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Bioactive lipids, antiradical activity and stability of rosehip seed oil under thermal and photo-induced oxidation

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SUMMARY: In the present report, the fatty acids, tocopherols, and sterol profiles as well as the total phenolics and carotenoids of rosehip (*Rosa canina*) seed oil were determined. The major fatty acids in the oil were linoleic and linolenic acids, comprising 54.80% and 23.47% of the total fatty acids, respectively. Other bioactive lipids in the oil included total tocopherols (786.3 mg/kg), total phenolics (37.97 mg/kg) and total carotenoids (218.8 mg/kg). Rosehip oil was rich in γ-tocopherol (472.0 mg/kg) and β-sitosterol (78.0% of total sterols). The DPPH· (2,2′-diphenyl-1-picrylhydrazyl) radical scavenging activity of the oil showed 1.08 mg α-tocopherol/g oil and 4.18 μmol TEAC (Trolox equivalent antioxidant capacity)/g oil, respectively. The $ABTS^+$ (2,2′-Azino-bis-3-ethylbenzothiazoline-6-sulphonic acid) radical scavenging activity of the oil showed 1.00 mg α-tocopherol/g oil and 3.02 μmol TEAC/g oil, respectively. The induction period (IP) of the oil was 3.46 h for the Rancimat test (110 °C), while the IP of oil in differential scanning calorimetry (DSC) test (100-150 °C) ranged between 0.26 and 58.06 min. The oxidative stability of the oil was determined under thermal and photo oxidation conditions. The progression of oxidation at 30 °C (under UV light) and at 60 °C (in the dark) was followed by recording the ultraviolet absorption (K_{232} and K_{270}) and degradation of total tocopherols, γ-tocopherol and total carotenoids. Rapid deterioration occurred in the oil stored under UV light conditions. The information provided in the present work is of importance for using rosehip seed oil in different food and non-food applications.

KEYWORDS: *Differential scanning calorimetry; Induction period; Oxidation;* Rosa canina *L.; UV light*

RESUMEN: ***Lípidos bioactivos, actividad antirradical y estabilidad de aceites de semillas de rosa mosqueta bajo oxidación térmica y fotoinducida.*** En este trabajo se determinaron los ácidos grasos, tocoferoles, el perfil de esteroles, así como los fenoles totales y los carotenoides de aceites de semillas de rosa mosqueta (*Rosa canina*). Los principales ácidos grasos fueron linoleico y linolénico, que representan el 54,80% y 23,47% de los ácidos grasos totales, respectivamente. Otros lípidos bioactivos incluyen tocoferoles totales (786,3 mg/kg), fenoles (37,97 mg/kg) y carotenoides (218,8 mg/kg). El aceite de rosa mosqueta es rico en γ-tocoferol (472,0 mg/kg) y β-sitosterol (78,0% del total de los esteroles). La actividad captadora de radicales DPPH· (2,2′-difenil-1-picrilhidrazilo) fue 1,08 mg de α-tocoferol/g de aceite y 4,18 μmol de TEAC (capacidad antioxidante equivalente de Trolox)/g de aceite, respectivamente. La actividad captadora de radicales ABTS+ (2,2'-Azino-bis-3-etilbenzotiazolin-6-sulfónico) fue de 1,00 mg de α-tocoferol/g de aceite y 3,02 μmoles de TEAC/g de aceite, respectivamente. El período de inducción (IP) del aceite fue 3.46 h Rancimat (110 °C), mientras que el IP del aceite para la prueba de calorimetría de barrido diferencial (DSC) (100-150 °C) osciló entre 0,26-58,06 min. La estabilidad oxidativa del aceite se determinó en condiciones térmicas y de fotooxidativas. El progreso de la oxidación a 30 °C (bajo luz ultravioleta) y 60 °C (en oscuridad) fue determinado mediante las medidas del K232 y K270 mediante la degradación de tocoferoles totales, γ-tocoferol y carotenoides totales. El rápido deterioro se produjo en el aceite almacenado bajo condiciones de luz UV. La información proporcionada en el presente trabajo es de importancia para usar aceite de semilla de rosa mosqueta en diferentes aplicaciones alimentarias y no alimentarias.

PALABRAS CLAVE: *Calorimetría diferencial de barrido; Oxidación; Periodo de inducción;* Rosa canina *L.; Ultravioleta*

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1. INTRODUCTION

The value of the rose flower is well known, but rose plants have been valued also for their fruits, the rosehips (Nybom and Werlemark, 2015). Rosehip (*Rosa canina* L., family Rosaceae) fruits are rich in ascorbic acid (Tumbas *et al*., 2012), phenolics and carotenoids (Gao *et al.,* 2000; Böhm *et al*., 2003). The plant materials have been preferably used in foods such as herbal teas (Tumbas *et al*., 2012), marmalades (Sagdic *et al*., 2015), and juices (Böhm *et al.,* 2003). Rosehip fruits are used as an ingredient in probiotic drinks, yoghurts and soups (Demir *et al.,* 2014). In certain cultures, rosehips have medical applications for gastric disorder, gallstones, constipation, dropsy, flu, inflammation, osteoarthritis, rheumatoid arthritis and chronic pain (Patel, 2017; Nybom and Werlemark, 2015).

