IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)
e-ISSN: 2319-2402, p- ISSN: 2319-2399.Volume 18, Issue 12 Ser. 3 (December 2024), PP 18-23
www.iosrjournals.org

Chemical Parameters, Antioxidants, And Polyphenols In Extra Virgin Olive Oil And Olive Pomace Oil

Obaidh Alabdulla
(Food Science Department, Faculty Of Agriculture /Damascus University, Syria

Abstract:
This study examines two types of olive oil: extra virgin olive oil (EVOO) and olive pomace oil (OPO). EVOO is known for its high quality and health benefits, while OPO is a by-product obtained through solvent extraction. We compare their physical and chemical parameters, highlighting differences in quality, nutritional value, and market demand. EVOO is recommended for health benefits, whereas OPO serves as a cost-effective industrial alternative. Significant differences in polyphenols, carotenoids, and FTIR analysis were found, with a notable difference (143%) at 1720 cm^{-1} between the two oils.

Key Word: *Extra Virgin olive oïl, Pomace olive oïl, Polyphenols, FTIR.*

Date of Submission: 17-12-2024 Date of Acceptance: 27-12-2024

I. Introduction

Extra virgin olive oil is the only vegetable oil that does not undergo a refining process and is consumed directly after being extracted from olive Fruits. Extra virgin olive oil is not refined because it contains beneficial chemical compounds that are highly valuable for human health and play a significant role in disease prevention: In contrast to other olive oils (olive pomace oil), which require refining before human consumption. Olive oil has attracted considerable attention from scientists because of the numerous health benefits associated with its consumption (Garcia et al, 2006). It is widely recommended for preventing cardiovascular diseases and its antioxidant effects (Mansouri et al., 2016, Selaimia et al, 2017). Historically, the beneficial properties of olive oil have been attributed to its high content of monounsaturated fatty acids (MUFAs), particularly oleic acid, which accounts for 70-80% of the total fatty acids in virgin olive oil. In addition to MUFAs, virgin olive oil contains a minor yet important fraction of phenolic compounds, which have drawn significant interest due to their potential health-promoting effects (Goldsmith et al., 2014, Irmak et al,2017).

Olive pomace is rich in polyphenols, making it a potential source of antioxidants for dietary supplementation (Romeu et al, 2024). Additionally, olive pomace oil retains some polyphenols, highlighting its health benefits.

Due to the rising prices of edible oils, including olive oil, manufacturers and traders wholly or partially substitute them with cheaper oils. Mixing with any other substance which affects quality is called adulteration. Such adulteration is an economic fraud that can endanger a consumer´s life. Due to fraud in the olive oil supply chain, food control authorities need efficient detection methods (Poiana et al., 2012). The probability is high that most commercial and governmental laboratories have an adaptation capable of identifying the adulterants of olive oil. Still, it is slow and requires movement to the laboratory. FT-IR spectroscopy is a quicker analysis method that can quickly find the presence of certain chemical functional groups and structural fragments in a compound (Poiana et al., 2012, Selaimia et al, 2017).

This study aimed to compare the spectroscopic properties of olive pomace oil and extra virgin olive oil using FTIR, providing a reliable method for their identification and detection.

II. Material And Methods

Olive fruits (Maraki variety) were harvested at the end of the maturation period in November 2015 and processed using a two-phase extraction system (Mini Frantoio Oliomio-50-60 Centrifuge, Italy). Oil samples were extracted by centrifugation at 5200 rpm/ min. After filtration, the virgin olive oil samples were stored at -18º C in dark glass bottles until analyses. The pomace was dried in an oven at 70°C under vacuum. Dried samples were extracted with petroleum ether (b.p. 40-60°C) to obtain crude olive pomace oil using a Soxhlet apparatus.

