

RELATIONSHIP BETWEEN VOLATILE COMPOUNDS OF OLIVE OIL AND SENSORY ATTRIBUTES

Shaker M. Arafat, Azza A. Ahmed

*Oils & Fats Department, Food Technology Research Institute, Agriculture Research Centre. Giza, Egypt.
e-mail: dr_shakerarafat@yahoo.com*

Abstract. This study was carried out to study some quality indices (acid value, peroxide value and UV absorption K_{232nm} , K_{270nm} and ΔK) of virgin olive oil of three varieties (Coratina, Koronakii and Picual) at two stages of ripening. Also, organoleptic tests phenolic content, α -tocopherol and oxidative stability measured by Rancimat method at 100°C were determined. Fatty acid composition and volatile compounds of virgin olive oil samples were analyzed by gas chromatography (GC) and gas chromatography mass spectrum (GC-MS) system. Twenty-five compounds were isolated and characterized by GC-MS. The presence of some of these compounds in virgin olive oil had not been previously reported. All results indicated that there was a wide variability in the chemical and aroma characteristics of the selected virgin olive oils.

Key words: Olive oil, volatile compounds, quality indices, stability.

Introduction

Virgin olive oil represents the main fats in the countries of the Mediterranean basin where the olive oil production is concentrated. Nowadays, there are some studies [LUNA *et al.*, 2005] indicated the beneficial effects on the health of the so called "Mediterranean diet" found on the consumption of great amounts of vegetables, cereals, fish and olive oil. The cultivation of the olive trees is spreading in countries where the virgin olive oil consumption is very modest like Australia, Argentina and South Africa [ANGEROSA *et al.*, 1999]. But another reason, owing to the increasing demand for olive oils of high quality, seems to be related to the increased popularity of this commodity, in addition to its health properties [ANGEROSA *et al.*, 2004]. It is represented by its peculiar sensory characteristics that, because of use of virgin olive oil as a seasoning of cooked and especially raw foods have great repercussions on their acceptability [BACCOURI *et al.*, 2007].

The distinctive aroma of virgin olive oil is attributed to a large number of chemical compounds of different chemical classes, i.e. aldehydes, alcohols, esters, hydrocarbons, ketones and probably, to other unidentified volatile compounds [VICHI *et al.*, 2003 & KALUA *et al.*, 2007]. The volatile composition of virgin olive oil depends on the levels and activities of the enzymes involved in the various pathways [ANGEROSA, 2002] which are genetically determined [CAMPEOL *et al.*, 2001]. The pathway starts with the production of 9 and 13 hydroperoxides of linoleic and linolenic acids

mediated by lipoxygenase. The subsequent cleavage of 13-Hydroperoxides of catalyzed by very specific hydroperoxidelyases and leads to C₆ aldehydes, whose unsaturated ones can isomerizes from cis-3 to the more stable trans-2 from. The mediation of alcohol dehydrogenase reduces C₆ aldehydes to corresponding alcohols, which can produce esters because of the catalytic activity of alcohol acetyl transferase [ANGEROSA *et al.* 2004]. But an additional branch of the lipoxygenase pathway is active when the substrate is linolenic acid [ANGEROSA *et al.*, 2000]. Lipoxygenase would catalyze besides the hydroperoxides formation, also its cleavage via an alkoxy radical giving rise to the formation of stabilized 1, 3-pentene radicals.

These last can dimerize leading to C₁₀ hydrocarbons (known as pentene dimmers) or couple with a hydroxy radical present in the medium producing C₅ alcohols, which can be enzymatically oxidized to corresponding C₅ carbonyl compounds [ANGEROSA *et al.*, 1999].

A recent investigation pointed out that olive seeds contain enzymatic activities metabolizing 13-Hydroperoxides other than hydroperoxidelyase that are responsible for a decrease in the content of C₆ unsaturated aldehydes during the olive oil extraction [ANGEROSA *et al.*, 2002].

The other accumulation products come from possible fermentations or conversion of some amino acids or from enzymatic activities of moulds or finally from oxidative processes but are generally related to the off-flavour of virgin olive oil [ANGEROSA



et al., 1998]. Other factors that influence the volatile are ripening cycle of the fruits [APARICIO *et al.*, 1998] and the processing equipment [ANGEROSA *et al.*, 2001]. The effects of climate and soil type have also been studied [COSIO *et al.*, 2006].

Many studies have been carried out in order to characterize the composition of the aroma of some olive oils [HADDADA *et al.*, 2007]. The aim of this work was to investigate the influence of ripening degree of olive fruits on aroma composition of olive oil by GC-MS and quality indices (acid value, peroxide value, UV absorption K_{232nm} , K_{270nm} and ΔK).

Also determination of organoleptic testes, phenolic content, α -tocopherol, oxidative stability measured by Rancimat method and fatty acids composition by gas chromatography.

Material and methods

- **Source of olive fruits:** Three varieties of olive fruits, i.e. Coratina, Koronakii and Picual were obtained from a private farm at El-Khtatba, Giza Governorate, Egypt. All varieties were collected by hand at the mid. of October and November during the crop season 2010. Only healthy fruits, without any kind of infection or physical damage were processed.
- **Reagents, solvents and standards:** All solvents in this study were purified and distilled before use. Folin-Ciocalteu reagent was obtained from Gerbsaure Chemical Co. Ltd., Germany. α -tocopherol and gallic acid standards were obtained from Koch Light Laboratories Ltd. England.
- **Oil extraction:** After harvest, fresh olives (1.5–2.0 kg) were washed and deleafed, crushed with mill and pressed using hydraulic laboratory (Carver) press. Oil produced from each extraction was 200–250 (ml/kg), filtered and then transferred into dark glass bottles and stored in the dark at 4°C until analysis.
- **Quality parameters:** Acidity, peroxide value and UV absorption characteristics, K_{232nm} (conjugated dienes) and K_{270nm} (conjugated trienes) and ΔK were carried out following the analytical methods described by A.O.A.C. [A.O.A.C. 2005].
- **Oil stability:** Oxidative stability was evaluated by the Rancimat method [GUTIERREZ, 1989]. Stability was expressed as the oxidation induction time (h), measured with

the Rancimat 679 apparatus (Metrohm Co., Herisou, Switzerland), using an oil sample of 5.00 g heated to $100^{\circ}\text{C}\pm 2^{\circ}\text{C}$ with an air flow of 20 l/hr^{-1} .

