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Stability and volatile oxidation compounds of grape seed, flax seed and black cumin seed cold-pressed oils as affected by thermal oxidation

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SUMMARY: The old-pressed oils (CPO) from grape seeds (GSO), flax seeds (FSO) and black cumin seeds (BSO) were analyzed for their fatty acid profiles, tocopherols, total phenolics, bioactives and phenolic compositions. The stability of CPO under thermal oxidation conditions was evaluated. The main fatty acid in FSO was linolenic acid (56.5% of total fatty acids); while GSO and BSO were rich in linoleic acid, which accounted for 66.8 and 56.8%, respectively. GSO was rich in α-tocopherol (123.0 mg/kg), while γ-tocopherol was a prevalent isomer in FSO and BSO (137.9 and 128.9 mg/kg, respectively). The total phenolic contents in the oils ranged from 554 mg GAE/kg oil (FSO) to 1140 mg GAE/kg oil (BSO). Luteolin, dihydroquercetin and benzoic acids were the dominant bioactives and phenolics in FSO, GSO and BSO, respectively. Based on the oxidative stability index (OSI) value, BSO showed the highest value (6.14 h) among the other oils. The oxidative stability of FSO and BSO were higher than GSO according to peroxide value (PV) and conjugated diene (CD) values of the oils during storage at 60 °C. Hexanal, 2,4-heptadienal and (*E,E*)-2,4-heptadienal were the major volatile oxidation compounds (VOC) in FSO. Hexanal and (*E*)-2-heptanal were the main identified VOC in the GSO and BSO under the same oxidation conditions.

KEYWORDS: Linum usitatissimum*;* Nigella sativa*; Quality control; SPME–GC/MS; Vegetable oils;* Vitis vinifera*; Volatile oxidation compounds*

RESUMEN: ***Estabilidad y compuestos de oxidación volátiles de aceites prensados en frío de semillas de uva, lino y comino negro, afectados por la oxidación térmica.*** Los aceites prensados en frío (CPO) de semilla de uva (OSG), semilla de lino (FSO) y semilla de comino negro (BSO) se analizaron para determinar su perfil de ácidos grasos, tocoferoles, compuestos fenólicos totales, compuestos bioactivos y composición fenólica. Se evaluó la estabilidad del CPO en condiciones de oxidación térmica. El ácido graso principal en FSO fue ácido linolénico (56,5%), mientras que GSO y BSO fueron ricos en ácido linoleico que representó el 66,8% y 56,8%, respectivamente. La OSG fue rica en α-tocoferol (123,0 mg/kg), mientras que el γ-tocoferol fue el tocoferol mayoritario en el FOE y BSO (137,9 y 128,9 mg/kg, respectivamente). El contenido fenólico total de los aceites varió de 554 mg GAE/kg de aceite en FSO a 1140 mg GAE/kg de aceite en BSO. La luteolina, la dihidroquercetina y los ácidos benzoicos fueron los bioactivos y fenólicos dominantes en FSO, GSO y BSO, respectivamente. En base al valor del índice de estabilidad de la oxidación (OSI), BSO mostró el valor más alto (6,14 h) entre los otros aceites. La estabilidad oxidativa de FSO y BSO fue mayor que la OSG según el valor de peróxido (PV) y los valores de dieno conjugado (CD) de los aceites durante el almacenamiento a 60 °C. Hexanal, 2,4-heptadienal y (E, E) -2,4-heptadienal fueron los principales compuestos de oxidación volátiles (VOC) en FSO. Hexanal y (E) -2-heptanal fueron los principales VOC identificados en la OSG y la BSO en las mismas condiciones de oxidación.

PALABRAS CLAVE*: Aceites vegetales; Compuestos de oxidación volátiles; Control de calidad;* Linum usitatissimum*;* Nigella sativa*; SPME-GC/MS;* Vitis vinifera

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1. INTRODUCTION

Oils and fats are important components of human nutrition. Grapes (*Vitis vinifera*) are utilized in different food products and grape seeds are important processing by-products. Grape seeds contain 10-20% oil, wherein the grape seed oil (GSO) contains high levels of unsaturated fatty acids (Apaydin *et al*., 2017). Grape seed extracts exhibit antibacterial and antioxidant potential (Da Porto *et al*., 2013). The unsaponifiable matter of GSO contains high levels of phytosterols. GSO exhibited many pharmaceutical properties, such as the prevention of thrombosis, the inhibition of cardiovascular diseases, properties against the oxidation of low-density lipoproteins (LDL), the dilation of blood vessel, cholesterol reduction, and the regulation of the autonomic nerve (Apaydin *et al*., 2017). Flax (*Linum usitatissimum*) is a commercially important oilseed crop worldwide. Flaxseed oil (FSO) contains high levels of *n*-3 fatty acids, which are linked to the prevention of cardiovascular diseases and blood pressure (Wei *et al*., 2015; Tańska *et al*., 2016). The production of high-quality cold-pressed oils (CPO) from flaxseed is difficult because of its high levels of polyunsaturated fatty acids (PUFA, *ca*. 50% of the total fatty acids in FSO). Studies have been reported on the physicochemical and biological properties of black cumin (*Nigella sativa*) oil (Ramadan, 2007; Ramadan *et al*., 2012; Kiralan *et al*., 2014). Black cumin seed oil (BSO) is rich in bioactive thymoquinone, phytosterols, tocols as well as essential fatty acids (Ramadan, 2013).

