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Effect of Light on the Oxidative Stability and Phthalate Levels of Black Cumin Oil-Corn Oil Blends in Plastic and Glass Bottling

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Abstract: Black cumin oil (BC) contains certain phytochemicals, including phenolics, tocopherols, and sterols, which show strong oxidation stability. In this study, BC was blended with refined corn oil (CO) at two concentrations (5% and 10%, w/w) and stored in plastic and glass bottles under light and dark conditions. Under light-storage conditions, blended oils in plastic bottles showed lower peroxide value (PV) and conjugated diene value (CD) compared to the control sample than dark-storage. It was also aimed to examine the phthalate levels in oil samples and evaluate the products' safety. Five main phthalates, namely di(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), butyl-benzylphthalate (BBP), diisononyl phthalate (DiNP), and diisodecyl phthalate (DiDP), were evaluated. In dark and light storage conditions, the phthalate level was determined below the LOQ value in CO without added BCO in the plastic and glass bottles. In the plastic-packaged blended samples, DEHP was determined above the LOQ value in dark storage, while BBP was detected in addition to DEHP in the samples stored under the light. On the other hand, phthalate values were determined below the LOQ value in all samples stored in glass packages under the light. DEHP was the most abundant phthalate in plastic-packaged blended oils under light storage, ranging from below the LOQ (0.23 mg/kg) to 0.83 mg/kg. Based on the present findings, BC improved the stability of CO under light storage, and the phthalate levels of blended oils did not exceed the specific migration limits (SMLs) for each phthalate.

Key words: black cumin oil, blended oils, oxidative stability, conjugated diene value, phthalate, peroxide value

1 Introduction

Black cumin (*Nigella sativa*) has been used for several health applications since ancient times. Many experimental studies indicated that black cumin's health properties are related to phenolics, especially thymoquinone, as well as tocols and phytosterols[1]. Therefore, black cumin seeds are used in various foodstuffs such as coffee, tea, pickles, and bread[2]. Moreover, black cumin oil is a valuable food product for its nutritional, health, and sensory attributes obtained from the seeds using the cold pressing method. Since cold-pressed black cumin oil is a rich source of thymoquinone and natural antioxidants, it is also suitable for direct consumption[3].

Black cumin oil has shown strong oxidative stability during thermal and photo-oxidation conditions. Kiralan *et al.*[4] evaluated the oxidative stability of cold-pressed black cumin oils at 60℃, wherein the oil showed higher stability than grape seed oil. Besides, the oxidative stability of black cumin oil was slightly higher than that of grape seed oil under photo-oxidation conditions[5]. Due to its strong oxidative stability, black cumin oil could be blended with common vegetable oils such as sunflower oil[6] and corn oil[7] to improve the oxidative stabilities of these oils. Mohamed *et al.*[8] demonstrated that cold-pressed black cumin oil is an excellent edible oil source to improve the oxidative stability of corn oil stored at thermal oxidation conditions (60℃) for 8 days. Ramadan[6] also investigated the improvement in sunflower oil stability by blending with black cumin oil (10% and 20%) under storage for 8 days at 60℃. In these oxidation experiments, glass bottles were used. Neverthe-

less, refined sunflower and corn oils are offered in plastic bottles in the markets.

Phthalates are environmental contaminants and act as plasticizers. They are widely used in the production of plastic packaging materials. According to Pereira *et al.*[9], some phthalates show toxic effects on reproduction and endocrine disruptors. Plastic bottles are generally used for packaging vegetable oils due to their relatively low price and weight and ease of handling[10]. Due to their lipophilic property, phthalates can be quickly released from plastic packaging and migrate into vegetable oils[11]. Phthalates have been detected in many vegetable oils such as olive, sunflower, corn, hazelnut, canola oils[12, 13]. Cold-pressed oils showed popularity among edible oils due to the advantages of non-thermal processing they possess. Besides, most bioactive compounds are present in cold-pressed oils, which contribute to human health, making these oils meet consumers' demands for natural and safe products[14]. As in vegetable oils, cold-pressed oils also suffer from phthalates. Kiralan *et al.*[15] evaluated main phthalates, including di (2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), butyl-benzylphthalate (BBP), diisononyl phthalate (DiNP), and diisodecyl phthalate (DiDP) in different cold-pressed oils sold in Turkish markets. These oils samples were packaged in glass bottles, while DEHP was found as major phthalate in contaminated oils (0.56-92.1 mg/kg). DEHP was identified in a high concentration in three black cumin oil samples (12.1-52.1 mg/kg), while in one black cumin oil sample, DBP was identified at a high level (51.6 mg/kg).