Quality indices of oils

Free acidity (oleic acid%) and peroxide value (mEq O2/kg oil) were determined according to AOCS (1998). K232 and K270 were determined with a UV spectrophotometer (Unico UV-2000, (USA) at 232 and 270 nm according to AOCS (1998). Spectra of virgin and crude pomace olive oils were measured in the UV region of 190–320 nm. Unsaponifiable matter of oil samples was determined according to IUPAC (1982). All parameters were determined in triplicate.

Total polyphenols content of olive oil

The total polyphenol content of the olive oil samples was determined according to the method explained by Laincer et al. (2014). Fifty g of the oil was dissolved in 50 mL of hexane; the solution was extracted successively three times with 30 mL of a methanol/water (80:20, v/v) solution. The extracts were collected and washed twice with 50 mL of hexane to dissolve the residual oil. The hexane phase was removed, and the methanolic solutions were concentrated and dried using a rotary evaporator (Eyela, Japan) under a vacuum at 40ºC. The residue was re-dissolved in a solution of methanol/water (80:20, v/v). Total polyphenol content was determined using Folin-Ciocalteu and colorimetric measurement at 765 nm.

Determination of chlorophyll and carotenoid compounds

Chlorophyll and carotenoid compounds were estimated from the absorption spectra of olive oil according to Fares et al. (2015). Chlorophyll and carotenoids were measured at 670 nm and 470 nm, respectively. The concentrations of chlorophyll and carotenoids were expressed as mg of pheophytin and lutein per Kg, respectively. Pigment contents were calculated as follows:

Chlorophylls (mg/kg) = (A670x106)/ (613x 1000x density)

Carotenoids (mg/kg) = (A470x106)/(2000x1000xdensity)

Identification and quantification of fatty acids by GC

The methyl esters of the fatty acids were prepared by using a mixture of methanol: concentrated sulphuric acid (99:1, v/v) and fatty acids: methylation mixture ratio of (1:13, v/v) at room temperature according to Morsi et al. (2008).

Fourier transform infrared spectroscopy (FTIR)

The infrared spectrum of olive oil was measured on an FT-IR spectrometer (Nicolet 6700, Thermo Fisher, Waltham, MA, USA) using KBr pellets in the infrared region of 4000−400 cm−1 at a resolution of 4 cm−1.

Statistical analysis

The data were analyzed using Assistat statistical software version 7.7. The significance of the differences of the means at a 5% level was determined using a one-way analysis of variance (ANOVA).

III. Result

Analytical data in Table.1 indicates deviation in characteristics of oil obtained from Maraki fruits using a two-phase centrifugal decanter and crude pomace oil from Maraki fruit. Notably, the values of acidity and peroxide of the crude pomace oil were higher than those of virgin olive oil. Furthermore, the K_{232} and K_{270} values of crude pomace oil were four (4) and six (6) times higher than virgin olive oil (Table 1). As per the 2015 standards set by the International Olive Council (IOC), the extra virgin olive oil (EVOO) must have an acidity of less than 0.8%, a peroxide value of less than 20 (meq O2/kg oil), and extinction coefficients at 232 nm and 270 nm of less than 2.50 and 0.25, respectively. The samples of virgin olive oil studied were below these values, and therefore they are classified as EVOO. Unlike crude olive oil, there are no limits on the acidity, peroxide value, and extinction coefficients of crude olive pomace oil (IOC, 2015).

Table 1. Characteristics of virgin olive oil and crude olive pomace oil.

Parameter	Virgin olive oil		Crude olive pomace oil
	EVOO*	Sample	
Free fatty acids %(as oleic acid)	≤0.8	0.05±0.01[b]	0.78±0.13[a]
Peroxide value (meq O2/kg)	≤20	2.17±0.14[b]	7.79±0.35[a]
K232	≤2.5	0.460	1.575
K270	≤0.22	0.039	0.289
ΔK	≤0.01	0.001	0.003
Total polyphenols (µg GAE /g)		146.44±1.34[b]	201±2.00[a]
Chlorophyll (mg pheophytin/kg)		3.77±0.08[b]	23±0.33[a]
Carotenoids (mg lutein/ kg)		1.32±0.02[b]	1.47±0.02[a]
Unsaponifiable matter (%)		1.5±0.10[b]	2.44±0.02[a]

