

# Frying Quality and Stability of Low- and Ultra-Low-Linolenic Acid Soybean Oils

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**ABSTRACT:** To determine effects of very low levels of linolenic acid on frying stabilities of soybean oils, tests were conducted with 2% (low) linolenic acid soybean oil (LLSBO) and 0.8% (ultra-low) linolenic acid soybean oil (ULLSBO) in comparison with cottonseed oil (CSO). Potato chips were fried in the oils for a total of 25 h of oil use. No significant differences were found for either total polar compounds or FFA between samples of LLSBO and ULLSBO; however, CSO had significantly higher percentage of polar compounds and FFA than the soybean oils at all sampling times. Flavor evaluations of fresh and aged (1, 3, 5, and 7 wk at 25°C) potato chips showed some differences between potato chips fried in different oil types. Sensory panel judges reported that potato chips fried in ULLSBO and aged for 3 or 7 wk at 25°C had significantly lower intensities of fishy flavor than did potato chips fried in LLSBO with the same conditions. Potato chips fried in ULLSBO that had been used for 5 h and then aged 7 wk at 25°C had significantly better quality than did potato chips fried 5 h in LLSBO and aged under the same conditions. Hexanal was significantly higher in the 5-h LLSBO sample than in potato chips fried 5 h in ULLSBO. The decrease in linolenic acid from 2 to 0.8% in the oils improved flavor quality and oxidative stability of some of the potato chip samples.

Paper no. J10457 in *JAOCs* 80, 275–280 (March 2003).

**KEY WORDS:** Cottonseed oil, flavor, fried food, frying, linolenic acid, low-linolenic acid soybean oil, oxidation, polar compounds, potato chips, soybean oil.

Linolenic acid-containing vegetable oils such as canola and soybean produce off-flavors and odors when they are oxidized. In the late 1940s, Evans and co-workers began publishing a series of papers on the flavor problems of soybean salad oil. Some of these studies reported that the linolenic acid content of soybean oil was a major source of the flavor problems for this oil (1–3). In these investigations, “painty” was a primary flavor characteristic in oxidized soybean salad oils that was attributed to the linolenic acid content. Evans *et al.* (2) found that the linolenic acid content needed to be decreased to less than 5% to improve the flavor quality and oxidative stability of soybean oil. Similar results with canola oil have shown that linolenic acid is a major factor in the instability of this oil in autoxidation studies (4). On the other hand, when linolenate-containing oils are heated to high temperatures as

in frying, linolenic acid is thought to be responsible for the fishy odor and flavor in these heated oils and in the resulting fried food. In attempts to solve the linolenic acid problem, studies on soybean and canola oils with a wide range of linolenic acid contents have been published (5–18). Methods to reduce the linolenic acid content in soybean oil from the usual 8–9% include blending with more saturated or monounsaturated oils, hydrogenation, and plant breeding. Mounts *et al.* (18) compared three unhydrogenated soybean oils of reduced linolenic acid content (1.7, 1.9, and 2.5%) with unhydrogenated soybean oil containing 6.5% linolenic acid and reported improved room odor of heated oils with decreasing linolenic acid. Many researchers found that reducing the linolenic acid level to less than 3% improved heated oil stability. Tompkins and Perkins (17) reported that a reduction of linolenic acid to 2.3% in a modified soy oil was not as good as hydrogenated soybean oil with 1.4% linolenic acid as judged by instrumental and chemical analyses of the oil. Warner and Mounts (10) compared frying stability of low-linolenic, unhydrogenated, and hydrogenated soybean and canola oils to unhydrogenated soybean and canola salad oils. The oils that had linolenic acid contents ranging from 3.7 to 0.4% were rated as having less room odor intensity; lower FFA contents, polar compounds, and foam heights; lower intensity of off-odors; and they produced better-quality fried food than the unmodified oils. However, hydrogenated oils were found to have waxy, fruity odors/flavors typical of some hydrogenated oils, but oils that had the linolenic acid content reduced by plant breeding did not have this flavor problem. Plant geneticists need recommendations on the levels of fatty acids to target in modifying oilseed composition. The optimal level of linolenic acid in soybean oil has never been established, because the level of linolenic acid needed to eliminate off-flavors and odors probably varies depending on the type of oil and on the type of fried food. Previously, the linolenic acid content of soybean oils has not been reduced below 1% except by hydrogenation or by a combination of modified oilseed plus later hydrogenation. A new cultivar of soybean yielding oil with only 0.8% linolenic acid was of interest because of the low linolenate level produced without the need for hydrogenation. The objectives of this study were to determine whether reducing the linolenic acid content to very low levels (0.8%) and to low levels (2%) by plant breeding improved soybean oil compared to cottonseed oil (CSO) in frying stability tests and in shelf-life tests of potato chips fried in these oils.

