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Headspace Volatile Analysis to Evaluate Oxidative and Thermal Stability of Soybean Oil. Effect of Hydrogenation and Additives

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Headspace gas chromatographic analysis of heated soybean oil was investigated as a tool to determine what effect hydrogenation and additives have on the formation of total and individual volatile components. Soybean oil was hydrogenated to varying linolenate (Ln) contents with either nickel (Ni) or copper catalysts. Oils were stabilized with citric acid (CA) or a combination of CA with tertiary butyl hydroquinone (TBHQ) and/or methyl silicone (MS). Volatiles were analyzed with a capillary gas chromatograph equipped with a headspace sampler positioned on the injector. Oxidative stability was determined after storage of the oils at 60 C. To study thermal abuse and frying performance of oils, samples were heated for several hours with prolonged bread frying. The deterioration of the oils was accelerated further by static heating in air within the headspace sampler. All hydrogenated oils produced less total volatiles than the unhydrogenated control oil after prolonged heating and bread frying. Static heating at 190 C for one hr showed that the oil hydrogenated with Ni to 0.4% Ln was the most stable. MS decreased the formation of volatiles in all samples and was particularly effective in stabilizing the hydrogenated oils. However, MS had little effect on volatiles in the oil hydrogenated to 0.4% with Ni. Unique volatile compounds identified included 2,4-heptadienal in nonhydrogenated soybean oil and 2-nonenal in most hydrogenated oils. On heating, the amount of 2-heptanal decreased significantly in the Ni hydrogenated oils compared to the control. Hexanal, on the other hand, decreased in all hydrogenated oils compared to the control.

When fats and oils are heated to frying temperatures, many oxidation reactions occur which produce desirable and undesirable flavors. Polyunsaturated fatty acids are most susceptible to oxidation and promote the formation of volatile compounds in the oils (1-3). Hydrogenation of soybean oil can be effective in producing a more stable cooking oil as determined by the room odor test (4). In this paper, the oxidative and thermal stability of hydrogenated cooking oils and the effect of additives were studied by analyzing for volatile compounds by gas chromatography. Volatile compounds formed in fried bread cubes also were evaluated to determine the effects of food frying.

EXPERIMENTAL

Soybean oil was hydrogenated in a continuous reactor (5-6) with nickel (Ni) or Copper (Cu) catalyst to reduce the linolenate content to a range of 0.4% to 2.7%. The products were compared to a commercially Ni-hydrogenated and winterized soybean oil containing 4.6% linolenate. After hydrogenation, each oil was bleached, deodorized and stabilized with citric acid (CA) or with CA in combination with methyl silicone (MS) or tertiary butyl hydroquinone (TBHQ). The fatty acid composition of the oils determined by gas chromatography (GC) is summarized in Table 1. The hydrogenated oils are identified by the type of catalyst and the amount of triene present in each sample (Table 1). These labels are used throughout this paper to distinguish samples. When soybean oil was hydrogenated with Ni, the formation of stearate increased from 4.4% to 7.1% in the Ni-2.7 hydrogenated oil and to 16.4% in the Ni-0.4 hydrogenated oil.

Volatile analyses were made for each oil after storage for eight days at 60 C. Prolonged frying tests were conducted by heating 100 g of each oil and reheating two more times to a temperature of 190 C with intermittent frying of bread cubes. Each oil was heated for a total of 17 hr, and bread cubes were fried in the oil for 2.5 hr of that time (8). The bread cubes were stored at 60 C for four days. An accelerated heating test was also carried out by heating a small sample of oil in air for one hr.

