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Physicochemical properties of cold pressed sunflower, peanut, rapeseed, mustard and olive oils grown in the Eastern Mediterranean region

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ABSTRACT

Fatty acid composition and stability of vegetable oils have taken more attention as an essential source of biologically active compounds in a good balanced diet. The purpose of the study was to determine peroxide value, free fatty acids, unsaponifiable matter, total carotenoid content, iodine value and fatty acid composition of sunflower, rapeseed, mustard, peanut and olive oils. Rapeseed and peanut oils had the highest peroxide values, while sunflower oil had the lowest peroxide values. The free fatty acid value of the tested oils varied between 0.43 and 1.36% oleic. The peanut oil had the highest free acid value and the mustard oil had the lowest one. Total carotenoid contents of mustard and rape seed oil were higher than those of the other oils tested. Palmitic acid (C16:0), oleic acid (C18:1) and stearic acid (C18:0) were the common main fatty acid components of the vegetable oils tested. Followed by linoleic acid, the amount of oleic acid was the highest among other fatty acid components. Mustard oil had the highest erucic acid (C22:1) with the amount of 11.38%, indicating that it cannot be used for human consumption. Among the oils investigated, sunflower and mustard oils were more stable than rapeseed, peanut and olive oils.

1. Introduction

Edible vegetable oils supply most of the dietary intake of the lipids vitally needed for daily life that provide energy, essential fatty acids and fat soluble vitamins (Yang et al., 2018; Dorni et al., 2018). As the world population grows, global oil demand remains strong. Edible oils are commonly used for frying, baking, cooking, salad and various other industries (O'Brien, 2004; Majchrzak et al., 2018). Mustard (*Brassica campestris*), rapeseed (*Brassica napus*), sunflower (*Helianthus annuus*), peanut (*Arachis hypogea*) and olive (*Olea europaea*) are top five oil crops cultivated worldwide, and their oils are the most common healthy cooking oils used. Sunflower oil, olive oil and rapeseed oils are among the edible vegetable oils mostly consumed in Turkey. Currently, oil crop production is not sufficient to meet the national demand of Turkey. Consequently, Turkey imports 60% of edible oil evaluated as seed or crude oil (Gul et al., 2016).

The quality of the vegetable oils is one of the most important factors that effect their acceptability and market value (O'Brien, 2004). Diet with higher amount of saturated fats is one of the major reasons of coronary heart diseases. Therefore, increasing intake of polyunsaturated fatty acids instead of saturated fatty acid decreases the risk of cardiovascular diseases (Assmann et al., 1999; Ganesan et al., 2018). Vegetable oils are recommended for healthy life due to their high content of polyunsaturated fatty acids (Indelicato et al., 2017). However, the amount of saturated and unsaturated fatty acids varies in different oil crops. The ratio of omega-3 and omega-6 fatty acids are important to provide cardiovascular health benefits (Okuyama, 2001; Gonzalez-Fernandez et al., 2017). It is estimated that the dietary omega-6/omega-3 fatty acids ratio is between 14:1 and 20:1. Changing this ratio can alter metabolic and inflammatory rate of human body (Tribole, 2007). However, higher rate of unsaturated and polyunsaturated fatty acids such as linoleic acid and linolenic acid promote oxidation that affect the oil stability. Oil stability is one of the most important factors that effect the oil quality (Redondo-Cuevas et al., 2018). Since instable oils have undesirable taste and flavor, they may lose

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nutritional value and may produce toxic compounds. Antioxidants such as vitamin E (tocopherol) in oils promote the oxidative stability and prevent the oxidative degradability of oils (Tawfik and Huyghebaert, 1999; Cayuela and García, 2017).

Crude oil quality is very important since it determines the upcoming processing and it is a good indicator of necessary treatments (Ceriani et al., 2008). Different physical and/or chemical properties of vegetable oils such as acidity, density, viscosity, color, refractive index, moisture, volatility, dielectric constant, total polar compounds, saponification, peroxide, iodine, ester and carbonyl values, determine the quality and the stability of oils which are necessary for any specific purpose (Mousavi et al., 2012). These physical parameters greatly vary in temperature on the stability, viscosity, peroxide value, and iodine value to assess the quality and functionality of the oil (Jinfeng et al., 2011).

