Effects of Expeller-Pressed/Physically Refined Soybean Oil on Frying Oil Stability and Flavor of French-Fried Potatoes

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ABSTRACT: To determine effects of expeller pressing/physical refining of soybean oil (SBO) on frying, studies were conducted with expeller-pressed, physically refined, bleached, deodorized SBO (EPSBO); hexane-extracted, refined, bleached, deodorized SBO + TBHQ; and hydrogenated SBO (HSBO). Oils contained citric acid and dimethylpolysiloxane and were used for 35 h of frying french-fried potatoes. Polar compound levels in EPSBO were similar to SBO + TBHQ or HSBO. Flavor quality of potatoes was evaluated by trained, experienced, analytical sensory panelists. In early frying stages, potatoes fried in EPSBO had significantly lower intensities of fishiness than potatoes fried in SBO + TBHQ. Potatoes fried in HSBO were described as "hydrogenated." Because of differences in flavor intensities and types, potatoes prepared in EPSBO had significantly better quality scores than those fried in SBO + TBHQ or HSBO during the first 15 h of frying. During later stages (25 and 35 h), potatoes fried in EPSBO had significantly better quality scores than potatoes fried in HSBO. Variations in minor oil constituents may partly explain these differences. EPSBO had less total tocopherols and phytosterols than did SBO at 0-time. During frying, TBHQ in SBO and Maillard reaction products in EPSBO probably inhibited tocopherol loss and therefore improved quality.

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KEY WORDS: Expeller press, flavor, french-fried potatoes, frying, Maillard reaction products, phospholipids, physical refining, soybean oil, tocopherols.

Mechanical extraction or pressing of vegetable oils is an old technology that is considered an alternative to hexane extraction. Several groups of researchers have studied the characteristics of oils extracted with extruder/expeller processing (1–5). Wang and Johnson (1) found that crude extruder/expeller soybean oil (SBO) had lower levels of phosphorus and FFA than solvent-extracted oil. On the other hand, they showed that crude extruder/expeller SBO had higher PV and lower oxidative stability as measured by the Active Oxygen Method (AOM) than solvent-extracted SBO (1). They speculated that oil handling procedures after extraction rather than the extraction method itself were the cause of the stability effects on PV and AOM. Hill (3) studied stability characteristics of extruded/expelled SBO and found that they had lower FFA, peroxides, and metals compared with crude solvent-extracted SBO. In addition to these scientific studies, anecdotal information exists about the stability effects of expeller technology. For example, Watkins (6) reported anecdotal results of soybean oils processed using this technique that claimed increased fry life when compared with partially hydrogenated, solvent-extracted, refined, bleached, and deodorized SBO. Although the expeller oils had the typical level of linolenic acid in soybeans—6–9%—the source of the enhanced stability was not clear. One theory on the stability of expeller oils includes a possible negative effect on stability from the solvents and chemicals used in conventional processing so that oil processed without these, such as expelled oil, would have better stability (6). Others believe that physically refined expeller oil does not contain compounds that may be present in partially hydrogenated frying oils (6); however, if this is true, no one has determined what components are lacking in the expeller oil that might lead to a longer fry life. Conversely, there is a possibility that expeller oils may contain compounds that enhance stability but that are not present in nonexpeller oils. For example, cold-pressed olive oil has good oxidative stability not only because of its FA composition (high oleic acid) but also because of its minor oil constituents such as polyphenols. The cold pressing technology helps retain these inherent compounds that enhance stability. Expeller-processed oils would not have the polyphenols present in a cold pressed product; however, the thermal processing step used for expeller oil may produce Maillard reaction products (MRP) that are well known for their antioxidant characteristics. Recent studies have suggested MRP may influence lipid oxidation stability (7–9). MRP comprise a broad class of compounds that result from the covalent attachment of a primary amine to a carbonyl carbon. The initial stages of the Maillard reaction involve the formation of a Schiff base, which rearranges to form a more stable ketoamine or Amadori product (10). Amadori products can then undergo numerous types of reactions depending on the system. Amadori products can crosslink forming polymeric compounds collectively referred to as advanced glycation end products (10). High antioxidant capacity generally has been associated with these colored advanced glycation end products (11). The role of these compounds in the oxidative stability of processed oils is poorly understood and is actively being investigated (12). To determine possible sources of the enhanced stability of EPSBO, we evaluated the composition of the oils; the fry life of oils and the quality of french-fried potatoes; the types and amounts of

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minor oil constituents present in the oils; and the effects of frying on the levels of some these compounds.

