Efficacy of Tertiary Butylhydroquinone on the Storage and Heat Stability of Liquid Canola Shortening

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The sensory (odor and flavor) and physicochemical characteristics of tertiary butylhydroquinone (TBHQ) treated and butylated hydroxyanisole/toluene (BHA/BHT) treated liquid canola shortenings, subjected to accelerated storage (Schaal oven test at 65°C) and deep fat heating (at 185°C), were determined. Data for the Schaal oven test indicate that TBHQ was effective in retarding oxidative rancidity in liquid canola shortenings. However, addition of the commonly used mixture of BHA/BHT to canola shortenings resulted in only a slight decrease in oxidation during Schaal oven storage. The results obtained from deep fat heating of canola liquid shortening show that neither TBHQ nor BHA/BHT was effective in enhancing oxidative and thermal stability of this product.

KEY WORDS: Liquid canola shortening, sensory/physicochemical characteristics, storage/heat stability, tertiary butylhydroquinone.

Canadian statistics show an increase in the use of vegetable oils and frying shortenings in household, restaurant and institutional settings (1). However, knowledge about the storage and heat stability of untreated or antioxidant treated frying shortenings is limited. There are a few reports on the performance of fluid shortenings during deep fat frying under institutional conditions (1-3). However, information about oxidative changes occurring in untreated and antioxidant treated canola frying shorteinings subjected to storage and deep fat frying conditions similar to those used in the home is lacking.

Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), in combination or singly, are commonly added to oils and shortenings during processing to retard oxidative deterioration due to storage and heat. However, recent studies have found only slight differences in the storage and heat stability of fats and oils with and without added BHA/BHT (4-11). Several reports have demonstrated a greater potency of tertiary butylhydroquinone as compared with BHA/BHT in fats and oils (5,6,9,12-15).

This study was conducted to evaluate the efficacy of TBHQ and BHA/BHT in enhancing the storage (Schaal oven test) and heat (deep fat frying at 185°C) stability of a canola frying shortening.

EXPERIMENTAL PROCEDURES

Fresh "Tasty-fry" liquid canola shortening, containing 2 ppm dimethylpolysiloxane (an antifoaming agent) was obtained from Canbra Foods, Lethbridge, Alberta. Antioxidants: TBHQ, BHA, BHT and monoglyceride citrate (CA) were obtained from Griffiths Laboratory, Toronto, Ontario.

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In order to establish its initial quality, the fresh canola shortening was analyzed for fatty acid composition (16), peroxide (17) and iodine (18) values. The shortening was then divided into three batches. Each batch of the shortening was subjected to the following treatments (T): T1, canola shortening with no antioxidant (control); T2, canola shortening with BHA/BHT (100 ppm ea.) and CA (50 ppm); T3, canola shortening with TBHQ (200 ppm); T4, canola shortening with TBHQ (100 ppm) and CA (50 ppm); T5, canola shortening with TBHQ (200 ppm) and CA (50 ppm); and T6, canola shortening with no antioxidant—frozen (-25°C) at time 0 (a hidden control that was not subjected to the storage or heating tests. It was used as a reference for sensory evaluation). For T2, T4 and T5, the 50 ppm CA was added as monoglyceride citrate.

For each antioxidant treatment, the shortening was heated to 80°C, and then appropriate amounts of antioxidants were incorporated. BHA, BHT and CA were added directly to the canola shortening; TBHQ was incorporated as a 5% solution in ethanol. The shortening was stirred for 30 min at 80°C, followed by 30 min stirring without heat.

For the Schaal oven test, three samples (75 mL) of each shortening treatment (one from each of three replications) were placed in 100-mL beakers, covered loosely with aluminum foil lids and held in a forced air oven at 65°C for up to 16 days. Samples were removed for analyses after 0, 4, 8, 12 and 16 days. Immediately after each storage period, the shortening samples were portioned into 20 mL glass vials and frozen (-25°C) for later sensory evaluation, chemical analyses and gas liquid chromatographic (GLC) testing.