Vegetable oils are a complex mixture of various saturated and unsaturated fatty acids, phosphatides, pigments, sterols, and tocopherols. The rate of saturated to unsaturated fatty acids is very important for human nutrition (Przybylski and McDonald, 1995; Ganesan et al., 2018). Higher rate of saturated fatty acids is important for oil stability while higher rate of unsaturated fatty acids is important to decrease the concentration of low density lipoproteins, affecting the ratio of low density lipoproteins to high density lipoproteins, and preventing clotting and vascular smooth muscle proliferation (Dzisiak, 2004).

Two types of long chain polyunsaturated fatty acids, alpha-linolenic acid (18:3, n-3) and linoleic acid (18:2, n-6) fatty acids are considered as essential fatty acids since they are not synthesized by human body due to the absence of necessary enzymes, and they must be taken from the foods (Mišurcová et al., 2011). Alpha-linolenic (18:3, n-3) fatty acid, and linoleic acid, namely omega-6 fatty acids, (18:2, n-6) are two important long chain polyunsaturated fatty acids (Dubois et al., 2007). Having higher rate of alpha-linolenic acid (omega-3) and linolenic acids (omega-6) in diet increases high density lipoproteins-cholesterol and decreases low density lipoproteins-cholesterol. However, having higher rate of oleic acid decreases low density lipoproteins-cholesterol in diet does not affect high density lipoproteins-cholesterol levels (Przybylski and Mcdonald, 1995; Gonzalez-Fernandez et al., 2017).

Therefore, it is needed to investigate the physical and chemical properties of peanut, rapeseed, sunflower, mustard and olive oils on health consequences of consuming oil associated with the choice of consumers. The purpose of the present study is to determine the fatty acid composition, tocopherol content and quality parameters such as free fatty acid content, saponification value, peroxide value and induction time of peanut, rapeseed, sunflower, mustard and olive oils.

2. Material and methods

Peanut, sunflower, rapeseed, mustard plants grown in the experimental field of Mustafa Kemal University were used for cold pressing. After harvesting, seed of each crop was dried at 35 °C. Oil extraction was carried out by using a screwexpeller (Kocmaksan, İzmir, Turkey) An oilscrew expeller, powered by a 10 kW electric motor, was used to extract oil from the seeds of the tested plants. The oil expeller was cleaned after each extraction. Olive oil samples were extracted from olives by a laboratory scale mechanical mill (Hakkı Usta, Turkey) with a crusher, a vertical malaxer and a two-phase centrifuge. Malaxation and centrifuge processes were performed at 25 °C for 30 min and at 5000 rpm, respectively. The oil was separated by decanting process, and then it was put into dark glass bottles. Oil samples were kept at 4 °C until chemical analysis which were triplicated.

Free acidity (% oleic acid) and peroxide value (meq O_2/kg) analysis were performed according to the AOCS Official methods Ca 5a-40 and Cd 8–53, respectively. The presence of carotenoids in each oil sample of the tested plants was measured at 472 nm as a neat sample and in a 1:1 mixture with UV-grade acetone (Shimadzu UV-2401PC), and results were expressed as lutein mg/kg (Minguez-Mosquera et al., 1991).

The fatty acid percentage was used to calculate iodine values (I_2N) according to the following formula: (Torres and Maestri, 2006).

$$I_2N = (\%\text{Palmitoleic acid} \times 1.001) + (\%\text{oleic acid} \times 0.899) + (\%\text{linoleic acid} \times 1.814). \quad (1)$$

For the determination of fatty acid composition (ISO:12966-2, 2011), the methyl ester of each oil sample was prepared by shaking each oil solution vigorously in *n*-heptane (0.1 g in 2 mL) with 2 N methanolic potassium then unsaponifiable matter was extracted. Approximately 0.5 µl of fatty acid methyl esters was injected into the gas chromatography (GC) using a Shimadzu GC apparatus (Model 14B) equipped with a hydrogen flame ionization detector (FID) and a capillary column DB-23 of 60 m length × 0.25 mm i.d. and 0.25 µm of film thickness (Agilent J & W, US) in order to determine the fatty acid composition of each vegetable oil. The carrier gas was helium at 1 cm^3/min and the temperatures of injector, oven and detector were 270, 230 and 280 °C, respectively. The results were expressed as peak area (relative) percent. The fatty acid composition of each sample was determined in triplicate.

