Journal of Physical Science, Vol. 25(1), 33–43, 2014

Storage Age Dependence of Olive Oil Acidity in Different Locations in Palestine

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Abstract: *The acidity of olive oil samples from different locations and of different storage ages was measured on a yearly and weekly basis. In this work, the overall results of olive oil acidity as a function of storage age on a yearly basis indicate deterioration of oil quality. The acidity results for some olive oil samples suggest that the oil can be stored for a period of not more than 12 years without deterioration. The overall results from measuring on a weekly basis indicate that the acidity increases incrementally as a function of storage age. The relationships between the acidity and storage age were described by fitting the data to equations.*

Keywords: Acidity of oil, storage ages, olive oil, fitting equations, effect of acidity

1. INTRODUCTION

Acidity is the oldest parameter used for evaluating olive oil quality, because it is closely related to the quality of raw material and reflects the extent of hydrolytic activities. The excellent quality of virgin olive oil is the culmination of a process that begins with the tree and ends in the bottle. Thus, it is necessary to care for each step of the process and the factors that can affect its commercial life (oxygen, light, temperature and metals) and lead to deterioration in quality as a consequence of oxidative and hydrolytic degradation.

Similar to other products that are produced within a limited period of time—but consumed throughout the year—olive oil must be stored, and these storage and packing conditions will determine the commercial life of the olive oil. Moreover, hydrolysis during storage, especially a partial loss in the minor constituents, is considered primarily responsible for its beneficial health effects.[1] To assess the role of the different modes of storage on the quality of olive oil, the literature concerning the analytical definition of the quality and composition of stored oils was critically reviewed.

There have been some data published on the effect of olive storage before oil extraction.[2–4] For instance, in a study by Nabil et al.,[2] two Tunisian cultivars of olive oil, i.e., Chemlali and Chetoui olive fruits, were stored for different periods of time before oil extraction. The results showed that fruit storage led to deterioration of the oil quality parameters, such as acidity, and that this deterioration was more rapid in the Chemlali oils than in the Chetoui cultivar.[2] The effect of machinery groups, packing materials and light intensities on the extra virgin olive oil (EVOO) quality indexes were studied, where EVOO for one season of olive harvesting was stored for sixth months. The acidity was affected by the type of machinery and packing material.[3] In addition, the influence of olive storage period on oil quality was studied by Pereira et al.[4] The results confirm that storage of the fruits reduces the olive oil quality. Acidity indicates a progressive deterioration of oil quality as the fruit is stored.[4]

The effect of some storage conditions and packaging material on olive oil quality and on EVOO quality was studied by several authors.[3–7] Changes in oil quality are also reflected in the standardised quality indices. Dabbou et al. studied the effect of packaging materials on the quality of EVOO as a function of storage time (0 to 12 months).[5] The results show that quality indexes were strongly influenced by the type of packaging material and the time of storage, whereas free fatty acids increased with storage time.[5] Another study by Falque et al. corroborates those findings. In the Falque et al. study,[6] four commercial samples of EVOO were analysed to evaluate the influence of storage time on quality. The quality parameters were determined after 3 and 6 months of storage. The results showed a gradual loss of quality during storage that included increases in acidity.[6]

In their study, Bouaziz et al.[7] analysed olive oil samples to evaluate the influence of storage time on oil quality. Six months of storage at 50ºC in the dark revealed a loss in oil stability. This finding was reflected by an increase in the peroxide value and a decrease in sterol content. During oil storage, as in the study, no significant variation in fatty acid composition was observed.[7]

Chemical analyses such as acidity, peroxide value, specific extinction coefficient at 232 and 270 nm, fatty acid composition, pigments, total phenols, oxidative stability and others were carried out by numerous researchers to evaluate the effect of storage age on oil quality. The results showed that quality indexes were strongly influenced by storage time.[2–7]

It has been known that olive oil quality and behaviour can be influenced by the cultivars, the degree of ripeness, and the industrial processes employed for oil extraction, as well as environmental conditions (mineral nutrition, room temperature, light and availability of water) and cultural practices.[2,4]

The main goal of this work was to study the dependence of the acidity of olive oil samples from different locations in Palestine on storage age. The relationship between acidity and storage age will be described by fitting equations.

