Antipolymerization Activity of Oat Extract in Soybean and Cottonseed Oils Under Frying Conditions

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A methanolic extract of Noble oat (*Avena sativa* L.) was tested for its antipolymerization activity in soybean and cottonseed oils heated to 180°C for 10 h per day for 10 d and for its carry-through properties in fried bread cubes. The soybean and cottonseed oils containing 0.005 or 0.007% oat extract (based on total phenolic content) formed significantly lesser amounts of polar compounds with high molecular weight than did the oils containing 0.02% tertiary butyl hydroquinone (TBHQ), 1 ppm dimethylpolysiloxane (DMS) and oils containing no additives (control) as measured by high-performance size-exclusion chromatography. Fatty acid composition, also monitored, showed that oils with either level of oat extract maintained a significantly higher linoleic-to-palmitic acid ratio (18:2/16:0) than did the other treatments. Oil extracted from bread cubes fried (180°C) in oils containing TBHQ and oat extract and then stored at 60°C in the dark for up to 14 d had significantly lower ($P \leq 0.05$) peroxide values and higher ($P \leq 0.05$) 18:2/16:0 ratios than did oil extracted from cubes fried in oil containing DMS and in the control oil.

KEY WORDS: Antioxidant, autoxidation, cottonseed oil, oat, oxidation, polymerization, soybean oil.

Commercially used antioxidants, such as tocopherol, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and tertiary butyl hydroquinone (TBHQ), are effective in protecting oxidation at ambient temperatures, but these antioxidants are heat-sensitive and volatile, so they quickly lose antioxidant activity at frying temperature (1,2). Buck (3) analyzed the volatility of BHA, BHT and TBHQ in soybean oil at 180°C with or without steam injection. After 4 h of heating, the initial concentration of 200 ppm for all the additives had fallen to 60 ppm.

The use of dimethylpolysiloxane (DMS) at a low level (0.2–25 ppm) is effective in extending the frying life of oils (4–6). The DMS is thought to act as an antifoaming agent for fats and oils at frying temperatures, thereby slowing the convection currents in the frying oil. A protective inert surface to the atmosphere is formed, which inhibits oxidation and polymerization of the oil. Although DMS is effective, the current interest by consumers in eating "all natural" products is limiting its usage.

The use of natural compounds as polymerization inhibitors in oils has been described. Musher (7) first reported that the aqueous extract of cereals and grains such as corn (*Zea mays* L.), barley (*Hordeum vulgare* L.), oats (*Avena sativa* L.), rice (*Oryza satuva* L.), wheat (*Triticum aestivum* L.) and rye (*Secale cereale* L.) not only were unaffected by heat treatment but also were actually activated under conditions of heat. In his study, refined cottonseed oil containing 0.5% of oat extract and a control oil with no additives were heated to 204°C, cooled immediately and then stored at 78°C with bubbling of air until rancidity was observed. The treatment with oat extract was much more stable than the control. The treated oil also was much more stable than a treatment containing oat extract without initial heating.

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White and Armstrong (8) reported that a specific sterol found in oats, Δ^5-avenasterol, and removed with alcoholic extraction was effective in retarding soybean oil deterioration at 180°C. The antipolymerization activity of the sterol at frying temperature is thought to reside in its side chain, which contains an ethylidene group. A tertiary free radical in the ethylidene group reacts rapidly with free radicals from the heated oils to produce a stable, isomerized allylic free radical, which interrupts the oxidation (9). When added at levels of 0.05 or 0.1%, the methanolic and petroleum ether extracts from Noble and Ogle oats and hulls, containing Δ^5-avenasterol and phenolic antioxidants, reduced polymerization of soybean oil, held at frying temperature for 14 d, but did not improve stability of the oil when stored at 60°C (10). An improved procedure for producing the methanolic extract from oat resulted in effective antioxidant activity in soybean and cottonseed oils stored at 30°C in the light and dark and at 60°C in the dark (11).

The purpose of the present study was to examine the ability of the new methanolic extract of Noble oat, previously described (11), to reduce polymerization of oils held at frying temperature. In addition, bread cubes were fried in these oils and stored to test the carry-through property of the antioxidants in the oat extract. The polymerization and antioxidant activities of the extract were compared with those of TBHQ, the best synthetic antioxidant, and DMS, the only available antipolymerization additive.

EXPERIMENTAL PROCEDURES

Oat extract. The methanolic oat extract was obtained as previously described (11). The total phenolic content was measured by the standard method (9.110) of the Association of Official Analytical Chemists (AOAC) (12). Alcoholic extracts of oat previously have been reported to contain caffeic and ferulic acids and their long-chain alcohol esters (13–17), as well as avenanthramides and orthoaminobenzoic acids (18,19). Also reported to be present in methanolic oat extracts is Δ^5-avenasterol (8).

Heating tests. Soybean and cottonseed oils were obtained in bulk from commercial sources and contained citric acid with no other additives. All tests were run on duplicate oil samples. In preliminary experiments, a methanolic oat extract was effective at fairly low levels, so amounts of 0.005 and 0.007% oat extract (based on phenolic content) were used for the tests. The phenolic content accounted for about 0.003% of the oat groat, and the oat extract was composed of approximately 0.1% phenolics (wt/vol) (11).

The oat extract was added to 50-mL beakers that had been previously cleaned with a potassium ethanol solution as previously described (11). The extract was partly dried under nitrogen, and then the oils were added. The extract was dark in color, slightly darkening the oils containing the extract. Sensory analyses of the samples were not conducted to accurately measure flavor and odor changes; however, as judged by the authors, there was no noticeable change in odor of the oils containing the extract.

