Effect of Water Content on Volatile Compounds Derived from Soybean Oils in Cans

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Soybean oil-water cans with different soybean oil/water ratios were prepared and stored. The volatiles and POV values of these samples were monitored. Water in cans caused the production of larger amounts of volatiles just after sterilization, however, during the storage period, cans without water had a higher rate of production of volatile compounds. It was postulated that POV values do not reflect the changes of volatile compounds in cans.

Rancidity resulting from the oxidation or hydrolysis of lipids is a primary consideration in the storage stability of food products. In the study of stability of dehydrated foods, the foods were always more rancid at lower moisture contents, but fatty acid hydrolysis proceeded more rapidly at higher relative humidities. Therefore, it appears that conditions for optimum stability include low temperature storage to prevent hydrolysis, and a moisture content near the monolayer moisture value to retard oxidation (1). The fact that instant fried noodles developed rancid off-flavors the slowest at aw 0.3, which was equivalent to 5.16% moisture, was also reported (2). In freeze-dried foods the lipid is spread on a large porous matrix, thus, oxygen is readily available for reaction and the food oxidizes even at low oxygen partial pressures. However, the presence of small amounts of water markedly inhibits rancidity, and the inhibitory effect of water was related to the water sorption isotherm because the adsorption of the water on the surface of the food excluded oxygen from reacting with the lipids (3).

Different kinds of canned foods contain different lipid and water contents, but the volatile constituents from lipids as well as the effect of water content on a generation of volatiles from the lipids in cans have never been reported. In this study, soybean oil-water cans with different soybean oil/water ratios were prepared and stored. The volatile constituents and POV values of these samples were monitored.

EXPERIMENTAL PROCEDURES

Preparation and storage of cans. Commercial soybean oil and distilled water were poured together with different ratios in Taiwan No. 7 epoxy-phenolic resin lacquered cans. The cans were deaerated by heating them for 10 min in a steam chamber. Their central temperature reached 80°C before sealing, and they were sterilized at 121°C for 20 min. Each can contained 270 ml liquid, the ratio of soybean oil to water was based on volume. The cans were stored at 37°C for subsequent analysis.

Flavor isolation. Volatile compounds of the samples were extracted for 2.5 hrs in a Likens-Nickerson apparatus (4). The 5 l sample flask contained 100 ml soybean oil and 3000 ml distilled water. Soybean oil was from cans. Distilled water was added to make up the volume. Redistilled pentane and diethyl ether (1:1) were used as the extracting solvent. n-Heptadecane (E. Merck, Dormsadt, Federal Republic of Germany) was added as an internal standard. The volatile extracts were dried with anhydrous Na_2SO_4 and concentrated to about 0.5 ml by using a spinning band distillation apparatus (Kontes Co., Vineland, NJ). The concentrate was then transferred to a one-ended, sealed, glass capillary tube and heated in a water bath at 40°C to a volume of about 50 μl.

POV value. POV value was determined by the AOAC procedure (5).

Gas chromatography. Gas chromatography was conducted using a Shimadzu GC-8APF equipped with a flame ionization detector. Two 50 m × 0.2 mm fused silica columns, coated with Carbowax-20M and OV-1 (Chrompack International, B.V., Middleburg, The Netherlands), respectively, were used. The oven temperature was programmed from 50-200°C at 2°C/min, and then held at 200°C for 55 min. The injector and detector temperatures were both 250°C. The carrier gas was hydrogen at a flow rate of 2.0 ml/min. The data were recorded on a Hewlett Packard 3390A integrator. Values reported were from the average of two analyses. The linear retention indices of the volatile components were calculated using n-paraffin (C_8-C_{25}, Alltech Associates, Ontario, Canada) according to Majlat *et al.* (6).

Gas chromatography-mass spectroscopy (GC-MS). GC-MS was conducted with a Hewlett-Packard 5985B system, and operational parameters were as follows: carrier gas, helium; ionization voltage, 70 eV; electron multiplier voltage, 2400 V; ion source temperature, 200°C.

