Gaziosmanpaşa Üniversitesi Ziraat Fakültesi Dergisi
Journal of Agricultural Faculty of Gaziosmanpasa University
http://ziraatdergi.gop.edu.tr/

Araştırma Makalesi/*Research Article*

JAFAG
ISSN: 1300-2910
E-ISSN: 2147-8848
(2018) 35 (2), 152-163
doi:**10.13002/jafag4376**

Stability of Sunflower Oil Enriched with Olive Phenolics in Deep Frying Condition

Ayşe Burcu ATALAY[1] Ahmet Levent INANC[2*]
[1]Department of Food Engineering, Engineering Faculty, Munzur University, Tunceli
(Orcid.org/0000-0002-2882-7865)
[2]Department of Food Engineering, Engineering Faculty, Kahramanmaras S.U University, Kahramanmaras
(Orcid.org/0000-0002-7363-5096)
[*] e-mail: linanc@ksu.edu.tr

Alındığı tarih (Received): 07.11.2017 Kabul tarihi (Accepted): 19.06.2018
Online Baskı tarihi (Printed Online): 08.08.2018 Yazılı baskı tarihi (Printed): 29.08.2018

Abstract: Sunflower oil was enriched separately with olive fruit, olive leaf and olive pomace phenolic extracts for deep-frying. Sets of 250 g of potatoes were fried discontinuously 7 times in 2 L of the enriched or non-enriched (control) sunflower oils at 180±5 °. The total phenol contents (initially 200 mg kg-1 oil) in the oils decreased as increasing the frying number but it was not determined phenolic content in the frying oils after 5 frying processes. Free fatty acids and peroxide values significantly increased and the oil with olive fruit extract contained the lowest free fatty acids (0.99 %, as oleic acid) and peroxide value (37.11 meqO_2 kg^{-1} oil) after 7 fryings. The initial antioxidant activity capacities of all oils significantly reduced to respectively about 69%, 68%, 60% and 50% for the oil with olive leaf, olive fruit, olive pomace extract and control after final frying due to oxidation.

Keywords: Frying, olive fruit, olive leaf, olive pomace, oxidative stability

Derin Yağda Kızartma Koşulunda Zeytin Fenolikleri ile Zenginleştirilmiş Ayçiçek Yağının Stabilitesi

Öz: Ayçiçek yağı; zeytin meyvesi, zeytin yaprağı ve pirinadan ekstrakte edilen fenolik esktraktlarla derin kızartma işlemi için ayrı ayrı zenginleştirilmiştir. Her bir kızartma işleminde patatesler, 180±5°C'de 2 L zenginleştirilmiş ve zenginleştirilmemiş (kontrol) ayçiçek kızartma yağlarında aralıklı olarak 7 defa 250 gramlık setler halinde kızartılmıştır. Yağlardaki toplam fenol içeriği (başlangıçta 200 mg kg^{-1} yağ), kızartma sayısının artmasıyla azalmış, ancak 5 kızartma işleminden sonra kızartma yağlarında fenolik içerik belirlenememiştir. Serbest yağ asitleri ve peroksit değerleri önemli oranda artmış ve zeytin meyve ekstraktlı yağ, 7. kızartmadan sonra en düşük serbest yağ asitleri (%0,99 oleik asit cinsinden) ve peroksit değeri (37.11 meqO_2 kg^{-1} yağ) içermiştir. Zeytin yaprağı, zeytin meyvesi, pirina ekstraklı yağ ve kontrol örneklerinin başlangıç antioksidan aktivite kapasiteleri son kızartmadan sonra oksidasyona bağlı olarak sırasıyla yaklaşık %69, %68, %60 ve %50'ye düşmüştür.

Anahtar Kelimeler: Kızartma, zeytin meyvesi, zeytin yaprağı, pirina, oksidatif stabilite

1. Introduction

Frying which is one of the most popular practices is preferred both for preparation of industrial and domestic food (Casal et al. 2010). Oxidation, oil hydrolysis, polymerization and decomposition of compounds take place at high temperatures and in the presence of oxygen and food, and inevitably the shelf life of fried product reduces (Nor et al. 2008). Numerous researches have extensively reported that the physical and chemical changes occurring in frying oils result in undesirable effects on human health (Abdulkerim et al. 2007). If edible oils contain a high amount of unsaturated fatty acids, especially polyunsaturated fatty acids, the oxidation is inevitable (Zhang et al. 2010). Oxidation of oils does not cause only to rancid odors, unpleasant flavors and discoloration, nutritional value and safety loss but also occur due to the formation of degradation products (Lercker and Rodriguez-Estrada, 2002). Because of these reasons, consumers do not accept oxidized products (Mohdaly et al. 2010).

Heating time, initial quality of frying oil, food materials subjected to frying, the presence and

concentration of antioxidants, especially the amount of unsaturated fatty acids and oxygen concentration effect the oxidation reactions throughout deep-fat frying (Orozco-Solano et al. 2011). Recently, the use of natural antioxidant extracts was preferred to reduce oxidation in food lipids (Naz et al. 2005). Synthetic antioxidants such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) are preferred to retard oxidation reactions of oils (Nor et al. 2008). However, synthetic antioxidants cause toxic and carcinogenic effects (Delfanian et al. 2015). Nowadays, there is a trend for replacement of synthetic antioxidants with natural ones (Yanishlieva and Marinova, 2001; Bouaziz et al. 2008).

Recently, special attention would be focused on the antioxidative ability of various natural components such as phenolic compounds (Frankel et al. 1993; Xiuzhen et al. 2007). The phenolic compounds that are very rich in some agro-food industrial by-products show higher antioxidant capacity and prevent lipid oxidation (Peschel et al. 2006). Particularly, olive fruit contain polyphenols with antioxidant and free radical-scavenging activity. Also, olive pomace and leaves from Olea europaea cultivars are in fact, main sources of olive phenols and can be used for supplementation of refined edible oils with polyphenols (Sanchez de Medina et al. 2012). While many researches have been made on other plant extracts for frying conditions, there are very few researches on olive fruit and olive pomace extracts which are the subjects of this research (Farag et al. 2003; Farag et al. 2007; Lafka et al. 2011).

