Effects of different postharvest storage conditions of black cumin seeds on the oxidative stability of cold pressed oil

Derya Arslan*
Ayşenur Acar

Department of Food Engineering
Faculty of Engineering
Necmettin Erbakan University
Koycegiz Campus
Konya, Turkiye

The high peroxide values encountered in black cumin seed oil, even when obtained from newly harvested seeds can be closely related to the storage conditions of the seeds. The oxidative stability of black cumin seed oil from unroasted and mildly roasted (65°C) seeds was evaluated under three different storage conditions; refrigerated at 4°C, shaded and exposed to direct sunlight both at room temperature. Seeds were stored in airtight jars or tied cloth bags as two different storage materials under these conditions. Storage in jars under shaded storage and in cloth bags at refrigeration condition resulted in lower free fatty acidity in the oils. Shaded storage showed better results in terms of PV, TPC and DPPH (4 months). Refrigerated conditions in cloth bags provided higher values of total phenolics and DPPH radical scavenging activity for the unroasted seeds. Mild roasting produced oils with lower free fatty acidity, higher amounts of total phenolics and stronger DPPH radical scavenging activity, however reduced the oxidative stability. A positive correlation was detected between the peroxide values of the oil and the L* values of the oil, and a negative correlation with the induction time. Free fatty acidity and induction time of the oil obtained from minimally heat-treated seeds showed a strong negative correlation.

Keywords: Black cumin seed oil; Cold pressing; Oxidative stability; Peroxide value; Storage conditions

1. INTRODUCTION

For many years, black cumin seeds (*Nigella sativa* L.) have been used for medicinal and culinary purposes [1]. Black cumin seeds (BCS) contain a high amount of oil and have an important place in the formulation of cosmetic and dietary supplement products, as well as health and nutrition due to their phytochemical content (phenolic and bioactive compounds) [2].

Black cumin seed oil (BCSO) is usually extracted by cold pressing, which is an inexpensive, safer and simpler process than solvent extraction [3]. Since it is unrefined, cold-pressed BCSO contains high amounts of natural antioxidants and thymoquinone, which is a main bioactive component of BCSO [1,2]. Due to the increasing demand of consumers for safe and native food products, cold-pressing has become an alternative to conventional extraction procedures [1].

Lipid oxidation, which has adverse effects on human health and food quality, is one of the major causes for the loss of quality characteristics such as colour, odour, taste and nutritional value [1]. For this reason, some measures should be taken to reduce oxidation and increase the oxidative stability of lipid products [4]. Autoxidation and light-sensitive oxidation are responsible for the oxidation of edible oils during processing and storage. Due to the crude oils obtained after extraction not being processed, phenolic compounds with high stability against autoxidation and polar lipids are protected [5].

✉ CORRESPONDING AUTHOR:
Derya Arslan
NEÜ Köyceğiz Yerleşkesi, 42080 Meram
Konya, Turkiye
Email: dears@erbakan.edu.tr
Tel: +905355640994

ORCID ID
https://orcid.org/
0000-0002-6655-9312

Received: April 14, 2023
Accepted: February 9, 2024

Considering the results of many studies, it was understood that BCSO showed peroxide values varying between a wide range [6-10]. Notably some literature data are high in terms of peroxide value [11, 12]. We believe that these high peroxide values are due to storage conditions of BCS. Accordingly, the effects of factors such as storage temperature, storage media and packages (light exposure and air) and duration, which is thought to cause an increase in peroxide value of BCSO, were investigated.
Thus, in this study, BCSs were stored in cloth bags and jars under different conditions (refrigerator temperature, shaded at room temperature and directly sun exposure). The impact of these storage materials and conditions on oxidative stability and some quality characteristics of the corresponding oils was examined. On the other hand, effect of roasting was also evaluated with this regard, since roasting is a process with important contributions in oil extraction.

2. MATERIALS AND METHODS

2.1. BLACK CUMIN SEEDS

BCSs were obtained in a week after harvest in December 2019 from Konya, Turkiye. BCS (24 kg for each replicate) were brought to the laboratory having 3 replicates for each treatment. Equal batches (1 kg) of BCS were packed in two types of storage materials, sealed airtight jars and tied cloth bags, which were stored at three different conditions as 4°C in a laboratory refrigerator, shaded and exposed to direct sunlight, both at room temperature (Fig. 1). Samples were analysed for oxidative stability on months 4 and 8 of storage time.
A mild roasting step was included in the experimental design for some batches of the stored seeds. For this purpose, water with a ratio of 10% of seed weight was homogeneously sprayed onto the ground seeds. Samples were incubated for 3 h, at 60°C and mixed at regular intervals.

2.2. OIL EXTRACTION FROM SEEDS BY COLD-PRESSING

BCSO was extracted using a manual screw press extractor (Karaerler NF 500, Turkiye, 1.5 kW power, 50 kg seed.h^{-1} capacity, single head, 15 hz rotation speed). The temperature remained below 50°C during the extraction. The oils were filled in dark coloured glass bottles and kept at +4°C.

2.3. DETERMINATION OF FREE FATTY ACIDITY (FFA) AND PEROXIDE VALUES (PV) OF BCSO

FFA and PV were measured according to practices Ca 5a-40 and Cd 8b-90 recommended by AOCS, respectively [13]. PV was given as milliequivalent active oxygen per kg of oil (meq O_2/kg oil) while FFA was expressed as a percentage of oleic acid (% oleic acid).

