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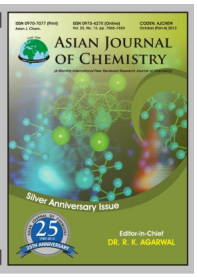

Some Properties and Antioxidant Potential of Olives and Their Corresponding Extra Virgin Olive Oils in Turkey

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Some of the properties of olives and their corresponding extra virgin olive oils were evaluated. It was found that variety has significant effect on properties and antioxidant activity of olives and their corresponding extra virgin olive oils. Ayvalik, Nizip and Odemis olives had higher oil content and their corresponding extra virgin olive oils had higher chlorophyll, caretenoid content ($p < 0.05$). Ayvalik, Halhali, Hasebi, Nizip and Odemis olive extracts were more effective as radical scavenger than BHT and BHA ($p < 0.05$). Ayvalik, Nizip and Odemis olive extracts showed better or similar antioxidant activity in bulk refined olive oil than control, BHT and BHA ($p < 0.05$). Halhali, Nizip and Odemis extra virgin olive oil extracts showed better protection in refined olive oil-in-water emulsions than control, BHT and BHA ($p \leq 0.05$). It was concluded that extracts from some olives and extra virgin olive oils may have food additive value for oils and oil containing foods.

Key Words: Olives, Virgin olive oil, Antioxidant activity, DPPH, Oil, Emulsion.

INTRODUCTION

There are around 130 million olive trees in Turkey, of which 30 % is used for edible olive production and 70 % is used for olive oil production and 160,000 tons of olive oil is produced. Most of the production occurs in the Aegean, Mediterranean, Marmara and South-eastern Anatolia regions of the country[1-3]. Turkey is one of the major olive oil producers and there are several studies about the chemical and analytical properties of Turkish olive oils from Ayvalik and Eastern Mediterranean cultivars[4].

It is known that fats and oils undergo various deleterious changes including hydrolytic, oxidative, isomerization and polymerization reactions during heat treatment at elevated temperature. However, olive oil shows a high resistance to these non-desirable changes. The addition of antioxidants is one of the most well-known strategies applied to delay lipid oxidation reactions. Antioxidant compounds can increase shelf life by retarding the process of lipid oxidation during processing and storage of different lipid systems[5-7]. Crude extracts can be refined to obtain concentrates with enhanced purity and antioxidant activity, suitable for specific food applications. The protective action of antioxidants has been frequently studied in oils, model foods, foods and cosmetic emulsions[8]. The synthetic antioxidants such as butylated hydroxyl toluene (BHT) and butylated hydroxyl aniline (BHA) which are use is being restricted due to safety concerns have been widely used to control lipid oxidative rancidity in foods[7]. Currently, there is a strong global interest in exploring new sources of natural antioxidants such as olive products and by products that are safe, low cost and do not cause the adverse effects produced by synthetic antioxidants. Phenolic compounds of olive fruit and olive oil have been widely explored due to their powerful antioxidant effect and potentially beneficial effects on human health. The antioxidant activity, olive oil polyphenols[9,10] as well as antioxidant activity of table olives[6,11] were studied. Numerous studies have been carried out dealing with oxidation mechanisms in bulk oils although, in most processed foods, lipids are found as oil-in-water or water-in-oil emulsions. Virgin olive oil in Mediterranean countries is mostly consumed, mainly in food emulsions or in the presence of a water phase including soup, stews and sauces[12]. Antioxidants in an edible form are needed to stabilize and to control rancidity and keeping nutritional and sensorial quality a wide variety of oils and oils enriched foods[13-15].

The purpose of this work was to study some properties of Ayvalik, Halhali, Hasebi, Odemis and Nizip olive varieties and their corresponding virgin olive oils. The antioxidant activity of the phenolic fraction of olives and their corresponding virgin olive oil was characterized by its activity in stabilizing oils and emulsions against oxidative deterioration and by the DPPH test and to compare their effectiveness to synthetic antioxidants.

EXPERIMENTAL

Olive varieties namely Ayvalik, Halhali, Hasebi, Nizip and Odemis were collected from Aegean, Eastern Mediterranean and South-eastern Anatolian regions of Turkey in 15th of December 2011. Refined olive oil for thermal oxidation studies was obtained from local markets. All chemicals and reagent were obtained from Sigma-Aldrich and Merck Co Ltd. (Turkey).

The cultivars were chosen since they were the predominating varieties in each location. 25 kg of olive fruits were manually collected from the three olive trees and the virgin olive oils from different olive varieties were produced by using dual-phase centrifuge system (PMS 470-PX40, Polat Machinery, Aydin, Turkey) in Bilaloglu Olive Oil factory, Karaisali, Adana, Turkey. The produced olive oils were put in tinted glass bottles (1 L) and kept at cold room at 4 ºC until they were used.