TBHQ, the best commercially used synthetic antioxidant, was tested at its legal limit of 0.02% (20). DMS, the only available additive used to reduce polymerization in heated oils, was used at the suggested level of 1 ppm (5). A control oil with no additives also was included for comparison. The soybean and cottonseed oils (400 g) were heated in Fry Baby® electric deep-fat fryers (Presto Company, Eau Claire, WI; model 05430) to 180 ± 5°C for 10 h per day for up to 10 d. The temperature of each fryer was controlled by a rheostat. Oils were sampled every 2 days and stored under nitrogen at −10°C until analyzed.

Bread cube frying tests. Oils were heated to 180°C within 10 min. Bread cubes, 16 g total (1 × 1 × 0.5 cm^3; HyVee White Bread), were fried for 1 min in the oils just after the temperature reached 180°C (0 min). After frying, the bread cubes were drained for 1 min, loosely wrapped in aluminum foil and stored at 60°C in the dark for up to 14 d. Bread cubes (2 g) were sampled every 4 d for cottonseed oil and every 7 d for soybean oil. Oil was extracted from the bread cubes twice with 50 mL hexane for 30 min each time, and the solvent was evaporated with a rotary evaporator at 40°C (21). The oil was analyzed for peroxide value (PV) and fatty acid composition (methods are described later) on the day of sampling.

High-performance size-exclusion chromatography (HPSEC). The polar compounds with high molecular weight (MW), formed during the heating of the oils, were measured by following the procedure of White and Wang (22). The HPSEC system included a Beckman 110A pump (Fullerton, CA), Beckman 210 sample injector, 20-μL injector loop, Hitachi 100-1 variable-wavelength UV/VIS detector set at 254 nm (Tokyo, Japan) and a Fisher Recordall® Series 5000 recorder (Fisher Scientific, Itasca, IL). The size-exclusion column series included two Beckman μ-Spherogel columns of 500Å (0.8 × 30 cm) and 1000Å (0.77 × 30 cm). Methylene chloride (HPLC-grade; Fisher Scientific) was used as the mobile phase at the rate of 1 mL/min. The solvent and samples were precleaned by passing through a 0.45-μm tetrafluoroethylene filter (Alltech Associates, Deerfield, IL) before injection to protect against blocking of the columns. Polystyrene standards (Supelco, Inc., Bellefonte, PA) of specified MW of 800, 2000, 4,000, 17,500, 50,000 and 70,000 g/mole were used as external standards to help estimate MW of the peaks. Oil samples were dissolved in methylene chloride to a concentration of 25 mg/mL before injection onto the columns.

In these tests, peak 4, which represented the compounds having MW greater than tetrameric triacylglyerols, was measured as a way to determine heat damage of the oils. The area of peak 4 was measured by drawing a vertical line from the lowest point of peak 4 to the baseline; then, the area was determined by using a planimeter. All tests were run in duplicate, and the results were averaged for each replicate. A typical chromatogram is described in the Results and Discussion section.

Gas chromatography (GC). Soybean and cottonseed oil samples from the heating tests and extracted from the fried bread were analyzed for fatty acid composition by following a procedure for fatty acid methyl esters (FAME) conversion (23). The FAME were injected onto a Hewlett-Packard 5890 Series II gas chromatograph (Kennett Square, PA) equipped with a flame-ionization detector and split/splitless injector. A DB-23 fused-silica capillary column was used with dimensions of 0.25 mm × 15 m × 0.25 μm film thickness (J&W Scientific Inc., Rancho Cordiva, CA). Chromatographic parameters were set as follows: injector temperature, 250°C; detector temperature, 250°C; column temperature programming, 140 to 200°C at 12°C/min with 5°C min holding time at 200°C; and carrier gas (He) at 100 mL/min. All tests were run in duplicate, and the results were averaged for each replicate. The linoleic-to-palmitic acid ratios of the oils were calculated from the FAME data.

PV. The PV of soybean and cottonseed oils extracted from the bread cubes were measured by the Stamm test as modified by Hamm *et al.* (24). All tests were run in duplicate, and the results were averaged for each replicate.

Data and statistical analyses. The least-square means of the areas of peak 4, the linoleic-to-palmitic acid ratios, each fatty acid amount and PV were calculated by the Statistical Analysis System (SAS) (25). The significance level was accepted at $P \leq 0.05$.

RESULTS AND DISCUSSION

Heating tests. To estimate the MW of the unknown compounds in the heated oils, polystyrene standards of known MW were run on the same columns. The correlation obtained between retention time of the standards and MW was linear (r = 0.99), as shown in Figure 1. From the retention time of each unknown peak, the approximate corresponding MW range was obtained.