- **Total phenolic content:** Total phenol content was calorimetrically quantified [RANALLI *et al.*, 1999]. Phenolic compounds were isolated by triple extraction of a solution of oil (10 g) in hexane (20 ml) with 30 ml of a methanol–water mixture (60:40, v/v). The Folin-Ciocalteu reagent was added to a suitable aliquot of the combined extracts, and the absorption of the solution at 725nm was measured. Values are given as milligrams of gallic acid per kilogram of oil [GÜTFINGER, 1991].
- **α -tocopherol content:** α -tocopherol was estimated by HPLC with direct injection of an oil-in-hexane solution: 1.5 ± 0.01 g of oil dissolved in hexane to 10 ml [SALAS *et al.*, 2000]. The volume of injection was 20 μl . The mobile phase consisted of hexane / ethyl acetate (70:30) at a flow rate of 1 ml/min α -tocopherol was quantified by the external standard method. Results are given as milligrams of α -tocopherol per kilogram oil.
- **Fatty acids composition:** The fatty acid methyl esters were prepared as described in the International Olive Oil Council [IOOC, 2009]. Methyl esters were prepared from olive oil, after saponification and analyzed by gas chromatography (Pye-Unicam model 104) equipped with flame ionization detector and glass coiled column (1.6 X 4 mm) supported on Chromosorb W-AW 100–200 mesh, was used. The samples (μl) were injected into the column using a Hamilton microsyringe. The gas chromatographic conditions for isothermal analysis were: temperatures: column 170°C detector 300°C and injector 250°C , flow rate: hydrogen 33 ml/min., nitrogen 30 ml/min and air 330 ml/min. Peak areas were measured using a spectra physics chronjet integrator according to the method of Farag [FARAG *et al.*, 1984].
- **Organoleptic test:** The organoleptic test was determined for the extracted oil according to the International Olive Oil Council [IOOC, 2009]. The oil samples (15 ml) were presented in covered blue glasses (diameter, 70 mm, capacity, 130 ml) at



28°C±2°C. The glass warmed and after removing the cover, the samples were smelled and then tested by the panelist to judge its flavour. The different attributes of the oils were assessed and their intensities were evaluated as a mean value of the panelists score.

Analysis of volatile compounds:

A-Extraction: About (100g) of olive oil was placed in a distillation flask with a little amount of distilled water. Steam was allowed to pass for four hours. The distillate was collected in an ice-cooled receiver, saturated with sodium chloride and extracted for several times with pure ether. The extract was kept at -10°C until analysis by GC-MS.

B- Identification: A GC Varian 240-MS equipped with a 1078 split/ splitless injector coupled with a mass spectrometer Varian Saturn 3 was used. A fused-silica capillary column VF-5MS, 30 m X 0.25 mm i.d., 1µm film thickness was employed. Helium Was used as a mobile phase at a pressure of 15 psi with a flow rate of 2.2 ml/ min and a linear velocity of 30.7 cm/s at 35°C. The GC oven heating was started at 35°C. This temperature was maintained for 8 min. then increased to 45°C at rate of 1.5°C/ min, increased to 150°C at a rate of 3°C/ min. there increased to 180°C at rate of 4°C/ min, and finally increased to 210°C at a rate 3.6°C/ min. and maintained at temperature for 14.5°C/ min: the total time of analysis was 80 min. The injector temperature was maintained at 250°C. The temperature of the transfer line was fixed at 220°C. The mass spectrometer was operated in the electron ionization mode at an ionization voltage of 70 eV in the mass range of 10-350 amu at a scan rate of 1s/ scan and a manifold temperature of 180°C. The GC-MS was

operated through the software Saturn GC-MS version 5.2 (Varian). The volatile compounds were identified by comparison of their mass spectra and retention times with those of authentic reference compounds. When standards were not available, identification of the volatile compounds was obtained by comparing their mass spectral data with those of the NIST-92 library. Integration of all of the chromatographic peaks was performed choosing the three masses [SERPVILI *et al.*, 2003].

Statistical analysis: The results are reported as the mean values. Data were compared on the basis of standard deviation of the mean values. In addition, Duncan's multiple range tests were used to determine significant differences among data. Statistical analysis was performed using the Statistical 5.00 Package (Stat Soft 97 edition).

Results and discussion

Chemical composition of olive fruits:

Table 1 shows the chemical composition of Coratina, Koronakii and Picual olive fruits during two stages of ripening. All varieties contained more than 50% moisture and 12% ash.

Crude proteins and carbohydrates were present in equal proportions. The crude fiber level was about twice that of proteins and carbohydrates.

The oil content of olive fruits (Coratina, Koronakii and Picual) during mid. October was lower than that mid. of November.

The chemical compositions of both cultivars were in accordance with the chemical composition reported by Raina and Basuny [RAINA *et al.*, 1986, BASUNY *et al.*, 2004].

Table 1.

Chemical composition (% on dry basis) of three investigated olive fruits harvest at two repining stags

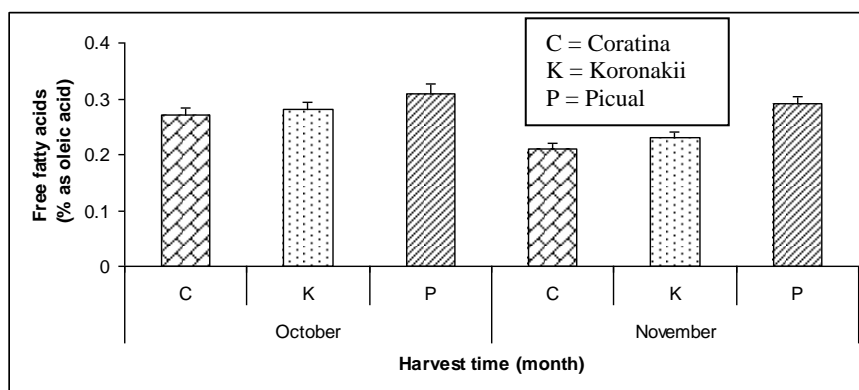
Constituents	Coratina		Coronakii		Picual	
	Harvest months					
	Mid. October	Mid. November	Mid. October	Mid. November	Mid. October	Mid. November
Moisture	60.32±5.00	54.60±3.90	57.93±4.01	55.40±4.15	62.53±6.11	57.60±4.22
Crude oil	41.03±3.25	47.71±4.72	38.86±3.02	43.92±4.10	36.43±2.95	40.28±3.15
Crude proteins	10.90±1.10	9.32±1.00	11.33±2.15	10.62±1.55	11.31±1.90	10.61±1.33
Crude fibers	18.15±2.50	15.22±2.01	21.75±3.00	19.82±2.90	20.10±3.02	18.40±2.80
Ash	12.84±1.60	12.45±1.22	13.54±1.78	13.30±1.53	13.80±2.10	13.67±3.02
Total hydrolysable carbohydrate	17.08±2.00	15.30±1.90	19.52±2.33	12.31±2.15	18.36±2.80	17.04±2.50

Results are the means of three replications ± SD.