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## EXPERIMENTAL PROCEDURES

**Materials.** Cottonseed oil (CSO) (Archer, Daniels, Midland Company, Decatur, IL), low-linolenic acid soybean oil (LLSBO) (Protein Technologies International, St. Louis, MO) and ultra-low-linolenic acid soybean oil (ULLSBO) (Protein Technologies International) were commercially processed. No oils contained additives other than citric acid. No. 1 Idaho Russet potatoes were obtained from a local market.

**Methods.** FA compositions of the initial oils were determined by capillary GC analysis with a Hewlett-Packard 5890 gas chromatograph equipped with an SP2330 column (30 m, 0.20 mm i.d., 0.20  $\mu$ m film thickness) (Supelco, Bellefonte, PA). Column temperature was held at 190°C for 5 min and temperature was programmed to 230°C at 20°C/min. Other GC conditions were: injector, 250°C; detector, 260°C. FFA values were measured as percent oleic acid by AOCS method Ca 5a-40 (19). Initial oxidation of the fresh oils was measured in duplicate by PV (AOCS method Cd 8-53) (19). Total polar compound levels of the oils were determined in duplicate by the AOCS column chromatography method (19). Hexanal content of the aged potato chips was analyzed in triplicate with a purge-and-trap apparatus equipped with a test tube adapter (Tekmar model 3000; Tekmar-Dohrmann Co., Cincinnati, OH) coupled with a Varian model 3400 gas chromatograph and a Saturn model 3 ion trap mass spectrometer (Varian, Inc.). A 50-mg potato chip sample was placed in a 1.9  $\times$  7.6 cm test tube and heated at 100°C for 9 min preheat time. Volatile compounds were trapped on a 30.5 cm Tenax #1 trap, with 10 min sample purge time, 170°C for 6 min desorbing, 180°C MCS desorb temperature, 160°C GC transfer line and valve temperature. Volatile compounds were introduced onto a DB-1701 GC capillary column (30 m  $\times$  0.32 mm with 1  $\mu$ m film thickness) (J&W Scientific, Folsom, CA). The column was held at -20°C for 2 min, then heated from -20°C to 233°C at 3°C/min. Column helium flow rate was 2 mL/min with 28 mL/min injector split vent flow. The GC injector was set at 240°C, and the line to the mass spectrometer was set at 230°C. The ion trap mass spectrometer operated in EI mode with mass scan range 23 to 400  $m/z$  over 0.8 s. Filament emission current was 25  $\mu$ A, axial modulation was 2.1 V, manifold heater was set at 160°C, and filament/multiplier delay was 2.5 min. Compound structural identifications were made both from spectral comparisons with the NIST 92 MS library (Varian, Inc.) and from retention time comparisons with standard compounds.

**Frying stability.** Frying protocol included intermittent frying at 190°C with total heating/frying time of 25 h over a 3-d period. At the start of each frying test, 9 L of each oil was placed in 16-L capacity fryers (Model EL250; Cecilware, West Palm Beach, FL). Fresh Idaho Russet potatoes were peeled then sliced 1-mm thick and rinsed several times in cold water. Slices were dried, then fried in 120-g batches. Oil samples were taken at the end of 5, 15, and 25 h of frying. Fresh oil was added as makeup oil after 5, 10, 15, and 20 h of frying to maintain the original amount of oil in the fryer. Samples of potato