Figure 2 shows typical HPSEC chromatograms of fresh soybean oil at day 0, a soybean oil control heated for 10 d at 180°C and soybean oil with 0.007% oat extract after 10 d of heating at 180°C. Peak 1 represents triacylglycerols and fatty acid trimers, peak 2 represents dimeric triacylglycerols, peak 3 represents tetrameric triacylgly-

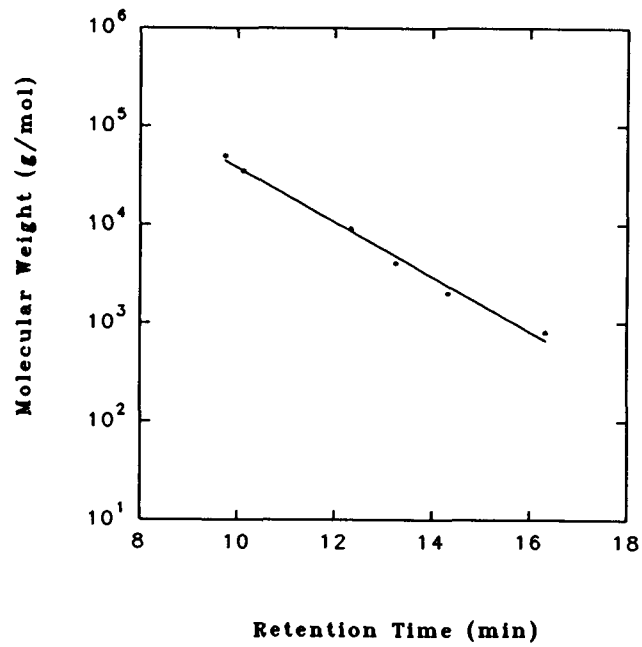

FIG. 1. Correlation of molecular weight and retention time of standard compounds.

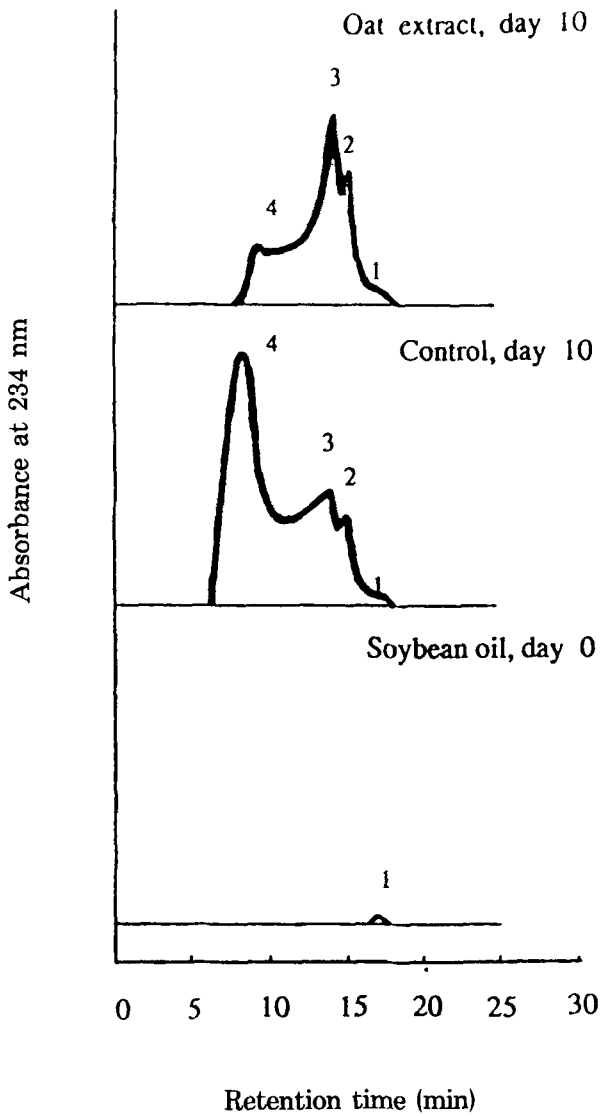

FIG. 2. Typical high-performance size-exclusion chromatography chromatograms of fresh soybean oil (day 0), soybean oil with no additives (control) and soybean oil with 0.007% added oat extract, both after 10 d of heating at 180°C.

