SHORT COMMUNICATION

Quantitation of Volatile Compounds in Heated Triolein by Static Headspace Capillary Gas Chromatography/Infrared Spectroscopy-Mass Spectrometry

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Static headspace and capillary gas chromatography/infrared spectroscopy–mass spectrometry were used to collect, separate, identify and quantitate the oxidative and thermal decomposition products in heated triolein. Approximately 4 L of triolein was heated in a deep-fat fryer at 190°C for 12 h each day for a total of 60 h, until it contained ≥20% polymeric material. The concentration of heptane and octane increased after 12 h heating, then decreased upon further heating, while the concentration of volatile aldehydes decreased gradually during heating. After 12 h of heating, the concentrations of the major volatiles changed as follows: heptane (16.36 to 30.17 ppm), octane (24.48 to 40.77 ppm), heptanal (21.68 ppm to 9.11 ppm), octanal (35.53 to 36.64 ppm), nonanal (68.95 to 43.16 ppm), (E)-2-decenal (135.00 to 89.00 ppm) and (E)-2-undecenal (88.50 to 61.00 ppm). After 60 h of heating, when the oil contained over 20% polymeric material, the concentrations of heptane, octane, heptanal, octanol, nonanal, (E)-2-decenal and (E)-2-undecenal were 5.16, 4.39, 5.45, 7.02, 18.07, 12.50 and 6.00 ppm, respectively.

KEY WORDS: Capillary gas chromatography/infrared spectroscopy and mass spectrometry, static headspace, triolein, volatile oxidation products.

Several reports on the volatile compounds formed by oxidized oleates have been published (1-5). Dynamic headspace (DHS) (6) and static headspace (SHS) (7) techniques have been used for the volatile analysis of vegetable oils. A comparison of three methods (direct injection, DHS and SHS) for the volatile analysis of soybean oil showed that, for routine analysis, SHS gas chromatography (GC) is superior (8).

The application of HS and capillary GC in quantitative analysis requires that the solute concentrations in the sample be determined from measurements of their corresponding concentrations in the vapor phase (9). Because of the increased vapor pressure of the low-molecular weight compounds, they occur in greater concentration at equilibrium in the headspace (6,8). Thus, SHS, which favors the detection of low-molecular weight compounds (8) associated with the flavor development of fried foods (5,10,11), is a useful technique when combined with gas chromatography/infrared spectroscopy–mass spectrometry (GC/IR-MS) for the identification and quantitation of volatiles in heated triglycerides. However, no work has been published that examines the change in concentration of volatiles in heated triglycerides that occurs during heating. The objective of this work was to use SHS in combination with capillary GC/IR-MS to determine the effect of heating on the concentration of volatiles in heated triolein as a function of heating time. The information derived from this work is important in determining the concentrations of volatiles consumed in fried foods because the volatiles may occur in the food product if the food absorbs any oil.

EXPERIMENTAL PROCEDURES

Materials. Triolein, synthesized from oleic acid (99%) and glycerol (ARCO Chemical Co., Newtown Square, PA), was heated at 190°C for 12 h for 5 consecutive days. The triolein did not contain any added antioxidants. An electric deep-fat fryer (model F175A; Intedge Industries Inc., Whippany, NJ) was used for heating the oil. After each 12-h heating period, the oil was allowed to cool to <95°C. A 100-mL sample was removed, placed in a brown glass bottle, purged with nitrogen and stored in the dark at 3–5°C until the following day for analysis. This heating process was repeated each day until the oil contained at least 20% polymeric material, as determined with high-performance size-exclusion chromatography (HPSEC) (12, 13). A high-performance liquid chromatography system (Rainin Instruments, Woburn, MA) with 2 size-exclusion columns in series (each column was 500 mm × 8 mm) with a particle size of 5 μ was used for the HPSEC. The packing in the first column had a pore size of 100 Å. The detector was an evaporative light scattering detector, ELSD II (Varex, Burtonsville, MD).