chips were collected for analyses when oil had been used for 5, 15, and 25 h. Potato chips were placed in 1-L wide-mouth glass jars with air in the headspace, and jars were closed with screw-caps. Potato chips were either aged in the jars in the dark for 1, 3, 5, and 7 wk at 25°C, then frozen until analyses, or frozen immediately as 0-time samples. The 16 members of an analytical descriptive sensory panel, trained and experienced in evaluating fried foods, were presented with 5 g crushed potato chip samples in 59.2 mL (2 oz) plastic souffle cups with snap-on lids (Solo Cup Company, Urbana, IL). Panelists rated the potato chips for intensities of individual flavors including fried food, stale, cardboard, rancid, old oil, and fishy on a 10-point intensity scale with 0 = no intensity and 10 = strong flavor intensity. They also rated overall flavor quality of the potato chips on a 10-point quality scale with 10 = excellent and 1 = bad. All sensory evaluations were conducted in a panel room with individual booths, temperature control, and red lighting to mask color differences between samples (20).

**Statistical analysis.** Data were evaluated by ANOVA (21). Statistical significance was expressed at the  $P < 0.05$  level unless otherwise indicated. Error bars indicate SD of each mean.

## RESULTS AND DISCUSSION

**FA composition.** Compositions of the oils showed that the linolenic acid contents were 2.0 and 0.8% for the LLSBO and ULLSBO, respectively (Table 1). In comparison to an unmodified soybean oil, the linoleic acid contents of these oils were increased slightly from the typical 55% because of the decreased linolenic acid levels. Linoleic acid contents were slightly less for CSO (52.3%) compared to 58.2% for ULLSBO and 59.7% for LLSBO. Saturated fat levels were similar in both soybean oils. Oleic acid levels were 24.8% in the ULLSBO and 22.4% in the LLSBO. Composition of the CSO was standard for this oil type (22).

**Initial oil quality.** Initially, all PV were zero or at low levels of 0.9 or less. In the fresh oils, total polar compound levels (Fig. 1) were low in the ULLSBO at 1.5%, and in the LLSBO at 2.8%, but the CSO had 5.7% total polar compounds, which is typical for a fresh unheated CSO (22). In the fresh oils, FFA levels were 0.07% for LLSBO, 0.08% for ULLSBO, and 0.10% for CSO (Fig. 2).

**Frying stability.** Total polar compound formation was used as a chemical measure of high-temperature degradation of the

**TABLE 1**  
Fatty Acid Compositions (%) of Cottonseed Oil (CSO), Low-Linolenic-Acid Soybean Oil (LLSBO), and Ultra-Low-Linolenic Acid Soybean Oil (ULLSBO)

Fatty acid	CSO	LLSBO	ULLSBO
14:0	0.9	0.0	0.0
16:0	25.5	11.3	11.5
18:0	2.5	4.7	4.6
18:1	17.7	22.4	24.8
18:2	52.3	59.7	58.2
18:3	0.1	2.0	0.8

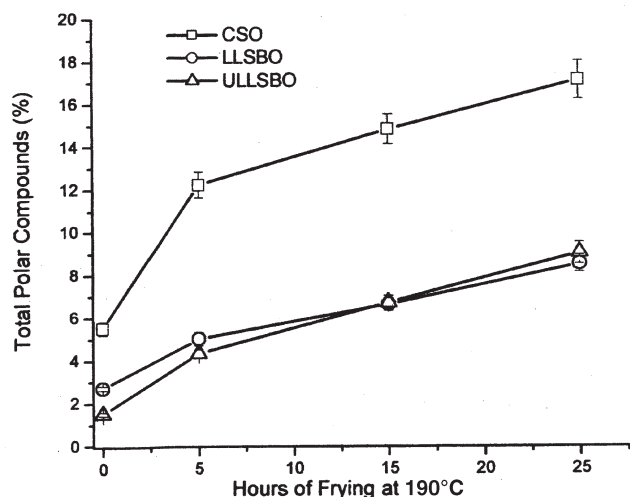


FIG. 1. Total polar compounds (%) in cottonseed oil (CSO), low-linolenic-acid soybean oil (LLSBO), and ultra-low-linolenic acid soybean oil (ULLSBO) at 0-time and after frying potato chips for 5, 15, and 25 h at 190°C. Error bars indicate SD of each mean.