2.4. OXIDATION STABILITY OF BCSO (RANCIMAT TEST)

Oxidative stability stated as the induction time (h) was evaluated with an accelerated controlled test

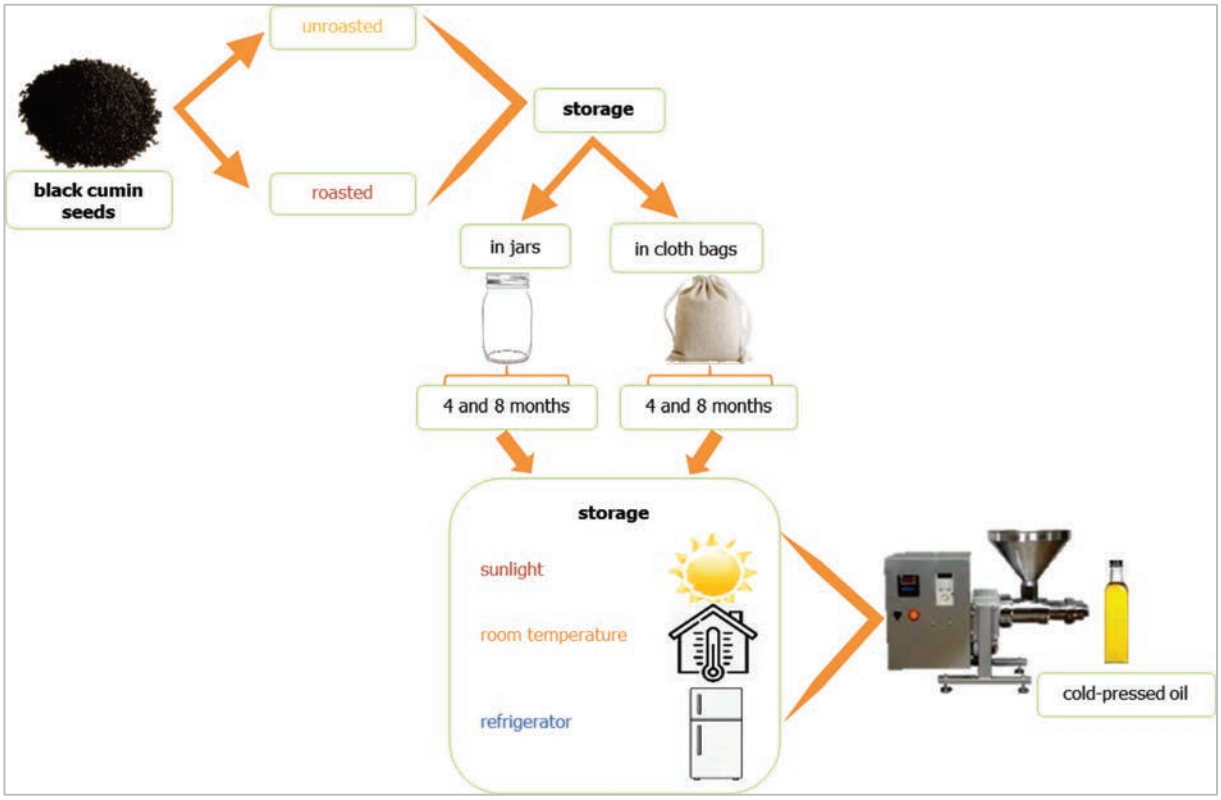

Figure 1 - Flow chart of the process of obtaining oil from BCSs stored at different conditions

on Rancimat device (Metrohm Co., Herisau, Switzerland). By passing an air flow of 20 L/h from inside 3 g oil heated at 120°C, volatile degradation products were kept in distilled water and the conductivity of the water increased [13].

2.5. COLOR MEASUREMENT

The colour of the oils was determined using the Minolta CR400 (Minolta Co., Osaka, Japan) instrument according to the Hunter colour system. Measurements were performed in triplicate [14].

2.6. TOTAL PHENOLIC COMPOUNDS (TPC)

n-hexane (5 mL) and methanol water (10 mL, 80:20, v/v) were added to 10 g BCSO and vortexed for 2 min. The mixture was centrifuged at 3000 rpm for 5 min and the extract was separated from the lipid phase through a separatory funnel. Extraction was performed by adding 3 mL of n-hexane and 5 mL of methanol water to the oily residue and this procedure was repeated. Purified phenolics were concentrated in a vacuum evaporator (Heidolph, Hei-Vap Core, Germany) at 40°C. The TPC of oil samples was determined by spectrophotometric method described previously by Rigane et al. [15].

2.7. 2,2-DIPHENYL-1-PICRYLHYDRAZYL RADICAL SCAVENGING ACTIVITY (DPPH-RSA) ANALYSIS

The antioxidant activity was evaluated by measuring the radical scavenging effect of BCSO phenolic extracts towards the DPPH radical [16]. 2 mL of DPPH and 0.9 mL of HCl buffer (pH 7.4) solutions were added to 0.1 mL of the BCSO extracts. The tubes were allowed to stand at room temperature for 30 min. The change in absorbance was determined at 517 nm in a spectrophotometer (Biochrom LibraS22, UK). DPPH-RSA was calculated as percent inhibition (%) with the following formula:

Inhibition % = $[(Abs_{control} - Abs_{sample}) / Abs_{control}] \times 100$.

