Dynamic Headspace Capillary Gas Chromatographic Analysis of Soybean Oil Volatiles

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To develop new knowledge on preventing or eliminating the formation of undesirable flavors in soybean oil, we analyzed quantitatively the major volatile products in samples that were oxidized during storage in the dark at ambient conditions. The volatiles formed were recovered and separated by dynamic headspace capillary gas chromatography. The effect of sampling temperatures was investigated by heating the sample, sweeping the volatiles with helium and trapping and desorbing them from a porous polymer Tenax trap. The volatiles were flushed from the trap onto a fused silica capillary column with a bonded mixed dimethyl-diphenyl siloxane phase. At peroxide values between 2 and 13, the major volatile products found were acrolein, pentene, pentane, 1-penten-3-ol, pentanal, hexanal, 2-hexenal, 2-heptenal, 2,4-heptadienal, 2-octenal and 2,4-decadienal. The profile of volatiles was significantly affected by the sampling temperature used and by the presence or absence of citric acid in the oils before storage. The relative amounts of volatile thermal decomposition products of linolenate and linoleate hydroperoxides, such as 2,4-heptadienal and 2,4-decadienal, increased significantly when samples were heated above 90 C. Dynamic headspace gas chromatography made it possible to analyze the volatiles in samples heated to 60 and 90 C. These volatiles may be representative of those present in oils at time of tasting.

The analysis of volatile compounds in heated edible oils by different gas chromatographic (GC) techniques has received much attention in recent years (1–8). A comprehensive review (9) has been published on different GC methods for the determination of flavor stability of fats and its correlation with flavor responses. GC analyses for volatile flavor compounds not only correlate with flavor scores by sensory analyses (10–13), but also provide sensitive means of detecting low levels of oxidative deterioration in a variety of lipid-containing foods (14–16). Numerous applications of static and dynamic headspace techniques have been developed recently for the analyses of volatiles in foods (17–19). Headspace GC is now regarded as the method of choice for characterizing odors and flavors in foods and beverages. The advantages and disadvantages of static versus dynamic headspace techniques have been reviewed recently (20). However, in spite of the considerable progress achieved in the analysis of flavor compounds, it has been difficult to relate information on volatile flavor compounds to practical problems in foods, especially those containing polyunsaturated fats. Improved quantitative methods are needed to evaluate oxidative and flavor stability of fats to gain a better understanding of factors contributing to the development of oxidatively derived flavor problems in vegetable oils.

We previously reported a gas chromatographic method to evaluate and predict the flavor stability of soybean oil using a direct injection technique with packed columns (21). This method was later improved by the use of capillary GC columns. In other studies we applied a static headspace GC technique with capillary columns to examine the volatiles formed in different vegetable oils (22) and to determine the effect of hydrogenation and additives on the oxidative and thermal stability of soybean oil (23). GC volatile analysis of vegetable oils by the direct injection technique has been improved by the use of a capillary column (24). A GC method to determine oxidative stability of vegetable oils was also recently developed by incorporating oxygen in the purge gas (25). The present paper describes a dynamic headspace technique using capillary GC columns to quantitatively examine the volatile flavor compounds formed in soybean oil stored at ambient conditions in the dark. The volatiles were identified by capillary GC-mass spectrophotometry (MS).

EXPERIMENTAL PROCEDURES

Materials. Refined and bleached soybean oil was deodorized in the laboratory with and without the addition of 0.01% citric acid. Storage in air was carried out in the dark at ambient conditions in quart bottles wrapped with aluminum foil and containing 600 g oil. Peroxide values were determined by the AOCS method CD 8-53 (26) after storage and prior to headspace GC analyses.

Dynamic headspace volatile concentration. A Tekmar dynamic headspace concentrator (Model 4000, Cincinnati, Ohio) was used with a 5-ml sample of soybean oil. The oil was heated in a glass tube (6 × 0.75″) and the headspace was swept with helium (He) onto a porous polymer Tenax (Anspec Co., Ann Arbor, Michigan) trap column (7 × 0.25″) at room temperature. The volatiles trapped on the Tenax column were thermally desorbed and swept directly into the split/splitless injection port of a capillary gas chromatograph. A flame ionization detector was used for quantitative analyses and a mass spectrophotometer for qualitative analyses. Peak integration and matching were electronically computerized. To prevent fogging and contamination of tubing lines in the concentrator, it was important to sweep the samples with gas above the oil and not to purge or bubble through the oil. Operational parameters for volatile concentration from soybean oil were as follows: prepurge, 2.5 min with He above the oil at 40 ml per min at room temperature; purge-preheat, 6.0 min at 60 to 180 C (without He flow); purge, 15 min with He at 40 ml per min at sampling temperature (60 to 180 C); desorb-preheat, Tenax trap heated to 120 C with no He flow; desorb, Tenax trap heated at 170 C for 5 min with He flow; bake-out, Tenax trap heated to 220 C for 15 min with He flow.