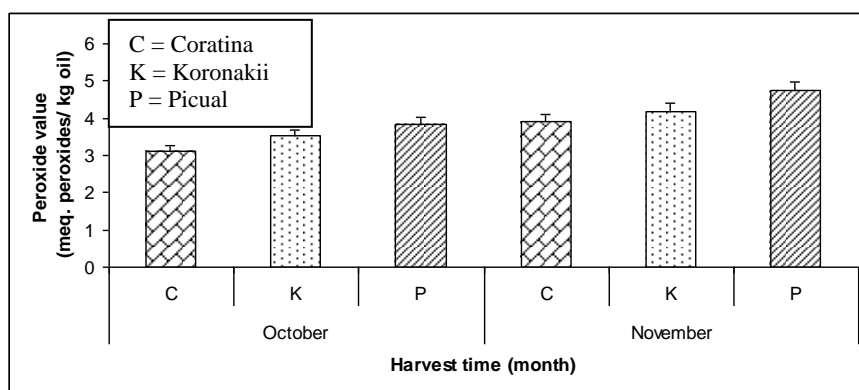
Quality indices: some physico-chemical characteristics of olive oil samples of the three varieties (Coratina, Koronakii and Picual) during two stages of ripening (mid-October and November) were analysed. [Figures 1, 2, 3, 4](#) and [5](#) show very low values for the classical physico-chemical parameters

(acidity ≤ 0.80 ; peroxide value ≤ 20.00 meq.O₂/kg; K₂₃₂ ≤ 2.50 ; K₂₇₀ ≤ 0.22 and $\Delta K \leq 0.01$) and the values were falling within the "extra virgin" category, as stated by Regulation International Olive Oil Council [IOOC, 2009].



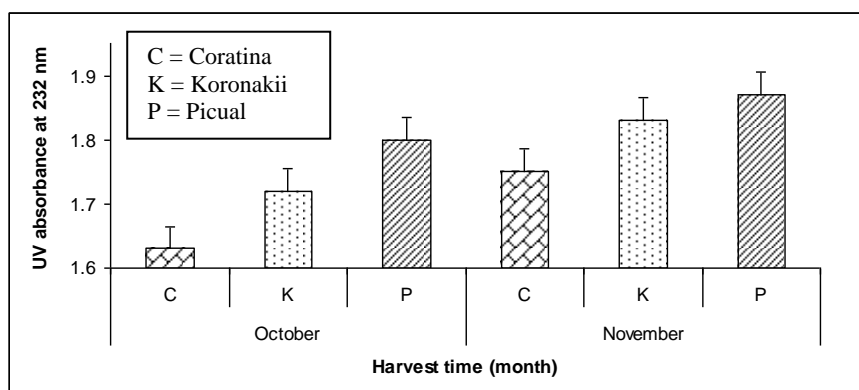
Results are the means of three replications \pm SD.

Figure 1. Effect of ripening stages on the free fatty acids (% as oleic acid) of virgin olive oil extracted from Coratina, Koronakii and Picual varieties.



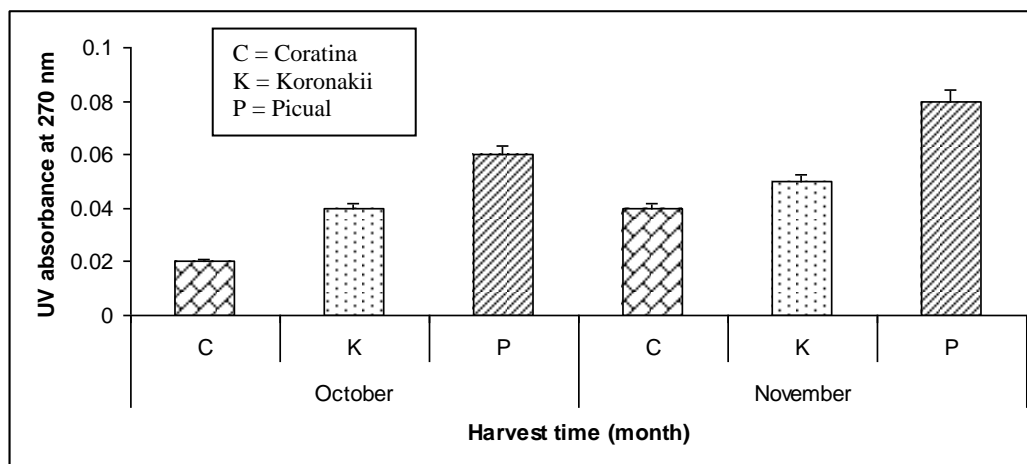
Results are the means of three replications \pm SD.

Figure 2. Effect of ripening stages on the peroxide value (meq. peroxides/kg oil) of virgin olive oil extracted from Coratina, Koronakii and Picual varieties.



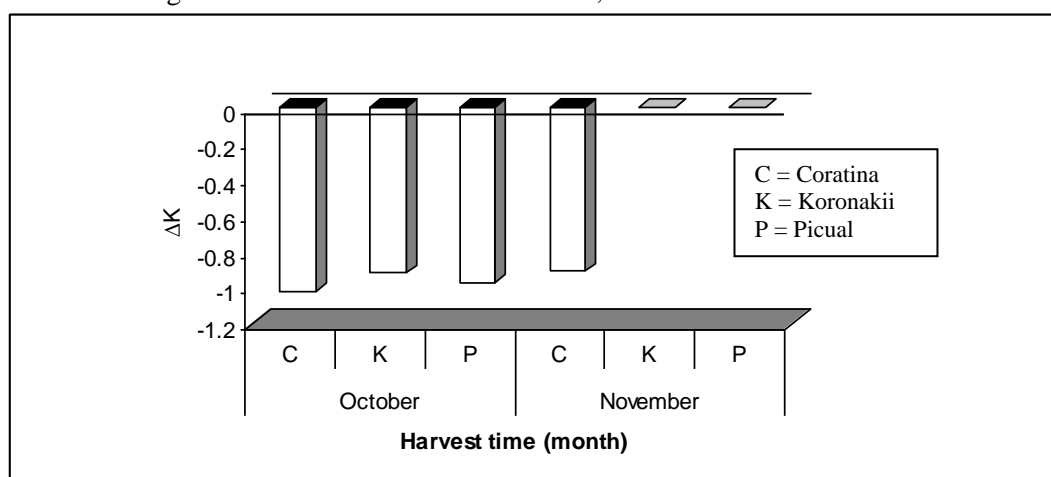
Results are the means of three replications \pm SD.