*** EVOO: Extra virgin olive oil Standard (International Olive Council, 2015). Data are expressed as mean±SD. Means with the same letter in the same row are not significantly different at 0.05 level of significance.**

Crude olive pomace oil obtained from the centrifugation of olive paste had a significantly higher content of total polyphenols (201±2.00µg GAE/g) compared with that of EVOO (146.44±1.34µg GAE /g) and, consequently, a Polyphenols are recognized as important antioxidant compounds that protect the oil against auto-oxidation. Total polyphenols of the Egyptian Maraki extra virgin olive oil ranged from 130.8 mg/kg to 198.20 mg Caffeic acid/kg oil) (Arafat et al., 2016). The unsaponifiable matter of the crude pomace oil (2.44%) was significantly higher than that of the extra virgin olive oil (1.5%). Moussaoui and Youyou et al. (2006) found that unsaponifiables content of Chemlal olive cake oil was 1.48%.

The virgin olive oil's green-yellowish color is a key quality parameter and significantly affects consumer preference. It is produced from the presence of chlorophylls and carotenes. According to the findings, the chlorophylls of Maraki crude pomace oil were most importantly ($p<0.05$) significantly higher (23 mg pheophytin/kg) than that of the EVOO samples from the same variety (3.77 mg pheophytin/kg) as well as the carotenoids (1.47 mg lutein/kg) same trend was observed for those of the EVOO (1.32 mg lutein/kg). According to a study done by Gallardo et al. (2002), the loss of pigment during the olive oil extraction process was due to the pigments remaining in the alperujo, not their destruction. Most of the chlorophyll fraction was found in the alperujo, while carotenoids were transferred to the oil. The olive variety, fruit ripeness stage, environmental conditions, production year, oil extraction process, as well as storage conditions affect the levels of chlorophylls and carotenoids in olive oil (Sarolic et al., 2016).

Absorbance at 232 nm, 270 nm, and ΔK correlate with the state of oxidation by detecting specific oxidized compounds. The higher the absorption at these wavelengths the greater the degree of oxidation. The increase of ΔK indicates lower-quality olive oil (Houshia et al., 2014). UV spectra of the investigated virgin olive oil and pomace oil samples exhibit remarkable differences (Fig.1). The absorbency at 232 nm in crude olive pomace oil is caused by hydroperoxides and conjugated dienes while the absorbency at 270 nm is caused by carbonylic components and conjugated trienes (Houshia et al., 2014).

Measurements of absorbance at 232 nm, 270 nm, and ΔK can be used to detect oxidation compounds. Higher absorbance at these wavelengths reveals a greater extent of oxidation. Houshia et al. (2014) informs that an Increase ΔK leads to a decline in the quality of olive oil. The UV spectra of virgin olive oil and pomace oil samples studied show significant differences (Fig. 1). The absorbance at 232 nm in crude olive pomace oil is caused by hydroperoxides and conjugated dienes, and the absorbance at 270 nm caused by carbonyl compounds and conjugated trienes (Houshia et al., 2014).

