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ORIGINAL PAPER

Effect of Bene Kernel Oil on the Frying Stability of Canola Oil

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Abstract Canola oil (CAO) with (0.05–0.4%) and without added bene kernel oil (BKO) and *tert*-butylhydroquinone (TBHQ, 100 ppm) was used for deep-fat frying of potatoes at 180 °C for 48 h. Frying stability of the oil samples during the frying process was measured based on the variations of total polar compounds (TPC) content, conjugated diene value (CDV), acid value (AV), carbonyl value (CV) and total tocopherols (TT). In general, frying stability of the CAO significantly ($P < 0.05$) improved in the presence of the TBHQ and BKO. The best frying performance for the CAO was obtained by using of 100 ppm TBHQ and 0.1% BKO. The effectiveness of TBHQ and BKO at these levels was found to be nearly the same. Increasing the level of BKO from 0.1 to 0.4% caused a decrease in the oxidative stability of the CAO, indicating the pro-oxidant effect of the oils added at these levels.

Keywords Canola oil · Frying · Bene kernel oil · TBHQ · Stability

Introduction

Deep-fat frying is one of the oldest and most popular methods for the preparation and manufacture of foods in the world [1]. During deep-fat frying of food, in the presence of air, a number of chemical reactions such as hydrolysis, thermal degradation, oxidation, polymerization, isomerization and cyclization occur in the oil, thus leading to the decomposition of the frying oil and formation of volatile oxidation products, non-volatile oxidized derivatives, and dimeric, polymeric, or cyclic substances, thereby affecting both the oil and finished product qualities [2]. There is evidence that some products of triacylglycerol oxidation reactions, particularly those with an altered chemical nature, may pose potential hazards to human health [3]. Therefore, use of oil that can resist oxidation as much as possible is very important.

Various methods to improve oxidative stability of frying oils have been developed and studied. Partial hydrogenation, addition of antioxidants or other oils which have a lower content of highly unsaturated fatty acids have been attempted [4]. Low cost synthetic antioxidants such as propyl gallate (PG), butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and *tert*-butylhydroquinone (TBHQ) alone or in combination, are commonly added to fats and oils to inhibit the development of off-flavors arising from the oxidation of unsaturated fatty acids. They are very effective during storage and transport of oils and fats, but are less effective at frying temperatures because of their volatility and decomposition [5, 6]. Furthermore, toxicity and carcinogenicity effects of synthetic antioxidants [7–9], and increasing consumer concern about food additives and their safety have directed our attention toward the use of natural antioxidants as alternatives to synthetic compounds.

Canola (low-erucic acid rapeseed) is one of the most important oil-seed crops in the world. Research indicates that the fatty acid composition of canola oil (CAO) is especially favorable in terms of health benefits when used as part of a nutritionally balanced diet. CAO is high in monounsaturated fatty acids (MUFA, 60%), of which most is oleic acid (18:1ω9), and has moderate levels of

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polyunsaturated fatty acids (PUFA, 30–37%), of which most are linoleic (18:2ω6, 22–25%) and linolenic (18:3ω3, 8–12%) acids. Moreover, it contains the lowest concentration of saturated fatty acids (SFA, 7%) among vegetable oils [10]. The lack of frying stability and poor frying oil performance of CAO related to high levels of linoleic and linolenic acids has been documented [11, 12].

Pistacia atlantica widely grows in the Zagrossian region of Iran at 600–3000 m above the sea level [13]. Its fruits, which are called bene in Iran, are round to oval, somewhat flat, 0.5–0.7 cm in diameter, and covered with a rather dry hull that can be easily removed by pressing between fingers. A previous study on *P. atlantica* dealt with the chemical composition and oxidative stability of the kernel oils from its current subspecies in Iran [14]. Regarding the fatty acid composition and total tocopherols and phenolic compounds determined, the oil extracted from the kernel of *P. atlantica* sub sp. *mutica* (bene kernel oil, BKO) was considered as one of the most oxidatively stable vegetable oils in the world. Our initial findings have indicated that the oxidative stability of less stable vegetable oils can be improved by BKO. Hence, this research has been undertaken to investigate the antioxidative effect of BKO on the CAO during the frying process at 180 °C, and to compare its strength with that of the powerful synthetic antioxidant *tert*-butylhydroquinone (TBHQ) in order to understand the potential use of BKO as a natural antioxidant in food industries.

Materials and Methods

Materials

The ripe fruits of bene were collected from the fields of Islamabad in the Ilam province. Refined, bleached and deodorized CAO with no added antioxidants was supplied by Segol (Nishaboor, Iran). The ripe fruits of bene and oil samples were stored at −18 °C until use. The BKO was added to the CAO at 0.05, 0.1, 0.2 and 0.4% w/w. Fatty acid methyl ester (FAME) standards, and all chemicals and solvents used in this study were of analytical reagent grade and were purchased from Sigma–Aldrich (St. Louis, MO) and Merck (Darmstadt, Germany).

Oil Extraction

After drying in the shade, the pericarps of the *Pistacia* fruits were removed and the kernels were ground to powder in a grinder. The powders were extracted with *n*-hexane (1:4 w/v) by agitation in the dark at ambient temperature for 48 h. The solvent was evaporated to dryness in vacuo at 40 °C.

