Volatiles from Microwave-Treated, Stored Soybeans[1]

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Soybeans were microwaved to inactivate enzymes and prevent oil deterioration during storage. Microwave time was varied from 4 to 10 min, in 2-min increments, and the treated and control soybeans were stored for 8 weeks at 40°C. Damage was monitored by analysis of peroxide value and free fatty acid content of the extracted oil and by volatile analysis of the full-fat meal and extracted oil. Volatiles were measured by multiple headspace extraction, and the formation of hexanal was monitored in both oil and meal. During storage of the control beans, peroxide value increased from 0.41 to 1.20 meq/kg, hexanal concentration changed from 29 to 94 ppb and free fatty acid content increased from 0.4 to 1.7%. Oils extracted from soybeans that were microwaved for 4 or 6 min had peroxide values of about 1 meq/kg and hexanal concentrations of 39–44 ppb after storage, indicating partial inactivation of lipoxygenase enzymes. However, soybeans that were microwaved for 8 min or more tended to oxidize during storage to a greater extent than the control soybeans, showing higher peroxide values and greater formation of hexanal in the samples. This suggests that soybeans microwave-treated in excess of 8 min are heat-damaged and susceptible to deterioration during storage. Free fatty acid content of the oils from all of the microwave-treated soybeans was about 0.4% initially, and did not increase with storage, indicating inactivation of hydrolytic enzymes.

KEY WORDS: Free fatty acid, hexanal, meal, microwave, oil, peroxide value, soybean, static headspace, storage, volatile.

Soybeans are susceptible to damage during storage and transportation under adverse conditions. Lipoxygenase activity has been reported to promote oxidation in soybean meal and its products, resulting in undesirable flavors in the finished products (1–3). Oil processed from soybeans stored at high moisture is also affected, and off-flavors are generated in the oil (4–6). Storage of soybeans at moisture contents of less than 12% has been reported to improve the storability of the beans (7). High moisture content is also responsible for the formation of free fatty acids, which can cause increased damage to the beans (8,9). Steam heating of the soybeans prior to processing decreases the action of lipoxygenase, producing a stable meal (10) and an oil with little off-flavor (11). The effects of microwave heating of soybeans on the molecular species of triacylglycerols (12,13) and the tocopherol content (14) of the extracted lipids has been reported by Yoshida and Kajimoto. They determined that microwave heating for 8 min caused a significant decrease in molecular species containing more than four double bonds. Microwave treatment of soybeans for 6 min, which was optimal to prepare full-fat soy flour without a burnt odor, retained about 90% of the tocopherols. In the current study, the soybeans were subjected to microwave treatments and stored for eight weeks. The conditions of the beans was monitored by measuring peroxide values (PV) and the free fatty acid (FFA) content, and an analysis of the volatile compounds formed in the soybean meal and the extracted oil.

[1]The mention of firm names or trade products does not imply that they are endorsed or recommended over other firms or similar products not mentioned.

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EXPERIMENTAL PROCEDURES

Four portions of soybeans at 15% moisture were microwaved for 4, 6, 8 and 10 min at 0.6 milliamp current at 2450 MHz by using a Despatch Unit (style # SMC 1-33H, Despatch Oven Co., Minneapolis, MN) equipped with a revolving carousel. This moisture content was selected to enhance the differences seen during microwaving. Soybeans (500 g) were placed in a flat dish, microwaved and immediately transferred to a 1-L screw-capped bottle for storage; bean temperature was measured by placing a thermocouple in the middle of the sample in the bottle. Triplicate samples were obtained from soybeans at each treatment time for further analysis. Control beans (no microwave treatment) and the microwaved beans were stored in the capped bottles for eight weeks at 40°C and 12% moisture; samples were removed at two-week intervals. Whole beans were cracked, flaked and dehulled as described previously (6). Oil was Soxhlet-extracted with hexane (15) and analyzed according to AOCS methods (16) for peroxide values (Cd 8-53) and free fatty acid content (Ca 5a-40), and for headspace volatiles as described below. The full-fat meal was also analyzed for volatile content.