The limited literature studies mentioned above show that oxidation experiments on black cumin seed oil are carried out in glass packaging materials and generally at high temperatures. However, plastic bottles are preferred in commercially refined vegetable oils packaging. Therefore, this study aimed to evaluate the oxidative deterioration of corn oil blended with cold-pressed black cumin oil (5% and 10%, w/w) packaged in both plastic and glass bottles stored under light or dark conditions by evaluating peroxide and conjugated diene values. Besides, the changes in the levels of phthalates [di (2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), butyl-benzylphthalate (BBP), diisononyl phthalate (DiNP), and diisodecyl phthalate (DiDP)] in oil samples stored under these oxidation conditions were evaluated.

2 Materials and Methods

2.1 Materials

Refined corn oil (CO) and cold-pressed black cumin oil (BC) were purchased from local markets in Turkey. The mixing ratio of CO:BC was 95:5 and 90:10 w/w, with a rigorous mixing at room temperature. All solvents and reagents were of analytical grade and were supplied from Merck (Darmstadt, Germany).

2.2 Storage experiments

The CO and blended oils (85 g) were poured into 100 mL clear plastic PET and glass bottles, leaving 2 mL headspace for air. The bottles were sealed and grouped into two series. The first series was placed on a dark cabinet shelf for dark-storage conditions, while the second series was stored under daylight. Oxidation was monitored for a 120-day storage period by taking samples every 30 days. In addition, the peroxide value (PV) and conjugated diene value (CD) analyses were carried out to monitor the oxidative changes.

PV and CD (K_{232}) were measured according to the official methods of the American Oil Chemists' Society [PV (AOCS Cd 8-53)] and conjugated diene and triene (AOCS Ch 5-91)[16]. The average temperature during the storage period was approximately 20℃. The initial PV and K_{232} values of CO and BC were 0.62 meq O_2/kg & 3.78, and 15.5 meq O_2/kg & 3.87.

2.3 Phthalates analysis

The oil sample (1 g) was placed in a 10-mL glass tube, and 10 μL of the internal standard solution in BHT (butylated hydroxytoluene, internal standard) was introduced with each sample. After vigorous shaking for 5 min, 10 mL of acetonitrile was added and vortexed for 10 min. Then, the mixture was centrifuged for 10 min at 2500 rpm to accelerate phase separation. The upper phase was transferred into a 10 mL test tube. The remaining solvent was evaporated under nitrogen at 40℃ until the final extract volume reached 1 mL. The extracts were then transferred into an autosampler vial and analyzed by GC-MS with electron ionization in SIM (selected ion monitoring) mode. A procedural blank sample was prepared and analyzed in each sample batch to evaluate possible contamination properly.

The GC-MS system used was an Agilent 6890N gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) connected to an Agilent 5973N mass spectrometer (Agilent Technologies, Palo Alto, CA, USA). The operation was performed at electronic impact (EI) ionization mode (70 eV). An HP-5MS capillary column (30 m × 0.25 mm I.D. × 0.25 mm film thickness, Agilent) was used for separation. The carrier gas was helium with a 1 mL/min flow rate. The injector and detector temperatures were both set to 280℃. The oven temperature program was as follows:

· Start at 80℃ and hold for 1 min.
· Step up 15℃/min until it reaches 280℃.
· Hold at 280℃ for 15 min.

A split ratio of 1:40 was used to inject samples (1 mL). Selected ion monitoring (SIM) mode was used to determine the peaks. The validation parameters were according to the

Table 1 Retention times, target and qualifier ions of phthalate esters and the internal standard.