Cold-pressing extraction is a solvent-free technique for oil production which is applied to seeds at low temperatures (Parker *et al*., 2003; Yu *et al*., 2005; Van Hoed *et al*., 2006; Siger *et al*., 2008; Ramadan *et al*., 2012; Prescha *et al*., 2014; Ramadan, 2013, Kiralan *et al*., 2014; Kiralan *et al*., 2018). In the process of cold-pressing, oil recovery is lower than in solvent extraction or hot-pressing techniques. CPO are important and rich sources of essential fatty acids, phenolics, sterols, tocols, carotenoids, and bioactive phytochemicals with health-promoting properties (Ramadan, 2013). Moreover, CPO have a characteristic taste, aroma and color (Matthäus and Brühl, 2003; Emir *et al*., 2014). Therefore, CPO could be classified as a "natural product" and consumed without a refining process.

Cold-pressing could avoid the deterioration of the thermo-sensitive compounds, wherein CPO could retain more bioactive compounds including pro-oxidant (i.e. hydroperoxides, free fatty acids, and chlorophylls) (Parry *et al*., 2005, Ramadan 2013; Wei *et al*., 2015; Kiralan and Ramadan, 2016). The fatty acid profile and other compounds such as phenolics, sterols and tocols affect lipid oxidation (Koski *et al*., 2002; Parker *et al*., 2003; Ramadan 2013; Kiralan and Ramadan, 2016). The stability of CPO is often from 6 to 12 months, which is limited by the amounts of PUFA, the antioxidant profile of the oil and the storage conditions (Choe and Min, 2006; Prescha *et al*., 2014).

Thermal and photo oxidation of CPO were previously determined using different techniques (Kiralan and Ramadan, 2016; Wroniak *et al*., 2016, Takeyama and Fukushima, 2013). In addition, headspace analysis can also be used for that purpose by determining some key volatile compounds which are markers for oxidation (Gromadzka *et al*., 2008; Vujasinovic *et al*., 2010; Lutterodt *et al*., 2011; Ramadan, 2013).

The goals of this research were to assess and compare the oxidative stability of selected CPO including flax seed oil (FSO), grape seed oil (GSO) and black cumin seed oil (BSO) under accelerated thermal oxidation conditions such as heating at 60 °C (Schaal oven test) or higher (Rancimat test at 110 °C). Oxidative stability parameters including conjugated diene (CD), and peroxide value (PV) were used to detect the oxidation during storage for six days. In addition, VOC were determined as oxidation markers in the CPO as affected by storage under thermal oxidation (60 °C) for 6 days.

2. MATERIALS AND METHODS

2.1. Oils and chemicals

Flaxseed, grape seed and black cumin seed CPO were obtained from a local cold-pressing company (Oneva Cold Pressing, Istanbul, Turkey). Chemicals and solvents with the highest purity available were used without further purification.

2.2. Accelerated thermal oxidation tests

2.2.1. Rancimat Test

The oxidative stability index (OSI) values of CPO were determined with the Rancimat assay according to AOCS 111 Official Method Cd 12b-92. (1997). The oil stability index (OSI) value was calculated and expressed as the induction time (h), measured by a Rancimat 743 apparatus (Metrohm) using 3 g of CPO sample heated at 110 °C with an air flow of 20 L/h.

2.2.2. Schaal oven test

Three grams of CPO sample were weighed and placed in a 20-mL brown headspace vial capped with a Teflon-lined septum. The oxidation was performed for 6 days in a forced-draft air oven at 60 °C. Samples were analyzed daily for conjugated diene (CD), peroxide value (PV), and VOC to monitor the oxidative stability.

2.3. CD and PV values

CD and PV values of CPO during thermal oxidation at 60 °C were measured according to AOCS methods Cd 8-53 and Cd 18-90 (AOCS, 1997).

2.4. GC analysis of fatty acid composition

Fatty acid methyl esters (FAME) were prepared according to IUPAC (1987). GC analysis was carried out with a Shimadzu GC-2010 chromatograph equipped with a fused capillary DB-23 fused-silica column (0.25 mm i.d., 60 m, 0.25 µm film thickness, Agilent J&W, USA). The carrier gas was helium at a flow rate of 0.70 mL/min. The column temperature was set to isothermal at 190 °C for 95 min, wherein the injector and detector temperatures were 230 °C and 240 °C, respectively. FAME peak areas were identified by the comparison of retention times with reference standards.