Approximately 29% of rosehip weight is the seeds, and these seeds are discarded as waste after the processing of rosehip (Szentmihályi *et al*., 2002). Based on rosehip species grown in Turkey, the oil content of the seeds contained up to 7.95% (Çelik *et al*., 2010). Rosehip seed oil has been revealed as a valuable nonconventional oil due to the fact that it is rich in polyunsaturated fatty acids (PUFA). The most abundant fatty acid is linoleic acid (41.1-51.0%), followed by α-linolenic (19.6-23.8%) and oleic (20.3-23.0%) acids (Çelik *et al*., 2010). Machmudah *et al*., (2007) extracted rosehip seed oil using supercritical CO_2, and found the oil to contain linoleic acid as the most abundant acid followed by linolenic, palmitic and stearic acids. Topkafa (2016) reported that cold-pressed rosehip seed oil contained high amounts of OLL, PLL, LLLn and LLL triacylglycerols as well as tocols (1124 mg/kg).

Although the oil content in rosehip seeds is low, the oil is rich in bioactive lipids including tocols and sterols that contribute to healthy traits (Fromm *et al*., 2012; Grajzer *et al*., 2015, Ramadan, 2015). The oil also contains high levels of carotenoids (i.e., lycopene, β-carotene and rubixanthin) (Franco *et al*., 2007; Silva *et al*., 2008). Rosehip seed oil could be used in the treatment of pigmentation, ulceration and scarring problems. The oil could be also applied in dermatological and cosmetic applications (Contri *et al*., 2016). Due to its high levels of bioactive compounds, rosehip oil has antibacterial, antifungal, and anti-inflammatory traits and could inhibit cancer cell proliferation (Olsson *et al*., 2004; Silva *et al*., 2008). Paladines *et al*., (2014) and Martínez-Romero (2017) added rosehip oil to improve the beneficial effect of Aloe Vera gel in delaying the ripening and maintaining the postharvest quality of several stone-fruits and plums.

Rosehip oil contains more than 77% PUFA, and therefore the oil is susceptible to oxidation (Concha *et al*., 2006). There is limited published research on rosehip seed oil. The tocopherols, phenolics and sterols of rosehip oil were investigated (Grajzer *et al*., 2015; Ilyasoğlu *et al*., 2014; Zlatanov, 1999). Recently, de Santana *et al*. (2016) used mid-infrared (MIR) spectroscopy and partial least square discriminant analysis (PLS-DA) to discriminate authentic rosehip oil from adulterated rosehip oil containing soybean, corn and sunflower oils. The oxidative stability of rosehip oil under accelerated oxidation conditions was investigated in one article (Grajzer *et al*., 2015).

The goals of this study were (1) to investigate the fatty acid, tocopherol and sterol composition of solvent-extracted rosehip seed oil, (2) to evaluate the antiradical traits of the oil using DPPH and $ABTS^+$ tests, and (3) to compare the induction periods (IP) and oxidative stability of rosehip oil under thermal and photo oxidation conditions.

2. MATERIALS AND METHODS

Rosa canina fruits were purchased from a local market in Bolu (Turkey). The seeds were removed from the pulp then left for 48 h at room temperature to remove pulp residue. Dried seeds were ground in a coffee-grinder and sieved with a sieve of 1 mm in diameter. Twenty grams of powdered seeds were mixed with 150 mL of petroleum ether in an Erlenmeyer flask and the mixture was shaken at 100 rpm in a water bath for 4 h. The mixture was filtered and the solvent was removed using a rotary evaporator at 40 °C under vacuum. The extracted oil was stored at -18 °C until analysis.

2.1. Gas chromatography (GC) analysis of fatty acids

Fatty acid methyl esters (FAMEs) were prepared in accordance with the method developed by AOCS Ce 2-66 (AOCS, 2000). The separation of FAMEs was performed by gas chromatography on a Shimadzu GC-2010 equipped with a flame ionization detector and the capillary column TR-CN 100 (60 m x 0.25 mm x 0.2 µm, Teknokroma, Barcelona, Spain). One µL of FAMEs was injected in split mode at a ratio of 50:1. Helium was used as carrier gas at a flow rate of 1 mL/min. The injector and detector temperatures were 250 °C. Separation was carried out at a temperature of 190 °C for 30 min. FAME identification was based on retention times as compared with those of a standard FAME mixture. The results were expressed as the percentage of total peak area. The analyses were carried out in triplicate.