AOCS Oven Storage Test for Accelerated Aging of Oils (Cg 5-97; 7) conducted at 60 ºC in the dark can be used to evaluate oxidative stability of oils[16] and the heating at 100 ºC simulates the cooking conditions[17]. Virgin olive oils and refined olive oils (2 × 25 g) containing 100 mg kg^{-1} olive or olive oil extracts, BHT and BHA each in a 50 mL beaker covered with aluminium foil were allowed to spontaneously oxidize in dark at both 60 and 100 ºC in the oven. Oil-in-water emulsions (30 %) by using olive, olive oil extracts as well as BHT and BHT were prepared as described previously in details by Keceli and Gordon[18]. Refined olive oil emulsion prepared without extracts and emulsions prepared by adding BHT and BHA were used as control. Emulsions were allowed to spontaneously oxidize at 60 ºC in the dark[19]. The aliquot of emulsion were removed from the oven after 7 days of oxidation, the oil was separated after freezing thawing and centrifuging and the progress of oxidation was monitored.

Detection method: The ripening index (RI) of the olive fruit was determined according to Artazo *et al.*[14] based on an evaluation of 100 olives skin and pulp colours. The average weights were determined by measuring the weights and width and length was measured by using a calliper of 50 olive fruits and their pits. The total oil content was determined by using a Soxhelt extractor and the results are given as percentage of oil yield[11].

The quality parameters of the olive oils (FFA, peroxide value specific extinction coefficients at 232 and 270 nm) were analyzed according to the European Union Commission Regulation[20] (Communication No: 2568/91) and Turkish Food Codex, Regulations for Olive and Olive Pomace oil (Communication No: 2010/35). Chlorophyll and carotenoid content of virgin olive oils were measured according to method of Allaout *et al.*[21]. A colorimeter (Colourquest XE, Hunter Lab) was used to assess the oil colour. 20 mL of olive oil sample was placed into the glass cell and the colour of each sample, in terms of L, a and b, was measured[22]. The extraction phenolic compounds from olives was performed according to the modified methods of Fernandez-Orozco *et al.*[23] and from olive oils a method proposed by Murkouic *et al.*[24] were used. Each olive and their olive oil extracts were kept at -18 °C for enrichment of oils to detect antioxidant activity of olives and olive oils against 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical and in bulk oil and oil-in-water emulsions. The total phenolic content (TPC) of the olive and olive oil samples were determined according to method of Gutfinger[25]. The total phenols concentration was determined from a caffeic acid calibration curve and expressed in mg/kg, as caffeic acid equivalents[10]. The free radical-scavenging activity (RSA) was evaluated by the DPPH assay following the method of Mishra *et al.*[26].

The progress of oxidation of oil samples was monitored in terms of peroxide value, conjugated dienes (CD) and *p*-anisidine (*p*-AV) values according to AOCS Official Method Cd-8b, Ti 1a-6 and Cd 18-90, respectively[27]. The results were evaluated by analysis of variance (ANOVA) by using SPSS 13 for windows. According to the results of ANOVA test Duncan's multiple range test was used to determine the significance at $p < 0.05$ levels[28].

RESULTS AND DISCUSSION

The average values for physical properties of different olive varieties were presented in Table-1. Ripening index and oil content of olive varieties were ranged between 1.0-5.9 and 26-49 %. Olive maturity significantly affects the oil extraction yield from olives, which increases during ripening. Ayvalik, Nizip, Odemis and Halhali olives had higher oil content due to their higher ripening index value than Hasebi (Table-1). Nizip variety was also reported to be high oil producing variety[22,29]. The results obtained here are in the range of previously reported values of Arslan[22] and Tanilgan *et al.*[30].

The pit and pulp weight values (g) of the olives ranged from 0.5 to 1.0 and 1.6 to 2.6, respectively (Table-1). Halhali variety had the lowest pit and pulp weight value. The fruit pulp weight, width and length of Odemis and Hasebi variety was higher than other olive varieties ($p < 0.05$). This is actually quite common with the fact that in Turkey Ayvalik, Halhali and Nizip are generally processed for olive oil Odemis and Hasebi are used for both table olive and olive oil extraction purposes reported[31]. Tanilgan *et al.*[30] reported that the fruit weight as 3.5 and 3.9 g and pit weight as 0.3-0.5 g for edible oil olives. The results obtained here are in the range of previously reported values[22,32]. Recently, Yorulmaz *et al.*[33] reported the average weight of Halhali, Hasebi and Nizip as 2.3, 4.0 and 2.5 g, respectively, these values were slightly higher than our results. All olive varieties were harvested at the same time manually and stored under same conditions until analysis, differences between physical values may be due to variety, growth conditions, soil and climate for olives obtained from three different regions of Turkey.

The characteristics of the main quality indices of extra virgin olive oils extracted from all olive varieties are shown in

TABLE-1
SOME PROPERTIES OF OLIVES

Properties	Olive varieties				
	Ayvalik	Halhali	Hasebi	Nizip	Odemis
Ripening Index	2.4	3.4	1.0	3.9	5.9
Total oil (%)	33.2	32.2	25.6	36.1	49
Dry matter (%)	58.9	67.9	62.1	45.0	69.4
Pit weight (g)	1.0	0.5	0.9	0.7	0.61
Pulp weight (g)	1.6	1.0	**2.3**	1.5	**2.6**
Fruit width (mm)	15.1	13.2	**16.9**	15.3	**17.0**
Fruit length (mm)	18.8	15.0	**20.9**	17.1	**21.2**

*Values are means of three measurements.