2.5. Total phenolic content (TPC)

Aliquots of CPO were dissolved in *n*-hexane (5 mL) and mixed with 10 mL methanol: water (80:20, v/v) in a glass tube for two min in a vortex (Ramadan *et al*., 2012). After centrifugation for 10 min at 3000 rpm, the hydroalcoholic extract was separated from the lipid phase using a Pasteur pipette and then combined and concentrated *in vacuo* at 30 °C. The oily residue was re-dissolved in 10 mL methanol: water (80:20, v/v) and the extraction process was repeated three times. Hydroalcoholic extracts were re-dissolved in acetonitrile (15 mL) and the mixture was washed three times with *n*-hexane (15 mL each). Purified phenolics were concentrated *in vacuo* at 30 ˚C and then dissolved in methanol. The phenolic extracts (40 µL) and 30 mL of water were poured into a tube. 200 µL of Folin-Ciocalteu reagent were added to the mixture. After 7.5 min, 600 µL of sodium carbonate (38%) were mixed into the solution and the mixture was left for 180 min at room temperature. The absorbance was measured at 765 nm using a UV-VIS spectrophotometer (PG Instruments, England). Gallic acid was used as a standard and TPC was calculated and expressed as mg GAE/kg oil.

2.6. HPLC analysis of bioactives and phenolic compounds

Phenolic and bioactive compounds were measured by reversed-phase high-performance liquid chromatography (RP-HPLC, Shimadzu Scientific Instruments, Tokyo, Japan). Identification and quantification were performed with a ShimadzuLC-10ADvp pump, a CTO-10Avp column heater, a Diode Array Detector, SCL-10Avp system controller, DGU-14A degasser and SIL-10ADvp autosampler (Shimadzu, Columbia, MD). Separations were performed at 30 °C on Agilent-Eclipse XDB C-18 reversed-phase column (4.6 mm length, 250 mm, 5 µm particle size). The mobile phases were A: 2.0% acetic acid in distilled water and B: methanol. The flow rate was 0.8 mL/min. For analysis, 25 mg of the extract was dissolved in 1 mL methanol wherein the injection volume was 10 µL. A modified gradient elution of two solvents was used: solvent A consisted of acetic acid: water (3:97, v/v), solvent B: methanol. The gradient program used is given in Table 1 according to Caponio *et al*., (2001). Identification and quantitative analyses were performed by comparison with standards. The limit of detection (LOD) and the limit of quantification (LOQ) were 0.01 and 0.02 µg/mL for gallic acid, 0.05 and 0.16 µg/mL for protocatechuic acid, 0.02 and 0.05 µg/mL for caffeic acid, 0.005 and 0.01 µg/mL for *p*-hydroxy benzoic acid, 0.02 and 0.07 µg/mL for chlorogenic acid, 0.01 and 0.02 µg/mL for syringic acid, 0.01 and 0.03 µg/mL for *p*-coumaric acid, 0.01 and 0.02 µg/mL for ferulic acid, 0.06 and 0.19 µg/mL for benzoic acid, 0.005 and 0.01 µg/mL for *o*-coumaric acid, 0.10 and 0,31 µg/mL for catechin, 0.05 and 0.15 µg/mL for (¯)-epicatechin, 0.03 and 0,10 µg/mL for vanilic acid, 0.01 and 0.04 µg/mL for vanilin, 0.06 and 0.18 µg/mL for rutin, 0.03 and 0.08 µg/mL for apigenin, 0.11 and 0.32 µg/mL for quercetin, 0.03 and 0.10 µg/mL for luteolin and 0.02 and 0.06 µg/mL for campherol, 0.73 and 2.21 µg/mL for thymoquinone, 2.49 and 7.56 µg/mL for thymol, 0.12 and 0.35 µg/mL for acacetin, respectively. The levels of phenolics in the extracts were calculated as mg/ kg oil. All extractions and chromatographic analyses were performed in triplicate and the results were averaged.

TABLE 1. Solvent gradient conditions of HPLC

Time (min)	3	20	28	35	50	60	62	70	73	75	80	90
A %*	93	72	75	70	70	67	58	50	30	20	0	93
B %	7	28	25	30	30	33	42	50	70	80	100	7

*Solvent A: acetic acid:water (3:97, v/v); solvent B: methanol.

2.7. HPLC analysis of tocopherols (α, β, γ, and δ)

Tocopherols were analyzed according to the American Oil Chemists' Society method Ce 8-89 (AOCS, 2003). Tocopherols (α, β, γ, and δ) were analyzed using normal-phase HPLC by the direct injection of CPO samples dissolved in a mixture (95:5, v/v) of heptane:tetrahydrofuran (THF). HPLC analysis was carried out with an SCL-10Avp System controller, LC-10ADvp pump, SIL-10ADvp Autosampler, CTO-10 Avp column heater and fluorescence detector set at 295 nm for excitation and 330 nm for emission. The 150 cm x 4.6 mm i.d. column filled with Supelcosil Luna, 5m (Supelco, Bellefonte, PA) was used. The mobile phase was a mixture of heptane:THF (95:5, v/v) at a flow rate of 1.2 mL/min wherein the injection volume was 10 mL. The standard samples used for identification and quantification were α, β, γ and δ-tocopherols (Sigma, St. Louis, Mo., USA). The data were analyzed and integrated using the Shimadzu Class-VP Chromatography Lab Automated Software. The levels of tocopherols in CPO were calculated as mg/kg oil using the external calibration curves obtained for each tocopherol standard. The LOD and the LOQ were 0.03 and 0.08 μg/mL for α-tocopherol, 0.02 and 0.06 μg/mL for β-tocopherol, 0.04 and 0.13 μg/mL for γ-tocopherol, and 0.03 and 0.08 μg/mL for δ-tocopherol. The chromatographic analysis was performed three times and the results were averaged.