2.2. Gas chromatography (GC) analysis of sterols

Sterols were determined according to the AOCS Official Method of Ch 6-91 (AOCS, 2000). The sterols were analyzed on an Agilent 7890A gas

chromatograph, equipped with a FID and a capillary column HP-5 (30 m × 0.32 mm id × 0.25 µm film thickness). The carrier gas was nitrogen with a flow rate of 1 mL/min and a split ratio of 5:1. The injector and detector temperatures were set at 300 °C. The oven temperature was held at 235 °C for 75 min. The identification of peaks was done by comparing the retention time of external standards (cholesterol, brassicasterol, campesterol, stigmasterol and β-sitosterol). The result of each sterol compound was expressed as percent concentration. LOD was 0.005% and LOQ was 0.05%. The analyses were done in triplicate.

2.3. Determination of total phenolic content (TPC) and total carotenoids

Phenolic compounds were extracted from the oils as described by Yılmaz and Durmaz (2015). An oil sample (2 g) was dissolved in 5 mL of *n*-hexane and then the solution was extracted with 3 mL of aqueous methanol (80%). The mixture was blended in a vibration mixer for 3 min. After 5 min of centrifugation at 600 g the hydrophilic layer was filtered and the combined extract was brought to dryness in a rotary evaporator at 38 ºC. The TPC in the oil extract was determined colorimetrically at 760 nm, using the Folin-Ciocalteau reagent (Singleton *et al.*, 1999; Ramadan *et al.*, 2012) and expressed as gallic acid equivalents (GAE). Total carotenoids were determined according to the method of Silva *et al.* (2011). Carotenoids were measured at 455 nm and the results were presented as mg β-carotene per kg of oil. The analyses were done in triplicate.

2.4. High performance liquid chromatography (HPLC) analysis of tocopherols

The Tocopherols were determined following the AOCS Method Ce 8-89 (AOCS, 2000). External standards of α, β, γ and δ-tocopherols (Sigma-Aldrich, Inc., St. Louis, MO) were used to calculate the individual amounts of each tocopherol in the oil. An aliquot of sample (20 µL) was injected into a Shimadzu HPLC system equipped with a PDA detector and a silica gel column (Intertsil SIL 100 A, with a 5-mm particle diameter, 4.6 x 250 mm in size, Tokyo, Japan). The separation of tocopherols was achieved with an isocratic elution of hexane: isopropanol (99.5:0.5, v/v) at 1.0 mL/min flow rate. The tocopherols were measured at 292 nm and expressed as mg/kg. The analyses were done in triplicate.

2.5. DPPH· (2,2-diphenyl-1-picrylhydrazyl) radical scavenging activity

The DPPH· method described previously (Espín *et al.*, 2000; Yılmaz and Durmaz, 2015) was used for the determination of the radical scavenging capacity of the oil samples. In brief, 100 µL of ethyl acetate extract from the oil was added to 2.9 mL of DPPH· methanol solution (25 mg/L). The mixture was shaken vigorously and left in the dark for 30 min. The absorbance was measured at 520 nm against pure ethyl acetate (blank) using a spectrophotometer in a 1-cm quartz cell. The radical scavenging activity was expressed as the inhibition percentage and was calculated using the following formula:

% Radical scavenging activity = (control OD-sample OD/control OD) × 100

The obtained data were used to calculate the α-tocopherol and trolox equivalents that correspond to the oil. The analyses were done in triplicate.

2.6. $ABTS^+$ (2,2'-Azino-bis 3-ethylbenzothiazoline-6-sulfonic acid) radical scavenging activity

The antioxidant capacity of the oils was estimated using the $ABTS^+$ method (Yılmaz and Durmaz, 2015). The $ABTS^+$ radical solution was obtained by incubating 7 mM potassium peroxidisulfate solution in distilled water for 16 h in the dark at room temperature. The absorbance was maintained in the 0.700±0.010 range with a methanol:chloroform (1:1, v/v) mixture before the assay. A 100 µL oil sample, diluted 10-fold in methanol:chloroform (1:1, v/v) was allowed to react with 2.9 mL of the $ABTS^+$ solution and the absorbance was recorded at 752 nm. The results of the $ABTS^+$ tests were expressed as α-tocopherol and trolox equivalents. The analyses were done in triplicate.

2.7. Determination of induction period (Rancimat test and DSC)

The induction period (IP) of the oil samples was determined using a 679 Rancimat device (Metrohm Ltd., Herisau, Switzerland). Briefly, 3 g of oil sample were used at 110 °C with an air flow of 20 L/h. Each measuring vessel contained distilled water (60 mL) and the experiments were done in duplicate.