fraying oils. Polar compound levels increased to 4 and 4.1% for the SBO samples and to 12.1% for the CSO after 5 h frying (Fig. 1). By 25 h frying, the CSO had 17% polar compounds and the SBO samples had 8.5 and 9%. Initially, the fresh oils showed significant differences in polar compound levels with CSO having the highest amount at 5.7% and ULLSBO the lowest at 1.7%. At 0-time and after 5 h, significant differences were noted between the two soybean oils; however, at 15 and 25 h, polar compound levels were not significantly different between these two oils. Both soybean oils had significantly lower polar compound formation than did the CSO at all sampling times. Tompkins and Perkins (17) reported that the polar compound levels in soybean oil with 2.3% linolenic acid ranged from 3.3% initially to 16.8% after 120 h of frying fish and potatoes in small fryers, which tend

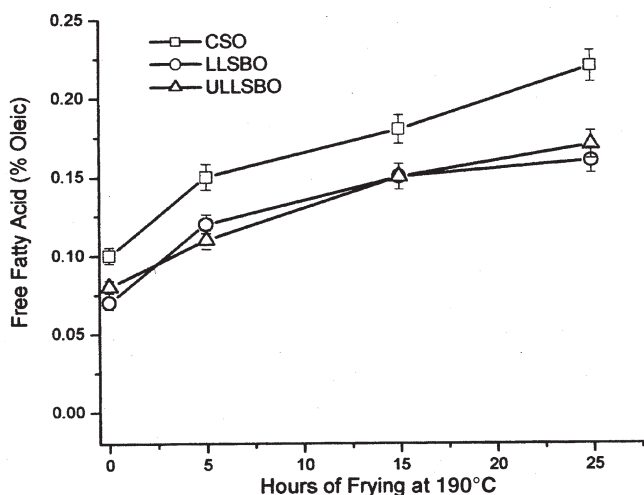


FIG. 2. FFA (% oleic acid) in CSO, LLSBO, and ULLSBO at 0-time and after frying potato chips for 5, 15, and 25 h at 190°C. For abbreviations see Figure 1.

to increase oil degradation compared to larger fryers. FFA analysis was used to determine effects on hydrolysis in the frying oils. FFA increased with increasing frying time in all oils (Fig. 2). No significant differences were noted between the FFA for the two soybean oils; however, FFA levels were significantly higher in the CSO than in either of the soybean oils at all sampling times.

*Flavor quality of potato chips.* The best index of the quality of frying oils is the flavor of the fresh and aged food fried in the oil. Sensory analyses were conducted on potato chips sampled after the oils were used for 0, 5, 15, and 25 h of frying. Sensory panelists evaluated the potato chips for both positive flavors, such as fried food and potato, and negative flavors, such as stale, cardboard/flat, fishy, and rancid. These negative flavors are usually produced by increased fry time of the oil and/or by increased aging time of the fried food. For potato chips fried in oils used for only 5 h, quality ratings did not decrease much because of aging (Fig. 3). The only significant difference between oil types was at 7 wk when the potato chips fried in ULLSBO had a significantly higher quality score than the potato chips fried in LLSBO or CSO. The potato chips fried in the oils used for 5 h are typical of potato chips fried in commercial operations because the chemical indices of FFA and total polar compounds for the soybean oils in this study were similar to what might be found commercially. For potato chips fried in oils used for 15 or 25 h, all oil types showed significant decreases in flavor scores between the 0-time and 7-wk aging, although the scores indicated the ratings decreased only from good to fair quality (Fig. 3). In the oils used for frying for longer periods of time (15 and 25 h), no significant differences were noted between oil types in the overall flavor quality of the potato chips.

Some of the reasons for the changes in flavor quality scores are related to the intensity levels of both the positive and negative flavors that can have significant effects on the quality of the potato chips. For example, the fried food flavor intensity of the potato chips fried in the 5-h ULLSBO and aged for 7 wk (Fig. 4) was significantly higher than for the potato chips fried in CSO. This result can help explain the higher flavor quality score for the sample fried in ULLSBO (Fig. 3), although lower intensities of negative flavors also affect the overall flavor quality as can be seen in Figures 5–7. Fried food flavor intensities of potato chips fried in oils used for 15 or 25 h (data not presented) were similar to those of the 5-h oils (Fig. 4).