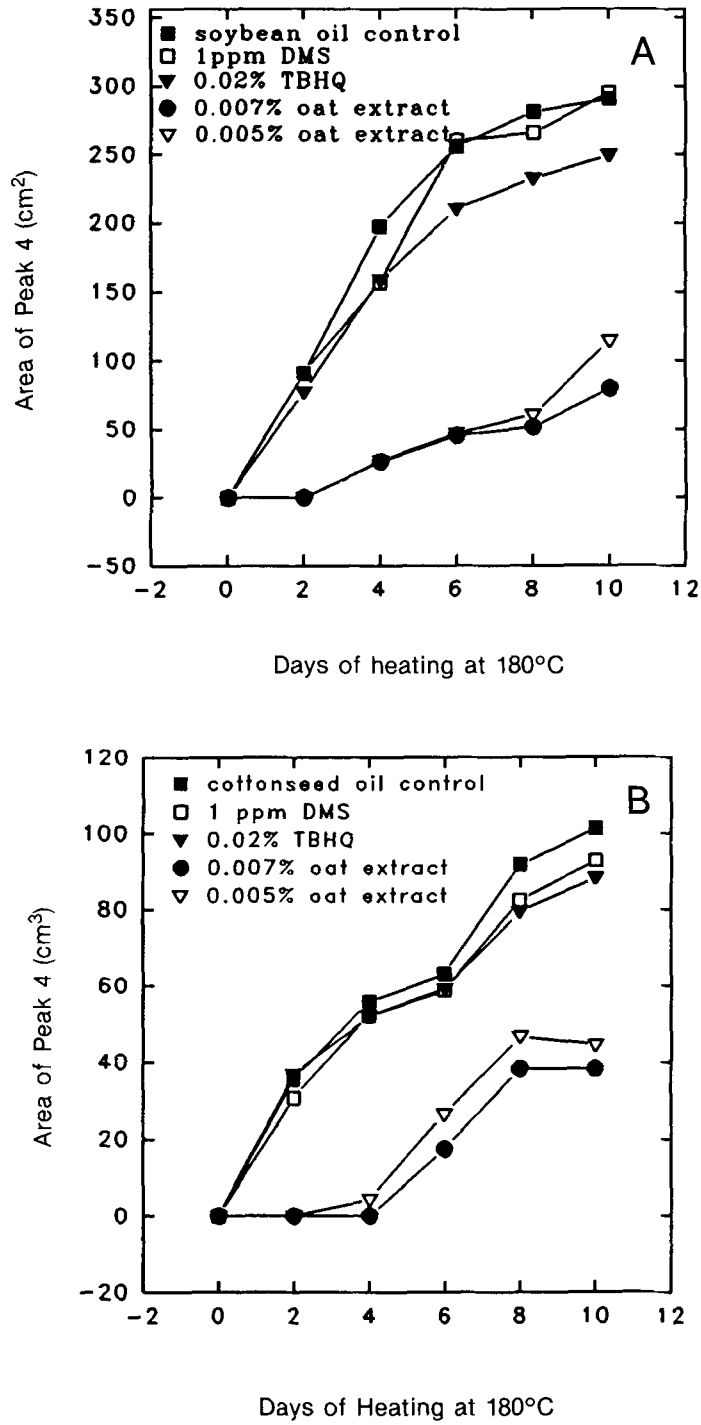

FIG. 3. Area of peak 4 by high-performance size-exclusion chromatography of soybean oil (top) and cottonseed oil (bottom) with different additives during 10 d of heating at 180°C. DMS = dimethylpolysiloxane; TBHQ = tertiary butyl hydroquinone.

cerols and peak 4 represents compounds with MW higher than tetrameric triacylglycerols (22). The increases of dimeric, tetrameric and higher MW peaks, the results of polymerization during thermal oxidation, indicate oil deterioration. In the current study, the area of peak 4 was reported as an indication of heat damage. The area of the peak was measured by drawing a vertical line from the lowest point of each peak to the baseline, and then the area was measured with a planimeter.

HPSEC of soybean oils. Great differences were observed in the areas of peak 4 among soybean oil treatments heated at 180°C (Fig. 3). By day 2 of heating, peak 4 was not observed in the treatments containing either level of oat extract; whereas the rest of the treatments showed already rapid increases of peak 4 after 2 d of heating. Peak 4 was observed in the treatments containing either level of oat extract after 4 d of heating, but the peak areas were much smaller than in the rest of the treatments. Oils containing either level of oat extract had significantly smaller areas for peak 4 than did all other treatments at any day of heating from day 2 through day 10. There were no significant differences between the oils containing either level of oat extract.

The oil containing DMS had a significantly smaller area of peak 4 than did the control on day 4 of heating, but

was not different from the control on days 6, 8 and 10 of heating. Perhaps, the amount of DMS was insufficient to protect against thermal decomposition of the soybean oil. The oil containing TBHQ had a significantly smaller area of peak 4 than did the control after 4 d of heating. These results are similar to those of Duve and White (10) in which 0.02% TBHQ did not significantly protect against thermal oxidation of soybean oil, although a tendency for improvement was noted with the addition of TBHQ.

HPSEC of cottonseed oils. Trends similar to those for soybean oil were seen for cottonseed oil (Fig. 3). After 2 d of heating, the areas of peak 4 of the oils containing either level of oat extract were significantly lower than the peak 4 areas of oils containing TBHQ, DMS and the control oil. The oils containing TBHQ and DMS also had slightly smaller areas for peak 4 than did the control after 2 d of heating, but the differences were not significant.

The peak-4 areas of all cottonseed oil treatments were smaller than the areas of the soybean oil treatments for the same heating times, indicating more high-MW compounds formed in the soybean oils. These differences likely are due to greater unsaturation of soybean oil than of cottonseed oil. The rate of thermal decomposition is roughly proportional to the degree of unsaturation of the fatty acids present (26). The speed of degradation approximates the ratio of 1:10:100:200, for stearic (18:0)/oleic (18:1)/linoleic (18:2)/linolenic acids (18:3) (27).

FAME of soybean oil. The FAME and the 18:2-to-palmitic acid (16:0) ratios (18:2/16:0) for the soybean oil treatments are shown in Table 1. For all treatments, the relative percentages of polyunsaturated fatty acids (18:2 and 18:3) generally tended to decrease during heating, whereas the relative percentages of the saturated fatty acids (16:0 and 18:0) and 18:1 generally tended to increase during heating. The oils containing oat extract at either level maintained levels of 18:2 and 18:3 that were significantly higher and levels of 16:0 and 18:0 and 18:1 that were significantly lower than those of the control oil and of the oils containing TBHQ and DMS. Throughout heating, few significant differences in levels of the FAME were found between the oils containing either level of oat extract or among the control and the oils containing TBHQ and DMS.

