Original scientific paper
UDC 665.327.3(496.5)

PHYSICAL AND CHEMICAL CHARACTERISTICS OF OLIVE OILS FROM AUTOCHTHONOUS ALBANIAN OLIVE VARIETIES

Marinela Muço[1*], Anila Kopali[2], Lumturi Xhelilaj Muço[3]

[1]Faculty of Technical Science, University of Vlora, Hajredin Haxhiraj 1, 9400 Vlora, Albania
[2]Faculty of Biotechnology and Food, Agricultural University of Tirana, Myslym Shyri 60, 1001 Tirana, Albania
[3]Center of Agricultural Technology Transfer, Lef Sallata 3, 9401 Vlora, Albania

[*]e-mail: marinela.muco@gmail.com

Abstract

The purpose of this study was to evaluate the physical and chemical characteristics of olive oils from some autochthonous Albanian olive varieties and allowed us to identify and classify the oils.

The studied samples which were collected from autochthonous Albanian olive varieties, specific to the region of Vlora, Berati, Elbasan, Tirana, were examined for physical and chemical properties (acidity, pH, peroxide values, saponification number, iodine value, ultraviolet spectrophotometric analysis (k232 and k270), refractive index), fatty acids composition and total phenol content. Olive oil was analyzed by GC gas-chromatography for fatty acids commonly present in olive oils which are: palmitic, palmitoleic, stearic, oleic, linoleic, linolenic, and arachidic.

Oleic acid was found in high percentage ranged from (59.3 to 77.3%), followed by palmitic, linoleic, palmitoleic, stearic and linolenic. Arachidic acid was detected in all olive oil samples, but in low percentage. Total phenol contents expressed as gallic acid of olive oils values ranged from 117 to 304 mg/kg.

All olive oil samples were compared with International Olive Oil Council (IOOC) about quality and purity criteria for olive oil. The samples exhibited remarkable physicochemical properties and could be useful as edible oils. The leader is *Kalinjot* cultivar, which covers about 40% of the total plantations known for oil and table use, which gave very good parameters for the quality of olive oil.

***Key words**: Olive oils, Physical and chemical properties, Fatty acids, Total phenol.*

1. Introduction

The olive tree (*Olea europaea* L.) is one of the most important crops in the Mediterranean countries. The origins of the cultivation of the olive tree lie rooted in legend and tradition. It probably started about 5000 - 6000 years ago within a wide strip of land by the eastern Mediterranean Sea and in the adjacent zones comprising Asia Minor, part of India, Africa, and Europe (Fernandez [1], Muzzalupo and Perri [2]). Others believe that the olive tree originated from Africa (Ethiopia, Egypt). Despite that olive can grow in different corners of the world, it yields abundantly in places of Mediterranean or semi Mediterranean climates and these places are considered optimal for olive farming (Angiolillo *et al.,* [3]). The figure 1 shows an olive tree cultivated in Albania which is a Mediterranean country.

Figure 1. The "Kalinjoti" cultivar in Vlora, Albania

Olive (*Olea europea, Oleaceae*) is a slow-growing, long-lived, evergreen tree uniquely adapted to the climate of the Mediterranean basin and is considered as a

defining feature of this climate (Smartt and Simmonds [4]). The olive tree, olive fruit and olive oil have been at the core of Mediterranean agriculture and trade since early cultivation times, providing sustenance to various cultures and civilizations of the Mediterranean basin (Vossen and Devarenne [5]). The Mediterranean people considered olive oil not only as an excellent food but also as a healing agent. Olive oil is a key component of the traditional Mediterranean diet, which is believed to be associated with a relatively long life in good health (Visioli and Galli [6], Tamilgan [7]). During the past four decades a renewed interest in the nutritional and health aspects of olive oil has been generated.

The Mediterranean diet includes the consumption of large amounts of olive oil, which contains high amounts of phenolic substances (Garcia *et al.,* [8]).