Static HS-GC/IRD-MSD analysis. A static HS sampler HS-40 (Perkin-Elmer, Norwalk, CT) with a heated 150-cm transfer line was used to transfer the volatiles to the GC capillary column. A 5890 series II capillary GC was connected to an IRD 5965B and an MSD 5970 (Hewlett-Packard, Naperville, IL). Approximately, 1 g of sample was weighed into each HS vial, and the vial was placed in the HS-40. PTFE/silicone vial septa, secured by aluminum caps, were used to seal the sample vials. The septa were held at 55°C under vacuum for ≥2 d to remove contaminating volatiles. The oil sample was held at 150°C for 10 min in the vial. The HS injection needle was maintained at 170°C, while the transfer line temperature was 175°C. The sample vial was pressurized for 7 min at 22500/kg/m^2 (32 psi). Then the volatiles were transferred for 5 min and simultaneously collected at the head of the capillary column (−50°C). The column was held at the cryofocusing temperature of −50°C for 1 min after sample transfer. Next, the column temperature was programmed at 20°C/min to 60°C, then 10°C/min to 120°C and finally 20°C/min to 220°C. Helium was used as the carrier gas. A fused-silica capillary column (crosslinked 5% phenyl methyl silicone; 50 m × 0.32 mm, $d_f = 0.52$ μm; Hewlett-Packard) was used. The injection port temperature was 200°C. A column head pressure of 17,600 kg/m^2 (25 psi) with a volumetric flow rate of 10 mL/min were used. The injector purge was off from 0 to 0.5 min, then continually on after 0.5 min. The detector B (IRD 5965B) temperature was 250°C. Each sample was analyzed in triplicate.

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TABLE 1

External Standards Used to Quantitate the Volatile Compounds in Triolein

Compound	Standard used
Heptane, 1-heptene	Heptane
Octane, 1-octene	Octane
Nonane	Nonane
Propanal	Propanal
Acetic acid, pentanal	Pentanal
Heptanal, 1-heptanol	Heptanal
Octanal, 1-octanol	Octanal
Nonanal, E-2-nonenal	Nonanal
E-2-Decenal, E-2-undecenal	Decanal

Quantitative analysis. For quantitative work, external standards were used. External standards were used to avoid confusing any volatiles from the standards with those derived from the oil. Solutions were prepared in fresh soybean oil that had no detectable volatiles. The standard samples were analyzed under the same conditions as the unknown. A calibration curve of total ion chromatogram (TIC) peak area vs. concentration was plotted (14). The data from the calibration curves were used to quantitate the volatiles in heated triolein. For example, a linear plot of TIC peak area vs. concentration (0–50 ppm) for heptane had a correlation coefficient of 0.98 and a slope of 0.23. Thus, for heptane, as well as 1-heptene, their TIC peak areas were divided by 0.23 to determine the 1-heptene and heptane concentrations (ppm) in the triolein samples. Table 1 shows the standards used for quantitation of the volatiles in the unstabilized triolein samples.

p-*Anisidine value* (p-*AV*). The *p*-AVs of the oil samples were determined in triplicate by the official method Cd 18-90 of the American Oil Chemists' Society (15).

RESULTS AND DISCUSSION

The triolein, without added antioxidants, attained approximately 20% polymeric materials after approximately 60 h of heating. A polymeric material concentration of 20% corresponds to 27% polar materials, which is the maximum amount of polar material recommended in frying oil (16). The major volatile compounds (concentrations ≥10 ppm), heptane, heptanal, octane, octanal, nonanal, (E)-2-decenal and (E)-2-undecenal, were the same throughout the 60-h heating period. The concentration of dissolved volatiles from heated triolein are shown in Table 2. Selke *et al.* (1) observed earlier that heptane, octane, heptanal,