The 18:2/16:0 has been reported to correlate with the iodine value and dielectric constant, thus providing a reliable indication of oil deterioration (28). In the current experiment, the soybean oils containing 0.005 or 0.007% oat extract generally maintained significantly greater 18:2/16:0 throughout heating than did the oils containing TBHQ or DMS and the control. The 18:2/16:0 of the

TABLE 1

Fatty Acid Composition (%) of Soybean Oil Treatments Heated at 180°C

Treatments	16:0	18:0	18:1	18:2	18:3	18:2/16:0
Day 0						
Fresh oil	11.1	4.0	23.9	53.6	7.7	4.8
Day 2						
0.007% Oat[d]	11.2[a]	4.8[b]	26.4[a]	50.0[a]	5.8[b]	4.5[a]
0.005% Oat	11.3[a]	4.6[b]	26.3[a]	50.1[a]	5.9[b]	4.5[a]
0.02% TBHQ[e]	13.0[a]	5.6[a]	28.6[a]	45.9[b]	4.5[a]	3.6[a,b]
1 ppm DMS[f]	13.9[a]	5.4[a]	28.4[a]	45.8[b]	4.4[a]	3.4[b]
Control	14.1[a]	5.6[a]	29.0[a]	44.6[b]	4.1[a]	3.2[b]
Day 4						
0.007% Oat	12.1[b]	4.5[b]	25.4[b]	50.7[a]	5.7[a]	4.2[a]
0.005% Oat	11.9[b]	4.9[b]	27.3[a,b]	48.9[a]	5.4[a]	4.2[a]
0.02% TBHQ	15.0[ab]	6.3[a]	31.2[a]	41.4[a]	3.4[b]	2.8[b]
1 ppm DMS	14.5[ab]	6.7[a]	32.2[a]	41.4[b]	3.3[bc]	2.9[b]
Control	16.0[a]	6.8[a]	32.0[a]	39.1[b]	2.9[c]	2.4[b]
Day 6						
0.007% Oat	12.5[b]	5.5[b]	27.9[c]	46.9[a]	4.6[a]	3.8[a]
0.005% Oat	12.5[b]	5.3[b]	28.4[c]	47.5[a]	4.8[a]	3.9[a]
0.02% TBHQ	16.5[a]	7.3[a]	34.1[a]	37.3[b]	2.5[b]	2.4[b]
1 ppm DMS	16.7[a]	7.0[a]	32.8[b]	36.3[b]	2.4[b]	2.2[b]
Control	17.4[a]	7.7[a]	35.1[a]	35.1[b]	2.1[b]	2.0[b]
Day 8						
0.007% Oat	12.9[b]	5.6[c]	29.3[b]	45.8[a]	4.2[a]	3.6[a]
0.005% Oat	13.0[b]	5.5[c]	28.0[b]	47.1[a]	4.5[a]	3.7[a]
0.02% TBHQ	17.6[a]	7.6[b]	35.8[a]	34.1[b]	2.1[b]	2.0[b]
1 ppm DMS	17.4[a]	8.1[a]	35.7[a]	33.2[b]	1.8[b]	1.9[b]
Control	18.7[a]	8.1[a]	34.6[a]	32.5[b]	1.8[b]	1.8[b]
Day 10						
0.007% Oat	14.1[b]	5.6[b]	29.6[b]	44.0[a]	3.7[a]	3.2[a]
0.005% Oat	14.0[b]	5.6[b]	29.6[b]	45.5[a]	4.0[a]	3.3[a]
0.02% TBHQ	18.9[a]	8.3[a]	36.2[a]	31.1[b]	1.5[b]	1.8[b]
1 ppm DMS	19.0[a]	7.6[a,b]	34.9[a,b]	32.9[b]	1.8[b]	1.8[b]
Control	19.7[a]	8.0[a]	36.3[a]	30.4[b]	1.5[b]	1.6[c]

[a–c]Values in the same column within the same day with different supercript letters are significantly different ($P \leq 0.05$).
[d]Oat extract.
[e]Tertiary butyl hydroquinone.
[f]Dimethylpolysiloxane.

oils containing different levels of oat extract were not significantly different from each other throughout the study. The 18:2/16:0 of the oils containing THBQ or DMS and the control were not significantly different from each other until day 10 of heating, when the ratio of the control was significantly lower than those of the other treatments.

These results are in agreement with those of Duve and White (10) in which soybean oil containing oat extract maintained significantly higher levels of polyunsaturated fatty acids (18:2 and 18:3) and of 18:2/16:0 than did the treatments containing 0.02% BHT and TBHQ after 14 d of heating at 180°C. In addition, no significant differences were found among the control and oils containing TBHQ or BHT.

FAME of cottonseed oils. Heating tests on cottonseed oil showed results similar to those of the soybean oil (Table 2). The FAME of 16:0, 18:0 and 18:1 of the treatments containing either level of oat extract generally were significantly lower, and the FAME of 18:2 were significantly higher than were those of the control and of oils containing TBHQ and DMS. The 18:2/16:0 for treatments containing oat extract at either level were significantly higher than the ratios for the rest of the treatments, especially after day 2 of heating. In contrast to soybean oil, the treatment containing 0.007% oat extract had a significantly higher 18:2 and 18:2/16:0 than did the treatment containing 0.005% oat extract at 10 d of heating. No significant differences in FAME levels or 18:2/16:0 occurred among the control and the oils containing TBHQ and DMS throughout heating, except for the amount of 18:0 at day 2.

Interpretation of effectiveness of polymerization inhibitors. DMS is thought to indirectly inhibit oxidation by suppressing the accumulation of foam-promoting oxidation products such as free fatty acids and food exudates in heated oils (6). The results of the current experiment, however, did not show any protective activity of this additive. This may be because the bread cubes, when fried in the oils, carried away the DMS; thus, the amount of remaining DMS in the oils may have been too low to prevent the thermal and oxidative decomposition.