For deep fat frying, four samples (450 g) of each shortening treatment were placed in 100-mL heavy duty pyrex beakers (specific surface 0.189 cm^2/g), heated to 185°C and held at 185°C (±5°C) for up to 60 min. Heated shortening samples were removed at 0, 20, 40 and 60 min, portioned into 20-mL glass vials and stored at -25°C for later sensory and physicochemical determinations.

For sensory evaluation, 14 panelists were screened, on the basis of 12 triangle tests. The selected panelists were intensively trained, according to the procedures of Cross *et al.* (19) and Hawrysh *et al.* (9) over a seven-week period. In order to teach the panelists to identify and quantify odor and flavor types and intensities, the panelists were presented with a range of prepared canola oil samples which were similar in quality to that expected in the study. During the training, as well as the experimental period, panelists evaluated oil odor and flavor intensity using a 10-point scale (10 = bland, 1 = extremely intense). Near the end of the training period, six panelists were selected to participate in the study. Evaluations were conducted in a taste panel room, equipped with individual booths and red lights. Each panelist received a total of six samples per session (T1-T5 and a reference sample). The order of sample presentation was randomized for each panelist. Oil samples (5 g) were served warm

TABLE 1

Chemical Properties of Liquid Canola Shortening Upon Receipt

Parameter		Oil (no antioxidant)
Iodine value		91.66
Peroxide value (meq/kg)		0.25
Fatty acid composition [%]		
Palmitic acid	(C16:0)	5.4
Palmitoleic acid	(C16:1)	0.4
Stearic acid	(C18:0)	2.9
Oleic acid	(C18:1)	81.7
Linoleic acid	(C18:2)	5.2
Linolenic acid	(C18:3)	0.8
Octadecatetraenoic acid	(C18:4)	0.6
Arachidic acid	(C20:0)	0.5
Gadoleic acid	(C20:1)	1.3
Arachidonic acid	(C20:4)	0.2
Behenic acid	(C22:0)	0.2
Erucic acid	(C22:1)	0.4
Docosapentaenoic acid	(C22:5)	0.1

[50-55°C as per AOCS standards (17) and Warner (20)] in 20-mL capped glass vials. Initially each panelist was asked to assess the odor intensity of each of the oil samples by holding the vial to the nose and taking several short sniffs. Secondly, the flavor intensity of each oil sample was evaluated. Approximately 3 g of warm oil was taken into the mouth and, during 15 seconds, exhaled through the nose several times. The sample was expectorated. Warm lemon water (1%), unsalted soda crackers and distilled warm water were provided to clear the palate between samples. Panelists waited at least 30 seconds before evaluating a subsequent sample.

Chemical analyses of the liquid canola shortenings subjected to the Schaal oven test included determinations of peroxide value (17), thiobarbituric acid (TBA) value (21) and UV absorbances at 234 and 268 nm (18). The "off flavor" compounds developed in the shortening samples during Schaal oven storage test were determined by GLC, using the method described by Tokarska *et al.* (8). Physicochemical analyses of shortenings subjected to deep fat frying included determinations of color (22), p-anisidine value (18), smoke point (17), viscosity (using Brookfield viscometer, model RUT-D) and UV absorbance at 234 and 268 nm (18).

For statistical analyses, a strip-plot experimental design (23) involving treatments and storage times was used for each experiment. Data for sensory evaluation and physicochemical analyses were subjected to the analyses of variance outlined by Milliken and Johnson (23). Student-Newman Keul's Multiple Range test (24) was used to identify significant differences among treatment means.

RESULTS AND DISCUSSION

The fresh "Tasty-fry" liquid canola shortening was of good initial quality with reasonably low peroxide (0.25 meq/kg) and iodine (91.66) values. The shortening contained 0.4% erucic acid and 0.8% linolenic acid.

Sensory evaluation data for the Schaal oven storage test (Table 2) indicate that both the odor and flavor intensities of the liquid canola shortening were improved by the addition fo TBHQ. In contrast, data for the untreated control (T1) and BHA/BHT treated (T2) liquid canola shortenings show a rapid progressive deterioration in the quality of these samples. After 16 days of storage, the odor intensity scores for both T1 and T2 were similar and significantly lower, respectively, than that of the hidden control. Relative to the bland hidden control (T6), at 16 days the flavor of T1 and T2 was described as definite. In contrast, the odor and flavor of the TBHQ treated samples (T3,T4,T5) were scored as slightly intense compared to the bland hidden control (T6) at 16 days of storage.