2.8. GC-MS analysis of VOC

CPO samples stored under accelerated oxidation conditions at 60 ºC were used to determine volatile compounds and VOC. Equilibration took place for 15 min at 35 °C followed by extraction (45 min) from the headspace at 35 °C then a 10 min of desorption in the GC injection port with the aid of a CTC Combi PAL (CTC Analytics AG, Zwingen, Switzerland) autosampler with 75 μm carboxen/polydimethylsiloxane solid-phase micro-extraction (SPME) fiber. GC-MS analyses were carried out with an Agilent system (GC 7890, MS 5975 N MSD, Santa Clara, CA, USA) using an analytical column of medium polarity (DB-624, 30 m length × 0.25 mm ID × 1.4 μm film thickness, Agilent Technologies, CA, USA). The following temperature program was applied: hold for 5 min at 40 °C; 3 °C/min up to 110 °C; 4 °C/min up to 150 °C; 10 °C/min up to 210 °C and hold for 12 min. The temperatures for the injection port, ion source, quadrupole, and interface were 250 °C, 230 °C, 150 °C, and 240 °C, respectively. Mass spectra were recorded in full scan mode at the electron impact of 70 eV with a scan range from m/z 41 to 400. The identification of volatile compounds was made by comparing mass spectra, Kovats index (KI) with the authentic standards and published data, as well as by comparing their mass spectra with Wiley7.0 (Wiley, NY, USA) and the mass spectrometry library of Nist 05 (National Institute of Standards and Technology, Gaithersburg, MD, USA). The KI parameters were calculated using the n-hydrocarbons (C4 to C20) series. One vial for daily assessment from sets of replicate vials for every CPO was used throughout the study.

2.9. Statistical analysis

Results are shown and expressed in terms of the mean and standard deviations. Significant differences were calculated using ANOVA in combination with Duncan's test with a significance level of α=0.05.

3. RESULTS AND DISCUSSION

3.1. Composition of CPO

The fatty acid profiles of the CPO samples are shown in Table 2. The main fatty acids in FSO were linolenic acid (56.5%), followed by oleic acid (18.0%) and linoleic acid (15.9%). The fatty acid compositions of GSO and BSO included linoleic acid (66.8% and 56.8%, respectively) as the major fatty acid, followed by oleic acid (19.5% and 23.8%) and palmitic acid (8.25% and 12.4%), respectively. The fatty acid composition of FSO was in agreement with those reported by others (Brühl *et al.*, 2008; Ivanova-Petropulos *et al.*, 2015; Raczyk *et al.*, 2016; Teh and Birch, 2013). The results of the FAME profile of GSO fall within similar ranges reported (Tuberoso *et al.*, 2007; Lutterodt *et al.*, 2011; Wen *et al.*, 2016). In addition, the fatty acid composition of BSO was in accordance with those previously reported in the literature (Cheikh-Rouhou *et al.*, 2007; Lutterodt *et al.*, 2010; Ramadan *et al.*, 2012).

The TPC of CPO is given in Table 3. The highest TPC was found in BSO (1140 mg/kg oil), while FSO contained the lowest TPC (554.4 mg/kg). The TPC in BSO was similar to the values (1.02-1.40 mg GAE/g) reported by Lutterodt *et al.*, (2010). The TPC of FSO was lower than the values reported by Kasote *et al.*, (2013) who determined that the TPC of cold-pressed linseed oils ranged from 10 to 26 mg GAE/100 g oil. In addition, the TPC of cold-pressed GSO was similar to the values (0.16-0.80 mg GAE/g) reported by Lutterodt *et al.*, (2011).

The phenolic and bioactive compound profiles of CPO are also given in Table 3. In the FSO, luteolin and apigenin were detected and their amounts were 0.76 and 0.02 mg/kg oil, respectively. In GSO, 8 compounds including vanillin, vanillic acid, *p*-coumaric acid, dihydroquercetin, luteolin, campherol, apigenin and acacetin were identified. GSO contained the highest dihydroquercetin content (2.49 mg/kg oil). Luteolin and apigenin were not detected in FSO or GSO in the research of Tuberos *et al.*, (2007). The differences in bioactive and phenolic compound profiles could be due to differences

Table 2. Fatty acid composition (relevant content, %) of CPO (n=2, mean ± SD)

