Original scientific paper
UDC 664.3-021.465:543(496.5)

COMPARISON OF THE PHYSICO-CHEMICAL PROPERTIES OF SOME EDIBLE OILS FROM THE ALBANIAN MARKETS

Lorena Memushaj[1*], Afërdita Shtëmbari[2]

[1]Department of Pharmacy, Faculty of Medical Sciences, Aldent University, Dibrës 235, 1001 Tirana, Albania
[2]Department of Industrial Chemistry, Faculty of Natural Sciences, University of Tirana, Boulevard Zogu I 25, 1016 Tirana, Albania

[*]e-mail: lorena.memushaj@ual.edu.al

Abstract

Edible oils had made an important contribution to the diet of people in many countries serving as a good source of proteins, lipids, and fatty acids. The purpose of this study is to evaluate the quality of the oils, based on the physicochemical parameters of some vegetable oils.

Five edible oils were obtained, of which 2 were imported (avocado oil, palm oil), and 3 of them were domestically produced (olive oil, corn oil, sunflower oil). The samples were taken randomly in local markets in Tirana, Albania. Selection of the representative samples for each type of oil was carried out starting from the products that are widely used by consumers. The quality of these oils was analyzed by determining physicochemical properties such as density, index of refraction, acid value, saponification value, and peroxide value. Classical methods of analysis were used.

The palm oil sample has high values of density (0.9152 g/mL) compared to the FAO/WHO standards. This shows that we have the presence of other added oils. Acid value is often used as a general indication of the condition and edibility of the oil. The acid value for all edible oils were below 0.6 mgKOH/g obtained from FAO/WHO recommendation. Olive oil has refractive index values of 1.4685 which is within the standards obtained from FAO/WHO, while the values of other oils are different from the required standards, or: avocado oil - 1.4734, maize oil - 1.4764, sunflower oil - 1.4764, and palm oil -1.4757, respectively. The different value of the refractive index indicates that foreign fats are present. It is noted that maize oil, sunflower oil, and palm oil have a lower number of saponification compared to the FAO/WHO recommendations: maize oil - 177.68 mg KOH/g, sunflower oil - 182.39mg KOH/g, and palm oil - 184.80 mg KOH/g, respectively. The lower saponification value indicates a low triacylglycerol content, consistent with the low ester value, and also indicates that the oil has no potential to be used for the cosmetic industry.

We observed that palm oil had the lowest quality according to standards recommendation.

***Key words**: Acidity, Peroxide, Refraction, Saponification.*

1. Introduction

It is commonly known how important edible oils are to fields including food, energy, cosmetics, pharmaceuticals, and lubricants. Vegetable oils' physical characteristics are primarily influenced by composition (and thus biological origin) and temperature. However, physico-chemical characteristics have a significant role in determining the overall stability and quality of a food system. Vegetable oil density has been demonstrated to decrease linearly with rising temperature. A vegetable oil's density, saponification value, iodine value, acid value, and peroxide value are a few of its key traits. The primary elements of a healthy daily diet are macronutrients like proteins, carbohydrates, and lipids as well as micronutrients like vitamins, minerals, and antioxidants. When used as food or as an ingredient in food products, edible oils are a significant component of the human diet [1].

Vegetable oils are composed of triglycerides. Triglycerides are molecules that contain carbon, hydrogen, and oxygen, and their structure includes glycerol and three fatty acids. Triglycerides can contain the same fatty acids or various types of fatty acids. Monoglycerides, diglycerides, free fatty acids, phosphates, esters, tocopherols, and tocotrienols are present in trace amounts. Since the fatty acid composition of triglycerides directly affects their physical properties, vegetable oils will typically contain fatty acids with chains of hydrocarbons of 12 to 22 carbons, with 16 and 18 carbons being the most prevalent, and with or without unsaturated carbon atoms, that is, with the presence of double links. Saturated, monounsaturated, and polyunsaturated are thus possible names for these fatty acids. More so than altering the triglycerides' molecular mass, this unsaturation has a direct impact on the physicochemical properties of vegetable oils. When used as food or as an ingredient in food products, edible oils are a significant component of the human diet [2].

The purpose of this study is to evaluate the quality of the 5 edible, domestic and imported oils, found in local markets in Tirana, Albania, based on the physicochemical parameters of some vegetable oils.