Analyses of the volatiles were made in duplicate with a Perkin Elmer Sigma 3B GC equipped with a Perkin Elmer HS-6 headspace sampler (Norwalk, Connecticut). Oil samples (0.5 g) to which 200 ppm dodecane had been added were weighed in 10-ml vials, purged with nitrogen for two min and sealed with a septum secured by an aluminum cap. The vials containing oil were placed in the headspace magazine and heated to 190 C for 10 min to vaporize the volatile compounds; then the headspace sampler was placed into the injection position and pressurized for 0.5 min to equilibrate the gas and liquid phase. Volatiles were then transferred into a 30-m Durabond-5 chemically bonded capillary column (30 m × 0.32 mm ID; 1 micron film thickness) (J&W Scientific, Rancho Cordova, California) by splitless injection. The GC oven temperature was held at 0 C for 10 min, then programmed to 250 C at 5 C/min. Helium flow was one ml/min through the column. Analysis of volatiles generated from fried bread cubes also was accomplished with the headspace sampler. Bread cubes were crushed, and 0.5 g samples were weighed in the 10-ml vials, purged with nitrogen for two min and sealed. The bread cube samples were heated to 90 C for 20 min. After 0.5 min pressurization, the volatiles were eluted onto the Durabond-5 capillary column under the same GC conditions as the oil samples. Individual volatile compounds were identified by comparing retention times of GC peaks with those from known standards, and confirming by GC-MS analysis with a Finnigan mass spectrometer (7).

Peroxide values were determined by the Official AOCS method Cd 8-53.

RESULTS AND DISCUSSION

Hydrogenation of soybean oil decreased the formation of volatiles during storage (Table 2). Many volatile compounds were derived from the oxidation of methyl linoleate, especially pentane, hexanal and 2-heptenal (3,7). Therefore, the samples with the largest quantity of linoleate had the highest levels of total volatiles. These results agree with previous work showing that increased amounts of saturates in oils tended to reduce the total volatile compounds derived from oxidation of unsaturated fatty acids (9,10). When only CA was used, there was little difference in the total volatiles formed from hydrogenated oils Cu-0.5 and Cu-2.4 and also Ni-4.6 and Ni-2.7, but Ni-0.5 gave the least volatile formation. However, with the other additives Cu-2.4 oil produced fewer volatiles than Cu-0.5. Of the additives tested with the stored oils, only MS reduced volatile formation during storage in Cu-2.4 hydrogenated oil, while TBHQ acted as a good antioxidant. With TBHQ alone or in combination with MS, all hydrogenated oils except Ni-4.6 showed a decrease in volatile formation compared to the unhydrogenated control. Peroxide values for the stored oils decreased in all hydrogenated oils and in the

TABLE 1

Fatty Acid Composition of Oils

		Fatty acids by GC, %				
Sample	Identification	C16:0	18:0	18:1	18:2	18:3
Soybean oil	SBO	10.3	4.4	22.7	54.1	8.5
Ni hydrogenated (commercial)	Ni-4.6	11.2	3.5	37.8	42.9	4.6
Ni hydrogenated	Ni-2.7	10.2	7.1	49.3	30.7	2.7
Ni hydrogenated	Ni-0.4	10.2	16.4	62.8	10.2	0.4
Cu hydrogenated	Cu-2.4	10.4	4.2	30.4	52.6	2.4
Cu hydrogenated	Cu-0.5	10.1	4.4	39.7	45.3	0.5

TABLE 2

Effect of Hydrogenation and Additives on Volatiles and Peroxide Value

	After storage at 60 C for 8 days							
	Volatiles[a]				Peroxide values[b]			
Samples[c]	CA	CA + MS	CA + TBHQ	CA + TBHQ + MS	CA	CA + MS	CA + TBHQ	CA + TBHQ + MS
SBO	14.0	16.2	10.0	7.5	5.3	6.4	1.5	1.5
Ni-4.6	9.1	9.9	9.3	8.1	2.5	1.5	0.9	0.9
Ni-2.7	10.0	8.8	5.5	4.9	2.4	2.2	0.4	0.4
Ni-0.4	0.5	1.3	0.3	0.4	0.6	0.3	0.3	0.3
Cu-2.4	9.3	6.0	4.9	3.3	4.0	2.9	0.4	0.6
Cu-0.5	9.4	9.1	8.6	5.0	2.1	2.9	0.4	0.6

[a] Volatile GC peak area (× 10^{-3}). Average standard deviation of duplicate analyses ±0.65.
[b] Peroxide value, me/kg.
[c] Identification from Table 1.