Fatty acid	Flax seed oil (FSO)	Grape seed oil (GSO)	Black cumin seed oil (BSO)
C12:0	0.04±0.00*	0.05±0.00	0.14±0.00
C14:0	0.02±0.00	0.01±0.00	0.03±0.00
C16:0	5.43±0.00	8.25±0.00	12.46±0.48
C16:1	0.05±0.00	0.09±0.00	0.18±0.01
C17:0	0.06±0.00	0.07±0.00	0.07±0.01
C17:1	0.04±0.00	0.03±0.00	0.04±0.00
C18:0	3.50±0.00	4.29±0.00	3.27± 0.18
C18:1	18.01±0.02	19.58±0.09	23.85±0.04
C18:2	15.95±0.01	66.86±0.07	56.80±0.56
C18:3	56.55±0.02	0.28±0.00	0.23±0.00
C20:0	0.11±0.00	0.14±0.00	0.20±0.00
C20:1	0.10±0.00	0.14±0.00	0.28±0.01
C20:2	0.03±0.00	ND*	2.41±0.03
C22:0	0.04±0.00	0.01±0.00	ND
C24:0	0.09±0.00	0.21±0.01	0.09±0.00

*ND: not detected

Table 3. TPC, bioactive compounds, phenolic compounds and tocopherol composition of CPO (n=2, mean ± SD)

	Flax seed oil	Grape seed oil	Black cumin oil
TPC (mg GAE/kg oil)			
	554.4±17.86*	924.2±20.41	1140.4±14.67
Bioactive compounds and phenolic compounds (mg/kg oil)			
***p*-hydrobenzoic acid**	ND*	ND	1.47±0.00
Vanillic acid	ND	0.39±0.00	ND
Vanillin	ND	0.33±0.00	ND
***p*-coumaric acid**	ND	0.08±0.01	ND
Benzoic acid	ND	ND	228.5±9.68
Dihydroquercetin	ND	2.49±0.02	ND
Luteolin	0.76±0.01	0.67±0.00	2.12±0.02
Campherol	ND	0.34±0.01	0.28±0.00
Apigenin	0.02±0.01	0.01±0.01	0.17±0.01
Thymoquinone	ND	ND	97.58±0.14
Thymol	ND	ND	4.80±0.20
Acacetin	ND	0.31±0.04	ND
Tocopherols (mg/kg oil)			
α-tocopherol	6.33±0.01***	123.0±1.76	22.04±0.62
γ-tocopherol	137.9±1.19	16.70±0.01	128.9±1.61
δ-tocopherol	3.73±0.01	0.56±0.01	0.61±0.01

*ND: not detected

in cultivar, variety, location and extraction conditions. The most abundant compound in black cumin oil was benzoic acid (228.5 mg/kg oil), followed by thymoquinone (97.58 mg/kg oil). The amounts of thymoquinone and benzoic acid in our study were higher than those reported by Kiralan *et al*., (2014) who determined that the levels of benzoic acid and thymoquinone were 4.15 and 14.4 μg/g, respectively.

Table 3 shows the tocopherol contents of CPO. γ-Tocopherol was found as the major tocopherol isomer in the FSO (137.9 mg/kg oil) and BSO (128.9 mg/kg oil). The main tocopherol in the GSO was the α form (123.0 mg/kg oil). The γ- tocopherol content in the FSO was in accordance with the values (10.5-15.0 mg/100 g seed) reported by Choo *et al*., (2007). The α-tocopherol value in the GSO in our work showed similarity to that determined by Fernandes *et al*., (2013) for oils of Portuguese GSO (85.5-244 mg/kg). The content of γ-tocopherol in the BSO was lower (0.225 g/kg) than that reported by Ramadan and Moersel (2004). The differences in the contents and composition of tocopherols in the CPO under study may be due to differences in cultivar, variety and origin of the investigated seeds.

3.2. Stability of CPO as affected by thermal oxidation

The OSI values of CPO according to the Rancimat test revealed that BSO had the highest OSI (6.14 h), followed by GSO (4.06 h), while FSO had the lowest (2.63 h) OSI value. The results can be explained by the fatty acid profile of the CPO under study. The oxidative stability of FSO was very low in comparison to the other oils under Rancimat oxidation conditions. This might be explained by the fact that FSO is rich in linolenic acid, which has a high susceptibility to oxidation. Likewise, BSO had a better OSI value than GSO. GSO contained a higher level (66.8%) of linoleic acid than BSO (56.8%).

The OSI of FSO was higher than the OSI values (1.43-1.52 h) reported by Bozan and Temelli (2008). The results obtained for GSO heated at 110 °C were lower than those reported by Hassanien *et al*., (2014) for hexane-extracted GSO (8 h). However, the OSI of GSO was similar to those reported for refined GSO (3.3-5.3 h) under similar conditions (Hidalgo *et al*., 2002). The OSI value for BSO was lower than that (16.9 h) reported by Hassanien *et al*., (2014) and (*ca*. 22 h) Rudzińska *et al*., (2016), but higher than that reported by Kiralan *et al*., (2014) for cold-pressed BSO (3.48 h). These differences in OSI values might be due to the composition and amounts of natural antioxidants in the CPO samples.