DSC was also used for the determination of the IP of rosehip seed oil. The IP of the oil sample was analyzed by DSC (Shimadzu Corporation, Tokyo, Japan) at different temperature ranges (100-150 °C). For this purpose, 3.0 mg of the oil were weighed in an aluminum pan while an empty pan was employed as the reference. The oven was heated from 50 °C to 150 °C at a rate of 10 °C/min under a nitrogen gas flow of 50 mL/min. After reaching 150 °C, oxygen gas was released into the sample instead of nitrogen at the same flow rate and the sample was held at 150 °C during analysis (Suja *et al.*, 2004). The experiments were done in duplicate.

2.8. Oxidative stability of oil under accelerated thermal oxidation conditions (60 °C)

An oil sample (15 g) was weighed into glass *Petri* dishes (70 mm diameter) and placed in the dark in an oven at 30 °C and 60 °C. The oxidative stability of the oil was examined using the specific extinction (K_{232} and K_{270}) values of the samples taken during the oxidation period (0-500 h) according to the AOCS Official Method of Ch 5-91 (AOCS, 2000). The experiments were done in duplicate. The tocopherol and carotenoid degradation in the oil were investigated during oxidation storage (0-160 h).

2.9. Oxidative stability of oil under accelerated photo oxidation conditions (UV light)

Accelerated photo oxidation was performed in a UV-light cabin (110 cm x 55 cm x 55 cm) fitted two 30 W UV lamps (254 nm wavelength). *Petri* dishes containing 15 g of oil were irradiated at a distance of 27 cm during 21 h. The temperature in the cabin was maintained at 30 °C. The oxidative stability of the oil was monitored by the determination of K_{232} and K_{270} values (AOCS, 2000). The experiments were done in duplicate. The tocopherol and carotenoid contents in the oil samples were also determined during photo oxidation.

3. RESULTS AND DISCUSSION

3.1. Fatty acids and bioactive lipids of rosehip seed oil

The fatty acid composition of rosehip seed oil is shown in Table 1. The main fatty acid found in the oil sample was linoleic acid (54.8%), followed by linolenic acid (23.4%) and oleic acid (14.7%). These fatty acid profiles are similar to previous reports (Ilyasoğlu *et al.*, 2014; Prescha *et al.*, 2014). Grajzer *et al.*, (2015) found fatty acid profiles in cold-pressed rose hip oils that were similar to those reported by Ozcan (2002) and Szentmihályi *et al.*, (2002) for oils extracted from rose hip seeds. They concluded that rose hip oil is a valuable source of PUFA in the human diet.

The sterol composition of rosehip seed oil is also presented in Table 1. The main sterol component found in the oil was β-sitosterol (78%), followed by campesterol, Δ7-stigmastenol and Δ5-avenasterol, with 4.3%, 4.3% and 3.9%, respectively. Our results for β-sitosterol were similar to those reported by Grajzer *et al.*, (2015) and Ilyasoğlu (2014). They stated that β-sitosterol was the most abundant sterol in rosehip oil. The percentages of campesterol, Δ7-stigmastenol and Δ5-avenasterol were similar to the data of Ilyasoğlu (2014). Grajzer *et al.*, (2015) reported that the sterol levels of cold-pressed rose hip oils were high and ranged from 5891.6 mg/kg to 6485.4 mg/kg. The presence of brassicasterol reported by Zlatanov (1999) and Δ7-stigmastenol reported by Ilyasoğlu (2014) (5.4% and 6.2% of total sterols, respectively) were confirmed in our results. Phytosterols have health-promoting traits and aid in preventing cardiovascular diseases by inhibiting the intestinal absorption of cholesterol. Thus, sterols have been incorporated into functional foods (Ramadan, 2015).

Table 1. Fatty acid and sterol composition of rosehip seed oil (n=3, mean ± SD).

Component	Relative content (%)
Fatty acids	
Myristic acid (C14:0)	0.03 ± 0.00
Palmitic acid (C16:0)	3.66 ± 0.00
Stearic acid (C18:0)	2.19 ± 0.01
Oleic acid (C18:1)	14.79 ± 0.05
Linoleic acid (C18:2)	54.80 ± 0.38
Linolenic acid (C18:3)	23.47 ± 0.50
Arachidic acid (C20:0)	0.93 ± 0.05
Behenic acid (C22:0)	0.14 ± 0.00
Saturated fatty acids	6.94
Unsaturated fatty acids	93.06
Monounsaturated fatty acids	14.79
Polyunsaturated fatty acids	78.19
Unsaturated/saturated fatty acid	13.41
Sterols	
Cholesterol	0.4 ± 0.0
Brassicasterol	0.1 ± 0.0
Campesterol	4.3 ± 0.1
β-sitosterol	78.0 ± 0.1
Δ5-avenasterol	3.9 ± 0.1
Δ7-stigmastenol	4.3 ± 0.2
Δ7-avenasterol	1.5 ± 0.4