2. Materials and Methods

2.1 Chemicals

All reagents used in this study were of analytical grade. The solutions were prepared with distilled water. All the following reagents used for this study were: potassium hydroxide, ethanol, phenolphthalein, hydrochloric acid, acetic acid, chloroform, potassium iodide, and sodium thiosulfate from Merck, Germany.

2.2 Sample collection

The purpose of the experimental part was to evaluate the quality of the oils, based on the physico-chemical parameters of the 5 vegetable oils that we took in the study, such as: avocado oil, olive oil, corn oil, and sunflower oil and palm oil, taken in country markets. The main purpose is to compare the results of these analyzes between the oils that we analyzed, and to determine whether they are within the standards [17]. The quality of these oils was analyzed by determining physicochemical properties such as: density, index of refraction, acid value, saponification value, and peroxide value. The values of each parameter are measured two times for each sample.

2.3 Density measurement

Density of oil samples were measured by a relative density (R.D) of bottle with a capacity of 10 mL according to the following formula [3]:

$$\text{Density } (\rho) = \frac{\text{Mass of the oil sample (M)}}{\text{Volume of the R.D bottle (V)}} \text{ g/mL}$$

2.4 Index of refraction

The index of refraction of a type of fat moves with the change in temperature, and as the temperature increases, the index of refraction decreases [4]. Refractive index measurement was done at ambient temperature. The determination of the refractive index was done on the completely dry and filtered sample using an Abbe refractometer [5, 6].

2.5 Acid value

The acidity number indicates how many milligrams of potassium hydroxide are needed to neutralize the free fatty acids contained in one gram of fat. 5 g of olive oil were weighed in a 250 mL Erlenmeyer flask. 50 mL of alcoholic solution (diethyl ether/ethanol (1:1 v/v)) were added and heated in a furnace, mixing it well until the alcohol begins to boil. Then a few drops of phenolphthalein were added and the mixture is titrated with 0.1 N KOH solution stirring continuously until the liquid acquires a stable pink color [7, 8].

2.6 Saponification value

Saponification number refers to the amount of potassium hydroxide (KOH) in milligrams needed to completely saponify one gram of oil. The amount of free and combined fatty acids contained in the fat is derived from this number.

In a conical flask with a volume of 250 mL, accurately 2 grams of oil were weighted, and 25 mL of alcoholic KOH solution 0.5N were added. The flask was connected to a vertical glass tube under a reserved condenser and placed in a water bath for 60 minutes with constant shaking. After heating, the flask was removed from the bath and 3 - 4 drops of phenolphthalein were added to the saponified solution. The excess KOH is titrated while still warm with 0.5 N HCl solution until the pink color disappeared [9, 10].

2.7 Peroxide value

The number of peroxides is the mass of total peroxides in olive oil expressed as milliequivalents of O_2 meq/kg oil. This value is known as a quality guideline. In other words, the peroxide value is a measure of active oxygen which reflects the values of hydroxyperoxides.

2 grams of oil were added into an Erlenmeyer flask and rapidly 30 mL of acetic acid-chloroform mixture were added, by continuous stirring in order to dissolve the fat. Then 1 mL of saturated potassium iodide solution was added. 75 mL of distilled water were added, and the solution was slowly titrated until it turns into light yellow. After that, 0.5 mL of starch solution were added, and the titration with 0.01 N $Na_2S_2O_3$ solution continued, by mixing it in order to get all the iodine from the chloroform layer until the blue color disappears [10, 11].

3. Results and Discussion

3.1 Density measurement

In determining the density, it is not necessary to keep the temperature exactly for liquid fats (oils) at 20 ^{0}C or 15 ^{0}C. Determination can be made at temperatures close to those mentioned above. In determining the density, it is not necessary to maintain the temperature exactly for liquid fats (oils) at 20 ^{0}C or 15 ^{0}C. Determinations can be made at temperatures close to those mentioned above. The values found can be calculated by means of the correction coefficient.

Figure 1 below shows the average density values for the analyzed vegetable oil samples, to see the difference in this parameter between them [12].

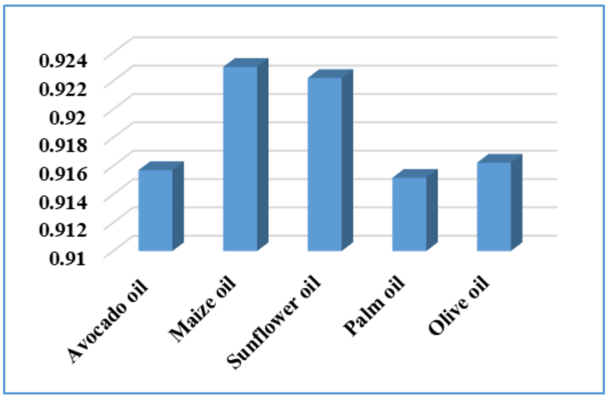

Figure 1. Density value (g/mL) distribution for the 5 oil samples

From the measurements carried out in the laboratory, the samples of maize oil and sunflower oil have the highest density. Their density values are related to their physical properties.