Virgin olive oil (VOO), an excellent natural food, is obtained from olive fruit (*Olea europaea* L.) by mechanical or physical procedures. Its composition varies widely, depending on fruit variety, degree of fruit ripeness, environmental conditions, growing region, and techniques of processing and storage (Barranco *et al.,* [9]). The nutritional value of VOO arises from high levels of oleic acid and phenolic compounds ([Caravita *et al.,* [10], and De Nino *et al.,* [11]). Nutritional value and pleasant flavour have contributed to an increase in consumption of olive oil which has fostered cultivation of olives outsides the traditional olive oil producing region of the Mediterranean and into newer areas where cultivars adaptability, different climatic conditions and different agronomic practices may alter olive quality (Patumi *et al.,* [12]).

Albania as a Mediterranean country, situated on the eastern shore of the Adriatic Sea, may be divided into two major regions: a mountainous highland region (north, east, and south) constituting 70% of the land area, and a western coastal lowland region that contains nearly all of the country's agricultural lands and is the most densely populated part of Albania. Due to the mountains landscape and especially because of its many divisions, the climate varies from region to region. It is warmer in the western part of the country which is affected by the warm air masses from the sea (the Adriatic costal region has a typical Mediterranean climate). This climate makes Albania an important producer of olives and olive oil for the region (Kapaj A. and Kapaj I. [13]). The major part of production is generated in the production of olive oil. Olive oil has a unique position among edible oils due to its delicate flavour, stability and health benefits (Vekiari *et al.,* [14]).

The olive and olive oil sector is an important segment of Albanian primary production and agro industry (Kapaj A. and Kapaj I. [13]). Albania can meet its demand for olives and olive oil, and even achieve surplus, by simply improving services to the current olives; moreover, even without further support for new plantings, the expansion of the production base will continue, even if at a slower pace (Leonetti *et al.,* [15]). Recently, according the data on country' olive oil quantity has ranked Albania as 16th country in world production (Topi *et al.,* [16]).

The International Olive Council (IOC, [17]) and the European Commission (EEC, [18]) have defined the quality of olive oil based on parameters that include: free acidity, peroxide value (PV), UV specific extinction coefficients (K_{232} and K_{270}) and sensory score. In particular, the quantity of free acidity is an important factor for classifying olive oil into commercial grades (Boskou [19], Rossell [20]). The general classification of olive oils into the different commercial grades is based on free acidity and sensory characteristics (taste and aroma). The commercial grades separate oil obtained from the olive fruit solely by mechanical or physical means (virgin) from the other oils that contain refined oils (Kalua *et al.,* [21]). The organoleptic quality of olive oils depends on several factors, one of which is the cultivar.

Some studies were already published concerning the influence of these factors on some: French (Amiot *et al.,* [22]), Spanish (Botia *et al.,* [23]), Italian (Esti *et al.,* [24], Muzzalupo *et al.,* [25]), Portuguese (Ferreres *et al.,* [26]) and Tunisian (Lazzez *et al.,* [27]) cultivars.

The aim of this study was to evaluate the physical and chemical properties, fatty acid composition and total phenol contents of olive oils from nine different autochthonous Albanian olive varieties. All olive oil samples were compared with International Olive Oil Council (IOOC) about quality and purity criteria for olive oil.

2. Materials and Methods

2.1 Olive oils samples

Nine (09) olive oils samples were collected from five locations such us Vlora, Berati, Tirana, Elbasan and Kruje in the year 2014. Samples were collected during the period when olives are usually harvested for oil production (November 2014). The olive oils samples were placed into sterilized bottles.

2.2 Physical and chemical analysis

The pH measurements of olive oils were obtained with a pH meter (HANNA), calibrated with two standard solutions buffered at pH = 4.00 and pH = 7.00. The impurities and moisture were determined according to the method described by Lecoq [28].

Free acidity, peroxide value (PV) and UV light absorption (K_{232}, K_{270}, ΔK) were determined following the official analytical methods described in EC Regulation 2568/91 (Commission Regulation, [29]). The mean of the data was calculated from three biological repeats obtained from three independent experiments.

Saponification number was determined using the method described by Lecoq [28]. For the free oil acidity, a known weight of olive oil was dissolved in a mixture of diethyl ether/ethanol (1 : 1 v/v). The mixture was titrated with potassium hydroxide in methanol (0.05M) in the presence of phenolphthalein as indicator.