Sunflower seed oil production makes up around 8% of the total global vegetable oil production. Sunflower oil is reported to be the third largest vegetable oil worldwide, following soybean and palm. India, Turkey, and Egypt are some of the major sunflower oil consumers that have participated in market growth by increasing their consumption without increasing the local production (MMR, 2017). The oil derived from sunflower is used for cooking and frying purpose globally. Sunflower oil is rich in oleic acid, linoleic acid and other nutrients which helps in lowering bad cholesterol and increases good cholesterol in blood (TMR, 2017). Dorni et al. (2018) reported that fatty acid profile of sunflower oil revealed that linoleic acid was the major fatty acid (62.69%), followed by oleic acid, 25.92%. Moderate amount of total saturated fatty acid (11.39%) was also noticed with palmitic (6.43%) and stearic (3.69%) acid being the major contributors. In general, the content of oleic and linoleic acid in sunflower oil accounts between 85 to 90% of total fatty acid which makes it unique among edible oils.

The purpose of this study was to investigate the effects of the total phenolic compounds extracted from olive leaf and olive fruit collected from Olive (*Olea europaea* L.) tree, and from olive pomace (also called olive pulp or olive cake; residual after olives are crushed and the olive oil is extracted) obtained from an olive oil plant on the stability of the frying oil during deep-oil frying process of potato chips in sunflower oil and in order to delineate the differential antioxidant activities of these extracts by the extent of their abilities to scavenge the free radical (DPPH) activity.

2. Methodology

The fruits, leaf and pomace of olives were obtained from an olive oil plant (Remzibey) in Kahramanmaras, Turkey during 2015 harvest season. Refined sunflower oil (SF) and potatoes were purchased from a local supermarket. For the analyses, the analytical grade chemicals were used and these were obtained either from Merck Co. (Darmstadt, Germany) and Sigma Chem. Co. (St. Louis, MO, USA).

Fresh olive leaf was washed with distilled water and dried at 65±5 ^{o}C for 6 h in a drying oven. The dried material was ground by a grinder and passed through 35 mesh (particle size ≤0.5 mm) sieve. The olive leaf powder (600 g) was extracted at 5:1 liquid/solid ratio (L kg^{-1}) with 78 % (v/v) ethanol at room temperature for 24 h, and the extraction was repeated three times. Olive leaf extracts; coded as L, were dried over anhydrous sodium sulphate and filtered through whatman filter paper (No. 2), and then ethanol was evaporated in a rotary vacuum evaporator (Heidolph, Germany, Heizbad Hei-VAP) (Harp, 2011). The olive fruit extract (F)

and the olive pomace extract (P) obtained by modifying the methods of Amiot and Fleuriet (1986), and Pagnanelli et al. (2010). Briefly, olive pomace was dried at 65±5 °C for 6 h and ground, and olive fruit was crushed in a grinder. Both samples (100 g each) were mixed with 500 ml of ethanol-water (78%) and stirred for 30 min. Then ethanol was evaporated under vacuum.

The total phenolic contents of olive leaf, fruit, pomace, their extracts and sunflower oil were detected. It was used 4 frying oils for frying processes of potatoes. Thus, it was prepared 3 frying oils containing 3 different extracts. Sunflower oil was supplemented with an appropriate quantity of the olive phenolic extracts corresponding to the supplementation of approximately 200 mg total polyphenols per kg of oil. Then, oil samples were homogenized by vortex homogenizer. Samples were coded as SF+F for sunflower oil with olive fruit extract, SF+L for sunflower oil with olive leaf extract, SF+P for sunflower oil with olive pomace extract and SF for control (sunflower oil-free the extract). Aqueous methanol (60%) was used to extract the polyphenols in the oils. The polyphenols in the aqueous fractions were extracted with ethyl acetate and then with n-butanol. The extracts were dried over anhydrous sodium sulphate and evaporated to dryness (Gutfinger, 1981; Capasso et al. 1992).

Potatoes were peeled, washed, and then cut into uniform pieces (8 x 0.5 x 0.5 cm). Frying was carried out in a home-style fryer (Tefal Filtra One Deep Fat Fryer FF162140, 2.1 L oil capacity). The proportion of potatoes to frying oil in the first frying was adjusted to 125 g L^{-1} oil and then it was not added any additional oil to the fryer for other 6 frying. Temperature of the fryer was set to 180 °C. Time required to reach and maintain the frying oil at that temperature before introduction of potatoes was 5 min. Potato slices were then fried for 3 min. After each frying, the oil was allowed to cool to room temperature until the next 6 hours. The oil was again heated to 180 °C for the next frying. Every 6 hours the same frying procedure was repeated (totally 7 fryings). The frying oil samples were taken for the analyses after each frying. After cooling to room temperature, the oil samples were stored in a freezer at -20 °C under nitrogen atmosphere until analyses.

The Folin–Ciocalteu reagent was used to determine the total phenol content (TP) of oil and the extracts spectrophotometrically (PG Instruments 25 UV/VIS) by reading the absorbance at 760 nm. Tannic acid was used for the preparation of a calibration curve (R^2= 0.993).TP was expressed as mg of tannic acid/kg^{-1} of sample (Folin and Denis, 1915). Free fatty acid (FFA; %, as oleic acid), was determined by titration of the oil samples dissolved in (1:1, v v-1) ethanol/ether with potassium hydroxide (TSE, 2003). Peroxide value (PV), a measurement of oxidative rancidity was determined according to the AOAC Method Cd 8-53 and expressed in milliequivalents of active oxygen per kilogram ($meqO_2$ kg^{-1}) oil (AOAC, 1989a). Ultraviolet absorbances (expressed as K232 and K270), spectrophotometric measurements of conjugated dienes and trienes as the primary and secondary oxidation products of oils, were determined at 232 and 270 nm, respectively by dissolving the oil samples in hexane (AOAC, 1989b). The antioxidant activity of the oil samples was measured by the DPPH* radical scavenging assay. The variation of free radical scavenging activity by the time was carried out by reaction using DPPH (2, 2-diphenyl-1-picrylhydrazyl) in methanol at 515 nm by spectrophotometer (PG Instruments 25 UV/VIS). The antioxidant activity was calculated as the percent of inhibition by using the equation (1) (Kaya, 2009):

$$\%Inhibition=[1-(Asample/Acontrol)]x100 \quad (1)$$

All measurements were repeated three times. The results were expressed as mean values and standard deviations. The data was statistically compared by Student's t-test and Duncan's multiple range tests (SPSS v.23, IBM, USA). Statistical significance was accepted at a level of $P<0.05$ (Draper and Smith, 1998).

