High-Temperature Stability of Soybean Oils with Altered Fatty Acid Compositions

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One canola oil and six soybean oils with different fatty acid compositions were heated intermittently, and bread cubes were fried in them to determine the stability of the oils. Two of the soybean oils were commercial varieties Hardin and BSR 101. The other soybean oils were from experimental lines developed at Iowa State University, and included A17 with 1.5% linolenate (18:3) and 15.1% palmitate (16:0), A16 with 1.9% 18:3 and 10.6% 16:0, A87-191039 with 1.8% 18:3 and 29.1% oleate (18:1) and A6 with 27.7% stearate (18:0). The soybean seeds were cold-pressed and crude canola oil was obtained without additives. Oils were refined, bleached and deodorized under laboratory conditions with additions. Each oil (300 mL) was heated to 180 ± 5°C in a minifryer. Bread cubes were fried at the beginning of heating, and half of the cubes were used for analyses. The second half was analyzed after storage at 60°C for seven days. Heating of the oils was continued for 20 h, cooled for 10 h, and then reheated for another 20 h, after which additional bread cubes were fried and analyzed. Results of sensory evaluation of the fried cubes, the peroxide values (PV) of oils extracted from the cubes and the conjugated dienoic acid values of the oils showed that the A17, A16, A87-191039 and A6 oils had better stabilities than did Hardin, BSR 101 and canola oils. The initial 18:3 contents of oils predicted their oxidative and flavor stabilities under heating and frying conditions (for PV *vs.* 18:3, r = 0.89, $P = 0.008$; for flavor quality *vs.* 18:3, r = −0.93, $P = 0.002$; for flavor intensity *vs.* 18:3, r = −0.91, $P = 0.004$).

KEY WORDS: Fatty acid composition, frying stability, high-temperature stability, soybean oils.

Deep fat frying is one of the most commonly used methods of food preparation because of its convenience, rapidity, economy and the appealing flavor, odor and texture of fried foods. Traditional soybean oils are considered suitable for use in salad dressings and sauces, but they are not stable during heating and frying (1,2) and may develop an objectionable fishy odor (3). Unhydrogenated corn, sunflower and cottonseed oils may be more suitable for frying than soybean oil because they contain only minor amounts of linolenate (18:3), the fatty acid believed to be most prone to autoxidation (3).

Hydrogenation is used to improve the stability of soybean oil during frying and at room temperature (4,5) by decreasing the amount of 18:3 (6). In 1973, France set a legal limit of 2% of 18:3 in oils to be used for deep-fat frying because oils with 18:3 exceeding that percentage are prone to oxidation (2). Other researchers, however, have shown that although the oxidative stability at room and frying temperatures was improved when the 18:3 content was reduced, the flavor quality of the hydrogenated soybean oil was not improved (4,7,8). Blumenthal *et al.* (7) concluded that, in general, unhydrogenated soybean oils had better flavor than did hydrogenated ones.

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Besides hydrogenation, the 18:3 content of soybean oil can be reduced through breeding. New soybean lines with different fatty acid compositions have been produced through such a breeding program at Iowa State University (Ames, IA) (9,10). These lines include A17 with 1.5% 18:3 and 15.1% palmitate (16:0), A16 with 1.9% 18:3 and 10.6% 16:0, A87-191039 with 1.8% 18:3 and 29.1% oleate (18:1) and A6 with a stearate (18:0) content of 27.7%. The purpose of this research was to evaluate the high-temperature stability of soybean oils (with different fatty acid compositions) and canola oil.

EXPERIMENTAL PROCEDURES

Extraction, refining and deodorization. Soybean seed of six genotypes [Hardin, BSR 101, A17, A16, A87-191039 (A87) and A6] and crude canola oil were produced, obtained, processed and analyzed as described in the previous paper (11).

Heating and frying process. Each oil (300 mL) was measured into a teflon-coated electric minifryer with a total capacity of 473 mL (Presto Fry Baby Electric Fryer, National Presto Industries, Inc., Eau Claire, WI) and heated to 180 ± 5°C within 10 min. Two batches (40 g each) of 2.54 cm^3 crust-free bread cubes (Hy-Vee white bread) were fried for one minute each and then drained. One batch was loosely covered and stored at 60°C for seven days. The other batch was used immediately for sensory evaluation and chemical analysis. Heating of the oils was continued for 20 h, the oils were cooled down for 10 h and then heated at 180 ± 5°C for another 20 h. After a total of 40 h of heating, additional bread cubes (40 g) were fried for one minute and evaluated by sensory and chemical tests.