Frying Process

Potatoes were peeled and cut into pieces (7.0 × 0.5 × 0.3 cm) and submerged in water until needed. Potato pieces were fried in the frying oils. The oil (2.5 L) was placed in a 2.5-L capacity bench-top deep-fryer (Tefal model 1,250, Paris, France) and heated to 180 °C. Potato pieces were fried in 20 g batches at a constant frying temperature. The batches were fried at 7 min intervals for 8 h per day for six consecutive days. At the end of each 4 h, about 10 g of the frying oil was filtered into a screw-cap vial and promptly stored in the dark at 4 °C until analyzed. The volume of oil was not replenished during the frying process. Frying experiments were conducted in duplicate on each frying medium [15].

Chemical Analyses

Fatty acid composition of the oils was determined by gas–liquid chromatography and is reported in relative area percentages. Fatty acids were transesterified into their corresponding FAMEs by vigorous shaking of a solution of oil in hexane (0.3 g in 7 mL) with 2 mL of 7 M methanolic KOH at 50 °C for 10 min. The FAMEs were identified using an HP-5890 chromatograph (Agilent, Palo Alto, CA) equipped with a CP-Sil 88 (Supelco, Bellefonte, PA) capillary column of fused silica, 60 m in length × 0.22 mm in internal diameter, 0.2 mm film thickness, and a flame ionization detector. Nitrogen was used as carrier gas with a flow rate of 0.75 mL/min. The oven temperature was maintained at 198 °C, and that of the injector and the detector at 250 °C [16].

A Metrohm Rancimat model 743 (Herisau, Switzerland) was used for the OSI (oil/oxidative stability index) analysis. The tests were done with 3-g oil samples at temperatures of 120 °C at an airflow rate of 15 L/h [17].

The content of total phenolic (TP) compounds was determined spectrophotometrically using Folin–Ciocalteu's reagent according to the method described by Capannesi et al. [18]. A calibration curve of gallic acid in methanol was performed in the concentration range of 0.04–0.40 mg/mL. Total tocopherols (TT) content was determined according to the colorimetric method described by Wong et al. [19].

The spectrophotometric method of the International Dairy Federation, as described by Shantha and Decker [20], was used to determine the peroxide value (PV). The acid value (AV) was determined according to AOCS Official Method Cd 3d-63 [21]. The total polar compounds (TPC) content was determined according to the economical micro method developed by Schulte [22]. For the conjugated diene value (CDV) the oil samples were diluted to 1:600 with hexane and measured spectrophotometrically at 234 nm and read against HPLC-grade hexane as a blank. An extinction coefficient of 29,000 mol/L was used to quantify the concentration of conjugated dienes formed during oxidation [23]. The carbonyl value (CV) of the oils was measured according to the method developed by Endo et al. [24] using 2-propanol and 2,4-decadienal as solvent and standard, respectively [25].

Statistical Analysis

All experiments and measurements were carried out in triplicate, and data were subjected to analysis of variance (ANOVA). ANOVA and regression analyses were performed according to the MstatC (Michigan State University, East Lansing, MI) and SlideWrite (Advanced Graphics Software, Carlsbad, CA) software. Significant differences between means were determined by Duncan's multiple range tests. P values less than 0.05 were considered statistically significant.

Results and Discussion

The fatty acid composition and chemical characteristics of the CAO and BKO are shown in Table 1. The PV and AV of the oils were less than 1.7 mequiv/kg and 0.6 mg/g, respectively, indicating that they were unoxidized and of high initial quality. Oleic acid (C18:1) was the most abundant mono-unsaturated fatty acid in the CAO and BKO. Oleic acid is more resistant toward oxidation, both at ambient storage and at high temperatures [26]. It can be observed that the CAO and BKO are distinguished from each other mainly due to the significant differences in the percentage of linoleic (18:2, 23.98 vs. 32.94%) and linolenic (C18:3, 8.02 vs. 1.22%) acids. Even though the CAO and BKO presented a similar ratio of unsaturated to saturated fatty acids (USFA/SFA), the OSI for the BKO (10.70 h) was considerably higher than that of the CAO (3.85 h). In fact, the fatty acid composition alone may not adequately explain the stability of frying oils [27]. In other words, oxidative stability of edible oils depends on their fatty acid composition and also the content and composition of minor components, especially tocopherols and polyphenols. The TT and TP contents of the BKO (817.92 and 213.47 mg/kg, respectively) were significantly higher than those of the CAO (627.39 and 44.29 mg/kg, respectively). Tocopherols and phenolic compounds are particularly important functional constituents of vegetable oils. Tocopherols are the most important natural antioxidants for vegetable oils and they are active as vitamin E, which makes them particularly important for human health. Interest in phenolic compounds is related primarily to their antioxidant activity; nevertheless, they also show important biological activity in vivo and may be beneficial in combating diseases related to excessive oxygen radical formation exceeding the antioxidant defense capacity of the human body [28, 29].

Table 2 shows the CDV of the CAO as affected by the BKO and TBHQ during the frying process at 180 °C. CDV can be used as a relative measure of oxidative stability of the oils [30, 31]. The CDV for all treatments studied increased linearly during the 48 h frying process. The results calculated from the linear relationship between the CDV and frying time are shown in Table 3. The slope of the linear equations (a value) was considered to be a measure of the rate of CDV increase during the frying process. The different levels of BKO and 100 ppm TBHQ caused a values decrease to less than that of the CAO (0.66), indicating their antioxidative activities. The level of conjugated dienes throughout the frying process was lowest in the CAO containing 100 ppm TBHQ ($a = 0.41$), followed by the CAO containing 0.1% BKO ($a = 0.54$). Higher a values (>0.6) were observed when the level of BKO was higher than 0.1%. Accordingly, the BKO at the