Phthalate esters and internal standard	Retention time (min)	Target Ion	Qualifier Ions
BHT*	8.099 ± 0.5	205	145, 177, 220
DBP	11.354 ± 0.5	149	150, 205, 223
BBP	13.748 ± 0.5	149	91, 150, 206, 238
DEHP	14.750 ± 0.5	149	150, 167, 279
DIDP	17.909 ± 2.0	307	149, 150, 167
DINP	16.074 ± 2.0	293	149, 150, 167

* Butylated hydroxytoluene, internal standard

study of Kiralan *et al.*[15]. LOQ (mg/kg) values for DBP, BBP, DEHP, DINP and DIDP were 0.09, 2.28, 0.23, 1.75 and 1.40, respectively. The initial phthalate analysis showed that only one phthalate (DEHP) was identified in CO and BC with 0.29 mg/kg and 0.35 mg/kg, respectively. The other phthalates were lower than the LOQ value determined for each phthalate. The retention times of both phthalate esters and the internal standard and the targeted ions and qualifier ions are given in **Table 1**.

2.4 Statistics

Statistical analyses were conducted using SPSS (Statistical Program for Social Sciences, SPSS Corporation, Chicago, IL, USA) version 16.0 for Windows. Experimental data were evaluated using analysis of variance (ANOVA), and significant differences between the means of the groups from PV and K_{232} during storage ($p < 0.05$) were determined by Duncan's multiple range test.

3 Results and Discussion

3.1 Effect of blending on the stability of oils

Figure 1 shows the changes in PV during the storage of blended samples stored in plastic (a) and glass (b) bottles under light at room temperature for four months. In plastic bottling, the control sample without BC reached a maximum PV of 17.9 meq O_2/kg after four storage months. Significant differences in PV were observed between control and blended oils, which exhibited the rate of peroxide formation. At the end of storage, the PV of BC5 and BC10 were 10.1 and 9.66 meq O_2/kg, respectively. In glass bottling, the PV of blended oil samples were found higher than control in the first two months of storage; however, the PV of the control sample presented a rapid increase in the third and fourth months, and the PV values of control and blended samples were close to each other. Therefore, it was thought that high PV for blended oils was due to the high levels of PV of added BCO, which was a normal situation regarding the nature of the highly unsaturated oil.
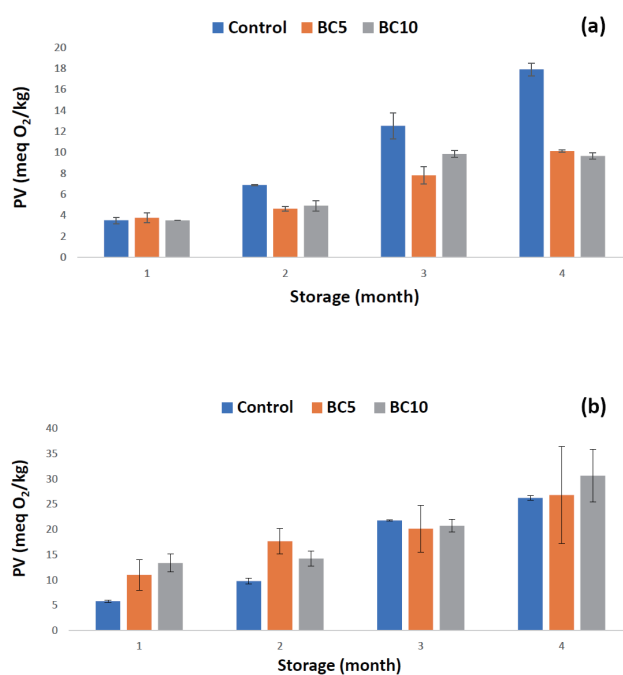

Fig. 1 Changes in PV of oils during storage under light. (a): plastic bottling, (b): glass bottling. Error bars represent the standard deviation obtained from duplicate experiments. Means with different letters show the variation between samples on the same storage month ($p < 0.05$).