2.8. STATISTICAL METHODS

The experimental procedure was conducted with three replications. Analysis of variance (ANOVA) was performed using a factorial experiment in a completely randomised design. Significant differences at 0.05 level were determined using Duncan's multiple range post hoc experiment. Pearson correlation analysis was conducted separately for the oil samples from roasted and unroasted seeds (SPSS 16.0 statistical software (Chicago, IL, USA).

3. RESULTS AND DISCUSSION

Regarding the unroasted samples, at the end of 8 months of storage, free fatty acids were higher in sun exposed samples for both in jar and cloth bag storage. FFA was lower in cloth bags under refrigerated conditions. Lower moisture levels retained in cloth bag might have contributed to suppressing the FFA formation. The acidity was lower in the jar for 4 months of storage; however, it was impossible to reach this conclusion for 8 months of storage. In other words, a significant increase was detected in the samples stored in the jar at the 8th month compared to the 4th month. It can be said that roasting provides a slight decrease in acidity in general, which was most likely due to moisture loss during roasting regarding the stored seeds, but in the case of unstored samples FFA of cold-pressed fresh seed oil was lower than the results of unroasted samples (Table I, Table II). According to Mazaheri et al. [17], the FFA of BCSO was comparatively high owing to the lipase activity, which was significantly decreased by pretreatments such as microwaving and roasting. For sto-

Table I - Effects of different storages condition on some analytical parameters of oil from unroasted BCSs (mean ± SD, n=3)

	Storage conditions	Storage time (month)	Free fatty acids (% oleic acid)	Peroxide value (meq O_2/kg oil)	Induction time (h)
	fresh seeds	0	8.72±0.07^{h†}	13.76±0.11^{f}	7.07±0.05^{a}
Cloth bag	sunlight	4	11.71±0.36^{d}	18.05±0.52^{e}	4.07±0.28^{b}
		8	12.15±0.08^{c}	29.34±0.20^{a}	3.16±0.26^{d}
	shaded	4	11.71±0.16^{d}	13.93±0.48^{g}	3.88±0.83^{bc}
		8	11.96±0.04^{cd}	25.26±0.82^{c}	3.33±0.11^{cd}
	refrigerator	4	10.35±0.10^{f}	19.27±0.69^{e}	3.96±0.45^{bc}
		8	10.57±0.09^{ef}	29.42±0.16^{a}	0.97±0.10^{f}
Jar	sunlight	4	11.66±0.15^{d}	25.25±0.54^{c}	4.35±0.16^{b}
		8	14.76±0.44^{a}	29.59±0.34^{a}	2.22±0.27^{e}
	shaded	4	9.15±0.07^{g}	22.80±1.80^{d}	3.85±0.30^{bc}
		8	10.82±0.22^{e}	26.77±0.25^{b}	2.04±0.32^{e}
	refrigerator	4	10.49±0.08^{ef}	15.43±0.51^{f}	3.42±0.26^{cd}
		8	12.63±0.39^{b}	29.39±0.67^{a}	1.73±0.20^{e}

† Small case letters within a column show significant differences between values belong to oils of samples stored at different conditions (P≤0.05).

rage in jars, the refrigerator was superior to the shaded storage with FFA values at levels as low as those of oil from the fresh sample. The negative effect of sun exposed storage became evident, especially after 8 months of storage. The hydrolysis and translation of triglycerides to free fatty acids during extraction and storage occur by hydrolytic reactions caused by the lipolytic activity of enzymes [3, 6].

The PVs of oils ranged between 15.43-29.59 meq O_2/kg (Table I). Considering the recommended PV of 10 meq O_2/kg [18] in edible oils, the high PV of BCSO even immediately after extraction is attributed to the lipoxygenase enzyme activity [17, 19]. On the other hand, Ramadan and Mörsel [20] attributed the high PV of black cumin oil to its relatively high free fatty acidity. High free fatty acidity increases the solubility of oxygen in oil due to the emulsion medium it creates. Indeed, also in this study, the free fatty acidity of the samples was considerably high with values varying between 8.85 and 13.14%.

For both roasted and unroasted samples, 4 months of shaded storage in a cloth bag had a significant suppressive effect on the increase of peroxide value even ensured that PV of unroasted seeds remained at almost the same value as the fresh sample. However, this effect was not observed in samples stored in jars. Regarding storage in jars, refrigeration provided lower peroxide formation compared to the sun exposed and shaded storage. These evaluations are relevant for the analysis performed on the 4th month, as the difference between PVs got closer each other at the 8th month. Roasting had no positive effect in terms of PV. In fact, in case of storage in cloth bags, unroasted samples showed lower PVs compared to the roasted samples (4th month values). Consistent with this, when the induction time is taken into account, it is obvious that the time was shorter for the roasted samples compared to the unroasted ones. A 4-month storage in jars under refrigerated conditions resulted in the lowest PV values. At the end of 8 months of storage, it was understood that shaded storage showed the best values in terms of oxidative stability. The induction time decreased gradually with increasing storage time (from 4 to 8 months) in oils from unroasted and roasted BCS. The lowest induction time was found in the oils pressed from seeds (unroasted and roasted) stored in the refrigerator in cloth bags for 8 months. As expected, oxidative stability decreased with extended storage time in all samples. Even the longest induction time detected in oils from stored samples was half the induction time of oil from fresh seeds.

At the end of the 8-month storage period, BCSOs stored in both jars and cloth bags at refrigerator had higher PVs than that of oils of shaded storage and oxidised rapidly during Rancimat analysis. However, the study of Aidos et al. [21] showed that the lipid hydroperoxides formed 3.7 times faster at 0°C than at 20°C. Thus, the authors recommend 0°C as the best temperature to keep the fish oil.