2. EXPERIMENTAL

The acidity of olive oil samples from different locations, namely Jeet (L_1), Saida (L_2), Al-Yamun (L_3), Beita (L_4), Jenin (L_5), Arraba (L_6), Meithaloon (L_7) and Asira Al-Shamaliyeh (L_8), and of different storage ages were measured using the titration method. The acidity of the oil was determined using the recommended official method.[8]

The acidity of olive oil samples (2010) from three locations [Meithaloon (L_7), Al-Yamun (L_3) and Beita (L_4)] were measured weekly during the period from June 2011 till January 2012. The experimental data were fitted, and the correlation constants of the best fit were estimated.

2.1 Quality of Olive Oil

According to the International Olive Oil Council (IOOC),[9] virgin olive oil is the oil obtained from the fruit of the olive tree solely by mechanical or other physical means under conditions that do not lead to alteration of the oil, which cannot undergo any treatment other than washing, decantation, centrifugation or filtration, to the exclusion of oils obtained using solvents or using an adjuvant that has a chemical or biochemical action.[9]

2.2 Free Fatty Acids Percent (%FFA) or the Acidity

The "acidity" in olive oil is the result of the degree of breakdown of triacylglycerols due to a chemical reaction called hydrolysis or lipolysis, where "broken off" fatty acids, called free fatty acids (FFAs), were formed. Table 1 shows the maximum levels that have been established by the IOOC for each category.[9]

Table 1: Limits of free fatty acid concentration, as oleic acid percent, established by the IOOC for each olive oil category.

Category	FFA%
Extra virgin olive oil	≤ 0.8
Virgin olive oil	≤ 2.0
Ordinary virgin olive oil	≤ 3.3
Lampante oil	>3.3
Refined olive oil	≤0.3

Oils obtained from healthy fruits, regardless of the cultivar, that are processed just after harvesting show very low values of free acidity that are well under 0.5% FFA. If fruits are damaged, hydrolytic enzymes become active and the free acidity of the oil slightly increases. The increase in acidity might also be due to delay between harvesting and extraction (especially if the fruit has been bruised or damaged during harvesting). The prolonged contact between oil and vegetation water after extraction increases the acidity. Careless extraction methods, as well as storing olives in heaps or silos, will lead to increase in the acidity of the oil. The free fatty acid concentration is thus a direct measure of the quality of the oil and reflects the care taken right from fruit blossoming to the eventual sale and consumption of the oil.[10–12]

3. RESULTS AND DISCUSION

3.1 Statistical Analysis

Some empirical relations were found to describe the storage age-dependent acidity using the MS Excel program. The correlation coefficients for the best fit were estimated. The best fit equation was chosen based on the percentage of average absolute deviation (AAD%) and standard deviation (SD) of the data.[13]

3.2 Olive Oil Crop (2010)

The acidity of olive oil samples from 2010 crop from different locations in Palestine was measured after storage for 5 months. The experimental data are shown in Figure 1.

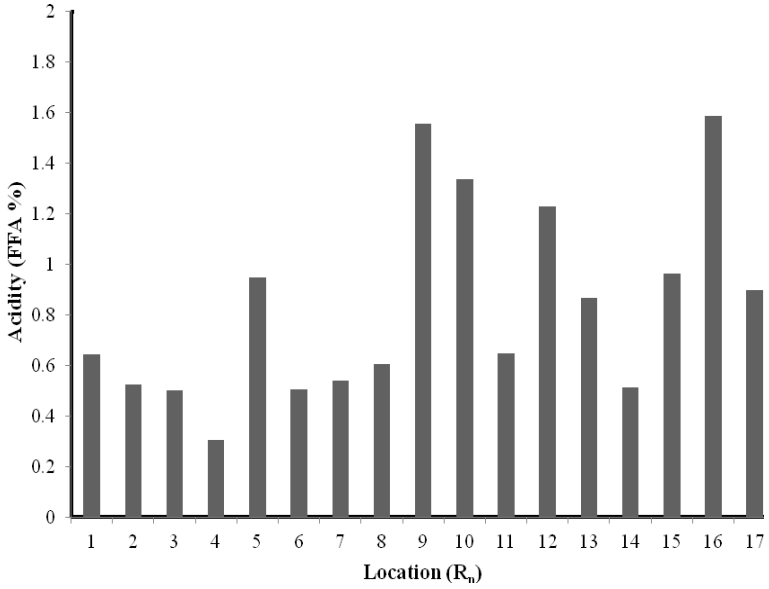

Figure 1: The acidity of olive oil samples of 2010 crop from different locations.