Chemical data for peroxide value, TBA value and absorbance ($E^{1\%}_{1cm}$) at 234 and 268 nm (Table 3), also show marked oxidative changes in the canola shortening samples stored without antioxidant (T1) and with BHA/BHT (T2). After 16 days of Schaal oven storage, the peroxide value for the untreated control (T1) increased from 0.28 meq/kg (fresh shortening) to 18.99 meq/kg, and for the BHA/BHT treated canola frying shortening from 0.26 (fresh shortening) to 6.72 meq/kg. In contrast, during the entire storage period, the peroxide values for TBHQ treated samples (T3,T4,T5) increased from 0.21-0.24 meq/kg to 2.00-2.09 meq/kg.

Generally, the TBA values, indicating presence of diunsaturated aldehydes, show that more rapid oxidative changes occurred in untreated control (T1) and the BHA/BHT treated (T2) canola frying shortenings than in TBHQ treated sampled (T3,T4,T5). During the entire storage period, the TBA values of untreated control (T1) and BHA/BHT treated shortening (T2) increased nine and five times, respectively. However, in the TBHQ treated samples, only a two-fold increase in the TBA values was detected after 16 days of storage.

Data for absorbance at 234 nm, indicating the presence of linoleic hydroperoxide and conjugated dienes, show that after the first four days of storage at 65°C, all samples were similar. However, after eight days of storage the TBHQ treated shortenings (T3,T4,T5) tended to have lower absorbance values (at 234 nm) than the untreated control (T1), which was similar to T2. At each subsequent storage period, the TBHQ treated shortenings (T3,T4,T5) had significantly lower absorbance values at 234 nm than that for the BHA/BHT treated samples (T2) which, in turn, differed significantly from the untreated control (T1). After storage from 0 to 12 days, no significant differences in absorbance at 268 nm, indicating presence of conjugated trienes, were detected among the treatments. However, at 16 days of storage at 65°C, all antioxidant treated shortenings (T2,T3,T4,T5) had slightly but significantly lower absorbance values (268 nm) than the untreated control (T1).

Gas liquid chromatographic data (Table 4) show a substantially slower development of "off flavor" compounds in the shortening samples stabilized with TBHQ (T3,T4,T5) than in the untreated control (T1) and BHA/BHT treated shortening (T2). After storage for 16 days, the amount of total "off flavor" volatiles in both the untreated control (T1) and BHA/BHT (T2) stabilized shortenings increased from 5.10 ppm and 6.85 ppm (at 0 storage) to 101.08 ppm and 45.67 ppm, for T1 and T2, respectively. The addition of TBHQ had a marked effect on slowing the rate of oxidation in canola shortening. All three samples containing TBHQ (T3,T4,T5) had substantially lower levels of total volatiles (an increase from 4.15-4.96 ppm to a range of 9.62-17.12) than T1 and T2.

TABLE 2

Average Scores for Odor and Flavor Intensity of Antioxidant Treated Liquid Canola Shortenings Following Accelerated Storage at 65°C

Characteristic	Canola shortening treatment							
	Storage time (days)	Untreated control (T1)	BHA/BHT (100 ppm ea) + CA (T2)	TBHQ (200 ppm) + CA (T3)	TBHQ (100 ppm) (T4)	TBHQ (200 ppm) (T5)	Hidden control (T6)	Standard error
Overall odor intensity	0	9.7	9.9	9.6	9.7	9.9	9.9	0.14
	8	6.4[c]	5.7[c]	8.1[b]	8.6[b]	7.6[b]	9.9[a]	0.28[e]
	12	6.1[c]	5.9[c]	8.0[b]	8.5[b]	7.9[b]	9.8[a]	0.28[e]
	16	5.8[c]	4.9[c]	7.7[b]	7.3[b]	7.7[b]	9.8[a]	0.31[e]
Overall flavor intensity	0	9.7	9.6	9.8	9.7	9.6	9.9	0.12
	8	5.7[c]	5.8[c]	6.8[c]	7.7[b]	6.7[c]	9.8[a]	0.26[e]
	12	5.7[c]	5.5[c]	7.5[b]	7.9[b]	7.7[b]	9.7[a]	0.23[e]
	16	4.4[c]	4.3[c]	7.3[b]	6.8[b]	7.1[b]	9.9[a]	0.27[e]

[a,b,c,d]Means within the same row sharing a common letter are not significantly different at $p < 0.05$.