TABLE-2
SOME PROPERTIES OF EXTRA VIRGIN OLIVE OILS

Properties	Extra Virgin Olive Oils					EVOO (EEC, 2003, Turkish Food Codex, 2010)
	Ayvalik	Halhali	Hasebi	Nizip	Odemis	
FFA (%)	0.4 ± 0.0c	0.6 ± 0.0a	0.5 ± 0.0b	0.5 ± 0.0b	0.5 ± 0.0b	≤ 0.8
Peroxide value (meqO_2/kg)	23.5 ± 0.1b	**27.1 ± 0.1a**	23.5 ± 0.0b	21.2 ± 0.1c	21.7 ± 0.7c	≤ 20
K 232	1.52 ± 0.0c	1.00 ± 0.0a	1.48 ± 0.0c	1.28 ± 0.0 b	1.60 ± 0.0c	≤ 2.5
K 270	0.15 ± 0.0a	0.14 ± 0.0ab	0.15 ± 0.0a	0.13 ± 0.0b	0.14 ± 0.0ab	≤ 0.22
Chlorophyll (mg kg^{-1})	**14.5 ± 0.3a**	4.8 ± 0.6c	8.2 ± 0.9b	**12.2 ± 0.9a**	**13.8 ± 0.2a**	–
Carotenoid (mg kg^{-1})	**7.9 ± 0.1b**	4.4 ± 0.2d	6.9 ± 0.4c	**8.8 ± 0.6a**	**9.5 ± 0.2a**	–
L	35.03 ± 0.1c	56.6 ± 1.1b	35.02 ± 0.1c	75.7 ± 2.4a	35.02 ± 0.1c	–
a	2.2 ± 0.1b	-0.25 ± 0.1c	2.2 ± 0.1b	2.8 ± 0.2a	2.2 ± 0.1b	–
b	2.9 ± 0.1c	36.7 ± 0.1b	2.9 ± 0.1c	77.83 ± 2.2a	2.9 ± 0.1c	–

*Mean ± SD. Significant differences in a same row are showed by different letters ($p < 0.05$).

Table-2. Ayvalik extra virgin olive oil had the lowest 0.4 % FFA where as Halhali extra virgin olive oil had the highest 0.6 % of FFA . Although peroxide value values of the were slightly high for Halhali olive oils, FFA and specific extinction coefficients values of olive oils were well below the limit established by EC Regulation[20] and Turkish Food Codex, Regulations for Olive and Olive Pomace oil (Communication No: 2010/35) for extra virgin olive oils (Table-2). Colour is one of the major attributes that affects consumer perception of quality of the virgin olive oil.

In olive oils, the main carotenoids and chlorophylls are lutein and pheophytin, respectively and they are mainly responsible for the colour of virgin olive oil, ranging from yellow-green to greenish gold as well as oxidative stability due to their antioxidant nature in the dark and pro-oxidant activity in the light[34]. The results showed that there were some differences between extra virgin olive oils chlorophylls' and carotenoids' content ($p < 0.05$). The highest chlorophyll concentration were observed in Ayvalik, Odemis and Nizip extra virgin olive oils with 14.5, 13.8 and 12.2 mg kg^{-1}, respectively, from Aegean and South-eastern region (Table-2). Similar trend was also observed for carotenoid content (Table-2) of virgin olive oils. Manai-Djebali *et al.*[34] found the chlorophyll and carotenoid content between 1.2 and 6.2, 1 and 3.8 mg kg^{-1}, respectively, for different type of extra virgin olive oils. L values show the lightness or whiteness value of extra virgin olive oils. L values indicate the lightness/darkness of extra virgin olive oils ranged between 35 and 76. On the other hand b value which indicate yellowness of the extra virgin olive oils and ranged between 3 and 79 (Table-2). It was found that Nizip and Halhali extra virgin olive oils had the highest whereas, Ayvalik, Odemis and Hasebi extra virgin olive oils had the lowest L and b values ($p < 0.05$). The results showed that Ayvalik, Hasebi and Odemis had same L, a and b values (Table-2). Present results were in accordance with the findings of Ogutcu and Yilmaz[3] who analyzed extra virgin olive oils obtained from different parts of Turkey. L, a and b values were found as 24.5 and 24.9, -0.48 and -2.1 and 10.1 and 13.3, respectively for Ayvalik and Nizip according to studies of Ocakoglu *et al.*[29].

Colour development using a Folin-Ciocalteu reagent (Folin-Ciocalteu assay) is the generally preferred method for measuring phenolics[35]. The content of phenolic compounds is an important parameter in the evaluation of extra virgin olive oil quality due to its correlation with peroxide number, acidity, oxidative stability and sensorial quality[36,37]. Table-3 shows total phenolic content and radical-scavenging activity of olives and their corresponding extra virgin olive oils.

