

Oxidative Stability of Hydrogenated Menhaden Oil Shortening Blends in Cookies, Crackers, and Snacks

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ABSTRACT: The oxidative stability of partially hydrogenated menhaden fish oil (PHMO) shortening/canola oil blends with added antioxidant tertiary butylhydroquinone (TBHQ) and various blended partially hydrogenated vegetable oil (PHVO) shortenings without antioxidant in aged cookies and crackers was analyzed by anisidine value (AV), peroxide value (PV), and Totox value. The results showed no significant differences ($P < 0.05$) for PV, AV, or Totox value between the PHMO shortening containing TBHQ and the PHVO shortening in cookies, crackers, and deep-fried extruded snacks, except for the AV and Totox value of crackers.

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Cookies and other baked products usually have a shelf life that is limited by staling, which occurs before any other deteriorative reaction. Not considered a major problem, oxidative stability in baked products has seldom been investigated. Because cookies and other baked products contain fat, however, the oxidative stability may be of concern to the food industry, especially if previously unused fat sources are proposed.

Lipid oxidation is affected by many factors, including the presence of antioxidants or prooxidants (trace metals, chlorophyll), abuse (regarding storage conditions), or age, chelating agents, and fatty acid composition (1). The number, position, and geometry of the double bonds affect the rate of oxidation. *Cis* acids oxidize more readily than their *trans* isomers. Conjugated double bonds are more reactive than nonconjugated bonds, and polyunsaturated fatty acids are more reactive than saturated ones. Relative rates of oxidation for the arachidonic, linolenic, linoleic, and oleic fatty acids are approximately 40:20:10:1, respectively (2). Polyunsaturated lipids in vegetable and fish oils produce a complex array of low- and high-molecular-weight secondary products, many of which are volatile.

Fish oil oxidizes at a greater rate than do most vegetable

or animal fats, due to the much greater content of long-chain polyunsaturated fatty acids with five and six double bonds [21% for menhaden oil; 0% for lard and soy, canola, palm, olive, and sunflower oils (3,4)]. The oxidative instability of n-3 polyunsaturated lipids in fish oil is well established. The principal marine oil polyunsaturated fatty acids are n-3 fatty acids, while the major vegetable oil polyunsaturates are n-6. The n-3 eicosapentaenoic acid (EPA) (20:5n-3) and docosahexaenoic acid (DHA) (22:6n-3), found in high amounts in fish oil, are much more susceptible to oxidation than is linolenic acid (18:3n-3), which is found in high amounts in unsaturated vegetable oils, such as soybean and canola oils. Also, DHA and EPA produce flavors and odors that are objectionable as a result of the formation of low-molecular-weight carbonyl compounds (5,6).

The use of fish oil in salad oils and other fish oil products has been discouraged because of reversion or “fishy” flavors (7) that may result from oxidation (8–10). The literature cites several products that have been successfully developed from fish oil, however. Specially deodorized and stabilized menhaden–fish-oil mayonnaise was prepared with tertiary butylhydroquinone (TBHQ) (0.02%) and nitrogen packaging (11). The all–fish-oil mayonnaise was acceptable in sensory tests after storage at 2°C for 14 wk and was not significantly different (as measured by the triangle test) from all–soy-oil mayonnaise. Moreover, chemical analyses showed that oxidation in the deodorized and stabilized fish-oil mayonnaise was minimal. French-type salad dressings (12) were made with menhaden/soybean oil blends of 10, 20, and 30% menhaden oil (w/w) with added antioxidant and stored in the dark at 22°C for 20 wk. Initially, the sensory scores were not significantly different between the blends and the control (100% soybean oil). After 6 wk of storage, the salad dressings made with 10 and 20% fish oil had similar ratings for aroma, aftertaste, and flavor, with no significant differences between the samples. They were rated as significantly less desirable, however, than the 100% soybean control. The addition of menhaden oil to the salad dressing imparted a lingering unpleasant taste that the spices in the formula were not able to overcome. The 30%–fish-oil salad dressing was rated as being different from the control by week 4 and was eliminated from the study.

