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# An investigation on Libyan olive oil in the western region

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## Abstract

Thirteen Olive oil samples were collected from five different places in the western Libyan region with different cultivation periods. The physical and chemical properties of samples were investigated and classified whether they comply with the Libyan standard specification number 8/2002 or not. The density and refractive index of almost all samples were found within the normal range (0.908-0.919) and (1.4688-1.4705) respectively whereas the chemical properties showed a range of fluctuated values such as peroxide number (11.20-60.40), acidity value (0.737-17.94), saponification number (185.34-199.65), esterification number (173.84-194.36) and iodine number (71.00-94.10). A third of the investigated samples are considered to be of good quality mainly the newer samples

***Keywords:*** *Olive oil, Iodine value, Acid number, peroxide number.*

# 1. Introduction

In many parts of the plants, seeds in particular contain oils, whereas Olive oil is obtained from the fruit of the tree *Olea europea*. Olive oil is well known in the Mediterranean basin and is considered as an economically important crop constituting the Mediterranean diet to a great extent.[1] Olive oil is a healthy edible oil, increasingly popular food produced worldwide, over three million tons are produced annually most of which are produced in Spain, Italy and Greece.[2] . Legally olive oil is classified into several categories which are further subdivided, mainly virgin olive oil (VOO) and olive-pomace oil (OPO). VOO is obtained simply by physical processes excluding any changes in the oil particularly thermal. This category includes extravirgin olive oil (EVOO) (% oleic acid <0.8g/100g), ordinary VOO (max acidity 3.3g/100g), lampanite (LVOO) subjected to refining (acidity >3.3g/100g). On the other hand oil extracted with organic solvents from the mills waste solids is classified as crude olive-pomace oil. Other commercial oils include olive oil (OO) formed by mixing VOO with refined Olive Oil in different proportions (max. acidity (1g/100g) and olive-pomace oil (OPO) resulted by mixing VOO with refined pomace oil.[3]. Most edible oils are similar in many respects, but a few factors have significant effects on the oil characteristics. Different grades of olive oil are available, each differing in flavor and quality depending on olive type, growing region, fruit maturity and the process of extraction. For example, olives when handled by the farmer may control the quality of the olive oil such as storage, harvest period and conditions of olives (bruising or damage of fruit).[4] Depending on olive processing method, olive oil is classified into three major types: extra virgin olive oil, virgin olive oil and lampanite olive oil.[5a, 5b]. The main components of olive oil are fatty acids with carbon chains C16 or C18. Most edible oils have an even number of carbons although olive oil contains a small proportion of odd number fatty acid C17. The number of carbon atoms will determine the physical properties of oils whether they are volatile (C4), solids at room temperature (palmitic acid, C16) or liquids (oleic acid, C18). Fatty acids may be saturated or unsaturated, bound in groups of three with a unit of glycerol, known as triglycerides (TAG's). About 95-98% of olive oil consists of TAG's the remaining may be phenolics and sterols which are responsible for giving olive oil its unique flavor and contribute greatly to the nutrition benefits. Olive oil with high phenolic content has a better shelf-life than oil with lower phenolic content.[4] Hydroxytyrosol, oleuropein are the main phenolics in olive oil having antioxidant activity[6]. Free fatty acids 'acidity' in olive oil are particularly important in determining the quality of the oil, based on extent of TAG's breaking down into free fatty acids (hydrolysis or lipolysis). Many factors play a significant role in this process such as status of the olives, bruised or damaged during harvesting, fungal disease in the olives and careless extraction methods. It has been reported that the legal limit of 0.8% for extra-virgin olive oil is not very demanding. A good oil should have a free acidity value less than 0.5% and an excellent oil less than 0.3%.[7]. Almost 75% of olive oil is oleic acid, the monounsaturated fatty acid, which plays an important role in cancer prevention and increases the shelf life of olive oil.[6]

# 2. Materials and methods

### *2.1 Samples*

Samples (13) of virgin olive oil have been investigated in this study from different cities in the western region of Libya as shown in table 1. These oils were produced between 2007-2015 and collected from individuals.