Oils containing the oat extract at either level, compared with all other treatments, maintained the highest 18:2/16:0, the greatest amount of 18:2 and 18:3 (for soybean oil), the lowest 16:0, 18:0 and 18:1 contents and the least amount of high-MW compounds as measured by HPSEC. The control oils and some of the treatments in these tests obviously were heated well beyond the stages of being edible. By the authors' estimations, for soybean oil, an 18:2/16:0 of less than 3.8 and an area for peak 4 by HPSEC of greater than about 40 cm^2 was completely undesirable. For cottonseed oil, this subjective cut-off was at about an 18:2/16:0 of 1.7 and an area for peak 4 by HPSEC of greater than 35 cm^2.

White and Armstrong (8) studied the antipolymerization properties in soybean oil of a highly purified sterol fraction of a methanolic oat extract that contained

TABLE 2

Fatty Acid Composition (%) of Cottonseed Oil Treatments Heated at 180°C

Treatments	14:0	16:0	18:0	18:1	18:2	18:2/16:0
Day 0						
Fresh oil	0.9	24.8	2.3	17.7	53.7	2.1
Day 2						
0.007% Oat[d]	1.2[a]	27.7[b]	2.0[c,d]	14.4[b]	54.1[a]	2.0[a]
0.005% Oat	1.1[a]	27.5[b]	1.9[d]	14.2[b]	54.0[a]	2.0[a]
0.02% TBHQ[e]	1.6[a]	33.7[a]	2.3[c,b]	15.3[a,b]	46.8[b]	1.4[b]
1 ppm DMS[f]	1.1[a]	31.2[a]	2.6[c,b]	16.9[a]	47.2[b]	1.5[b]
Control	1.1[a]	31.9[a]	2.8[a]	17.0[a]	46.6[b]	1.6[ab]
Day 4						
0.007% Oat	1.1[a]	28.6[b]	2.1[b]	15.1[b]	52.2[a]	1.8[a]
0.005% Oat	1.1[a]	28.4[b]	2.0[b]	15.3[b]	52.5[a]	1.9[a]
0.02% TBHQ	1.5[a]	38.7[a]	3.0[a]	17.3[a]	38.7[b]	1.0[b]
1 ppm DMS	1.4[a]	38.6[a]	3.1[a]	17.6[a]	38.3[b]	1.0[b]
Control	1.6[a]	39.6[a]	3.0[a]	17.3[a]	37.6[b]	1.0[b]
Day 6						
0.007% Oat	1.1[a]	29.3[b]	2.2[b]	15.9[b]	50.1[a]	1.7[a]
0.005% Oat	1.1[a]	29.7[b]	2.3[b]	16.6[b]	49.6[a]	1.7[a]
0.02% TBHQ	1.7[a]	41.0[a]	3.0[a]	18.1[a]	36.3[b]	0.9[b]
1 ppm DMS	1.7[a]	41.3[a]	3.0[a]	18.0[a]	35.6[b]	0.9[b]
Control	1.1[a]	40.4[a]	3.3[a]	18.3[a]	35.3[b]	0.9[b]
Day 8						
0.007% Oat	1.2[a]	31.8[b]	2.3[b]	16.5[b]	47.9[a]	1.5[a]
0.005% Oat	1.2[a]	32.8[b]	2.5[b]	16.3[b]	46.4[a]	1.6[a]
0.02% TBHQ	1.5[a]	42.1[a]	3.4[a]	19.0[a]	32.4[b]	0.8[b]
1 ppm DMS	1.3[a]	42.2[a]	3.6[a]	19.1[a]	32.5[b]	0.8[b]
Control	1.4[a]	42.1[a]	3.5[a]	19.2[a]	31.4[b]	0.8[b]
Day 10						
0.007% Oat	1.2[a]	33.3[b]	2.6[b]	17.5[a]	44.6[a]	1.3[a]
0.005% Oat	1.2[a]	33.5[b]	2.5[b]	16.1[a]	39.4[b]	1.2[a]
0.02% TBHQ	1.5[a]	43.1[a]	3.5[a]	19.6[b]	29.6[c]	0.7[b]
1 ppm DMS	1.6[a]	44.1[a]	3.4[a]	19.2[b]	28.9[c]	0.7[b]
Control	1.5[a]	43.3[a]	3.5[a]	19.8[b]	29.4[c]	0.7[b]

[a-f]See footnotes to Table 1.

Δ^5-avenasterol. The oat sterol retarded thermal degradation as measured by FAME, conjugated dienoic acids and high-MW compounds as measured by HPSEC. They found that the area of peak 4 from the soybean oil containing the oat sterol fraction remained at 0 until 14 h of heating, whereas the area of peak 4 from a control oil increased dramatically during the same heating period. These results agree with those of the current experiment.

PV of oils from stored bread cubes. Figure 4 shows the PV of oils extracted from the bread cubes stored at 60°C in the dark after frying in soybean oil containing one of the following additives: 0.005 or 0.007% oat extract, 0.02% TBHQ, 1 ppm DMS or a control that contained no additives. At 7 and 14 d of storage, the treatments containing either level of oat extract or TBHQ had significantly lower PV than did the treatments containing DMS and the control. The oil with DMS had a significantly lower PV than did the control, although its PV was still great. Small but significant differences in PV were found among the oils containing either level of oat extract and TBHQ. At day 7, the treatment containing 0.007% oat extract tended to have the smallest PV, but by day 14, the treatment containing TBHQ had the smallest PV, followed by treatments containing 0.007 and 0.005% oat extract, respectively.