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Margarine containing 16% unhydrogenated fish oil had a shelf life of at least 10 wk when stored at 5°C and was similar to the all-vegetable control margarine (13). Low-calorie spreads (40% fat) containing unhydrogenated fish oil had an adequate shelf life (12 wk) when stored at 5°C, similar to the shelf life of dairy- and vegetable-oil-based spreads (14).

Hydrogenation is used to improve the oxidative stability of the oil because it converts the polyunsaturated fatty acids to mono- and diunsaturated forms. In an unpublished study by the American Institute of Baking (Manhattan, KS) concerning the same products in this paper, 20 untrained panelists found that products made with blended, partially hydrogenated menhaden oil (PHMO) plus TBHQ and with bleached and deodorized shortening/canola oil were not significantly different by the triangle testing method (Stauffer, C., A.P. Bimbo, and J.B. Crowther, personal communication, 1993).

No literature was found on oxidative stability of baked goods or on tests determining stability in these products. Hsieh and Regenstein (15), however, found that the most sensitive analytical tests for early detection of oxidation of mayonnaise containing fish oil were peroxide value (PV) and thiobarbituric acid (TBA), while total carbonyl compound (TCC) and anisidine value (AV) were used to measure later oxidation. Our objective was to determine the oxidative stability of cookies, crackers, and deep-fried snack crackers containing either PHMO shortening/canola oil blend with antioxidants or partially hydrogenated vegetable oil (PHVO) shortening blend without antioxidants.

EXPERIMENTAL PROCEDURES

Raw materials. Menhaden oil (Zapata Protein, Inc., Reedville, VA) was extracted, refined, bleached, and deodorized by standard methods (16). Hydrogenation, analysis, blending of basestocks, and preparation of shortenings were carried out at POS Pilot Plant (Saskatoon, Saskatchewan, Canada).

Table 1 shows the characteristics of PHMO basestock and hardstock (Stauffer, C., A.P. Bimbo, and J.B. Crowther, personal communication, 1993). The PHMO shortening was

TABLE 1
Characteristics of Partially Hydrogenated Menhaden Oil Basestocks and Hardstock

| | Basestock #1 | Basestock #2 | Hardstock |
|-------------------------------|--------------|--------------|-----------|
| Temperature (°C) | 175–200 | 160 | 175–200 |
| H ₂ pressure (psi) | 20 | 40 | 20 |
| Ni concentration (%) | 0.1 | 0.1 | 0.1 |
| Time (min) | 103 | 99 | 150 |
| Melting point (°C) | 35.8 | 38.9 | 58.2 |
| Iodine value | 76.0 | 71.0 | 4.6 |
| Solid fat index (°C) | | | |
| 10.0 | 33.1 | 39.5 | 78.2 |
| 21.1 | 20.3 | 27.0 | 80.3 |
| 26.7 | 13.5 | 21.0 | 82.0 |
| 33.3 | 1.1 | 9.6 | 85.8 |
| 40.0 | 0.0 | 0.0 | 88.5 |

TABLE 2
Composition of Partially Hydrogenated Menhaden Oil Shortenings

| | All-purpose spray oil | Filler fat, frying fat |
|-----------------------------|-----------------------|------------------------|
| Basestock #1 | 60% | — |
| Basestock #2 | — | 100% |
| Hardstock | 10% | — |
| RBD ^a canola oil | 30% | — |

^aRefined, bleached, and deodorized.

composed of 60% basestock, 10% hardstock, and 30% refined, bleached, and deodorized canola oil (iodine value of 110–126) (Esprit; Can Amera Foods, Edmonton, Alberta, Canada), which had an initial PV of 0.68 (Table 2). The fatty acid composition of the blend was not measured. Because menhaden oil can vary in its fatty acid composition according to season of the year and location of catch, the exact composition cannot be taken from the literature. Fatty acid composition of the blend, however, was calculated by determining the typical fatty acid composition of each component and then multiplying it by its percentage (Table 3) (Bimbo, A.P., personal communication, 1994). The PHMO was stabilized with 200 ppm TBHQ.