Table 1 Fatty acid composition (%) and chemical characteristics of the canola (CAO) and bene kernel (BKO) oils

Parameter	CAO	BKO
C14:0	0.32 ± 0.04 a	0.21 ± 0.03 b
C16:0	10.00 ± 0.04 b	10.82 ± 0.01 a
C16:1	0.28 ± 0.03 b	1.54 ± 0.03 a
C18:0	3.65 ± 0.07 a	3.03 ± 0.01 b
C18:1	50.51 ± 0.13 a	49.01 ± 0.12 b
C18:2	23.98 ± 0.06 a	32.94 ± 0.27 a
C18:3	8.02 ± 0.11 a	1.22 ± 0.12 b
C20:0	0.26 ± 0.07 b	0.76 ± 0.00 a
C20:1	1.62 ± 0.04 a	0.61 ± 0.00 b
C22:0	0.71 ± 0.03 a	0.26 ± 0.13 b
C22:1	0.44 ± 0.03	–
SFA	14.93 ± 0.06 a	15.01 ± 0.05 a
MUFA	52.85 ± 0.23 a	50.55 ± 0.15 b
PUFA	31.99 ± 0.18 b	34.16 ± 0.15 a
USFA/SFA	5.63 ± 0.03 a	5.64 ± 0.02 a
AV	0.20 ± 0.00 b	0.51 ± 0.01 a
PV	0.51 ± 0.07 b	1.65 ± 0.04 a
TP content	44.29 ± 3.42 b	173.62 ± 4.88 a
TT content	627.39 ± 13.23 b	817.92 ± 3.90 a
OSI	3.85 ± 0.32 b	10.70 ± 0.12 a

Means ± SD (standard deviation) within a row with the same lowercase letters are not significantly different at $P < 0.05$

AV acid value (mg KOH per g oil); *SFA* saturated fatty acids; *MUFA* monounsaturated fatty acids; *PUFA* polyunsaturated fatty acids; *USFA* unsaturated fatty acids; *PV* peroxide value (mequiv O_2 per kg oil); *TP* total phenolics (mg gallic acid per kg oil); *TT* total tocopherols (mg α-tocopherol per kg oil)

Table 2 Conjugated diene value (CDV) of the canola oil (CAO) as affected by the bene kernel oil (BKO) and *tert*-butylhydroquinone (TBHQ) during the frying process at 180 °C

Time (h)	CAO	BKO (%)				TBHQ (100 ppm)
		0.05	0.1	0.2	0.4	
0	8.72 ± 0.22 Kab	8.33 ± 0.18 Mab	8.03 ± 0.46 Lb	8.81 ± 0.26 Ja	8.85 ± 0.63 La	8.43 ± 0.22 Jab
4	12.44 ± 0.29 Ja	11.28 ± 0.22 Lbc	10.59 ± 0.43 Kc	12.18 ± 0.29 Iab	11.65 ± 0.83 Kabc	10.96 ± 0.66 Ic
8	15.52 ± 0.28 Ia	13.56 ± 0.28 Kbc	12.86 ± 0.24 Jc	14.93 ± 0.92 Hab	14.34 ± 0.96 Jabc	13.02 ± 0.50 Ic
12	19.68 ± 0.56 Ha	16.48 ± 0.54 Jb	15.31 ± 0.36 Ib	18.98 ± 1.63 Ga	18.47 ± 1.26 Ia	16.31 ± 0.97 Hb
16	22.30 ± 1.10 Ga	18.35 ± 0.77 Ic	16.93 ± 0.81 Hc	22.21 ± 0.61 Fa	20.49 ± 1.29 Hb	17.79 ± 1.05 GHc
20	25.23 ± 0.52 Fa	22.11 ± 1.02 Hb	19.83 ± 1.16 Gc	26.42 ± 1.47 Ea	22.74 ± 0.69 Gb	19.02 ± 0.58 FGc
24	28.01 ± 0.79 Ea	23.62 ± 0.54 Gc	22.98 ± 0.40 Fc	28.34 ± 1.35 Ea	25.29 ± 1.22 F b	20.14 ± 0.93 EFd
28	28.83 ± 0.20 Ebc	27.25 ± 0.51 Fcd	25.61 ± 0.47 Ed	31.17 ± 3.07 Da	29.68 ± 0.63 Eab	21.79 ± 1.64 DEe
32	31.44 ± 1.26 Dab	28.51 ± 0.26 Ec	27.23 ± 0.66 Dc	32.20 ± 1.47 CDa	30.41 ± 1.16 Eb	23.75 ± 1.68 CDd
36	36.29 ± 0.73 Ca	30.81 ± 0.89 Dc	29.03 ± 0.15 Cd	34.15 ± 2.14 BCb	31.84 ± 1.00 Dc	25.81 ± 1.09 BCe
40	37.16 ± 0.18 Ca	31.96 ± 0.54 Cbc	30.96 ± 0.59 Bc	36.47 ± 2.68 ABa	33.27 ± 0.78 Cb	26.24 ± 1.63 ABd
44	38.75 ± 1.19 Ba	33.86 ± 0.50 Bcd	31.61 ± 0.54 ABd	37.78 ± 1.89 Aab	35.86 ± 0.70 Bbc	27.27 ± 3.19 ABe
48	40.02 ± 0.55 Aa	35.07 ± 0.84 Ab	32.32 ± 0.57 Ac	38.02 ± 2.18 Aa	38.42 ± 0.47 Aa	28.44 ± 2.48 Ad

Means ± SD (standard deviation) within a column with the same uppercase letters are not significantly different at $P < 0.05$