[e]Significant at $p < 0.001$.

TABLE 3

Peroxide and TBA Values for Antioxidant Treated Liquid Canola Shortenings Following Accelerated Storage at 65°C

Test	Canola shortening treatment						
	Storage time (days)	Untreated control (T1)	BHA/BHT (100 ppm ea) + CA (T2)	TBHQ (200 ppm) (T3)	TBHQ (100 ppm) + CA (T4)	TBHQ (200 ppm) + CA (T5)	Standard error
Peroxide value (meq/kg)	0	0.28	0.26	0.21	0.21	0.24	0.03
	4	1.61[a]	1.45[b]	1.16[c]	1.13[c]	1.22[c]	0.03[f]
	8	4.63[a]	2.80[b]	1.47[c]	1.37[c]	1.56[c]	0.06[f]
	12	10.49[a]	4.33[b]	1.80[c]	1.73[c]	1.70[c]	0.17[f]
	16	18.99[a]	6.72[b]	2.09[c]	2.04[c]	2.00[c]	0.20[f]
TBA (532 nm)	0	0.82	0.85	0.78	0.75	0.74	0.05
	4	1.85[a]	1.61[b]	1.19[c]	1.16[c]	1.14[c]	0.04[f]
	8	3.74[a]	2.62[b]	1.36[c]	1.46[c]	1.34[c]	0.10[f]
	12	6.08[a]	3.15[b]	1.50[c]	1.42[c]	1.46[c]	0.11[f]
	16	7.38[a]	4.18[b]	1.52[c]	1.52[c]	1.58[c]	0.12[f]
$E^{1\%}_{1cm}$[d] (234 nm)	0	11.88	11.83	11.85	11.69	11.83	0.05
	4	11.82	11.82	11.79	11.77	11.77	0.02
	8	12.19[a]	12.05[a,b]	11.82[c]	11.78[c]	11.89[b,c]	0.05[e]
	12	12.58[a]	12.07[b]	11.75[c]	11.75[c]	11.74[c]	0.06[f]
	16	13.31[a]	12.31[b]	11.78[c]	11.84[c]	11.88[c]	0.06[f]
$E^{1\%}_{1cm}$[d] (268 nm)	0	0.84	0.85	0.84	0.83	0.83	0.01
	4	0.84	0.84	0.84	0.83	0.83	0.01
	8	0.90	0.91	0.88	0.90	0.89	0.01
	12	0.88	0.87	0.86	0.86	0.87	0.01
	16	0.97[a]	0.92[b]	0.92[b]	0.91[b]	0.91[b]	0.01[f]

[a,b,c]Means within the same row sharing a common letter are not significantly different at $p < 0.05$.

[d]Not corrected for triglyceride absorption.

[e]Significant at $p < 0.01$.

[f]Significant at $p < 0.001$.

The data from the present Schaal oven storage experiment are in agreement with the results of our previous study (9), which demonstrated the efficacy of TBHQ in enhancing the storage stability of canola oil subjected to 16 days of Schaal oven test.

Results of sensory evaluation of the shortenings subjected to deep fat frying (Table 5) show that the fastest rate of oxidative degradation occurred during the initial heating (a total of 22.5 ± 2.5 min) of the shortening samples from room temperature to 185°C. During the entire heating period, only minor differences in shortening odor and flavor intensity scores were determined.