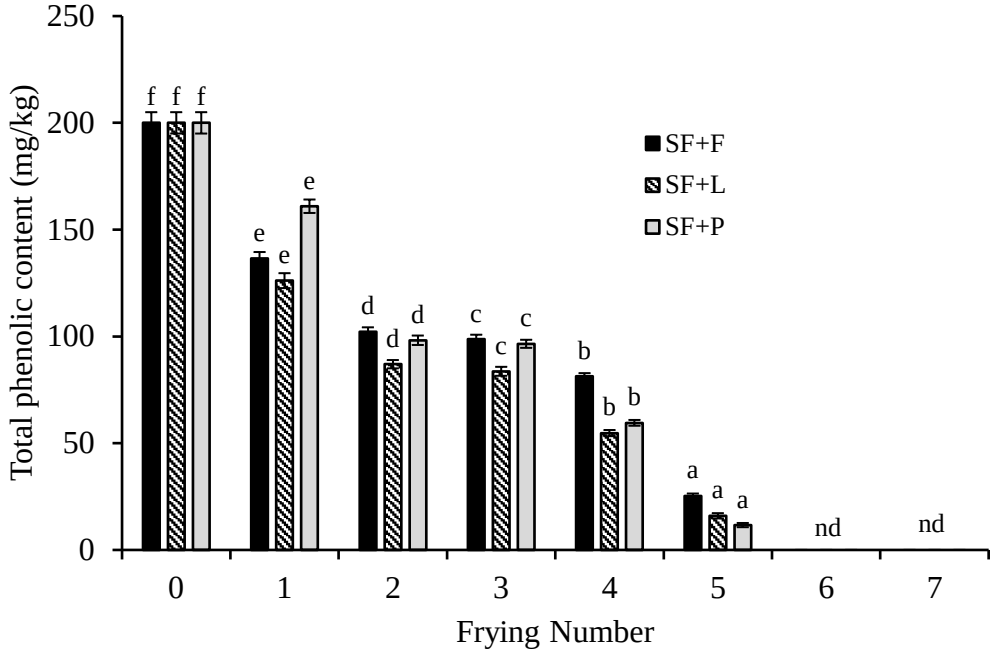
3. Results and Discussion

The total phenolic contents of F, L and P extracts were 528.53, 380 and 209.90 mg kg^{-1},

respectively as tannic acid equivalents (TAE). In a previous study, the total polyphenol contents were determined in range of 485-495, 234-250, 185-195, 65-73 and 193 and 170 mg kg^{-1} TAE for olive fruits, leaves, oils, pomaces, aqueous extracts, respectively as tannic acid equivalents (Farag et al., 2003). Farag et al. (2007) found that the total polyphenol content of crude olive leaf juice was 280 $mgkg^{-1}$ TAE. In another study, the total phenol content of olive oil mill waste was 16.33 mg kg^{-1} TAE for ethanolic extract (Lafka et al. 2011). These differences between the values in the previous works and the present results may be due to several factors such as differences in harvest year, climatic conditions, maturity stage of fruits, solvents, extraction methods, locality, and cultivar of fruits.

Figure 1 shows TP contents of the frying oils during frying processes. The initial TP content in SF (control) was very low (0.06 mg kg^{-1}), and completely decomposed after the first frying. Therefore, it was not shown in the figure. SF+P had higher TP content (160.95 $mgkg^{-1}$) than other oil samples (136.52 mg $kg^{-1}$for SF+F and 126.11 mg kg^{-1} for SF+L) after 1st frying. It showed that initiation reaction ability of the phenols extracted from olive pomace was low. Increasing the frying number caused a significant decrease in TP of the samples ($P<0.05$). TP losses % after the 5th frying were calculated as 87%, 92% and 94% for SF+F, SF+L and SF+P, respectively. SF+L had the lowest amount of phenols than other oils, with exception of the 5th fryings ($P<0.05$).

It was not detected TP contents in all frying oils after 6th fryings. The results were in agreement with the findings of Farag et al. (2007). The amounts of phenolic compounds decreased constantly during heating process. Salta et al. (2007), studied oil stability of edible vegetable oils by rancimat method at 110 °C before and after supplementation of polyphenols with olive leaf extract. In that study, total polyphenols were not detected in sunflower oil and was determined 202.49 $mgkg^{-1}$ TAE before and after supplementation. And oxidative stability was determined as 1.3 and 2 induction time in hour before and after enrichment with the olive leaf extract (254.75 $mgkg^{-1}$ TAE). So, it was stated that addition of polyphenolic extract into oils caused to an increase of the induction time in percentages that ranged from 19 to 54%. Moreover, Aydeniz and Yılmaz (2012) measured total phenolic content of the enriched and the non-supplemented oil samples for 7 days of frying and the total phenolic content of control oil was not detected for all days of frying. The total phenolic content of the enriched oil with olive leaf decreased by increasing frying day number, similarly. Total phenolic content decreased from 80 to 20 $mgkg^{-1}$ TAE in the enriched oil. Gallic acid equivalent (GAE) and caffeic acid equivalent (CAE) units expressed for the units of total phenolic contents in the works done by Farag et al. (2007), (Lafka et al. 2011), Salta et al. (2007) and Aydeniz and Yılmaz (2012) were converted to TAE by using TAE=1.3292*GAE equation derived from the data of Bizuayehu et al. (2016) for the conversion of GAE to TAE and TAE=1.3064*CAE equation derived from the data of Vinayak et al. (2015) for the conversion of CAE to TAE. The changes in FFA values of the frying oils were shown in figure 2. FFA increased with increasing frying number. The initial FFA (oleic acid %) values were 0.07 for SF+F, 0.08 for SF+L and SF+P, and 0.06 for SF. The FFA values after 7th. frying process were determined as 1.49, 1.24, 1.13 and 0. 99 for SF, SF+P, SF+L, SF+F, respectively. A series of reactions is initiated by air and water while frying process of a food is performed in frying oil at high temperature. Triglycerides are decomposed by water and converted to monoacylglycerol, diacylglycerol, and eventually to glycerol (Dobarganes and Marquez Ruiz, 1996).