The K_{232} values of the samples during photo-oxidation are shown in **Fig. 2**. During light-storage conditions, the blending of BC with CO in plastic bottles caused small decreases in K_{232} values compared to the control sample. After four months of storage, the K_{232} value of the control sample reached up to 5.44. The values for blended oils at 5% and 10% were 4.68 and 4.44, respectively. Regarding glass bottling, the K_{232} values of the blended oils exhibited an increase during the overall storage period. However, this increase was much higher in the second month of storage than in the 1st month. At the end of the storage period, the K_{232} values of both control and blended samples
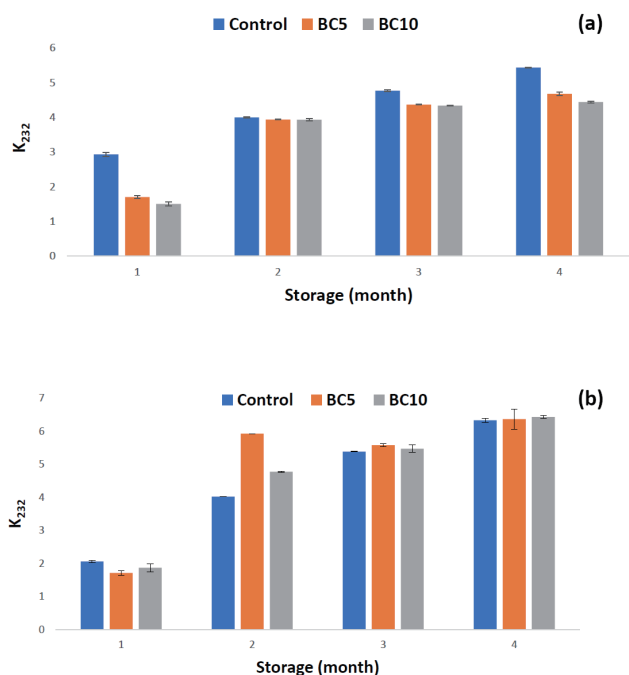
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Fig. 2 Changes in K_{232} values of oils during storage under light. (a): plastic bottling, (b): glass bottling. Error bars represent the standard deviation obtained from duplicate experiments. Means with different letters show the variation between samples on the same storage month ($p < 0.05$).
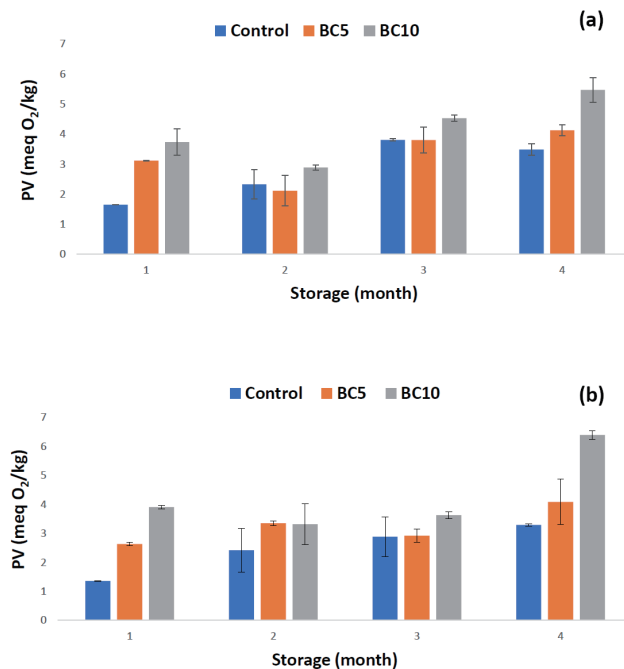

Fig. 3 Changes in PV of oils during storage under dark. (a): plastic bottling, (b): glass bottling. Error bars represent the standard deviation obtained from duplicate experiments. Means with different letters show the variation between samples on the same storage month ($p < 0.05$).

were close to each other, as they were 6.33, 6.36, and 6.43 for the control, BC5, and BC10, respectively. The results from PV and K_{232} values during storage under light indicate that BC has an antioxidant effect and protected CO against primary lipid oxidation, as the final values of blended samples for PV and K_{232} were comparable to those of the control.

Under dark-storage conditions, the changes in PV in the samples stored in plastic and glass bottles are shown in Fig. 3. In plastic bottling, the final PV of the control, BC5, and BC10 samples were 3.49, 4.13, and 5.47 meq O_2/kg, respectively. After the second month of the storage period, the PV of blended samples tended to increase compared to control. BC10 sample had the highest PV value in the overall storage samples. A similar phenomenon was also observed among the samples stored in glass bottles. After three months of storage, the PV of control (2.89 meq O_2/kg) and BC5 (2.92 meq O_2/kg) were almost identical. However, BC10 had the highest PV of 6.40 meq O_2/kg at the end of the storage. Also, the blended samples' initial PV was higher than the control due to higher PV of BCO, as previously discussed for light-storage conditions.