The changes in PV in CPO during storage for 6 days at 60 °C are shown in Figure 1. The PV values for fresh CPO were 1.82, 12.2 and 26.5 for FSO, GSO and BSO, respectively. After 48 h of storage under oxidation conditions, the PV of FSO increased sharply and reached up to 29.97 meq O_2/

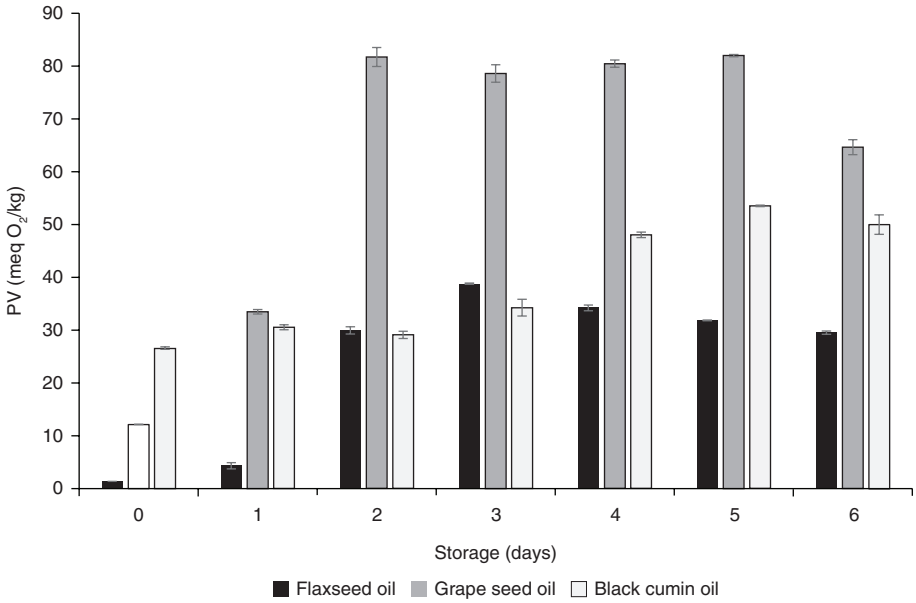

FIGURE 1. Changes in the PV of CPO during storage at 60 °C (n=2, mean ± SD). Error bars show the variations of two determinations in terms of standard deviation.

kg. After that, PV values were recorded to show stabile behavior till the end of storage period. In addition, the PV values of GSO increased sharply after 48 h of storage and the highest values were recorded (81.6 meq O_2/kg). After 48 h of storage, the PV values for GSO slightly decreased to *ca*. 87-81 meq O_2/kg until the 5th day of storage, when the PV of GSO decreased to 64 meq O_2/kg. In the BSO, the PV increased gradually with increasing storage period. The highest PV value (53.5 meq O_2/kg) for BSO was measured after 5 days of storage. Based on PV values, it could be concluded that BSO had the greatest oxidative stability among the CPO under study.

The changes in CD (K_{232} values) of the CPO stored for 6 days under thermal oxidation are exhibited in Figure 2. The rate of increase in K_{232} values showed similar behavior to that of the PV values. The K_{232} values for FSO increased gradually with the increase in storage time, reaching the maximum value (6.41) at the end of the storage period. There was a significant increase in the K_{232} values for the GSO with increasing storage time. In addition, a stable increase in the K_{232} values of BSO was observed until the 6th day of storage.

Our CD results for FSO are in agreement with Hamed and Abo-Elwafa (2012), who reported that the PV and CD values of FSO increased sharply when stored at 60 °C. Similar observations on PV and K_{232} values of GSO stored under thermal conditions have been reported (Jang *et al*., 2015). In addition, similar increases in PV and CD values have been observed in BSO as affected by thermal oxidation conditions (Kiralan, 2014; Kiralan *et al*., 2017). However, our results might somehow differ from the results previously reported in the literature. In our experiment, small oil samples were used in headspace vials, as opposed to the use of large amount of oil samples in the above-mentioned literature. In addition, the differences in the results might be due to the distinctive experiment oxidation conditions, genotype and growing condition of plants.

3.3. Changes in the VOC as affected by thermal oxidation

An in-depth search in the scientific literature indicated that studying VOC in FSO, BSO and GSO during storage at thermal oxidation conditions had not yet been performed. The changes in the VOC and volatile compounds in CPO during storage under thermal oxidation conditions are given in Table 4. Six volatile compounds, including aldehydes and alkadienes, are detected in the headspace of FSO. During storage, hexanal was the major compound among VOC. 2,4-heptadienal, and (*E,E*)-2,4-heptadienal were formed upon oxidation and at the end of the storage period, both compounds increased up to the maximum values of 16.84 and 16.09x10^6 AU, respectively. 2-hexenal, 2,4-hexadienal and *E*-2-heptenal were VOC detected after 3 days of FSO storage and their levels increased with the increase in storage time.