It cannot be said that there was a strong relationship between peroxide values and induction times. The formation of high amounts of hydroperoxides does not always mean that high amounts of secondary oxidation products will be formed [22].

The oxidative stability of oil, which is a safety and quality parameter, has an important place for its use in food products and potential commercial applications. OSI, which closely depends on the content of antioxidants in oils, basically evaluates the formation of oxidation products (primary or secondary) [23]. Peroxides that increase during storage, after that are

Table II - Effects of different storages condition on some analytical parameters of BCSO from roasted seeds (mean ± SD, n=3)

Packaging material	Storage conditions	Storage time (month)	Free fatty acids (% oleic acid)	Peroxide value (meq O_2/kg oil)	Induction time (h)
	fresh seeds	0	8.72±0.07^{g†}	13.76±0.11^{h}	7.07±0.05^{a}
Cloth bag	sunlight	4	10.75±0.08^{e}	26.76±0.71^{bc}	3.37±0.10^{b}
		8	11.62±0.18^{cd}	28.15±0.37^{ab}	1.71±0.22^{de}
	shaded	4	10.74±0.11^{e}	16.05±0.88^{g}	2.92±0.10^{c}
		8	11.90±0.03^{c}	25.09±1.50^{d}	2.06±0.45^{d}
	refrigerator	4	11.39±0.08^{d}	20.09±0.18^{f}	3.55±0.20^{b}
		8	13.14±0.08^{a}	28.19±0.26^{ab}	0.91±0.06^{f}
Jar	sunlight	4	9.04±0.07^{f}	25.19±2.20^{cd}	2.85±0.36^{c}
		8	12.41±0.30^{b}	29.29±0.49^{a}	1.49±0.09^{e}
	shaded	4	8.45±0.09^{g}	22.39±0.76^{e}	3.39±0.34^{b}
		8	11.85±0.28^{c}	23.02±0.20^{e}	2.00±0.14^{d}
	refrigerator	4	8.49±0.21^{g}	16.18±0.05^{g}	3.15±0.27^{bc}
		8	11.65±0.30^{cd}	26.22±0.17^{cd}	1.57±0.26^{de}

† Small case letters within a column show significant differences between values belong to oils of samples stored at different conditions (P≤0.05)

transformed into secondary oxidation products (such as alcohol, aldehyde, ketone). During the oxidation of fat and oil, sudden oxidation, i.e., the propagation period, occurs after the induction period once the antioxidants in food have been consumed during the induction period [24]. When the results of induction time and phenolic content are examined, it can be said that there is a relationship among these data. Phenolic compounds are able to delay lipid oxidation as they are effective antioxidants [25].

The TPC of the oils increased with the roasting process (Table III, Table IV). Roasting is known to increase the phenolic content and antioxidant activity of the oil [26]. TPCs of oils of unroasted samples were in the range of 2730.83 and 4751.01 mg GAE/kg oil. After 4 months of storage, lower levels of TPC were detected in the samples stored in the refrigerator than those exposed to the sun and shade. However, contrary to this situation, phenolic values were found to be higher in samples stored under refrigerated conditions after 8 months compared to 4 months (in all storage materials and conditions). The increase in TPC with storage can be explained by the breakdown of complex phenolic compounds in oils into simple phenols

Table III - Effects of storage on total phenolics and DPPH radical scavenging activity of oils from unroasted BCSs (mean ± SD, n=3)

Packaging material	Storage conditions	Storage time (month)	Total phenolics (mg GAE/kg oil)	DPPH-RSA (% inhibition)
	fresh seeds	**0**	4410.41±88.60^{a†}	69.81±1.61^{a}
Cloth bag	sunlight	**4**	3088.38±42.01^{e}	50.07±1.33^{d}
		8	2808.31±16.12^{g}	38.67±0.59^{h}
	shaded	**4**	3156.98±20.88^{d}	50.44±1.00^{d}
		8	2965.70±41.75^{f}	38.81±1.09^{h}
	refrigerator	**4**	2785.71±54.57^{gh}	40.04±1.71^{gh}
		8	3648.51±55.55^{c}	47.33±0.68^{e}
Jar	sunlight	**4**	4751.01±43.94^{a}	66.93±0.46^{b}
		8	2730.83±17.01^{h}	38.41±0.76^{h}
	shaded	**4**	4142.45±56.54^{b}	57.33±0.78^{c}
		8	3591.20±51.15^{c}	43.63±1.48^{f}
	refrigerator	**4**	2838.98±24.21^{g}	41.15±1.01^{g}
		8	2807.34±12.43^{g}	36.33±1.46^{i}

† Small case letters within a column show significant differences between values belong to oils of samples stored at different conditions (P≤0.05).

