INFLUENCE OF MODIFIED ATMOSPHERIC CONDITIONS AND DIFFERENT PACKAGING MATERIALS ON PISTACHIO (Pistacia vera L.) OIL QUALITY.

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Abstract—Pistachio as a strategic product has a particular position among Iranian productions and is one of the most important non-oil exports after carpet. In this study, after primary processing such as dehulling, washing, drying and roasting, pistachio nuts were packed in four different atmospheres including N₂, CO₂, vacuum and ambient air. Storage temperatures were 20°C and 40°C for a 12 month period. The evaluated packaging materials were a plastic compound five layers film, a modified polypropylene pouch, and a metalized plastic pouch (polypropylene with a layer of aluminum). After extracting pistachio oil with hexane, thiobarbituric acid (TBA) index, free fatty acids (FFA), and induction time (IT) were measured at three-month intervals. Statistical analysis of our data revealed that stored samples under N₂, CO₂ and vacuum had a lower TBA index compared with air-packed ones, and the IT of pistachio oil was longer at 20°C than at 40°C.

Keywords—Packaging, pistachio oil, free fatty acids, oxidation, shelf life.

1. INTRODUCTION

Pistachio is a rich source of nutritional substances, especially fat, since it has high amounts of unsaturated fatty acids, which are essential in human diets for health reasons. Iran is one of the most important countries regarding producing and exporting pistachio in the world. Among non-oil exports of Iran, pistachio is in the second ranking after carpet. Annual production of pistachio at 2010 in Iran was 162,000 Mt which constitutes 55% of the world pistachio production (Iran Pistachio Association, 2011) followed by U.S.A and Turkey. Pistachio nut is mainly consumed as salted, roasted or added in confectionery and snack foods (Amirteimoori and Chizari, 2008). It is also used as the main ingredient of desserts, such as baklava and nut paste in Turkey.

Pistachio contains around 23% protein, 19% carbohydrate and 5% moisture. It also contains high amounts of K and P, and various amounts of Ca, Mg and Fe (Kucukoner and Yurt, 2003; Pala et al., 1994). In a research carried out on 8 varieties of pistachio in Greece, the fatty acid composition of kernel oil averaged 61.88 % oleic, 17.52 % linoleic, 9.26 % palmitic and 0.4 % linolenic acid (Tsantli et al., 2010). Great differences in fat content of pistachio nut were reported by several researchers, such as 56% by Kucukoner and Yurt (2003), Pala et al. (1994) and between 40.6% and 53.5% by Koroglu (1997). Therefore, pistachio is a nut with high nutritional value, lipid content and very rich in unsaturated fatty acids. However, the unsaturated fatty acids make pistachio susceptible to oxidation, producing a variety of off-flavors and off-aroma.

Fats oxidation is one of the main factors for quality loss in pistachio. Factors affecting fat oxidation are free fatty acids, oxygen, water activity, temperature, heavy metals, light, enzymes, and antioxidants. There are different ways to evaluate oils and fats deterioration, such as sensory evaluation, determination of peroxide and thiobarbituric acid (TBA) values, measurement of the induction time period (IT), etc. (Ellis and Mam, 2000; Maskan and Karatas, 1997). Comparing with other food products, studies on the storage stability of pistachio nuts are very limited. In a study by Faruk Gamli and Hayoğlu (2007), samples of pistachio paste were produced by boiling a mixture of 51% sucrose, 16% pistachio, 8% glucose, and 25% water as long as final brix equaled 75. These samples were stored in 4°C and 20°C inside three types of packages, including polypropylene (pp) as a packaging material sealed either under vacuum or without vacuum, and glass jars sealed. This study showed that pistachio paste stored at 4°C in sealed glass jars had better acceptance with respect to chemical properties compared with other samples.