MATERIALS AND METHODS

Materials. The oils used in this study included expeller-pressed, physically refined, bleached and deodorized SBO (EPSBO) (Endura Products LLC, Springfield, IL); hexane-extracted, refined, bleached, and deodorized soybean oil (SBO) containing 200 ppm TBHQ (FAB Inc., Norcross, GA); and partially hydrogenated SBO (HSBO) (ACH Foods, Memphis, TN). All oils contained 50 ppm citric acid and 1 ppm dimethylpolysiloxane. No. 1 Idaho Russet potatoes were obtained from a local market to prepare french-fried potatoes. Pure tocopherol standards were obtained from Matreya (Pleasant Gap, PA).

Frying stability tests. Frying protocol included intermittent frying at 180°C with total heating/frying time of 35 h over 5 d. Nine hundred grams of each oil was heated in 3-L capacity fryers (Model 2540; Presto Industries, Eau Claire, WI) for 7 h each day for 5 d. Fresh Idaho Russet potatoes were cut into 8 cm lengths of shoestring size (0.5 × 0.5 cm), rinsed twice with water, and fried in 120-g batches. Potatoes were fried every 15 min and samples taken every 5, 15, 25, and 35 h of frying for sensory analysis. Potatoes used for sensory testing were par fried in 120-g batches for 2 min/batch just prior to testing, then finish-fried for 2 min during each 30 min sensory panel session. Frying oils were sampled every 5, 15, 25, and 35 h of frying and were frozen with argon in the headspace for later analyses. After 6, 16, and 26 h of frying, 90 g of fresh oil was added to each fryer.

Instrumental and chemical analyses of oils. FA compositions of the initial oils were determined in duplicate by capillary GC analysis with a Hewlett-Packard 5890 gas chromatograph (Wilmington, DE) equipped with an SP2330 column (30 m, 0.20 mm i.d., 0.20 mm film thickness; Supelco, Bellefonte, PA). Column temperature was first held at 190°C for 5 min and then was programmed to 230°C at 20°C/min. The injector was held at 250°C and the detector at 260°C. FFA values were measured in duplicate as percent oleic acid by AOCS method Ca 5a-40 (13). The initial oxidation level in the fresh oils was measured in duplicate by PV (AOCS method Cd 8-53) (13). The oxidative stability index (OSI) of the fresh oils was measured at 110°C in triplicate according to AOCS method Cd 12b-92 (13). Levels of total polar compounds in the fresh and used frying oils were determined in duplicate by the AOCS column chromatography method Cd 20-91 (13). Tocopherols were measured in duplicate in the fresh oils and fryer oils by HPLC with a polar phase column coupled with a fluorescence detector. The HPLC column used was a 3-μm particle size ultra silica HPLC column (250 × 4.9 mm) from Phenomenex (Torrance, CA). The solvent system was 2% 2-propanol in hexane. The solvent was pumped at 0.5 mL/min. The sample size was 10 μL of 50 mg solute per mL of the mobile solvent. The fluorescence detector was a programmable unit, model HP1046 A (with excitation wavelength set at 298 nm and emission wave length set at 345 nm with gain at 6) (Hewlett-Packard Co., Palo Alto, CA). The data output from the fluorescence detector was processed by a Star Chromatography Workstation with version 4.0 software (Varian Associates, Inc., Walnut Creek, CA). The tocopherol standards were prepared by appropriate dilutions of the standard tocopherol, 50 mg tocopherol, 99.4% pure, in 1 mL hexane, for a total of four separate standards. Phytosterols were measured by GC using the method of Vlahakis and Hazebroek (14). Phospholipids were analyzed by a published method (15).

Fluorescence spectroscopy. Fluorescence has long been associated with MRP and is indicative of their presence (16). Samples were analyzed for potential Maillard products using fluorescence spectroscopy as previously described by Leclère and Birlouez-Aragon (17). Samples for fluorescence analysis were diluted 1:50 (w/w) in $CHCl_3$. Spectra were recorded on a Fluorolog 3 fluorimeter (Jobin-Yvon Inc., Edison, NJ). Emission spectra were recorded from 360 to 600 nm with excitation at 350 nm. Spectra were recorded at 22°C and a bandpass of 2 nm for both excitation and emission.

