TABLE V

Effect of Work Softening on Viscoelastic Parameters of Butter and Margarine at 5 C

Sample	Treatment	Instantaneous elasticity	Retarded elasticity	Viscous flow	Deformation % of total[a]		
		$Pa.10^{-4}$	$Pa.10^{-4}$	$Pa.s.10^{-8}$	Inst.	Ret.	Perm.
Butter	Before working	1539.5	1902.7	2098.4	16.2	13.9	69.9
Butter	4 hr after working	834.5	503.1	782.3	8.0	18.5	73.5
Butter	7 days after working	987.3	591.3	1093.2	13.4	22.3	64.4
Margarine	Before working	994.3	767.3	2073.5	19.2	25.2	55.7
Margarine	4 hr after working	248.4	143.8	208.3	8.5	19.4	72.1
Margarine	7 days after working	405.7	356.1	506.8	13.6	16.3	69.8

[a]Instantaneous, Retarded, Permanent.

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♣Capillary Gas Chromatographic Analyses of Headspace Volatiles from Vegetable Oils[1]

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ABSTRACT

Eight different vegetable oils obtained commercially were analyzed for volatiles by capillary gas chromatography (GC). Volatiles generated in a GC static headspace sampler at 180 C were injected automatically onto a chemically bonded capillary column. Only a small number of GC peaks of low intensity were observed in the fresh samples, which varied in peroxide values from 0.2 to 3. Several major peaks were evident in the oils aged eight and 16 days at 60 C with peroxide values ranging from 16 to 65. Thirty-four GC peaks were identified on the basis of relative retention time of reference compounds and on the basis of gas chromatography-mass spectrometry (GC-MS). Volatile compounds identified were those expected from the autoxidaion of principal unsaturated fatty acid components of each vegetable oil tested. The relative concentrations of volatile components increased with the level of oxidation as determined by peroxide value.

INTRODUCTION

Different GC methods for the determination of volatile compounds formed in heated vegetable oils have been reviewed by Waltking and Goetz (1). However, there is a lack of quantitative studies using fats of different origins. Methods using GC with packed columns have been limited by the instability of the liquid phase, resulting in bleeding and poor reproducibility of peak retentions. Although capillary GC has been used for the analysis of volatiles in different foods (2), very little work has been reported on its application to analysis of volatiles in vegetable oils. Newly developed capillary GC systems with chemically bonded stationary phase have diminished problems with column bleed and afforded more reproducible peak retention than GC with packed column (3). Quantitative headspace analysis of volatile compounds by pneumatic sampling has been achieved (4). A headspace GC technique also has been developed to measure changes in light oxidized soybean oil (5). This work has been aimed at developing a reproducible capillary GC method to analyze headspace volatiles in different vegetable oils and to identify volatile components producing GC peaks by GC-MS.

[1]Presented at the AOCS Meeting in Chicago, May 1983.

EXPERIMENTAL PROCEDURES

Commercially processed canola, corn, cottonseed, olive, peanut, safflower, soybean and sunflower seed oils were obtained from various industrial sources or purchased at local stores, and analyzed initially for volatiles (zero-time). Each sample was subjected to accelerated oxidation by a modified Schaal oven test (6) by storing 50 g of oil at 60 C for eight days in 8-oz clear glass bottles containing air in the headspace by using loosely stoppered corks lined with cellophane paper. Twenty g of the aged oils were analyzed and the remaining 30 g were again stored at 60 C for eight additional days. Fatty acid composition of each oil was determined by GC analysis of the methyl esters with a Silar-10C column (50 m × 0.4 mm). Peroxide values were determined by AOCS Method CD 8-53 (7).

For volatile analyses, a Perkin Elmer Model Sigma 3B gas chromatograph (Norwalk, Connecticut) was equipped with a Perkin Elmer Model HS-6 Headspace Sampler. The oil sample (0.5 g) was weighed into a vial, which was then purged with nitrogen for two min and sealed with a septum secured by an aluminum cap. The vials were placed in the headspace magazine and heated to 180 C for 10 min. The magazine was placed into injection position, and the pressure within the vial and between the vial and the column was equalized for 0.5 min before injection of the sample. When the carrier gas was switched off, the sample volatiles were transferred through the sampling needle into the injector. After the injection period, the carrier flow was switched on again and the volatiles eluted onto a Durabond-5 fused silica column [30 m × 0.32 mm, film thickness - 1 m (J&W Scientific, Rancho Cordova, California)]. Column temperature was programmed between O C (hold 10 min) and 250 C at 5 C/min. Volatile analyses were performed in duplicate on each oil. For quantitative evaluation of the data on volatiles, an internal standard, dodecane, was used. Response factors were calculated and used for correction of GC peaks areas (8).