As fried food ages during storage, fried food flavor intensity can increase in the early stages of storage, especially if the fried food flavor intensity is not high in the freshly prepared food (22). Potato chips fried in ULLSBO showed a slight increase in the intensity of fried food flavor from the 0-time sample to the sample aged 1 wk at 25°C (Fig. 4).

Cardboard/flat flavor can be evident in slightly aged fried food and usually is indicative of very early oxidation. For example, cardboard flavor increased slightly in the early stages of oxidation (Fig. 5) for potato chips fried in the oils used for 5 h; however, the differences were not significant. The intensities of the cardboard flavor were low at all times for all samples

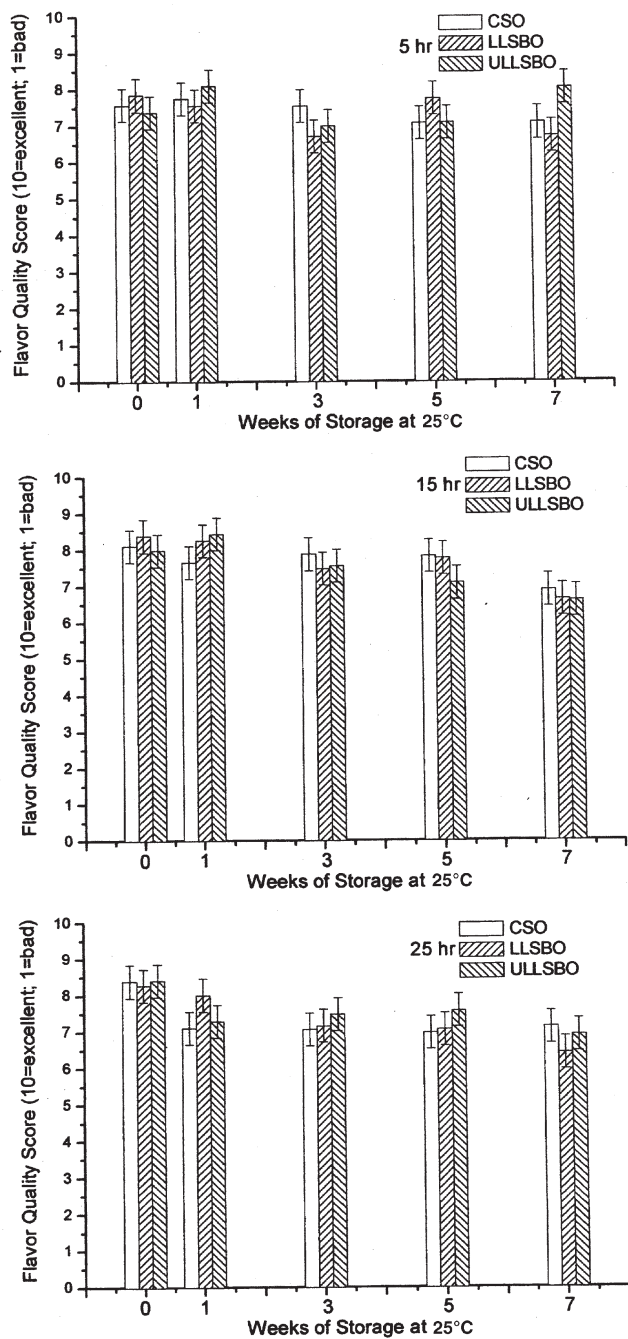


FIG. 3. Flavor quality scores of potato chips fried in CSO, LLSBO, and ULLSBO used 5, 15, or 25 h and aged for 0, 1, 3, 5, or 7 wk at 25°C. For abbreviations see Figure 1.

fried in oils used for 5 h. The profile for the cardboard flavor intensity at 5 hr was similar to the results for samples at 15 and 25 h. Stale flavor is usually evident after the early stage of oxidation as the intensity of positive flavors such as fried food decrease but before any flavors indicative of greater oxidation such as rancid or painty can be detected. Potato chips aged 3 wk at 25°C had the highest intensities of stale flavor, although the intensity values were only at the weak level (2.2) (Fig. 6). Potato chips fried in ULLSBO had significantly less