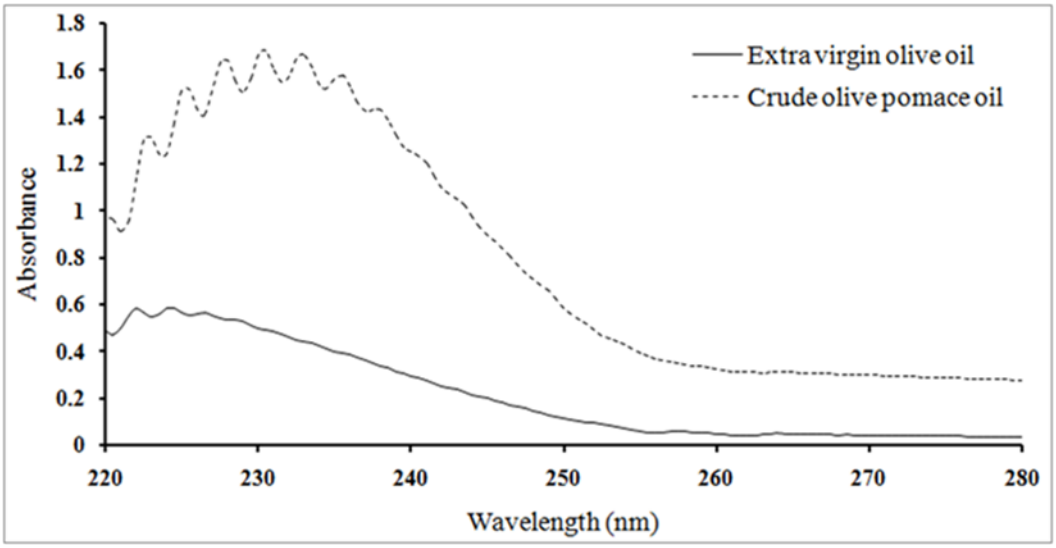

Fig. 1 Ultraviolet spectra of extra virgin olive oil and olive pomace oil.

Fatty acid composition of extra virgin olive oil and pomace olive oil

The fatty acid composition, expressed as a percentage of the total identified fatty acids, is summarized in Table 2. The results indicate that the fatty acid profiles of extra virgin olive oil (EVOO) and pomace oil fall within the normal range, as reported by the International Olive Council (IOC) in 2015. The primary fatty acids identified were oleic acid (C18:1), linoleic acid (C18:2), and palmitic acid (C16:0), with oleic acid being the most predominant in the samples analyzed. The oleic acid content was measured at 61.21% for EVOO and

60.79% for pomace oil. Monounsaturated fatty acids are significant due to their beneficial effects on the oxidative stability of oils. Palmitic acid represents the major saturated fatty acid in olive oils, accounting for 15.95% in crude olive pomace oil and 16.18% in extra virgin olive oil. The oleic/linoleic acid ratio ranged from 3.5 to 3.7, which can be useful for characterizing different olive cultivars (Uluata et al., 2016). Low levels of palmitoleic acid (C16:1), stearic acid (C18:0), linolenic acid (C18:3), arachidic acid (C20:0), 9-Eicosenoic acid (C20:1), and behenic acid (C22:0) were recorded in both oil samples. Furthermore, the ratio of unsaturated to saturated fatty acids was 4.19 for EVOO and 4.25 for crude olive pomace oil. Overall, the results showed that both oils had similar fatty acid profiles, as illustrated in Table 2

Table 2. Fatty acid composition of extra virgin olive oil and crude olive pomace oil

Fatty acid	Extra virgin olive oil	Crude olive pomace oil
C16:0	16.18	15.95
C16:1	1.87	1.85
C18:0	2.48	2.50
C18:1	61.21	60.79
C18:2	16.33	16.94
C18:3	0.92	0.94
C20:0	0.43	0.44
C20:1	0.27	0.28
C22:0	0.11	0.12
Σ Saturated	19.20	19.01
Σ Unsaturated	80.60	80.80
Σ Unsaturated /Σ Saturated	4.19	4.25
Σ Monounsaturated	63.35	62.92
Σ Polyunsaturated	17.25	17.88
Σ Polyunsaturated /Σ Saturated	0.90	0.94

Fourier Transform Infrared Spectroscopy (FTIR)