Raei et al. (2010) evaluated storage stability of pistachio cv. Ohadi under four different packaging materials and various storage conditions. They found that five layer plastic films or metallized films under N₂/CO₂ or vacuum kept the quality of pistachios for long time, while storage at 40°C was better than at 20°C for quality maintenance. Metal cans were not good barriers against oxygen and water vapor as expected. Kader et al. (1982) investigated the effect of temperature (0, 5, 10, 20 and 30°C) on chemical and sensory characteristics of pistachio nut during storage time of 6-12 months. Their results revealed that a moisture level of 4-6% resulted in the best quality. Dried pistachio nuts can be kept for 12 months at 20°C. Maskan and Karatas (1998) studied the storage stability of pistachio nuts under various conditions. Lowest rate of product oxidation and hydrolysis occurred at or near the monolayer moisture content and under CO₂ atmosphere. In another research, they showed that fatty acid reduction and peroxide formation were higher in ambient storage, but storing at monolayer moisture content and under CO₂ atmosphere improved the stability of pistachio nuts (Maskan and Karatas, 1999).
Tavakkolipour et al. (2010) evaluated the storage stability of whole split Kerman pistachio nuts (Pistacia vera L.) stored at 5, 15, 25 and 35 °C with a relative humidity range of 11 to 87 %. They found that rate constants of lipid oxidation reaction at 5 to 35 °C varied between 0.145 and 0.567 (month⁻¹). Also, the oxidation activation energy was 31.46 kJ/mol and lowest product oxidation and lipolysis occurred at or near monolayer moisture content. Some researchers have worked on new methods of pistachio preservation. For example, ozone was used for degradation of aflatoxins in pistachio (Akbas and Ozdemir, 2009). It was found that increasing of the exposure time and ozone concentration increased aflatoxin degradation, whereas fatty acid composition and other quality factors of pistachios didn’t change significantly after ozonation treatments.

The aim of this research was to evaluate qualitative properties of pistachio oil in nuts, packaged in different materials using modified atmosphere packaging (MAP) and stored at different temperatures.

II. MATERIALS AND METHODS

Pistachios (cv. Ohadi) were picked from Feizabad area in Khorasan province (north east of Iran), from randomly selected trees and were transported to a local pistachio terminal for processing. After washing and drying the samples, three packaging materials were used for product packaging and one sample (in bulk without packaging) was considered as control. Packaging materials were: (a) five layers of plastic compound film (including 2 layers of polyethylene, 2 layers of polyamide and 1 layer of glue with 80 μ thickness), (b) modified propylene with PCG code and 20 μ thickness and (c) metalized plastic film (polypropylene with a layer of aluminum). These materials were provided by the local commercial suppliers. Packages were sealed by a heat sealer. The applied gases inside packages were: N₂, CO₂, ambient air and no gases (vacuum). Packaging was done by Henkleman machine (model 200A, Germany). Each pack consisted of 300 g, roasted pistachios.

The pistachio samples were stored for one year at two conditions: ambient temperature and 40°C in an oven (Memmert). All measurements were performed in triplicate based on a fully randomized factorial design. Obtained data were analyzed by Minitab (version 14) software at a 95 % significance level and the Figures were drawn by Microsoft Excel (2007). Analyses were carried out at 3 months time intervals.

For determination of pistachio oil attributes, ground samples were extracted using hexane (at a ratio of 3:1 w/w with pistachio) for 24 h in darkness at ambient temperature (Raie et al., 2010). The solvent was evaporated under vacuum at 30°C (Maskan and Karatas, 1998). Free fatty acids were determined by titration method based on oleic acid percent (AOACS, 2005). Thiobarbituric acid value (TBA) was measured by centrifugation and spectroscopic absorbance reading at 532 nm (AOCS, 2005). Induction time (IT) was measured with Rancimat (Metrohm 743, Germany) by application of the method of Ellis and Mam (2000).

III. RESULTS AND DISCUSSION

A. Thiobarbituric acid index (TBA)

Previous researchers have shown that peroxide value of pistachio oil cannot be determined by current standard methods because in food products with low peroxide value, little amount of iodine is released and is absorbed by unsaturated bonds of fatty acids that are rich in pistachio oil. In this case, phenomena of discoloration and titration termination are difficult to detect. Therefore, for monitoring pistachio oil deterioration during storage, more accurate indices, including TBA, will be measured by spectrophotometry (Yaman, 2004; Sedaghat, 2004). Our results revealed that changes of TBA are significantly (P<0.01) affected by storage temperature (Fig. 1), storage time (Fig. 2), and filling gas type (Fig. 3). Also, interaction of gas and time was significant on this index (P<0.05).