2,4-heptadienal was formed in canola and soybean oil with high linolenate (Snyder *et al*., 1985). (*E,E*)-2,4-heptadienal was also identified in soybean oil stored under thermal oxidation conditions (Snyder *et al*., 1988). Hexanal, 2-hexenal, (*E*)-2-heptenal, (*E,E*)-2,4-heptadienal and

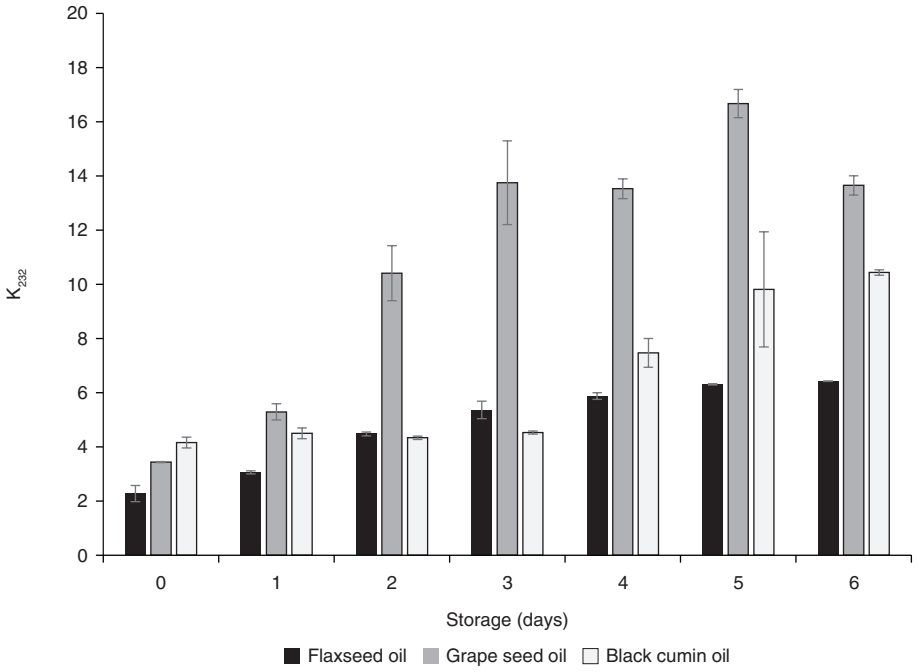

FIGURE 2. Changes in CD levels of CPO during storage at 60 °C (n=2, mean ± SD). Error bars show the variations of two determinations in terms of standard deviation.

(*E,E*)-2,4-hexadienal were detected in fresh FSO without oxidation treatments (Krist *et al*., 2006; Wei *et al*., 2015). The results of our study on the VOC in FSO are in agreement with Abuzaytoun and Shahidi (2006) who reported an increase in hexanal levels during the storage of FSO at 60 °C.

Table 4 listed the VOC identified in the GSO during storage. Thirteen compounds were detected, including alkane (2-octene), aldehydes ((*E*)-2-heptenal, hexanal, (*E*)-2-octenal), ketones (3-octanone, 6-methyl-5-hepten-2-one, 2-heptanone, 2-octanone), and alkadienals (2,4-hexadienal, 2,4-heptadienal, 2,4-nonadienal, 2,4-decadienal, (*E,E*)-2,4-decadienal). (*E*)-2-heptenal was detected as the main VOC during storage, followed by hexanal. At the end of storage, the other most abundant aldehyde found in GSO was (*E*)-2-octenal. In addition, at the end of the storage experiment, diverse alkadienals were formed. However, the levels of these compounds remained limited among the VOC.

Hexanal, (*E*)-2-heptenal and (*E*)-2octenal were determined as the decomposition products of linoleate hydroperoxides (Frankel *et al*., 1981). The increase rate of forming hexanal and (*E*)-2-heptenal during storage at 60 °C was observed in the study by Jelen *et at*., (2000), who reported that the increase in 2-heptenal was more than that in hexanal in the headspace of cold-pressed rapeseed oil at the end of storage (60 °C). No literature report could be found about the volatile compounds of GSO during thermal oxidation but only one published work (Bail *et al*., 2008) reported on the volatile compounds of nine GSO. In this work (Bail *et al*., 2008), hexanal, 2-heptanone, (*E*)-2-heptenal and (E)-2-octenal were observed in the volatiles of oil samples. These compounds were also identified in our analyzed cold-pressed grape seed oil.

Five VOC were identified in the headspace of BSO during storage as given in Table 4. Most of the identified volatiles were aldehydes and only one ketone (2-heptanone) was detected in the headspace of the BSO sample. Among the aldehydes, hexanal and (*E*)-2-heptenal were formed as the main VOC during storage. Lower contents of 2-hexenal and (*E*)-2-octenal in the headspace of BSO were identified. The study by Kiralan *et al*. (2017) concluded that hexanal and (*E*)-2-heptenal were the major VOC formed during the oxidation of BSO at 60 °C.