Figure 3. Effect of ripening stages on the conjugated diene formation (UV absorbance at 232 nm) of virgin olive oil extracted from Coratina, Koronakii and Picual varieties.



Results are the means of three replications \pm SD.

Figure 4. Effect of ripening stages on the conjugated triene formation (UV absorbance at 270 nm) of virgin olive oil extracted from Coratina, Koronakii and Picual varieties.



Results are the means of three replications \pm SD.

Figure 5. Effect of ripening stages on the Δk refractive index of virgin olive oil extracted from Coratina, Koronakii and Picual varieties.

Fatty acid composition: The distribution of fatty acids, from all olive oil samples extracted from Coratina, Koronakii and Picual fruits during two ripening stages covered the normal composition range expected for olive oil (Table 2).

Oleic acid is the main monounsaturated fatty acid, representing high concentrations (59.17–67.66%) according to varieties. Palmitic acid, the major saturated fatty acid, ranged between 14.83% and 19.67%, whereas linoleic acid was dominant polyunsaturated fatty acids ranging from 11.68% and 13.95% (Table 2).

Variations in fatty acids contents observed in olive oil samples obtained from

all varieties are probably related to cultivar–environmental interaction during the development and the maturity of the fruits [LAVEE & WODNER, 1995].

The results of the present study are in agreement with the finding of other authors [BRUNI *et al.*, 1994, SCHIRATTI, 1999].

It was observed that olive oil products during mid. October was rich in total USFA, essentially due to its higher content in oleic acid, while, mid. November was rich in total SFA due to its high content in palmitic acid.

These values are similar to those reported by some authors for other olive oil varieties [BEN TEMIME *et al.*, 2006 & KRICHENE *et al.*, 2007].



Table 2. Fatty acid composition of virgin olive oil extracted from Coratina, Koronakii and Picual varieties.

Name of fatty acids	Variety					
	Coratina		Koronakii		Picual	
	Mid. October	Mid. November	Mid. October	Mid. November	Mid. October	Mid. November
C16:0	15.01±1.50	16.40±1.80	14.73±1.22	16.78±1.91	18.57±2.00	19.67±2.13
C16:1	0.82±0.01	1.57±0.15	1.38±0.10	1.85±0.20	1.82±0.20	2.49±0.25
C17:0	0.03±0.001	0.08±0.001	0.05±0.001	0.08±0.001	0.09±0.001	0.00±0.00
C17:1	0.06±0.01	0.11±0.01	0.08±0.01	0.12±0.01	0.12±0.01	0.13±0.01
C18:0	1.84±0.20	2.42±0.35	2.56±0.40	2.21±0.25	3.61±0.50	2.85±0.56
C18:1	66.65±5.50	64.40±5.20	67.66±5.77	64.12±5.13	62.05±4.88	59.17±3.90
C18:2	12.89±2.10	12.56±2.00	11.68±1.95	12.89±2.11	12.31±1.89	13.95±2.33
C18:3	0.87±0.10	0.95±0.10	0.70±0.10	0.94±0.10	0.81±0.10	0.91±0.10
C20:0	0.44±0.01	0.42±0.01	0.42±0.01	0.41±0.01	0.45±0.01	0.33±0.01
C20:1	0.48±0.01	0.37±0.01	0.27±0.01	0.00±0.00	0.23±0.01	0.17±0.01
C22:0	0.11±0.001	0.12±0.001	0.10±0.001	0.11±0.001	0.00±0.00	0.00±0.00
C24:0	0.59±0.01	0.60±0.01	0.37±0.01	0.49±0.01	0.00±0.00	0.00±0.00
Monounsaturated	68.01±6.50	66.45±5.90	69.39±6.71	66.09±5.81	64.20±5.50	61.96±4.91
Poly unsaturated	13.76±2.50	13.51±2.30	12.38±2.00	13.83±2.66	13.12±2.15	14.86±3.00
Total saturated	18.23±3.10	20.04±3.22	18.23±3.00	20.08±3.30	22.72±3.50	23.18±3.60
Total unsaturated	81.77±8.00	79.96±7.90	81.77±8.00	79.92±7.80	77.32±7.22	76.82±6.90

Results are the means of three replications ± SD.

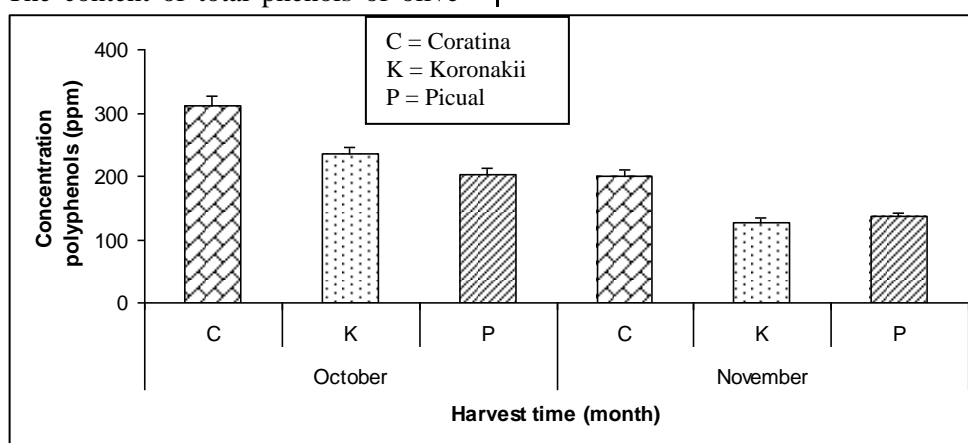
Total phenolic content: Olive oil is the only vegetable oil which contains remarkable amounts of phenolic compounds (which were represented basically by ortho-diphenols) acting as antioxidant substances and conferring to it a greater stability against oxidation during storage [BENDINI *et al.*, 2007].

The content of total phenols of olive

oils extracted from all varieties during mid.