TABLE 3

Effect of Hydrogenation and Additives on Volatiles after Frying or Heating at 190 C for 1 hr

	GC Peak Area (×10^{-3})							
	Frying[a]				Static heating[b]			
Samples[c]	CA	CA + MS	CA + TBHQ	CA + TBHQ + MS	CA	CA + MS	CA + TBHQ	CA + TBHQ + MS
SBO	47.1	40.6	49.7	33.0	178	160	175	158
Ni-4.6	35.4	16.6	35.3	15.5	147	124	146	120
Ni-2.7	29.7	11.3	22.3	19.1	148	125	139	116
Ni-0.4	16.1	10.0	16.8	9.5	98	75	87	43
Cu-2.4	14.2	10.6	14.4	14.7	161	148	162	147
Cu-0.5	33.1	27.6	30.9	27.3	160	125	161	140

[a] Frying—heating oil 3 times for a total of 17 hr and frying bread cubes. Average standard deviation of duplicate analyses is ± 1.2.
[b] Static heating—0.5 g oil heated in air at 190 C for 1 hr. Average standard deviation of duplicate analyses is ± 3.7.
[c] Identification from Table 1.

oils containing TBHQ (Table 2). With CA and CA+MS, peroxide values followed the same trend as volatiles, and these additives were not as effective as TBHQ in reducing oxidation compounds. These results agree with previous studies in showing that partial hydrogenation improved the oxidative stability based on peroxide values but not the flavor stability of soybean oil (11).

To determine the thermal stability of the oils, total volatiles were measured after prolonged frying (F) or after static heating (S) (Table 3). After frying, the total volatiles decreased as the extent of hydrogenation of soybean oil with Ni increased. However, with Cu catalysts the lightly hydrogenated oil Cu-2.4 produced less volatiles than the more highly hydrogenated oil Cu-0.5. Static heating of the oils at 190 C for one hr provided an accelerated thermal oxidation test (Table 3). After static heating the hydrogenated Ni-0.4 oil was the most stable, and the total volatile concentration from all hydrogenated oils was less than SBO. However, static heating of Cu-hydrogenated oils did not confirm results obtained with frying.

MS was effective in reducing the volatiles from all oils tested after frying and static heating. TBHQ alone did not have any significant effect on the volatiles except with hydrogenated oil Ni-0.4. When TBHQ and MS were used in combination, the total volatiles generally were reduced to the same extent as when MS was used alone.

In the fried bread analyses, after 17 hr of heating and intermittent frying, all breads fried in hydrogenated oils formed less volatiles than breads fried in the unhydrogenated soybean oil (Table 4). After storage for four days at 60 C, bread fried in hydrogenated Ni-0.4 oil was the most stable. Although TBHQ had an effect on limiting volatile formation, MS had a much greater effect, and MS plus TBHQ further decreased the total volatiles.

Individual volatiles from soybean oil were compared with those of hydrogenated oils. 2,4-Heptadienal

TABLE 4

Effect of Hydrogenation and Additives on Volatiles of Fried Bread Cubes[a] after Storage[b]

	Volatile GC peak area (× 10^{-3})			
Samples[c]	CA	CA + MS	CA + TBHQ	CA + TBHQ + MS
SBO	246.6	6.2	146.8	3.5
Ni-4.6	127.0	4.8	76.1	1.3
Ni-2.7	130.5	1.9	56.3	0.4
Ni-0.4	31.7	1.7	23.2	0.2
Cu-2.4	204.5	3.7	56.9	0.5
Cu-0.5	107.4	2.0	58.4	0.8

[a] Bread cubes from final frying during 17 hr heating of oils.
[b] Storage—4 days at 60 C.
[c] Identification from Table 1.

formed from linolenate (3) was found as a significant peak in soybean oil. After hydrogenation to a linolenate content of 0.5% with each catalyst, only a trace of 2,4-heptadienal was found. Octanal and nonanal formed from oleate (3) increased, while pentane, hexanal, 2-heptenal and 2,4-decadienal, which are formed from linoleate, decreasd. *cis*-6-Nonenal, found in trace amounts in most of the hydrogenated oils, previously was identified in hydrogenated soybean oil by GC-MS. The precursor of this compound is apparently 9,15-diene, which is expected to be formed in hydrogenated oils in small amounts (12).