Radical-scavenging assay. Samples were analyzed for their ability to quench 1,1-diphenyl-2-picrylhydrazyl (DPPH) radicals in toluene as previously described by Ramadan *et al*. (7). Briefly, a DPPH radical solution was freshly prepared at a concentration of 10^{-4} M in toluene. Oil (15 mg) was added to 7 mL of DPPH solution. The mixture was vortexed for 20 s and maintained at room temperature. The decrease in absorption at 515 nm was monitored for 15 min. Absorption was recorded with a PerkinElmer (Wellesley, MA) Lambda 4B UV/vis spectrophotometer with a bandpass of 5 nm. Radical-scavenging activity was estimated from the differences in absorbance (Abs) of toluenic DPPH solution with and without sample (control). The percent DPPH remaining was calculated from the following equation:

$$\%\ \text{DPPH remaining} = \{[(\text{Abs of control}) - (\text{Abs of sample})]/(\text{Abs of control})\} \times 100 \quad [1]$$

Three replicates for each sample were assayed. Error bars are reported at 2 SD.

Sensory analysis. A 15-member analytical descriptive sensory panel, trained and experienced in evaluating fried foods, rated the french-fried potatoes for intensities of individual flavors including deep-fried, potato, stale, cardboard, waxy, hydrogenated, and fishy on a 10-point intensity scale with 0 = no intensity and 10 = strong flavor intensity (18). They also rated overall flavor quality of the potatoes on a 10-point quality scale with 10 = excellent and 1 = bad. Panelists were presented with the freshly fried potato samples in 59.2 mL (2 oz) plastic souffle cups (Solo Cup Company, Urbana, IL). All sensory evaluations were conducted at our research center in a temperature-controlled room with individual booths and with red lighting to mask color differences between samples. Data from two frying series were pooled and statistically analyzed.

Statistical analysis. Data were evaluated by ANOVA (19). Statistical significance is expressed at the $P \leq 0.05$ level unless otherwise indicated.

RESULTS AND DISCUSSION

FA composition. The two unhydrogenated SBO had typical FA compositions that varied only slightly from one another (Table 1). The linolenic acid contents were similar at 7.4% for EPSBO and 7.3% for the SBO + TBHQ. The iodine values were identical at 130.1. The HSBO had 2.5% linolenic acid and an iodine value of 104.9. Linoleic acid (C18:2*c*) contents were 37.7% for HSBO, 52.5% for EPSBO, and 53.2% for SBO + TBHQ.

Initial oil quality. All oils were evaluated before frying using a variety of tests to measure initial oil quality (Table 2). The PV for EPSBO was 1.0, and the PV for the SBO + TBHQ and the HSBO were 0.4 each. In the fresh oils, total polar compound levels were low with 1.4% in the HSBO, 1.6% in the SBO + TBHQ, and 1.9% in the EPSBO. FFA levels were 0.06% for HSBO, and 0.08% for both EPSBO and SBO + TBHQ. OSI measurements were similar for EPSBO and HSBO. The OSI for the oils were 6.8 h for HSBO, 6.5 h for EPSBO, and 12.5 h for SBO + TBHQ. The SBO + TBHQ OSI was significantly higher, probably because of the addition of TBHQ. In the zero-time (0-time) oils, SBO + TBHQ had significantly higher total tocopherols than EPSBO and HSBO with the amount of γ-tocopherol showing the most difference between the two oils. Based on the compositional analyses, the HSBO had been formulated to contain very low amounts of tocopherols because the total tocopherol content was 112 ppm compared with 922 ppm for EPSBO and 1148 ppm for the SBO + TBHQ. The amounts of total sterols were lower in the HSBO than in the other two oils, which had similar levels. Phospholipids were not detected in the SBO + TBHQ or in the HSBO; however, 2 ppm was measured in the EPSBO. Only the total polar compounds and the levels of tocopherols were monitored during frying.

Frying stability of oils. Total polar compounds are one measure of the frying stability or fry life of an oil. In this study, we did not see differences in the levels of polar compounds formed during frying of any of the three oils (Fig. 1). After 15 h of frying, all oils still had low amounts of total polar compounds with 5.7% in EPSBO, 5.5% in the SBO + TBHQ, and 5.6% for the HSBO, thus showing there was little effect of FA composition, oil processing, or additives. By 35 h of frying, the oils still had similar amounts of total polar compounds with 9.1% in EPSBO, 8.9% in the SBO + TBHQ, and 9.7% for the HSBO. The use of hydrogenation, TBHQ, or expeller pressing/physical refining had similar effects in inhibiting formation of polar compounds.