Volatile analyses of the oil and meal were accomplished with a Perkin Elmer Model 2000 GC equipped with a HS-100 headspace sampler (Perkin Elmer, Norwalk, CT) and fitted with a DB-1701 capillary column (0.32 mm × 30 m) (J&W, Cardova, CA). Soybean oil (0.5 g) was weighed into a 20-mL vial and sealed. The vial was thermostatted at 50°C for 30 min, pressurized for 0.5 min, and then volatiles were injected onto the column for a 0.3-min interval. The gas chromatographic (GC) column temperature was held at −30°C for 5 min, then raised to 250°C at 5°C/min. Each vial was analyzed by multiple headspace extraction by using three extractions to accurately determine the concentration (17). Sampling was repeated three times to determine repeatability. Soybeans were ground in a small mill; 0.5 g of the full-fat meal was weighed into a 20-mL vial and sealed, the vial was thermostatted and pressurized, and volatiles were sampled as above. Gas chromatographic conditions for the volatile analysis of the meal were the same as for the oil. Individual volatile compounds were identified by capillary GC (column, DB-1701 0.32 mm × 30 m) coupled to a Finnigan 1020 mass spectrometer (Finnigan, Inc., San Jose, CA) and by retention times of standard compounds.

RESULTS AND DISCUSSION

The temperature of the soybean samples, determined after each treatment, increased from 25°C to 123°C, and

moisture content decreased from 15% to 7.6% as the time of microwave treatment was increased to 10 min (Table 1). There was no mold evident in any of the sample bottles after storage.

Results of PV and FFA analyses of the extracted soybean oil are presented in Table 2 for all microwave treatments at each period of storage. The PV of the control (0 min) bean oil increased significantly during storage, from 0.2 to 1.2 meq/kg. Beans subjected to microwave energy for 4 to 6 min showed no increase in the PV during storage. It has been demonstrated that microwave treatment for 4 min inactivates the lipoxygenase enzymes (18). However, when the time of microwave treatment exceeded 8 min, a large increase in peroxide formation was observed. This may be attributed to the decrease in tocopherol content of the oil previously reported (14) or to heat damage from "hot spots" generated by the microwave treatment, causing further degradation. FFA increased during storage only with the control sample. The inhibition of formation of FFA during storage observed with oil from microwave-treated soybeans may indicate inactivation of lipase.

TABLE 1

Microwave Treatment of Soybeans

Microwave time (min)	Moisture content (%)	Temperature (°C)
0	15.0	25
4	13.6	88
6	12.8	101
8	11.3	114
10	7.6	123