Chemical analyses were done on 3-mL samples of the oils removed from the fryer at the beginning of heating, immediately before the second 20-h heating period, and immediately after the second 20-h heating period. The oil was not replenished or filtered and, after the last batch of cubes had beed fried, approximately 150 mL of oil remained in the fryer. Two replications of the heating and frying procedure were conducted on each of the seven oils.

Additional bread cubes were fried in fresh Crisco® oil (unhydrogenated soybean oil) or in Puritan® oil (unhydrogenated canola oil), which were purchased from a local grocery store. These cubes were stored at −10°C in double freezer bags with the air pressed out by hand and they were used as references during sensory evaluation.

Chemical analyses. The tocopherol and sterol contents of oils were determined by gas-liquid chromatography of the saponified and extracted compounds on a 30 m × 0.32 mm i.d. capillary column (with a 0.5-μm film of cross-linked 5% phenylsilicone and 95% methylsilicone; Supelco, Bellefonte, PA). A Hewlett-Packard Model 5890A gas-liquid chromatograph (GLC) (Palo Alto, CA) equipped with a split-splitless injector (split ratio 100:1) and a flame ionization detector was used. Column temperature was 265°C and injector and detector temperatures were 300°C. Helium, the carrier gas, was set at a flow rate of 1.1

mL/min. Peak areas were measured with a Hewlett-Packard 3390A reporting integrator. Samples were saponified with potassium hydroxide and extracted with ether in a 30-min distillation. The solvents were removed by evaporation under nitrogen. The saponified tocopherols and sterols were dissolved in cholesteryl isovalerate pyridine/butyric anhydride solution and then determined by GLC.

Fatty acid compositions of the oils were measured both at the beginning and at the end of the frying and heating process. Methyl esters of the fatty acids (FAME) of the frying oils were prepared by transesterification of the oils with sodium methoxide in methanol (12). Fatty acid compositions were determined by GLC of the methyl esters with a 6.0 ft × 0.085 in stainless-steel packed column (100/120 Gas Chrom QII with 10% Silar 10°C coating; Alltech Associates, Deerfield, IL). A Varian Aerograph series 3700 GLC (Varian Associates, Palo Alto, CA) equipped with a flame ionization detector was used. Chromatographic parameters were as follows–injector, detector and column temperatures, 220°C, 250°C and 170°C, respectively; carrier gas, nitrogen, at 20 mL/min. The peak areas were measured with a Hewlett-Packard 3390A reporting integrator.

Peroxide values (PV) of the oils extracted from the bread cubes and conjugated dienoic acid (CDA) values of the oils used for heating and frying were used to determine the extent of deterioration of oils during the test conditions. The CDA of the unheated oils (0 h, 20 h and 40 h of heating and frying) were measured according to AOCS official method Ti-la-64 (13).

Because peroxides are unstable and do not accumulate in heated oil, the PV is not a good indicator of frying oil deterioration (14,15). However, the PV can be used to measure oil oxidation once a fried product has been cooled and/or stored. The PV of the oils extracted from the cubes were determined by the Stamm test (16) whenever sensory tests were held. The oil was extracted from 20 bread cubes by 25 mL distilled hexane in a 20-min extraction, and the solvent was removed by rotary evaporation as described elsewhere (17). All test results are the averages of duplicate analyses from duplicate heating and frying procedures.

Sensory evaluation. Twelve trained panelists evaluated the fried bread cubes at room temperature for quality of fried bread flavor (18) and intensity of oxidized flavor (19). On the flavor quality scale, 10 is excellent and 1 is extremely poor; on the flavor intensity scale, 10 is bland and 1 is an extremely intense flavor. The panelists were trained by judging fresh and stored bread cubes fried in Crisco and Puritan vegetable oils as previously described (18). Five training sessions were conducted to develop agreement on oxidized flavor scores.

The fried cubes were presented at room temperature and in random order. The panelists were instructed to smell the cubes first and then to taste them in an approximate order of increasing odor intensity. This procedure reduced the possibility of a strongly oxidized sample overwhelming a panelist's ability to evaluate less oxidized cubes before all samples were judged. Panelists were instructed to expectorate after chewing and evaluating each sample. Distilled water and unsalted crackers were provided to rinse and remove the oxidized flavor from their mouths. The thawed fresh cubes that had been fried in Crisco oil and stored at −10°C were provided as a reference in judging the samples. Sensory evaluations were conducted on cubes fried at 40 and 0 h of heating and then stored at 60°C for seven days.

Statistical analysis. The data were analyzed by Analysis of Variance (ANOVA), Duncan's Multiple Test (Duncan's Test) and linear regression (20). Pearson correlation coefficients were determined from mean values of the two replicates. Statistical significance was accepted at a level of $P < 0.05$.

