luna, Morales & Aparicio, 2006; Bendini et al., 2007), it ranged from 0.26% up to 1.03%, respectively in Kenine and Achajara almoubaraka OO samples. C5 alcohols such as 1-penten-3-ol and 2-methyl-1-butanol, compounds that are linked to "mouldy" and "rancid" defects (Koprivnjak et al., 2000), were found only in Achajara almoubaraka OO at a low amount (0.54%; 0.85% Respectively).

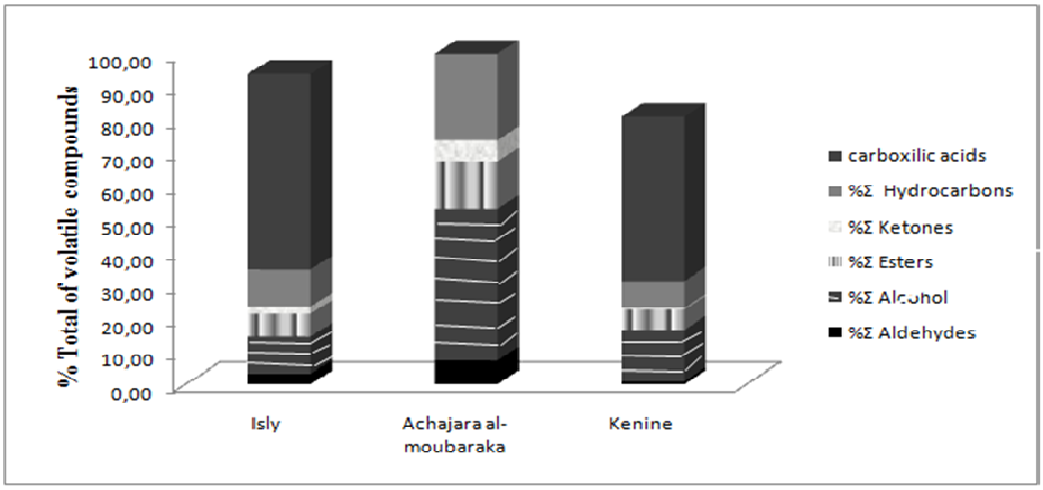

Figure 1. Distribution of carboxylic acids; hydrocarbons; ketones; esters; alcohols and aldehydes in relation to total volatile compounds

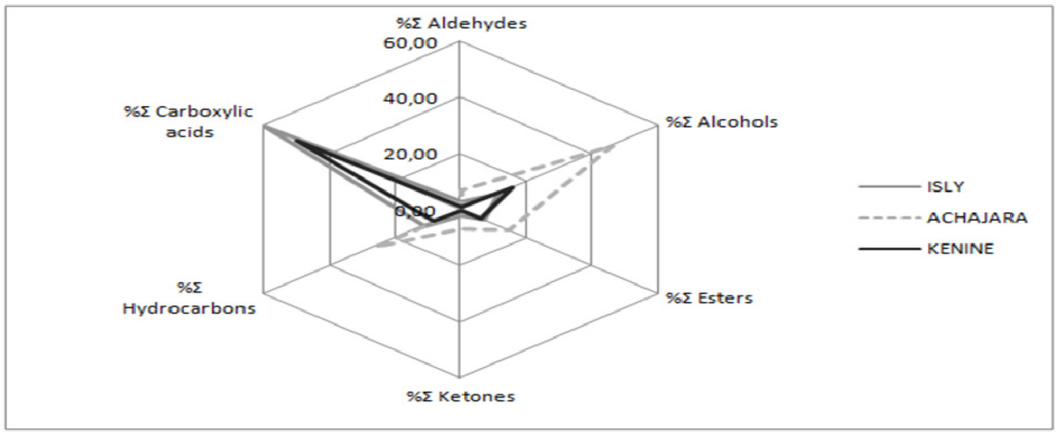

Figure 2. The average of the percentage of volatile compounds for the Isly, Achajara almoubaraka and Kenine OO

The chemical composition of all the OO headspace was characterized by the presence of 12 volatile compounds in most of the all analyzed samples; however, their proportions were substantially different (Table 3), as follows: E-2-hexenal; ethanol; 3-methyl-1-butanol; Z-3-hexen-1-ol; 1-hexanol, methyl acetate; ethyl acetate; 3-pentanone; Z-3,7-dimethyl-1,3,6-octatriene; 5-E-3-ethyl-1,5-octadiene; E-4,8-dimethyl-1,3,7 nonatriene; Methyl-cyclodecane.