Flavor quality of french-fried potatoes. Flavor analyses were conducted on french-fried potatoes sampled after the oils were used for 5, 15, 25, and 35 h of frying. Sensory panelists evaluated the potato samples for positive flavor attributes of deep-fried flavor and potato flavor and for negative flavors of stale, fishy, cardboard, waxy, and hydrogenated and for overall flavor quality. Overall flavor quality scores generally decreased with in-

TABLE 1
FA Compositions (%) of Expeller-Pressed/Physically Refined Soybean Oil (EPSBO), Soybean Oil (SBO) + TBHQ, and Partially Hydrogenated Soybean Oil (HSBO)

FA	EPSBO	SBO + TBHQ	HSBO
C14:0	0.1	0.1	0.1
C16:0	10.6	10.8	11.7
C18:0	5.3	4.7	9.5
C18:1*t*	0.0	0.0	5.4
C18:1*c*	23.0	23.0	30.3
C18:2*t*	0.0	0.0	1.4
C18:2*c*	52.5	53.2	37.7
C18:3	7.4	7.3	2.5
C20:0	0.5	0.5	1.0
C22:0	0.4	0.4	0.5

TABLE 2
Initial Oil Analyses[a] for EPSBO, SBO, and HSBO

Analyses	EPSBO	SBO + TBHQ	HSBO
PV	1.1a	0.4b	0.4b
FFA (% oleic)	0.08a	0.08a	0.06a
Oxidative stability index (h)	6.5a	12.5b	6.8a
Total polar compounds (%)	1.9a	1.6b	1.4b
Tocopherols (ppm)			
α	59a	97b	19c
β	18a	23a	0b
γ	592a	768b	75c
δ	253a	260a	8b
Sterols (ppm)			
Campesterol	383a	362a	196b
Stigmasterol	297a	251b	155c
β-Sitosterol	1051a	1233b	811c
δ 5-Avenasterol	34a	36a	23b
δ 7-Stigmasterol	107a	114a	73b
δ 7-Avenasterol	29a	29a	19b
Total phospholipids (ppm)	2a	0b	0b

[a]Values with letters in common in each row are not significantly different ($P > 0.05$). For abbreviations see Table 1.

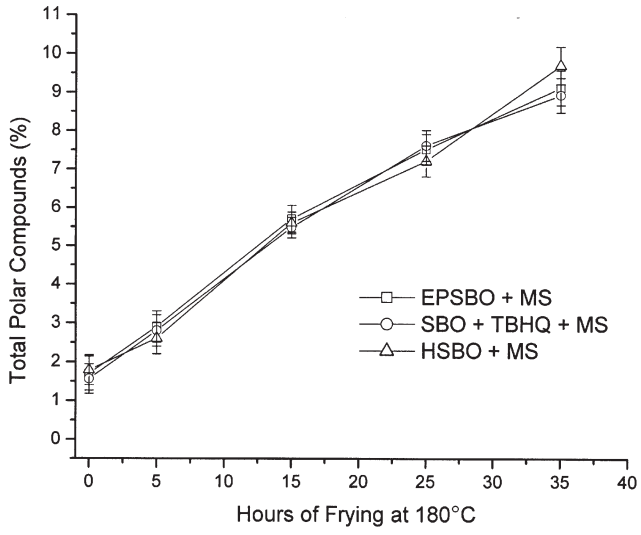

FIG. 1. Total polar compounds (%) in expeller-pressed soybean oil (EPSBO) + methyl silicone (MS), soybean oil (SBO) + TBHQ + MS, and hydrogenated SBO + MS used to fry french-fried potatoes for up to 35 h.

