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Dedicated to Professor Claude Nicolau
on the occasion of his 80th anniversary

QUALITY EVALUTION OF THE OLIVE OIL DURING STORAGE TIME

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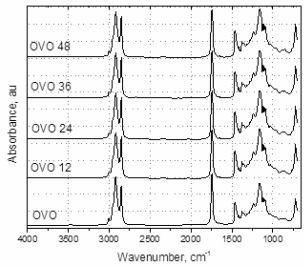
In this paper, the quality of olive oil during storage time has been investigated. Parameters like free fatty acids (FFA), anisidine value (AV), iodine value (IV), saponification number (SN) were studied and identification of the molecular structure through FT-IR method have been made. During storage time (48 months) an increase in the values of parameters FFA and AV took place that measures the oxidative degradation of the oil. The oxidative stability of the sunflower oil samples stored at room temperature was high. However, the acidity of the sunflower oil increases very little during storage time.



INTRODUCTION

Olive oil is one of the oldest known vegetable oils mainly produced in the countries surrounding the Mediterranean Sea. It is obtained from the fruit of the *Olea europea L* tree and it has a unique composition and quality.[1] Olive oil is recognized worldwide for its nutritional value, health benefits, and is appreciated for its aroma and taste.[2] Also, comparative with sunflower oil, olive oil is one of the very few oils that can be consumed only in its natural form, thus preserving all the constituents.

According to the literature, the chemical composition of the olive oil (% w/w) is: myristic 0.1%, palmitic 7-20%, palmitoleic 0.3-3.5%, stearic 1-4%, oleic 56-84%, linoleic 3-21% and linolenic 0.2-1.5% acids.[3] Besides mono-unsaturated fatty acids, olive oil contains phenolic compounds, tocopherol, and carotenoids making the olive oil to be more stable than other edible oils.[4-6] Also, the olive oil contains vitamins, aromas and other components.[7]

Olive oil quality depends on many factors such as: olive tree cultivation, the harvesting, processing and storage time. Furthermore, the most significant factors which affect the olive oil quality after processing and during storage are environmental, temperature, exposure to light and contact with oxygen. Thus, light, oxygen and heat reduce the organoleptic and nutritional properties of the product through oxidation[8].

These reasons explain the opportunity of our study where we investigate the quality of a olive

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oil during storage time. Thus, we monitored the olive oil during 48 months to reveal the changes in their composition in terms of acidity (determination of free fatty acids), lipid oxidation (determination of anisidine value), oxidative rancidity (determination of iodine value and saponification number), identification of the molecular structure (FT-IR method).

EXPERIMENTAL

Materials and method

For this study, refined virgin olive oil commercially available has been used. The samples of the olive oil were stored in bottles at room temperature during the analysis period. Samples of oil were took and analyzed at five time intervals, namely: freshly bought, after 12 months, 24 months, 36 months and 48 months. The samples were denoted as OVO; OVO 12; OVO 24; OVO 36 and OVO 48.

Chemical reagents used for determination of the free fatty acids (FFA), the anisidine value (AV), the iodine value (IV) and saponification number (SN) for the all samples were purchased from Merck.

The free fatty acid (FFA) value in terms of % oleic acid, the saponification number (SN) and the iodine value were determined through methods of analysis detailed in literature.[9] Also, anisidine value was determined by the standard method[10] using a Shimadzu UV-Visible Spectrophotometer. The analyses were conducted in triplicate for each oil sample and the arithmetic averages have been noted in the paper.

FT-IR Analysis

All infrared spectra (4000-650 cm^{-1}) were acquired with a Perkin Elmer Spectrum 100 FT-IR spectrometer. This instrument was equipped with a horizontal attenuated total reflectance (HATR) sampling accessory and ZnSe crystal. HATR accessory was used to collect the spectral data of oil. The resolution was set at 2 cm^{-1} and the number of scans collected for each spectrum was 128. The ZnSe crystal was cleaned with ethanol in between sample runs. Measurements were conducted in duplicate or triplicate for each oil sample and the arithmetic media have been noted in the paper.

RESULTS AND DISCUSSION

Free fatty acid value (FFA)

According literature, the free fatty acidity is a measure of the quality of the oil and reflects the care taken in producing and storage processes of the oil**,** stability of oil and its susceptibility to rancidity.[11] The fatty acids are simple structures made up of long chains of various numbers of carbon atoms. We found that there are only a few types of fatty acids in olive oil, but the proportions of each strongly influence the characteristics and nutritive value of the oil.[12]

The changes in the free fatty acid value (FFA) for all samples during storage time, expressed in terms of % oleic acid are presented in Fig. 1.