Two types of cookies were tested—a rotary sandwich cookie (14.35% shortening) with a cream filling (33.33% oil) and a wire-cut butter crunch cookie (18.70% shortening). The experimental sandwich cookie and the butter crunch cookie

TABLE 3
Typical Analysis of Fats and Oils Containing Menhaden Oil^a

| | All-purpose spray oil | Filler fat, frying fat |
|------------------------|-----------------------|------------------------|
| | (% total fatty acids) | |
| Fatty acid composition | | |
| C _{14:0} | 5.5 | 8.0 |
| C _{16:0} | 16.5 | 23.5 |
| C _{16:1} | 8.0 | 10.5 |
| C _{18:0} | 5.5 | 8.3 |
| C _{18:1} | 26.1 | 12.1 |
| C _{18:2} | 7.5 | 1.2 |
| C _{18:3} | 3.3 | — |
| C _{20:0} | 2.8 | 10.9 |
| C _{20:1} | 7.5 | 9.5 |
| C _{20:2} | 2.6 | — |
| C _{20:3} | 0.4 | — |
| C _{20:5} | 0.6 | 0.1 |
| C _{21:5} | 1.1 | 0.8 |
| C _{22:0} | 7.0 | 6.8 |
| C _{22:1} | 1.5 | 4.7 |
| C _{22:3} | 1.0 | 2.1 |
| C _{22:4} | 1.2 | 2.0 |
| AOM (h) | 162.0 | 273.0 |
| Smoking point (°C) | 248.0 | 240.0 |
| Melting point (°C) | 43.6 | 38.9 |
| Maximum iodine value | 84.0 | 85.0 |
| Solid fat index (°C) | | |
| 10.0 | 25.4 | 39.5 |
| 21.1 | 19.2 | 27.0 |
| 26.7 | 16.5 | 21.0 |
| 33.3 | 11.1 | 9.6 |
| 40.0 | 3.6 | 0.0 |

^aSource: Bimbo, A.P., personal communication, 1994.

TABLE 4
Typical Analysis of Vegetable Oil Shortenings^a

| | All-purpose | Spray oil | Filler fat | Frying fat |
|-------------------------|----------------------|-----------|------------|------------|
| | (% total fatty acid) | | | |
| Fatty acid composition | | | | |
| C _{6:0} | — | — | 0.4 | — |
| C _{8:0} | — | — | 6.8 | — |
| C _{10:0} | — | — | 5.7 | — |
| C _{14:0} | 0.2 | 0.1 | 18.2 | — |
| C _{16:0} | 12.3 | 5.4 | 9.2 | 10.2 |
| C _{16:1} | — | 0.4 | — | 0.1 |
| C _{17:0} | — | — | — | 0.1 |
| C _{18:0} | 11.8 | 5.1 | 11.5 | 11.8 |
| C _{18:1} | 62.3 | 66.7 | 0.9 | 72.9 |
| C _{18:2} | 12.1 | 17.5 | 0.1 | 2.2 |
| C _{18:3} | 0.3 | — | — | — |
| C _{20:0} | 0.4 | 1.6 | 0.2 | 0.3 |
| C _{20:1} | 0.4 | 1.7 | — | 0.2 |
| C _{22:0} | 0.4 | 0.4 | — | 0.3 |
| C _{22:1} | — | 0.4 | — | — |
| AOM (h) | 150.0 | 75.0 | 350.0 | 300.0 |
| Smoking point (°C) | ND | ND | ND | 230.0 |
| Peroxide value (meq/kg) | 0.5 | 1.0 | 1.0 | 0.2 |
| Melting point (°C) | 46–49 | 20–22 | 33–36 | 38 |
| Iodine value | 70–75 | 90 | ND | 69.5 |
| Solid fat index (°C) | | | | |
| 10.0 | 25–30 | 10 | ND | 50 |
| 21.1 | 17–22 | 3 | ND | 36 |
| 26.7 | 15–20 | — | ND | 28 |
| 33.3 | 11–15 | — | ND | 14 |
| 40.0 | 8.5–13 | — | ND | 1 |