Figure 4 also shows the PV of cottonseed oil extracted from bread cubes stored at 60°C for up to 12 d. The treatments were the same as for soybean oil. Results were similar to those for soybean oil except for greater differences among PV of the treatments containing oat extract and TBHQ. At day 4, the treatments containing either level of oat extract and THBQ had PV that were not significantly different from each other. At days 8 and 12, however, the treatment containing TBHQ had the lowest PV, followed by the treatments containing 0.007% oat extract, 0.005% oat extract, DMS and the control, respectively. Interestingly, the oat extract was more effective, and the TBHQ was slightly less effective in soybean than in cottonseed oils. Some differences in effectiveness of the antioxidants in the two oils should be expected, based on differences in the unsaturation of the oils; however, one might expect greater overall stability of cottonseed oil than of soybean oil, based on unsaturation. These results suggest that stability of oils with added antioxidants depends not only on the level of unsaturation of the fatty acids but also on interactions among antioxidants and minor components inherent in the oils.

FAME of extracted oils from stored bread cubes. The data from the FAME of soybean oil extracted from fried bread cubes were in general agreement with the PV results, showing that treatments with either level of oat extract or TBHQ changed less than other treatments during storage and were not significantly different from each other (Table 3). The 18:2 and 18:3 contents of the oils containing either level of oat extract or TBHQ were generally higher, and 16:0 and 18:0 were generally lower than those of the control and the oil containing DMS throughout the storage. On day 7, the treatment containing DMS had significantly less decrease in 18:2 and 18:3 and significantly less increase in 16:0, 18:0 and 18:1 contents than did the control; however, by day 10, the differences were not significant. The 18:2/16:0 of the treatment containing DMS and the control were significantly lower than ratios of all other treatments on days 7 and 14. Indeed,

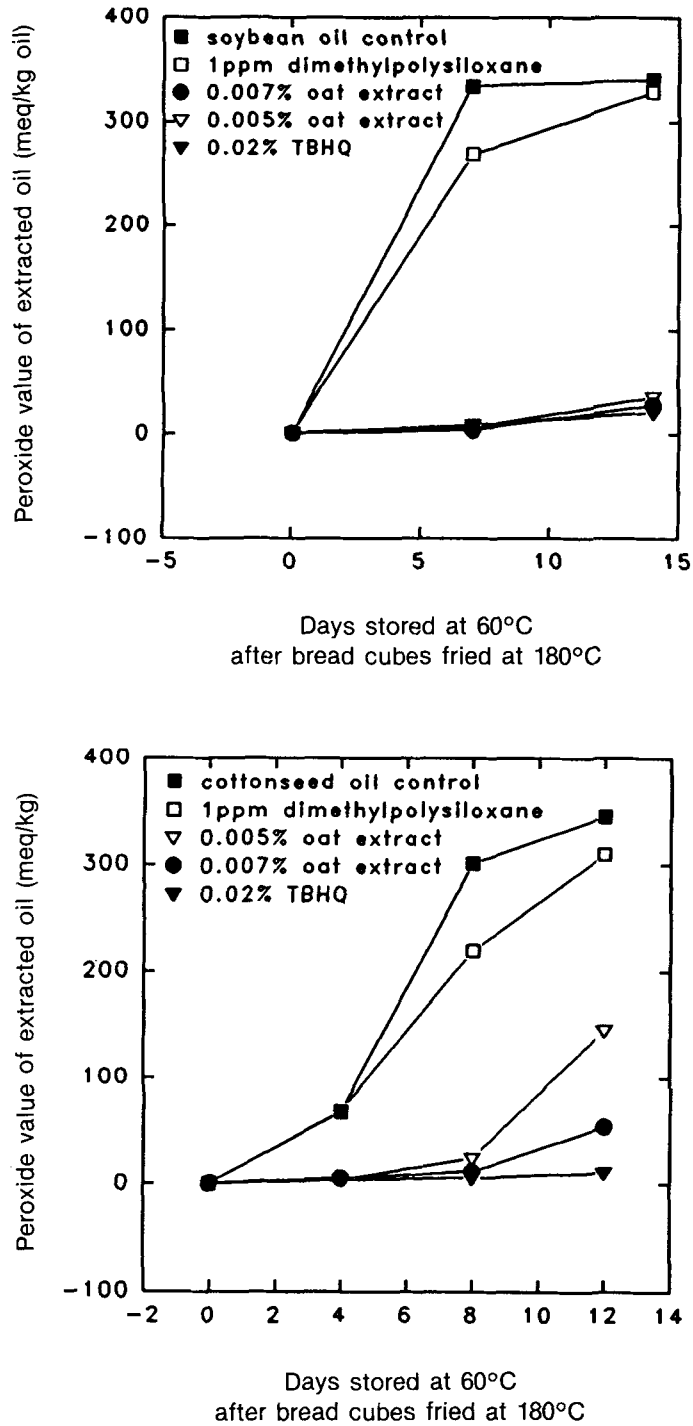

FIG. 4. (a) Peroxide value of oil extracted from bread cubes fried in soybean oil; (b) cottonseed oil with different additives and stored at 60°C. Abbreviations as in Figure 3.

ratios of the treatments containing oat extract or TBHQ changed little during storage of the bread cubes after frying and were not significantly different from each other. The treatment with DMS maintained a significantly higher 18:2/16:0 than did the control at day 7, but by day 10, both treatments decreased greatly in this ratio with no significant difference between them.