RESULTS AND DISCUSSION

Figure 1 shows the gas chromatogram of the isolated volatiles of soybean oil cans. Table 1 shows the volatile constituents identified in the samples. Most of the compounds were identified by comparing the mass spectra and GC retention times (Carbowax-20M and OV-1 columns) of the components with authentic samples. It contained 12 aldehydes, 3 acids, 2 ketones, 2 furans, 2 hydrocarbons, 1 alcohol and 1 ester. All these compounds are the oxidation products of fatty acids and have been reported in many studies (7-12). However, some differences exist, as more than one-half of the compounds were aldehydes. These are the inital products of the degradation of fatty acids. We used soybean oil instead of pure fatty acids or their esters. The heating condition is also a critical factor. Cans were heated at 121°C for 20 min in this study. All these facts may explain the differences. The simplicity remained during the storage period. This information reflects the real situation of the canned foods.

Table 2 shows the comparison of the major volatile compounds and total volatile compounds among the samples. Figures 2 and 3 show changes of total volatile

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TABLE 1

Volatiles Compounds Identified in Canned Soybean Oil

Peak no.[a]	Compound	MW	ID	Ik[d] CW-2-M	Ik[d] OV-1
2.	ethyl acetate	88	A[b]	891.5	800
3.	ethyl furan	96	B[c]	951.0	800
4.	pentanal	86	A	984.5	800
5.	n-hexanal	100	A	1038.8	800
6.	(E)-2-pentenal	84	A	1129.4	800
7.	xylene	106	A	1135.4	851.8
8.	2-pentanone	86	A	1148.5	800
9.	n-heptanal	114	A	1184.2	879.8
10.	2-n-pentyl furan	138	A	1225.0	978.4
11.	cyclohexanone	98	A	1290.2	860.4
12.	(E)-2-heptenal	112	A	1321.3	929.9
13.	n-nonanal	142	A	1389.9	1086.2
14.	(E)-octenal	126	A	1412.3	1037.2
15.	1-octen-3-ol	128	A	1434.8	955.6
16.	(E,Z)-hepta, 2.4-dienal	110	B	1457.3	—
17.	(E,E)-hepta, 2.4-dienal	110	A	1488.2	1187.2
18.	(E,E)-nona, 2.4-dienal	138	A	1586.2	1212.6
19.	n-heptadecane	240	A	1700.0	1700.0
20.	(E,Z)-deca, 2.4-dienal	152	B	1774.5	—
21.	(E,E)-deca, 2.4-dienal	152	A	1806.9	1355.3
22.	hexanoic acid	116	A	1880.1	1018.5
23.	heptanoic acid	130	A	1999.2	1107.1
24.	octanoic acid	144	A	2111.4	1201.9

[a] Peak number refers to Figure 1.

[b] comparison of GC retention time and mass spectrum with that of authentic compound.

[c] mass spectrum or GC retention time was consistent with that of published data (tentative identification).

[d] calculated Kovat's indices.

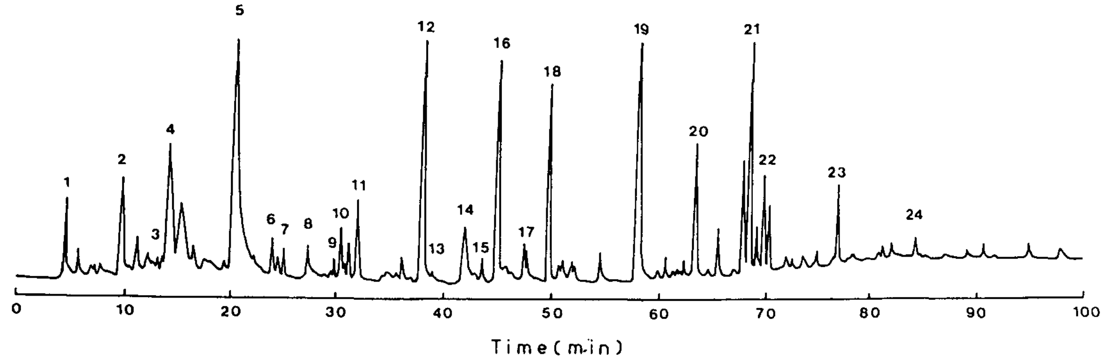

FIG. 1. Gas chromatogram of volatile compounds of soybean oil can (Carbowax-20M column).