Regarding K_{232}, a slight difference in the variation of K_{232} values among the plastic-bottled samples stored at dark was noted (Fig. 4). Contrary to PV, the K_{232} value recorded

slightly higher values in the control sample than the blended samples. After four months of storage, the K_{232} values for the control, BC5, and BC10 were 4.15, 3.90, and 4.01, respectively. In glass-bottled samples, the K_{232} value of the control was always higher among the tested samples. In the second and third months of the storage, the K_{232} values of BC5 and BC10 were close to each other; however, BC5 exhibited a higher K_{232} than BC10 at the end of the storage period. The K_{232} values of the samples after four months of storage were 4.04, 3.95, and 3.86 for the control, BC5, and BC10, respectively. In conclusion, we suggest that the differences among PV and K_{232} values may result from the color components naturally present in BCO.

Similar results were observed in the study of Pignitter *et al.*[17], who demonstrated that PV and CD values were higher in soybean oil stored under light compared with the oils stored under dark. The light-induced lipid oxidation promotes the oxidation parameters, including PV and K_{232} values. Besides, Méndez and Falqué[18] emphasized that olive oil stored in plastic bottles showed higher PV and K_{232} values than in the other packagings, including opaque plastic, glass, tin plate, and Tetra-brik®. The authors also demonstrated that light is an efficient factor in the increased photo-oxidation of olive oil stored in plastic bottles. Cecchi *et al.*[19] evaluated the PV and CD values in
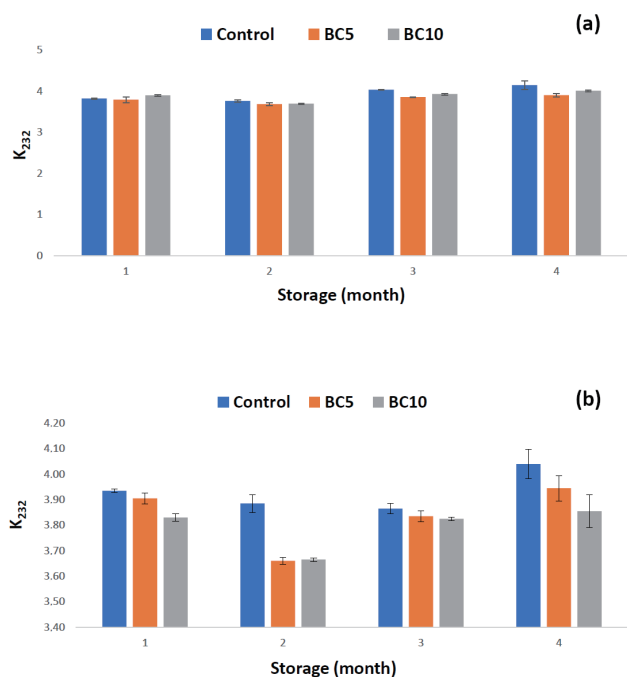
Fig. 4 Changes in K_{232} values of oils during storage under dark. (a): plastic bottling, (b): glass bottling. Error bars represent the standard deviation obtained from duplicate experiments. Means with different letters show the variation between samples on the same storage month ($p < 0.05$).

the olive oil packed in PET bottles and stored in the dark or light at room temperature. They reported a fluctuation in the PV during storage in light and dark conditions. The authors explained the decrease in PV during the middle storage stage with the consumption of peroxides in PET bottles. The authors also determined the slight increases in the K_{232} value of olive oil stored at dark and light. Our results showed similarities with the results of Cecchi *et al.*[19], wherein the fluctuation in PV of oils could be related to plastic materials. According to Kiralan *et al.*[5], the fluctuations were also noted in the PV and K_{232} values of grapeseed oil and BCO samples during their photo-oxidation processes. Anwar *et al.*[20] determined a rapid increase in soybean oil's PV and CD values during photo-oxidation. Their findings revealed that the samples' PV and CD values stored under light were found higher than those of the samples stored in the dark. Dedebas *et al.*[21] also studied the differences in the PV and CD values of different cold-pressed oils stored at different temperatures in the dark. Their results suggested that the PV and CD values of grapeseed oil and BCO increased during storage conditions at room temperature. In another study about the effects of different ambient conditions on oil oxidation during storage, Wroniak and Rękas[22] stated that the PV of rapeseed oil samples stored at 20℃ in the dark was higher than

those of samples stored at 4℃ while in dark-storage. Moreover, the authors noted that the PV of oil samples were close to each other in light- and dark-storage at the same temperature of 20℃.