Table 3. Percentage of volatile compounds present in all samples

	Isly	Achajara almoubaraka	Kenine
E-2-hexenal	1.49	1.75	0.29
ethanol	2.62	20.77	10.63
3-methyl-1-butanol	0.46	0.87	0.34
Z-3-hexen-1-ol	5.46	14.12	2.35
1-hexanol	2.72	5.41	1.48
methyl acetate	2.04	6.30	2.17
ethyl acetate	1.52	8.00	2.25
3-pentanone	0.36	4.59	0.43
5-E-3-ethyl-1,5-octadiene	1.25	2.19	0.39
Z-3,7-dimethyl-1, 3,6-octatriene	0.98	1.30	0.82
E-4,8-dimethyl-1, 3,7-nonatriene	1.51	1.40	0.67
methyl cyclodecane	4.96	8.26	3.68

The E-2-hexenal derives from the enzymatic transformation of the fatty acids (Angerosa, D'Alessandro, Basti & Vito 1998) and mainly contributes to "lawn, banana" and "almond" notes (Angerosa, 2000; Koprivnjak et al., 2002; Morales et al., 2005), given also to extra VOO the typical "green" note, "apple like" and "fruity" (Aparicio & Luna, 2002; Baccouri et al., 2008; Morales et al., 2005; Reiners & Grosch, 1998). This compound can be used as quality-freshness markers of VOO (Cavalli, Fernandez, Lizzani-Cuvelier, & Loiseau, 2004) and which is inversely related to the oxidation degree of virgin olive oil (Vichi et al., 2003b). In fact, E-2-hexenal is produced from Z-3-hexenal by an isomerization factor (Morales & Aparicio, 1999) with the aid of cis-3: trans-2-enal isomerase (Williams, Salas, Sanchez, & Harwood, 2000) and it is itself reduced to form E-2-hexen-l-ol (Williams, Morales, Aparicio, & Harwood, 1998). Isly and Achajara almoubaraka OO samples present higher level of E-2-Hexenal than Kenine OO, accounted for 1.49%; 1.57%; 0.29% respectively.

As far as alcohol is concerned, ethanol was higher in the Achajara-almoubaraka and Kenine OO (Table3). The C6 alcohol Z-3-Hexen-1-ol was higher in Isly and Achajara-almoubaraka OO and it ranged from 5.46% up to 14.12%, respectively. In fact, this compound has been correlated with the "green" sensory perception (Morales & Aparicio, 1999) and responsible for the "cut grass" odor and could have a role in the enhancement of bitterness (Caporale, Policastro, & Monteleone, 2004). Bedoukian reported that the cis forms of hexenol were characterized by a more pleasant sensory perception than their corresponding transforms. The high level of 1-Hexanol was found only in Achajara almoubaraka OO (5.41%); it contributed to "fruity, grassy" and "soft" sensory notes (Gomez-Rico, Salvador, & Fregapane, 2009). The sensory characterization of hexanol demonstrates that different sensory descriptions exist and in some cases contradictory, for instance "fruit, banana, grassy, soft" and undesirable notes were identified for this same volatile compound (Aparicio & Morales, 1998). 1-Hexanol can be used to separate cultivars and maturity stages (Prenzler et al., 2007). C5 alcohols such as 3-methyl-1-butanol was present at low amount in the all samples analyzed, this compounds is associated with sensory defects (Angerosa, Mostallino, Basti, & Vito, 2001; Ranalli, Pollastri, Contento, lannucci, & Lucera, 2003) "woody, whiskey, sweet" (Morales et al., 2005).

Regarding methyl acetate, contributing to "green" sensory notes (Morales & Tsimidou, 2000), Achajara almoubaraka OO contained higher levels of this volatile compound compared to other samples (6.30%). Achajara almoubaraka OO showed also high amount of ethyl acetate (8%), responsible of sensory descriptor "sticky; sweet" (Morales et al., 2005) and "Crust; crumb" (Bianchi, Careri, Chiavaro, Musci & Vittadini, 2008). However Di Giovacchino and Serraiocco (1995) have shown that the high concentrations of ethyl acetate were found in olive oils obtained by pressure systems from poor quality olive fruits giving sensory defects such as "fusty" and "winey" defects.