Individual volatile compunds analyzed by headspace GC were first identified by comparing retention times of the GC peaks with those of standards. Further identification was accomplished by GC-MS [Finnigan OWA/1020 system (San Jose, California) interfaced with a Tekmar Headspace Concentrator (Cincinnati, Ohio)]. For this analysis, five g of oil was heated in a tube in the Tekmar Concentrator at 170 C for 10 min; the oil was purged for eight min with helium, and the volatiles from the oil were collected on a Tenax trap (Anspec Co., Ann Arbor, Michigan). Volatiles were thermally desorbed (180 C) from the Tenax trap onto the Durabond-5 capillary column. Oven temperature was held at −50 C for eight min during desorption, then the temperature was programmed to 250 C at 5 C/min.

RESULTS AND DISCUSSION

The fatty acid composition of the eight oils examined was expected to influence the total volatile profile of each oil (9). We found the volatile compounds present in each stored vegetable oil sample related to the main fatty acid components of the oil (Table I). Safflower, sunflower seed, corn and cottonseed oil, with the highest amount of linoleate, tended to produce the greatest amount of volatiles, especially pentane and hexanal. Canola and soybean oils, which contain linolenate, both formed measurable amounts of 2,4-heptadienal. Olive oil, with the largest quantity of oleate, produced the most octanal and nonanal.

Chromatograms of volatile compounds in soybean oil were determined at O-time and after the first eight-day storage period at 60 C (Fig. 1). The peaks numbered on the chromatogram were identified by GC-MS and by comparison of their retention times with those of reference standards (Table II). Each oil sample was analyzed in duplicate. The reproducibility of GC peak areas was estimated by the average standard deviations varying from ± 0.02 for pentene (mean area 0.1 × 10^3) to ± 1.07 for propane (mean areas 0.7 to 12.7 × 10^3). The average standard deviation for the total volatile area was 3.2. Most of the individual volatiles identified in this work were reported previously in the literature (9,10). Volatile compounds formed in each of the other seven oils were typical volatile products of triglyceride oxidation, but show varying intensities of the major volatile peaks (11-15). Also, some volatiles were found in only one or two of the different types of vegetable oils. A high concentration of propane, tentatively identified by retention times, was present in most of the oil

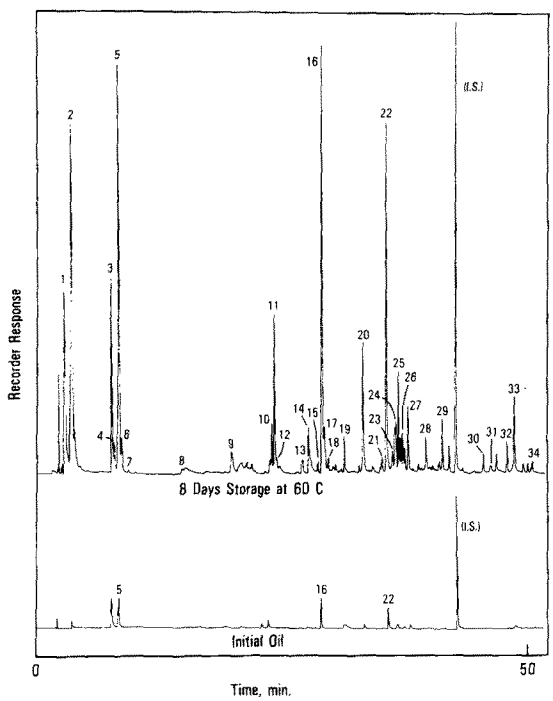

FIG. 1. Capillary GC chromatogram of volatiles in soybean oil: effect of storage at 60 C.

TABLE I

Fatty Acid Composition of Vegetable Oils

Fatty Acid	Vegetable Oils (Relative Area %)							
	Canola	Corn	Cottonseed	Olive	Peanut	Safflower	Soybean	Sunflower
14:0	----	----	1.0	----	----	----	----	----
16:0	3.9	11.2	20.7	15.2	11.3	6.3	11.1	6.0
16:1	0.2	0.2	0.5	1.8	----	0.2	----	----
18:0	1.6	1.9	2.5	2.4	2.1	1.9	3.7	3.8
18:1	60.0	24.9	18.5	65.1	46.5	9.7	24.2	17.2
18:2	22.0	60.6	56.6	14.5	35.1	81.8	54.1	73.0
20:0	1.3	0.3	0.2	0.3	0.8	0.1	0.1	----
18:3	10.1	0.9	----	0.7	----	----	6.8	----
20:1	----	----	----	----	1.5	----	----	----
22:0	0.2	----	----	----	2.7	----	----	----
22:1	0.7	----	----	----	----	----	----	----