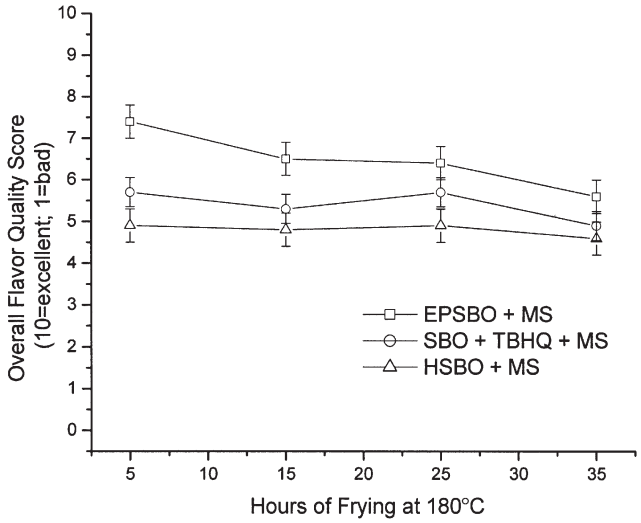

FIG. 2. Overall flavor quality scores for french-fried potatoes fried in EPSBO + MS, SBO + TBHQ + MS, and hydrogenated SBO + MS. For abbreviations see Figure 1.

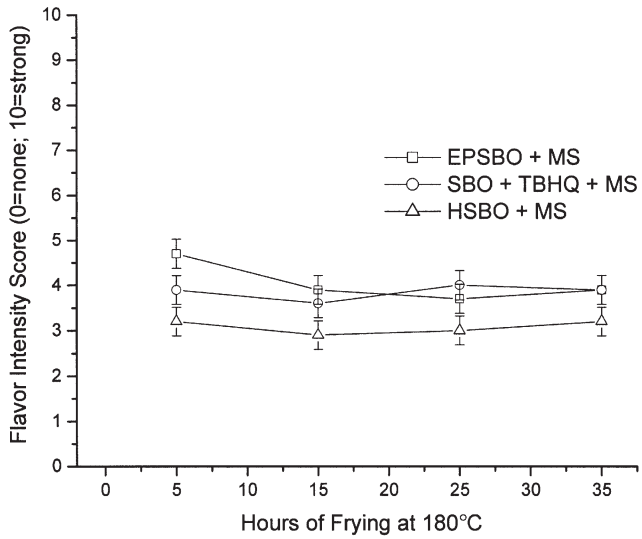

FIG. 4. Intensity scores for potato flavor in french-fried potatoes fried in EPSBO + MS, SBO + TBHQ + MS, and hydrogenated SBO + MS. For abbreviations see Figure 1.

creasing frying times except for the potatoes fried in HSBO, which remained fairly constant. In french-fried potatoes sampled after 5 and 15 h of frying, the EPSBO samples had significantly higher (better) flavor quality scores than potatoes fried in the other two oils (Fig. 2). After 25 and 35 h of frying, sensory panelists found that the potatoes fried in the EPSBO still had the highest quality scores, but there were no significant differences between the scores of potatoes fried in EPSBO and SBO + TBHQ. However, scores for potatoes fried in HSBO were significantly lower than the scores of potatoes fried in EPSBO. The overall flavor quality scores for the potatoes fried in HSBO were stable throughout the frying times, but the scores were low with a score of 4.9 because of negative flavors such as waxy and hydrogenated at all frying times and because of the low intensity of deep-fried flavor at 5 h. The intensity levels of other flavors such as stale and cardboard were at the weak level of 0.6–1.2 and did not differ much between oils (data not shown). Fishy flavor intensity was one of the primary differences between the potatoes fried in EPSBO and SBO + TBHQ (Fig. 3). The intensity was significantly higher in the potatoes fried in SBO + TBHQ than in the EPSBO at all frying times. Fishy flavor intensity was low in the potatoes fried in either EPSBO or HSBO. As discussed later in this paper, the MRP formed in the EPSBO can serve as antioxidants. These compounds may therefore be one possible explanation for the difference in fishy flavor intensity between EPSBO and SBO with TBHQ. Soybean and canola oils with 7–10% linolenic acid typically have a characteristic fishy odor