Table IV - Effects of storage on total phenolics and DPPH radical scavenging activity (DPPH-RSA) of oils from roasted BCSs (mean ± SD, n=3)

Packaging material	Storage conditions	Storage (month)	Total phenolics (mg GAE/kg oil)	DPPH-RSA (% inhibition)
	fresh seeds	0	4410.41±88.60^{b†}	69.81±1.61^{a}
Cloth bag	sunlight	4	3403.95±20.16^{g}	52.78±1.17^{c}
		8	3111.78±53.34^{i}	39.48±1.11^{fg}
	shaded	4	4215.90±40.61^{d}	59.96±1.19^{b}
		8	3180.39±32.03^{h}	39.52±1.48^{fg}
	refrigerator	4	3071.43±25.28^{i}	41.48±1.07^{f}
		8	4365.21±49.88^{c}	48.70±1.58^{de}
Jar	sunlight	4	4992.33±53.34^{a}	75.63±1.49^{a}
		8	3043.18±42.79^{j}	38.93±1.54^{g}
	shaded	4	4653.35±46.09^{b}	60.81±1.57^{b}
		8	3524.21±24.21^{f}	39.89±0.56^{fg}
	refrigerator	4	3184.42±32.96^{h}	50.70±1.51^{cd}
		8	3685.63±32.52^{e}	47.70±1.52^{e}

† Small case letters within a column show significant differences between values belong to oils of samples stored at different conditions (P≤0.05).

[7]. For both the roasted and unroasted samples, the highest TPC values (4142-4992 mg GAE/kg oil) were determined in the oils of seeds stored under sun and shade for 4 months in the jar. Additionally, high values were determined for the roasted samples in cloth bags after 4 months in the shade and 8 months in the refrigerator (4213 and 4365 mg GAE/kg oil, respectively). All these high values are close to the value detected in fresh seeds on average. BCSOs from the seeds exposed to sun contained the lowest levels of total phenolics. Hydrolytic activities and oxidation are probably caused by temperature, oxygen and enzymes during storage that leads to a decrease in phenolic concentration. TPC, which is a significant quality parameter

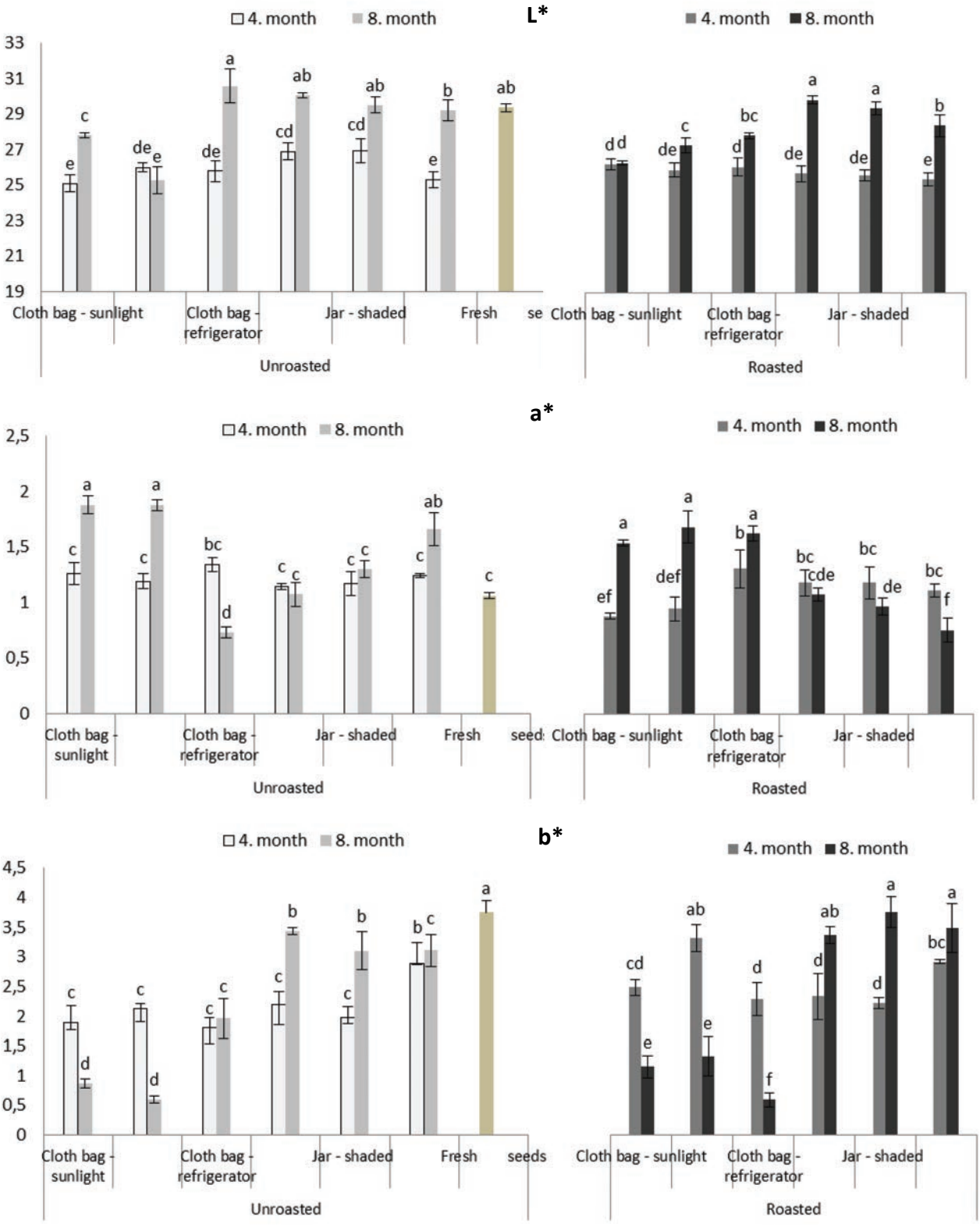

Figure 2 - Effects of the storage conditions on color indices of BCSO from unroasted and roasted seeds (mean ± SD, n=3).

especially as an antioxidant in oil, has nutritional and organoleptic properties [7]. It has been indicated that BCSO is a rich source of polyphenols, which possess antihydrolytic effect and antioxidant activity [27]. Total phenolic component content of BCSO was found 2-3.5 times higher in the present study compared to that reported by Lutterodt et al. [1] (1.02-1.40 mg /g). This difference may be due to the variety of seeds, growing conditions, and methods and conditions of obtaining both the oil and the phenolic extract.