3.2 Effect of blending on the phthalate content of oils

The individual phthalate contents of oil samples during storage of different conditions in plastic and glass bottles are exhibited in **Tables 2** and **3**, respectively. DBP, BBP, DINP, and DIDP were at the LOQ level in the initial samples of refined CO and BC. However, DEHP was determined in 0.29 mg/kg and 0.35 mg/kg for refined CO and BC, respectively. These values are below the specific migration limit (SML) of 1.5 mg/kg established in EU 2011/10[23]. Similar results were found in other vegetable oil surveys[15, 24, 25].

According to **Table 2**, DEHP was determined in blended oils during light storage conditions. BBP was only determined in blended oils stored for two months, while this phthalate was at the LOQ level. BBP concentration of BC10 was slightly higher than the BC5. Like BBP, the highest value of DEHP was found in blended oils after two months of storage, while after that, the concentration of DEHP decreased with storage and eventually reached the LOQ level. Under dark storage conditions, DEHP was found in blended oils at higher concentrations than control at the LOQ level. Besides, DBP, BBP, DINP, and DIDP were lower than their LOQ in all samples. The highest value of DEHP was recorded in BC10 at 0.61 mg/kg after two months of storage. DEHP concentration of blended oils decreased with the storage period and eventually was lower than its LOQ value. Our data indicated that the blended oils stored in the light showed higher DEHP values than those kept in the dark. Besides, BBP was detected in the blended oils after two months of storage in the light, while this phthalate was lower than its LOQ level stored in dark conditions. Considering phthalate concentrations, all oil samples stored at light and dark conditions do not exceed the SML value for each phthalate established in EU 2011/10[23]. On the other hand, the phthalate concentrations in the samples stored in glass bottles were all below their respective LOQs, and this situation was expected as there was no migration from the glass material (Table 3).

Our results agree with Xu *et al.*[26], who demonstrated an increasing trend in the phthalate levels of cooking oil stored at 20℃ for two months. Besides, DEHP was reported to highly migrate in the cooking oil. Oh *et al.*[27] investigated the presence of DBP and DEHP in 12 different vegetable oils, and they concluded that DEHP was the most abundant phthalate in their samples, having a maximum level of 806 µg/kg in grape seed oil. In another study by Fusari and Rovellini[28], DEHP was also determined in many oil samples, including olive, sunflower, corn, peanut, and grape seed oils, in concentrations ranging between 0.39-2.67 mg/kg. Vavrouš *et al.*[29] stated that DEHP was present

Table 2 Changes in phthalates (mean ± SD) in CO with and without BC during the storage in plastic bottles (n = 2).

Phthalate (mg/kg)	Sample	Storage (month)-dark condition				
		1	2	3	4	6
DBP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BBP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DEHP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	0.42 ± 0.00	0.43 ± 0.01	0.35 ± 0.05	<LOQ	<LOQ
	BC10	<LOQ	0.61 ± 0.03	0.35 ± 0.03	0.24 ± 0.01	<LOQ
DINP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DIDP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Phthalate (mg/kg)	Sample	Storage (month)-light condition				
		1	2	3	4	6
DBP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BBP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	0.20 ± 0.04	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	0.26 ± 0.02	<LOQ	<LOQ	<LOQ
DEHP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	0.57 ± 0.01	0.26 ± 0.02	<LOQ	<LOQ
	BC10	0.55 ± 0.01	0.83 ± 0.01	0.42 ± 0.01	0.28 ± 0.01	<LOQ
DINP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DIDP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

in their vegetable oil samples, having a minimum concentration of 0.18 mg/kg in rapeseed oil and a maximum of 4.7 mg/kg in olive oil samples. DEHP presence in cold-pressed black cumin oil was also reported by Kiralan *et al.*[15]. According to the researchers, the concentrations of DEHP varied between 12.09-52.11 mg/kg in their samples.

4 Conclusion

Cold-pressed oils are considered safe and more consumer-desired products. However, cold-pressed oils could be blended with refined vegetable oils characterized by poor oxidative stability due to their high content of PUFA. On the other hand, many refined vegetable oils are sold in plastic bottles. Phthalates are possible contaminants in plastic bottles and cause a significant health risk for

Table 3   Changes in phthalates (mean ± SD) in CO with and without BC during the storage in glass bottles (n = 2).