The total phenols in the olives ranged between 133 and 217 mg kg^{-1} as expressed as caffeic acid of fruit. The total phenolic content of Ayvalik, Nizip and Odemis olives were higher than Hasebi and Halhali olives ($p < 0.05$). Halhali variety had the lowest total phenolic content 133 mg kg^{-1} (Table-3). Similarly, Arslan[22] reported the total phenolics content of Halhali olive variety from the Hatay region of Turkey ranged between 178 and 231 mg kg^{-1}. Boskou *et al.*[11] found that total phenol content of Greek table olives between 52-171 mg 100 g^{-1} of olives as expressed as caffeic acid. The total phenols in the extra virgin olive oils ranged between 44 and 97 mg caffeic acid per kg of oil (Table-3). The total phenolic content of Halhali, Nizip and Odemis extra virgin olive oils were the highest, Ayvalik and Hasebi oils had the lowest ($p < 0,05$) content. However, recently, total phenol concentrations of Southeast Anatolian oils were found to be lower than those of the other regions[33]. Present results are in accordance with the results of Ogutcu and Yilmaz[3] who found total phenolic content content of extra virgin olive oils ranging from 32 and 208 mg gallic acid kg^{-1} oil. Ocakoglu *et al.*[29] studied the total phenolic content

TABLE-3
TOTAL PHENOLIC CONTENT AND DPPH RADICAL SCAVENGING ACTIVITY OF OLIVES AND EXTRA VIRGIN OLIVE OILS

	Olives TPC (mg kg^{-1})	EVOO TPC (mg kg^{-1})	Olives RSA (%)	EVOO RSA (%)
Ayvalik	**216.7 ± 2.5a**	43.7 ± 0.3c	**84.1 ± 0.4a**	69.3 ± 1.9c
Halhali	133.3 ± 1.8c	**97.0 ± 0.8a**	**82.9 ± 0.8a**	68.9 ± 0.8c
Hasebi	137.5 ± 1.7c	44.1 ± 0.9c	**83.3 ± 1.01a**	68.5 ± 1.7c
Nizip	**191.5 ± 0.6a**	79.5 ± 0.1b	**84.2 ± 0.23 a**	**73.5 ± 1.5b**
Odemis	**179.9 ± 2.4b**	72.9 ± 0.2b	80.5 ± 1.0b	**77.9 ± 0.5a**
BHT	n.d	n.d	64.6 ± 1.5d	64.6 ± 1.5d
BHA	n.d	n.d	73.3 ± 2.1c	73.3 ± 2.1b

*Mean ± SD. Significant differences in a same column are showed by different letters ($p < 0.05$)

content of different extra virgin olive oils from different olive cultivars in Turkey were 67 and 112 for Ayvalik and Nizip varieties as mg gallic acid kg^{-1} oil. However, Manai-Djebali *et al.*[34] found total phenol content of five different extra virgin olive oils between 253 and 1400 mg kg^{-1} expressed as caffeic acid per kg of oil which were quite higher than our findings. Although, olive fruits are rich in polyphenols, only 2 % of the total phenolic content passes to the oil phase whilst the remaining 98 % is lost in the waste waters (black water, alpechin) and in the solid phase (pomace, alperujo)[38]. The amount of total phenols extra virgin olive oils normally ranges between 50 and 1000 mg kg^{-1}, depending on various factors[34]. Since same extraction procedures were used in this study the difference between total phenolic content of extra virgin olive oils might be mainly attributed to cultivar and degree of maturation rather than other factors.

Measurement of radical scavenging activity using discoloration has been widely used due to its stability, simplicity and reproducibility[26,35] and has been extensively applied on the study of antioxidant activity of food items, such as olives and olive oil[5,11,39]. Table-3 showed that the olives had higher DPPH radical scavenging activity than their corresponding olive oils. Among the olives Ayvalik, Halhali, Hasebi and Nizip had higher radical-scavenging activity than Odemis olive, BHA and BHT ($p < 0,05$). Interestingly, for corresponding extra virgin olive oils, Odemis had the highest radical-scavenging activity than other extra virgin olive oils, BHT and BHA ($p < 0.05$). The radical-scavenging activity of Nizip extra virgin olive oil (73.5 %) was comparable to BHA (73.3 %), ($p > 0.05$) and higher than BHT (64.6 %). A higher radical scavenging capacity of olives in comparison to their corresponding extra virgin olive oils might be attributed to higher total phenolic contents of olives (Table-3). A correlation between radical-scavenging activity and total phenolic content of samples were also found[3,4,13,36,37]. Keceli and Gordon[10] found that olives from Ayvalik, Sari Ulak Ege and Sari Uak Tarsus were more effective at scavenging DPPH radicals than their extra virgin olive oils. Nakbi *et al.*[40] found that Chetoui oil had higher Radical scavenging activity (78.56 %) than Chemlali oil (37.23 %). Our findings for extra virgin olive oils obtained from Odemis and Nizip were similar to DPPH radical scavenging activity of Chetoui olive oil and higher than Chemlali olive oil. Kiralan *et al.*[41] found that 87, 49 and 96 % radical-scavenging activity for Halhali, Hasebi and Nizip extra virgin olive oils, respectively. Recently, Kyralan and Bayrak[2] found the radical-scavenging activity activity of Ayvalik olive oil as 37 % which was quite lower than our values found for Ayvalik extra virgin olive oil.