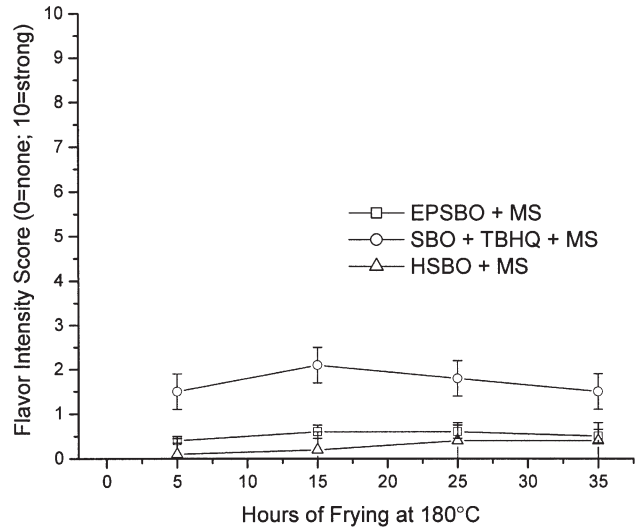

FIG. 3. Intensity scores for fishy flavor in french-fried potatoes fried in EPSBO + MS, SBO + TBHQ + MS, and hydrogenated SBO + MS. For abbreviations see Figure 1.

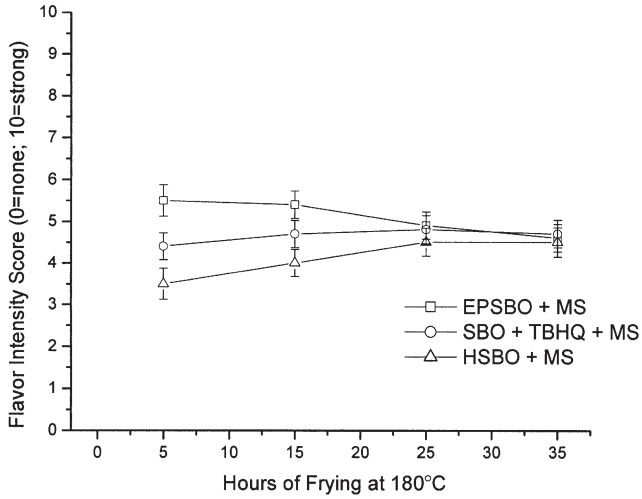

FIG. 5. Intensity scores for deep-fried flavor in french-fried potatoes fried in EPSBO + MS, SBO + TBHQ + MS, and hydrogenated SBO + MS. For abbreviations see Figure 1.

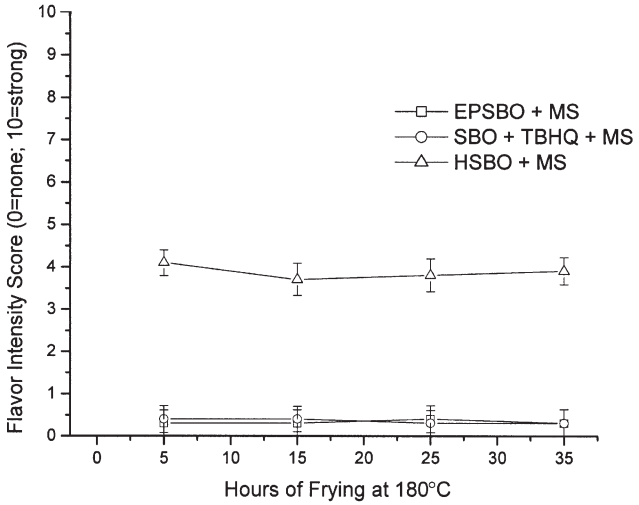

FIG. 6. Intensity scores for hydrogenated flavor in french-fried potatoes fried in EPSBO + MS, SBO + TBHQ + MS, and hydrogenated SBO + MS. For abbreviations see Figure 1.

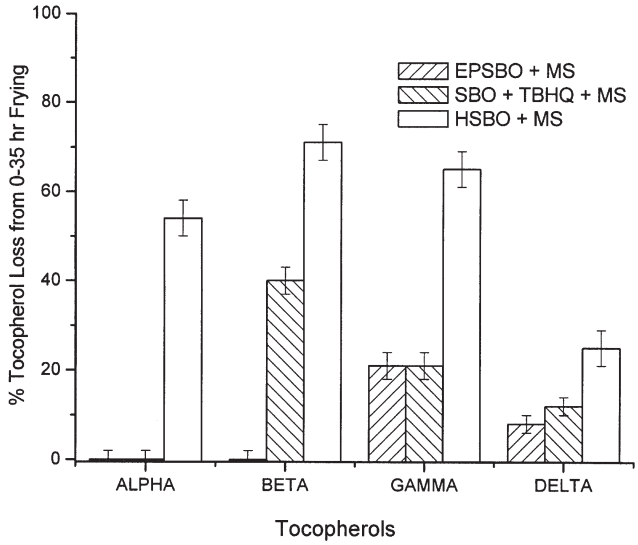

FIG. 8. Loss of tocopherols in EPSBO + MS, SBO + TBHQ + MS, and hydrogenated SBO + MS used for frying french-fried potatoes for 35 h. For abbreviations see Figure 1.