Avocado, maize, sunflower and olive oil samples present density values within the standards [17]. This indicates that they have been produced and stored in suitable conditions. Only the palm oil sample has high values of density (0.9152 g/mL) compared to the standards. This indicates that the palm oil may have been stored in inappropriate conditions, but it may also be mixed with other oils.

3.2 Refractive index

Refractive index is an important constant of fats because various adulterations can be detected as well as the presence of foreign fats. As known, the refraction ability of fats is conditioned by their physico-chemical properties. In particular, the refractive index depends on the structure of the fatty acids that make it up. It has been found that with the increase in the molecular mass of fatty acids, unsaturated bonds as well as the presence of hydroxyl groups, the ability to refract light increases [13].

Figure 2 below shows the average values of the refractive index for the analyzed vegetable oil samples, to see the difference of this parameter between them.

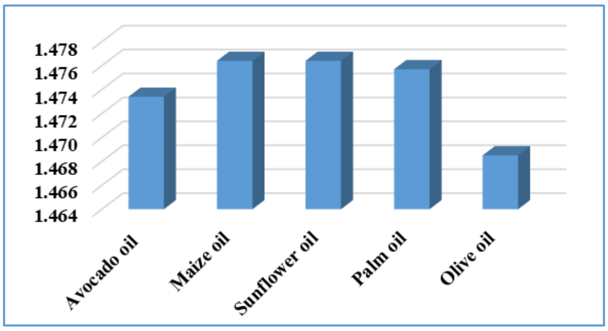

Figure 2. Distribution of refractive index values for 5 oil samples

From the data obtained, the corn and sunflower oil samples have the highest refractive index. Olive oil and palm oil have the lowest refractive index. The different values of the refractive index indicate that the oils consist of different amounts of fatty acids. We can conclude that olive oil has refractive index values (1.4685) within the standards [17]. This shows that the olive oil has been saved under suitable conditions and has not been mixed with other oils. The values of other oils are different from the required standards respectively: avocado oil (1.4734), maize oil (1.4764), sunflower oil (1.4764), and palm oil (1.4757).

3.3 Acid value

Free acidity is the oldest parameter used to evaluate oil quality. Acidity in oil means the degree of rupture of ester bonds in triacylglycerol molecules, as a result of hydrolysis (lipolysis) releasing free fatty acid molecules. Usually, every fat contains a certain amount of free fatty acids. In general, fresh fats do not contain free acids or are present in small amounts. The increase in the content of free fatty acids in fats comes as a result of hydrolytic breakdowns of glycerides, which arise if the fat is not stored in suitable conditions. In the Figure 3 are presented the acidity values for the 5 samples taken in the analysis [14].

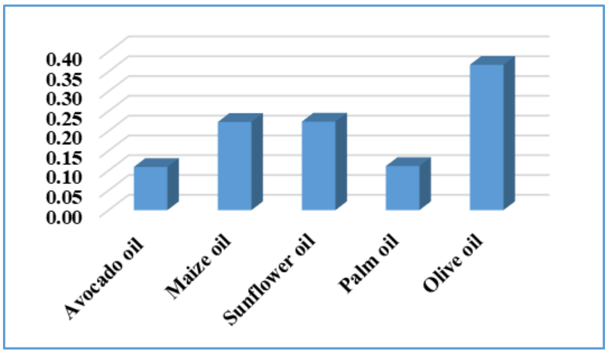

Figure 3. Distribution of free acidity values (mg KOH/g) for 5 oil samples

The acid value for all edible oils were below 0.6 mg KOH/g. Acid value is often used as a general indication of the condition and edibility of the oil. As we noticed, the olive oil sample has higher acidity value compared with others. The acid value of the olive oil compared to the standards shows that the analyzed oil is extra virgin oil. All samples have acidity within the standards and this indicates that these oils are produced from quality raw material and packaged in more suitable conditions.