TABLE 2

Effect of Heating on Concentration of Individual Volatiles Formed by Triolein

Volatile compound	Concentration (ppm)					
	0 h	12 h	24 h	36 h	48 h	60 h
Propanal	0.07 ± 0.03[a]	0.25 ± 0.00	ND[b]	0.13 ± 0.00	ND	0.25 ± 0.21
Pentanal	ND	3.07 ± 0.41	2.68 ± 0.22	1.95 ± 0.34	2.68 ± 0.00	1.17 ± 0.27
Acetic acid	1.95 ± 0.73	ND	ND	ND	ND	ND
1-Heptene	1.02 ± 0.03	1.02 ± 0.19	0.68 ± 0.15	0.42 ± 0.00	ND	ND
Heptane	16.36 ± 1.99	30.17 ± 1.19	26.14 ± 0.97	13.18 ± 0.81	10.55 ± 0.18	5.16 ± 0.97
1-Octene	1.12 ± 0.08	ND	ND	ND	ND	ND
Octane	24.48 ± 0.21	40.77 ± 1.68	33.93 ± 0.87	17.96 ± 1.07	15.10 ± 0.21	4.39 ± 1.12
Heptanal	21.68 ± 1.49	9.11 ± 3.96	7.52 ± 1.39	9.01 ± 0.84	11.49 ± 1.19	5.45 ± 0.77
1-Heptanol	7.82 ± 1.29	3.96 ± 0.00	2.67 ± 0.00	3.37 ± 0.10	5.25 ± 0.10	1.09 ± 0.30
Nonane	ND	1.86 ± 0.09	1.22 ± 0.14	0.83 ± 0.00	ND	ND
Octanal	35.53 ± 2.13	36.64 ± 0.53	13.19 ± 1.81	15.21 ± 0.45	18.19 ± 2.23	7.02 ± 2.34
1-Octanol	6.91 ± 0.30	4.89 ± 0.00	3.72 ± 0.38	3.83 ± 0.45	4.68 ± 0.62	1.91 ± 0.68
Nonanal	68.95 ± 2.81	43.16 ± 4.74	41.23 ± 4.04	40.53 ± 0.00	49.47 ± 6.32	18.07 ± 6.14
(E)-2-Nonenal	2.28 ± 1.39	ND	ND	4.74 ± 0.00	6.84 ± 2.11	0.61 ± 0.00
(E)-2-Decenal	135.00 ± 8.00	89.00 ± 13.00	74.50 ± 7.00	65.00 ± 7.00	89.0 ± 10.50	12.50 ± 0.50
(E)-2-Undecenal	88.50 ± 4.00	61.00 ± 11.00	50.00 ± 7.50	45.50 ± 3.55	79.00 ± 13.00	6.00 ± 2.55

[a] Mean concentration ± standard deviation; n = 3.
[b] ND = not detected.

octanal, nonanal, (E)-2-decenal and (E)-2-undecenal were the major volatile compounds in heated triolein. The triolein did not contain any added antioxidants.

The concentration of heptane and octane in unstabilized triolein increased after heating for 12 h. However, upon further heating, there was a continual decrease in the concentrations of heptane and octane. It is likely that heptane and octane, similar to other volatiles, are formed rapidly during deep-fat frying until a balance is reached between the rate of formation and the rate of evaporation (17). After a 12-h heating period, the rate of evaporation exceeded the rate of formation.

The volatile aldehydes in unstabilized triolein decreased significantly during heating. The concentrations of (E)-2-decenal and (E)-2-undecenal after 60 h of heating were 9.3 and 6.8%, respectively, of the concentrations in the unheated triolein. A similar trend was observed for the saturated aldehydes, heptanal, octanal and nonanal with concentrations at 60 h that were 25.1, 19.8 and 26.2%, respectively, of the concentrations at time 0. This observation concurs with previous work, which reported that aldehyde concentrations in oils decrease with time due to their oxidation to acids (18). For (E)-2-decenal and (E)-2-undecenal, the decrease in concentration could also be due to their decomposition to lower-molecular weight compounds, a phenomena that has been observed for 2,4-decadienal (19).

The AVs for the heated triolein increased with an increase in heating time (Table 3). However, the total volatile aldehydes generally decreased (Table 3), suggesting that they are not the only ones contributing to the AVs. Although the unheated triolein had a low AV, the AVs after each heating interval indicated an increase in aldehyde concentration with an increase in heating time. As heptane and octane are formed, 11-oxo-9-undecenoate and 10-oxo-8-decenoate are formed, both of which remain attached to the rest of the triacylglycerol (3). The formation of the volatile alkenes 1-nonene and 1-decene would result in the formation of 9-oxononanoate and 8-oxooctanoate, respectively, which will remain attached to the remainder of the original triacylglycerol. Thus, the formation of nonvolatile oxo-compounds would account for the increase in AV, despite a decrease in the concentration of volatile aldehydes on heating. Even though volatile formation continued during heating, the concentrations did not increase during heating due to evaporation, effectively preventing buildup of the volatiles in the oil. In contrast, the concentration of the nonvolatiles will increase during heating as a result of dimer and polymer formation (11–13,20). Further oxidation/thermal degradation and not evaporation would be the only mechanism of nonvolatile loss.

TABLE 3

Anisidine Values and Total Volatile Aldehydes in Heated Triolein

Heating time (h)	Anisidine values	Total volatile aldehydes (ppm)
0	2.06 ± 0.44	352.01
12	48.29 ± 0.29	242.33
24	72.84 ± 0.41	189.12
36	87.89 ± 1.53	182.07
48	97.89 ± 2.38	256.67
60	98.26 ± 2.18	51.07

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