Means ± SD (standard deviation) within a row with the same lowercase letters are not significantly different at $P < 0.05$

Table 3 The results calculated from the linear relationship between the conjugated diene value (CDV) and frying time for the canola oil (CAO) as affected by the bene kernel oil (BKO) and *tert*-butylhydroquinone (TBHQ) during the frying process at 180 °C

	CDV = a (time) + b		
	a ± SE	b ± SE	R^2
CAO	0.66 ± 0.03 a	10.75 ± 0.73 ab	0.983
BKO (%)			
0.05	0.57 ± 0.02 b	9.47 ± 0.54 c	0.988
0.1	0.54 ± 0.02 c	8.91 ± 0.60 d	0.983
0.2	0.63 ± 0.03 a	11.13 ± 1.01 a	0.966
0.4	0.61 ± 0.02 a	10.18 ± 0.62 bc	0.986
TBHQ (100 ppm)	0.41 ± 0.02 d	10.11 ± 0.52 b	0.970

Means ± SE (standard error) within a column with the same lowercase letters are not significantly different at $P < 0.05$

levels $\leq$0.1% had a stabilizing effect whereas at the higher levels exerted pro-oxidant activity, possibly due to free radicals generated under the frying conditions. With regard to the information from Table 1 and the levels of BKO added, the stabilizing effect can probably be attributed to the presence of powerful antioxidant constituents in the phenolic fraction of the BKO. Besides, the unsaponifiable matter fraction of vegetable oils naturally contains hydrocarbons, carotenes, tocopherols and tocotrienols, linear and triterpenic alcohols, methyl sterols, sterols, and triterpenic dialcohols, and typically constitutes 0.5–2.5% of the vegetable oils, although some vegetable oils have exceptional amounts of 5–6% [32]. As can be seen, most of these compounds are particularly important functional compounds which have potentials to retard the degradation of unsaturated fatty acids in lipid systems. The effectiveness of the unsaponifiable matter fraction of vegetable oils in retarding oil deterioration has been demonstrated by many investigators [33–36].

Analysis of polar compounds content is one of the most reliable methods for the assessment of used frying oils [37, 38]. All treatments had statistically the same initial TPC contents in the range of 3.79–3.95%. The TPC contents linearly increased with high correlation coefficients ($R^2 > 0.98$). Both BKO and TBHQ were significantly capable of lowering the percentage of polar compounds in the CAO. The amounts of TPC is an important criterion in evaluation of frying oil quality for human consumption, and many European countries have set a polar compounds maximum level to between 24 and 27% [39]. Assuming that the limit of acceptance for the TPC content is 24%, the time required to reach this limit was considered as a measure of frying stability (t_{24}). As shown in Fig 1, the CAO showed a frying stability significantly lower (32.64 h) than those of CAOs containing the BKO and TBHQ (34.92–51.80 h). The highest t_{24} value was observed in the presence of TBHQ (51.74 h), followed by the BKO at the levels 0.1 (45.47 h), 0.2 (42.34 h), 0.3 (38.88 h), and 0.4% (34.92), respectively.

Changes in the AV of the oil samples during the frying process at 180 °C are given in Table 4. The AVs significantly increased in all treatments as frying progressed. The change in the AV as a measure of stability for the CAO was considerably higher (6.74 Units) than that for the CAOs containing the BKO and TBHQ (4.12–6.02 Units) after

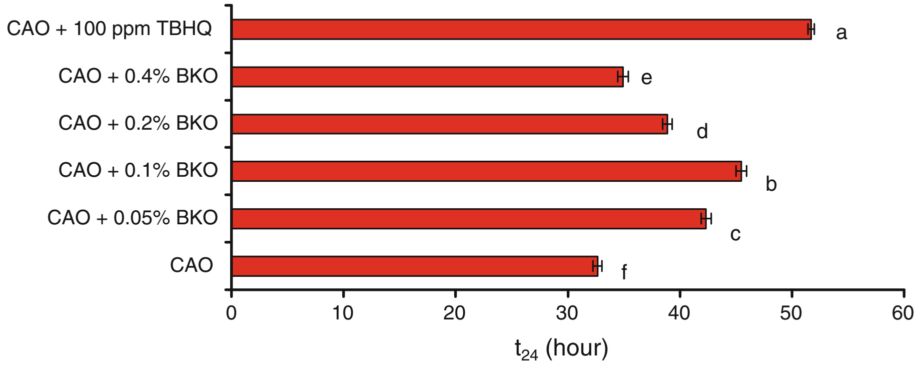

Fig. 1 The time required to reach total polar compounds (TPC) content of 24% (t_{24}) for the canola oil (CAO) as affected by the bene kernel oil (BKO) and *tert*-butylhydroquinone (TBHQ) during frying at 180 °C. The corresponding linear equations: CAO, $y = 0.614\ x + 3.973$, $R^2 = 0.997$; CAO + 0.05% BKO, $y = 0.440\ x + 5.350$, $R^2 = 0.987$; CAO + 0.1% BKO, $y = 0.426\ x + 4.630$, $R^2 = 0.985$; CAO + 0.2% BKO, $y = 0.532\ x + 3.310$, $R^2 = 0.992$; CAO + 0.4% BKO, $y = 0.557\ x + 4.551$, $R^2 = 0.991$; CAO + 100 ppm TBHQ, $y = 0.393\ x + 3.665$, $R^2 = 0.993$. Means ± SE (standard error) with the same lowercase letters are not significantly different at $P < 0.05$

48 h of frying, indicating that both BKO and TBHQ were able to retard oxidative and also hydrolytic reactions. The protective effect of (the change content in AV) 0.1% BKO on the CAO (4.44 Units) was higher than that of the levels of 0.05% (4.76 Units), 0.4% (4.80 Units), and 0.2% (6.02 Units), respectively. It was interesting to find that there was no marked difference between the effect of 0.1% BKO and 100 ppm TBHQ (4.12 Units).