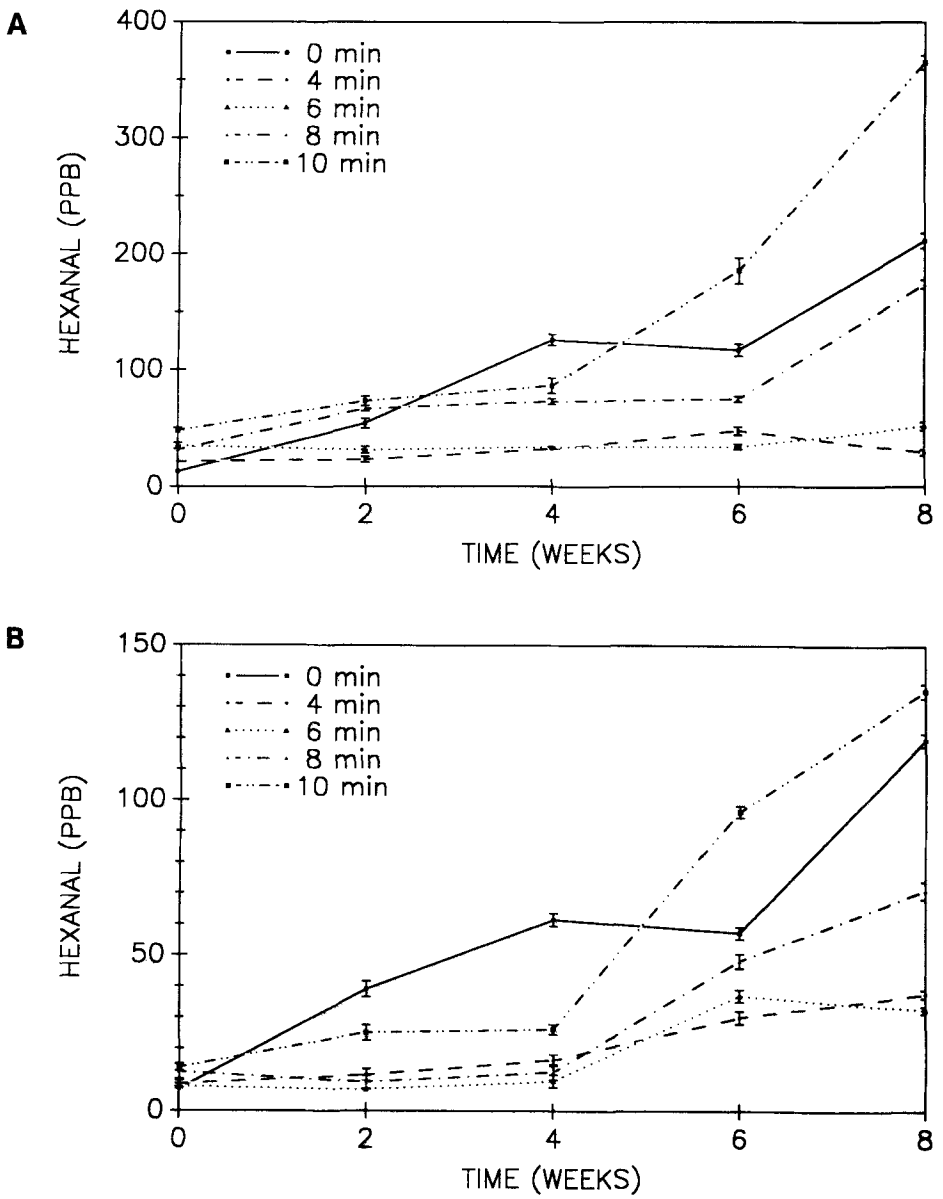

FIG. 1. Hexanal content in microwave-treated soybeans: a, soybean oil; b, soybean meal. Each data point is the average of three samples with the standard deviation shown by the error bars.

TABLE 2

Effect of Microwave Treatment of Soybeans on Extracted Soybean Oil as a Function of Storage Time

Microwave time (min)	PV		FFA	
	0 weeks	8 weeks[a]	0 weeks	8 weeks[a]
0	0.2	1.2	0.4	1.7
4	0.6	0.6	0.3	0.4
6	0.8	0.6	0.3	0.2
8	1.2	7.6	0.4	0.3
10	0.6	15.9	0.5	0.4

[a]Soybeans with 12% moisture stored at 40°C.

We have previously reported that hexanal content is a good indicator of oxidative deterioration (19). Volatile analysis of soybean oil showed that hexanal content remained low during storage for eight weeks in the oil from the beans microwaved for 4 and 6 min and, as with the PV analysis, increased in the oil from the soybeans microwaved for 8 and 10 min (Fig. 1a). The hexanal content in the full-fat soybean meals (Fig. 1b) showed the same trend as in the soybean oil, but the concentration was lower. Other volatile compounds formed in oil and meal after storage of soybeans for eight weeks at 40°C are shown in Figure 2. Chromatograms for the control beans (no microwave treatment) and beans after 10-min microwave treatment are presented.

The volatile analyses accomplished by static headspace tend to show the lower-boiling compounds (with lower molecular weight) to be larger peaks on the chromatogram than the higher-boiling compounds (19). Volatile compounds that increase with storage due to oxidation, such as pentane, propanal and 2-heptenal, tended not to change in concentration during storage in the control and 10-min microwave oil. Comparing the chromatograms of volatiles from the oil extracted from the control beans and beans after 10-min treatment with microwave energy shows that several peaks are present only in the oil from microwaved soybeans. Xylene and naphthalene are compounds reported by Schwab *et al.* (20) to be formed from the pyrolysis of soybean oil.

Chromatograms of control soybean meal and the meal from beans after 10-min treatment with microwave energy indicated some differences in the stored soybeans. Ethanol, found in all of the samples of soybean meal, did not increase during storage; however, it was present in greater amounts in the control beans than in the beans that were microwaved for 10 min. Formation of ethanol in oilseeds