RESULTS

Chemical analyses. The FAME compositions of the oils at the beginning (0 h) and at the end (40 h) of the heating and frying process are shown in Table 1. The FAME compositions of the fresh commercial oils used as controls for sensory analysis also are shown. The A17 and A16 oils had less 18:3 and 18:2, and more 18:1, 18:0 and 16:0 than did Hardin and BSR 101 oils. The A87 oil had slightly more 18:1 and 18:0 than did Hardin and BSR 101, whereas A6 oil had less 16:0, 18:1 and 18:2, but about seven times more 18:0 than the two commercial varieties. Canola oil was high in 18:3 and 18:1, but low in 18:2, 18:0 and 16:0 as compared with soybean oils.

A decrease in the relative percentage of unsaturated fatty acids and an increase in the relative percentage of saturated fatty acids occur when oils are heated (17,21). This pattern was observed in all oils after 40 h of heating and frying (Table 1). The higher the initial 18:3 content of the oil, the greater the loss of the 18:3 during heating and frying. In a previous study (22), however, no change was found in fatty acid compositions after partly hydrogenated canola oil and partly hydrogenated soybean oil were heated at 185 ± 2°C for 75 h. But oils used in that study contained an antifoam agent and stabilizers and had lower 18:3 contents than those used in the present study.

The PV of oils extracted from bread cubes fried at 0 h and 40 h of heating and from bread cubes fried at 0 h of heating and stored at 60°C for seven days are shown in Table 2. Significant differences were noted in the oils from bread cubes fried in fresh oils (0 h) and stored for seven days. The oils extracted from the cubes fried in the A17, A87 and A6 oils had significantly lower PV ($P < 0.05$) than did those from the cubes fried in Hardin, BSR 101, A16 and canola oils. The amounts of peroxides formed after seven days of storage tended to follow the order of the initial amounts of 18:3 and the polyunsaturated fatty acid (PUFA) (18:2 and 18:3) contents of the oils. Canola oil also had a significantly higher PV ($P < 0.05$) at 0 h of heating than did the other oils. No significant difference was observed among the oils extracted from the cubes fried at 40 h of heating. During storage of the cubes, canola oil deteriorated faster than did the oils from A17, A87 and A6 and tended to be higher than the other soybean oils, likely because of its higher 18:3 content.

The CDA values of oils heated for up to 40 h (Table 3) did not differ significantly ($P < 0.05$) from one another after 0 h of heating, but the CDA value of BSR 101 tended to be higher than the other oils at 20 and 40 h of heating. At 0 h of heating, the CDA value of canola oil was significantly higher ($P < 0.05$) than that of the other oils, likely because of canola oil's high 18:3 content. The

TABLE 1

Fatty Acid Composition (relative area %) of Oils Before and After Heating and Frying Bread Cubes at 180°C

Oil type	Relative fatty acid composition by GLC, %[a]					
	16:0	18:0	18:1	18:2	18:3	18:2 + 18:3
Hardin						
Beginning values	10.6	3.6	25.2	54.8	5.9	60.7
Ending values[b]	18.1	6.8	37.5	36.1	1.2	37.3
BSR 101						
Beginning values	10.2	3.8	22.6	56.7	6.8	63.5
Ending values	18.1	7.0	34.0	39.4	1.6	41.0
A17						
Beginning values	15.1	5.1	29.3	49.4	1.5	50.9
Ending values	25.5	9.3	39.3	25.3	0.3	25.6
A16						
Beginning values	10.6	5.6	31.8	50.7	1.9	52.6
Ending values	17.9	9.6	42.8	29.0	0.3	29.3
A87						
Beginning values	10.3	4.5	29.1	54.7	1.8	56.5
Ending values	17.2	7.3	40.7	33.9	0.5	34.4
A6						
Beginning values	8.5	27.7	21.5	40.4	4.1	44.5
Ending values	11.9	38.9	26.1	21.8	1.2	23.0
Canola						
Beginning values	3.8	1.4	63.0	21.3	10.3	31.6
Ending values	5.6	2.1	74.4	13.1	3.8	16.9
Crisco®[c]	10.7	4.1	24.8	53.5	6.7	60.2
Puritan®[c]	4.2	1.9	65.0	20.4	8.6	29.0

[a]Values represent the average of duplicate runs of two replicates.

[b]After 40 h heating and frying.

[c]Values of fresh oils used as controls for sensory analyses.