Table 5 shows the CV of the CAO as affected by the BKO and TBHQ during the frying process at 180 °C. Determination of CV in rancid oils has been shown to be a quick, simple, and cheap test [40]. This criterion does not measure primary products of oxidation (hydroperoxides), but secondary decomposition products such as aldehydes and ketones [41]. According to Woyewoda et al. [42], peroxides are transformed into secondary products that contain carbonyl groups. These compounds are more stable than peroxides and the CV is considered to be a good index of oxidative changes in lipids. There were no significant differences among the initial CV of the oil treatments, ranging from 8.03 to 8.80 µmol/g. During the frying process of CAO, the CV increased and reached a maximum value of 39.93 µmol/g after 24 h of the frying process and then decreased as a result of further heat treatment (Table 5). This phenomenon has been attributed to the decomposition of carbonyl compounds during a prolonged

Table 4 Acid value (AV) of the canola oil (CAO) as affected by the bene kernel oil (BKO) and *tert*-butylhydroquinone (TBHQ) during the frying process at 180 °C

Time (h)	CAO	BKO (%)				TBHQ (100 ppm)
		0.05	0.1	0.2	0.4	
0	0.36 ± 0.04 Jab	0.34 ± 0.04 Mab	0.38 ± 0.02 Ja	0.35 ± 0.02 Jab	0.31 ± 0.00 Mb	0.38 ± 0.02 La
4	0.49 ± 0.06 Jb	0.49 ± 0.02 Lb	0.50 ± 0.04 Jab	0.56 ± 0.00 IJa	0.53 ± 0.00 Lab	0.53 ± 0.04 KLab
8	0.77 ± 0.10 IJa	0.59 ± 0.00 Kc	0.69 ± 0.02 Ib	0.77 ± 0.02 IJa	0.74 ± 0.02 Kab	0.71 ± 0.01 JKab
12	1.06 ± 0.04 HIa	0.77 ± 0.02 Jb	0.84 ± 0.16 Hb	1.04 ± 0.12 HIa	0.88 ± 0.02 1 J b	0.87 ± 0.12 IJb
16	1.39 ± 0.02 GHa	0.92 ± 0.00 Ic	0.81 ± 0.04 HIc	1.39 ± 0.22 GHa	1.15 ± 0.04 I b	1.04 ± 0.12 Ib
20	1.78 ± 0.01 Ga	1.20 ± 0.04 Hc	1.37 ± 0.04 Gb	1.78 ± 0.29 FG a	1.42 ± 0.02 H b	1.27 ± 0.06 Hbc
24	2.27 ± 0.16 Fa	1.43 ± 0.04 Gb	1.41 ± 0.05 Gb	2.24 ± 0.36 EFa	1.62 ± 0.08 Gb	1.58 ± 0.14 Gb
28	2.90 ± 0.34 Ea	1.74 ± 0.16 Fb	1.74 ± 0.04 Fb	2.72 ± 0.44 DEa	2.02 ± 0.08 Fb	1.97 ± 0.22 Fb
32	3.66 ± 0.30 Da	2.18 ± 0.12 Ecd	2.13 ± 0.04 Ed	3.26 ± 0.37 CDb	2.41 ± 0.07 Ecd	2.42 ± 0.26 Ec
36	3.92 ± 0.00 Da	2.81 ± 0.06 Db	2.83 ± 0.28 Db	3.75 ± 0.47 Ca	2.91 ± 0.16 Db	2.96 ± 0.26 Db
40	5.08 ± 0.57 Ca	3.20 ± 0.02 Cd	3.18 ± 0.02 Cd	4.36 ± 0.50 Bb	3.50 ± 0.20 Ccd	3.70 ± 0.12 Cc
44	6.12 ± 0.93 Ba	4.33 ± 0.14 Bc	4.18 ± 0.27 Bc	5.52 ± 0.04 Ab	4.17 ± 0.21 Bc	4.03 ± 0.16 Bc
48	7.10 ± 0.42 Aa	5.10 ± 0.08 Ac	4.82 ± 0.00 Ad	6.37 ± 0.09 Ab	5.11 ± 0.03 Abc	4.50 ± 0.02 Ae

Means ± SD (standard deviation) within a column with the same uppercase letters are not significantly different at $P < 0.05$

Means ± SD (standard deviation) within a row with the same lowercase letters are not significantly different at $P < 0.05$

Table 5 Carbonyl value (CV) of the canola oil (CAO) as affected by the bene kernel oil (BKO) and *tert*-butylhydroquinone (TBHQ) during the frying process at 180 °C