In a study in which various cooking oils were exposed to heat and light, it was reported that the change in peroxide values differed according to the oil [28]. While this conversion was reported to be fast in olive oil and rapeseed oil it was slower in sunflower oil and safflower oil as the conversion began when the hydroperoxide concentration reached a certain amount [22]. Likewise, the rate of hydroperoxides formation was different for walnut, linseed and rapeseed oils in the study of Guillén and Ruiz [29]. The difference between the conversion of primary oxidation products to secondary oxidation products from oil to another oil was attributed to the degradation rate of acyl groups which is closely related to the formation and degradation of primary and secondary oxidation compounds and the nature and evolution of these products. In addition to the degree of unsaturation of these oils, they stated that different behaviours were observed in their oxidation due to the difference in the minor components they contain. For instance, it has been previously shown that tocopherols are more effective in delaying the formation of hydroperoxides than carbonyls. It was stated that total polar compounds and phenolic compounds, rather prevent the formation of off-flavour, that means delay in secondary oxidation [30]. BCSO is rich in linoleic and oleic acids and contains high amounts of unsaponifiable elements. Tovar et al. [31] did not detect a direct correlation between phenolic compounds and oxidative stability in some oils examined in their study. It was suggested that stability in oils was not related to total phenolics but to some major phenolic compounds. Similarly, Lutterodt et al. [1] samples with the highest phenolic content showed the lowest oxidative stability. Therefore, they stated that phenolic components partially affect oil stability.

The DPPH inhibition rate results were in line with the concentrations of total phenolics. As shown in Table III, oils from stored seeds exhibited lower DPPH-RSA than the oil of fresh seeds. Roasting of the seeds resulted in higher DPPH-RSA in the pressed oils. In this respect, higher activity was obtained with storage in a jar than with storage in a cloth bag, except for samples stored in the refrigerator for 8 months. For both unroasted and roasted BCSOs, the highest DPPH-RSA was observed in oils from seeds stored in cloth bags at room temperature and in jars exposed to sunlight for 4 months. Storage for 4 months produced higher DPPH-RSA than 8 months of storage (except for storage in the cloth bag under refrigerated conditions). Roasting revealed higher DPPH-RSA in BCSOs mostly overall storage conditions, so that it was also mentioned above that roasting resulted in higher TPC in the oils. Liang et al. [32] reported that the RSA increased in BCSs when the time of heating was prolonged. Lutterodt et al. [1] reported that DPPH-RSA may vary depending on the seed variety and growing conditions of BCSs and was significantly affected by seed storage and processing practice.

At the end of 8 months of storage, L* values increased compared to 4 months of storage. This means there was some lightening of the colour. Roasting did not show any significant effect on the L* values (Fig. 2). The L* values of the seeds stored for 4 months under all packaging and ambient conditions were lower than those of the oil obtained from the fresh sample. The highest L* values were determined at samples stored in jars for 8 months exposed to sunlight which were similar to the L* values of fresh seed oil (the free acidity of these samples was also higher than the others). Although this phenomenon was the same for roasted and unroasted seeds, slightly higher L* values were obtained for the unroasted samples.

Regarding the roasted samples, there was an increase in the a* values (more redness) of the samples stored in cloth bags, and decrease (less redness) in those stored in jars (regarding all storage conditions) after 8 months compared to 4 months. a* values of the unroasted seed oils were closer to that of fresh seed oil, however the oils of unroasted seeds stored in a cloth bag under sun or shade showed higher a* values compared to fresh seed oil. Likewise, 8 months storage in the cloth bag resulted in higher a* values in the oils of roasted seeds. Lower b* values were measured in stored samples compared to fresh seed oil. Storage in cloth bags resulted in lower b* values for both roasted and unroasted seeds, although roasted seed oils had even lower values. In all the three conditions, the oils of roasted seeds stored in jars had b* values equivalent to the fresh seed oil. Both roasted and unroasted samples showed lower b* (more yellowness) values at the 8th month compared to the 4th month when stored in cloth bags, and b* values increased as the storage progressed when the seeds were stored in jars. The oils from seeds stored in jars had significantly higher b* values than those from seeds stored in cloth bags, indicating a decrease in red colour. Roasting had a clear impact on the a* and b* values of BCSOs stored in cloth bags, at room temperature and under sunlight. A similar effect was also seen in the study of Suri et al. [33].