compounds and POV of soybean oil cans during storage at 37°C, respectively. From these data we can draw two conclusions: (i) Water (20-80%) in cans accelerated the autoxidation of fatty acids as evidenced by the increasing POV values, and the order was 80% > 60% > 40% > 20% > 0%. Cans that contain more water should have a higher oxygen content as one volume of oxygen gas can be dissolved in 32 volumes water at 20°C, while oxygen that can be dissolved in oils just ranges in several ppms (13). More water represents more oxygen and less soybean oil in cans because the total volume of a can is constant. It is reasonable to conclude that more water in the ranges of 20-80% causes more lipid oxidation. (ii) Water in cans caused the production of larger amounts of volatiles just after sterilization (1000-2000 μg/100 g), while cans without water contained only 188 μg/100 g. This means that water serves as an oxidant in high temperatures of sterilization. However, during the eight weeks of the storage period, cans with 80% or 60% water either remained about the same or decreased; cans with 40% or 20% water increased 1.5-3.0-fold; and cans without water increased 10-fold. The above data showed that the total volatile contents of oils containing 80% or 60% water decreased during storage even though the peroxide values of these samples increased during the same period of storage. This contradiction can be postulated by the following two reasons: (i) POV values reflect only the first stage of autoxidation of fatty acids, the

TABLE 2

Comparisons of the Major and Total Volatile Compounds among the Samples During Storage at 37°C.

	Soybean Oil				
Time (Week)	100%	80%	60%	40%	20%
Ethyl acetate					
0	29.66	224.52	170.53	122.20	119.37
1	37.33	929.63	385.52	116.84	160.37
2	13.83	1111.34	516.26	45.39	39.84
4	338.34	134.13	625.80	78.99	370.42
6	341.91	317.51	640.78	75.79	335.08
8	344.33	246.70	631.26	64.08	262.78
n-Hexanal					
0	42.84	282.83	305.28	351.95	224.47
1	173.76	955.05	654.07	399.25	147.28
2	54.65	778.21	676.16	259.27	82.86
4	399.42	339.21	170.88	125.09	273.15
6	419.33	356.80	142.43	135.80	297.15
8	359.75	321.51	113.72	127.33	276.54
(E)-2-Octenal					
0	2.17	3.69	4.83	9.53	5.78
1	1.55	5.01	17.34	3.52	14.77
2	30.04	21.40	20.35	43.16	5.22
4	44.33	35.47	21.61	46.27	6.77
6	51.46	41.86	29.90	46.39	3.90
8	54.62	18.16	37.16	45.96	4.90
(E,E)-Deca-2.4-dienal					
0	4.75	22.90	43.99	51.96	87.23
1	22.72	28.49	111.84	42.25	217.96
2	36.17	31.59	143.17	92.78	199.77
4	90.83	41.35	64.69	37.58	58.55
6	96.58	70.45	74.68	61.59	84.40
8	107.55	128.03	71.42	81.83	90.68
(E)-2-heptenal					
0	7.84	5.85	13.80	8.53	13.72
1	7.84	3.29	56.53	2.86	2.74
2	7.81	8.03	38.60	3.62	5.21
4	10.17	7.25	18.83	13.70	11.11
6	13.06	10.91	16.60	23.02	12.32
8	14.75	13.83	9.45	22.50	10.73
1-octen-3-ol					
0	8.57	35.66	53.17	105.45	88.85
1	8.57	55.55	79.88	13.67	57.54
2	56.13	102.05	229.68	9.24	9.25
4	68.86	47.55	112.62	20.65	55.64
6	75.37	62.45	151.37	25.45	52.58
8	72.50	53.05	148.74	35.93	59.57
(E,E)-hepta, 2.4-dienal					
0	7.70	28.05	49.14	33.03	53.76
1	7.70	95.25	91.80	10.43	27.94
2	34.09	32.50	147.49	9.32	12.81
4	101.18	80.75	100.77	10.00	44.02
6	123.54	90.14	94.20	11.65	50.73
8	115.85	69.25	77.21	10.93	15.60

TABLE 2—*(continued)*

Comparisons of the Major and Total Volatile Compounds among the Samples During Storage at 37°C.

	Soybean Oil				
Time (Week)	100%	80%	60%	40%	20%
hexamoic acid					
0	20.14	18.79	31.05	16.58	50.73
1	20.14	22.65	25.97	6.76	40.48
2	16.59	14.85	20.92	20.80	41.81
4	24.01	51.36	28.45	21.21	61.50
6	33.85	57.84	17.69	10.74	28.74
8	42.85	43.21	22.14	54.53	15.41
Total volatiles					
0	188	993	1144	1317	1219
1	450	2644	2115	878	1074
2	507	2689	2751	651	698
4	1746	1167	2458	624	1332
6	1917	1493	3750	725	1352
8	1927	1372	3304	849	1210

Unit:μg/100 g oil.