Time (h)	CAO	BKO (%)				TBHQ (100 ppm)
		0.05	0.1	0.2	0.4	
0	8.39 ± 0.94 Ga	8.40 ± 0.39 Ga	8.03 ± 0.52 Ga	8.80 ± 0.27 Ha	8.12 ± 0.38 Ea	8.85 ± 0.64 Ha
4	8.77 ± 1.82 Gb	13.06 ± 2.23 Fa	8.42 ± 1.11 Gb	13.53 ± 2.04 Ga	8.59 ± 1.34 Eb	9.97 ± 1.48 GHb
8	17.43 ± 2.97 Fa	15.53 ± 2.02 Eab	8.92 ± 0.95 Gd	14.14 ± 0.92 FGbc	12.95 ± 1.58 Dbc	12.93 ± 1.40 FGbc
12	25.16 ± 1.87 Ea	19.50 ± 0.53 Db	14.63 ± 1.48 Fc	16.18 ± 1.03 Fc	14.60 ± 1.60 Dc	15.25 ± 2.44 Fc
16	27.96 ± 2.37 Ea	20.72 ± 0.90 Db	16.00 ± 2.40 Fcd	28.08 ± 1.247 Da	14.74 ± 1.31 Dd	19.35 ± 3.99 Ebc
20	28.24 ± 3.56 Ea	24.03 ± 1.72 Cabc	21.65 ± 6.84 Ebc	26.70 ± 1.87 DEab	19.23 ± 1.53 Cc	20.52 ± 2.58 DEc
24	39.93 ± 2.03 Ca	25.98 ± 3.06 Cb	22.77 ± 2.51 Ebcd	24.46 ± 2.40 Ebc	19.56 ± 2.31 Cd	21.28 ± 1.85 DEcd
28	33.76 ± 2.70 Da	26.15 ± 1.46 Cb	24.60 ± 2.73 DEb	25.63 ± 2.70 Eb	20.64 ± 1.19 Cc	24.15 ± 3.65 CDbc
32	35.80 ± 1.46 Da	18.25 ± 1.05 Dd	26.98 ± 2.17 CDc	31.35 ± 1.45 Cb	24.82 ± 4.57 Bc	24.26 ± 2.33 CDc
36	55.67 ± 2.80 Ba	31.10 ± 1.72 Abc	28.10 ± 2.33 BCcd	33.97 ± 1.058 Bb	27.62 ± 2.44 Bc	26.46 ± 2.82 BCd
40	63.98 ± 1.76 Aa	31.93 ± 1.30 Ac	29.86 ± 2.40 BCb	34.13 ± 1.59 Bbc	35.10 ± 2.92 Abc	28.47 ± 1.83 ABd
44	58.04 ± 1.40 Ba	29.71 ± 2.48 ABc	31.64 ± 1.51 ABc	36.17 ± 1.86 Bb	19.64 ± 2.57 Ce	29.37 ± 2.45 ABd
48	47.50 ± 3.42 Ba	28.83 ± 1.21 Be	34.78 ± 1.45 Ac	41.61 ± 0.10 Ab	24.37 ± 1.12 Be	30.98 ± 2.51 Ad

Means ± SD (standard deviation) within a column with the same uppercase letters are not significantly different at $P < 0.05$

Means ± SD (standard deviation) within a row with the same lowercase letters are not significantly different at $P < 0.05$

Table 6 Total tocopherols (TT) content of the canola oil (CAO) as affected by the bene kernel oil (BKO) and *tert*-butylhydroquinone (TBHQ) during the frying process at 180 °C

Time (h)	CAO	BKO (%)				TBHQ (100 ppm)
		0.05	0.1	0.2	0.4	
0	817.91 ± 3.90 Aab	817.34 ± 14.30 Aab	814.37 ± 11.05 Aab	820.97 ± 15.12 Aa	802.49 ± 3.60 Ab	820.41 ± 12.62 Aa
4	758.73 ± 6.54 Bb	749.53 ± 15.78 Bbc	790.03 ± 13.36 Ba	728.61 ± 8.18 Bd	738.23 ± 15.85 Bcd	768.20 ± 12.36 Bb
8	717.71 ± 6.65 Cc	669.75 ± 5.01 Cd	771.84 ± 10.85 Ca	705.21 ± 15.76 Cc	648.34 ± 16.10 Ce	754.64 ± 10.60 Bb
12	578.69 ± 15.39 De	631.73 ± 14.02 Dd	746.05 ± 7.33 Da	590.80 ± 13.07 De	555.03 ± 9.79 Df	708.19 ± 10.73 Cb
16	538.62 ± 17.59 Ee	635.81 ± 4.33 Dc	690.01 ± 10.47 Ea	558.68 ± 10.255 Ed	522.95 ± 11.17 Ee	656.89 ± 8.57 Db
20	507.31 ± 8.74 Fe	583.10 ± 6.56 Ed	615.06 ± 9.14 Fb	482.11 ± 12.67 Ff	480.01 ± 9.68 Ff	630.58 ± 10.15 Ea
24	477.32 ± 9.87 Gd	539.46 ± 5.36 Fc	600.42 ± 6.61 Ga	476.65 ± 13.83 Fd	469.09 ± 12.82 Fd	607.17 ± 11.84 Fa
28	359.41 ± 6.04 He	476.67 ± 11.06 Gc	567.82 ± 7.72 Ha	448.60 ± 11.95 Gd	449.68 ± 5.52 Gd	550.31 ± 10.32 Gb
32	355.83 ± 3.77 He	457.55 ± 17.39 Hc	534.63 ± 9.58 Ib	435.25 ± 6.07 Ge	451.35 ± 3.50 Gd	543.29 ± 3.54 GHb
36	340.81 ± 5.74 If	441.12 ± 9.50 Ic	530.97 ± 3.96 IJb	399.45 ± 2.13 He	426.23 ± 13.10 Hd	531.62 ± 7.50 HIb
40	336.15 ± 6.16 Je	420.20 ± 7.30 Jc	519.35 ± 3.33 Jb	391.62 ± 1.82 HId	411.20 ± 14.35 HIc	525.90 ± 13.414 IJb
44	312.89 ± 7.23 Jf	386.56 ± 10.59 Kde	502.57 ± 7.38 Kc	378.20 ± 3.04 IJe	397.32 ± 9.15 Id	520.92 ± 8.28 IJb
48	309.65 ± 13.80 Kf	328.07 ± 9.24 Le	490.45 ± 5.02 Kc	365.09 ± 2.14 Jd	321.58 ± 11.55 Jef	515.26 ± 6.06 Jb