TABLE II

Identification of Volatile Compounds in Vegetable oils After Eight Days Storage at 60 C

Peak no. from Fig. 1	Volatile[a] compound	Retention time (min)	GC Peak Area ($\times 10^3$) Mean ± Standard Deviation (S.D.)								
			Canola	Corn	Cottonseed	Olive	Peanut	Safflower	Soybean	Sunflower Seed	Ave S.D.
1	Ethane[b]	3.4	1.0±.07	1.0±.07	0.8±0	0.2±0	8.0±2.26	0.2±.07	0.9±.07	1.0±.71	.41
2	Propane[b]	4.1	0.7±0	10.6±.35	12.6±.99	0.6±.07	——	10.4±.70	9.1±.71	12.7±4.67	1.07
3	Propenal	8.0	1.5±.07	2.3±.35	2.1±.21	1.7±.14	2.4±.07	2.3±.42	4.5±.14	2.9±.21	.20
4	Pentene[c]	8.3	0.2±.07	——	——	——	——	——	0.3±.14	——	.11
5	Pentane	8.7	0.5±.07	24.3±.28	32.7±1.13	14.9±.85	19.0±.28	54.1±4.10	11.1±.28	41.5±.71	.96
6	Propanal	9.0	1.0±.07	——	——	0.3±.07	0.6±.28	——	0.7±0	——	.04
7	Pentene[c]	9.6	0.1±0	——	——	0.1±.07	——	0.1±0	0.1±0	——	.02
8	Hexane	15.2	1.1±.42	0.4±.07	0.3±0	0.3±0	0.2±.07	0.4±.28	0.3±.07	0.1±0	.13
9	2-butenal	19.6	0.5±.07	0.2±0	0.2±.21	——	0.3±0	——	0.5±0	0.1±.07	.35
10	1-penten-3-ol	22.0	0.4±.14	——	——	——	——	——	0.8±.14	0.1±.07	.42
11	Pentanal	22.7	0.5±0	1.0±0	1.3±0	1.8±.07	2.8±.07	1.9±.07	2.9±.14	2.4±.14	.06
12	Heptane	23.0	0.2±.14	0.2±.07	——	2.2±.42	0.5±.07	0.2±.07	0.1±0	0.4±.35	.15
13	Pentenal	26.7	0.3±0	0.1±.71	0.1±0	——	——	——	0.6±.07	——	.20
14	Pentanol	27.0	0.3±.14	0.5±.71	0.8±.14	0.5±0	1.4±.57	2.0±.28	1.5±.28	1.3±.21	.29
15	Octene[c]	28.0	——	0.1±0	0.1±0	0.2±.07	0.5±0	0.1±0	0.2±.14	——	.04
16	Hexanal	28.3	3.1±.71	9.8±.28	10.3±.28	5.8±.42	7.6±.14	11.1±.28	10.7±.28	10.5±.57	.37
17	Octane	28.4	3.7±.35	2.2±.42	3.9±0	4.1±.14	0.3±.07	0.2±.07	0.3±.07	4.5±.21	.17
18	Octene[c]	29.0	——	0.1±0	——	0.1±0	0.2±.14	0.1±0	0.2±.07	——	.04
19	t-2-hexenal	30.8	0.2±0	0.3±.14	0.5±.14	0.2±.21	0.8±0	0.3±0	0.5±.14	0.7±.07	.09
20	Heptanal	32.8	0.8±.07	0.6±.07	2.2±.07	1.8±.14	2.0±.14	3.2±.07	2.1±.21	1.8±.42	.15
21	c-2-heptenal	34.7	0.2±0	0.2±0	0.1±0	0.1±.07	——	0.3±.07	0.2±.07	——	.04
22	t-2-heptenal	35.1	0.9±.21	1.3±.49	3.6±.07	2.6±.07	1.5±0	5.6±.28	5.1±.42	3.4±.14	.21
23	1-octen-3-ol	36.0	0.1±.07	0.3±0	0.2±.14	0.3±0	0.3±0	0.1±0	0.3±.14	0.3±0	.04
24	pentyl furan	36.3	0.2±0	0.5±.57	0.8±.07	0.2±.07	0.7±.07	0.7±.07	1.0±.57	0.6±.42	.24
25	t, c-2, 4-heptadienal	36.5	0.5±.28	——	——	——	——	——	0.6±.07	——	.17
26	octanal	36.7	0.5±0	0.3±0	0.4±0	1.1±.14	0.6±0	0.4±0	0.5±0	0.3±0	.07
27	t, t-2, 4-heptadienal	37.2	0.8±0	——	——	——	——	——	0.8±.07	——	.04
28	Octenal	39.0	0.2±.14	0.5±.14	0.5±.07	0.6±0	0.7±.28	0.6±.07	0.4±0	0.5±.07	.10
29	Nonanal	40.6	1.2±0	0.5±.42	0.6±.07	2.8±.14	0.5±0	0.4±.07	0.6±0	0.4±.28	.13
i.s.	Dodecane	42.4									
30	t-2-decenal	44.6	0.2±0	0.2±0	0.3±0	0.7±.14	0.2±.14	0.2±0	0.3±.14	0.3±0	.07