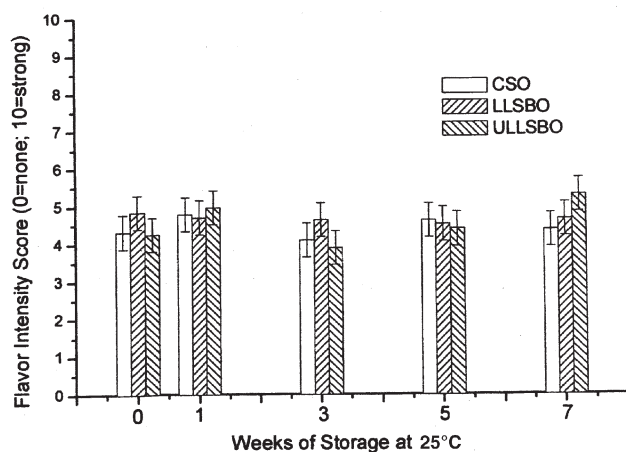


FIG. 4. Fried food flavor intensity of potato chips fried in CSO, LLSBO, and ULLSBO used 5 h and aged for 0, 1, 3, 5, or 7 wk at 25°C. For abbreviations see Figure 1.

stale flavor than the potato chips fried in CSO at the 7-wk storage time. This is another possible reason why this potato chip sample had a significantly higher overall flavor quality score than the other samples at 5 h (Fig. 3). Fishy flavor is usually characteristic of oils containing linolenic acid. Soybean and canola oils typically have a characteristic fishy odor and flavor when they are heated to frying temperature and foods fried in these oils can have this same odor and flavor. In previous studies of fried foods, we reported that the fishy flavor was most noticeable in foods fried in fresher rather than abused oils and in fresh and slightly aged foods rather than those aged for longer periods (Warner, K., and W.E. Neff, unpublished data). As frying time and aging increase, flavors that develop as a result of the degradation of other fatty acids such as linoleic acid could possibly mask the fishy flavor, and/or the compounds that are responsible for the fishy attribute can decompose to produce other flavors. In this study, we found only low levels of fishy flavor in the potato

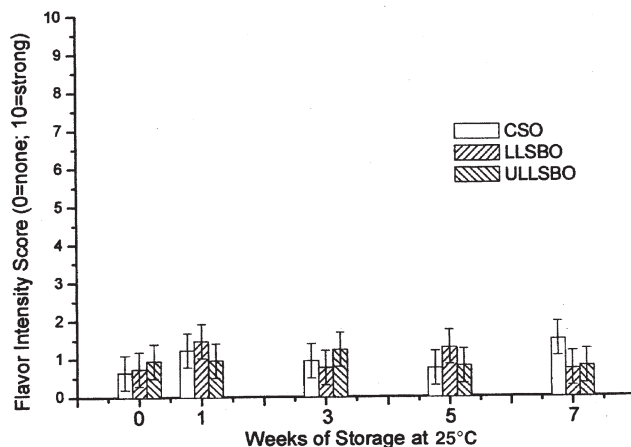


FIG. 5. Cardboard flavor intensity of potato chips fried in CSO, LLSBO, and ULLSBO used 5 h and aged for 0, 1, 3, 5, or 7 wk at 25°C. For abbreviations see Figure 1.

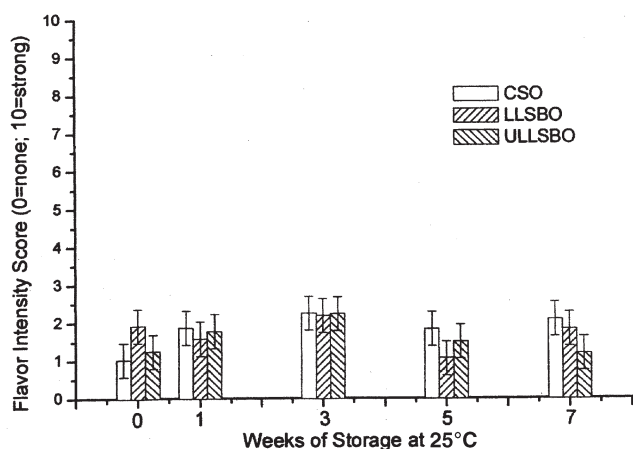


FIG. 6. Stale flavor intensity of potato chips fried in CSO, LLSBO, and ULLSBO used 5 h and aged for 0, 1, 3, 5, or 7 wk at 25°C. For abbreviations see Figure 1.