TABLE 4

Content of Total Off-Flavor Volatiles in Antioxidant Treated Liquid Canola Shortening Following Accelerated Storage at 65°C

Compounds[a]		Canola shortening treatment				
	Storage time (days)	Untreated control (T1)	BHA/BHT (100 ppm ea) + CA (T2)	TBHQ (200 ppm) (T3)	TBHQ (100 ppm) + CA (T4)	TBHQ (200 ppm) + CA (T5)
Total volatiles	0	5.10	6.85	4.96	4.38	4.15
	8	41.21	29.64	6.13	7.09	6.15
	12	47.53	23.64	7.33	8.00	7.66
	16	101.08	45.67	13.98	9.62	17.12

[a]Determined as ppm from gas liquid chromatographic analyses.

TABLE 5

Average Scores for Odor and Flavor Intensity of Antioxidant Treated Liquid Canola Shortenings Following Extended Heating (185°C)

Characteristic		Canola shortening treatment						
	Heating time (min)	Untreated control (T1)	BHA/BHT (100 ppm ea) + CA (T2)	TBHQ (200 ppm) (T3)	TBHQ (100 ppm) + CA (T4)	TBHQ (200 ppm) + CA (T5)	Hidden control (T6)	Standard error
Overall odor intensity	0	5.8[b]	5.8[b]	6.5[b]	5.9[b]	6.3[b]	10.0[a]	0.26[c]
	40	5.8[b]	5.5[b]	6.3[b]	5.7[b]	5.8[b]	10.0[a]	0.28[c]
	60	5.7[b]	5.1[b]	5.7[b]	6.1[b]	5.7[b]	9.9[a]	0.34[e]
Overall flavor intensity	0	6.2[b]	6.3[b]	6.4[b]	6.1[b]	6.2[b]	10.0[a]	0.27[c]
	40	6.0[b]	5.4[b]	5.6[b]	5.4[b]	5.8[b]	10.0[a]	0.27[c]
	60	5.7[b]	5.4[b]	5.6[b]	5.6[b]	5.4[b]	10.0[a]	0.27[c]

[a,b]Means within the same row sharing a common letter are not significantly different at $p < 0.05$.
[c]Significant at $p < 0.001$.

TABLE 6

Data for Color, Free Fatty Acid Content, Smoke Point and Viscosity of Antioxidant Treated Liquid Canola Shortenings Following Extended Heating (185°C)

Test		Canola shortening treatment					
	Heating time (days)	Untreated control (T1)	BHA/BHT (100 ppm ea.) (T2)	TBHQ (200 ppm) + CA (T3)	TBHQ (100 ppm) + CA (T4)	TBHQ (200 ppm) (T5)	Standard error
Color	0	0.085[a,b]	0.087[a]	0.082[c]	0.085[a,b]	0.084[b,c]	0.00[e]
	20	0.087[b]	0.089[a]	0.085[c]	0.086[b,c]	0.086[b,c]	0.00[f]
	40	0.089[b]	0.092[a]	0.086[c]	0.089[b]	0.089[b]	0.00[e]
	60	0.091[b]	0.094[a]	0.088[c]	0.091[b]	0.090[b]	0.00[e]
FFA (%)	0	0.02	0.04	0.03	0.04	0.04	0.00
	20	0.03	0.03	0.03	0.04	0.03	0.00
	40	0.02[b]	0.04[a]	0.03[b]	0.04[a]	0.04[a]	0.00[f]
	60	0.02[b]	0.04[a]	0.03[a]	0.04[a]	0.03[a]	0.00[d]
Smoke point (°C)	0	239.0	240.0	240.7	240.0	236.0	1.12
	20	242.7	239.3	240.7	240.0	237.3	1.22
	40	239.7	238.3	240.0	238.3	239.7	0.79
	60	240.7	239.3	239.7	237.3	238.3	1.30
Viscosity (cps)	0	41.7[a]	41.7[a]	41.2[b]	41.5[a,b]	41.3[b]	0.08[e]
	20	41.6	41.6	41.2	41.2	41.4	0.08
	40	41.4	41.3	41.0	41.1	40.9	0.13
	60	41.9	42.0	41.5	41.7	41.2	0.17

[a,b,c]Means within the same row sharing a common letter are not significantly different at $p < 0.05$.
[d,e,f]Significant at $p < 0.05$, $p < 0.01$ and $p < 0.001$, respectively.