TABLE 3

Fatty Acid Composition (%) of Soybean Oil Extracted from Bread Cubes Stored at 60°C in the Dark

Treatments	16:0	18:0	18:1	18:2	18:3	18:2/16:0
Day 0						
Fresh oil	11.1	4.0	23.9	53.6	7.7	4.8
Day 7						
0.007% Oat[d]	10.6[a]	4.2[a]	26.2[a]	51.0[a]	6.5[a,b]	4.8[a]
0.005% Oat	10.4[a]	4.9[b]	26.9[a]	50.7[a]	6.3[a,b]	4.9[a]
0.02% TBHQ[e]	10.3[a]	4.4[a]	26.0[a]	51.4[a]	6.6[a]	5.0[a]
1ppm DMS[f]	11.1[a]	4.9[b]	28.7[b]	47.1[b]	5.8[b]	4.3[b]
Control	15.4[b]	6.7[c]	35.8[c]	37.2[c]	2.8[c]	2.4[c]
Day 14						
0.007% Oat	11.0[a]	4.9[a]	25.9[a]	50.4[a]	6.1[a]	4.7[a]
0.005% Oat	10.9[a]	4.7[a]	25.7[a]	50.6[a]	6.3[a]	4.7[a]
0.02% TBHQ	10.8[a]	4.9[a]	26.5[a]	50.2[a]	6.1[a]	4.7[a]
1 ppm DMS	26.3[b]	11.4[b]	45.4[b]	10.7[b]	0.9[b]	0.4[b]
Control	27.0[b]	12.2[b]	44.0[b]	9.8[b]	0.7[b]	0.4[b]

[a–f]See footnotes to Table 1.

The FAME of cottonseed oil extracted from bread cubes stored at 60°C for 12 d (Table 4) showed changes different from those of soybean oil. At 4 d of storage, no significant differences occurred among all treatments. At 8 d of storage, the 18:2 levels of the treatments containing oat extract at either level or TBHQ were significantly higher than the 18:2 content of the treatments with DMS and the control. By day 12, the levels of 18:2 from the treatments with DMS and the control had dropped dramatically. The 14:0, 16:0, 18:0 and 18:1 contents of the treatments containing DMS and the control were significantly higher than these values for the treatments containing oat extract and TBHQ at 12 d of heating. Some significant differences in the FAME for these treatments occurred at day 8. The 18:2/16:0 of oil extracted from bread cubes fried in cottonseed oil containing oat extract or TBHQ remained essentially unchanged during storage for up to 12 d, even though some differences were calculated as significant (Table 4). The 18:2/16:0 for the treatment containing DMS was essentially the same as for treatments other than the control on day 8; however, by day 12, the ratio for the DMS treatment had dropped greatly.

Interpretation of effectiveness of oat extract. Bread cubes fried in oils containing oat extract or TBHQ and then stored were more stable as measured by PV and by FAME than those fried in control oils containing no additives or in oils containing DMS. The oat extract was as effective as TBHQ in protecting the FAME of the oils in the stored bread cubes for both cottonseed and soybean oils, but the PV were generally slightly higher in stored cubes from the oat extract treatments than from oils with TBHQ.

Although TBHQ is somewhat volatile at frying temperatures, in the current tests, the bread cubes were fried at time 0 of heating, allowing little time for the TBHQ to volatilize before being transferred from the oil to the bread

TABLE 4

Fatty Acid Composition (%) of Cottonseed Oil Extracted from Bread Cubes Stored at 60°C in the Dark

Treatments	14:0	16:0	18:0	18:1	18:2	18:2/16:0
Day 0						
Fresh oil	0.9	24.8	2.0	15.5	53.7	2.1
Day 4						
0.007% Oat[d]	0.7[a]	23.7[a]	2.2[a]	15.8[a]	55.2[a]	2.4[a]
0.005% Oat	0.7[a]	23.7[a]	2.2[a]	15.9[a]	56.2[a]	2.4[a]
0.02% TBHQ[e]	0.7[a]	24.1[a]	2.3[a]	15.6[a]	56.7[a]	2.4[a]
1 ppm DMS[f]	0.7[a]	23.9[a]	2.3[a]	16.0[a]	56.3[a]	2.4[a]
Control	0.7[b]	23.7[a]	2.3[a]	16.0[a]	56.2[a]	2.4[a]
Day 8						
0.007% Oat	0.7[a]	23.7[b]	2.3[a,b]	16.4[b,c]	56.2[a]	2.4[b]
0.005% Oat	0.8[a]	23.4[b,c]	2.2[b]	16.0[c]	56.7[a]	2.4[b]
0.02% TBHQ	0.7[a]	23.1[c]	2.3[a,b]	16.0[c]	56.7[a]	2.5[a]
1 ppm DMS	0.6[b]	23.6[b,c]	2.4[a]	16.8[a,b]	55.4[b]	2.4[b]
Control	0.7[b]	24.9[a]	2.4[a]	17.0[a]	53.6[c]	2.2[c]
Day 12						
0.007% Oat	0.7[b]	23.3[b]	2.2[c]	16.1[c]	56.4[a]	2.5[a]
0.005% Oat	0.7[b]	23.1[b]	2.2[c]	16.4[c]	56.1[a]	2.4[a]
0.02% TBHQ	0.7[b]	23.2[b]	2.2[c]	15.9[c]	56.8[a]	2.5[a]
1 ppm DMS	1.6[a]	52.4[a]	4.6[b]	24.6[b]	14.8[b]	0.3[b]
Control	1.5[a]	53.5[a]	5.3[a]	26.7[a]	10.4[c]	0.2[b]

[a–f]See footnotes to Table 1.

cubes. Therefore, TBHQ likely was present in the bread cubes during storage at essentially its original level and was able to act as an antioxidant. Oat antioxidants have not been tested for their volatility, but would have had the same advantage as the TBHQ.

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