^aND = not determined; sources: Dunford, D., and T. Ingala, personal communication, 1994.

basecake were made with all-purpose PHMO shortening; the control cookie basecake contained refined, bleached, and partially hydrogenated and deodorized soybean/cottonseed oil shortening (BBS-C; Capital City Co., Karlshamns, Columbus, OH) (Tables 4 and 5). The experimental sandwich cookie's cream filling was made with PHMO filler fat, and the control was made with refined, bleached, partially hydrogenated, filtered, and deodorized coconut oil filler fat (Pureco 92; Capital City Co.).

Experimental snack crackers (7.49% shortening) were prepared with all-purpose PHMO shortening and were sprayed with all-purpose PHMO. Control crackers contained partially hydrogenated soybean/cottonseed oil shortening and were sprayed with refined, bleached, partially hydrogenated, filtered, and deodorized canola oil (Lobra 70; Capital City Co.).

TABLE 5
Types and Amounts of Vegetable Oil Used in Controls

| Test material | Oil | Use (%) | Trade name |
|----------------------|--|---------|------------------------|
| Sandwich cookie | All-purpose partially hydrogenated soybean/cottonseed-oil shortening | 14.35 | BBS-C ^a |
| Cream filling | Partially hydrogenated coconut oil filler-fat shortening | 33.33 | Pureco 92 ^a |
| Butter crunch cookie | All-purpose partially hydrogenated soybean/cottonseed-oil shortening | 18.7 | BBS-C |
| Snack cracker | All-purpose partially hydrogenated soybean/cottonseed-oil shortening | 7.49 | BBS-C |
| Snack cracker | Partially hydrogenated canola spray oil | 12–15 | Lobra 70 ^a |
| Extruded snacks | Partially hydrogenated soybean oil | | XXX Vream ^b |

^aCapital City Co., Karlshamns, Columbus, OH. ^bBunge Corp., Bradley, IL.

The spray oil, which was 12–15% of the product's weight, was applied to the hot crackers as they exited the oven.

Experimental extruded snack pellets were deep-fried in PHMO frying-fat shortening, while the control snacks were deep-fried in partially hydrogenated soybean oil (XXX Vream; Bunge Corp., Bradley, IL). Extruded snack pellets were fried in a floor-model fryer (Filter Magic; Fry Master Corp., Shreveport, LA) at 204°C for 10 s. Baking and deep-frying were done at the American Institute of Baking with standard cookie and cracker formulas for ingredient and process testing.

Storage. The products were packaged in polystyrene packing trays, wrapped in polyethylene bags, and held at approximately 25°C for about 15 d, before their arrival at Cornell University (Ithaca, NY). The products were stored at 20°C ± 4°C for up to 9.5 mon in the original packaging. Because the cookies and crackers were packed in clear plastic bags, they were exposed to fluorescent light and some sunlight during the 9.5 mon at Cornell.

AV. AV was measured by the method for fish oil as published in the International Association of Fish Meal Manufacturers (IAFMM) Fish Oil Bulletin (17). AV is a measure of the alpha-beta unsaturated aldehydes of fats and oils.

To prepare samples for AV analysis, the cream layer was scraped from the cookie layers, and cookies or crackers were blended to make crumbs in a Handy Chopper (Black & Decker, Shelton, CT). Crumbs (2 g) or cream layer (3 g) were combined with 20 mL isooctane (Fisher, Spectranalyzed, Fairlawn, NJ). Samples were centrifuged (Sorvall RC2-B, Norwalk, CT) at 8,500 rpm (13,000 × g at the tube bottom) for 20 min, and the supernatant was removed with a pipet. The absorbance of the supernatant (Ea) was measured at 350 nm (1-cm pathlength) on a Hitachi 100–60 spectrophotometer (Hitachi Corp., Tokyo, Japan) against pure isooctane. Then 5 mL supernatant or 5 mL isooctane blank were reacted with 1 mL *para*-anisidine (0.25% solution in glacial acetic acid) in Pyrex test tubes (Corning, Inc., Corning, NY). The test tubes were capped, shaken vigorously, and kept in the dark for 10 min. The absorbance (Eb) was measured at 350 nm against isooctane plus *para*-anisidine. AV was calculated from the following formula:

$$AV = 25 \times (1.2Eb - Ea) / \text{sample weight} \quad [1]$$

PV. Fat was extracted for PV analysis by the procedure of Ke and Woyewoda (18). PV was determined by American Oil