The oils exhibit variations in the chain lengths of their acyl moieties, as well as differences in their degree of unsaturation and the position of these double bonds. These distinctions are evident in the FTIR spectra (Maggio et al., 2010). The significance of infrared (IR) spectroscopy in identifying molecular structures stems from specific absorption bands associated with different functional groups (Bendini et al., 2007). Extra virgin olive oil is considered the highest quality type of olive oil, making it the most expensive. As a result, it is sometimes adulterated with cheaper oils, such as olive pomace oil. The typical FTIR spectra for extra virgin olive oil and olive pomace oil are shown in Fig. 2. While the spectra of these two oils are quite similar due to their comparable chemical compositions, there are notable differences in the width and intensity of certain absorption bands. The results indicate that the absorbance of olive pomace oil is consistently higher than that of extra virgin olive oil across the FTIR spectrum. The smallest difference observed was 15% at 1764 cm−1, while the largest difference was 143% at 1720 cm−1. Absorbance at 3012 cm−1 corresponds to the stretching vibration of cis-double bonds. The absorbances at 2930 cm−1 and 2858 cm−1 are attributed to CH2 stretching vibrations, both asymmetric and symmetric, respectively. The peak at 1750 cm−1 is linked to the stretching vibration of the C=O double bond in saturated aldehyde groups. Peaks within the range of 1470–1380 cm−1 are associated with CH2 and CH3 vibrations, while bands observed at 1242 cm−1 and 1168 cm−1 have been identified as corresponding to saturated acyl groups (Guillén and Cabo, 1997)

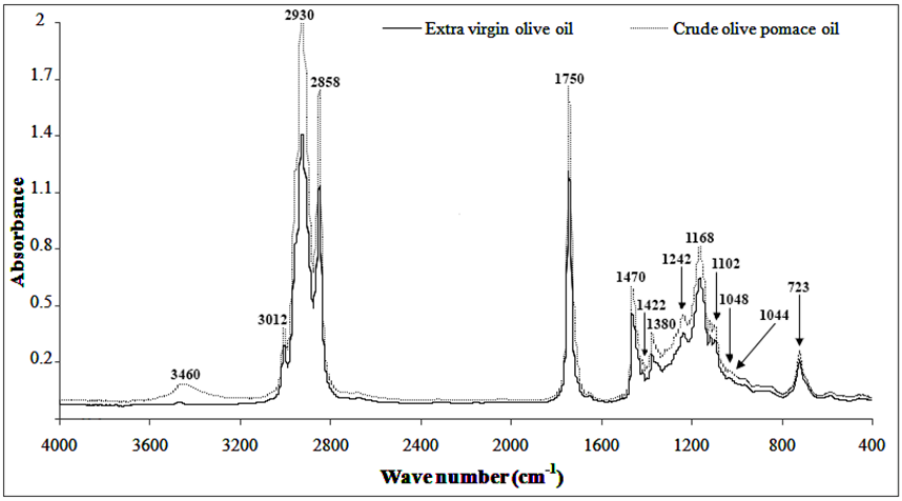

Fig. 2. FT-IR spectra of olive oil samples

The spectral region between 1500 and 900 cm^{-1} revealed significant differences in the absorption bands, particularly at 1168 cm^{-1} (assigned to -C-O stretching and CH_2 bending) and at 1122 and 1102 cm^{-1}. These findings align with the results reported by Yang and Irudayaraj (2001) for extra virgin olive oil and olive pomace oil. The strong intensities of the spectral bands at 3460 cm^{-1} (associated with the carbonyl C=O stretching bond, hydroperoxides; Guillén and Cabo, 1997) and 1750 cm^{-1} (related to the stretching vibration of saturated aldehyde groups, C=O) are noteworthy. Additionally, the absorbance ratio of peak heights (3012/3460 cm^{-1}) greater than 4 further characterizes the pomace oil.

IV. Conclusion:

Olive Pomace oil is abundant in polyphenols and antioxidants. After a refining process, it can be utilized in human nutrition. Additionally, it has industrial applications, including soap making and in the cosmetic and pharmaceutical industries.

References

[1]. Arafat, S.M.; Basuny, A. M. M.; Elsayed, M. E. And Soliman, H. M. (2016). Effect Of Pedological, Cultivar And Climatic Condition On Sterols And Quality Indices Of Olive Oil. Scientia Agriculturae., 1:23-29.