For peroxide value, about 5 g of olive oil was dissolved in a mixture of acetic acid/chloroform (3 : 2 v/v), and saturated solution of KI (1mL) was then added. The liberation iodine was titrated with sodium thiosulphate solution (0.05M) in the presence of starch as indicator.

For saponification number, a known weight of olive oil (1 g) was dissolved in alcoholic potassium hydroxide (25 mL) then evaporated for 30 min. The sample was titrated with chlorydric acid (0.5N) in the presence of phenolphthalein as indicator.

2.3 Analysis of fatty acids

The analyses of fatty acids were performed according to the official method of the European Community Regulation (Commission Regulation. [29]). The olive oil samples were esterified in a methanol solution of 2N KOH for 30 minutes at 50 ^{0}C. The gas-chromatographic analyses of fatty acid methyl esters were performed on a Perkin Elmer gas chromatograph, equipped with a flame ionisation detector (Shimadzu QP2010). The column was a fused silica capillary SE30 length 25 meters, diameter 0.25 µm. Helium was the carrier gas (6mL/min). The column temperature program was: initially isotherm at 140 ^{0}C for 10 min., an initial programmed rate of 1 ^{0}C/min. up to 160 ^{0}C, then a second rate of 2 ^{0}C/min. up to 220 ^{0}C and a final isotherm for 15 min. Samples were injected into the split mode. The apparatus itself carried out recording and integration. The gas-chromatographic peaks were identified as corresponding fatty acid methyl esters by check of the elution order on the column and compared the retention times with those of pure standards.

2.4 Determination of total phenol content

The total phenol content was determined according to the methods described by Tsimidou [30]. 100 g of oil was extracted three times with 500 mL of methanol (methanol/Water : 40v/60v). The total phenols in the oil extracts were measured by the Folin-Ciocalteu assay. The measurement was carried out at 765 nm via UV-spectrophotometer. Results were expressed as mg of gallic acid equivalent in one kg oil.

3. Results and Discussion

3.1 Chemical and physical properties of olive oils samples

The chemical and physical characteristics of olive oils sample are shown in Table 1. As is shown, differences were found in chemical values (free fatty acid, peroxide value) among olive oils samples. These properties especially depend on the initial quality of the olives samples. Acidity (% oleic acid) was in the range of 0.58% and 1.31% and fell within the accepted values for extra VOOs and VOOs as the standard free acidity limit for extra VOO and VOO are 0.8 and 2.0 g per 100 g maximum, respectively (IOC [17], EEC [18]). The acidity (% oleic acid) of olive oils samples is shown in Figure 2.

The PV is a measure of primary oxidation. The results obtained also indicated that peroxide values were not higher and ranged between 4.1 meq O_2/kg and 8.8 meq O_2/kg. The data (Table 1) revealed that in all cultivars the PVs were not higher than 8.8 meq O_2 kg^{-1}. None of the oil samples analysed exceeded the maximum for extra-VOO (20 meq O_2 kg^{-1}) (IOC [17]). The peroxide values are shown in Figure 3.

K_{232} parameter is mainly indicative of the conjugated dienes. Data in Table 1 showed that the minimum and maximum values for the absorbance at 232 nm were recorded respectively for Boç (1.300) and Kushan (1.711) oil. The absorbance at 270 nm, mainly indicative of the conjugation of trienes and of the presence of carbonylic compounds, gives the minimum value for Kushan oil (0.100) and the maximum value for Kotruvsi oil (0.176). The values recorded at 232 and 270 nm for all samples analysed complied with IOOC limits for extra VOO. Also, all the values for ΔK lie inside the limits specified for extra VOO in the standard (IOC, [17]).