Phenolic compounds, acting as natural antioxidants, increase the resistance of oil to storage and heating[42] are the most active antioxidants in virgin oil while enrichment of refined olive oil with phenolics increases its oxidative stability[14,43,44]. The relationship between the total phenolic content and the stability of extra virgin olive oils has been studied by several authors who tested stability to auto-oxidation through the measurement of both induction time and peroxide value. Peroxide value is used to measure the oxidation status of fats and oils (mainly as evidence of primary oxidation) after processing and storage[45]. Table-4 shows the peroxide value of oils stored at 60 ºC for 7 days. Although the oxidation was followed by measuring peroxide value, conjugated dienes and *p*-anisidine values only the peroxide values were shown here.

The initial peroxide value ranged between 21-27 and 5 meq O_2 kg^{-1} for extra virgin (EVOO) and refined olive oils (ROO), respectively. The peroxide value of oils reached up to 181, 61 and 352 meq O_2/kg for extra virgin olive oils and refined olive oil enriched with olive and olive oil extract, respectively after oxidation at 60 ºC for 7 days. However, the peroxide value of BHT and BHA were only 68 and 57 meqO_2/kg ($p < 0.05$) at the same time (Table-4). The results showed that extra virgin olive oils showed slight resistance to oxidation at 60 ºC compared to control ($p < 0.05$) and refined olive oil with BHA and BHT but they oxidised very fast at 100 ºC. Extra virgin olive oil extracts showed pro-oxidant activity in bulk oil oxidation when compared to that of control refined olive oil and refined olive oil with BHT and BHA ($p < 0.05$) oxidized at both 60 and 100 ºC (Table-4). It was reported that the antioxidants extracted from plants can show pro-oxidant activity at low concentration and antioxidant activity over certain critical values[46]. However, enrichments of the refined olive oils with 100 mg kg^{-1} olive extracts from Ayvalik, Nizip and Odemis caused significant antioxidant activity when compared to control and refined olive oils enriched with BHT and BHA ($p < 0.05$) at both 60 and 100 ºC (Table-4). Regarding the formation of primary oxidation products which is measured by peroxide value, Odemis, Ayvalik and Nizip olive extacts reduced the formation of peroxides of refined olive oil 88, 87 and 78 % respectively after 7 days oxidition at 60 ºC as

TABLE-4
EFFECT OF OLIVES AND THEIR CORRESPONDING EXTRA VIRGIN OLIVE OIL EXTRACTS ON THE OXIDATIVE STABILITY (FINAL PEROXIDE VALUE) OF BULK OIL STORED AT 60 AND 100 ºC FOR 7 AND 1 DAYS

Bulk oil	Peroxide values (meq O_2 kg^{-1} oil)							
	EVOO		Refined olive oil with EVOO extract		Refined olive oil with olive extract		Enhancement to oxidative stability (%)	
	60 ºC	100 ºC	60 ºC	100 ºC	60 ºC	100 ºC	60 ºC	100 ºC
Control	212 ± 4.6a	275	212 ± 4.6	275 ± 3.4	212 ± 4.6a	275 ± 3.4a	0	0
Ayvalik	179 ± 1.2b	875	262 ± 2.3	239 ± 1.2	27 ± 1.2e	66 ± 1.9e	87	76
Halhali	181 ± 1.2b	774	352 ± 5.4	301 ± 2.9	49 ± 3.4d	109 ± 2.9b	77	60
Hasebi	172 ± 2.3c	773	267 ± 3.9	331 ± 5.7	61 ± 3.4c	63 ± 1.2e	71	77
Nizip	178 ± 2.3b	920	296 ± 4.6	332 ± 2.3	47 ± 1.2d	53 ± 1.2f	78	80
Odemis	167 ± 1.2d	873	295 ± 1.2	233 ± 1.4	26 ± 2.2e	51 ± 1.2f	88	81
BHT	68 ± 2.3e	85	68 ± 2.3	85 ± 0.5	67.9 ± 2.3b	85 ± 0.5c	68	69
BHA	57 ± 2.5f	77	57 ± 2.5	77 ± 1.5	57.2 ± 2.5c	77 ± 1.5d	73	72

*Mean ± SD. Significant differences in a same column for each temperature are shown by different letters.