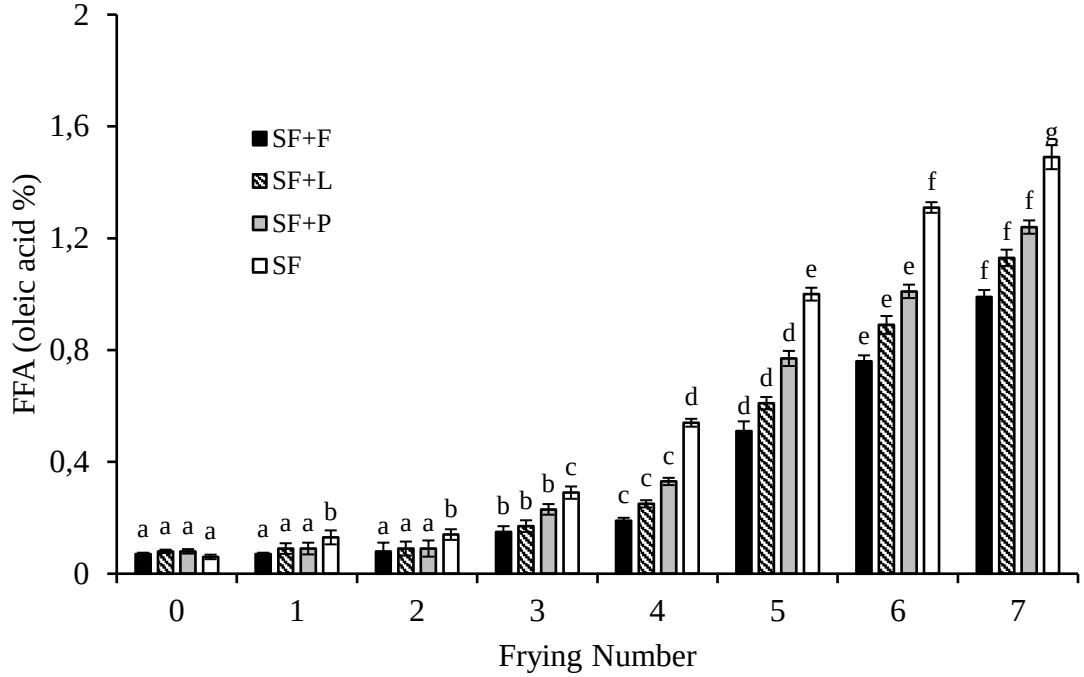
n = 3 ± standard deviation; There is no statistically significant difference among the values indicated by the same letters (p>0.05). The series are for comparasion of values in frying numbers of each sample, independently of the others.
nd: not detected, SF+F: sunflower oil with olive fruit extract, SF+L: sunflower oil with olive leave extract, SF+P: sunflower oil with olive fruit extract

Figure 1. Total phenolic content of the frying oils with olive fruit, olive leave and olive pomace extract
Şekil 1. *Zeytin meyvesi, zeytin yaprağı ve pirina ekstraktlı kızartma yağlarının toplam fenol içeriği*

For all fryings, FFA value of SF was the highest than other oils and also FFA value of SF+P was significantly highest as compared to FFA values of SF+L and SF+F ($P<0.05$). Similarly, with the present study, Abdulkerim et al. (2007), fried vegetable oils by using potatoes for 6 h a day up to a maximum of 5 days and observed that free fatty acid values increased constantly from the initial to final process of frying. The addition of polyphenolic extracts reduced the increase in the acid value during the deep-frying process. Casal et al. (2010), reported that stability of oil samples under deep-frying conditions decreased increasingly during 27 h of frying. Delfanian et al. (2015), investigated frying stability of sunflower oil enriched with jujube leaf extract. Potato slices were fried for 7 min as a raw material. FFA showed an increase from the initial to final of the experiment similar to the the results of this study. At the end of 24 h of frying, FFA values of oil samples enriched with natural and synthetic antioxidants were lower than the control oil. Similar to results reported by Aydeniz and Yılmaz (2012), the increase in free acidity of oil samples were observed during 7 days of frying.

Figure 3 shows the changes in PV of the oils after each frying. PV was 5.35 $meqO_2\ kg^{-1}$ for SF+F and SF+P, 5.30 $meqO_2\ kg^{-1}$ for SF+L and 5.40 $meqO_2\ kg^{-1}$ for SF before 1st frying. PV significantly increased with frying number for all oils. But, PV of SF increased more than that of the other oils after 7th fryings ($P<0.05$). Sequence of PV's after that frying was as follows:

SF (76.96 $meqO_2\ kg^{-1}$) > SF+P (60.76 $meqO_2\ kg^{-1}$) > SF+L (47.20 $meqO_2\ kg^{-1}$) > SF+F (37.11 $meqO_2\ kg^{-1}$)



There is no statistically significant difference among the values indicated by the same letters ($p>0.05$). The series are for comparasion of values in frying numbers of each sample, independently of the others.
SF+F: sunflower oil with olive fruit extract, SF+L: sunflower oil with olive leave extract, SF+P: sunflower oil with olive fruit extract, SF: sunflower without extract (control)

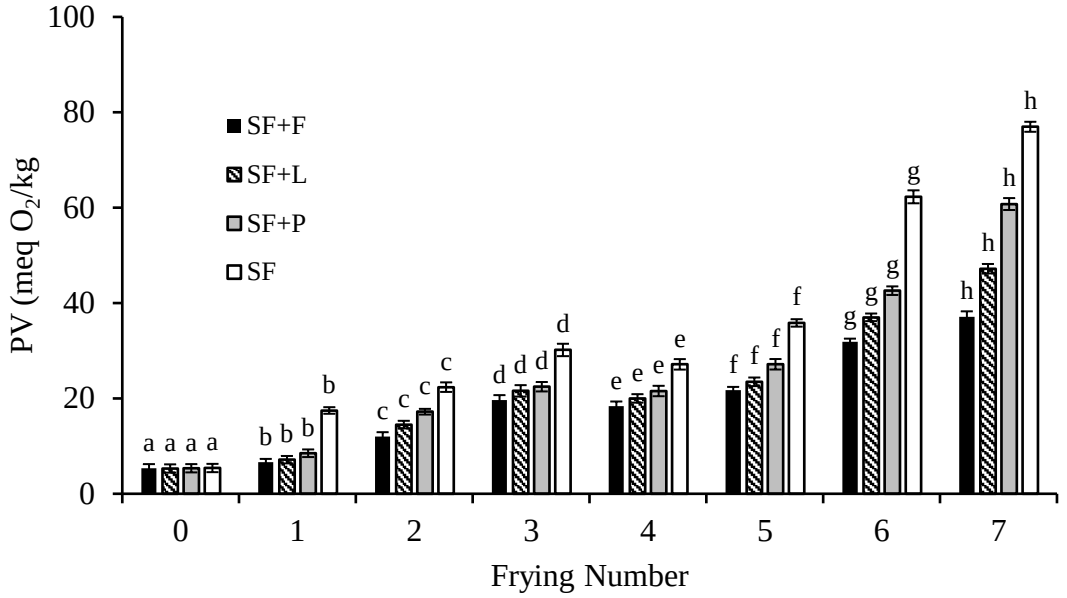
Figure 2. Free fatty acid (FFA) values of the frying oils with olive fruit, olive leave and olive pomace extract