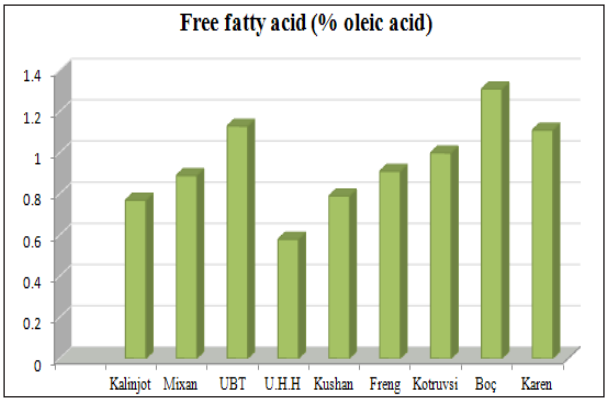

Figure 2. Free fatty acid (% oleic acid) of olive oils samples

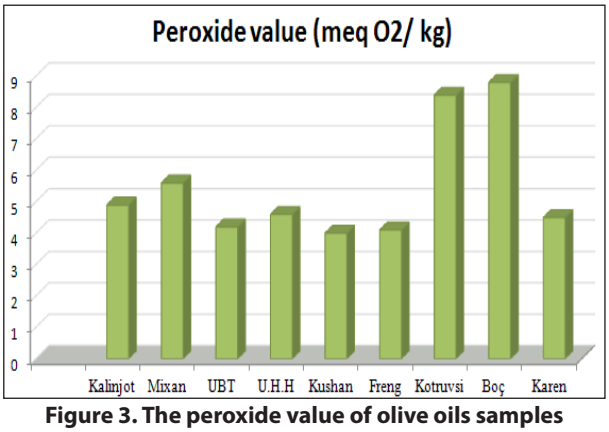

Figure 3. The peroxide value of olive oils samples

In Table 1, pH of all olive oils samples is ranged from pH 4.91 - 5.51.

Sample Freng had lowest pH (4.91), where approved; it had a high acidity value.

Saponification number of all olive oils samples ranged from 177 mg KOH/g to 189 mg KOH/g. All the samples were under the limits (184 - 196 mg KOH/g) established by C.O.I [31].

3.2 Fatty acid composition of olive oils samples

Fatty acid composition is an essential aspect of the qualitative assessment of olive oil. Unsaturated Fatty Acids (UFA) are of great importance because of their nutritional implications and effect on the oxidative stability of oils (IOC, [32]). The fatty acid compositions of the nine olive oils samples were determined by gas chromatography and the results are shown in Table 2.

When examining the fatty acid composition, differences among the samples were observed. It is clear that oleic acid was present in the highest concentration; the values were ranged between 59.3% (Boç) and 77.3% (Ulliri i Holle i Himares - U.H.H) (Figure 4).

It was followed by palmitic acid (4.33 - 8.99%), linoleic acid (4.55 - 17.2%), stearic acid (1.93 - 3.43%), linolenic acid (0.27 -1.02%) and palmitoleic acid (0.13 - 1.46%). Sample U.H.H contained the highest concentration of oleic acid (77.3%) but sample *Boc* has a lowest percentage of the same fatty acid (59.3%). Differences in these values can be due to species, genetics, variety, growing conditions, locality, climatic conditions and postharvest treatment (Patumi *et al.,* [12], and EEC [18]).

Table 1. Chemical and physical properties of olive oils samples

Sample	Free fatty acid (% oleic acid)	pH	Peroxide value (meq O_2/kg)	Saponification number (mg KOH/ g)	Iodine value	K_{232}	K_{270}	ΔK	Unsaponifiable matter
Kalinjot	0.77	4.92	4.9	181	78.8	1.698	0.102	-0.001	1.14
Mixan	0.89	5.02	5.6	181	79.9	1.676	0.106	0.001	1.19
UBT	1.13	5.11	4.2	176	79.6	1.670	0.123	-0.001	1.02
U.H.H	0.58	4.95	4.6	180	79.0	1.489	0.101	-0.001	1.32
Kushan	0.79	5.51	4.0	177	78.8	1.711	0.100	-0.001	1.25
Freng	0.91	4.91	4.1	188	78.9	1.655	0.111	0.000	1.27
Kotruvsi	1	5.07	8.4	178	79	1.347	0.176	0.001	0.77
Boç	1.31	4.93	8.8	177	79.1	1.300	0.167	0.003	0.59
Karen	1.11	4.95	4.5	189	78	1.651	0.107	0.002	0.88