Capillary GC-MS. A Finnigan MAT automated

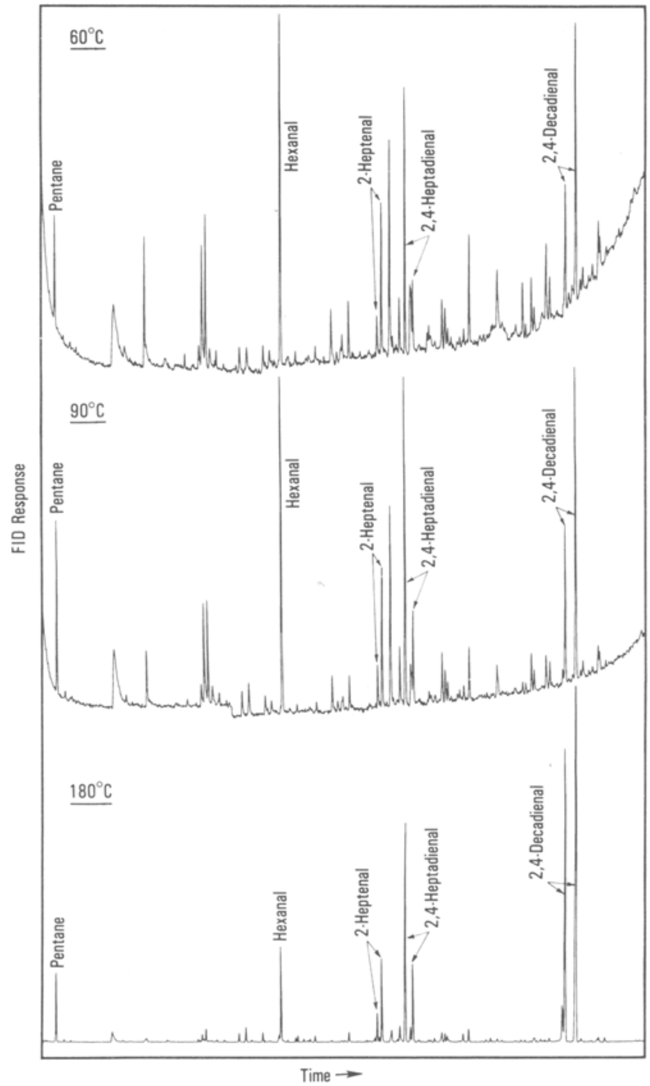

FIG. 1. Effect of sampling temperatures on dynamic headspace gas chromatograms of soybean oil oxidized at ambient temperature to a peroxide value of 9.5 in the absence of citric acid.