A positive relationship was detected between the peroxide value and the L* value of the oil, especially for unroasted samples (Table V). Consistent with this, a significant negative correlation was observed between the L* value and the induction time. The results showed that the oxidation products released during oil storage affected the darkening of the colour of the

Table V - Pearson correlation coefficients between the analyzed parameters of oils from unroasted and roasted BCSs

		L*	Free fatty acids	Peroxide value	Induction time	Total phenolics
unroasted	L*	1				
	Free fatty acids	-	1			
	Peroxide value	0.736**	0.259	1		
	Induction time	-0.784**	-0.220	-0.658**	1	
	Total phenolics	-	-0.429**	-	-	1
	DPPH-RSA	-	-0.373*	-	0.465**	0.911**
roasted	L*	1				
	Free fatty acids	-	1			
	Peroxide value	0.530**	0.548**	1		
	Induction time	-0.765**	-0.702**	-0.547**	1	
	Total phenolics	-	-0.386*	-	-	1
	DPPH-RSA	-	-0.676**	-	0.378*	0.851**

* and ** indicate significance at $p < 0.05$ and $p < 0.01$, respectively

oil. Data obtained especially in roasted seed oil showed positive correlations between free fatty acids and peroxide number and strong negative correlations between induction time. The increased formation of oxidation products due to the mild roasting process may have caused a significant correlation; in contrast no significant correlations were seen at this level for oil from unroasted seeds. There was also dependency of the increase in free fatty acidity and the decrease in DPPH-RSA which can probably be attributed to the fact that free fatty acids have emulsifying properties, making the extraction of antioxidant compounds with hydrophilic and lipophilic characters difficult. The strong positive correlations between DPPH-RSA and the induction time along with DPPH-RSA and total phenolics content were expected results.

CONCLUSIONS

The quality and functional properties of the oil were negatively affected when storage exceeded 4 months. Storage in a cloth bag under shaded conditions resulted in higher oxidative stability, confirmed by lower a peroxide value and prolonged induction time. Under shade, storage in jars is recommended for lower free fatty acidity in the oil. Additionally, if the seeds are stored unroasted under refrigerator conditions, the cloth bag has an advantage over the jar due to lower free fatty acid increase during storage and higher oxidative stability. However, in general, both total phenolic content and DPPH radical scavenging activity were lower in oils obtained from seeds stored in cloth bags. Minimal roasting of the seeds increased the peroxide value of the oil from the seeds stored in cloth bags and shortened the induction time. Sun exposure during storage showed the most notable negative effects on free fatty acidity and peroxide value. Correlation analysis revealed a positive relationship between increased oxidation in the oil and darkening of the oil color. The free fatty acidity of the oil and the induction time exhibited strong negative correlation due to the increased formation of oxidation products with mild roasting.

Conflict of interest

The author(s) declare no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

REFERENCES

[1] H. Lutterodt, M. Luther, M. Slavin, J.J. Yin, J. Parry, J.M. Gao, L.L.Yu, Fatty acid profile, thymoquinone content, oxidative stability, and antioxidant properties of cold-pressed black cumin seed oils. LWT - Food Science and Technology, *43*, 1409–1413 (2010).

[2] A. Hajib, H. Harhar, S. Gharby, I. Nounah, B. Matthäus, D. Guillaume, Z. Charrouf, Is geographic origin a good marker for cumin seed oil (*Cuminum cyminum* L.), Riv. Ital. Sostanze Grasse, *95*(3), 155-159 (2018).

[3] H. Bakhshabadi, H.O. Mirzaei, A. Ghodsvali, S.M. Jafari, A.M. Ziaiifar, V. Farzaneh, The effect of microwave pretreatment on some physico-chemical properties and bioactivity of black cumin seeds' oil. Industrial Crops and Products, *97*, 1–9 (2017).

[4] F. Shahidi, Y. Zhong, Lipid oxidation and improving the oxidative stability. Chemical Society Reviews, *39*, 4067–4079 (2010).

[5] M.T. Satue, S.W. Huang, E.N. Frankel, Effect of natural antioxidants in virgin olive oil on oxidative stability of refined, bleached, and deodorized olive oil. Journal of the American Oil Chemists' Society, *72*(10), 1131-1137 (1995).

[6] M. Soleimanifar, R. Niazmand, S.M. Jafari, Evaluation of oxidative stability, fatty acid profile, and antioxidant properties of black cumin seed oil and extract. Journal of Food Measurement and Characterization, *13*, 383–389 (2019).