The experiment was set up in a completely randomized design with three replicates. Variance analyses were conducted by using PROC GLM procedure of SAS (SAS Institute, 2002). The means were compared by using the least significant difference method (LSD) at 5% level ($P < 0.05$) of significance for all the parameters evaluated in the ANOVA.

3. Results and discussion

The physicochemical properties of cold extracted oil are given in Table 1. Free fatty acid values, expressed as % of oleic acid, varied between 0.43 and 1.36% oleic. The highest free acid amount was obtained from peanut oil followed by olive and sunflower oil, respectively.

When oil quality is considered, the amount of free fatty acids is shown to be a good indicator (Sharma et al., 2009). Oils, which have higher free fatty acids contents, posses poor quality, and significant losses occur during the refining process (Cornelius, 1966). Therefore, low free fatty acid in crude oil is a good physicochemical indicator for crude oil, and it could be useful for refining process. Low free fatty acid content of cold pressed mustard and rape seed oils shows their higher quality, and this can provide great advantage during the refining process. Esuoso and Odetokun (1995) stated that free fatty acid contents of oils should not exceed 5% in order to be suitable for edibility. According to this view, cold extracted mustard, rapeseed, sunflower, peanut and olive oils are edible. According to the International Olive Council (IOC) standard for free fatty acids extra virgin olive oil has a maximum of 0.8% free fatty acids. Olive oil obtained in the eastern Mediterranean region was within this range established for virgin olive oil.

The peroxide value varied between 9.46 and 4.19 meq O_2/kg, indicating that the tested vegetable oils are fresh. Rapeseed oil had the highest peroxide value, while sunflower had the lowest one. The fresh vegetable oils normally have peroxide values below 10 meq O_2/kg (Orhevba and Efomah, 2012). High temperature, visible light and oxygen can easily increase the peroxide value of the oils. Only cooking oils with the lowest initial peroxide value are

Table 1
Physicochemical parameters of cold extracted mustard, rapeseed, sunflower, peanut and olive oils.

Species	Free fatty acid (% oleic)	Peroxide value (meq O_2/kg)	Unsaponifiable matter (%)	Total carotenoid (mg/kg)	Iodine value
Mustard	0.43	3.66	1.01	18.93	94.95
Rapeseed	0.65	9.46	0.97	12.01	107.51
Sunflower	0.81	4.19	0.81	3.06	102.02
Peanut	1.36	8.39	0.94	1.83	111.19
Olive	0.82	6.39	1.23	6.21	80.03
LSD 0.05	0.16	0.99	0.12	0.44	7.14

suitable for consumption. Oils with peroxide value higher than 9 meq O_2/kg cause undesirable health problems by increasing reactive oxygen species as well as secondary products of lipid peroxidation that stimulate cardiovascular and inflammatory diseases (Lobo et al., 2010). Therefore, oils which have peroxide value should not be produced and some regulations must be put for sale of highly-oxidized cooking oils. Generally, oils with peroxide levels higher than 10 meq O_2/kg are considered to be less stable, and they have short shelf life. The present study showed that rapeseed and peanut oils have higher initial peroxide value, indicating that they have very short shelf life and they will quickly become unsuitable for human diets when compared with mustard, sunflower and olive oils.

Unsaponifiable matter of the tested plant oils varied between 0.81 and 1.23%. The highest unsaponifiable matter content was obtained from olive oil with 1.23%, and the lowest was obtained from sunflower oil with 0.81%. Unsaponifiable matters in the fats and oil are substances dissolved in oils. They cannot be saponified by the caustic alkalies but are soluble in the fat solvent.

Considerable variability in iodine value was detected among the vegetable oils tested. The iodine value varied between 80.03 and 111.19. The highest iodine value was obtained from peanut, and the lowest was obtained from olive oil. The iodine value of an oil is a indicator of the unsaturated fatty acid, that is iodine value is used as a indicator of unsaturation degree (Pomeranz and Meloan, 1987; Nielson, 1994). Among the vegetable oils tested, the best unsaturated oil was peanut oil followed by rapeseed and sunflower oils. Olive oil had low iodine value (80.3), indicating that it could be used for soap making and in human diets. Oils which have higher iodine values (about 190) are used for paint and varnish industries.