chips, with the highest intensity at 1.7 on the 0–10 intensity scale for the potato chips fried in the 5-h LLSBO and aged 3 wk at 25°C (Fig. 7). As expected, the potato chips sampled at 15 and 25 h had less fishy flavor than those sampled at 5 h (data not presented). In potato chips fried in the oils used for 5 h, potato chips prepared in LLSBO had significantly higher fishy flavor intensity than potato chips fried in ULLSBO or CSO at the 1-, 3-, and 7-week storage times (Fig. 6). Intensity levels of rancid flavor in the potato chips were at very low levels (<1.0) in all samples, and no significant differences were noted because of oil type, amount of frying time, or length of storage (data not shown). Panelists did not detect painty flavor in any of the samples.

*Oxidative stability of potato chips.* Volatile compounds indicative of linolenic acid degradation showed few differences between samples. Therefore, hexanal, which is an excellent marker for the oxidative stability of linoleic acid-containing oils and foods (23), was chosen as the primary compound to

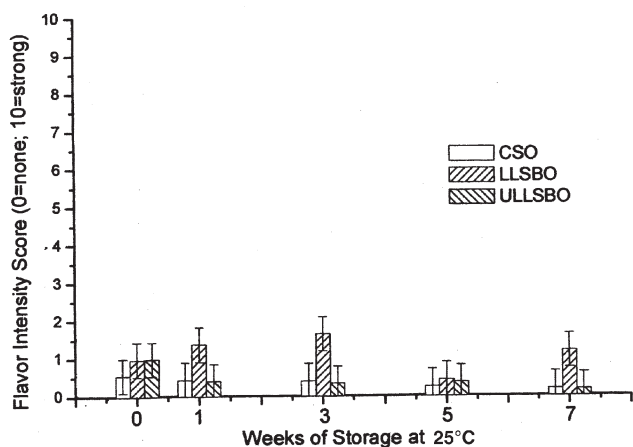


FIG. 7. Fishy flavor intensity of potato chips fried in CSO, LLSBO, and ULLSBO used 5 h and aged for 0, 1, 3, 5, or 7 wk at 25°C. For abbreviations see Figure 1.

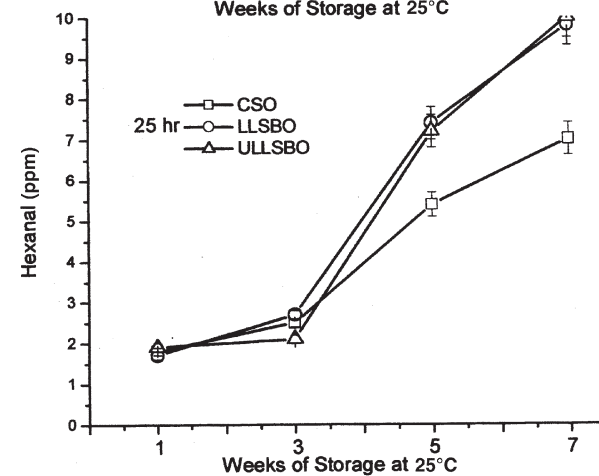
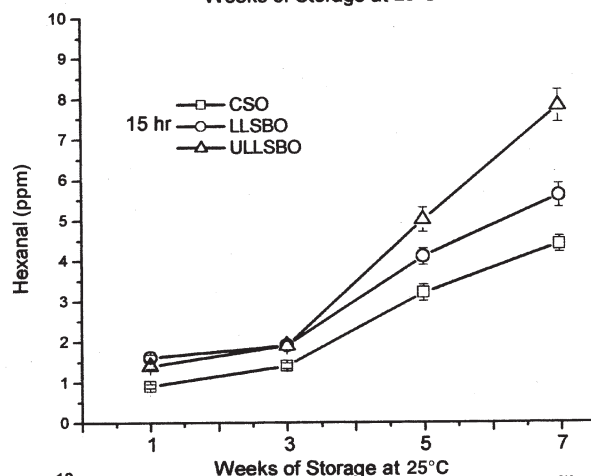
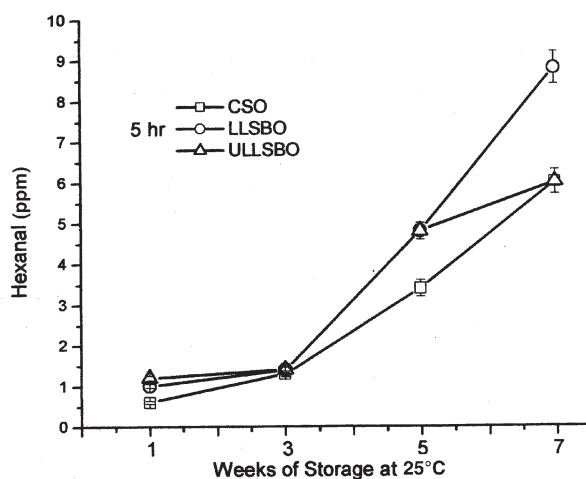