October showed the highest values in phenols with, 311.40, 235.00 and 202.30mg/kg, respectively, whereas, mid.

November recorded the lowest ones with 199.00, 127.30 and 135.60 mg/kg, respectively (Figure 6).



Results are the means of three replications ± SD.

Figure 6. Effect of ripening stages on the polyphenol content (ppm) of virgin olive oil extracted from Coratina, Koronakii and Picual varieties.

α -tocopherol content: Figure 7 shows the main components that are related to oil stability. The tocopherol content of virgin olive oil is important factor to protect lipids

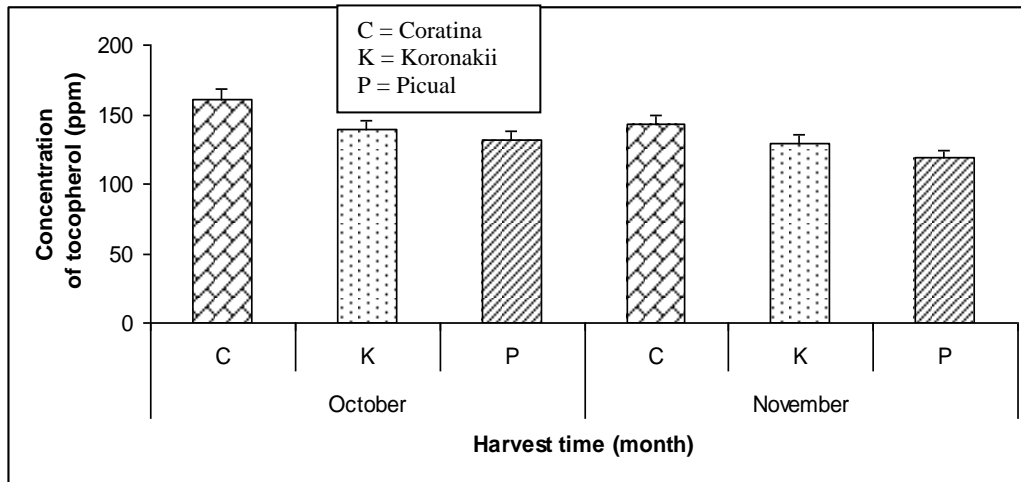
against autoxidation and, thereby, to increase its storage life. The range of α -tocopherol contents in virgin olive oil of the olive varieties (Coratina, Koronakii and Picual) was



between 118.90 to 160.60 mg/kg. There were differences in the α -tocopherol content between the harvest periods. Oils from the

mid. November contained lower α -tocopherol than oils extracted during mid.

October of the all varieties (Figure 7).



Results are the means of three replications \pm SD.

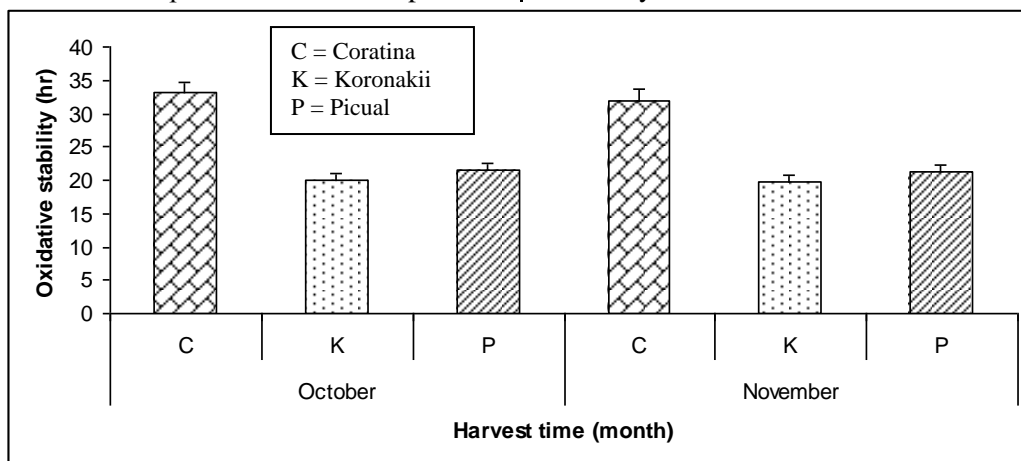
Figure 7. Effect of ripening stages on the total tocopherol content (ppm) of virgin olive oil extracted from Coratina, Koronakii and Picual

Oxidative stability: Stability to oxidation is an important property of olive oil which is improved by synergistic interactions between the various antioxidants present in the oil itself, and also depends on the lipid composition.

Oxidative stability of the olive oils showed the same trend in relation to harvest period as the total phenol and α -tocopherol

contents of the oil differences were between the stability of virgin olive oils from the different harvesting time.

The higher stability of olive oil in the first harvest period (mid. October) than the second harvest period (mid. November) this fact could be explained by a degradation of phenolic compounds, mainly implicated in oil stability [GUTIERREZ *et al.*, 2001].



Results are the means of three replications \pm SD.

Figure 8. Effect of ripening stages on the oxidative stability (hr) of virgin olive oil extracted from Coratina, Koronakii and Picual varieties.

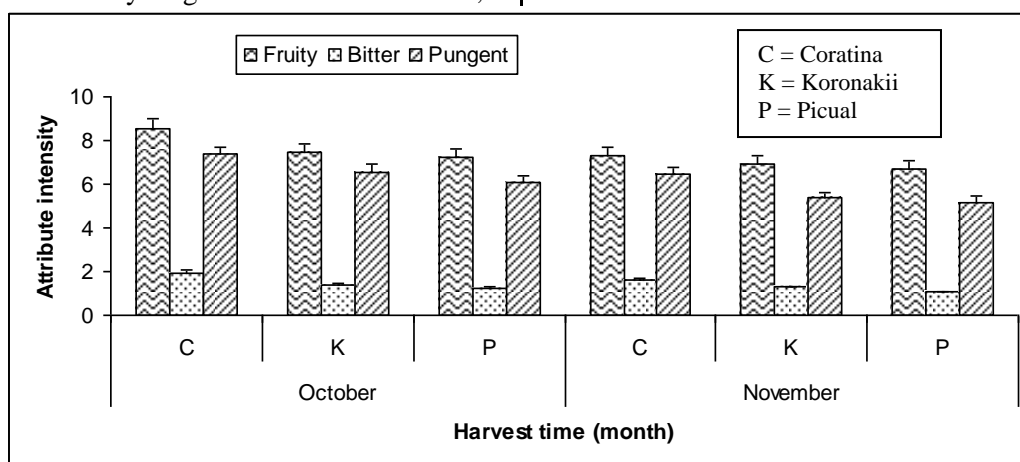
Organoleptic test: Organoleptic test of olive oil samples extracted from Coratina, Koronakii and Picual varieties during two ripening stages (mid. October and November) were evaluated by 10 panelists (Figure 9).