The fatty acid composition of sunflower, rapeseed, mustard, peanut and olive oils are shown in Table 2. It was found that the main fatty acids of tested oils were palmitic acid (C16:0), oleic acid (C18:1n9c) and stearic acid (C18:0). The highest rate of palmitic acid was obtained from olive oil with 15.11% followed by mustard and peanut oils with 10.24 and 9.37%, respectively. Low level of palmitoleic acid was detected in the olive (1.24%), sunflower (0.95%) and rapeseed oil (0.17%). When stearic acid (C18:0) was considered, it varied between 2.02 and 3.73% among the tested plant oils. The highest stearic acid was obtained from peanut and olive oils followed by sunflower, rapeseed and mustard oils, respectively.

Oleic acid (C18:1n9c) content had the highest ratio, and it ranged between 36.65 and 68.85%. Rapeseed and olive oils include higher amount of oleic acids than those of sunflower, peanut and mustard oils. Olive oil is one of the healthiest oils in human diet due to its higher mono unsaturated fatty acid content, namely higher oleic acid (55–83%) (Salimon and Farhan, 2012; Esmaeili and Shaykhmoradi, 2012; Matthäus and Ozcan, 2011; Dabbou et al., 2011). Therefore, people living in the Mediterranean region have low incidence of coronary heart diseases, colon, breast and skin cancer.

Linoleic acid (C18:2n-6) was detected in all of the oils tested, but its amount showed differences among the tested oils. The highest linoleic acid was obtained from peanut, mustard and sunflower with 23.69, 22.06 and 21.58%, respectively. Sunflower, rapeseed mustard and peanut oils include similar amount of linoleic (C18:2n6) acids. Linoleic acid (C18:2n6), which is found in sunflower, rapeseed, mustard, peanut and olive, are essential fatty acid that is vital in the maintenance of some key physiological functions of the human body. The omega-3 family consists of α-linolenic acid and its long chained derivatives, eicosapentaenoic acid and docosahexaenoic acid. However, only olive oil has small amount of α-linolenic acid (C18:3n3) with the amount of (0.54%). Moreover, all of other tested oils were lack of α-linolenic acid. Dupont et al. (1990) stated that linoleic acid is essential for human body to maintain the integrity of the skin, cell membranes, the immune system, and eicosanoids synthesis.

Mustard oil had high eicosenoic acid (C20:1n9) with the amount of 13.38%, whereas small amount of eicosenoic acid in sunflower, rapeseed, peanut and olive oils was found. Rapeseed and mustard oils had γ-linolenic acid (C18:3n6) with the content of 6.75 and 8.06%, respectively. However, sunflower, peanut and olive oil did not include γ-linolenic acid. The omega-6 fatty acid family consists of linoleic acid and its longer chain derivatives such as γ-linolenic acid and arachidonic acid. Rapeseed, mustard and sunflower oils had the highest rate of omega-6 fatty acid family.

Table 2
Fatty acid compositions of sunflower, rapeseed, mustard, peanut and olive oils.

Fatty acid profile	Sunflower	Rape seed	Mustard	Peanut	Olive
Palmitic acid(C16:0)	$5.94_{\pm0.84}$	$3.97_{\pm0.07}$	$10.24_{\pm0.09}$	$9.37_{\pm0.11}$	$15.11_{\pm0.36}$
Palmitoleic acid(C16:1n7)	$0.95_{\pm0.14}$	$0.17_{\pm0.02}$	–	–	$1.24_{\pm0.03}$
Stearic acid(C18:0)	$2.53_{\pm0.05}$	$2.12_{\pm0.02}$	$2.02_{\pm0.02}$	$3.73_{\pm0.04}$	$3.08_{\pm0.03}$
Oleic acid(C18:1n9c)	$68.88_{\pm0.94}$	$63.68_{\pm1.56}$	$36.65_{\pm0.19}$	$55.33_{\pm0.18}$	$68.85_{\pm0.29}$
Vaccenic acid(C18:1n7c)	–	–	–	–	$2.58_{\pm0.06}$
Linoleic acid(C18:2n6)	$21.58_{\pm0.22}$	$17.43_{\pm0.02}$	$22.06_{\pm0.09}$	$23.69_{\pm0.03}$	$8.50_{\pm0.11}$
γ-linolenic acid(C18:3n6)	–	$6.75_{\pm0.02}$	$8.06_{\pm0.03}$	–	–
α-linolenic acid(C18:3n3)	–	–	–	–	$0.54_{\pm0.01}$
Arachidic(C20:0)	$0.28_{\pm10}$	$0.70_{\pm0.01}$	$0.92_{\pm0.01}$	$1.83_{\pm0.01}$	$0.50_{\pm0.18}$
Gadoleic acid(C20:1n11)	–	–	$0.40_{\pm0.01}$	0.00	–
Eicosenoic acid(C20:1n9)	$0.23_{\pm0.11}$	$2.82_{\pm0.01}$	$13.38_{\pm0.04}$	$1.57_{\pm0.07}$	$0.29_{\pm0.2}$
Behenic acid(C22:0)	$0.49_{\pm0.24}$	$0.37_{\pm0.02}$	$0.72_{\pm0.02}$	$3.25_{\pm0.05}$	–
Erucic acid(C22:1n9)	–	$1.93_{\pm0.04}$	$11.38_{\pm0.08}$	0.00	–
Lignoceric acid(C24:0)	$0.31_{\pm0.16}$	–	$0.81_{\pm0.02}$	$1.62_{\pm0.25}$	–