Şekil 2. *Zeytin meyvesi, zeytin yaprağı ve pirina ekstraktlı kızartma yağlarının serbest yağ asitliği değerleri*

The increase in PV shows the increase in the formation of peroxides due to oxidation and F extract more prolonged peroxidation time than the others. Controlling the oxidative stability of oils is very difficult due to variables such as the presence of preservatives, unsaturation degree of oils, temperature, surface-oil volume ratio and other frying conditions (Dobarganes and Marquez Ruiz, 1996), so that peroxides are unstable under deep-frying conditions at high temperature. As oil continues to deteriorate, hydroperoxides break down, so carbonyl and aldehyde compounds contribute to reduction of peroxide values (Shahidi and Wanasundara, 1997). It was reported that the phenolic extracts obtained from olive leaves were more effective on the oxidative stability of vegetable oils as compared with synthetic antioxidants at accelerated test conditions (Jimenez et al. 2010; Harp, 2011). Casal et al. (2010) reported that there was firstly an increase in PV of deep frying oils during frying and then PV decreased after reaching to the highest value.

Spectrophotometric examination in the ultraviolet can provide information on the quality of a fat, its state of preservation and changes brought about by a process. In other words, it is a measure of oxidation/rancidity, oil quality and possibly refinement (IOC, 2015). The absorption at 232 and 270 nm is due to the presence of conjugated diene and triene systems resulting from oxidation processes. These absorptions are expressed as K_{232} and K_{270} (also referred to as

"extinction coefficients"). The changes in the extinction coefficients are shown in Figure 4. K_{232} values for SF+F, SF+L, SF+P and SF before 1st frying were 0.29, 0.27, 0.24 and 0.28, respectively. K_{232} for all oils significantly increased with frying number ($P<0.05$). But, K_{232} values for SF+F were lowest followed by SF+L, SF+P and SF after all frying processes.



There is no statistically significant difference among the values indicated by the same letters ($p>0.05$). The series are for comparasion of values in frying numbers of each sample, independently of the others.
SF+F: sunflower oil with olive fruit extract, SF+L: sunflower oil with olive leave extract, SF+P: sunflower oil with olive fruit extract, SF: sunflower without extract (control)

Figure 3. Peroxide values (PV) of the frying oils with olive fruit, olive leave and olive pomace extract
Şekil 3. *Zeytin meyvesi, zeytin yaprağı ve pirina ekstraktlı kızartma yağlarının peroksit değerleri*

K_{232} values for SF+F, SF+L, SF+P and SF after 7th fryings arose to 2.20, 2.22, 2.36 and 2.62, respectively. Besides, the same tendencies seen in K_{232} values were also observed in K_{270} values ($P< 0.05$), and the lowest conjugated triene formations (K_{270}) were determined in SF+F after all frying processes as compared to the other frying oils. The low levels of both conjugated dienes and trienes in SF+F indicate that SF+F had a good oxidative stability. Farmer and Sutton (2002) indicated that uptake of oxygen and formation of peroxides lead to the formation of conjugated diene and triene during the early stages of oxidation and so, an increase in the absorption was observed. Positive correlation between the extinction coefficients and PV was found. Conjugated dienes values were higher than conjugated trienes for all. The seconder polymer compounds like trienes would occur by the transformation of most of dienes with increase in frying time; however, the reason that the increase in conjugated dienes was considerably higher compared to the conjugated trienes, is specifically due to the high content of linoleic acid in sunflower oil (Bou et al. 2012). Similarly, with the present study Lee et al. (2009) reported that conjugated diene values of the control increased from 0.22 to 1.96 throughout heating treatment for 48 h.

fig. 4a

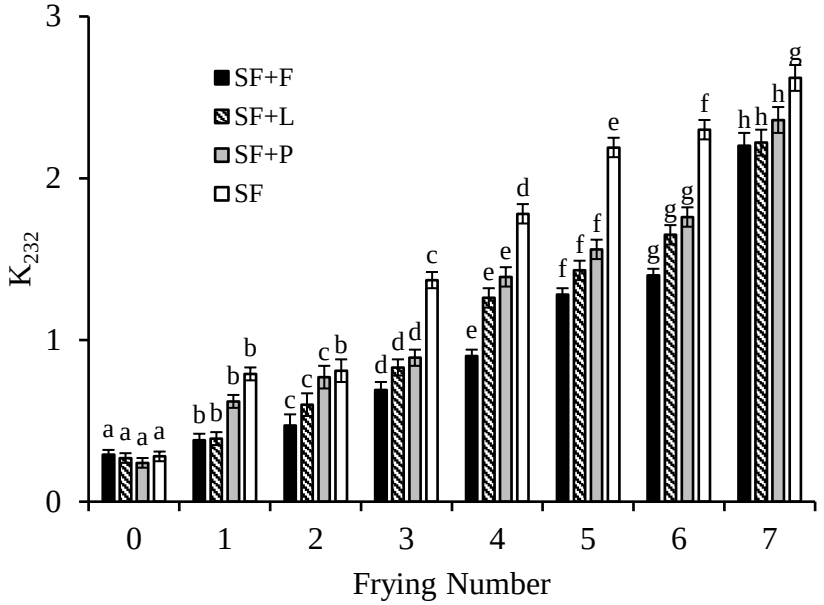
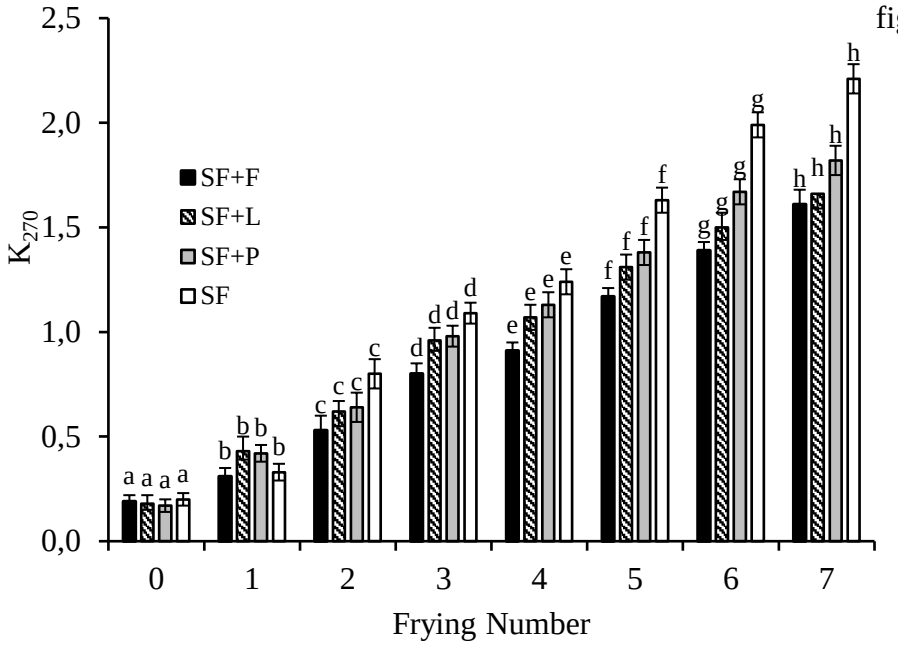