TABLE 6
Changes in Anisidine Value, Peroxide Value, and Totox Value in Sandwich Cookie Basecake with Time^a

| Month | Anisidine value | | Peroxide value | | Totox value | |
|-------------------|-----------------|-------------------|----------------|--------------|--------------|--------------|
| | Control | PHMO | Control | PHMO | Control | PHMO |
| 0.0 | 1.46 ± 0.62 | 2.54 ± 0.34 | 1.75 ± 0.55 | 1.96 ± 0.11 | 4.96 ± 0.99 | 6.46 ± 0.38 |
| 3.0 | 1.95 ± 0.30 | 1.82 ± 0.23 | 0.68 ± 0.29 | 0.82 ± 0.41 | 2.63 ± 0.51 | 3.24 ± 0.62 |
| 5.5 | 0.32 ± 0.03 | 0.50 ^b | 0.60 ± 0.18 | 0.71 ± 0.04 | 1.52 ± 0.26 | 1.92 ± 0.06 |
| 7.5 | 1.21 ± 0.19 | 1.36 ± 1.24 | 0.65 ± 0.55 | 0.78 ± 0.74 | 2.51 ± 0.80 | 2.92 ± 1.62 |
| 9.5 | 1.64 ± 0.76 | 1.54 ± 0.15 | 1.17 ± 0.50 | 1.69 ± 0.18 | 3.98 ± 1.04 | 4.92 ± 0.30 |
| Mean ^c | 1.32 ± 0.47a | 1.55 ± 0.58a | 0.97 ± 0.44a | 1.19 ± 0.39a | 3.26 ± 0.78a | 3.93 ± 0.80a |

^aExcludes cream filling, mean ± SD, n = 2, except as noted. PHMO, partially hydrogenated menhaden fish oil.

^bn = 1.

^cMeans in the same measurement category with different letters are significantly different at the 5% level.

Chemists' Society (AOCS) Official Method Cd 8-53 (19), based on iodometric titration.

The cream layer of the sandwich cookies was separated from the outer layers and extracted. Five grams of the cream layer and the same amounts as for the AV analysis were used. Cookies or crackers (10 g) were blended to crumbs and combined with 50 mL chloroform, 25 mL methanol, and 25 mL 2.5% aqueous CaCl₂ solution (Fisher, A.R. grade). Samples were centrifuged at 8,500 rpm for 20 min, and the chloroform layer was separated in separatory funnels. Glacial acetic acid (15 mL) and, after swirling, 0.5 mL saturated KI solution was added to 10 mL chloroform extract or chloroform blank. Samples were swirled occasionally for exactly 1 min, then 25 mL double-distilled water was added to stop the reaction. Samples were titrated with 0.01 N Na₂S₂O₃ (0.5 mL 1% starch was added as the indicator) until the blue color just disappeared. PV was calculated from the following formula:

$$PV \text{ (milliequivalents/kg)} = (S - B) \times 0.01 N \times 1000 \times 5/W \quad [2]$$

S is the volume of titrant for sample extract (mL); *B* is the volume of titrant for blank (mL); and *W* is the sample weight (g).

Totox value. Totox value was calculated as the AV plus twice the PV (20,21).

Statistical analysis. The general linear model of Minitab 7.2 (Minitab, Inc., State College, PA) was used for analysis of variance, analysis of covariance, and regression because it can be used with unbalanced designs and missing data. Means and standard deviations were determined on duplicate sam-

ples, except where noted. The standard deviation of the grand mean was the root mean square average within months.