[2]. American Oil Chemists' Society (Aocs). (1998) Official Methods And Recommended Practices Of The American Oil Chemists' Society. Champaign, Il.; 1998.

[3]. Barba, L.; Arrighetti, G. And Calligaris, S. (2013). Crystallization And Melting Properties Of Extra Virgin Olive Oil Studied By Synchrotron Xrd And Dsc. Eur. J. Lipid. Sci. Technol.,115:322–329.

[4]. Bendini, A.; Cerretani, L.; Di Virgilio, F.; Belloni, P.; Bonoli-Carbognin, M. And Lercker, G. (2007). Preliminary Evaluation Of The Application Of The Ftir Spectroscopy To Control The Geographic Origin And Quality Of Virgin Olive Oils. J. Food Quality., 30:424-437.

[5]. Cerretani, L.; Maggio, R.M.; Barnaba, C.; Toschi, T.G. And Chiavaro, E. (2011). Application Of Partial Least Square Regression To Differential Scanning Calorimetry Data For Fatty Acid Quantitation In Olive Oil. Food Chem., 127:1899-1904.

[6]. Chatziantoniou, S.E.; Triantafillou D.J.; Karayannakidis, P.D. And Diamantopoulos, E. (2014). Traceability Monitoring Of Greek Extra Virgin Olive Oil By Differential Scanning Calorimetry. Thermochimica Acta., 576:9-17.

[7]. Chiavaro, E.; Rodriguez-Estrada, M.T.; Barnaba, C.; Vittadini, E.; Cerretani, L. And Bendini, A. (2008). Differential Scanning Calorimetry:A Potential Tool For Discrimination Of Olive Oil Commercial Categories. Analytica Chimica Acta., 625:215–226.

[8]. Chiavaro, E.; Rodriguez-Estrada, M.T.; Bendini, A. And Cerretani, L. (2010). Correlation Between Thermal Properties And Chemical Composition Of Italian Extra Virgin Olive Oils. Eur. J. Lipid. Sci. Technol., 112:580–592.

[9]. Fares, N.; Karoui Jabri, I.; Sifi, S. And Abderrabba, M. (2016). Physical-Chemical And Sensory Characterization Of Olive Oil Of The Region Of Kairouan. Journal Of Chemical And Pharmaceutical Research., 7:2148-2154.

[10]. Gallardo-Guerrero, L.; Roca, M. And Mínguez-Mosquera, M. I. (2002). Distribution Of Chlorophylls And Carotenoids In Ripening Olives And Between Oil And Alperujo When Processed Using A Two-Phase Extraction System. J. Am. Oil. Chem. Soc., 79:105–109.

[11]. Gharby, S.; Harhar, H.; Mamouni, R.; Matthäus, B.; Addi, E.A. And Charrouf, Z. (2016). Chemical Characterization And Kinetic Parameter Determination Under Rancimat Test Conditions Of Four Monovarietal Virgin Olive Oils Grown In Morocco. O. C. L. J, 23:401-408.

[12]. Goldsmith, C.D.; Stathopoulos, C.E.; Golding, J.B. And Roach, P.D. (2014). Fate Of The Polyphenols During Olive Oil Production With The Traditional Press Method. International Food Research Journal, 21:101-109.

[13]. Guillen, M.D. And Cabo, N. 1997. Characterization Of Edible Oils And Lard By Fourier Transform Infrared Spectroscopy. Relationships Between Composition And Frequency Of Concrete Bands In The Fingerprint Region. J. Am. Oil. Chem. Soc., 74:1281-1286.

[14]. Houshia, O. J; Zaid, O.; Shqair H; Zaid, M.; Fashafsheh, N. And Bzoor, R. (2014). Effect Of Olive Oil Adulteration On Peroxide Value, Delta-K And On The Acidity Nabali-Baladi Olive Oil Quality. Advances In Life Sciences., 4:235-244.