compared to control. The reduction rate were 81, 80 and 76 % respectively after 1 day oxidation at 100 ºC for the refined olive oil enriched with same olive extracts (Table-4). Moreover, BHT and BHA could only reduce peroxides formation at 69 and 73 % under the same conditions (Table-4). In other words, these results indicated that the olive extracts mainly obtained from Ayvalik, Nizip and Odemis olives had better capacity to inhibit oxidative process in refined olive oil than BHT and BHA at both 60 and 100 ºC ($p < 0.05$). This result, well correlate with the higher total phenolic contents of Ayvalik, Odemis and Nizip olive fruits than Hasebi and Halhali varieties (Table-3). This result also confirmed the results of Ogutcu and Yilmaz[3], who showed the total phenolic content of extra virgin olive oils from Southeast and Aegean region of Turkey were found to be similar, while other regions are separate from each other. This study also confirmed the strong relationship between total phenolic content and peroxide value as stated before[37]. The results found in this study in accordance with previous research is quite important finding since there are some health concern about the potent antioxidants such as BHT and BHA and olives can be very important source of phenolics showing comparable or even better activity than BHT and BHA[46]. Our findings are in accordance with the results of studies which showed that the enrichment of oils with phenolics from different source increased oxidative stability different types of oils including olive, sunflower, corn, canola oils and butter[9,10,14,18,43,44,47,48] and antioxidants added from different natural sources being more effective than BHT and BHA[48] during storage and cooking.

The oxidative stability of food emulsions is normally lower than the stability of the corresponding edible bulk oils, giving to these foods a shorter shelf life[39]. Food emulsions may possess several native antioxidants for coping with oxidative stresses, but these compounds can be removed or inactivated during food processing operations and therefore exogenous antioxidants are often added to foods during processing in order to extend product shelf-life. Table-5 shows the peroxide value of oil-in-water emulsions stored in dark at 60 ºC for 7 days. The emulsions were physically stable during all the experiments. Although the emulsion samples were stored for 14 days and oxidation was monitored by measuring peroxide value, conjugated dienes and *p*-anisidine values of the emulsion samples, only the peroxide values of 7 days were shown here. The initial peroxide value of extra virgin olive oils was ranged between 21-27 and 5 meq O_2/kg for refined olive oils. Interestingly extra virgin olive oil-in-water emulsions were very stable against oxidation when compared to control ($p < 0.05$) and showed similar stability to the refined olive oil-in-water emulsions enriched with BHT and BHA ($p \leq 0.05$) at 60 ºC after 7 days of oxidation (Table-5). On the contrary to bulk oil, refined olive oil-in-water emulsions enriched with extra virgin olive oil extracts from Hasebi, Nizip and Odemis showed remarkable antioxidant activity compared to control refined olive oil emulsion ($p < 0.05$) and similar activity to that of the refined olive oil-in-water emulsions with BHT and BHA ($p \leq 0.05$) under the same conditions (Table-5).

Therefore in emulsions, Odemis, Nizip and Hasebi extra virgin olive oil extracts were most effective at showing similar antioxidant activity to that of BHT and BHA ($p \leq 0.05$). In fact, at the end of the heating process, the treatments that indicated the best percentages of protection of enriched refined olive oil-in-water emulsions against the formation of peroxides were the ones containing Odemis, Nizip and Hasebi extra virgin olive oil extracts at providing 84, 81 and 80 % protection, respectively (Table-5). Under the same conditions, refined olive oil-in-water emulsions enriched with BHT and BHA and oxidized at 60 ºC for 7 days could only provide 75 and 78 % protection, respectively (Table-5). It was also found that enrichment of refined olive oil with olive extracts to prepare oil-in-water emulsions lead to a pro-oxidant effect since by the end of the heating period, the peroxide values obtained were higher than in the control, refined olive oil-in-water emulsions enriched with BHT and BHA (Table-5).

Our findings are in accordance with previous studies of that showed an antioxidant activity of olive oil[39] as well as phenolics from different sources[8,12,19] showed considerable antioxidant activity in oil-in-water emulsions. The result of this study are in accordance with 'polar paradox' where explains the efficiency of hydrophilic antioxidants as in olive extracts would protect bulk oil from oxidation, whereas lipophilic antioxidants from olive oil would protect the oil-in-water emulsions from oxidation due to their partitioning at oil phase where lipid oxidation occur[16,42,49]. Our results also confirms the results of Mattia *et al.*[49], who stated that besides their healthy properties, olives and olive oil minor compounds can play an important role in the oxidative stabilization of olive oil-based emulsions and thus this work may provide new practical information that may increase the potentiality of utilization of

TABLE-5
EFFECT OF OLIVES AND THEIR CORRESPONDING EXTRA VIRGIN OLIVE OIL EXTRACTS ON THE OXIDATIVE STABILITY (FINAL PEROXIDE VALUE) OF OIL-IN-WATER EMULSIONS STORED AT 60 ºC FOR 7 DAYS