For each test, analysis of variance with respect to time, treatment, and the interaction of time and treatment was determined ($P < 0.05$). To determine significance ($P < 0.05$) between overall means of treatments, a one-way analysis of variance was done with time averaged out.

RESULTS AND DISCUSSION

Sandwich cookie. The differences in mean AV, PV, and Totox value between the experimental and control sandwich cookies were not significant ($P < 0.05$) for both the cookie and cream filling (Tables 6 and 7). The initial AV for the sandwich cookie basecake with PHMO was higher than the control, but was slightly lower after 9.5 mon. AV of both sets of cookies decreased and then increased toward the end of the study. The initial AV for the cream filling of the sandwich cookies containing PHMO was lower than that of the control and decreased over time. By the end of 9.5 mon, the differences between the control and PHMO were not significant.

PV and Totox value of the sandwich cookie basecake with PHMO and the cream filling were slightly higher than those of the control throughout most of the study. PV and Totox value for both PHMO and control cookies decreased with increasing storage, but increased at 9.5 mon. PV values at initial tests were high, perhaps due to the initial holding conditions prior to storage, but they were within the normal range

TABLE 7
Changes in Anisidine Value, Peroxide Value, and Totox Value in Cream Filling of Sandwich Cookie with Time^a

| Month | Anisidine value | | Peroxide value | | Totox value | |
|-------------------|-----------------|-------------------|----------------|--------------|--------------|--------------|
| | Control | PHMO | Control | PHMO | Control | PHMO |
| 0.0 | 2.14 ± 0.05 | 1.28 ± 0.37 | 1.76 ± 1.33 | 3.56 ± 2.70 | 5.66 ± 1.88 | 8.40 ± 3.84 |
| 3.0 | 0.99 ± 0.00 | 1.03 ± 0.32 | 0.52 ± 0.45 | 1.05 ± 0.16 | 2.04 ± 0.64 | 3.13 ± 0.39 |
| 5.5 | 0.39 ± 0.03 | 0.56 ^b | 1.04 ± 0.15 | 1.09 ± 0.07 | 2.47 ± 0.21 | 2.74 ± 0.10 |
| 7.5 | 0.42 ± 0.48 | 0.19 ± 0.04 | 0.78 ± 0.36 | 0.58 ± 0.67 | 1.98 ± 0.70 | 1.35 ± 2.09 |
| 9.5 | 0.27 ± 0.00 | 0.28 ± 0.05 | 1.22 ± 0.80 | 1.64 ± 0.33 | 2.71 ± 1.13 | 3.56 ± 0.47 |
| Mean ^c | 0.84 ± 0.22a | 0.67 ± 0.22a | 1.07 ± 0.74a | 1.58 ± 1.39a | 2.98 ± 1.07a | 3.83 ± 1.98a |

^aMean ± SD, n = 2, except as noted. Abbreviation as in Table 6.

^bn = 1.

^cMeans in the same measurement category with different letters are significantly different at the 5% level.

TABLE 8
Changes in Anisidine Value, Peroxide Value, and Totox Value in Butter Crunch Cookies with Time^a

| Month | Anisidine value | | Peroxide value | | Totox value | |
|-------------------|-----------------|-------------------|-------------------|--------------|-----------------|-----------------|
| | Control | PHMO | Control | PHMO | Control | PHMO |
| 0.0 | ND ^b | ND ^b | 1.37 ± 0.42 | 0.87 ± 0.13 | ND ^b | ND ^b |
| 2.0 | 2.37 ± 0.21 | 2.26 ^c | 0.73 ± 0.08 | 0.47 ± 0.30 | 3.84 ± 0.24 | 3.20 ± 0.42 |
| 4.0 | 3.01 ± 0.75 | 3.15 ± 0.37 | 0.71 ± 0.11 | 1.00 ± 0.01 | 4.43 ± 0.77 | 5.15 ± 0.37 |
| 6.0 | 2.29 ± 0.18 | 1.24 ± 0.49 | 0.78 ^c | 1.83 ± 1.30 | 3.85 ± 0.18 | 4.90 ± 1.90 |
| 8.0 | 1.94 ± 0.02 | 1.80 ± 0.66 | 1.70 ± 0.33 | 1.55 ± 1.90 | 5.34 ± 0.48 | 4.90 ± 2.77 |
| Mean ^d | 2.40 ± 0.40a | 2.11 ± 0.45a | 1.45 ± 0.25a | 1.32 ± 1.02a | 5.30 ± 0.53a | 4.75 ± 1.51a |