The bioactive lipids in rosehip seed oil including tocopherols, carotenoids and phenolics are given in Table 2. The Total amount of tocopherol, carotenoid and phenolic contents were 786.3 mg/kg oil, 218.8 mg/kg oil and 37.97 mg gallic acid/kg oil, respectively. Regarding TPC, Grajzer *et al.*, (2015) reported TPC in lower amounts (783.5 and 570.7 µg/kg) than those presented in our work. The level of total carotenoids in the oil was higher than those reported by Ilyasoğlu (2014) and Szentmihályi *et al.*, (2002). Grajzer *et al.*, (2015) reported that the carotenoid content of cold-pressed rose hip oils ranged from 36.4 mg/kg to 107.7 mg/kg mg/kg. Among tocopherol isomers, γ-tocopherol accounted for the highest value in rosehip oil (472.0 mg/kg oil). Besides, α-tocopherol (261.2 mg/kg oil) was found slightly higher than half of the γ-tocopherol, while

TABLE 2. Bioactive phytochemicals and antioxidant traits of rosehip oil (n=3, mean ± SD).

Component	Value
Total phenolic comounds (mg gallic acid/kg oil)	37.97 ± 1.45
Total carotenoids (mg/kg oil)	218.8 ± 1.9
Total tocopherols (mg/kg oil)	786.3 ± 0.7
Individual tocopherols (mg/kg oil)	
α-tocopherol	261.2 ± 0.3
γ- tocopherol	472.0 ± 0.4
δ- tocopherol	53.1 ± 0.7
Antioxidant capacity	
DPPH·	
Tocopherol equivalents (mg α-tocopherol/g oil)	1.08 ± 0.04
Trolox equivalents (μmol TEAC/g oil)	4.18 ± 0.14
$ABTS^+$	
Tocopherol equivalents (mg α-tocopherol/g oil)	1.00 ± 0.09
Trolox equivalents (μmol TEAC/g oil)	3.02 ± 0.28

TEAC: Trolox equivalent antioxidant capacity

δ-tocopherol was present only as a minor (53.1 mg/kg oil) isomer among the tocopherols. Grajzer *et al.*, (2015) reported higher levels of total tocopherols (1124.7 and 1037.6 mg/kg) in rosehip oil in comparison with our results. However, the total tocopherol content of rosehip oil in our study was higher than the values (89.4 mg/kg) reported by Zlatanov (1999).

Several studies mentioned that oil composition is affected by the method of extraction. Also, studies reported that the qualitative and quantitative compositions of fatty acids, sterols, tocopherols and carotenoids differed significantly among different genera and also among cultivars of the same species. Grajzer *et al.*, (2015) stated that γ- tocopherol was the major tocopherol isomer in rosehip oil. They found lower contents of α-tocopherol and higher contents of δ- tocopherol than those detected in our study (116.6, 147.3 mg/kg for α-tocopherol and 230.4, 259.9 mg/kg for δ- tocopherol). Andersson *et al.*, (2011) studied the levels of tocols in four species of *Rosa* (*R. dumalis*, *R. spinosissima*, *R. rubiginosa*, and *R. pimpinellifolia*) and found α- and γ-tocopherol only in the fleshy parts of the rosehip. The amount of tocols and vitamin E activity varied with the date of harvesting and species, while fruit ripening had little influence on this activity.

3.2. Antiradical properties and IP of rosehip seed oil

The antiradical activities of the extracts from oil samples were assessed using DPPH· and $ABTS^+$ radical scavenging tests. Both tests are commonly used to determine the antioxidant capacity of bioactive compounds. As exhibited in Table 2, the antioxidant activities of the extracts as assessed by the DPPH· test were 1.08 mg α-tocopherol/g oil and 4.18 μmol TEAC (Trolox equivalent antioxidant capacity)/g oil. The $ABTS^+$ values for the oil extracts were determined as 1.00 mg α-tocopherol/g oil and 3.02 μmol TEAC/g oil. The antioxidant activity tested by $ABTS^+$ for rosehip seed oil extracts was higher than the reported value (Ilyasoğlu, 2014) for the methanol extract of rosehip oil (1.77 μmol TEAC/g). The DPPH· results showed higher antiradical activity than those (2.32 mM TEAC/kg) reported by Prescha *et al.*, (2014) and Grajzer *et al.*, (2015), who reported that the antioxidant activity of rosehip oil extracts ranged between 2.32 and 3.00 mM TEAC/kg.