Figure 1 shows most of the olive oil samples of 2010 crop from different locations have an FFA% ≤ 0.65%, which indicates that most of the olive oil samples from crop 2010 from different locations are EVOO (< 0.8% FFA). In contrast, the olive oil samples that have an FFA% between 0.8% and 2% are considered to be virgin olive oil. The acidity of olive oil is influenced by different parameters, such as degree of ripeness, industrial processes employed for oil extraction, the cultivator, altitude, climate and several other factors.

3.3 Storage Age Dependence of Olive Oil Acidity

3.3.1 Yearly basis

The acidity of olive oil samples from four different locations (**L_1**, L_2, L_6 and L_7) with different storage ages was measured. The experimental data are shown in Figure 2. The acidity of the olive oil sample from L_8 (Asira Al-Shamaliyeh), which was stored for 12 years, was measured to be 2.92%.

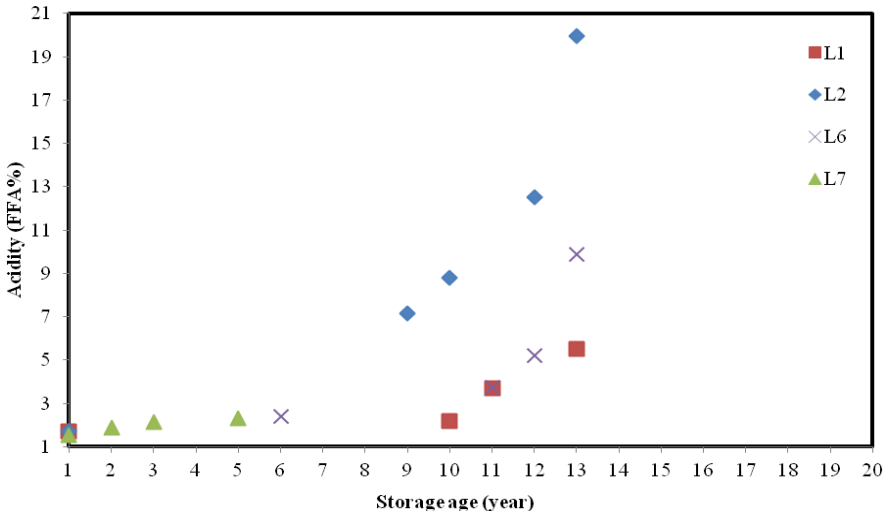

Figure 2: The measured values of acidity of olive oil samples from L_1, L_2, L_6 and L_7 locations as a function of storage age in years.

A multi-constant formula is proposed in this work to obtain a more suitable prediction of the storage age dependence of the acidity of olive oil samples. The AAD% and SD values were evaluated to select the suitable prediction. The experimental values of the acidity of the olive oil samples from L_1, L_2, L_6 and L_7 and of different storage ages were fitted using the following proposed multi-constant formula:

$$acidity(FFA\ \%) = At^2 + Bt + C + De^{Et} \quad (1)$$

where acidity is presented as grams of oleic acid per 100 g of oil, t is the storage age in years, and A, B, C, D and E are constants. The calculated values for A, B, C, D, E, AAD% and SD are given in Table 2.

Table 2 shows that most of the AAD% was 0%. Therefore, the proposed multi-constant formula was adequate to describe the storage age dependence of acidity of olive oil samples.

Table 2: Values of A, B, C, D and E, AAD% and SD using the proposed formula.

Location	A (1/years^2)	B (1/year)	C	D	E	AAD%	SD
L_1	0.0809	–0.8047	2.4088	–1.5000	–10.0000	0.6	0.2
L_2	0.0996	–0.3124	1.9170	5.2346	0.0003	0.0	0.0
L_6	0.4251	–7.0564	29.4518	–29.1479	–10.0000	0.0	0.4
L_7	–0.2093	0.2277	–1.1053	2.0070	0.2647	0.0	0.0

Figure 3 shows the experimental data and fitted curves using Equation 1 for the acidity of olive oil samples from L_1, L_2, L_6 and L_7 as a function of storage age in years.