Table 2. Fatty acid content of olive oils samples (%)

Sample	Palmitic acid	Palmitoleic acid	Oleic acid	Linoleic acid	Linolenic acid	Stearic acid	Arachidic acid
Kalinjot	7.88	0.39	74.2	7.32	0.44	2.99	0.44
Mixan	6.91	0.40	75.7	6.65	0.37	3.39	0.55
UBT	6.99	0.66	75.67	9.89	0.60	3.43	0.26
U.H.H	4.33	0.13	77.3	4.55	0.27	3.01	0.56
Kushan	5.55	0.32	75.68	7.88	0.33	3.31	0.45
Freng	5.33	0.23	76.88	7.07	0.34	3.13	0.33
Kotruvsi	7.71	0.94	68.3	12.12	0.88	2.67	0.12
Boç	8.99	1.46	59.3	17.2	1.02	2.23	0.13
Karen	8.44	1.03	70.02	11.7	0.66	1.93	0.44

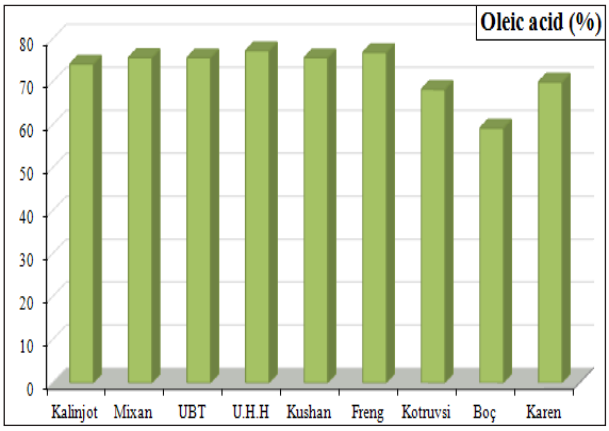

Figure 4. The concentration of oleic acid (%)

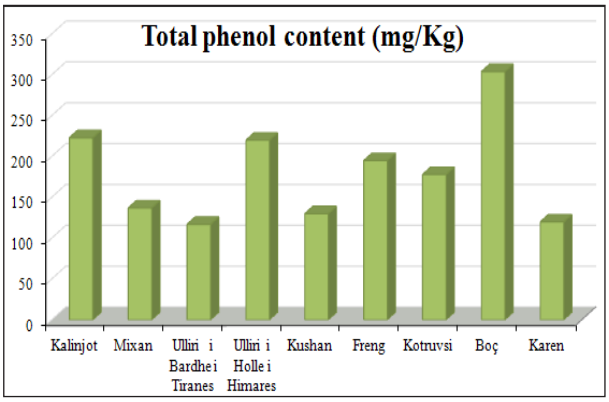

Figure 5. Total phenol contents of olive oils samples (expressed as gallic acid in mg/Kg)

The fatty acid composition of the studied olive oils complies with the requirements of the IOC trade standard (IOC, [17]).

These results of native varieties represent quality and balanced profile of fatty acids, comparable with the Mediterranean countries. Cultivar Kalinjot confirmed as a cultivar of interest for the production of a high quality olive oil, but also U.H.H that is increasingly used in the production of olive oil, presents quality profile of fatty acids.

3.3 Total phenol contents of olive oils

The results of total phenol contents of olive oils samples are shown in Table 3 and illustrated in Figure 5.

Table 3. Total phenol contents of olive oils samples (mg/kg)

Sample	Gallic acid equivalent
Kalinjot	223
Mixan	137
UBT	117
U.H.H	220
Kushan	130
Freng	195
Kotruvsi	178
Boç	304
Karen	120

Total phenol contents expressed as gallic acid of olive oils values ranged from 117 and 304 mg/kg. Total phenol content as gallic acid equivalent in sample "*Boç*" was the highest (304 mg/kg) but sample coded UBT has a lowest percentage of these components (117 mg/kg). These results showed a difference in total phenol contents of olive oils samples. These differences may be due to maturation state and nature of cultivar and total phenol contents of the samples can be considered medium-high levels.