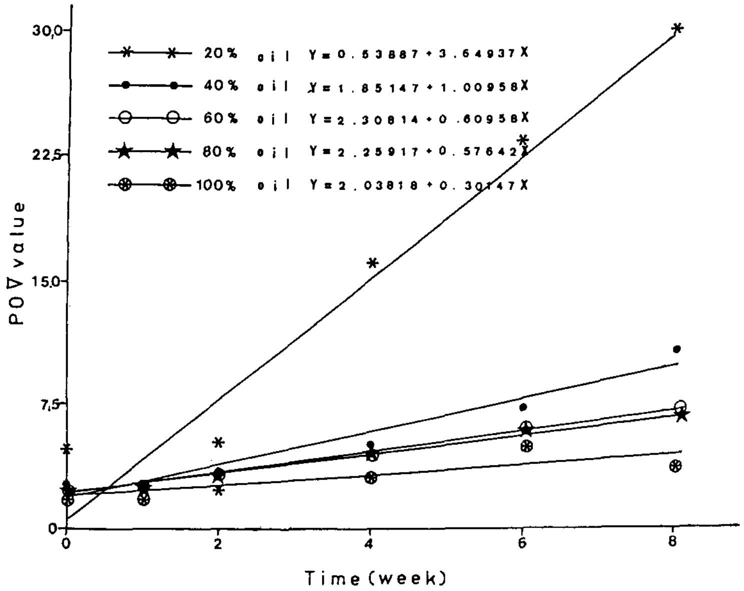

FIG. 2. Changes of POV values of the soybean oil from different soybean oil/water cans during storage at 37°C.

further reactions of volatile degraded compounds cannot be monitored by POV values. Water and volatile compounds exist in both vapor and liquid phases in storage. Small amounts of water can inhibit rancidity (1-3), i.e., it prevents the production of volatile compounds. (ii) The volatile compounds of oils containing 80% or 60% water decreased during storage, suggesting that they are produced and then consumed. Because there was no new volatile compound produced in the GC profiles, these volatile compounds should become nonvolatile compounds such as polymer, complex or other forms.

Volatile compounds can be used as a measure of rancidity of foods (14,15). The degradation products of fatty acids such as hexanal, hexanoic acid or 1-octen-3-ol are described as having green, rancid and mushroom aromas. This paper showed oil cans containing 80% or 60% water can reduce the volatile compounds contents in storage, i.e., to reduce rancidity.

Our previous work found that the main change in volatile constituents of stir fried bell peppers during aging is the production of volatile carbonyl compounds from autoxidative breakdown of unsaturated fatty acid (12). The pathway for the breakdown of 9-HPOD (9-hydroperoxyoctadeca-E-10, Z-12 dienoic acid) proposed by Grosch *et al.* (11) was postulated as the pathway for the autoxidation of stir fried oils, because no (E)-2-hexeanl

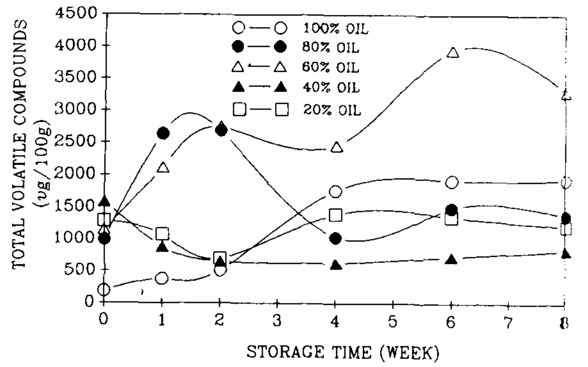

FIG. 3. Changes of total volatile compounds of different samples during storage at 37°C.

was found, except for the aged sample of stir fried bell pepper, which contained some amount of (E)-2-hexenal. Therefore, we can say that although oxidative cleavage was mainly at 9-position, it happened to some extent at the 13-position. This reaction occurs especially after aging. In this study, the heating of oils was in a closed system. All samples did not contain (E)-2-hexenal even after aging; only oxidative cleavage of 9-position was proposed.

This study reports the volatile compounds produced from a simple system which contained only water and oils, but this basic information should be beneficial to cans which contain foods and ingredients. However, water and oils are still the most common liquid form components in the cans.

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