—Continued

TABLE II (Continued)

Peak no. from Fig. 1	Volatile[a] compound	Retention time (min)	GC Peak Area ($\times 10^3$) Mean ± Standard Deviation (S.D.)								
			Canola	Corn	Cottonseed	Olive	Peanut	Safflower	Soybean	Sunflower Seed	Ave S.D.
31	Decenol	45.9	0.1±.07	0.1±.07	0.1±0	0.2±0	0.1±0	0.1±.07	0.1±0	0.1±.07	.03
32	t, c-2, 4-decadienal	46.9	0.3±0	0.3±.14	0.4±.28	0.1±0	0.3±0	0.3±0	0.6±.14	0.4±.14	.09
33	t, t-2, 4-decadienal	47.7	0.8±.14	1.0±.28	1.2±.07	0.8±.14	0.8±.14	1.5±.07	1.4±.57	1.4±.14	.19
34	Undecenal	49.4	0.1±.07	0.1±0	0.2±.14	0.2±.14	0.2±0	0.2±.14	0.1±.07	0.2±.14	.09
	Total Area		25.8±1.4	63.1±9.3	77.6±2.1	49.2±.70	53.6±1.3	99.6±3.9	40.2±.5	70.4±6.7	3.2

[a]Identified by GC-MS and by comparing retention times with standards.
[b]Identified only by retention times.
[c]Isomeric compounds not identified by GC-MS.

samples. Several volatile components formed from canola oil were not present in the other oils; trace amounts of tetrahydrofuran, ethyl furan and ethyl acetate were identified by GC-MS. In this study, the methyl ketones, C4 to C8, also were found in trace amounts in canola and in soybean oils, while corn, peanut and sunflower seed oils had small amounts of heptanone, and olive oil produced trace amounts of butanone and pentanone.

One of the major volatile compounds formed from cottonseed oil was 1-decyne, which was reported as a predominant volatile of photooxidized cottonseed oil formed from its precursor sterculic acid (16). Since 1-decyne was found at O-time, the cottonseed oil apparently was exposed to light at the store or during transportation. The amount of 1-decyne increased with storage but the intensity did not exceed the other volatiles, apparently because our storage tests were conducted in the dark and further photooxidation was limited.

GC volatile analyses, based on total peak area for each oil, increased with storage time and followed a trend similar to peroxide values (Fig. 2). Although labels did not indicate the presence of additives, MS provided evidence for BHT in canola oil, which remained the most stable oil during storage at 60 C. The peroxide values at O-time were less than 1 for each oil except corn oil, which had a value of 1.8, and olive oil, with a value of 2.5. After eight-day storage, the peroxide values increased and varied from six to 15. The total volatile pattern for each oil increased in the same manner as the peroxide values (Fig. 2) and appears related to linoleate content. As expected, the deterioration of the oils was much greater after 16 days. Total area for volatiles doubled for most of the oils. However, the peroxide values increased at a greater rate. Safflower oil had the highest peroxide value and greatest total area for volatiles after 16 days.

Major individual volatile compounds determined in duplicate runs were estimated quantitatively by flame ionization detection. Changes in each volatile compound were examined after storage at 60 C for eight and 16 days. Eight of the major volatile compounds common in each oil were compared to determine the effects of storage (Table III). Concentration (ppm) of the volatiles was determined using the internal standard dodecane to correct for GC response (8). Polyunsaturated oils were particularly susceptible to oxidation, as shown by the increase of volatile compounds formed from linoleic