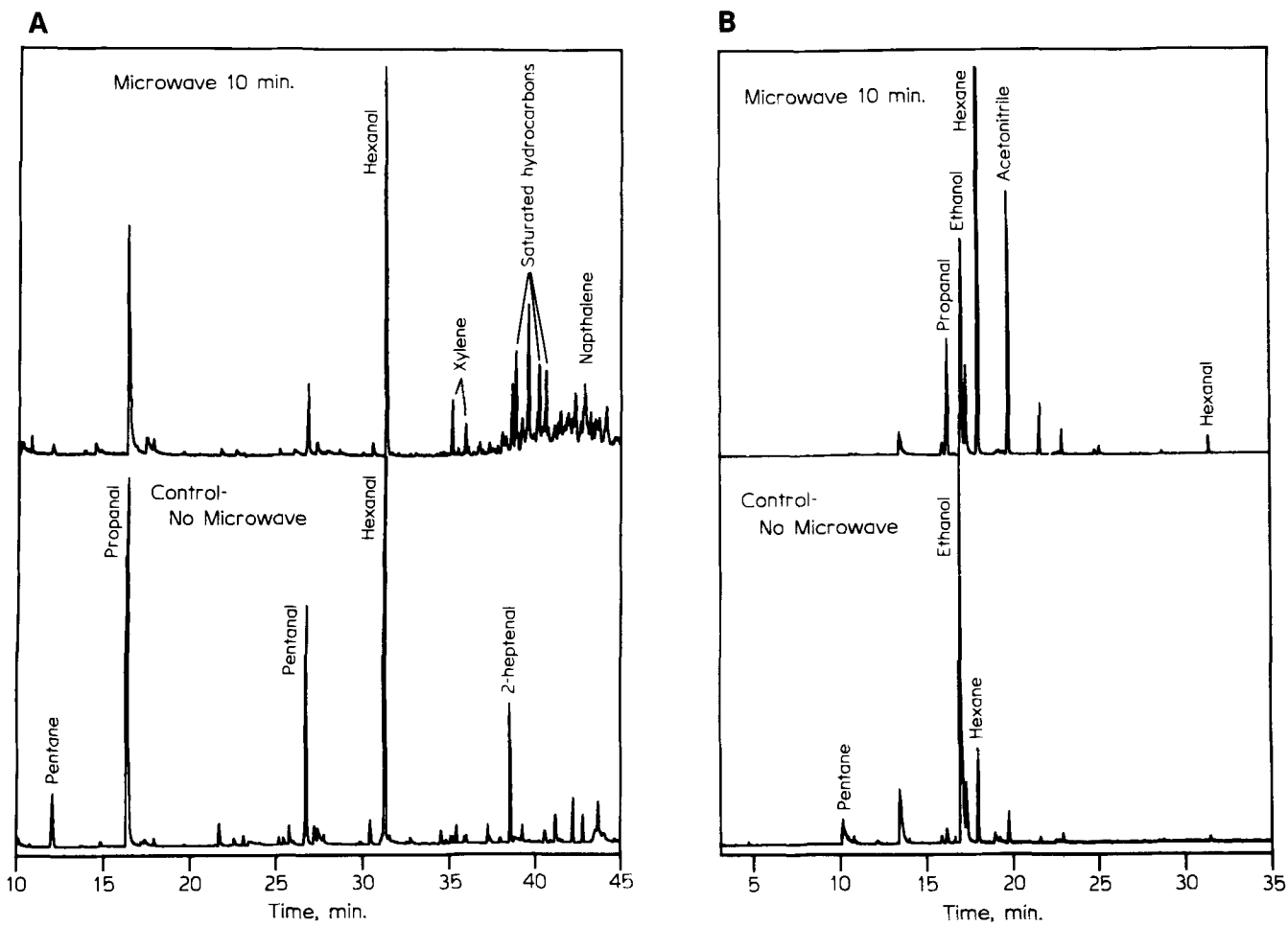

FIG. 2. GC chromatograms of volatiles from stored soybeans: a, soybean oil; b, soybean meal.

has been shown to be related to enzyme activity (21). Microwave treatment has been reported to deactivate enzymes (15,18) and, therefore, ethanol formation is inhibited.

Acetonitrile, found only with meal of microwaved soybeans, increased with the time of treatment with microwave energy. Acetonitrile was highest in the 8- and 10-min microwave treatments. There is no reference in the literature to indicate that acetonitrile is formed in soybean meal during storage or heating. However, pyrazine is a volatile formed from the decomposition of sugars (22), and we speculate that acetonitrile could be similarly formed from carbohydrates at high temperatures due to hot spots during microwave treatment.

The results presented here indicate that treatment of soybeans with microwave energy for 4–6 min is beneficial to the stability of oil and meal during soybean storage. However, treatment of soybeans with microwave energy for longer periods, such as 8–10 min, can damage oil and meal.

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[Received March 6, 1991; accepted July 30, 1991]