Figure 5 shows sample UBT had low percentage of total polyphenols; whereas sample coded Boç had a highest total polyphenols percentage.

Acknowledgement

This work was supported by IE Pescara and Center of Agricultural Technology Transfer, Vlora Albania.

4. Conclusions

- The aim of this study was to evaluate the quality and purity of olive oils, based on the standards and requirements of the national and European legislation, in order to provide a qualitative product to the customer. Albania has great potentials for olive cultivation and its processing, due to its suitable climatic conditions and quality of native cultivars.

- Native cultivars present good quality in chemical and organoleptic composition, comparable with countries of the Mediterranean basin. They provide quality and balanced profile of fatty acids.

- In this study, the obtained results revealed that the olive oils samples from autochthonous Albanian olive varieties were free from any defects and were classified as virgin olive oil according to international olive oils council, acidity and peroxide values were within the limits for virgin olive oil. The physical and chemical characteristics of olive oils samples showed somewhat considerable differences, but have good properties as they contain low percentages of acidity, therefore could be utilized successfully as a source of edible oil for human consumption.

5. References

[1] Fernandez Diez M. J. (1971). *The olive, in the biochemistry of fruits and their products*. Academic press, London 2, pp. 255-279.

[2] Muzzalupo I., and Perri E. (2008). *Genetic characterization of olive germplasms by molecular markers*. Eur. J. Plant Sci. Biotech., 2, pp. 60-68.

[3] Angiolillo A., Mencuccini M., and Baldoni L. (1999). *Olive genetic diversity assessed using amplified fragment length polymorphisms*. Theor. Appl. Genet., 98, pp. 411-421.

[4] Smartt J., and Simmonds N. (1995). *Evolution of Crop Plants*. Publisher: Wiley-Blackwell (2 Ed.), pp. 496-500.

[5] Vossen P. M., and Devarenne A. K. (2011). *The effect of minor constituents of olive oil on cardiovascular disease: new findings*. UC cooperative extension sensory analysis panel enhances the quality of California olive oil. California Agriculture, 65, pp. 1-13.

[6] Visioli F., and Galli C. (1998). *The effect of minor constituents of olive oil on cardiovascular disease*. Nutrition. Reviews, 56, p. 142.

[7] Tamilgan K., Ozcan M., and Unver A. (2007). *Physical and chemical characteristics of five Turkish olive (Olea europea L.) varieties and their oils*. Grasas y Aceites, 58 (2), pp. 142.

[8] Garcia A., Brenes M., Garcia P., Romero C., and Garrido A. (2003). *Phenolic content of commercial olive oils*. Eur. Food. Res. Technol., 216, pp. 520-525.

[9] Barranco D., Fernandez-Escobar R., and Rallo L. (1996). *Olive growing* (in Spanish). Junta de Andalusia, Consejeria de Agricultura y pesca and ediciones mundiprensa, Madrid, Barcelona, Mexico.

[10] Caravita M. A., Benincasa C., De Rose F., Muzzalupo I., Parise A., (2007). *Omega-3 / omega-6 fatty acids ratio in olive oils from Italian olive varieties*. Agro Food Ind. Hi Tec., 18, pp. 17-18.

[11] De Nino A., Mazzotti F., Perri E., Procopio A., Raffaelli A., and Sindona G. (2000). *Virtual freezing of the hemiacetal-aldehyde equilibrium of the aglicones of oleuropein and ligstroside present in olive oils from Carolea and Coratina cultivars by ionspray ionization tandem mass spectrometry*. J. Mass Spectrom., 35, pp. 461-467.

[12] Patumi M., D'andria R., Marsillio V., Fontanazza G., Morelli G., and Lanza L. (2002). *Olive and olive oil quality after intensive monocone olive growing (Olea europaea L., Cv. Kalamata) in different irrigation regimes*. Food Chem., 7, pp. 27-34.

[13] Kapaj A. M., and Kapaj I. (2012). *Olive Oil Sector in Albania and its Perspective*. In: Boskou D. (Ed.), Olive Oil - Constituents, Quality, Health Properties and Bioconversions, InTech, pp. 495-510, DOI: 10.5772/1378.