Oil-in-water emulsions	Peroxide values (meq O_2 kg^{-1} oil)			
	EVOO emulsions	ROO Emulsions with EVOO extract	Enhancement to oxidative stability (%)	ROO Emulsions with olive extract
Control	273 ± 1.3a	273 ± 1.3a	0	273 ± 1.3
Ayvalik	75 ± 1.2c	113 ± 1.4b	59	340 ± 7.2
Halhali	76 ± 1.5c	78 ± 1.7c	72	253 ± 1.4
Hasebi	66 ± 2.7c	59 ± 1.5cde	**80**	247 ± 1.4
Nizip	44 ± 3.0d	52 ± 2.7de	**81**	150 ± 1.7
Odemis	76 ± 1.5c	43 ± 1.3e	**84**	250 ± 1.4
BHT	68 ± 1.9c	68 ± 1.9cd	75	68 ± 1.9
BHA	61 ± 1.5cd	61 ± 1.5cde	78	61 ± 1.5

*Mean ± SD. Significant differences in a same column are shown by different letters ($p < 0.05$).

olive oil or recovered olive oil phenolic compounds in formulated foods.

Conclusion

As a result of this study, variety has significant effect on both some properties and antioxidant activity of olives and their corresponding extra virgin olive oils. All oils fell in the category of extra virgin olive oil with slightly high peroxide value possibly due to inhereted properties from each olive variety. Ayvalik, Nizip and Odemis olives and their corresponding extra virgin olive oils had higher oil and phenol, pigment content and showed better or similar antioxidant activity BHT and BHA in different lipid systems including bulk oil and o/w emulsions. The results clearly showed a correlation between radical scavenging activities (DPPH test) and antioxidant activities of olive extracts from Ayvalik, Nizip and Odemis toward bulk lipid oxidation but not in oil-in-water emulsions. It is evident that the radical scavenging properties of extra virgin olive oil extracts from Nizip and Odemis exhibited a higher correlation with the inhibition of oxidation in oil-in-water emulsion than in bulk oil oxidation. This study confirmed the system dependent antioxidant activity of phenolic compounds from olive cultivars and their corresponding extra virgin olive oils being better or similar than that of BHT and BHA as synthetic antioxidants. As a conclusion, the results demonstrate the potential usefulness of natural antioxidants extracted from olive cultivars and their corresponding olive oils for food preservation. Olive and extra virgin olive oil extracts are safe as food lipid antioxidants compared to synthetic antioxidants such as BHA and BHT. Especially, olives neither processed for table olives nor processed for oil production or extra virgin olive oils directly might be used for the extraction of phenolics to be used as food additive. Enrichment of oils or oil containing foods with the extracts from olives and olive oil and therefore, improving quality and healthiness of the target oils suggests a future possible use them as a natural antioxidant and as an ingredient at an industrial scale since they seem to be useful for lipid stabilization in processed foods.