[15]. International Olive Council (2015). Trade Standard Applying To Olive Oils And Olive-Pomace Oils. International Olive Council, Coi/T.15/Nc No 3/Rev 8.

[16]. Irmak S., Tokusoglu O., (2017). Saturated And Unsaturated Fatty Acids Composition Of Olive Oils Obtained From Less Salty Black Table Olives Preserved With Vacuum, Map And Gamma Irradiation Technologies. J. Nutr. Food Sci. 7: 582.

[17]. Iupac (1982). Standard Methods For The Analysis Of Oils, Fats And Derivatives, 6th Edn, Pergamon Press, Oxford.

[18]. Laincer, F.; Laribi, R. And Tamendjari, A. (2014). Olive Oils From Algeria:Phenolic Compounds, Antioxidant And Antibacterial Activities. Grasas Y Aceites., 65:67-77.

[19]. Maggio, R.M.; Kaufman, T.S.; Del Carlo, M.; Cerretani, L.; Bendini, A.; Cichelli, A. And Compagnone, D. (2009). Monitoring Of Fatty Acid Composition In Virgin Olive Oil By Fourier Transformed Infrared Spectroscopy Coupled With Partial Least Squares. Food Chemistry, 114: 1549–1554.

[20]. Mansouri, F.; Benmoumen, A.; Richard, G.; Fauconnier, M.L.; Sindic, M.; Serghini-Caid, H. And Elamrani, A. (2016). Characterization Of Monovarietal Virgin Olive Oils From Introduced Cultivars In Eastern Morocco. La Rivista Italiana Delle Sostanze Grass., 20:22-30.

[21]. Morsi, M.K.S.; Galal, S.M. And Elkholy, M. (2008). Synthesis And Evaluation Of Sucrose Esters. Egyptian J. Of Nutrition., 23:1-23.

[22]. Moussaoui, R. And Youyou, A. (2006). Oil Extraction From Olive Foot Cake With Acidic Ethanol. Journal Of Food, Agriculture And Environment., 4:61-63.

[23]. Poiana, M.A.; Mousdis, G.; Alexa, E.; Moigradean, D.; Negrea, M, Mateescu, C. (2012). Application Of Ft-Ir Spectroscopy To Assess The Olive Oil Adulteration, Journal Of Agroalimentary Processes And Technologies., 18:277-282.

[24]. Romeu, M.F.C; Bernardo,J; Daniel C.I; Crespo, J.G; Pinto, L,S; Ponte, M,N; Nunes, A,V,M: (2024). Hydroxytyresol Recovery From Olive Pomace: A Simple Process Using Olive Mill Industrial Equipment And Memberane Technology. J Food Sci Technology 61(1):161-168.

[25]. Sarolić, M.; Gugić, M.; Friganović, E.; Giovanni Tuberoso, C.I. And Jerković, I. (2016). Phytochemicals And Other Characteristics Of Croatian Monovarietal Extra Virgin Olive Oils From Oblica, Lastovka And Levantinka Varieties. Molecules., 20:4395-4409.

[26]. Selaimia,R; Oumeddour, R; Nigris, S; (2017). The Chemometrics Approach Applied To Ftir Spectral Data For The Oxidation Study Of Algerian Extra Virgin Olive Oil. International Food Research Journal 24(3): 1301-1307
[27]. Uluata, S.; Altuntas, Ü. And Özçelik, B. (2016). Biochemical Characterization Of Arbequina Extra Virgin Olive Oil Produced In Turkey. J. Am. Oil. Chem. Soc., 93:617-626.
[28]. Yang, H. And Irudayaraj, J. (2001). Comparison Of Near-Infrared, Fourier Transform-Infrared, And Fourier Transform-Raman Methods For Determining Olive Pomace Oil Adulteration In Extra Virgin Olive Oil. J. Am. Oil. Chem. Soc., 78:889- 895.