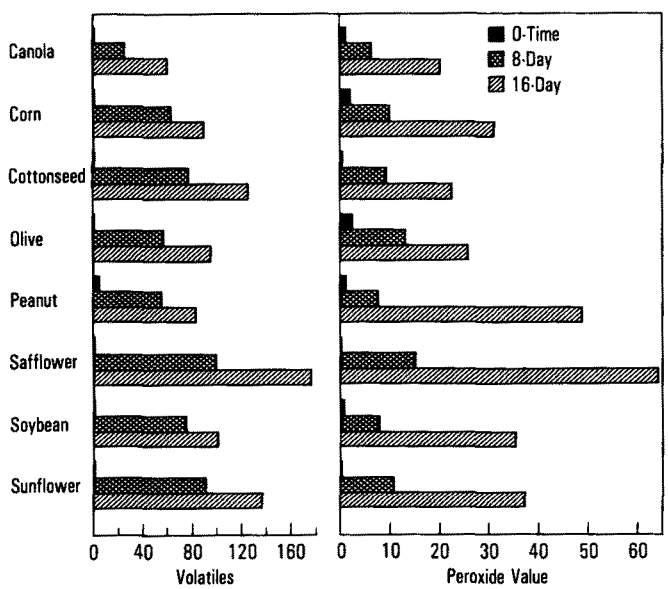

FIG. 2. Comparison of peroxide values and total GC volatiles of vegetable oils during storage at 60 C.

TABLE III

Effect of Storage on Intensity of Individual Volatiles

Volatile[a] compound	Storage time	Concentration, ppm							
		Canola	Corn	Cottonseed	Olive	Peanut	Safflower	Soybean	Sunflower seed
Pentane	0-time	0.5	1.3	1.1	0.4	4.5	1.6	0.6	0.9
	8-day	0.9	68.4	82.8	27.1	41.9	110.8	23.5	84.9
	16-day	26.3	76.4	117.9	57.2	75.7	144.7	66.7	127.8
Pentanal	0-time	0.5	0.4	--	--	--	0.4	--	--
	8-day	1.6	5.3	6.2	9.6	7.5	7.3	11.6	9.2
	16-day	2.2	21.0	20.8	25.6	19.2	20.8	15.9	28.0
Hexanal	0-time	1.7	0.8	1.2	1.2	1.1	0.8	0.8	0.8
	8-day	9.8	50.8	47.6	19.3	30.6	41.5	41.4	39.3
	16-day	45.5	60.3	59.3	32.2	59.7	110.6	62.8	81.8
Heptanal	0-time	--	--	--	--	--	--	--	--
	8-day	1.9	2.3	7.5	5.2	6.0	8.9	6.0	5.0
	16-day	5.9	4.1	8.9	3.9	5.1	10.0	7.3	8.0
2-Heptenal	0-time	0.6	0.6	0.6	0.6	0.5	0.5	0.5	0.5
	8-day	4.0	9.4	23.3	12.1	8.5	29.3	27.6	17.8
	16-day	14.7	27.9	39.1	27.8	41.5	56.3	38.2	36.3
Octanal	0-time	0.6	--	0.6	0.6	0.5	--	--	--
	8-day	2.2	2.1	2.5	5.0	3.3	3.6	2.6	1.5
	16-day	1.7	1.9	2.4	6.3	2.5	3.7	2.7	1.1
Nonanal	0-time	0.4	--	--	0.4	--	--	--	--
	8-day	3.8	2.5	2.7	3.6	4.0	1.5	2.3	1.5
	16-day	8.7	2.3	2.5	9.8	4.3	1.5	2.3	2.4
2,4-decadienal	0-time	--	0.4	--	--	--	--	0.2	--
	8-day	3.6	7.4	5.7	3.0	4.6	7.0	8.0	6.9
	16-day	7.8	11.5	10.0	5.5	11.2	14.8	12.2	14.4

[a]Major volatiles formed from each oil.

acid (9,10,17), especially pentane, hexanal and 2-heptenal; these compounds increased the greatest with storage. However, 2,4-decadienal, also expected from linoleic acid (9,10,17), was found in relatively low concentration under our instrumental conditions. Under the static headspace used in this study the volatile compounds are in equilibrium (18), and the high boiling volatiles such as 2,4-decadienal would be expected to be lower in concentration than the low boiling volatiles such as pentane and hexanal. Oxidation products from oleic acid, such as heptanal, octanal and nonanal, did not increase appreciably between eight and 16 days' storage. 2,4-Heptadienal, found in canola and soybean oil and derived from linolenic acid (9,10,19), increased after extended storage. The concentration of *trans, trans*-2,4-heptadienal in each oil was 3 ppm at eight days and increased to 4.8 ppm in canola oil and 5.9 ppm in soybean oil after 16 days at 60 C.

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