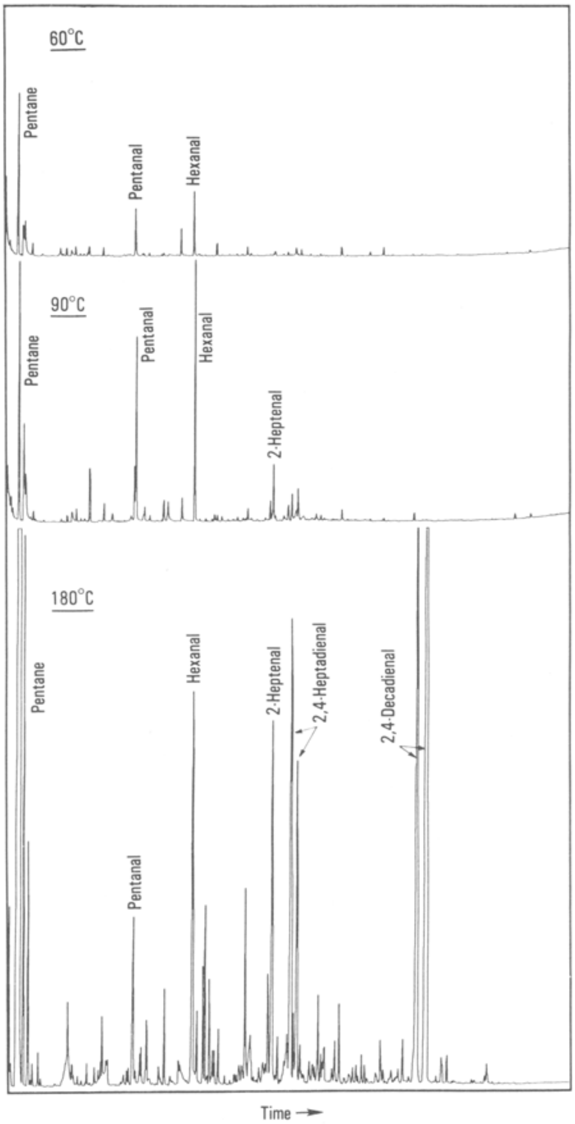

FIG. 2. Effect of sampling temperatures on dynamic headspace gas chromatograms of soybean oil oxidized at ambient temperature to a peroxide value of 5.3 in the presence of citric acid.

GC-MS system was used (Model 0WA/1020, San Jose, California), interfaced to a Perkin-Elmer gas chromatograph (Model Sigma 3B, Norwalk, Connecticut). A fused silica capillary column (60 m × 0.32 mm I.D.) coated with 1 μ bonded mixed dimethyl-diphenyl siloxane phases (Durabond DB-5, J&W Scientific Co., Rancho Cordova, California) was used. The column was cooled to −65 C with liquid nitrogen. The injector port was switched to the splitless mode during the desorption of volatiles from the Tenax trap. Immediately after desorption, the GC injector port was changed back to the split mode, and temperature programming started from −65 to 260 at 5 C per min followed by a final hold of 10 min. Volatiles were identified as described previously (27,28), by matching mass spectra with those of our reference library and by confirming with GC retention data.

RESULTS

Flavor deterioration in soybean oil occurs at relatively low levels of oxidation, usually at peroxide values between 5 and 10 or below, corresponding to a level of oxidation of 0.1% or less. Therefore, for studies of volatiles to be relevant to flavor problems, it is important to choose analytical methods sufficiently sensitive to detect less than 0.1% oxidation. Toward this goal, soybean oil was oxidized with and without citric acid at ambient conditions, and the volatiles were analyzed by dynamic headspace GC at different sampling temperatures. This parameter is defined as the temperature used to heat oil samples while headspace volatiles are swept with He and trapped onto a Tenax column. Figures 1 and 2 show the effect of sampling temperatures on the chromatograms obtained with soybean oil oxidized to two different peroxide values. Marked differences in volatile profiles can be noted depending on the sampling temperature and the absence or presence of citric acid in the oils.

Quantitative analyses in Table 1 show, in the oil oxidized without citric acid present, significantly more

TABLE 2

Dynamic Headspace Gas Chromatographic Analyses of Volatile Composition of Aged Soybean Oil[a]: Effect of Peroxide Value (PV), Citric Acid and Sampling Temperatures

	No additives						+0.01% Citric acid				
	Sample temp. 60 C			Sample temp. 180 C			Sample temp. 60 C		Sample temp. 180 C		
Major volatiles[b]	PV 1.0	PV 5.9	PV 9.5	PV 1.7	PV 4.9	PV 9.5	PV 1.2[c]	PV 5.3[c]	PV 1.2	PV 5.3	PV 13.1
Acrolein	0.00	0.00	0.00	0.00	0.30	0.26	11.65	8.77	0.74	3.34	3.42
Pentene	0.00	0.00	0.00	0.57	1.18	0.32	5.07	12.56	4.58	5.80	6.35
Pentane	13.31	2.52	3.84	13.81	10.43	3.63	30.59	43.14	49.23	48.00	54.96
1-Penten-3-ol	0.00	8.74	6.68	2.79	0.74	0.53	0.00	1.02	1.20	0.44	0.42
Pentanal	8.13	6.52	6.43	3.14	1.12	0.83	12.22	11.14	1.61	0.96	0.91
2-Pentenal	0.00	0.00	1.04	0.30	1.17	1.36	0.00	0.50	0.67	0.62	0.64
Hexanal	30.13	21.04	18.51	11.93	4.34	5.31	20.69	12.73	5.92	2.60	3.18
2/3-Hexenal	0.00	0.00	3.05	1.52	0.44	0.46	0.00	0.20	0.73	0.30	0.23
Heptanal	6.84	4.15	2.80	1.90	0.48	0.66	3.31	2.17	1.61	1.09	0.79
2-Heptenal	2.41	6.52	9.06	9.07	0.51	4.89	1.95	0.65	5.54	3.38	2.98
2,4-heptadienal	0.00	14.66	12.99	17.82	20.05	18.16	0.81	0.72	7.75	8.81	8.09
2-Pentyl furan	3.70	2.37	3.13	1.08	0.27	0.59	1.19	0.45	0.98	0.37	0.22
Octanal	7.40	4.89	2.55	0.61	0.15	0.33	4.20	2.36	0.24	0.09	0.06
2-Octenal	2.04	3.41	2.59	3.41	0.73	0.68	1.17	0.65	0.75	0.47	0.31
Nonanal	14.05	9.49	5.05	3.94	0.95	0.83	6.67	2.74	0.98	0.49	0.26
2-Nonenal	5.18	5.48	2.55	2.83	0.29	0.24	1.22	0.09	0.32	0.17	0.08
2,4-Decadienal	6.84	10.22	19.72	25.14	55.82	60.47	0.27	0.11	16.33	22.71	16.72
2,4,7-Decatrienal	0.00	0.00	0.00	0.13	1.04	0.44	0.00	0.00	0.80	0.33	0.39
Peak areas ratios	1.0	1.25	4.39	1.0	9.60	40.58	1.0	1.64	1.0	3.34	3.19