To relate hydrogenation with the total volatile profile of the stored oils, individual volatile compounds were plotted against their precursor. As expected, 2,4-heptadienal, formed essentially from linolenate, produced a linear relationship when the area of the GC peak due to this aldehyde was plotted against triene content (Fig. 1a). In the same manner, hexanal and 2-heptenal formed from linoleate also approximated a straight line when plotted versus diene content (Fig. 1b). Pentane plotted against diene showed a wide scatter of points. Volatile compounds that noticeably increased in hydrogenated oils included 2-decenal, 2-undecenal, octanal and nonanal. A linear relationship was apparent when nonanal was plotted against the monoene concentration (Fig. 1c).

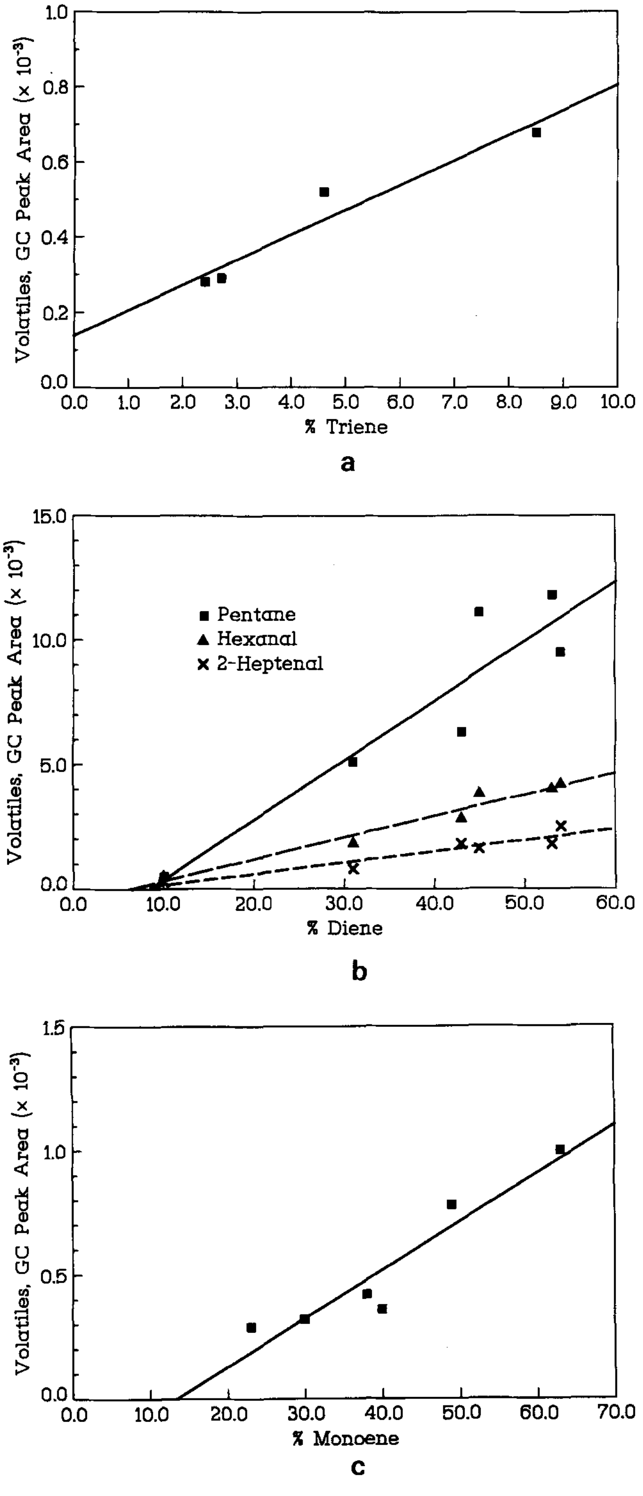

FIG. 1. Relationship of volatile compounds to their precursor fatty acids. All oils contain CA only and were stored at 8 days at 60 C. a, 2,4-heptadienal vs triene; b, pentane, hexanal, 2-heptenal vs diene; c, nonanal vs monoene.

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