Means ± SD (standard deviation) within a column with the same uppercase letters are not significantly different at $P < 0.05$

Means ± SD (standard deviation) within a row with the same lowercase letters are not significantly different at $P < 0.05$

frying period and formation of new compounds which are not detectable by the CV assay [42]. Similar changes in the CV were observed for CAOs containing 0.05% (26.15 µmol/g after 28 h), 0.2% (26.70 µmol/g after 20 h), and 0.4% (35.10 µmol/g after 40 h) BKO. However, the CV of CAOs containing 0.1% BKO and 100 ppm TBHQ increased consistently and reached maximum values of 34.78 and 30.98 µmol/g at the end of the frying process.

Tocopherols are important minor constituents in oils, acting as natural antioxidants by slowing the rate of oxidative degradation [27]. Verleyen et al. (2001) showed that heating triacylglycerol mixtures caused a marked reduction in residual α-tocopherol level (66–98%) [43]. The changes in TT content of the CAO and CAOs containing the BKO and TBHQ during the frying process at 180 °C are presented in Table 6. Tocopherols degradation increased as a function of frying time. At the end of the frying period, the remaining tocopherols content was highest in the CAOs containing the 0.1% BKO (60.22%) and TBHQ (62.80%), and was the lowest for the CAO (37.86%) and CAOs containing 0.05% (40.14%), 0.2% (44.47%), and 0.4% (40.07%) BKO. Since tocopherols act as antioxidants, oils in which tocopherols degrade rapidly would be expected to exhibit lower stability. Less stable oils, shown in this study, are ones having significantly higher rates of TPC, CDV, CV, and AV formation.

Conclusions

Based on the oxidative stability criteria investigated in this study, the BKO as a vegetable oil and not as a pure natural or synthetic antioxidant showed itself to be capable of retarding oxidation at a level as low as 0.1% (1,000 ppm). Its effectiveness at this level was found to be nearly the same as the powerful synthetic antioxidant TBHQ. A marked pro-oxidant effect was observed when levels higher than 0.1% of BKO were added to the CAO. In summary, the present study demonstrates the antioxidant properties of BKO and that this vegetable oil can be considered as a potential source of natural antioxidants in food industries. Nevertheless, the BKO is a new product and our research group is still working on gaining a better understanding of the most reactive antioxidants in the BKO and the possible mechanisms involved.