FIG. 8. Hexanal content of potato chips fried in CSO, LLSBO, and ULLSBO at 5, 15, or 25 h of frying time at 190°C and aged for 1, 3, 5, or 7 wk at 25°C. For abbreviations see Figure 1.

monitor because of the high levels of linoleic acid in the oils in this study. Analyses of volatiles were conducted on potato chips sampled at 5, 15, and 25 h of oil use, then aged at 1, 3, 5, and 7 wk at 25°C. The induction period for hexanal development was between 3 and 5 wk for all frying times and oil types (Fig. 8). Only slight increases were observed between 1 and 3 wk for potato chips fried in all oil types and at all frying times; however, after the 3 wk, hexanal in the potato chips

began to increase rapidly. With one exception, after 5 and 7 wk, potato chips fried in CSO had significantly less hexanal than did the potato chips fried in LLSBO or ULLSBO. No significant difference was noted between potato chips fried in CSO or ULLSBO for the 5-h/7-wk samples (Fig. 8). Low hexanal levels in this study at <10 ppm did not appear to have much effect on flavor scores. The primary reason for the differences in hexanal content of the potato chips is probably related to the differences in linoleic acid in the oil, with CSO containing 52.3%, ULLSBO 58.2%, and LLSBO 59.7%, respectively (Table 1).

Previous studies of soybean and canola oils with less than 1% linolenic acid required the combination of oilseed modification by plant breeding with later hydrogenation. Several studies that included chemical and physical analyses of these oils discovered that hydrogenation of LLSBO did not necessarily improve the oil further even though the linolenic acid content was lower. Warner and Mounts (10) found that hydrogenated LLSBO (0.4% linolenate) had higher FFA levels than the oil with 3.7% linolenic acid, which was confirmed by Tompkins and Perkins (17). Tompkins and Perkins (17) reported that hydrogenated LLSBO with 0.1% linolenic acid had lower polymeric content than LLSBO (2.3% linolenate) and two partially hydrogenated soybean oils (0.4 and 1.4% linolenate). However, the hydrogenated LLSBO showed no differences in polar compound content, foam height, and red color compared to the hydrogenated oils. Unfortunately, chemical and physical analyses cannot determine the flavor quality of heated oil or the food fried in it. Warner and Mounts (10) found that the overall room odor intensities of heated LLSBO and low-linolenic acid canola oils were lower than the intensities of the hydrogenated low-linolenic acid oils. The fishy odor intensities were lower in the hydrogenated low-linolenic acid oils than in the low-linolenic acid oils as might be expected, but the hydrogenated oil had the characteristic hydrogenation odors and flavors of waxy and fruity. Finally, the flavor scores of the french-fried potatoes evaluated in that study showed no difference between the low-linolenic acid oils and the hydrogenated low-linolenic acid oils probably because the improvement caused by the decreased fishy flavor intensity was nullified by the increase in undesirable hydrogenation flavor in the hydrogenated oils (10). Results from this present study showed that decreasing the linolenic acid to very low levels did improve the flavor quality of the fried food without the need for further hydrogenation.

## ACKNOWLEDGMENTS

The authors thank Linda Parrott, Wilma Rinsch, Kevin Steidley, and Katie LeGreco for technical assistance and also the NCAUR sensory panel.

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[Received September 30, 2002; accepted January 23, 2003]