Among the C5 compounds, 3-pentanone was the most important C5 ketone identified in all samples, this compound gives the typical notes associated with "green" (Morales & Tsimidou, 2000). High amount of this compound characterizes the aroma fraction of Achajara-almoubaraka with 4.59%.

The hydrocarbons like, methyl-cyclodecane; Z-3,7-dimethyl-1,3,6-octatriene; 5-E-3-ethyl-1,5-octadiene and E-4,8-dimethyl-1,3,7-nonatriene were detected in the all aroma fractions of the analyzed OO. However Jung, De Ropp and Ebeler (2000) reported that the presence of hydrocarbons, proteins and other minor components in OO can decrease the aroma intensity through sorption, binding and formation of intermolecular complexes. Moreover the role of these components in the definition of flavor is not clear. In fact, in the literature, only very few papers (Bentivenga, D'Auria, De Luca, De Bona, & Mauriello, 2001; Vichi et al., 2003b) report the presence of these compounds, which could play a very important role in the fragrance of this valuable food.

Finally, in each of the analyzed OO samples there were compounds which were identified but not found in others (Table2). They are as follows:

Aldehydes: Hexanal is among the main volatile components of OO (Williams, Morales, Aparicio & Harwood, 1998). It is present in Achajara-almoubaraka and Kenine OO at a low amount (5.06%; 0.25% respectively). The amount of hexanal is due to both autoxidation and the lipoxygenase cascade (through the formation of 13-LOOH) (Vichi et al., 2003b). The high amounts of hexanal, often related to a sweet (Morales & Tsimidou, 2000) green and apple sensory note (Morales & Aparicio, 1999; Koprivnjak et al., 2002).

Nonanal and E-2-decenal were identified at low amount in the headspace of Isly (0.57% for nonanal and 0.5% for E-2-decenal) and Kenine OO (0.15% for nonanal and 0.18% for E-2-decenal). In fact Bendini et al. (2010) reported that these two compounds with the E-2-heptenal are the most frequently used volatile markers of oxidation of VOO during storage. These compounds are characterized by low odor threshold (150, 100 and 5 μg/kg, respectively) and by negative off-flavors namely "oxidized", fatty and fish, that strongly contribute to the rancid defect perceived by assessors. Kanavouras, Hernandez-Munoz, Coutelieris (2004) carried out a storage study. They could select a group of volatiles such as hexanal, E-2-heptenal, nonanal, and E-2-decenal, highly correlated with oxidation in packaged extra virgin olive oil under various storage conditions for one year (glass/ PET/PVC bottles; 15°/30°/40°C temperature; light or dark conditions).

Esters: Esters are compounds associated with fruity sensory notes (Aparicio & Luna, 2002; Luna et al., 2006). The presence of C6 esters in virgin olive oils contributes to the positive sensory notes "sweet", "fruity" and "green leaf" (Inarejos-Garcia et al., 2010b), however Kenine OO samples showed a low concentration in Z-3-hexenyl acetate (0.27%). This could be due to the fact that the activity of the alcohol acyl transferase involved in the biogeneration of C6 esters is low (Olías, Pérez, Ríos & Sanz, 1993; Ridolfi, Terenziani, Patumi, & Fontanazza, 2002). Except the methyl and ethyl acetate, which were present in all samples, the majority of the

esters were identified only in Isly and Kenine OO at different percentages. Furthermore, Achajara almoubaraka OO was rich in ethers (14.31%) compared to other oils analyzed (Figure 2).

Ketones: C5 ketones such as 2-pentanone, increase during storage (Cavalli et al., 2004), this compound does not result from the lipoxygenase pathway by enzymatic actions, but from homolytic cleavage of 13-hydroperoxides (Angerosa, 2002) to the detriment of C6 aldehyde and alcohol formation. This compound was present in the headspace of the Achajara almoubaraka OO (1.12%).

Hydrocarbons: The hydrocarbon octane (sweet sensory characteristics) is due to autoxidation reactions (Morales et al., 2005; Morales et al., 1997) and it was the marker for storage in the light (Kalua et al., 2006). Low amounts of this compound were found in the headspaces of VOO Isly (0.4%) and Kenine (0.53%). Morales et al. (2005) reported that this volatile with other compounds which are also due to autoxidation reaction, are responsible for virgin olive oil off-flavors.