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 found that a fishy flavor was most noticeable in the foods fried in oil that had not been used very long rather than in abused oils (Warner, K., unpublished data). Although off-flavors are usually produced by increased fry time of the oil, fishy flavor is at higher intensity levels during the early stages of frying possibly because the volatile compounds producing this flavor degrade and/or the fishy flavor is partly masked by other off-flavors that develop during later periods of frying.

Potato and deep fried flavors are positive flavor attributes in french-fried potatoes. The intensities of the potato flavor differed between the EPSBO and the SBO + TBHQ only at the 5-h sampling time (Fig. 4). The intensity of potato flavor was significantly lower in the potatoes fried in hydrogenated oil than in potatoes fried in either EPSBO or SBO + TBHQ probably because the distinctive hydrogenation flavor partially masked the potato flavor. The intensity of deep-fried flavor was significantly higher in the samples fried in EPSBO than in the other oils possibly because of the off flavors (fishy and hydrogented/waxy) that were present in the other oils (Fig. 5). By 25 h of frying, the differences between the oils for this flavor were not significant. In contrast to the positive flavor attributes, hydrogenated and waxy flavors are considered negative attributes in french-fried potatoes. Both flavors are typical of hydrogenated oil, therefore, the intensities of these flavors are very low in the EPSBO and in the SBO + TBHQ (Figs. 6, 7). As expected, the intensities of hydrogenated flavor and waxy flavor were significantly higher in the potatoes fried in hydrogenated oil than in potatoes fried in either EPSBO or SBO + TBHQ.

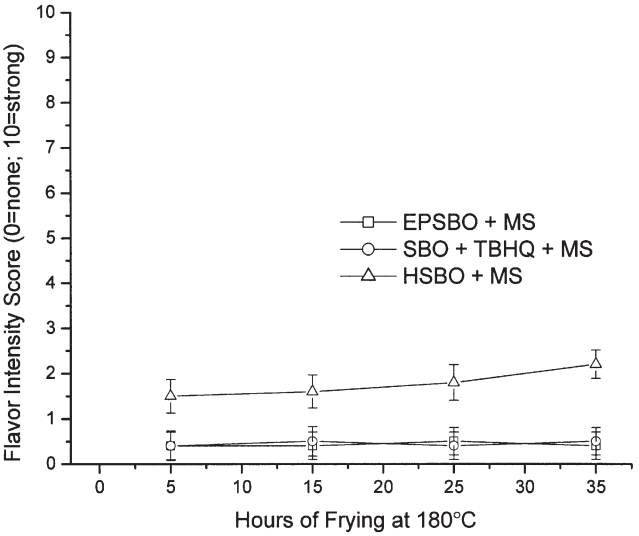

FIG. 7. Intensity scores for waxy flavor in french-fried potatoes fried in EPSBO + MS, SBO + TBHQ + MS, and hydrogenated SBO + MS. For abbreviations see Figure 1.

Retention of tocopherols. HSBO had the highest losses of tocopherols (Fig. 8), which is typical for a saturated oil (20). The SBO + TBHQ lost significantly more β-tocopherol and δ-tocopherol than did the EPSBO. No significant differences were found between the EPSBO and SBO + TBHQ samples for levels of α- and γ-tocopherols. The presence of TBHQ probably helped to inhibit the loss of tocopherols in the SBO + TBHQ; however, the EPSBO possibly had antioxidant compounds that helped to inhibit tocopherol loss as well, which will be discussed in the next section. The presence of methyl silicone (MS) was probably not a factor in retaining tocopherols because HSBO, which lost the largest percentage of tocopherols, also contained MS.