4. CONCLUSIONS

Based on the results of the Rancimat test, BSO had higher oxidative stability than GSO and FSO. In addition, FSO and BSO showed stronger oxidative stability than GSO after storage at 60 °C. The changes in PV and CD in FSO during storage at 60 °C were less than in BSO and GSO. The higher stability of FSO and BSO could be related to the levels of γ-tocopherol and individual bioactives and phenolic compounds in both oils. To the best of our knowledge, this is the first study on the effect of

TABLE 4. Changes in the volatile oxidation compounds of CPO during storge under thermal oxidation (n=2, mean ± SD)

	KI[A]	RI[B]	Compound	Storage (day) 0 (Fresh)	1	2	3	4	5	6
FLAX SEED OIL										
1	838	a	**Hexanal**	2.92±0.04c*	3.46±0.02c	5.00±0.02c	10.10±0.84b	26.63±1.55a	22.59±0.88a	24.28±4.15a
2	906	a	**2-hexenal**	ND	ND	ND	0.75±0.07b	1.43±0.19a	1.45±0.13a	1.58±0.11a
3	974	b	**2,4-hexadienal**	ND	ND	ND	1.05±0.13b	1.56±0.21a	1.58±0.08a	1.67±0.10a
4	1012	a	***E*-2-heptenal**	ND	ND	ND	2.01±0.30b	5.70±0.81a	5.29±0.62a	5.41±0.95a
5	1062	b	**2,4-heptadienal**	ND	ND	1.88±1.44d	6.80±1.28c	13.35±2.08b	12.92±1.55b	16.84±1.85a
6	1076	b	**(*E,E*)-2.4-heptadienal**	ND	ND	ND	5.82±1.61b	12.92±2.47a	12.77±2.02a	16.09±3.19a
GRAPE SEED OIL										
1	819	b	**2-octene**	ND	ND	ND	ND	0.76±0.02	0.78±0.04	0.72±0.07
2	838	a	**Hexanal**	11.98±0.01d	13.74±0.19cd	19.08±2.14bc	23.99±1.27b	32.25±2.67a	36.69±5.13a	36.79±1.56a
3	935	a	**2-heptanone**	ND	ND	ND	ND	4.14±0.23a	4.42±0.31a	3.63±0.10b
4	974	b	**2,4-hexadienal**	ND	ND	ND	ND	ND	ND	0.74±0.06
5	1012	a	***E*-2-heptenal**	2.01±0.54e	3.75±0.54de	12.27±0.50d	25.56±1.84c	35.02±4.62b	39.77±6.50b	67.53±5.41a
6	1029	b	**3-octanone**	3.00±0.03c	3.17±0.27c	4.19±0.54bc	5.81±0.87ab	5.49±1.19ab	5.21±0.41ab	6.65±0.74a
7	1034	b	**6-methyl-5-hepten-2-one**	1.48±0.01d	1.72±0.27d	2.97±0.43c	4.20±0.49b	4.02±0.47b	3.86±0.07b	5.17±0.05a
8	1037	b	**2-octanone**	1.27±0.01d	1.75±0.33d	2.95±0.28c	3.69±0.28b	3.38±0.37bc	3.32±0.16bc	4.36±0.32a
9	1076	b	**2,4-heptadienal**	ND	ND	ND	ND	0.72±0.12b	0.74±0.06b	1.44±0.20a
10	1118	a	***E*-2-octenal**	0.44±0.02c	0.61±0.12c	1.07±0.15c	2.30±0.51bc	3.36±0.02bc	4.32±1.30b	9.72±2.76a
11	1288	b	**2,4-nonadienal**	ND	ND	ND	0.25±0.08b	0.32±0.06b	0.35±0.08b	0.78±0.00a
12	1368	b	**2,4-decadienal**	ND	ND	ND	ND	ND	ND	0.76±0.08
13	1394	b	**(*E,E*)-2,4-decadienal**	ND	ND	ND	ND	0.39±0.14b	0.48±0.23b	1.60±0.26a
BLACK CUMIN OIL										
1	838	a	**Hexanal**	10.4±0.04d	17.19±0.53d	25.48±0.47cd	37.14±2.92c	55.82±0.33b	68.38±2.60ab	76.20±16.89a
2	906	a	**2-hexenal**	ND	ND	ND	ND	ND	3.46±0.46	4.01±0.91
3	935	a	**2-heptanone**	ND	ND	ND	ND	ND	1.13±0.01	1.19±0.13
4	1012	a	***E*-2-heptenal**	ND	ND	ND	ND	9.21±2.21b	22.88±4.86a	24.17±0.08a
5	1117	a	***E*-2-octenal**	ND	ND	ND	ND	0.65±0.33b	1.53±0.48a	1.89±0.09a

[a]KI = Kovats index calculated for DB-624 capillary column (J&W Scientific; 30 m, 0.25 mm id, 1.4 µm film thickness) installed on a GC equipped with a mass-selective detector.
[b]RI = reliability of identification; a = mass spectrum and retention time identical to the authentic sample; b = mass spectrum and Kovats index from the literature in accordance.
*Results are expressed as means of total ion current (TIC) area units ($\times 10^{-6}$); means with different letters given in the same row are significantly different at $p < 0.05$.

storage under thermal oxidation conditions on the VOC in the selected CPO. The identified VOC could be used as markers for detecting oils under study. The results could be used for the determination of the major and minor bioactive components responsible for the quality of CPO.

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Compliance with ethics requirements. This article does not contain any studies with human or animal subjects.

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