References

1. Pedreschi F, Moyano P, Kaack K, Granby K (2005) Color changes and acryl amide formation in fried potato slices. Food Res Int 38:1–9
2. Andrikopoulos NK, Kalogeropoulos N, Falirea AF, Barbagianni MN (2002) Performance of virgin olive oil and vegetable shortening during domestic deep-frying and pan-frying of potatoes. Int J Food Sci Technol 37:177–190
3. Dobarganes C, Marquez-Ruiz G (2003) Oxidized fats in foods. Curr Opin Clin Nutr Metab Care 6:157–163
4. Dobbs JE, Vaisey-Genser M, Diamant R (1978) Unpleasant odours of rape seed oil heated to frying temperatures. Can. Inst. Food Sci.Technol. J 11:66–70
5. Nawar WW (1996) Lipids. In: Fennema OR (ed) Food chemistry. Marcel Dekker, New York, pp 225–320
6. Fatihanim MN, Mohamed S, Nor Aini I, Razali I (2008) Antioxidative properties of *Pandanus amaryllifolius* leaf extracts in accelerated oxidation and deep frying studies. Food Chem 110:319–327
7. Ito N, Hirose M, Fukushima S, Tsuda H, Shirai T, Tatematsu M (1986) Studies on antioxidants: their carcinogenic and modifying effects on chemical carcinogenesis. Food Chem Toxicol 24:1071–1082
8. Whysner J, Wang CX, Zang E, Iatropoulos MJ, Williams GM (1994) Dose response of promotion by butylated hydroxyanisole in chemically initiated tumors of the rat forestomach. Food Chem Toxicol 32:215–222
9. Williams GM, Iatropoulos MJ, Whysner J (1999) Safety assessment to butylated hydroxyanisole and butylated hydroxytoluene as antioxidant food additives. Food Chem Toxicol 37:1027–1038
10. Ackman RG (1990) Canola fatty acids—an ideal mixture for health, nutrition and food use. In: Shahidi F (ed) Canola and rapeseed. Van Nostrand Reinhold, New York, pp 81–89
11. Petukhova I, Malcolmsona LJ, Przybylskia R, Armstrong R (1999) Frying performance of genetically modified canola oils. J Am Oil Chem Soc 76:627–632
12. Warner K, Mounts TL (1993) Frying stability of soybean and canola oils with modified fatty acid compositions. J Am Oil Chem Soc 70:983–988
13. Sabeti H (1994) Forest, trees, and shrubs of Iran. Iran University of Science and Technology Press, Tehran
14. Farhoosh R, Tavakkoli J, Hadad Khodaparast MH (2008) Chemical composition and oxidative stability of kernel oils from two current subspecies of Pistacia atlantica in Iran. J Am Oil Chem Soc 85:723–729
15. Tyagi VK, Vasisihtha AK (1996) Changes in the characteristics and composition of oils during deep-fat frying. J Am Oil Chem Soc 73:499–506
16. Farhoosh R, Niazmand R, Rezaei M, Sarabi M (2008) Kinetic parameter determination of vegetable oil oxidation under Rancimat test conditions. Eur J Lipid Sci Technol 110:587–592
17. Farhoosh R (2007) The effect of operational parameters of the Rancimat method on the determination of the oxidative stability measures and shelf-life prediction of soybean oil. J Am Oil Chem Soc 84:205–209
18. Capannesi C, Palchetti I, Mascini M, Parenti A (2000) Electrochemical sensor and biosensor for polyphenols detection in olive oils. Food Chem 71:553–562
19. Wong ML, Timms RE, Goh EM (1988) Colorimetric determination of total tocopherols in palm oil, olein and stearin. J Am Oil Chem Soc 65:258–261
20. Shantha NC, Decker EA (1994) Rapid, sensitive, iron-based spectrophotometric methods for determination of peroxide values of food lipids. J AOAC Int 77:21–424
21. AOCS (1993) Official methods and recommended practices of the American Oil Chemists' Society, Vol. 29. AOCS Press, Champaign, pp 573–577
22. Schulte E (2004) Economical micromethod for determination of polar components in frying fats. Eur J Lipid Sci Technol 106:772–776
23. Saguy IS, Shani A, Weinberg P, Garti N (1996) Utilization of jojoba oil for deep-fat frying of foods. Lebensm Wiss u-Technol 29:573–577
24. Endo Y, Li CM, Tagiri-Endo M, Fugimoto K (2001) A modified method for the estimation of total carbonyl compounds in heated and frying oils using 2-propanol as a solvent. J Am Oil Chem Soc 10:1021–1024
25. Farhoosh R, Moosavi SMR (2006) Determination of carbonyl value in rancid oils: a critical reconsideration. J Food Lipids 13:298–305
26. Warner K, Knowlton S (1997) Frying quality and oxidative stability of high-oleic corn oils. J Am Oil Chem Soc 74:1317–1321
27. Normand L, Eskin NA, Przybylski R (2001) Effect of tocopherols on the frying stability of regular and modified canola oils. J Am Oil Chem Soc 78:369–373
28. Aparicio R, Roda L, Albi MA, Gutierrez F (1999) Effect of various compounds on virgin olive oil stability measured by Rancimat. J Agric Food Chem 47:4150–4155
29. Morello JR, Motilva MJ, Tovar MJ, Romero MP (2004) Changes in commercial virgin olive oil (cv Arbequina) during storage,

with special emphasis on the phenolic fraction. Food Chem 85:357–364

30. Che Man YB, Tan CP (1999) Effects of natural and synthetic antioxidants on changes in refined, bleached, and deodorized palm olein during deep-fat frying of potato chips. J Am Oil Chem Soc 76:331–339
31. Shahidi F, Wanasundara UN (1997) Measurement of lipid oxidation and evaluation of antioxidant activity. In: Natural antioxidants, chemistry, health effects and applications. AOCS Press, Champaign, pp 1–10
32. Maleka M (1994) The effect of squalene on the thermostability of rapeseed oil. Nahrung 38:135–140
33. Abdel-Aziz SMG (1985) Chemical and biological evaluation of unsaponifiable matter of vegetable oils. Ph.D. Thesis, Faculty of Agriculture, Cairo University, Cairo (Egypt)
34. Awatif II, Khalil MF, Badawy HAA (1996) Effect of natural and synthetic antioxidants on the stability of virgin olive oil. Ann Agric Sci 41:269–280
35. Mohamed HAM, Awatif II (1998) The use of sesame oil unsaponifiable matter as a natural antioxidant. Food Chem 62:269–276
36. Gopala Krishna AG, Prashanth PA, Pragasam A, Raghavendra KV, Matoon S (2003) Unsaponifiable matter and oxidative stability of commercially produced Indian rice bran oils. J Food Lipids 10:329–340
37. Naghshine AA, Ariffi HM, Ghazal H, Mirhossein AS, Kunto (2009) Influence of partial replacement of olive oil on frying performance of palm olein. J Food Lipids 16:554–568
38. Fritsch CW (1981) Measurement of frying fat deterioration, a brief review. J Am Oil Chem Soc 58:272–274
39. Mariod A, Matthaus B, Eichner K, Hussein IH (2006) Frying quality and oxidative stability of two unconventional oils. J Am Oil Chem Soc 83:529–538
40. Schultz HW (1962) Symposium on foods: lipids and their oxidation, the second in series of symposia on foods held at Oregon State University. The AVI Publishing Company, Oregon, pp 294–320
41. Matthhaus B (2006) Utilization of high-oleic rapeseed oil for deep-fat frying of French fries compared to other commonly used edible oils. Eur J Lipid Sci Technol 108:200–211
42. Woyewoda AD, Shaw SJ, Ke PJ, Burns BG (1986) Recommended laboratory method for assessment of fish quality. Canadian Technical Report Fisheries and Aquatic Sciences No. 1448
43. Verleyen T, Kamal-Eldin A, Dobarganes C, Verhe R, Dewettinck K, Huyghebaert A (2001) Modeling of loss and products of α-tocopherol during thermoxidation in mixtures of triolein and tripalmitin. Lipids 36:719–726