According to European Union Commission[13] the free fatty acid value (FFA) expressed in terms of % oleic acid for the olive oil is 1.5%. As can be seen in Fig. 1, the FFA value of the fresh olive oil sample (OVO) is about 0.8% fact which denotes that an oil of high quality has been used in this study. However after 12 months of storage time the FFA is about 3.5% and this value increase continuous which marked the decreasing in its quality.

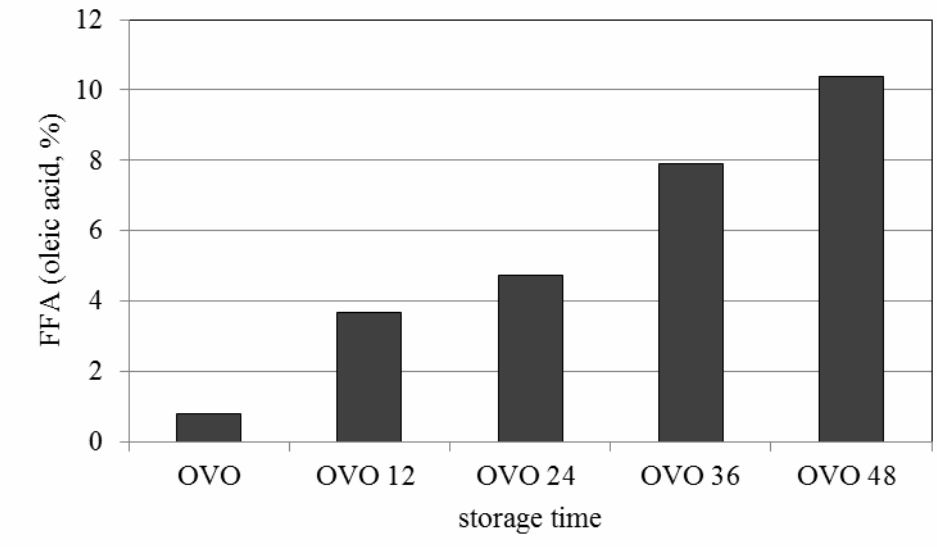

Fig. 1 – The FFA values of olive oil samples during storage period.

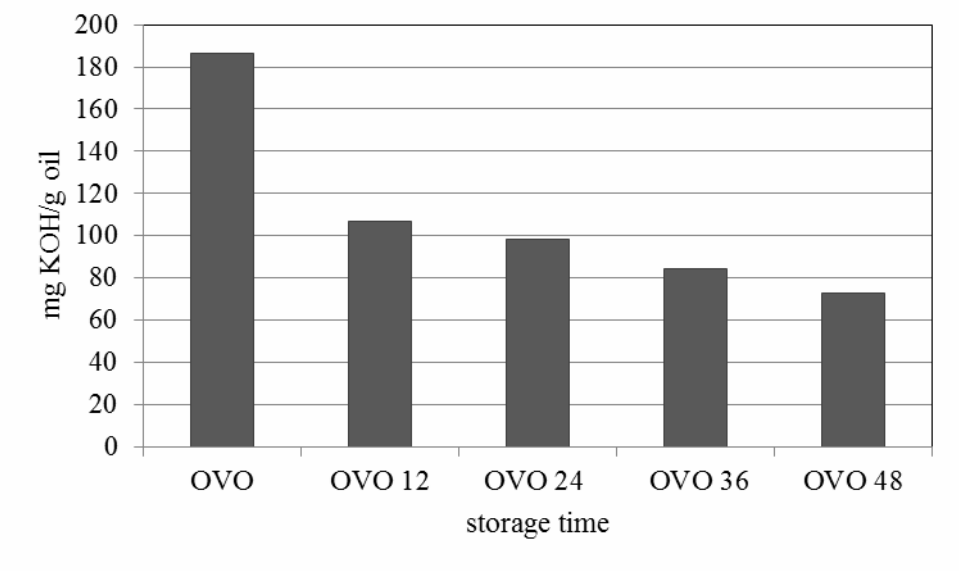

Fig. 2 – The saponification number for olive oil samples during storage period.

The increase in content of free fatty acids should be caused by the action of natural enzymes (for example, lipase) present in the olive fruit, which help the fatty acids to detach from the molecule of triglyceride. The action of lipase produces free fatty acids which are responsible for the acidity of the oil. Also, the same action can be caused by the enzymes produced by microorganisms which grow on the fruit.[11]

The saponification number (SN)

According to the literature, the saponification value is an indication of the molecular weights of triglycerides in oil. Higher saponification value indicates higher proportion of lower fatty acids because saponification value is inversely proportional with the average molecular weight or chain length of the fatty acids. Thus, shorter the average chain length, higher is the saponification number.[14] The saponification number (SN) for the all samples are presented in Fig. 2.