TABLE 3. Induction periods (min) for rosehip oil determined by Rancimat device and DSC (n=3, mean ± SD).

	IP (min)
Rancimat (110 °C, 20 L/h air flow rate, h)	3.46 ± 0.13
DSC	
100°C	58.06 ± 5.39
110°C	24.38 ± 3.35
120°C	6.93 ± 2.82
130°C	4.95 ± 0.65
140°C	1.02 ± 0.07
150°C	0.26 ± 0.05

The differential scanning calorimetry (DSC) method is a rapid method to evaluate the oxidative stability of oils. In addition to this method, the Schaal oven test could be used as an accelerated oxidation method (Ramadan, 2012). Arain *et al.*, (2009) determined the oxidative stability of *Bauhinia purpurea* oil and found a high correlation between DSC *T*0 values and the oxidative stability index (OSI) values. They concluded that the DSC method could be easily used as an alternative technique for the measurement of oil's oxidative stability. To get comprehensive data about stability against oxidation, different thermal oxidation values should be compared. The values for the IP obtained by the Rancimat test and DSC are given in Table 3. The IP measured by Rancimat was 3.46 h at 110 °C. Regarding the DSC test, the IP of the oil samples decreased with the increase in the DSC experiment temperature. As expected, the highest IP (58.06 min) was recorded at 100 °C, while the lowest IP of the oil was 0.26 min at 150 °C. The IP obtained by DSC was lower than that obtained by the Rancimat method. These differences could be related to the higher surface-to-volume ratio, small amount of sample and purified oxygen used in DSC (Tan *et al.*, 2002). In our study, the IP of rosehip oil determined by DSC was lower than the results reported by Grajzer *et al.*, (2015) for cold-pressed rosehip oils.

Tocols have vitamin E activity and they are compounds with the ability to scavenge free radicals, and even tocols could be considered as the most important antioxidants. The high amount of tocopherols found in rosehip oil could be the main reason for the strong oxidative stability of the oil.

3.3. Oxidative stability of rosehip oil as affected by thermal and photo oxidation

Lipid oxidation negatively influences the quality and nutritional value of foods during storage and this might also limit the utilization of oil in processed foods. Therefore, it is important to evaluate the stability of oils as affected by storage conditions (Mohdaly *et al*., 2010; Özkan *et al*., 2016). Several methods have been employed to measure the stability of oils and fats. The storage of oil samples under thermal and photo oxidation conditions was employed for monitoring the stability of oils (Özkan *et al*., 2016). On the other hand, the detection of conjugated dienes (CD) and conjugated trienes (CT) is a good parameter to determine the stability of oils. The formation of hydroperoxides is coincidental with the conjugation of double bonds in unsaturated fatty acids, as measured by absorption at the UV spectrum. Methylene-interrupted dienes or polyenes in lipids show a shift in their double bond position during oxidation. The resulting CD exhibit intense absorption at 232 nm, while CT exhibit intense absorption at 270 nm. The increase in CD and CT contents is proportional to the uptake of oxygen. The higher the levels of CD and CT in oil the lower the oil stability will be (Ramadan *et al*., 2006).

The changes in K_{232} values during thermal and photo oxidation experiments are illustrated in Figure 1A. At all stages, the highest K_{232} value of the oil was observed during UV light-induced oxidation. After 21 h, the K_{232} value increased from 4.94 to 40.64 in the photo oxidation experiment, followed by the oil stored at 60 °C in the oven (15.38). There was a lower increase in the K_{232} value in the oil during 21 h storage at 30 °C under dark conditions (8.47). With the increase in storage time, the K_{232} value of the oil was decreased after a certain point under thermal storage conditions (60 °C). This behavior of the decrease in CD when the heating times increased could be explained by the induction of secondary oxidation products (hydroperoxides) which formed in the primary stages of oxidation (Shahidi *et al*., 1992; Ramadan and Moersel, 2004; Iqbal and Bhanger, 2007). Regarding the oil stored at 30 °C in the dark, the maximum value for K_{232} was 17.69 after storage of up to 480 h.

The K_{270} values for the oil samples were determined during storage under thermal and UV light-induced conditions (Figure 1B). After 21 h of storage at UV light, the K_{270} value increased from

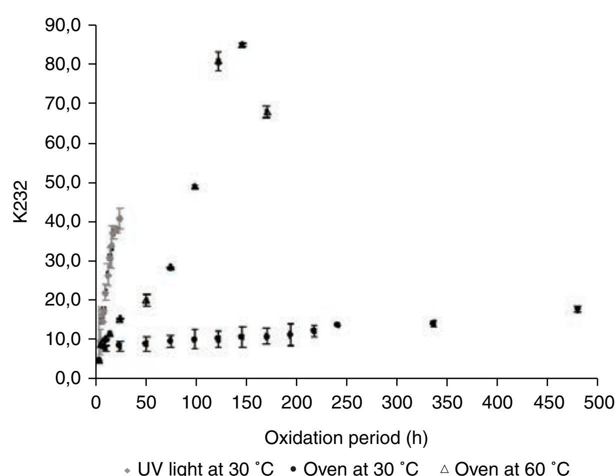

FIGURE 1A. Variation in K_{232} values for rosehip seed oil under different storage conditions (n=2, mean ± SD).