From a sensory point of view all the samples examined are belong to the extra virgin olive oil grade.

The direct observation of the intensities of attributes detected by tasters



showed that the oils studied were mainly characterized by high intensities of bitter, pungent, fruity.



Results are the means of three replications \pm SD.

Figure 9. Effect of ripening stages on the Sensory characteristics of virgin olive oil extracted from Coratina, Koronakii and Picual varieties.

Volatile compounds: Flavour is an important quality criterion for virgin olive oils. The identification of the compounds causing the flavour or off-flavour is therefore

the key for quality control. Virgin olive oil has delicate and unique flavour [LANGROSA *et al.*, 2000].

Table 3.

Volatile components (%) of virgin olive oil extracted from Coratina, Koronakii and Picual varieties.

No.	Volatile components	R.T	Variety					
			Coratina		Koronakii		Picual	
			Mid. October	Mid. November	Mid. October	Mid. November	Mid. October	Mid. November
1	3-Methyl-butanol	3.056	3.20 \pm 1.00	7.50 \pm 2.50	0.40 \pm 0.01	0.50 \pm 0.01	0.50 \pm 0.01	1.00 \pm 0.10
2	Pentan-3-one	3.644	5.30 \pm 1.13	3.70 \pm 1.00	5.70 \pm 1.50	4.90 \pm 1.30	1.50 \pm 0.10	4.00 \pm 1.15
3	2-Methyl butanal	4.233	3.00 \pm 1.00	2.56 \pm 0.90	0.37 \pm 0.01	0.40 \pm 0.01	0.53 \pm 0.01	0.33 \pm 0.01
4	1-Penten-3-one	4.345	14.50 \pm 3.00	8.30 \pm 2.20	2.50 \pm 0.95	1.20 \pm 0.10	5.60 \pm 1.52	5.00 \pm 1.50
5	Unknown	4.541	2.20 \pm 0.85	3.20 \pm 1.00	2.50 \pm 0.90	3.00 \pm 1.01	4.50 \pm 1.15	2.70 \pm 0.85
6	Unknown	4.849	2.00 \pm 0.70	2.15 \pm 0.72	8.50 \pm 2.35	8.00 \pm 2.00	3.10 \pm 1.00	2.66 \pm 0.95
7	Butyl acetate	7.035	5.50 \pm 1.30	5.10 \pm 1.15	7.25 \pm 2.40	7.00 \pm 2.00	5.90 \pm 1.53	4.70 \pm 1.00
8	Hexanal	10.790	1.20 \pm 0.10	2.30 \pm 0.70	0.95 \pm 0.10	1.00 \pm 0.10	3.10 \pm 1.00	5.90 \pm 1.55
9	E-2-Methyl-2-butenal	13.199	7.10 \pm 2.10	6.10 \pm 1.90	9.10 \pm 2.50	4.50 \pm 1.33	3.00 \pm 1.00	6.00 \pm 1.57
10	Ethylbenzene	14.404	14.50 \pm 3.50	12.70 \pm 2.90	12.50 \pm 2.81	7.90 \pm 2.00	4.90 \pm 1.77	4.00 \pm 1.183
11	2-Methyl-butyl acetate	22.698	1.40 \pm 0.20	2.30 \pm 0.80	1.80 \pm 0.51	2.00 \pm 0.50	5.80 \pm 1.50	3.70 \pm 1.00
12	Z-3-Hexenal	23.007	1.05 \pm 0.10	1.41 \pm 0.15	2.30 \pm 0.66	3.00 \pm 0.79	2.50 \pm 0.95	3.00 \pm 1.13
13	Z-3-Hexenal	31.049	0.43 \pm 0.10	0.55 \pm 0.10	0.75 \pm 0.10	0.90 \pm 0.15	2.50 \pm 0.88	1.80 \pm 0.55
14	E-2-Hexenal	37.830	8.40 \pm 2.50	9.60 \pm 2.80	9.50 \pm 2.77	8.40 \pm 2.40	14.50 \pm 3.22	10.30 \pm 2.90
15	Trans-2-Hexen-1-ol	44.527	6.10 \pm 1.80	5.50 \pm 1.50	4.50 \pm 1.30	3.80 \pm 1.15	3.00 \pm 1.01	1.90 \pm 0.80
16	Pentan-1-ol	49.515	3.40 \pm 1.15	0.95 \pm 0.15	1.10 \pm 0.20	2.90 \pm 0.71	2.50 \pm 0.66	8.00 \pm 2.30
17	Unknown	54.390	2.95 \pm 0.80	1.50 \pm 0.30	2.01 \pm 0.71	2.50 \pm 0.83	3.10 \pm 1.00	1.00 \pm 0.15
18	3-Methyl-2-butenylacetate	54.698	1.15 \pm 0.20	5.60 \pm 1.30	1.40 \pm 0.35	3.90 \pm 1.11	3.80 \pm 1.00	4.10 \pm 1.37
19	Hexyl acetate	57.809	1.10 \pm 0.12	2.50 \pm 0.83	1.90 \pm 0.66	2.10 \pm 0.70	2.30 \pm 0.75	5.30 \pm 1.60
20	E-2-Octenal	64.870	1.35 \pm 0.20	1.60 \pm 0.25	9.20 \pm 2.50	8.90 \pm 2.30	1.90 \pm 0.50	1.80 \pm 0.44
21	6-Methyl-5-hepten-2-one	67.252	1.70 \pm 0.20	1.50 \pm 0.15	1.00 \pm 0.10	0.85 \pm 0.01	7.80 \pm 2.50	3.80 \pm 1.31
22	Hexan-1-ol	68.204	2.15 \pm 0.70	2.20 \pm 0.63	4.30 \pm 1.15	4.25 \pm 1.11	2.30 \pm 0.88	6.90 \pm 2.15
23	Nonan-2-one	70.642	4.05 \pm 1.00	1.60 \pm 0.30	4.30 \pm 1.20	2.60 \pm 0.70	4.00 \pm 1.01	3.00 \pm 0.95
24	Unknown	71.345	2.46 \pm 0.70	2.66 \pm 0.85	3.45 \pm 1.00	3.44 \pm 1.00	2.33 \pm 0.90	2.38 \pm 0.95
25	Z-2-Hexen-1-ol	73.751	4.50 \pm 1.18	8.60 \pm 2.32	5.20 \pm 1.50	9.00 \pm 2.70	7.50 \pm 2.11	4.50 \pm 1.15

Results are the means of three replications \pm SD.