fig. 4b



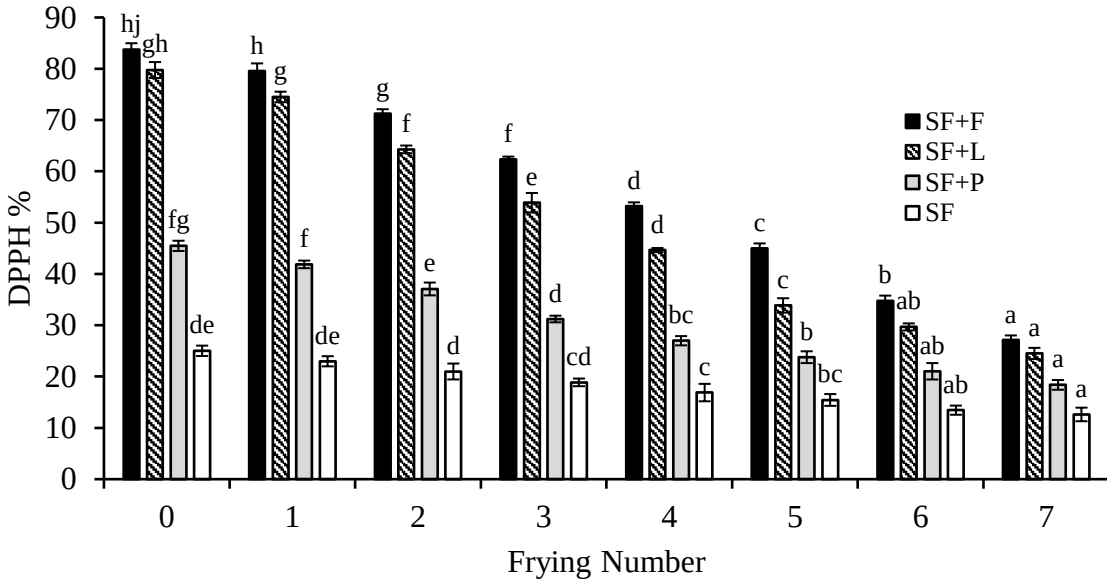
There is no statistically significant difference among the values indicated by the same letters ($p>0.05$). The series are for comparasion of values in frying numbers of each sample, independently of the others. SF+F: sunflower oil with olive fruit extract, SF+L: sunflower oil with olive leave extract, SF+P: sunflower oil with olive fruit extract, SF: sunflower without extract (control)

Figure 4. Conjugated diene (K_{232}) and conjugated triene (K_{270}) values in of the frying oils with olive fruit, olive leave and olive pomace extract

Şekil 4. *Zeytin meyvesi, zeytin yaprağı ve pirina ekstraktlı kızartma yağlarının konjuge dien (K_{232}) ve konjuge trien (K_{270}) değerleri*

Aydeniz and Yılmaz (2012), determined the conjugated dienoic acid in the frying oil samples and conjugated dienoic acid values ranged from 0.48 to 1.88% for control oil and from 0.52 to 1.70% for the enriched oil with olive leaf extract during 7 days of frying.

The present results for the conjugated diene and triene values is similar to those reported by Chirinos et al. (2011); Bou et al. (2012) and Delfanian et al. (2015) the conjugated diene and triene values increased with increasing frying time. The additions of phenolic extracts to frying oils retarded the formation of oxidation products. The antioxidant activity was calculated as the percent of inhibition. The changes in antioxidant activities (DPPH%) of all frying oils as the percent of inhibition are presented in figure 5. Antioxidant activities for all oils significantly decreased by increasing frying number ($P<0.05$). But the decreases in antioxidant activity of SF between consecutive fryings were very closed, as the initial activity was low ($P<0.05$). Additionally, the antioxidant activities of the frying oils used for 0. and 7. frying process were statistically compared by using Student's t-test for overall evaluation of frying process (Table 1). The antioxidant activities of the frying oils before frying process (frying number 0) followed the order: SF+F>SF+L>SF+P>SF ($P<0.05$). While the potential antioxidant activities of the enriched oils were compared with the control, the antioxidant activities of SF+F, SF+L and SF+P were calculated to be 70%, 68.6% and 45% higher than SF, respectively. The initial antioxidant activities significantly reduced to about 69%, 68%, 60% and 50% for SF+L, SF+F, SF+P and SF after the final frying (7th frying) due to the oxidation, respectively.



There is no statistically significant difference among the values indicated by the same letters ($p>0.05$). The series are for comparasion of values in frying numbers of each sample, independently of the others.