TABLE 2

Peroxide Values[a] of Oils Extracted from Bread Cubes Fried (180°C) at 0 h of Heating, after 40 h of Heating, and from Cubes Stored for Seven Days After Frying at 0 h

Oil type	Heating time of oil		Cubes stored for 7 days
	0 h	40 h	
Hardin	0.2[b]	3.1[b]	92.3[b]
BSR 101	0.1[b]	3.3[b]	81.4[b]
A17	0.2[b]	3.5[b]	63.8[c]
A16	0.2[b]	2.6[b]	76.5[b]
A87	0.1[b]	3.4[b]	66.7[c]
A6	0.2[b]	3.5[b]	65.1[c]
Canola	0.3[c]	4.3[b]	110.7[b]

[a]Values represent the average of duplicate analyses of two replicates.

[b,c]Values in the same column with different superscript letters are significantly different ($P < 0.05$) as measured by Duncan's Test.

TABLE 3

Conjugated Dienoic Acid Values[a] of Oils During Heating and Frying at 180°C

Oil type	0 h	20 h	40 h
Hardin	0.14[b]	3.38[b]	3.53[b]
BSR 101	0.16[c]	4.06[b]	4.48[b]
A17	0.16[c]	3.32[b]	3.60[b]
A16	0.12[b]	3.24[b]	3.39[b]
A87	0.13[b]	2.92[b]	3.38[b]
A6	0.28[d]	2.76[b]	2.93[b]
Canola	0.70[e]	2.17[b]	2.61[b]

[a]Values represent the average of duplicate analyses of two replicates.

[b-e]As in Table 2.

CDA values of canola oil at 20 and 40 h of heating tended to be lower than those of all the soybean oils used in this study, perhaps because the 18:3 double bonds stopped shifting after 20 h of heating and canola oil had a relatively low 18:2 content to contribute to additional CDA formation. The order of the CDA values of soybean oils at 40 h of heating tended to follow the order of the PUFA contents in the oils (Tables 1 and 3). The higher the PUFA content, the higher the CDA value.

Frankel (23) suggested that even a low level of 18:3 hydroperoxides might catalyze the oxidation of 18:2, the predominant fatty acid in soybean oils. The rapid oxidation of 18:2, catalyzed by the 18:3 hydroperoxides, may explain why the soybean oils formed CDA so quickly as compared with canola oil.

Sensory evaluation. Several studies have compared the sensory qualities of French fries or bread cubes fried in various types of oils and fats (1,2,4,19,21). Fresh bread cubes were chosen in this study because of their availability and their uniform size and moisture content.

The flavor quality and flavor intensity scores of the cubes fried at 0 and 40 h of heating of the oils and after storage of cubes fried at 0 h are shown in Tables 4 and 5, respectively. There were no significant ($P < 0.05$) differences in sensory quality or intensity scores among the cubes fried at 0 h and at 40 h of heating of the oils. But significant differences ($P < 0.05$) were noted after seven-day storage of the cubes fried at 0 h of heating. The cubes

TABLE 4

Flavor Quality Scores[a] of Bread Cubes Fried (180°C) at 0 h of Heating, After 40 h of Heating and of Cubes Stored for Seven Days After Frying at 0 h

Oil type	Heating time of oil		Cubes stored for 7 days
	0 h	40 h	
Hardin	8.2[b]	7.1[b]	3.7[b]
BSR 101	7.8[b]	6.3[b]	3.3[b]
A17	7.6[b]	6.3[b]	6.0[c]
A16	8.2[b]	6.7[b]	5.9[c]
A87	8.0[b]	7.3[b]	6.4[c]
A6	7.8[b]	6.6[b]	5.8[c]
Canola	6.9[b]	6.0[b]	2.9[b]

[a]Values represent the average of duplicate analyses of two replicates.
[b,c]As in Table 2.

TABLE 5

Flavor Intensity Scores[a] of Bread Cubes Fried (180°C) at 0 h of Heating, After 40 h of Heating and of Cubes Stored for Seven Days After Frying at 0 h

Oil type	Heating time of oil		Cubes stored for 7 days
	0 h	40 h	
Hardin	8.2[b]	7.2[b]	3.4[b]
BSR 101	8.0[b]	6.4[b]	3.1[b]
A17	7.5[b]	6.8[b]	6.1[c]
A16	8.3[b]	6.7[b]	6.0[c]
A87	8.2[b]	6.3[b]	6.8[c]
A6	7.5[b]	6.3[b]	6.1[c]
Canola	7.0[b]	5.7[b]	2.7[b]

[a]Values represent the average of duplicate analyses of two replicates.
[b,c]As in Table 2.

fried in the A17, A16, A87 and A6 oils were judged significantly ($P < 0.05$) higher in both flavor categories than the cubes fried in Hardin, BSR 101 and canola oils. Panel members described the cubes fried in canola oil as having a strong fishy odor, even when fried at 0 h of heating, which may have been caused by the high 18:3 content of the oil. The fishy odor became especially noticeable after storage for seven days, when the oil was highly oxidized, as measured by the PV test. In a related study of room-temperature storage (11), the A6 oil scored low in both flavor categories, perhaps because of its semi-solid properties at low temperature. When heated or used for frying, differences in oil consistency were not noticed.