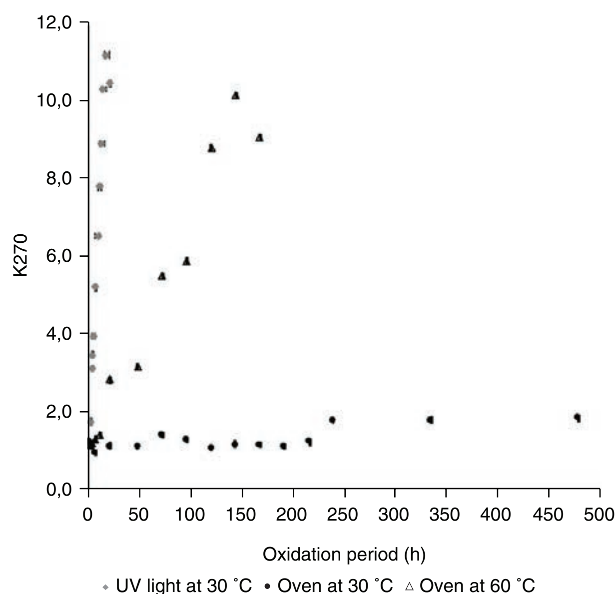

FIGURE 1B. Variation in K_{270} values for rosehip seed oil under different storage conditions (n=2, mean ± SD).

1.24 to 10.50. The K_{270} values for samples over the same period stored at 60 °C and 30 °C were 2.83 and 1.14, respectively. Up to 144 h of storage at 60 °C, the K_{270} value reached its maximum value (10.19) and after that, the value was decreased. However, the K_{270} value of the oil increased slightly during storage at 30 °C. The results for K_{232} and K_{270} values were similar to those reported in a study of rosehip oil stored at 20 °C (Prescha *et al*., 2014), where an increase was observed for CD and CT values in rosehip oil during 6 months of storage.

The amounts of total tocopherols in the oils during different storage periods are presented in Figure 2A. The highest decrease in total tocopherols occurred during storage under UV light conditions.

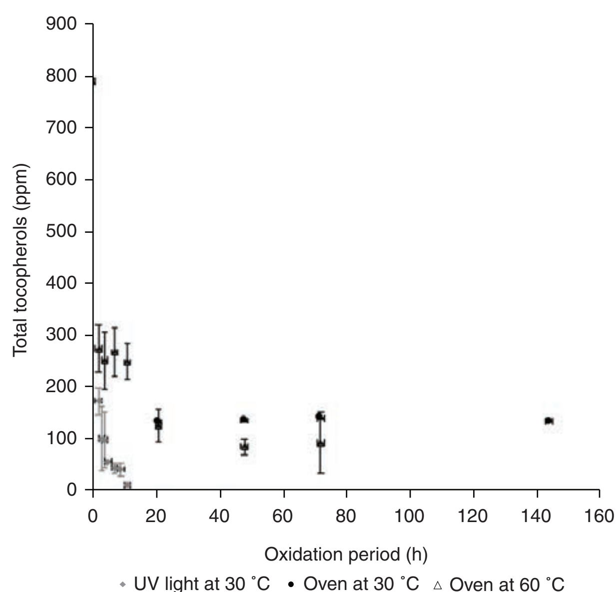

FIGURE 2A. Variation in total tocopherol contents in rosehip seed oil under different storage conditions (n=2, mean ± SD).

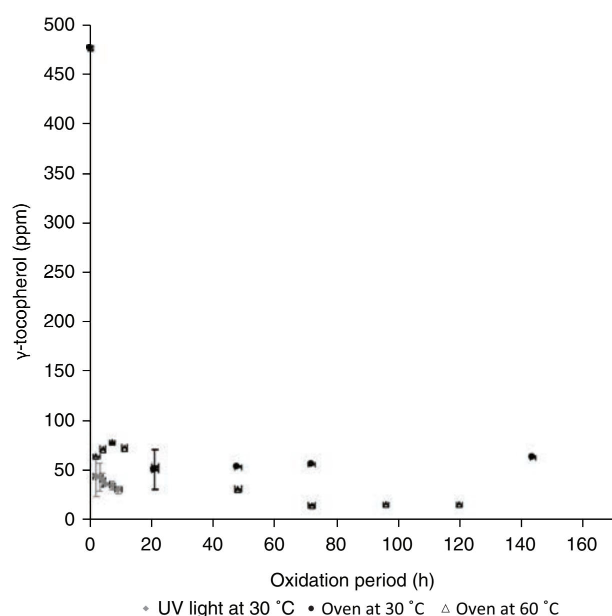

FIGURE 2B. Variation in γ-tocopherol contents in rosehip seed oil under different storage conditions (n=2, mean ± SD).