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REFERENCES

1. D. Arslan and M. Schreiner, *Sci. Horticul.*, **144**, 141 (2012).
2. M. Kýralan and A. Bayrak, *Int. J. Food Prop.*, **16**, 649 (2013).
3. M. Ogutcu and E. Yilmaz, *J. Sensory Studies*, **24**, 332 (2009).
4. H. Karaosmanoglu, F. Soyer, B. Ozen and F. Tokatli, *J. Agric. Food Chem.*, **58**, 8238 (2010).
5. J. Lee, H. Chung, P.-S. Chang and J. Lee, *Food Chem.*, **103**, 662 (2007).
6. A. Sousa, I.C.F.R. Ferreira, L. Barros, A. Bento and J.A. Pereira, *LWT-Food Sci. Technol.*, **41**, 739 (2008).
7. P. Terpinc, B. Èeh, N.P. Ulrih and H. Abramoviè, *Ind. Crops Prod.*, **39**, 210 (2012).
8. E. Conde, A. Moure, H. Dominguez, M.H. Gordon and J.C. Parajo, *J. Agric. Food Chem.*, **59**, 9158 (2011).
9. M.H. Gordon, F. Paiva-Martins and M. Almeida, *J. Agric. Food Chem.*, **49**, 2480 (2001).
10. T. Keceli and M.H. Gordon, *J. Sci. Food Agric.*, **81**, 1391 (2001).
11. G. Boskou, F.N. Salta, S. Chrysostomou, A. Mylona, A. Chiou and N. K. Andrikopoulos, *Food Chem.*, **94**, 558 (2006).
12. F. Paiva-Martins, V. Santos, H. Mangericao and M.H. Gordon, *J. Agric. Food Chem.*, **54**, 3738 (2006).
13. S. Achat, V. Tomao, K. Madani, M. Chibane, M. Elmaataoui, O. Dangles and F. Chemat, *Ultrason. Sonochem.*, **19**, 777 (2012).
14. L.S. Artajo, M.P. Romero, J.R. Morello and M.J. Motilva, *J. Agric. Food Chem.*, **54**, 6079 (2006).
15. I. Medina, S. Lois, D. Alcantara, R. Lucas and J. C. Morales, *J. Agric. Food Chem.*, **57**, 9773 (2009).
16. E.A. Decker, K. Warner, M.P. Richards and F. Shahidi, *J. Agric. Food Chem.*, **53**, 4303 (2005).
17. M. Nissiotis and M. Tasioula-Margari, *Food Chem.*, **77**, 371 (2002).
18. T. Keceli and M.H. Gordon, *J. Food Sci.*, **67**, 943 (2002).
19. P. Lisete-Torres, S. Losada-Barreiro, H. Albuquerque, V. Sanchez-Paz, F. Paiva-Martins and C. Bravo-Diaz, *J. Agric. Food Chem.*, **60**, 7318 (2012).
20. C.R. (EC), *Official J. Eur. Union*, **L295**, 57 (2003).
21. A. Allalout, D. Krichène, K. Methenni, A. Taamalli, I. Oueslati, D. Daoud and M. Zarrouk, *Sci. Horticul.*, **120**, 77 (2009).
22. D. Arslan, *Grasasy Aceites*, **63**, 158 (2012).
23. R. Fernandez-Orozco, M. Roca, B. Gandul-Rojas and L. Gallardo-Guerrero, *J. Food Comp. Anal.*, **24**, 858 (2011).
24. M. Murkovic, S. Lechner, A. Pietzka, M. Bratacos and E. Katzogiannos, *J. Biochem. Biophys. Methods*, **61**, 155 (2004).
25. T. Gutfinger, *JAOCS*, **58**, 966 (1981).
26. K. Mishra, H. Ojha and N.K. Chaudhury, *Food Chem.*, **130**, 1036 (2012).
27. AOCS, In ed.: D. Firestone, AOCS Press., Illionis, edn. 4 (1989).
28. SPSS, Base 13.0 Applications Guide SPSS Inc. Chigago, USA (2001).
29. D. Ocakoglu, F. Tokatli, B. Ozen and F. Korel, *Food Chem.*, **113**, 401 (2012).
30. K. Tanilgan, M.M. Ozcan and A. Ünver, *Grasasy Aceites*, **58**, 142 (2007).
31. N. Ozilbey, Zeytin Çeitlerimiz, Sidas Ltd. Sti., Ýzmir (2011).
32. H. Cetin, D. Arslan and M.M. Ozcan, *J. Sci. Food Agric.*, **91**, 498 (2011).
33. A. Yorulmaz, E.S. Poyrazoglu, M.M. Ozcan and A. Tekin, *Eur. J. Lipid Sci. Technol.*, **114**, 1083 (2012).
34. H. Manai-Djebali, D. Krichène, Y. Ouni, L. Gallardo, J. Sánchez, E. Osorio, D. Daoud, F. Guido and M. Zarrouk, *J. Food Comp. Anal.* (2012).
35. T. Katsube, H. Tabata, Y. Ohta, Y. Yamasaki, E. Anuurad, K. Shiwaku and Y. Yamane, *J. Agric. Food Chem.*, **52**, 2391 (2004).
36. M. Del Carlo, G. Sacchetti, C. Di Mattia, D. Compagnone, D. Mastrocola, L. Liberatore and A. Cichelli, *J. Agric. Food Chem.*, **52**, 4072 (2004).
37. J.R. Morello, S. Vuorela, M.P. Romero, M.J. Motilva and M. Heinonen, *J. Agric. Food Chem.*, **53**, 2002 (2005).
38. S. DeJong and M.C. Lanari, *Food Chem.*, **116**, 892 (2009).
39. S. Gomez-Alonso, G. Fregapane, M.D. Salvador and M.H. Gordon, *J. Agric. Food Chem.*, **51**, 667 (2003).
40. A. Nakbi, M. Issaoui, S. Dabbou, N. Koubaa, A. Echbili, M. Hammami and N. Attia, *J. Food Comp. Anal.*, **23**, 711 (2010).
41. M. Kiralan, A. Bayrak and M.T. Özkaya, *J. Am. Oil Chem. Soc.*, **86**, 247 (2008).
42. L. Cerretani, A. Giuliani, R.M. Maggio, A. Bendini, T.G. Toschi and A. Cichelli, *Eur. J. Lipid Sci. Technol.*, **112**, 1150 (2010).
43. B. Aydeniz and E. Yilmaz, *Eur. J. Lipid Sci. Technol.*, **114**, 933 (2012).
44. M. Suárez, M.-P. Romero, T. Ramo and M.-J. Motilva, *Eur. J. Lipid Sci. Technol.*, **113**, 894 (2011).
45. A. Rotondi and M. Magli, *J. Food Agric. Environ.*, **2**, 193 (2004).
46. T.-I. Lafka, A.E. Lazou, V.J. Sinanoglou and E.S. Lazos, *Food Chem.*, **125**, 92 (2011).
47. R.S. Farag, G.S. El-Baroty and A.M. Basuny, *Int. J. Food Sci. Technol.*, **38**, 81 (2003).
48. D.A.P. de Abreu, K.V. Rodríguez and J.M. Cruz Freire, *Eur. J. Lipid Sci. Technol.*, **113**, 1395 (2011).
49. C.D. Mattia, G. Sacchetti and P. Pittia, *Food Biophys.*, **6**, 295 (2010).