3.4 Saponification value

The determination of the number of saponification is based on the breakdown of the fat into its components in glycerol and fatty acids. Fatty acids bind to potassium hydroxide to form soap. Determining the number of saponification is important for distinguishing different fatty substances as well as for distinguishing mixtures of unsaponifiable substances such as mineral oils, etc. The presence of unsaponifiable substances reduce the number of saponification. It is a measure of the average molecular weight (or chain length) of all the fatty acids present in the sample in form of triglycerides. The higher the saponification value, the lower the fatty acids average length, the lighter the mean molecular weight of triglycerides, and vice versa [15, 19].

Distribution of saponification values is shown in Figure 4.

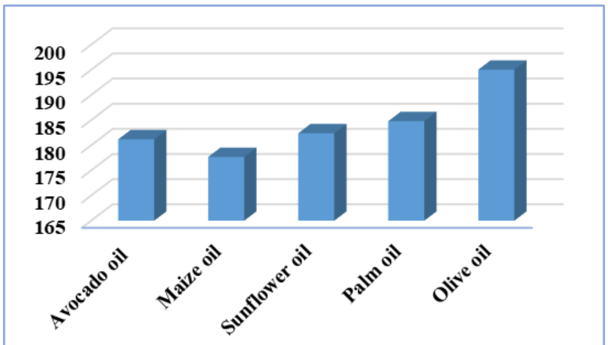

Figure 4. Distribution of saponification values (mg KOH/g oil) for 5 oil samples

It is noted that in maize oil, sunflower oil and palm oil have lower number of saponification compared to the FAO/WHO recommendations respectively: maize oil (177.68 mg KOH/g), sunflower oil (182.39mg KOH/g) and palm oil (184.80 mg KOH/g). This depends on the variety of fruit that was used, it also indicates the presence of unsaponifiable substances such as mineral oils or mixtures with waxes.

3.5 Peroxide value

Peroxide value is a parameter that increases and depends on storage conditions (acceptance of oxygen, light, temperature, and storage time). After reaching a maximum value, the value of peroxides decreases due to the formation of secondary products, typical of rancidity (bittering of fats) [16, 18].

This is an indicator of primary oxidations that have occurred, forming peroxide compounds, and indicates the age of the oil. Estimation of the degree of oil oxidation is based on the determination of both primary and secondary oxidation products. The primary stage of oxidation is the formation of peroxides from fatty acids through a radical mechanism. The analysis is performed by an iodometric procedure, which involves dissolving the oil in a mixture of acetic acid-chloroform, and adding potassium iodide solution. The iodine formed is titrated with sodium thiosulfate solution.

Peroxide values are shown in Figure 5.

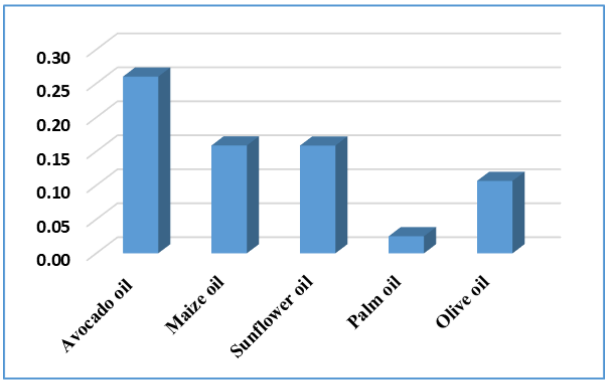

Figure 5. Distribution of peroxide values (meq O_2/kg) for 5 oil samples

From the measurements obtained, all the samples have values of peroxides less than maximum set by international organizations [17]. So we can say that these oils are not oxidized, because they do not contain many free radicals or they contain antioxidants that absorb these free radicals, thus preventing the oxidation. We can also say that the oil has been stored in suitable temperature conditions and in the dark, so it has not been exposed to natural and artificial light sources.

4. Conclusions

- Starting from the results obtained from the physico-chemical analyses, we can say that not all types of oils that were taken to be analyzed are within the limits allowed by international standards, for certain parameters. Olive oil and avocado oil were the oils that had most of the physical-chemical parameters analyzed within the parameters allowed by international standards. If we were to make a comparison between different types of oils, we can say that the palm oil sample, based on the values obtained during the experimental work, can be mixed with other oils. This can be seen from density value, refractive index and saponification number. The value of the olive oil compared to the standards shows that the analyzed oil is extra virgin oil. The samples of avocado oil, olive oil and sunflower oil have acidity within the standards and this indicates that these oils are produced from quality raw material and packaged in more suitable conditions.