SF+F: sunflower oil with olive fruit extract, SF+L: sunflower oil with olive leave extract, SF+P: sunflower oil with olive fruit extract

Figure 5. The antioxidant activities (DPPH%) of the frying oils with olive fruit, olive leave and olive pomace extract

Şekil 5. *Zeytin meyvesi, zeytin yaprağı ve pirina ekstraktlı kızartma yağlarının antioksidan aktiviteleri (DPPH%)*

The reason that a compound has higher binding capacity value is due to the ability to give too much hydrogen, and therefore it has higher antioxidant activity (Von et al. 1997; Kaya, 2009). Chiou et al. (2009), investigated oxidative stability of edible oils supplemented with olive leaf extract during pan-frying of french fries. Before and after addition of phenolic extracts, antioxidant capacity of both enriched and control oils for 7 days. The antioxidant capacities of control and treatment groups decreased by frying days. At the end of frying process, antioxidant capacity value of the enriched oil was higher than antioxidant capacity of control oil for first day. Antioxidant capacity of fresh and fried oil samples detected. For both fresh and fried oil samples, antioxidant capacities were found 1.5-6.9 times higher for enriched sunflower oils compared to the oils before enrichment. Aydeniz and Yılmaz (2012), studied to extend the usage life of oils with addition of plant phenolic extracts to canola oil. The doughs were fried in both the

control oil as the trolox equivalent (TE) decreased from 103.9 to 56.33 μmol TE g^{-1} oil. Also, the antioxidant capacity of the enriched oil with olive leaf extract decreased, similarly with the present results.

Table 1. The statistical comparison of the antioxidant activities (DDPH %) of the frying oils used for 0. and 7. frying process

Çizelge 1. *0. ve 7. kızartma işlemleri için kullanılan kızartma yağlarının antioksidan aktivitelerinin (DDPH %) istatistiksel olarak karşılaştırılması*

Frying Oil	Frying number	
	0	7
SF+F	83.73±1.25 $^{b, C}$	27.13±0.89 $^{a, D}$
SF+L	79.76±1.5 $^{b, D}$	24.51±1.09 $^{a, C}$
SF+P	45.48±1 $^{b, B}$	18.38±0.95 $^{a, B}$
SF	25.02±1.01 $^{b, A}$	12.62±1.32 $^{a, A}$

n = 3 ± standard deviation; there is no statistically significant difference among the values indicated by the same letters ($p>0.05$). Series 'a-b' for comprasion of values in row and series 'A and D' for in the column

4. Conclusions

Sunflower oil was enriched with three different phenolic extracts extracted from olive fruit, olive leaves and olive pomace to be observed the effects of these extracts on the performance of the frying oil during frying of potatoes. The enriched oils exhibited more DPPH radical scavenging activity percentages and so more antioxidant efficiency than the control oil. On the other hand, after fryings, the reduction of the percentages of DPPH radical scavenging activity was observed for all oils, but the protective antioxidant effects of the enriched oils were higher than that of the control. The extracts had positive effects on peroxide and free acidity which are basic parameters used for monitoring oxidative stability and rancidity deterioration of the oils, as well. It is concluded that the phenolic extract of the olive fruit resulted in better protection of the oil under the frying conditions than olive leave and olive pomace extracts. The results of this study show that natural phenolic extracts can enhance thermo-oxidative stability and shelf-life of vegetable oils. The enrichment of frying oils with phenolic extracts may retard the formation of oxidation products like conjugated diene and triene. Moreover, agricultural by-products such as olive leaf and olive pomace can be evaluated for regaining to food industry with health and economic benefits. The amounts of the extracts adding to the oils were kept constant to be observed the effects of the different phenolic sources on oxidative stability of oil in the present work. In further studies, the effects of adding different amounts of the extracts to frying oil on oxidative stability of oil should be investigated and which phenolics compounds are most effective on it.

Acknowledgements

This work was supported by Coordination Committee of Scientific Research Projects of Kahramanmaras Sutcu Imam University (Project no: 2011/ 3-39 YLS).

References

Abdulkerim SM, Long K, Lai OM, Muhammad SKS and Ghazali HM (2007). Frying quality and stability of high-oleic moringa oleifera seed oil in comparison with other vegetable oils. Food Chemistry, 105: 1382-1389.

Amiot MJ and Fleuriet JM (1986). Importance and evolution of phenolic compounds in olive during growth and maturation. Journal of Agricultural and Food Chemistry, 34: 823-826.

AOAC (1989a). Official Methods and Recommended Practices. Peroxide value analysis, Cd 8 - 53. Illionis, AOCS Press.

AOAC (1989b). Official and Tentative Methods of The American Oil Chemists' Society (4th Ed.). Conjugated diene and triene value analysis, Ti la - 64. Champaign, AOCS Press.

Aydeniz B and Yilmaz E (2012). Enrichment of frying oils with plant phenolic extracts to extend the usage life. Eur. J. Lipid Sci. Technol., 114: 933-941.

Bizuayehu D, Atlabachew M and Ali MA (2016). Determination of some selected secondary metabolites and their invitro antioxidant activity in commercially available Ethiopian tea (Camellia sinensis). SpringerPlus, 5: 412-421.

Bou R, Navas A, Tres R, Codony F and Guardiola A (2012). Quality assessment of frying fats and fried snacks during continuous deep-fat frying at different large-scale producers. Food Control, 27: 254-267.

Bouaziz M, Fki I, Jemai H, Ayadi M and Sayadi S (2008). Effect of storage on refined and husk olive oils composition: Stabilization by addition of natural antioxidants from Chemlali olive leaves. Food Chemistry, 108: 253-262.

Capasso R, Cristinzio G, Evidente A and Scognamiglio F (1992). Isolation, spectroscopy and selective phytotoxic effects of polyphenols from vegetable waste waters. Phytochemistry, 31: 4125–4128.

Casal S, Malheiro R, Sendas A, Oliveira PP and Pereira AJ (2010). Olive oil stability under deep-frying conditions. Food and Chemical Toxicology, 48: 2972-2979.

Chiou A, Kalogeropoulos N, Salta FN, Efstathiou P and Andrikopoulos NK (2009). Pan-frying of French fries in three different edible oils enriched with olive leaf extract: Oxidative stability and fate of microconstituents. Food Science and Technology, 42: 1090-1097.

Chirinos RM, Huaman I, Betalleluz-Pallardel R, Pedreschi D and Campos A (2011). Characterization of phenolic compounds of Inca muna (Clinopodium bolivianum) leaves and the feasibility of their application to improve the oxidative stability of soybean oil during frying. Food Chem., 128: 711-716.

Delfanian M, Kenari RE and Sahari MA (2015). Frying stability of sunflower oil blended with jujube (Ziziphus mauritiana Lam.) leaf extract. Food Science & Nutrition, 3: 548-556.

Dobarganes MC and Marquez Ruiz G (1996). Dimeric and Higher Oligomeric Triglycerides İn Deep Frying. Chemistry, Nutrition and Practical Applications. Illinois, AOCS Press.