Phthalate (mg/kg)	Sample	Storage (month)-dark condition				
		1	2	3	4	6
DBP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BBP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DEHP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DINP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DIDP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Phthalate (mg/kg)	Sample	Storage (month)-light condition				
		1	2	3	4	6
DBP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BBP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DEHP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DINP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DIDP	Control	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	BC10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

humans. In the current study, light storage induced higher PV and CD values of oils than dark storage. During light storage, BC showed a protective effect on CO oxidation, wherein lower PV and K_{232} values were observed in CO blended with BC at 5% and 10%. Nevertheless, slight increases in PV were observed in blended oil compared to the control sample. The studied phthalates in the control sample stored under light or dark did not exceed the LOQ value. Like the control sample, DBP, DINP, and DIDP were lower than LOQ in blended oils stored under light and dark conditions. However, DEHP was identified in blended oils at both light and dark conditions, while BBP was only present in blended oils after two months of storage under the light. This higher contamination could be due to the migration of plastic materials to blended oils as an effect of light and temperature. Mostly, this effect could be seen in

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blended oils with a high amount of BC.

Declaration

This study has not been funded by any commercial or not-for-profit organizations.

Author Contribution

The authors' contributions are as follows:

İ.T: sample preparation and performing analyses

M.K: contribution to the design of the work, preparation of the manuscript draft, interpretation of data

O.K: final manuscript check, manuscript formatting, manuscript submission, preparation of the figures, formatting of the tables

M.F.R: final manuscript check, contribution to the design of the work, improving text quality

All authors read and approved the final manuscript.

Conflict of Interest

The authors declare no conflict of interest.

References

1) Ramadan, M.F. Introduction to black cumin (*Nigella sativa*): Chemistry, technology, functionality and applications. in *Black cumin (Nigella sativa) seeds: Chemistry, Technology, Functionality, and Applications* (Ramadan, M.F. ed.), Springer International Publishing, Cham, pp. 1-7 (2021).

2) Ramadan, M.F. Nutritional value, functional properties and nutraceutical applications of black cumin (*Nigella sativa* L.): An overview. *Int. J. Food Sci. Technol.* 42, 1208-1218 (2007).

3) Lutterodt, H.; Luther, M.; Slavin, M.; Yin, J.-J.; Parry, J. *et al.* Fatty acid profile, thymoquinone content, oxidative stability, and antioxidant properties of cold-pressed black cumin seed oils. *LWT-Food Sci. Technol.* 43, 1409-1413 (2010).

4) Kiralan, M.; Çalik, G.; Kiralan, S.; Özaydin, A.; Özkan, G.; Ramadan, M.F. Stability and volatile oxidation compounds of grape seed, flax seed and black cumin seed cold-pressed oils as affected by thermal oxidation. *Grasas Aceites* 70, e295 (2019).

5) Kiralan, M.; Çalik, G.; Kiralan, S.; Ramadan, M.F. Monitoring stability and volatile oxidation compounds of cold-pressed flax seed, grape seed and black cumin seed oils upon photo-oxidation. *J. Food Meas. Charact.* 12, 616-621 (2018).

6) Ramadan, M.F. Healthy blends of high linoleic sunflower oil with selected cold pressed oils: Functionality, stability and antioxidative characteristics. *Ind. Crop Prod.* 43, 65-72 (2013).

7) Ramadan, M.F.; Wahdan, K.M.M. Blending of corn oil with black cumin (*Nigella sativa*) and coriander (*Coriandrum sativum*) seed oils: Impact on functionality, stability and radical scavenging activity. *Food Chem.* 132, 873-879 (2012).

8) Mohamed, K.M.; Elsanhoty, R.M.; Hassanien, M.F.R. Improving thermal stability of high linoleic corn oil by blending with black cumin and coriander oils. *Int. J. Food Prop.* 17, 500-510 (2014).

9) Pereira, J.; Selbourne, M.dC.; Poças, F. Determination of phthalates in olive oil from European market. *Food Control* 98, 54-60 (2019).

10) Coltro, L.; Padula, M.; Saron, E.S.; Borghetti, J.; Buratin, A.E.P. Evaluation of a UV absorber added to PET bottles for edible oil packaging. *Packag. Technol. Sci.* 16, 15-20 (2003).

11) Shi, L.-K.; Zhang, M.-M.; Liu, Y.-L. Concentration and survey of phthalic acid esters in edible vegetable oils and oilseeds by gas chromatography-mass spectrometry in China. *Food Control* 68, 118-123 (2016).