- The palm oil sample has higher acidity than the standard values and this shows that the conditions of obtaining (so, the raw material was not of good quality) and storage were not suitable. In conclusion, we can state that how edible oils are stored is crucial. It is advised against reusing frying oil since heat alters the structure of the carbon chains, endangering arteries and resulting in arteriosclerosis.

5. References

[1] O'Brien D. R. (2009). *Fats and Oils* (3rd Ed.). CRC Press, Boca Raton, USA, pp. 2-52.

[2] Artaud J. O., Pinatel C., Durbec J., Gue're M. (2006). *Differentiation of French virgin olive oil RDOs by sensory characteristics, fatty acid and triacylglycerol compositions and chemometrics*. Food Chemistry, 97, pp. 382-393.

[3] Lee D., Lee E., Kim H., Kim S., Kim K. (2001). *Reversed phase liquid chromatographic determination of triacylglycerol composition in sesame oils and the chemometric detection of adulteration*. Analytical Chemical Acta, 429, pp. 321-322.

[4] Schultz E., Pugh E. M. (2001). *Determination of the fatty acid content of biological membranes*. Journal of Chemical Education, 78, pp. 944-946.

[5] A.O.A.C. (2000). *Official Methods of Analysis* (17th Ed.). Association of Official Agric. Chem., Washington, USA.

[6] Salvador M. D., Aranda F., Gomez-Alanso S., Fregapane G. (2003). *Influence of extraction system, production year and area on cornicabra virgin olive oil: A study of five crop seasons*. Food chemistry, 80, pp. 359-366.

[7] Rotondi A., Bendini A., Cerretani L., Mari M., Lercker G., Toschi G. T. (2004). *Effect of olive ripening degree on the oxidative stability and organoleptic properties of cv. Nostrana di Brisighella extra virgin olive oil*. J. Agric. Food Chem., 52, pp. 3649-3654.

[8] Henna Lu F. S., Tan P. P. (2009). *A Comparative study of storage stability in virgin coconut oil and extra virgin Olive oil upon thermal treatment*. International Food Research Journal, 16, pp. 343-354.

[9] Waltking A. E., Wessels H. (1981). *Chromatographic separation of polar and nonpolar components of frying oils*. Journal of the Association of Official Analytical Chemistry, 64, pp. 1329-1330.

[10] Romero A., Bastida S., Sánchez-Muniz F. J. (2006). *Cyclic fatty acid monomer formation in domestic frying of frozen foods in sunflower oil and high oleic acid sunflower oil without oil replenishment*. Food Chem. Toxicol., 44, pp. 1674-1681.

[11] Siddique B. M., Anees A., Ibrahim M. H., Sufia H., Rafatullah M., Rafatullahb M., Omar A. K. M. (2010). *Physico-chemical properties of blends of palm olein with other vegetable oils*. Grasas y Aceites, 61, pp. 423-429.

[12] Codex Alimentarius. (1999). Codex Stan. 210-1999: Codex standard for vegetable oils amended in 2005, and 2011. Codex Alimentarius, Rome, Italy.

[13] Aparicio R., Roda L., Albi M. A., Gutiérrez F. (1999). *Effect of various compounds on virgin olive oil stability measured by Rancimat*. J. Agric. Food Chem., 47, pp. 4150-4155.

[14] International olive council. (2019). *COI/T.15/NC No 3/ Rev.15: Trade Standard applying to olive oils and olive pomace oils*. IOC, Madrid, Spain.

[15] Abdulkarim S. M., Myat M. W., and Ghazali H. M. (2010). *Sensory and physicochemical qualities of palm olein and sesame seed oil blends during frying of banana chips*. Journal of Agricultural Science, 2, (4), pp. 18-29.

[16] Freeman I. P., Melnikov M. S. (2005). *Margarines*. In: Elvers B. (Ed.), Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, Germany.

[17] AOCS. (2012). *Official methods and recommended practices of the American Oil Chemist Society: Fats and Oils* (6th Ed.). AOCS, Urbana, USA.

[18] Ranelli A., De Mattia G., Ferrante M. L., Giansante L. (1997*) Incidence of olive cultivation area on the analytical characteristics of the oil*. Notel - La Rivista Italiana Della Sostanze Grasse, 115, pp. 501-508.

[19] Schumann K., Kurt Siekmann K. (2005). *Soaps*. In: Elvers B. (Ed.), Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, Germany.