All the identified volatiles are listed in Table 3. Twenty-five compounds have been

characterized by GC-MS analysis. The major constituents of the volatile fraction of

Coratina oil in the first harvest (mid. October) were 1-penten-3-one (14.50%), ethylbenzene (13.50%), E-2-hexenal (8.40%), E-2-methyl-2-butenal (7.10%), trans-2-hexen-1-ol (6.10%), butylacetate (5.50%) and pentan-3-one (5.30%) (*Table 3*).

The volatile fractions of Koronakii oil (mid. October) were ethylbenzene (12.50%), E-2-hexenal (9.50%), E-2-octenal (9.20%), E-2-methyl-2-butenal (9.10%), butylacetate (7.25%), pentan-3-one (5.70%) and Z-2-hexen-1-ol (5.20%) (*Table 3*).

The main constituents of that characterized volatile fraction of Picual oil (mid. October) were E-2-Hexenal (14.50%), 6-Methyl-5-hepten-3-one (7.80%), Z-2-hexen-1-ol (7.50%), butyl acetate (5.90%), 2-methyl-1-butylacetate (5.80%), 1-penten-3-one (5.60%) and ethylbenzene (4.90%) (*Table 3*). These results indicated that there were quantitative differences between the

volatile profiles of the varieties analyzed (Coratina, Koronakii and Picual), the present results are in agreement with the other studies such as Youssef [YOUSSEF *et al.*, 2011], Luna and Baccouri [LUNA *et al.*, 2006, BACCOURI *et al.*, 2007].

Finally, results showed that there were quantitative significant ($P \geq 0.05$) difference during the olive ripeness (mid. October and November) the amount of volatile compounds in all varieties [ANGROSA *et al.*, 2004].

The role of volatile compounds in the sensory quality of virgin olive oils: *Table 4* shows the sensory characterization of the volatile compounds with the exception of a few that were mostly hydrocarbons.

Although a consensus was held on the sensory descriptors, the assessors were suggested to limit description of the sensory perceptions to the attributes defined by the International Olive Oil Council [IOOC, 1987].

Table 4.

Relationship between volatile components and sensory characteristics

No.	Volatile components	Sensory characteristics
1	3-Methyl-butanol	Fruity, sweet
2	Pentan-3-one	Fruity
3	2-Methyl butanal	Sweet
4	1-Penten-3-one	Pungent
5	Unknown	--
6	Unknown	--
7	Butyl acetate	Green, fruity, pungent
8	Hexanal	Green, grass
9	E-2-Methyl-2-butenal	Green fruit, aromatic
10	Ethylbenzene	Strong
11	2-Methyl-butyl acetate	Fruity, green,
12	Z-3-Hexenal	Green leaves, cut grass
13	Z-2-Hexenal	Fruity
14	E-2-Hexenal	Fruity, aromatic, cutgrass
15	Trans-2-Hexen-1-ol	Bitter almonds green-fruity
16	Pentan-1-ol	Pungent, strong
17	Unknown	--
18	3-Methyl-2-butenylacetate	Pungent
19	Hexyl acetate	Sweet, green, fruit
20	E-2-Octenal	Green, grassy
21	6-Methyl-5-hepten-2-one	Green, grassy, fruity, pungent
22	Hexan-1-ol	Fruity, aromatic
23	Nonan-2-one	Pungent, fruity
24	Unknown	--
25	Z-2-Hexen-1ol	Almond, grass

Results presented in the *Table 3*, it was found that the compound (1-penten-3-one and ethylbenzene) is the compounds, which distinguishes the olive oil (Coratina variety). On the other side, it was found that the compounds (e-2-methyl-2-butanol and

ethylbenzene) are characterized by the presence of olive oil (Koronakii variety).

Also found that the olive oil (Picual variety) is characterized by the presence of compound (E-2-hexenal) and the rate of the different of ripening stages.



From this we can deduce that each class of varieties of olive oils, oil is characterized by the presence of volatile compounds different from the other varieties.

Given the results presented in *Table 3* and *Table 4* we find that the variety (Coratina) gave the highest values in the organoleptic properties (Fruity, bitter and pungent) on the other varieties and found that the variety (Coratina) is characterized by the presence of compounds (1-penten-3-one, ethylbenzene) in the two ripening stages.

These compounds are directly related to an increase of concentration of the desired intensity of sensory attributes (fruity, bitter and pungent) *Figure 9*.

While characterized by the rest of the varieties under study, other compounds in different concentration (*Table 3*). From the above we can say that there is a direct relationship between volatile compounds and sensory properties of varieties of olive oil.

Conclusion

In conclusion, the results confirm that there is a great variation in all of the measured characters among the olive varieties. All these results indicate that olive oil aroma compounds accumulate differently according to the cultivar. In fact, accumulation of these metabolites has a close dependence on the enzymatic store, which is genetically determined, according to results of other researches [ANGROSA *et al.*, 1999].