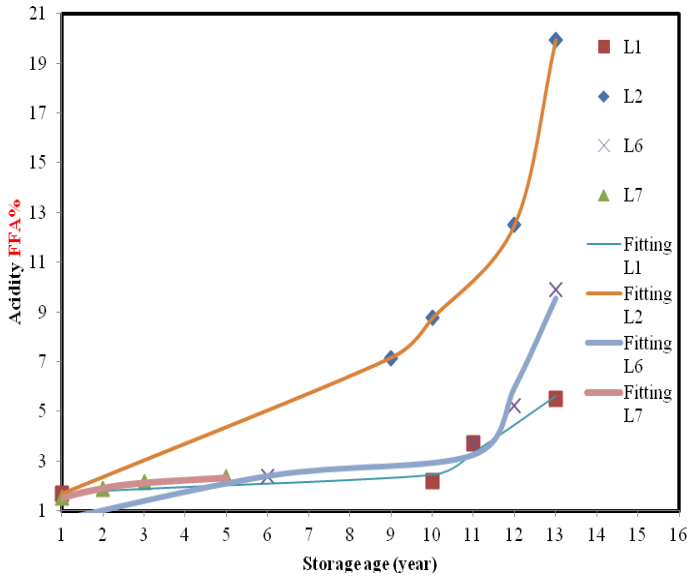

Figure 3: The acidity of olive oil samples from the L_1, L_2, L_6 and L_7 locations as a function of storage age in years. The solid lines represent the predicted values from Equation 1 and the points represent the experimental data.

3.3.2 Weekly basis

The acidity of olive oil samples from three different locations (L_3, L_4 and L_7) was measured at different storage ages on a weekly basis. The experimental data are shown in Figure 4.

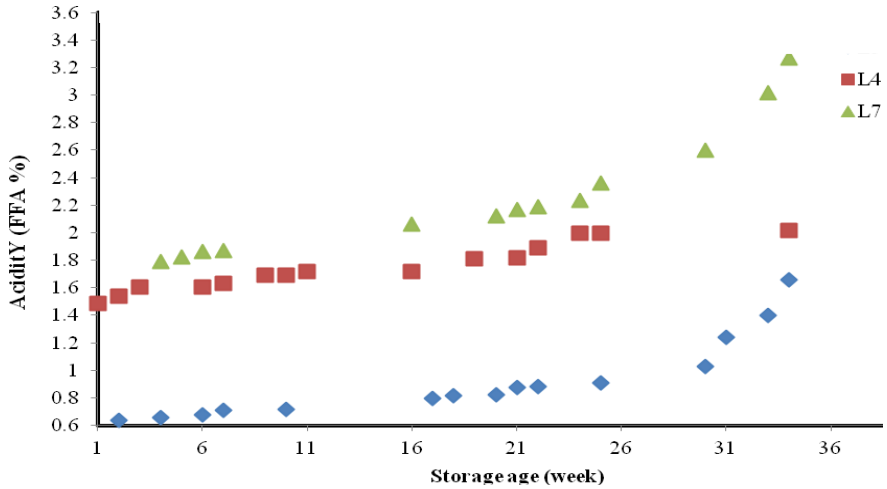

Figure 4: The measured values of acidity of olive oil samples from L_3, L_4 and L_7 as a function of storage age in weeks.

The experimental values of the acidity of olive oil samples from L_3, L_4 and L_7 and of different storage ages were fitted by using a multiple regression formula. The proposed formula is:

$$acidity(FFA\%) = At^{B} + Ct + D + Ee^{Ft} \quad (2)$$

where acidity is presented as grams of oleic acid per 100 g of oil, t is the storage age in weeks, and A, B, C, D and E are constants. The calculated values of A, B, C, D, E, AAD% and SD are given in Table 3.

Table 3: Values of A, B, C, D, E, F, AAD% and SD using the proposed formula.

Location	A (1/week^2)	B (1/week)	C	D	E × 10^{-6}	F	AAD%	SD
L_3	0.4871	0.0290	0.0089	0.1190	8.7517	0.3308	0.0	0.0
L_4	0.2039	–0.0400	0.0192	1.3006	–1.0548	0.3418	0.0	0.0
L_7	0.3102	–0.0431	0.0231	1.4137	7.098	0.3425	0.0	0.0

Table 3 shows that the AAD% was 0%. Accordingly, the proposed formula is adequate for describing the storage age dependence of the acidity of olive oil samples. Figure 5 shows the experimental data and fitting curves using Equation 2 for the acidity of olive oil samples from L_3, L_4 and L_7 as a function of storage age in weeks.