TABLE 7

p-Anisidine and Absorbance at 234 and 268 nm for Antioxidant Treated Liquid Canola Shortenings Following Extended Heating (185°C)

Test	Canola shortening treatment						
	Heating time (min)	Untreated control (T1)	BHA/BHT (100 ppm ea) + CA) (T2)	TBHQ (200 ppm) (T3)	TBHQ (100 ppm) + CA (T4)	TBHQ (200 ppm) + CA (T5)	Standard error
p-Anisidine value	0	3.96[a]	3.75[a]	2.68[b]	2.81[b]	2.49[b]	0.11[h]
	20	4.88[a]	4.54[b]	3.22[c]	3.26[c]	3.23[c]	0.07[h]
	40	5.51[a]	5.25[b]	3.81[c]	3.87[c]	3.43[d]	0.06[h]
	60	6.17[a]	5.98[a]	4.36[b,c]	4.72[b]	4.06[c]	0.13[h]
$E^{1\%}_{1cm}$[e] (234 nm)	0	11.76	11.64	11.61	11.67	11.66	0.06
	20	11.94	12.00	11.90	11.83	11.92	0.05
	40	12.20	12.16	12.08	12.02	12.01	0.06
	60	12.10	12.16	11.90	11.93	12.12	0.09
$E^{1\%}_{1cm}$[e] (268 nm)	0	0.89	0.89	0.86	0.88	0.87	0.01
	20	0.89[a,b]	0.90[a]	0.86[c]	0.87[b,c]	0.89[a,b]	0.01[f]
	40	0.98[a,b]	0.99[a]	0.95[b]	0.95[b]	0.95[b]	0.01[g]
	60	0.99	1.00	0.96	0.96	0.96	0.01

[a,b,c,d]Means within the same row sharing a common letter are not significantly different at $p < 0.05$.

[e]Not corrected for triglyceride absorption.

[f,g,h]Significant at $p < 0.05$, $p < 0.01$ and $p < 0.001$, respectively.

Also, no significant differences in odor and flavor attributable to antioxidant treatment were detected in the heated liquid canola shortenings.

Data for color, percent free fatty acids, smoke point and viscosity (Table 6) indicate very few differences among the canola frying shortening treatments following home-type deep frying for up to 60 min. During heating from 0 to 60 min, all the shortening samples darkened slightly (an increase in absorption of 0.006-0.007). Generally, only small differences in free fatty acid content among the treatments were determined after 40 and 60 min of heating. However, these differences are too small to affect the shortening quality. Moreover, between 0 and 60 min of deep fat heating, only very small differnces in the percentages of free fatty acid in all heated samples were determined. Data for smoke point indicate that no significant differences among the treatments were detected. After 60 min of heating, the smoke point of each of the canola frying shortening treatments was almost unchanged. Except for time 0, when small but significant differences in viscosity among the treatments occurred, the viscosity of the shortening samples was very similar at other heating periods. Therefore, even though some significant differences in physicochemical characteristics of the shortening treatments were detected among the samples, they were too small to be of practical significance.

Data for p-anisidine values and absorbance ($E^{1\%}_{1cm}$) at 234 and 268 nm (Table 7) also show few differences among the shortening treatments. The p-anisidine values indicate a slower development of aldehydes in the TBHQ treated canola frying shortenings that in the untreated control (T1) and the BHA/BHT (T2) treated samples. The results for absorbance at 234 nm show that after 60 min deep fat heating no significant differences among the treatments were observed. At 0 and 60 min of heating, no effect of antioxidant treatment on absorbance at 268 nm was determined. However, at 20 and 40 min, a few small but significant differences (probably not of practical importance) in absorbance at 268 nm occurred among the samples.

Generally, the results of this experiment are in agreement with the data from our previous study (11), which indicate that neither BHA/BHT nor TBHQ are effective in enhancing canola oil thermal stability.

In conclusion, data from the Schaal oven test indicate that TBHQ was effective in retarding oxidative rancidity in liquid canola shortenings. However, addition of the commonly used mixture of BHA/BHT to canola shortenings resulted in only a slight decrease in oxidation during Schaal oven storage. The results obtained from deep fat heating of canola frying shortenings show that neither TBHQ nor BHA/BHT was effective in enhancing oxidative and thermal stability of this product.

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