References

1. Angrosa, F.; Mostallino, R.; Basti, C. & Vito, R. (1998): Biogenesis of volatile compounds in virgin olive oil: Their evaluation in relation to malaxation time. *Journal of Agriculture and Food Chemistry*, 46: 2940–2944.
2. Angrosa, F.; Basti, C. & Vito, R. (1999): Virgin olive oil. Volatile compounds from lipoxygenase pathway and characterization of some Italian cultivars. *Journal of Agricultural and Food Chemistry*, 47: 836–839.
3. Angrosa, F. (2002): Influence of volatile compounds on virgin olive oil quality evaluated by analytical approaches and sensor panels. *European Journal of Lipid Science and Technology*. 104: 639–660.
4. Angrosa, F.; Servili, M.; Selvaggini, R.; Taticchi, A.; Esposto, S. & Montedoro, G. F. (2004): Volatile compounds in virgin olive oil: Occurrence and their relationship with the quality. *Journal of Chromatography*, 1054: 17–13.
5. A. C. (2005): Official Methods of Analysis of the Association of Official Analytical Chemists, 16th ed., published by Association of Official Analytical Chemists Arlington, Virginia, USA.
6. Aparicio, R. & Morales, M. T. (1998): Characterization of olive ripeness by green aroma compounds of virgin olive oil. *Journal of Agricultural and Food Chemistry*, 46: 1116–1122.
7. Baccouri, B.; Temime, S.; Campeol, E.; Cioni, P.; Daoud, D. & Zarrouk, M. (2007): Application of solid phase microextraction to the analysis of volatile compounds in virgin olive oils from five new cultivars. *Food Chemistry*, 102: 850–856.
8. Basuny, A. M. & Mostafa, M. D. (2004): Influence on minor components and pigments in the virgin olive oil quality. *Minufiya Journal of Agricultural Research*, 29: 1317–1327.
9. Benndini, A.; Cerratani, L.; Carrasco-pancorbo, A.; Goenez-caravaca, A. M.; Segura-carretero, A. & Fernandez-Gutierrez, A. (2007): Phenolic molecules in virgin olive oils: A survey of their sensory properties, health effects. Antioxidant activity and analytical methods. *Molecules*, 12: 1679–1719.
10. Ben Temime, S. E.; Campeol, E.; Cioni, P. L.; Daoud, D. & Zarrouk, M. (2006): Volatile compounds from chatoui olive oil and variations induced by growing area. *Food Chemistry*, 99: 315–325.
11. Bruni, U.; Cortesi, N. & Fiorino, P. (1994): Influence of agricultural techniques, cultivar and area of origin on characteristics of virgin olive oil and on levels of some of its minor components. *Olivae*, 53: 28–41.
12. Campeol, E.; Flamini, G.; Chericoni, S.; Catalano, S. & Cremonini, R. (2001): Volatile compounds from three Cultivars of *olea europaea* from Italy. *Journal of Agriculture and Food Chemistry*. 49: 5409–5411.
13. Cosio, M. S.; Ballabio, D.; Benedetti, S. & Gigliotti, C. (2006): Geographical origin and authentication of extra virgin olive oils by an electronic nose in combination with artificial neural networks. *Analytica Chimica Acta*, 567: 2002–2210.
14. Farag, R. S.; Abdel Rahim, E. A.; Elsharabasy, A. M.; Hewedy, F. M. & Ragab, A. A. (1984): Biochemical studies on lipids of hen's egg during incubation. *Seifen De-Fette, Wachse*, 100: 63–65.
15. Gutierrez, F. (1989): Determination de la estabilidad oxidativa de aceites de oliva



- virgrnes. Comparacion entre del metodo A. O. M. Y. el metodo Rancimat. *Grasa Y Aceities*, 40: 1–5.
16. Gutierrez, F.; Arnaud, T. & Garrido, A. (2001): Contribution of polyphenols to the oxidation stability of virgin olive oil. *Journal of Science and Food Agriculture*. 81:1–8.
 17. Gutfinger, T. (1981): Polyphenols in olive oils. *Journal of the American Oil Chemists Society*. 58: 966–968.
 18. Haddada, F. M.; Manai, H.; Doud, D.; Fernandez, X.; Culvelier, L. L. & Zarrouk, M. (2007): Volatile compounds from some monovarietal Tunisian virgin olive oils. Comparison with French PDO– *Food Chemistry*. 103: 467–476.
 19. IOOC (1987): International Olive Oil Council, DOC T.20/n.3, Madrid June 18th.
 20. IOOC. (2009): International Olive Oil Council. Trade Standard Applying to Olive Oil and Olive Pomace Oils. COI/T.15/NC no.3/Rev. 4 November.
 21. Lavee, S. & Wodner, M. (1995): The effect of growing region, maturation and fruit handling on oil quality of cv. "Nablei" olives in west Bank Mountains. *Agrmed*. 125: 395–403.
 22. Luna, G.; Morales, M. T. & Apaario, R. (2006): Characterization of 39 varietal virgin olive oils by their volatile compositions. *Food Chemistry*, 98: 243–252.
 23. Kaluo, C. M.; Allen, M. S.; Bedgood, D. R.; Bishop, A. C.; Prenzler, P.D. & Robards. K. (2007): Olive oil volatile compounds, flavour, development and quality: A Critical review. *Food Chemistry*, 100: 273–286.
 24. Krichene, D.; Taamali, W.; Daoud, D.; Salvador, M. D.; Fergapane, G.; Zarrouk, M. (2007): Phenolic compounds, tocopherol and other minor components in virgin olive oils of some Tunisian varieties. *Journal of Food Biochemistry*, 31: 179–194.
 25. Raina, B. C.; Bhata, A.; Katiyer, S. & Gupta, A. (1986): Quality characteristics of promising Himachal olive varieties *Olea europea*. *Journal Food Science and Technology*, 23: 237–239.
 26. Ranalli, A.; De Mattia, G.; Patuni, M. & Proietti, P. (1999): Quality of virgin olive oil as influenced by origin area. *Grasas Y Aceities*, 50: 249–259.
 27. Sales, J. J.; Sanchez, J.; Ramli, A. M.; Manaf, M.; Williams, M. & Harwood, J. L. (2000): Biochemistry of lipid metabolism in olive and other oil fruits. *Progress in Lipid Research*. 39: 151–180.
 28. Schiratti, G. (1999): Presentation de letude sur l influence des bariables environnementales. Agronomiques t technologiques sur les caracteristiques et les niveaux des composants majeurs de lhuile dolive extra vierge. *Olivae*, 59: 29–227.
 29. Servili, M. Selvaggini, R.; Taticchi, A.; Esposto, S. & Montedoro, G. (2003): Volatile compounds and phenolic composition of virgin olive oil: Optimization of temperature and time of exposure of olive pastes to air contact during the mechanical extraction process. *Journal of Agricultural Food Chemistry*, 51: 7980–7988.
 30. Vichis, S.; Castellote, A. I.; Pizzale, L.; Conte, L. S.; Buxaderas, S. & Lopez–Tamames, E. (2003): Analysis of virgin olive oil volatile compounds by headspace solid–phase microextraction coupled to gas chromatography with mass spectrometric and flame ionization detection. *Journal of Chromatography*, 983: 19–33.
 31. Youssef, O.; Guido, F.; Manel. I.; Yuossef, N.; Luigi, C.; Mohamed, H.; Daoud, D. & Mohhtar, Z. (2011): Volatile compounds and compositional quality of virgin olive oil from Questati varieti: Influence of geographical origin. *Food Chemistry*, 124: 1770–1776.

Received: August 1, 2011

Accepted: September 26, 2011