### *2.2 Reagents*

All chemicals and reagents were analytical grade unless mentioned. Phenolphthalein indicator, starch, hydrochloric acid, sodium carbonate, sodium hydroxide, phloroglucinol, glacial acetic acid, chloroform, potassium iodide, sodium thiosulphate, potassium hydroxide, Hanus reagent.

### *2.3 Analytical Methods*

The physical and chemical properties of the samples have been investigated such as: *relative density* (AOCS 28003), *refractive index*, *rancidity* (Hart and Fisher 13-18, P301), *turbidity* (AOCS 28.116), *peroxide number* was determined by directly titrating the oil in acidic medium against standard sodium thiosulphate solution (AOAC 28022), *acidity* was determined directly by titration of oil against alcoholic potassium hydroxide standard solution (AOCS Ca 5a-40), *saponification value* is determined by titration of oil sample after refluxing with alcoholic potassium hydroxide solution against standard hydrochloric acid solution (AOAC 28025) and *iodine value* by titrating treated oil sample with Hanus reagent against sodium thiosulphate in the presence of potassium iodide (AOCS Cd 1-25) according to standard methods of analyses as stated above.

**Table 1.** locations and year of production of the studied samples

| No. | Location | Year of production | No. | Location | Year of production |
|---|---|---|---|---|---|
| 1 | Kikla | 2012 | 8 | Gaser Khyar | 2015 |
| 2 | Kikla | 2013 | 9 | Ein Zara Tripoli | 2013 |
| 3 | Garian | 2013 | 10 | Ein Zara Tripoli | 2015 |
| 4 | Garian | 2014 | 11 | Al-Zawia | 2007 |
| 5 | Garian | 2015 | 12 | Al-Zawia | 2013 |
| 6 | Gaser Khyar | 2013 | 13 | Al-Zawia | 2015 |
| 7 | Gaser Khyar | 2014 | | | |

## 3. Results and Discussions

The physical properties of the analyzed samples are summarized in table 2, indicating that the density and refractive index of all samples are within the acceptable range. The chemical properties of the analyzed samples are summarized in table 3, showing fluctuated results. Samples from Garian showed acceptable peroxide values for two samples and the older sample (2013) exceeded the limit by 1.5 times, in contrast to that of the iodine values which was higher in the newer (2015) sample. Although the acidity value increased by storage time all showed acceptable values, the saponification number all are within the limited range. From figure 1 the overall Gaser khyar samples may not be classified as good quality, all showed high peroxide number and the acidity value was high in 2013 and 2015 samples whereas 2014 sample was acceptable. The iodide number is out of range for samples produced in 2013 and 2014 but acceptable in 2015 sample. While the saponification value was high for the older sample (2013) with about 0.8%. Al-Zawia samples showed poor results and may not be classified as good samples according to the Libyan standard specifications, the 2015 produce showed high acidity whereas the 2013 produce showed high peroxide number. Einzara 2015 produce showed good results and can be classified as virgin oil. Whereas the 2013 produce showed high iodine, acidity and peroxide number. Kikla samples both showed high peroxide number this may be due to long term storage since they are cultivated in 2012 and 2013. As shown in figure 1 the maximum value of peroxide number was Gaser khyar 2013 produce (60.40) while the produce of Garian 2015 showed the lowest peroxide number. The highest iodine number was for Garian 2015 while Gaser khyar 2013 showed the highest saponification value (197.45). Gaser khyar 2013 sample can be classified as poor quality olive oil due to its deviation from the Libyan standard specification for almost all the performed measurements.

On comparison of the results obtained according to their year of production as shown in the figures below one can deduce the following: Figure (2) shows that almost all samples showed high peroxide number except for those of the newer produce 2015 and 2014 Garian samples, Al-Zawia 2015 and Ein zara 2015.