3.2 Oxidative Stability

Stability to oxidation is an important property of olive oil, VOO is considered to be resistant to oxidation because of its low content of polyunsaturated fatty acids and the presence of natural antioxidants. The oxidative stabilities of the oils were measured as the induction time in response to forced oxidation, and they are shown in (Table 4). Oxidative stability of the VOOs analyzed varied according to the origin. It ranged from a minimum of 38.75-40.58h (Kenine) and 46.05-46.75h (Isly) to a maximum of 50.95-62.55h (Achajara almoubaraka). This difference of oxidative stability between the different VOOs analyzed could be explained by the different amounts of phenolic compounds (Lerma-García, Simó-Alfonso, Bendini, & Cerretani, 2009) and other natural antioxidants.

Compared to Achajara almoubaraka OO, Isly and Kenine OO, had lower stability values, their potential oxidative susceptibility was therefore much higher than Achajara almoubaraka. Table 4 indicates that Isly and Kenine OO showing a higher value for compounds responsible for off-flavor (COF). Aparicio, Roda, Albi & Gutierrez (1999) reported that high values of stability indirectly mean a low level of rancidity and hence low presence of the undesirable sensory descriptors such as rancidity. Nonanal and E-2-decenal are the most frequently used volatile markers of oxidation of virgin olive oil during storage (Bendini et al., 2010). These are characterized by low odour threshold (150 and 100 μg kg-1, respectively) and by negative off-flavours namely oxidized. These compounds were present in Isly and Kenine OO samples at a low amounts (Table 4). We have also noted that the oil having a low value of the oxidative stability (Isly & Kenine) were dominated by carboxylic acids, whereas carboxylic acids dominate the volatile compounds in oils stored in oxygenrich environments, and polymeric volatile compounds are produced at elevated temperatures. These volatile compounds, from oxidation, modify the sensory quality of olive oils (Vichi et al., 2003 a).

Table 4. Rancimat induction periode (hours) at 101°C and amount (%) of volatils compounds reponsible for off-flavor

	OS	Oct	Non	E-2-dec	Und	Σ carb	1-pen	2-met	3-met	Eth	Eth.ac	Σ COF
1	46.05	-	0.57	1.5	0.5	64.83	-	-	0.44	1.88	1.38	71.1
2	46.75	0.4	-	-	0.8	53.65	-	-	0.48	3.35	1.66	60.34
3	50.95	-	-	-	-	0	0.79	1.22	0.99	19.95	9.18	30.91
4	62.55	-	-	-	-	0	0.62	0.48	0.76	21.58	6.82	30.26
5	38.75	0.88	0.26	-	-	47.69	-	-	0.58	17.7	3.87	70.98
6	40.85	0.17	0.05	0.2	-	51.71	-	-	0.41	3.54	0.61	56.69

VOO reference number: VOO Isly: 1, 2; -VOO Achajara almoubaraka: 3, 4; -VOO Kenine: 5, 6.

OS: Oxidative stability; Oct: Octane; Non: Nonanal; Und: Undecenal; carb: carboxilic acids; 1-pen: 1-penten-3-ol; 2-meth: 2-methyl-1-butanol; 3-meth: 3-methyl-1-butanol. Eth: ethanol; eth. ac: ethyl acetate; Σ COF: Sum of the compounds responsible for off-flavor.

4. Conclusion

Analysis of the VOOs produced in the eastern of Morocco by SPME enabled us to identify 84 compounds, represented by different chemical classes. The volatile profiles of Isly and Kenine OO were similar. Most of the volatile compounds consist of carboxylic acids. There are volatile compounds that are formed in oxidized olive oil regardless of the external conditions. These results indicate that the volatile profiles of Isly and Kenine OO were distinctly different from those of Achajara almoubaraka characterized by significantly higher levels in Alcohols. It should be noted that the high concentration volatile compounds are not necessarily the major contributors of odor. For instance, Reiners and Grosch (1998) reported a concentration of 6770 μg/g for trans-2-hexenal with an odor activity value of 16 whereas 1-penten-3-one with a much lower concentration of 26 μg/g had a higher odor activity value of 36. The results of the oxidative stability have also demonstrated a difference between the analyzed VOOs, in fact compared to Achajara almoubaraka OO, Isly and Kenine OO, had lower stability values, and a higher value of COF's sum. However, in the analyzed samples, except carboxylic acids, the amounts of compounds formed from oxidation reactions were low (Table 3). Analysis of volatile compounds by SPME must be completed by a GC / olfactometry to determine the intensity of sensory descriptors for each compound and selected compounds that have a significant odor impact contributing to the aroma of oils olive studied.

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