^aMean ± SD, n = 2, except as noted. Abbreviation as in Table 6.^bND = Not determined.^cn = 1.^dMeans in the same measurement category with different letters are significantly different at the 5% level. For peroxide value (PV) we had data for 0, 2, 4, 6, 7, and 8.5 mon. To obtain PV (and, consequently, Totox value) for 6.5 mon, we interpolated halfway between months 6 and 7.

of 0–2 (except for PHMO cream filling), according to Stansby (22). Fresh alkali-refined sunflower seed and palm oil generally have Totox values of about 4 (23).

Butter crunch wire-cut cookie. The differences in mean AV, PV, and Totox value for butter crunch cookies were not significant ($P < 0.05$) (Table 8). AV for the butter crunch cookies made with PHMO shortening was generally slightly lower than that of the control. For both, AV increased during the first four months and then decreased. Initially and at the end of the study, PV was lower in the butter crunch cookies containing PHMO than that of the control. During the latter part of the study, the variation in data, as measured by the standard deviation for cookies made with PHMO, increased. Mean AV, PV, and Totox value were higher for the control butter crunch cookies than those of the cookies made with PHMO, but the differences were not significant. Trends in Totox value for the control cookies were higher at months 2 and 8 (3.84 and 5.34, respectively); and lower at months 4 and 6 (4.43 and 3.85, respectively) than PHMO cookies. Totox values of control cookies generally increased through the eighth month, and for the PHMO; Totox values increase through the fourth month, then level off.

Snack crackers. Mean AV and Totox value for PHMO were significantly higher than those of the control crackers ($P < 0.05$). There was no significant difference in PV, however. Snack crackers made with PHMO had higher mean values

than did the control in all three analyses (Table 9). All values generally decreased with time. PV of the PHMO snack crackers was similar to that of the control. For both, PV decreased (month 4), then increased (month 6.5), then decreased again (month 8.5). The final decrease can probably be explained by the fact that the hydroperoxides are early intermediate products and are therefore unstable. By the end of the study, however, PV and Totox value were not significantly different for the PHMO or the control crackers.

Deep-fried extruded snacks. No significant differences ($P < 0.05$) between overall means of the two treatments were noted for AV, PV, and Totox analyses (Table 10). Deep-fried extruded snacks made with PHMO shortening had a higher initial AV than did the control snacks but, by the eighth month, AV was lower, although not significantly. For both, AV increased until the fourth month and then decreased to a level below the initial AV. Extruded snacks, deep-fried in PHMO, generally had higher PV and Totox values than did the control. Overall, PV for both deep-fried extruded snacks increased over time to the fifth month. All deep-fried extruded snacks had low initial AV, PV, and Totox value. Extruded snacks, deep-fried in PHMO, had higher Totox values than the control throughout the study (except for month 6.5), for PHMO.

In summary, no significant differences in Totox value were found for cookies, crackers, and deep-fried extruded snacks

TABLE 9
Changes in Anisidine Value, Peroxide Value, and Totox Value in Snack Crackers with Time^a