Olive oil was only one of the oil which has vaccenic acid (C18:1n7c), a minor constituent of hardened vegetable oil, with the amount of 2.58%. Vaccenic acid is normally found in animal fat, but lower amount of vaccenic acid was detected in vegetable oils (Appelqvist, 1975).

Among the tested vegetable oils, peanut oil included the highest long chain saturated fatty acid ratio, containing 5.7% of arachidic, behenic and lignoceric fatty acids. Our findings are similar to the findings obtained by Zambiazi et al. (2007) and Kostik et al. (2013) who stated that the total content of arachidic, behenic and lignoceric fatty acid were found to be 6.18 and 7.2%, respectively. Our findings for palmitic, stearic, oleic, linoleic and arachidic acid contents in peanut oil were very similar to the results obtained by Ozcan and Seven (2003).

Mustard oil contained the higher amount of erucic acid (C22:1n9) with the amount of 11.38%. Oils including higher erucic acid are considered to be harmful for human beings (George and Suryavanshi, 1985; West et al., 2002; Food Standards Australia New Zealand, 2003) since it was reported that higher amount of erucic acid impairs myocardial conductance, causing lipidosis in children and increasing blood cholesterol (Ackman et al., 1977). Therefore, some countries have regulations about the maximum level of erucic acid which is between 2 and 5% of the total fatty acids owing to the potential public health risks of exceeding levels. Hence, mustard oil tested in the present study is a good alternative to fossil oils for industrial applications. Mustard oils including higher amount of erucic acid are used to produce important commercial products such as high grade lubricants, plastics, emulsifiers, coatings, textile softeners, surfactants and biodiesel (Kaimal et al., 1993; Friedt and Lühs, 1998; Piazza and Foglia, 2001).

Behenic acid is one of the minor saturated long-chain fatty acids found in sunflower, rapeseed, mustard and peanut oils with the content of 0.49, 0.37, 0.72 and 3.25, respectively (Table 2). Owing to its long chain, bioavailability of behenic acid is quite low (Webb and Sanders, 1991) and its effect on cholesterol content is less (Cater and Garg, 1997). Major amount of behenic acid was reported in sunflower oil (Cater and Denke, 2001; Salas et al., 2005; Izquierdo and Aguirrezábal, 2008). Minor amount of lignoceric acid was detected in the oil of sunflower, mustard and peanut oils with the amount of 0.31, 0.81 and 1.62%, respectively. Barkley et al. (2011) and Tang et al. (2013) detected lignoceric acid in peanut oil. The fatty acid composition of oils is significantly influenced by cultivar, ecological conditions, latitude and agricultural practices (Konuskan et al., 2017).

4. Conclusion

Peroxide value, free fatty acids, unsaponifiable matter, total carotenoid contents and fatty acid composition of oils determine the physical and chemical properties of the vegetable oils. Fatty acid composition of tested vegetable oil is within the range as explained in the literature except for mustard oil which had the highest erucic acid rate indicating that it cannot be used in human diet. Palmitic acid, oleic acid and stearic acid were the common major fatty acid components in the vegetable oils tested. Oleic acid was the highest fatty acid components followed by linoleic acid. It can be concluded that the sunflower, rapeseed, peanut and olive oils were within the acceptable levels of physical and chemical quality parameters indicated in the literature.

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