**Table 2.** Physical properties of the analyzed samples.

| Test & limit / Sample | Density | Refractive index |
|---|---|---|
| | 0.910-0.916 | 1.4705-1.4677 |
| Garian2015 | 0.912 | 1.4700 |
| Garian2014 | 0.912 | 1.4700 |
| Garian2013 | 0.911 | 1.4700 |
| Gaser Khyar 2015 | 0.909 | 1.4692 |
| Gaser Khyar 2014 | 0.910 | 1.4693 |
| Gaser Khyar 2013 | 0.908 | 1.4695 |
| Al-Zawia 2015 | 0.912 | 1.4688 |
| Al-Zawia 2013 | 0.909 | 1.4688 |
| Al-Zawia 2007 | 0.914 | 1.4689 |
| Ein zara 2015 | 0.911 | 1.4700 |
| Ein zara 2013 | 0.919 | 1.4701 |
| Kikla 2013 | 0.913 | 1.4700 |
| Kikla 2012 | 0.912 | 1.4700 |

**Table 3.** shows the chemical properties of the analyzed samples.

| Test & limit / Sample | Peroxide value | Acidity value | Saponification number | Esterification value | Iodine value |
|---|---|---|---|---|---|
| | 20 | 6.6 | 182-196 | - | 75-94 |
| Garian2015 | 11.20 | 0.737 | 185.34 | 184.60 | 97 |
| Garian2014 | 12.39 | 1.25 | 190.53 | 189.28 | 94.10 |
| Garian2013 | 29.26 | 2.50 | 189.40 | 186.9 | 85.26 |
| Gaser Khyar 2015 | 22.44 | 9.13 | 187.31 | 178.18 | 84.35 |
| Gaser Khyar 2014 | 56.38 | 1.6 | 191.27 | 189.67 | 71.69 |
| Gaser Khyar 2013 | 60.40 | 12.42 | 197.45 | 185.05 | 71.00 |
| Al-Zawia 2015 | 15.77 | 16.21 | 190.05 | 173.84 | 75.01 |
| Al-Zawia 2013 | 31.38 | 4.96 | 192.55 | 187.59 | 77.80 |
| Al-Zawia 2007 | 39.43 | 11.33 | 199.65 | 188.32 | 70.22 |
| Einzara 2015 | 19.05 | 1.71 | 186.2 | 184.49 | 83.61 |
| Einzara 2013 | 33.79 | 17.94 | 193.29 | 175.35 | 69.51 |
| Kikla 2013 | 31.38 | 2.74 | 197.10 | 194.36 | 77.21 |
| Kikla 2012 | 47.13 | 13.16 | 194.40 | 181.24 | 73.6 |