| Month | Anisidine value | | Peroxide value | | Totox value | |
|-------------------|-------------------|-------------------|----------------|--------------|--------------|--------------|
| | Control | PHMO | Control | PHMO | Control | PHMO |
| 0.0 | 1.72 ± 0.06 | 3.53 ± 0.34 | 1.30 ± 0.30 | 1.36 ± 0.07 | 4.32 ± 0.43 | 6.25 ± 0.35 |
| 2.0 | 1.13 ± 0.49 | 2.24 ± 0.23 | 1.15 ± 0.23 | 0.89 ± 0.16 | 3.43 ± 0.59 | 4.02 ± 0.32 |
| 4.0 | 0.44 ^b | 0.98 ^b | 0.66 ± 0.18 | 1.70 ± 0.18 | 1.76 ± 0.25 | 4.38 ± 0.25 |
| 6.5 ^c | 0.78 ± 0.25 | 1.24 ± 0.74 | 1.82 ± 0.33 | 2.16 ± 0.56 | 4.44 ± 0.54 | 5.56 ± 1.09 |
| 8.5 | 0.59 ± 0.31 | 1.07 ± 0.61 | 0.98 ± 0.28 | 0.85 ± 0.10 | 2.55 ± 0.50 | 2.77 ± 0.63 |
| Mean ^d | 0.93 ± 0.28a | 1.81 ± 0.47b | 1.29 ± 0.28a | 1.52 ± 0.40a | 3.51 ± 0.48a | 4.85 ± 0.74b |

^aMean ± SD, n = 2, except as noted. Abbreviation as in Tables 6 and 8.^bn = 1.^cInterpolated values for PV (at 6 and 7 mon) were used to calculate PV and Totox value for 6.5 mon.^dMeans in the same measurement category with different letters are significantly different at the 5% level.

TABLE 10
Changes in Anisidine Value, Peroxide Value, and Totox Value in Deep-Fried Extruded Snacks with Time^a

| Month | Anisidine value | | Peroxide value | | Totox value | |
|-------------------|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | Control | PHMO | Control | PHMO | Control | PHMO |
| 0.0 | 0.51 ^b | 0.86 ± 0.55 | 0.45 ± 0.11 | 0.81 ± 0.18 | 1.41 ± 0.16 | 2.48 ± 0.61 |
| 2.0 | 0.72 ^b | — ^c | 1.44 ± 0.17 | 1.88 ± 0.07 | 3.60 ± 0.24 | — ^c |
| 4.0 | 1.12 ± 0.03 | 1.12 ± 0.28 | 1.39 ± 0.15 | 1.71 ± 0.45 | 3.90 ± 0.21 | 4.54 ± 0.70 |
| 5.0 | ND ^d | ND ^d | 1.56 ± 0.37 | 2.13 ± 0.58 | ND ^d | ND ^d |
| 6.5 | 0.27 ± 0.02 | 0.50 ± 0.04 | 1.14 ± 0.65 | 1.09 ± 0.44 | 2.54 ± 0.92 | 2.24 ± 0.62 |
| 8.0 | 0.26 ± 0.23 | 0.06 ± 0.04 | ND ^d | ND ^d | ND ^d | ND ^d |
| Mean ^e | 0.58 ± 0.10a | 0.64 ± 0.31a | 1.20 ± 0.35a | 1.52 ± 0.39a | 2.98 ± 0.50a | 3.68 ± 0.63a |

^aMean ± SD, n = 2, except as noted. Abbreviation as in Table 6.

^bn = 1.

^cMissing anisidine value data because net absorbance of the fat-anisidine solution was smaller than net absorbance of the fat solution, producing negative anisidine value (see equation in anisidine value section).

^dND = Not determined.

^eMeans in the same measurement category with different letters are significantly different at the 5% level.

prepared with PHMO, containing TBHQ, compared to similar items made with PHVO shortening without antioxidants. Significant differences ($P < 0.05$) were noted between snack crackers made with PHMO plus TBHQ and PHVO for both AV and Totox value.

Similarities in the stability of the PHMO and control products were probably due to two factors. First, fatty acid composition of the menhaden oil changed with hydrogenation. The fatty acids, EPA and DHA (21% of menhaden oil), which are highly susceptible to oxidation, were eliminated. The percentage of long-chain polyunsaturated fatty acids decreased from about 21 to 0.6% (all-purpose and spray oil) or 0.1% (filler fat and frying fat) (see Tables 3 and 4). The other factor is that the TBHQ antioxidant was added to the PHMO but not to the vegetable oils. The products in this study made from menhaden oil and stabilized by hydrogenation and antioxidants, were equivalent in stability to products made from vegetable oil that was stabilized by hydrogenation only.

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