Dorni C, Sharma P, Saikia G and Longvah T (2018). Fatty acid profile of edible oils and fats consumed in India. Food Chemistry, 238: 9-15.

Draper NR and Smith H (1998). Applied Regression Analysis, 3rd ed. New York: Wiley.

Farag RS, El-Baroty GS and Basuny AM (2003). The influence of phenolic extracts obtained from the olive plant (cvs. Picual and kronakii) on the stability of sunflower oil. International Journal of Food Science and Technology, 38: 81-87.

Farag RS, Mahmoud EA and Basuny AM (2007). Use crude olive leaf juice as a natural antioxidant for the stability of sunflower oil during heating. International Journal of Food Science and Technology, 42: 107-115.

Farmer EH and Sutton DA (2002). Peroxidation İn Relation To Oleifenic Structure. Food lipids: Chemistry, Nutrition, And Biotechnology. New York, CRC Press.

Folin O and Denis W (1915). A colorimetric estimation of phenols (and phenolic derivatives) in urine. J. Bio. Chem. 22: 305-308.

Frankel EN and Kanner J (1993). Inhibition of oxidation of human low density lipoprotein by phenolic substances in red wine. Lancet, 341: 454-457.

Gutfinger T (1981). Polyphenols in olive oils. Journal of the American Oil Chemistry Society, 58: 966–968.

Harp F (2011). Determination of antioxidant effects of Gemlik, Domat, Adana Topagi and Adana local type olive leaves. MS.c. Thesis, Cukurova University, Institution of Natural and Applied Sciences, Adana, p23.

IOC (2015). COI/T20/Doc. No. 19/Rev. 3, method of analysis spectrophotometric investigation in the ultraviolet. International Olive Council.

Jimenez P, Masson L, Barriga A, Chavez J and Rober P (2010). Oxidative stability of oils containing olive leaf obtained by pressure, supercritical and solvent - extraction. European Journal of Lipid Science and Technology, 113: 497-505.

Kaya U (2009). The determination of some physical, chemical and antioxidant properties of Gemlik olives and oils grown in Iznik. MS.c. Thesis, Cukurova University, Institution of Natural and Applied Sciences, Adana.

Lafka TI, Lazou AE, Sinanoglu VJ and Lazos ES (2011). Phenolic and antioxidant potential of olive oil mill wastes. Food Chemistry, 125: 92-98.

Lee HO, Boo-Yong LJ, Hee-Bong L, Song-Youn S, Cheon-Seo P, Shetty K and Young-Cheul K (2009). Assessment of phenolics-enriched extract and fractions of olive leaves and their antioxidant activities. Bioresource Technology, 100: 6107-6113.

Lercker G and Rodriguez-Estrada MT (2002). Cholesterol Oxidation Mechanism. Champaign, AOCS Press.

MMR (2017). Sunflower Market - Industry Analysis, Growth and Trends: https://www.mordorintelligence.com/industry-

reports/global-sunflower-market (Accessed to web: 07.12.2017).

Mohdaly AA, Sarhan MA, Mahmoud A, Ramadan MF and Smetanska I (2010). Antioxidant efficacy of potato peels and sugar beet pulp extracts in vegetable oils protection. Food Chemistry, 123: 1019-1026.

Naz S, Siddiqi R, Sheikh H and Sayeed SA (2005). Deterioration of olive, corn and soybean oils due to air, light, heat and deep-frying. Food Research International, 38: 127-134.

Nor A, Mohamed A, Idris B, Nor A and Ismail R (2008). Antioxidative properties of pandanus amaryllifolius leaf extracts in accelerated oxidation and deep frying studies. Food Chemistry, 110: 319-327.

Orozco-Solano MI, Priego-Capote F and Luque De Castro MD (2011). Influence of simulated deep frying on the antioxidant fraction of vegetable oils after enrichment with extracts from olive oil pomace. J. Agricultural and Food Chemistry, 59: 9806-9814.

Pagnanelli F, Viggi CC and Toro L (2010). Development of new composite biosorbents from olive pomace wastes. Applied Surface Science, 256: 5492-5497.

Peschel W, Sanchez-Rabaneda F, Diekmann W and Plescher A (2006). An industrial approach in the search of natural antioxidants from vegetable and fruit wastes. Food Chemistry, 97: 137-150.

Salta FN, Mylona A, Chiou A, Boskou G and Andrikopoulos NK (2007). Oxidative stability of edible vegetable oils enriched in polyphenols with olive leaf extract. Food Science and Technology International, 13: 413-421.

8

Sanchez de Medina V, Priego-Capote F and Luque de Castro MD (2012). Characterization of refined edible oils enriched with phenolic extracts from olive leaves and pomace. J. Agricultural and Food Chemistry, 60: 5866-5873.

Shahidi F and Wanasundara UN (1997). Measurement of lipid oxidation and evaluation of antioxidant activity in Natural Antioxidants, Chemistry, Health Effects and Applications. Connecticut, IL, AOCS Press.

TMR (2017). Sunflower Oil Market - Global Industry Analysis, Size, Share, Growth, Trends, and Forecast 2017 – 2025: https://www.transparencymarketresearch.com/sunflower-oil-market.html (Accessed to web: 07.12.2017).

TSE (2003). Turkish Standardization Institute, TS 342 Edible Olive Oil İnspection And Testing Methods. Ankara.

Vinayak U, Sandeep RP and Hegde HV (2015). Effect of method and time of extraction on total phenolic content in comparison with antioxidant activities in different parts of Achyranthes aspera. Journal of King Saud University – Science, 27: 204–208.

Von Gadow A, Joubert E and Hansmann CF (1997). Comparison of the antioxidant activity of aspalathin with that of other plant phenols of rooibos tea (aspalathus linearis), α-tocopherol, BHT, and BHA. Journal of Agricultural and Food Chemistry, 45: 632-638.

Xiuzhen H, Shenemail T and Lou H (2007). Dietary polyphenols and their biological significance. International J. Molecular Science, 8: 950-988.

Yanishlieva NV and Marinova EM (2001). Stabilisation of edible oils with natural antioxidants. European Journal of Lipid Science and Technology, 103: 752-767.

Zhang Y, Yang L, Zu Y, Chen X, Wang F and Liu F (2010). Oxidative stability of sunflower oil supplemented with carnosic acid compared with synthetic antioxidants during accelerated storage. Food Chemistry, 118: 656-662.