By increasing temperature from 20°C to 40°C, TBA index showed almost a 50% rise (Fig. 1), which could be explained by the influence of temperature on the rate of chemical reactions. During storage, TBA index increased linearly from 0.2 at the beginning to 0.94 (A₅₃₂) one year later (Fig. 2). Other researchers (Sedaghat, 2004) have reported similar results. Considering filling gases inside packages, we found that N₂, vacuum, and CO₂ provided the highest quality in terms of TBA (Fig. 3), whereas air was the worst one. It is well known that oxidation of fat and production of oxidized products resulting in higher TBA values requires oxygen that is found in air stored pistachios. Applying N₂, vacuum, and CO₂, amounts of oxygen would be limited and therefore, TBA values will decrease.

![Figure 1. Influence of storage temperatures on the rate of TBA index, FFA and induction time in pistachio oil.](image1)

![Figure 2. Influence of storage time on the rate of TBA index and FFA in pistachio oil.](image2)
the oxidation. Changes in IT, in relation to filling gases or air storage, showed a trend similar to TBA and FFA (Fig. 4). For instance, the presence of oxygen (in air), led to an induction time (1.13 h) lower than that of CO₂ (approximately 1.4 h).

Regarding storage time (Fig. 5), the IT was almost half after one year of the value at the beginning of storage. Thus, the rate of IT decreased faster during the early time intervals of storage than the late ones. Concerning for the different packaging materials, no significant difference (P>0.01) was found between five layer film and OPP, but metallized film was more effective in terms of IT (Fig. 6), which makes it more suitable for pistachio packaging. This could be explained by low transmittance of light and permeability to oxygen through the metallized films, since light and oxygen are very important pro-oxidants in fats oxidation.

**B. Free fatty acids (FFA)**
Free fatty acids consist one of the quality factors of oils. The rate of free fatty acids formation was related with the development of lipolysis and production of oleic acid. Our data analysis showed that the influence of temperature (Fig. 1), storage time (Fig. 2), and kind of gas filling the packages were all statistically significant (P<0.05) on FFA value. Also, the interaction of time and temperature was significant (P<0.041). Stored pistachios at 40°C had higher FFA values compared with those at 20°C, and this could be attributed to faster chemical and enzymatic (lipolysis) reactions at the higher temperature than at the lower one.

In Fig. 2, it is obvious that storage time resulted in 250% (2.5-fold) increase in FFA value during storage for 12 months. Increases in FFA value were concomitant with increases in TBA index. The similar trends of FFA and TBA values during storage could be explained by the fact that FFA are precursors for the formation of oxidation products. It should be noted that the rate of FFA increase at later period of storage was higher than the initial storage time. With respect to highest FFA content (0.55% oleic acid) of pistachio oil (month 12 and 40°C), it can be concluded that quality of pistachio has been kept relatively well during 12 month-storage, since this value is 5% less than maximum FFA for human use (Kucukoner and Yurt, 2003).

Values of FFA did not differ among the packages filled with different gases or stored in air (Figure 3). This effect was confirmed statistically and was in partial disagreement with the effect of gases on TBA, since TBA values in samples stored with air were higher than in the samples stores in other gases.

**C. Induction time (IT) of pistachio oil**
The analysis of our data (Figs. 1, 4, 5, and 6) showed that IT was significantly (P<0.01) affected by the factors of storage temperature, type of filling gas, and storage time, and also by the interaction of packaging material and storage time (P<0.01). The higher the induction time, the better the quality of pistachio oil and the lower...
IV. CONCLUSION
In order to have pistachio products of high quality with long shelf-life, it is very important to package them in proper materials and store under appropriate conditions. Our results showed that higher temperatures and longer storage times would result in a product with minimum quality attributes. Considering different studies on packaging materials, we found that metallized film is the best one in terms of preventing oxygen permeability and maintaining the pistachio fat quality. Regarding TBA and FFA, storage in air resulted in poorer quality products since these indices were high.

REFERENCES
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