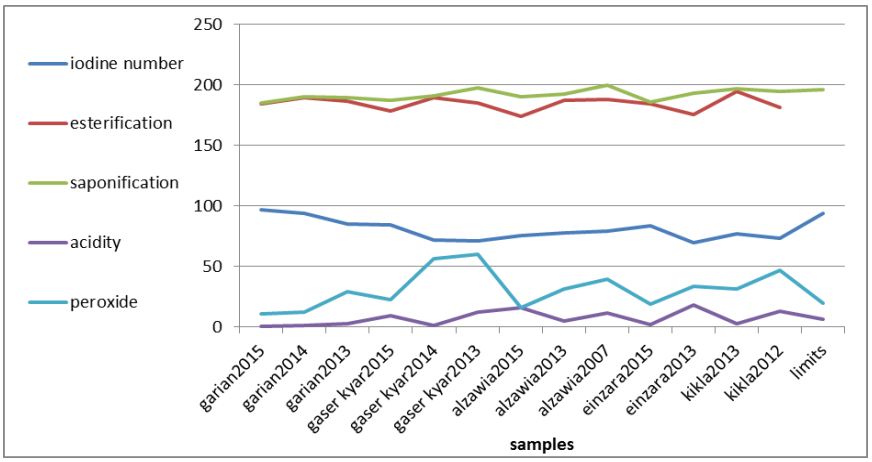


**Figure 1.** Overall result obtained for the investigated olive oil samples

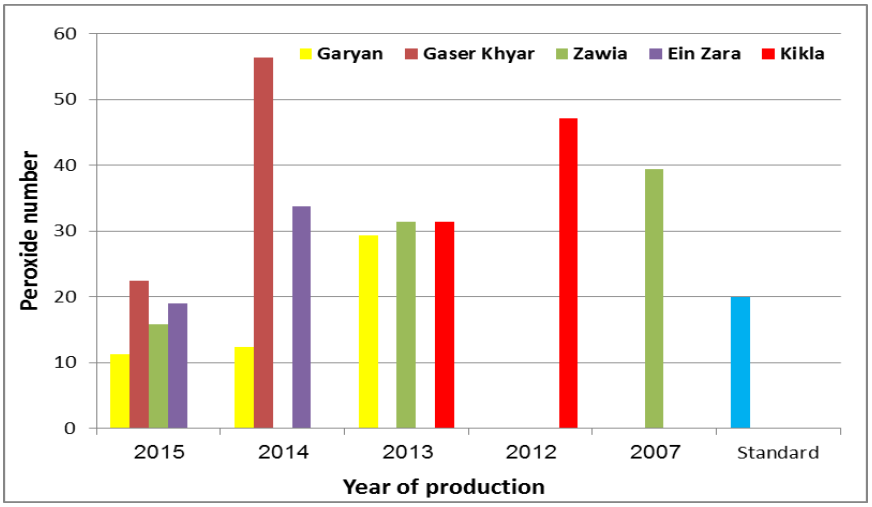


**Figure 2.** peroxide number in the olive oil samples in different sites

According to figure 3 all three samples taken from Garian region showed acceptable acid number in addition to Ein zara 2015, Al-Zawia 2013, Gaser khyar 2014 and Kikla 2013 samples.

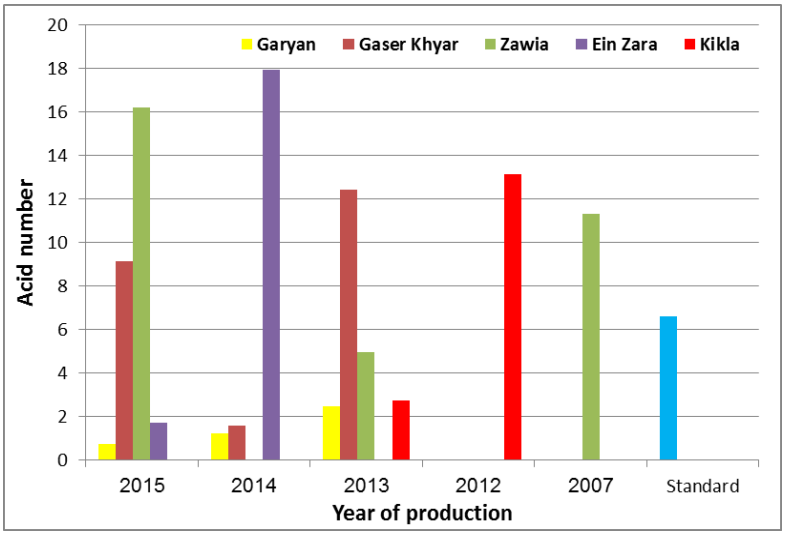


**Figure 3.** acid number in the olive oils samples in different sites

In accordance to figure 4 almost all samples showed consistent values to those of the limited range in terms of saponification number apart from the very old produce of 2007, Gaser khyar 2013 and Kikla 2013 and may be considered as acceptable values. From figure 5 it is observed that 4 samples showed iodine value lower that the limited range, while one sample showed higher value than the maximum limit.