[a] Calculated on the basis of integrated peak areas.

[b] Integrated values for pentene, 2,4-heptadienal, 2,4-decadienal and 2,4,7-decatrienal represented two or three peaks due to geometric isomers.

[c] Averages from duplicate runs.

gas chromatogram profiles of soybean oil were pentane, hexenal, 2-heptenal and 2,4-decadienal derived from the hydroperoxides of linoleate, and 2/3-hexanal and 2,4-heptadienal derived from the hydroperoxides of linolenate (30). At 60 C the volatiles from linoleate contributed 50–54% of the total GC peak area, compared to 74–76% at 180 C in both oils, with and without citric acid. On the other hand, in the oil without citric acid, the volatiles from linolenate contributed 16% of the total peak area at 60 C and 19% at 180 C, whereas in the oil with citric acid, linolenate volatiles contributed only 1% at 60 C and 9% at 180 C. Volatiles from linolenate are known to have lower flavor threshold values than volatiles from linoleate (31). Because different sampling temperatures result in different relative amounts of decomposition products from linoleate and linolenate, the interpretation of dynamic headspace GC volatile analysis in terms of flavor significance depends greatly on sampling temperature.

The remarkable effect of citric acid on the volatile profiles from soybean oil can be attributed to its well-known action in inactivating trace metals in vegetable oils. Hexanal derived from the 13-hydroperoxide of linoleate, 2,4-decadienal derived from the 9-hydroperoxide of linoleate and 2,4-heptadienal derived from the 12-hydroperoxide of linolenate (32) provided the largest contribution to the volatiles in soybean oil without citric acid. In oils containing citric acid, pentane and hexanal derived from the 13-hydroperoxide of linoleate contributed a larger proportion of the total volatiles. The greater effect of citric acid in decreasing the proportion of linolenate volatiles such as 2,4-heptadienal, especially at temperatures below 90 C, accounts for the important effect of this metal inactivator in greatly improving the flavor stability of soybean oil.

Fat hydroperoxides are known to undergo rapid decomposition when the temperature is raised above 100 C (33,34). Volatile profiles obtained by dynamic headspace GC at 60 to 90 C would, therefore, be representative of flavor compounds in oils at time of tasting, whereas those obtained above 90 C would reflect breakdown products of lipid hydroperoxides. Because dynamic headspace GC is sufficiently sensitive to analyze volatiles in oils at 60 to 90 C, it can be regarded as a method of choice for the analysis of volatile flavor compounds that affect the flavor score of vegetable oils.

A large body of work published on analyses of volatiles in vegetable oils by gas chromatography (1–13) was carried out at elevated sampling temperatures that would be expected to decompose flavor hydroperoxide precursors and with oil samples that contain citric acid, generally used in industry as a processing aid. In this paper, we showed that both sampling temperatures and the presence of citric acid have a significant effect on volatile profiles. A judicious choice of methods and sampling temperatures is therefore needed to distinguish between flavor volatile profiles reflecting the actual flavor of the oil at time of tasting and the breakdown of flavor precursors indicating the potential formation of flavor compounds on storage. Both of these aspects of volatile analyses should provide valuable information on the present and future flavor stability of vegetable oils.

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K.J. Moulton carried out the deodorizations, and R.K. Holloway determined the peroxide values.

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