[7] Y. Mazaheri, M. Torbati, S. Azadmard-Damirchi, G.P. Savage, Oil extraction from blends of sunflower and black cumin seeds by cold press and evaluation of its physicochemical properties. Journal of Food Processing and Preservation, *43*(10), pp. e14154 (2019b).
[8] M. Kiralan, G. Çalik, S. Kiralan, A., Özaydin, G. Özkan, M.F. Ramadan, Stability and volatile oxidation compounds of grape seed, flax seed and black cumin seed cold-pressed oils as affected by thermal oxidation. Grasas y Aceites, *70*(1), e295 (2019).
[9] T. Dedebas, L. Ekici, O. Sagdic, Chemical characteristics and storage stabilities of different cold-pressed seed oils. Journal of Food Processing and Preservation, *45*(2), e15107 (2021).
[10] Ž.Tarasevičienė, V. Laukagalis, A. Paulauskienė, A. Baltušnikienė, E. Meškinytė, Quality changes of cold-pressed black cumin (*Nigella sativa* L.), safflower (*Carthamus tinctorius* L.), and milk thistle (*Silybum marianum* L.) seed oils during storage. Plants, *12*(6), 1351 (2023).
[11] M. Kıralan, G. Özkan, A. Bayrak, M.F. Ramadan, Physicochemical properties and stability of black cumin (*Nigella sativa*) seed oil as affected by different extraction methods. Industrial Crops and Products, *57*, 52-58 (2014).
[12] M.A. Mamun, N. Absar, Major nutritional compositions of black cumin seeds – cultivated in Bangladesh and the physicochemical characteristics of its oil. International Food Research Journal, *25*(6), 2634-2639 (2018).
[13] AOCS, 1998. AOCS Official Methods and Practices of the AOCS (fifth ed.), AOCS Press, Champaign, USA (1998).
[14] S.M. Lee, K.T. Lee, S.H. Lee, J.K. Song, Origin of human colour preference for food. Journal of Food Engineering, *119*(3), 508-515 (2013).
[15] G. Rigane, A. Yahyaoui, A. Acar, S. Mnif, R.B. Salem, D. Arslan, Change in some quality parameters and oxidative stability of olive oils with regard to ultrasound pretreatment, depitting and water addition. Biotechnology Reports, *26*, e00442 (2020).
[16] K. Thaipong, U. Boonprakob, K. Crosby, L. Cisneros-Zevallos, D.H. Bryne, Comparison of ABTS, DPPH, FRAP and ORAC assays for estimating antioxidant activity from guava fruit extracts. Journal of Food Composition and Analysis, *19*, 669-675 (2006).
[17] Y. Mazaheri, M. Torbati, S. Azadmard-Damirchi, G.P. Savage, Effect of roasting and microwave pre-treatments of *Nigella sativa* L. seeds on lipase activity and the quality of the oil. Food Chemistry, *274*, 480– 486 (2019a).
[18] FAO/WHO, (2009). Report of the 21st session of the Codex Alimentarius Committee on fats and oils. Kola Kinabalu, Malaysia, 16-20 February (2009).
[19] M. Kıralan, M. Ulaş, A. Özaydın, N. Özdemir, G. Özkan, A. Bayrak, M.F. Ramadan, Blends of cold pressed black cumin oil and sunflower oil with improved stability: A study based on changes in the levels of volatiles, tocopherols and thymoquinone during accelerated oxidation conditions. Journal of Food Biochemistry, *41*, e12272 (2017).
[20] M.F. Ramadan, J.T. Mörsel, Oxidative stability of black cumin (*Nigella sativa* L.), coriander (*Coriandrum sativum* L.) and niger (*Guizotia abyssinica* Cass.) crude seed oils upon stripping. European Journal of Lipid Science and Technology, *106*(1), 35-43 (2004).
[21] I. Aidos, S. Lourenclo, A. Van der Padt, J.B. Luten, R.M. Boom, Stability of crude herring oil produced from fresh byproducts: influence of temperature during storage. Journal of Food Science, *67*(9), 3314-3320 (2002).
[22] M.D. Guillen, N. Cabo, Fourier transform infrared spectra data versus peroxide and anisidine values to determine oxidative stability of edible oils. Food Chemistry, *77*, 503-510 (2002).
[23] E. Pereira, M.C. Ferreira, K.A. Sampaio, R. Grimaldi, A.J. de Almeida Meirelles, G.J. Maximo, Physical properties of amazon fats and oils and their blends. Food Chemistry, *278*, 208-215 (2019).
[24] N. Gotoh, S. Wada, The importance of peroxide value in assessing food quality and food safety. Journal of the American Oil Chemists' Society, *83*, 473–474 (2006).
[25] A. Siger, M. Nogala-Kalucka, E. Lampart-Szczapa, The content and antioxidant activity of phenolic compounds in cold-pressed plant oils. Journal of Food Lipids, *15*(2), 137-149 (2008).
[26] N. Chandrasekara, F. Shahidi, Effect of roasting on phenolic content and antioxidant activities of whole cashew nuts, kernels, and testa. Journal of Agricultural and Food Chemistry, *59*, 5006–5014 (2011).
[27] A. Asdadi, H. Harhar, S. Gharby, Z. Bouzoubaâ, A. Yadini, R. Moutaj, M.E. Hadek, Chemical composition and antifungal activity of *Nigella sativa* L. oil seed cultivated in Morocco. International Journal of Pharmaceutical Science Invention, *3*, 9– 15 (2014).
[28] A. Kaleem, S. Aziz, M. Iqtedar, Investigating changes and effect of peroxide values in cooking oils subject to light and heat. Fuuast Journal of Biology, *5*(2), 191-196 (2015).
[29] M.D. Guillén, A. Ruiz, Monitoring the oxidation of unsaturated oils and formation of oxygenated aldehydes by proton NMR. European Journal of Lipid Science and Technology, *107*(1), 36-47 (2005).
[30] R. Farhoosh, S. Pazhouhanmehr, Relative contribution of compositional parameters to the primary and secondary oxidation of canola

oil. Food Chemistry, *114*(3), 1002-1006 (2009).
[31] M.J. Tovar, J. Motilva, M.P. Romero, Changes in the phenolic composition of virgin olive oil from young trees (*Olea europaea* L. cv. Arbequina) grown under linear irrigation strategies. Journal of Agricultural and Food Chemistry, *49*, 5502-5508 (2001).
[32] L.C. Liang, W. Zzaman, T.A. Yang, A.M. Easa, Effect of conventional and superheated steam roasting on the total phenolic content, total flavonoid content and DPPH radical scavenging activities of black cumin seeds. Pertanika Journal of Tropical Agricultural Science, *41*(2), 663-676 (2018).
[33] K. Suri, B. Singh, A. Kaura, M.P. Yadav, N. Singh, Impact of infrared and dry air roasting on the oxidative stability, fatty acid composition, Maillard reaction products and other chemical properties of black cumin (*Nigella sativa* L.) seed oil. Food Chemistry, *295*, 537-547 (2019).