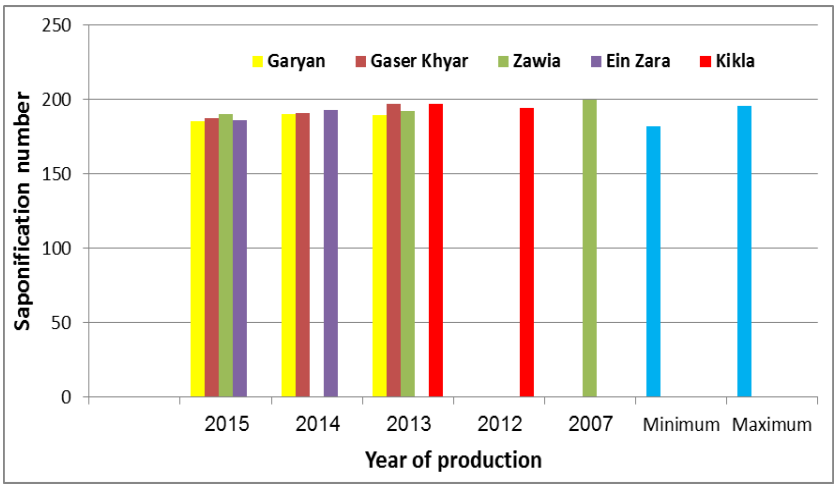


**Figure 4.** saponification number in the olive oil samples in different sites

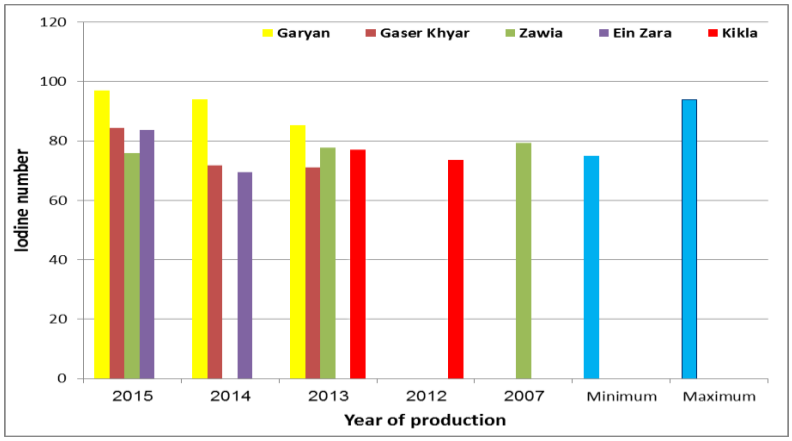


**Figure 5.** Iodine number in the olive oil samples in different sites

The results of physicochemical properties in this work demonstrate that typically on taking the produce of 2013 for example, it is clear that the acidity of samples from mountaneous regions (Garian, Kikla) showed better results than the coastal regions (Gaser khyar, Ein Zara and Al-Zawia) with a trend of 2.5, 2.74, 4.96, 12.42, 17.94 for the regions Garian, Kikla, Al-Zawia, Gaserkhyar, Ein Zara respectively. More than half the samples (54%) are considered to be acceptable according to Libyan standard specification regarding the acidity value. While 31% of the samples complied with the Libyan standard specifications regarding the peroxide value, i.e only 4 samples out of 13 are accepted representing the samples Garian 2015(11.20), Garian 2014 (12.39), Al-Zawia 2015 (15.77), Ein Zara 2015 (19.05). Whereas the saponification number and iodide numbers showed 77% and 62% of the samples that are consistent and comply with the Libyan standard specifications. Only 15% of the samples may be classified as good quality virgin olive oil, specifically the Garian 2014 and Ein zara 2015 which showed excellent results of all the measurements. This may be explained mainly due to the poor storage of the oil samples and the conditions at which the olives are processed.

## 4. Conclusion

From the obtained results it is clear that the longer the period of storage of the oil the more its susceptibility to deterioration. For example, the peroxide value was found to increase with storage time of all oil samples, since the peroxide value is a measure of the extent to which rancidity reactions have occurred during storage. Previous studies reported that storage techniques for olive oil are very important to prevent it from rancidity and preserve its delicate taste. Olive oil if properly stored can be kept for years without undergoing rancidity.[8] The best storage containers for olive oil are tinted glass, ceramic, porcelain or stainless steel.[9] Storage is very important in olive oils since rancid oils may cause cellular damages and have been associated with diabetes, Alzheimer`s disease due to free radial formation as well as cancer fostering, damaging to DNA and accelerates aging.[8] Accordingly, local farmers, cultivators and consumers should be aware of the importance of storage and conditions required for keeping olive oil safe without undergoing rancidity to prevent people from getting affected rather than being healthy.

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