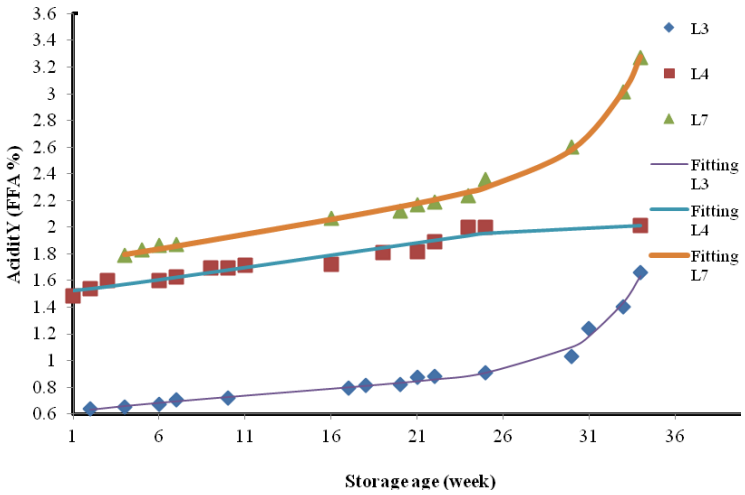

Figure 5: The acidity of olive oil samples from L_3, L_4 and L_7 locations as a function of storage age in weeks. The solid lines represent the predicted values from Equation 2 and the points represent the experimental data.

3.4 Discussion

The data regarding acidity as a function of storage age measured on a yearly basis show that acidity varied as follows: for location L_1, from 0.97% (0-year storage age) to 5.51% (13-year storage age); for location L_2, from 1.70% (1-year storage age) to 19.94% (13-year storage age); for location L_6, from 0.305% (0-year storage age) to 9.89% (13-year storage age) and for location L_7, from 0.90% (0-year storage age) to 2.34% (5-year storage age).

The overall results in this study of the level of acidity as a function of storage age measured on a yearly basis were over the limits established by IOOC ($\geq$ 3.3%). This indicates a deterioration of oil quality as olive oil is stored. The acidity values of some olive oil samples (from L_7) were below the maximum levels ($\leq$ 3.3%) established by IOOC, which suggests that the oil can be stored for a long period (> 12 years) without deterioration.

The results of the acidity level measured on a weekly basis show an increase as a function of storage age in weeks. The acidity levels increased as follows: location L_3 increased from 0.64% (2-week storage age) to 1.66% (34-week storage age); location L_4 increased from 1.48% (1-week storage age) to 2.01% (34-week storage age); location L_7 increased from 1.79% (4-week storage age) to 3.27% (34-week storage age). The overall results from measuring on a weekly basis in this study indicate that the fatty acid levels in the analysed olive

oil samples increased incrementally but within the limits established by IOOC ($\leq 3.3\%$).

The acidity levels of EVOO increased from 0.65% to 0.79% after three months and to 1.03% after 6 months. In their study,[6] Falque et al. found that the initial acidity levels of the EVOO stored in glass bottles was 0.39%, and the acidity levels after three and six months were 0.42% and 0.45%, respectively.[6] The results from the present study are in good agreement with those of Falque et al. The slightly different values from one location to another are most likely due to different parameters that influence the acidity of oil. The degree of ripeness is an important quality factor.[10] Olive oil quality and other properties can be influenced by the industrial processes employed for oil extraction. The acidity increases if the olive fruits are damaged. The main olive pests/diseases in Palestine that damage the fruits are the olive fly and the peacock eye spot. Fruits are also damaged if olives are picked by sticks from the trees. Acidity levels in previous studies[2,4] indicate a progressive deterioration of oil quality as the fruit is stored. Some empirical relations that describe the dependence of the acidity of olive oil on storage age were fitted to the experimental data in the present study. The constants for the best fit were calculated.

4. CONCLUSION

The acidity levels of some olive oil samples (from L_1) suggest that the oil can be stored for a period of not more than 12 years without deterioration. Much research is needed to understand the influence of storage age on other quality factors, such as peroxide index, impurity content (%), phenol content, iodine index, saponification index, fatty acid content, and absorption coefficients K270 and K232. The absorption coefficients K270 and K232 are used as quality factors because absorption at 232 nm is caused by hydroperoxides (primary stage of oxidation) and conjugated dienes (intermediate stage of oxidation). The absorption at 270 nm is caused by carbonylic compounds (secondary stage of oxidation) and conjugated trienes (technological treatments). The degree of oxidation of olive oil is reflected by its specific extinction at 232 nm and 270 nm.

These studies will assist in determining the possible storage age of olive oil without deterioration. In addition, future studies are needed to study the quality parameters as a function of storage age in ideal storage conditions. The ideal storage condition is when each bottle is flushed with nitrogen after filling to remove oxygen, and olive oil must be stone-stored in a temperature range of 16°C–18°C in the dark.

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