Fluorescence spectroscopy of MRP. Fluorescence is a general measure of MRP (10). In the current study, fluorescence spectroscopy was used to identify differences in EPSBO and SBO. This included monitoring the fluorescence emission with excitation at 350 nm (21). The fluorescence emission spectra

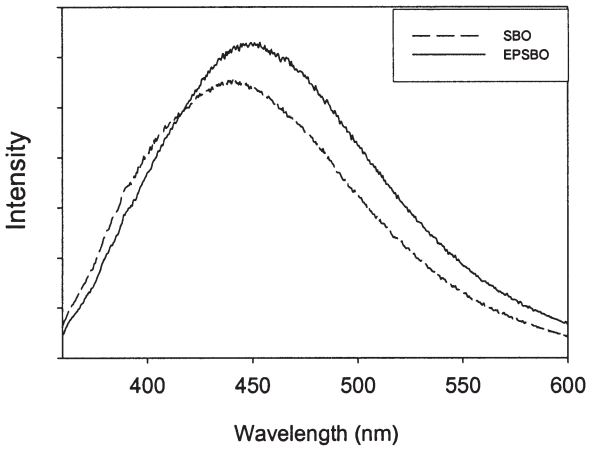

FIG. 9. Fluorescence emission spectra for EPSBO and SBO with excitation at 350 nm. For abbreviations see Figure 1.

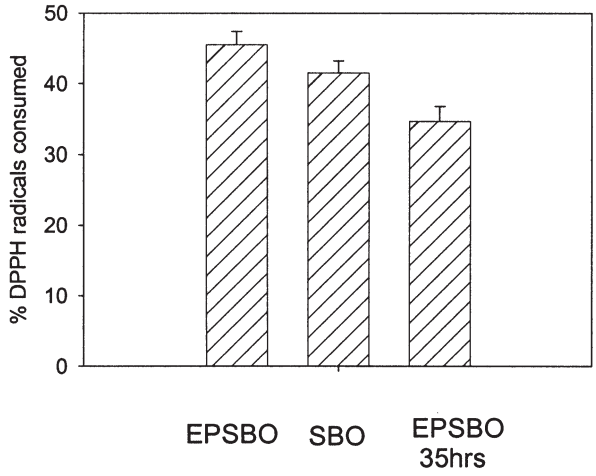

FIG. 10. Radical scavenging activity as measured by 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical consumption of 0-time EPSBO, 0-time SBO, and EPSBO used for 35 h of frying.

of ESPBO and SBO are presented in Figure 9. The results showed the EPSBO sample had a ~15% increase in signal intensity between emission maxima relative to SBO. The results also showed the EPSBO sample had an emission maximum that was red-shifted relative to SBO. EPSBO had an emission maximum of 452 nm, whereas SBO had an emission maximum of 442 nm. Fluorescence emissions in this wavelength range are consistent with MRP.

Radical-scavenging activity. The ability of MRP to scavenge free radicals has been long been associated with their antioxidant activity (22). The ability of EPSBO and SBO to scavenge free radicals was tested using the stable radical DPPH in toluene (7). In addition to testing EPSBO and SBO, EPSBO thatt had been used for 35 h of frying was examined. The results are reported in Figure 10. The results show EPSBO had 10% more radical-scavenging activity than SBO as measured by consumption of DPPH radicals after 15 min of incubation. EPSBO after 35 h of frying had the lowest radical-scavenging activity of the three samples, with a 22% decrease in radical-scavenging activity relative to EPSBO. These results for the oil used for 35 h of frying would be expected because of the loss of tocopherols during frying.

Heat treatments associated with processing have long been correlated with the formation of MRP for many food products (10). During the expeller-pressing process, soybeans can experience temperatures as high as 110–140°C and for as long as 30 s. SBO containing PE recently has been shown to form nonenzymatic browning products after heating to 160°C (23). MRP can have a significant effect on inhibiting lipid oxidation (20). In addition, phospholipids have an effect on oxidation because of a synergisim with α-tocopherol (20). The EPSBO used in this study contained 2 ppm total phospholipids, but no phospholipids were detectable in the other oils. Both Frankel (20) and Smouse (24) reported that unsaponifiable components such as tocopherols and phytosterols act synergistically to inhibit oxidation and that phospholipids also contribute to this effect. The fact that the EPSBO had frying stability equal to that of a SBO with TBHQ or to hydrogenated SBO indicated that some stability characteristic(s) were present in the EPSBO. We believe that the EPSBO performed well in these frying tests because the expeller processing enhanced antioxidant properties of the EPSBO in comparison with the conventional solvent–extracted SBO. EPSBO contained both MRP and phospholipids that acted to help inhibit oxidation in the frying oil and fried food.

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