From Fig. 2 it can be observed that the saponification number of the fresh sample (OVO) falls into the permitted standard level (184-196 mg KOH/g oil)[15] which suggest that it contain a high proportion of lower fatty acids. The decreasing below the permitted standard observed for OVO 12, OVO 24, OVO 36, and OVO 48 samples suggest that they have high content of long chain fatty acids hence are unsuitable for soap making and also unsuitable for human nutrition.[16] We can say that increase in content of long chain fatty acids should be caused by some processes which took place in during storage time (*e.g.* oligomerization).

The iodine value (IV)

According to the literature, the iodine value is an indicator of the lipid oxidation and the degree of unsaturation, a great iodine value indicating that the oils are prone to oxidation. Furthermore, the unsaturated character affects the stability of oils and leads to the appearance of degradation effects during storage.[17,18] The iodine value (IV) for all samples are presented in Fig. 3.

As can be seen in Fig. 3, the iodine value of the fresh olive oil sample (OVO) is in the permitted standard level (the standard iodine value of the olive oil is between 75 and 94.[15] The iodine value for other samples (OVO 12, OVO 24, OVO 36 and OVO 48 samples) decreases continuous thus that to the end of the 48 months it is below 40%. This fact can be attributed to the decreasing of the degree for unsaturation of the oil caused by the oxidation process that occurs during storage time.[19]

The anisidine value (AV)

It is well known that the secondary stage of oxidation occurs when the hydroperoxides decompose to carbonyls and other compounds, like aldehydes. These compounds give the oil a rancid smell and they are measured by the anisidine value (AV). The anisidine value (AV) for all analyzed samples are presented in Fig. 4.

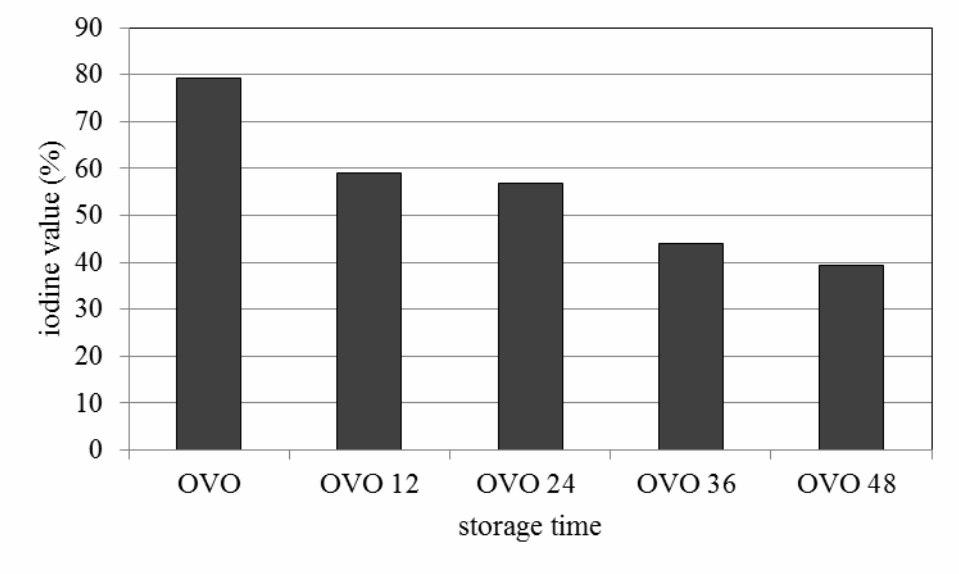

Fig. 3 – The iodine value (IV) for olive oil samples during storage period.