The amount of total tocopherols decreased from 784 mg/kg to 11.3 mg/kg after 11 h of storage under UV light. After that, the tocopherols were not detected in these samples. The other storage condition which caused a loss in tocopherols was the storage of oils at 60 °C. After 72 h of storage, total tocopherols decreased to 92.3 mg/kg; thereafter, tocopherols were not detected in the oil samples. The smallest loss in total tocopherols was determined at 30 °C of storage. Although there was a decline in the total tocopherols at the beginning of storage, after 21 h, the tocopherol

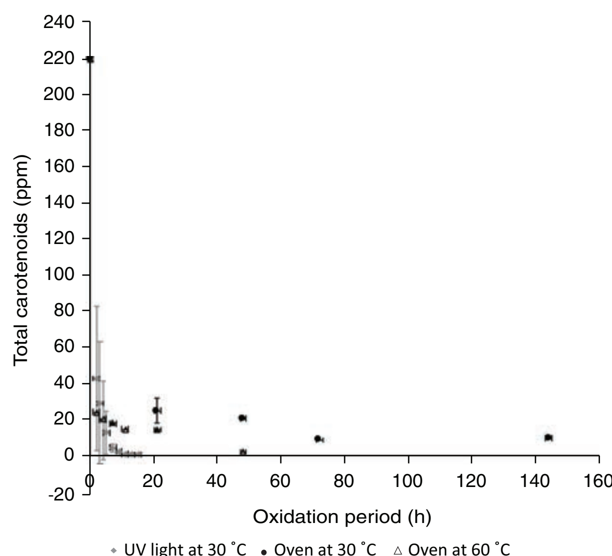

FIGURE 2C. Variation in total carotenoids in rosehip seed oil under different storage conditions (n=2, mean ± SD).

content in the oil (132.6-139.8 mg/kg) exhibited stabile behavior for 120 h of storage.

In addition to total tocopherols, the levels of γ-tocopherol, the main tocopherol isomer in oil, was assessed during different storage conditions. The changes in the amounts of this isomer in the oil during storage is exhibited in Figure 2B. The highest decline in the level of this isomer was observed in the oils during storage under UV light. During 9 h of storage under UV light, the amount of γ-tocopherol decreased to 30.3 mg/kg from the starting value (472.0 mg/kg). The other significant decrease in γ-tocopherol was detected during storage at 60 °C. After 120 h under thermal storage, the concentration of γ-tocopherol declined to 15.3 mg/kg. The lowest decrease in γ-tocopherol between among the storage conditions was determined under dark storage at 30 °C. The amount of γ-tocopherol was 62.3 mg/kg for rosehip oil at the end of 144 h of storage.

The carotenoid degradation of rosehip oil under different storage conditions is summarized in Figure 2C. The degradation rate of carotenoids was more noticeable under UV light storage than under storage in the dark at 30 °C and 60 °C. After 15 h of storage under UV light, there was a tremendous decline in the carotenoid level in rosehip oil, where the total carotenoid content decreased to 0.6 mg/kg from the initial value (218.8 mg/kg). The other dramatic decrease in the content of carotenoids was observed in the oil samples stored under thermal conditions at 60 °C. Total carotenoid content decreased to 2.3 mg/kg after 48 h storage under thermal storage conditions. During storage at 30 °C, the minimum losses in total carotenoids was detected, where the total carotenoid content was 9.6 mg/kg even at the end of 144 h storage in the dark at 30 °C.

4. CONCLUSIONS

Vegetable oils are bioactive ingredients in nutraceuticals, drugs, cosmetics and biofuels. Rosehip oil is valuable for food, pharmaceutical and cosmetic applications. Rosehip seeds are potential sources for the production of edible oil after marmalade production. Rosehip oil is rich in unsaturated fatty acids especially linoleic and linolenic acids and these fatty acids are an important part of the human diet because of their contribution to human health. In addition, the oil contains high contents of tocopherols, especially γ-tocopherol, which showed strong antioxidant traits. Considering the levels of bioactive phytochemicals in rosehip oil, the oil could be utilized in food, pharmaceutics, cosmetics, and other nonfood applications. The storage conditions for rosehip oil should be controlled, especially under UV light and temperatures above 30 °C which promote oil degradation.

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