[14] Vekiari S. A., Papadopoulou P., and Kiritsakis A. (2007). *Effects of Processing Methods and Commercial Storage Conditions on the Extra Virgin Olive Oil Quality Indexes*. Grasas y Aceites. 58, pp. 237.

[15] Leonetti L., Imami D., Stefanllari A., and Zhllima E. (2009). *The olive and oil value chain in Albania*. In: Formulation of a Technical Assistance Project in Support of Albania's Olive Oil Sector. DSA Project report, Tirana, Albania.

[16] Topi D., Beqiraj I., Seiti B., and Halimi E. (2014). *Environmental impact from olive mills waste disposal, chemical analysis of solid wastes and wastewaters*. Journal of Hygienic Engineering and Design, 7, pp. 44-48.

[17] IOC. (2006). *Trade standard applying to olive oils and olive pomace oils*. COI/T.15/NC 3/Rev. 2.

[18] EEC. (1991). *Regulation (EEC) No 2568/91 on the characteristics of olive oil and olive-residue oil and on the relevant methods of analysis*. Official Journal of the European Communities, L 248.

[19] Boskou D. (1996). *Olive oil chemistry and technology*. AOCS press, Champaigen, IL, USA.

[20] Rossell J. B. (1986). *Classical analysis of oils and fats*. In: Hamilton R. J., and Rossell J. B. (Eds), Elsevier Applied Science Publishers, Ltd, England.

[21] Kalua C. M., Allen M. S., Bedgood D. R., Bishop A. G., Prenzler P. D., and Robards K. (2007). *Olive oil volatile compounds, flavor development and quality. A critical review*. Food Chem., 100, pp. 573-575.

[22] Amiot M. J., Fleuriet A., and Macheix J. J. (1986). *Importance and evolution of phenolic compounds in olive during growth and maturation*. J. Agric. Food Chem., 34, pp. 823-826.

[23] Botia J. M., Ortuno A., Benavente-Gracia O., Báidez A. G., Frias J., Marcos D., and Del Rio J. A. (2001). *Modulation of the biosynthesis of some phenolic compounds in Olea europaea L. fruits: Their influence on olive oil quality*. J. Agric. Food Chem., 49, pp. 355-358.

[24] Esti M., Cinquanta L., and La Notte E. (1998). *Phenolic compounds in different olive varieties*. J. Agric. Food Chem., 46, pp. 32-35.

[25] Muzzalupo I., Stefanizzi F., Perri E., and Chiappetta A. (2011). *Transcript levels of CHL P gene, antioxidants and chlorophylls contents in olive (Olea europaea L.) pericarps: a comparative study on eleven olive cultivars harvested in two ripening stages*. Plant Food Hum. Nutr., 66, pp.1-10.

[26] Ferreres F., Vinha A. F., Silva B., Valentão P., Gonçalves A., Pereira J. A., Oliveira. M. B., Seabra R. M., and Andrade P. B. (2005). *Phenolic profiles of Portuguese olive fruits (Olea europaea L.): Influences of cultivar and geographical origin*. Food Chem., 89, pp. 561-568.

[27] [27] Lazzez A., Perri E., Caravita M. A., Khlif M., and Cossentini M. (2008). *Influence of olive maturity stage and geographical origin on some minor components in virgin olive oil of the Chemlali variety*. J. Agric. Food Chem., 56, pp. 982-988.

[28] Coq Le R. (1965). *Manual food testing and usual expertise* (in French). Ed Doin, Paris, .

[29] European Commission (1991). *Regulation No 2568/91 of 11 July 1991 on the characteristics of olive oil and olive-residue oil and on the relevant methods of analysis*. OJ L 248, pp. 1.

[30] Tsimidou Z. M. (1999) Sem. Food. Anal. 4, p. 13.

[31] C.O.I. (2003). *Commercial standards applicable to olive oils and olive-pomace oils* (in French). C.O.I/ T.15/ N.C.N°3/ Rev. 1

[32] IOC. (2007). *Sensory analysis of olive oil. Method for the organoleptic assessment of virgin olive oil*. COI/T.20/Doc. 15/Rev. 2.