DISCUSSION

The flavor quality and intensity scores of the cubes stored for seven days and the PV scores of the oils extracted from the cubes fried in fresh oils and stored for seven days generally followed an order similar to that of the 18:3 contents of oils before frying. Miller and White (17) reported that the 18:3 content sometimes predicts the relative flavor stabilities of oils at high-temperature oxidation. The A17, A87 and A6 oils were more stable to heat deterioration than Hardin, BSR 101 and canola oils as measured by PV and sensory evaluations.

TABLE 6

Correlation Coefficients and Probability Levels Among Selected Test Results

Total measurements	Correlation coefficients	Probability level
18:3[a] *vs.* PV[b]	0.89	0.008
18:3 *vs.* Flavor quality[c]	−0.93	0.002
18:3 *vs.* Flavor intensity	−0.91	0.004
PV *vs.* Flavor quality	−0.87	0.01
PV *vs.* Flavor intensity	−0.87	0.01
CDA[d] *vs.* PUFA[a]	0.87	0.01

[a]18:3, initial values; PUFA, initial values.
[b]PV of oils extracted from the fried cubes stored at 60°C for seven days.
[c]Flavor quality and flavor intensity scores of fried cubes stored at 60°C for seven days.
[d]CDA of oils heated for 40 h.

The oils from A17, A16 and A87 had similar 18:3 and PUFA contents and similar flavor quality and intensity scores for the bread cubes fried in the fresh oils and stored for seven days. The PV of the A16 oil extracted from the cubes fried in fresh oil and stored for seven days was significantly higher ($P < 0.05$) than those of the other two oils. The A6 oil had much less PUFA content than all other soybean oils, but an intermediate amount of 18:3, likely explaining its similar stability to that of A17 and A87 oils.

The CDA values of the oils at 40 h of heating, although showing no significant differences, tended to follow the order of the PUFA contents of the oils, except for canola oil. The flavor scores in both categories of the cubes fried at 40 h of heating were not significantly different from each other.

Formation of hydroperoxides normally coincides with the conjugation of double bonds of the PUFA of oils when oxidized at room temperature and at frying temperature (14,15). The conjugated dienes absorb UV light at a wavelength of 233 nm (11). The single allylic methylene group (-CH=CH-CH_2-) in oleate (18:1) has a bond strength estimated at 77 kcal/mole, whereas 52 kcal/mole is estimated for the double allylic methylene (-CH=CH-CH_2-CH=CH-) in linoleate (18:2) (4). Linolenate (18:3) has two double allylic methylene groups (-CH=CH-CH_2-CH=CH-CH_2-CH=CH-), but neither is activated by the other. Thus, the two double allylic methylene structures make 18:3 about two times more likely to shift and form a CDA than 18:2 (4).

The correlations between initial 18:3 contents of oils and PV of oils extracted from the fried cubes stored at 60°C for seven days, and of flavor quality and intensity scores of the fried cubes, are shown in Table 6. All correlations were high and were highly significant.

High correlations and probability levels between PV of oils from fried bread cubes after seven days storage at 60°C and flavor quality and flavor intensity scores of the stored cubes also are shown in Table 6. The CDA values of heated oils were highly correlated with their initial PUFA contents, and the flavor quality and intensity scores were highly correlated with each other ($r = 1.00$, $P = 0.001$). The PV of oils extracted from cubes stored for

seven days and the initial 18:3 content of the oils were poorly correlated with the CDA of the oils heated for 40 h ($r = -0.28$, $P = 0.54$ and $r = -0.20$, $P = 0.67$, respectively). During heating and frying, the initial PUFA content predicted the CDA values of oils better than their 18:3 contents did.

The results of sensory evaluations of fried bread cubes, the PV of the oils extracted from the fried cubes, and the CDA values of the oils during heating and frying showed significant ($P < 0.05$) improvement of these new experimental soybean oils over traditional soybean oils and canola oil, especially after storage of the fried bread cubes for seven days. The new soybean oils, with their improved flavor and oxidative stabilities, may be suitable as deep-fat frying oils. The initial 18:3 contents were excellent predictors of PV and of flavor scores, and PV correlated with the flavor scores. The CDA values were less useful in relating to other flavor predictors.

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