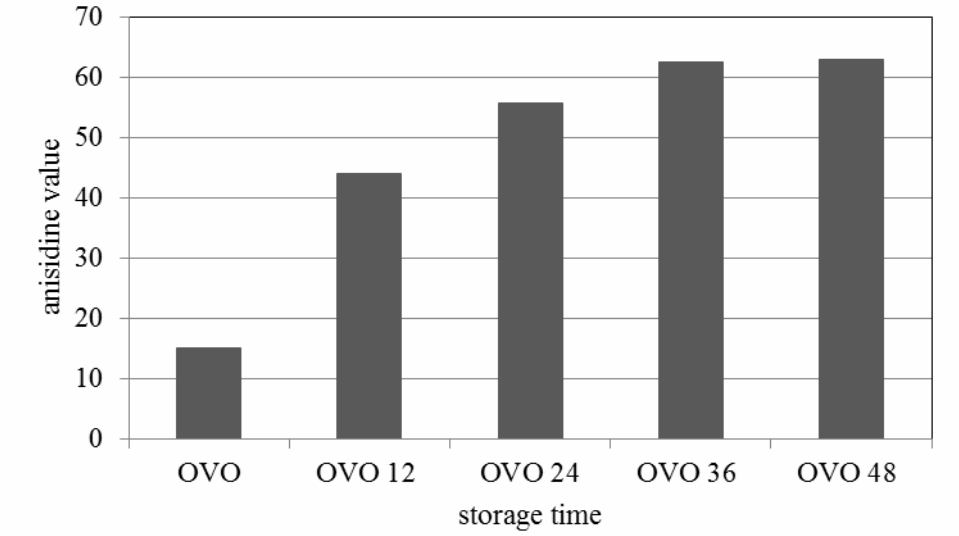

Fig. 4 – The anisidine value (AV) for olive oil samples during storage period.

From Fig. 4, we can see that the anisidine value of the analyzed olive oil increases continuously during the storage, related to the decrease in oil quality in time.[20] This fact can be attributed to the decomposition of hydroperoxides or of a non-volatile portion of the fatty acid that remains a part of the oil. This non-volatile reaction product causes an increasing in the anisidine value.[11]

FT-IR analysis

A study of literature suggests that IR spectroscopy can be considered as a vital technique for identification, analysis, determination of degree of saturation of fatty acids and detection of adulteration of oils of plant origin.[21] The FT-IR analysis for all olive oil samples are presented in Fig. 5.

Fig. 5 shows a representative olive oil spectrum in the 4000-900 cm^{-1} region, exhibiting several characteristic bands which are same or close to those from literature.[22,23] Thus, the peak near 3000 cm^{-1} (for all samples) is assigned to C-H stretching mode from methylene and methyl groups of fatty acid and triacylglycerol. For the OVO 12, OVO 24, OVO 36 and OVO 48 samples intensity peak near 3000 cm^{-1} is low and it can be explained by the CH=CH elongation.[24] The bands between 2922 cm^{-1} (observed in OVO sample) and 2852 cm^{-1} (observed to all samples) is attributed to the symmetric stretching vibration of the aliphatic CH_2 group. The band at the wavenumbers 1743 cm^{-1}

(observed to all samples) is the indicator of production of saturated aldehyde functional groups or other secondary oxidation products. The major peak at 1743 cm^{-1} arises from C=O stretching vibrations. This band is very strong for all samples and it can describe to the triacylglycerol C=O ester group.[24] The bands near 1238 cm^{-1} and 1161 cm^{-1} (observed to OVO, OVO 12, OVO 24, and OVO 48 samples) are associated with the stretching vibration of the C-O ester groups and with bending vibration of changes during oxidation period. The absorbance at 967 cm^{-1} (observed for all samples), is associate with bending vibrations of CH functional groups of isolated trans-olefins. All observations show that the quality olive oil decreases during storage time due to chemical change in oil structure.

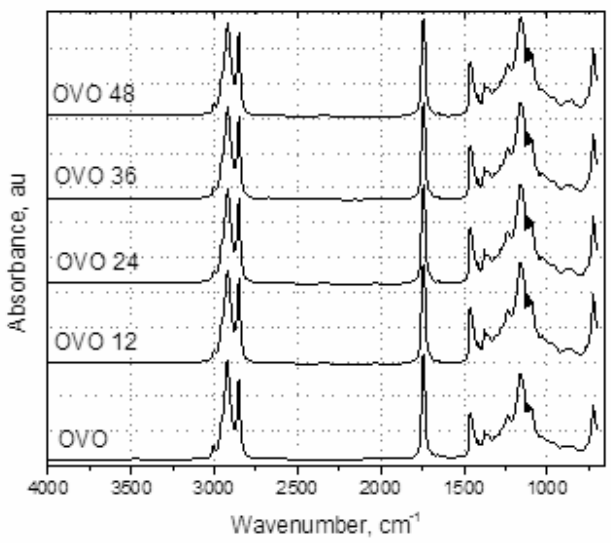

Fig. 5 – The FT-IR spectra for the analyzed olive oil samples.

CONCLUSIONS

This study evaluate the quality of an olive oil commercially available during storage time During storage (for 48 months) an increasing in the values of quality parameters FFA and AV took place that are the measures of oxidative degradation of oils.

It was concluded that while the initial quality of olive oil samples was good, it keeps decreasing during storage, reaching the worst level after 48 months storage. The results are verified by using spectrometric methods FTIR. The spectrum is in accordance with information obtained by the quantitative determinations.

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