12) Sungur, S.; Okur, R.; Turgut, F.H.; Ustun, I.; Gokce, C. Migrated phthalate levels into edible oils. *Food Addit. Contam. B* 8, 190-194 (2015).

13) Kıralan, S.S.; Toptancı, İ.; Öncül Abacıgil, T.; Ramadan, M.F. Phthalates levels in olive oils and olive pomace oils marketed in Turkey. *Food Addit. Contam. A* 37, 1332-1338 (2020).

14) Parker, T.D.; Adams, D.A.; Zhou, K.; Harris, M.; Yu, L. Fatty acid composition and oxidative stability of cold-pressed edible seed oils. *J. Food Sci.* 68, 1240-1243 (2003).

15) Kiralan, M.; Toptanci, İ.; Yavuz, M.; Ramadan, M.F. Phthalates levels in cold-pressed oils marketed in Turkey. *Environ. Sci. Pollut. Res.* 27, 5630-5635 (2020).

16) AOCS. *Official Methods and Recommended Practices of the American Oil Chemists' Society*. AOCS Champaign, IL, USA (2006).

17) Pignitter, M.; Stolze, K.; Gartner, S.; Dumhart, B.; Stoll, C.; Steiger, G.; Kraemer, K.; Somoza, V. Cold fluorescent light as major inducer of lipid oxidation in soybean oil stored at household conditions for eight weeks. *J. Agr. Food Chem.* 62, 2297-2305 (2014).

18) Méndez, A.I.; Falqué, E. Effect of storage time and container type on the quality of extra-virgin olive oil. *Food Control* 18, 521-529 (2007).

19) Cecchi, T.; Passamonti, P.; Cecchi, P. Study of the quality of extra virgin olive oil stored in PET bottles with or without an oxygen scavenger. *Food Chem.* 120, 730-735 (2010).

20) Anwar, F.; Shahid Chatha, S.A.; Ijaz Hussain, A. Assessment of oxidative deterioration of soybean oil at ambient and sunlight storage. *Grasas Aceites* **58**, 390-395 (2007).

21) Dedebas, T.; Ekici, L.; Sagdic, O. Chemical characteristics and storage stabilities of different cold-pressed seed oils. *J. Food Process. Pres.* **45**, e15107 (2021).

22) Wroniak, M.; Rękas, A. Nutritional value of cold-pressed rapeseed oil during long term storage as influenced by the type of packaging material, exposure to light & oxygen and storage temperature. *J. Food Sci. Technol.* **53**, 1338-1347 (2016).

23) EC. European Commission. Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. *J. Eur. Union* **L12**, 1-89 (2011).

24) Nanni, N.; Fiselier, K.; Grob, K.; Di Pasquale, M.; Fabrizi, L. *et al.* Contamination of vegetable oils marketed in Italy by phthalic acid esters. *Food Control* **22**, 209-214 (2011).

25) Liu, Y.; Wang, S.; Wang, L. Development of rapid determination of 18 phthalate esters in edible vegetable oils by gas chromatography tandem mass spectrometry. *J. Agr. Food Chem.* **61**, 1160-1164 (2013).

26) Xu, Q.; Yin, X.; Wang, M.; Wang, H.; Zhang, N. *et al.* Analysis of phthalate migration from plastic containers to packaged cooking oil and mineral water. *J. Agr. Food Chem.* **58**, 11311-11317 (2010).

27) Oh, M.-S.; Lee, S.-H.; Moon, M.H.; Lee, D.S.; Park, H.-M. Simultaneous analysis of phthalates, adipate and polycyclic aromatic hydrocarbons in edible oils using isotope dilution-gas chromatography–mass spectrometry. *Food Addit. Contam. B* **7**, 168-175 (2014).

28) Fusari, P., Rovellini, P. Liquid chromatography-Ion Trap-ESI-mass spectrometry in food safety assessment: Phthalates in vegetable oils. *Riv. Ital. Sostanze Grasse* **86**, 25-30 (2009).

29) Vavrouš, A.; Pavloušková, J.; Ševčík, V.; Vrbík, K.; Čabala, R. Solution for blank and matrix difficulties encountered during phthalate analysis of edible oils by high performance liquid chromatography coupled with tandem mass spectrometry. *J. Chromatogr. A* **1456**, 196-204 (2016).