SHORT COMMUNICATION

Quantitation of Volatile Compounds in Heated Trilinolein 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, detect and quantitate the oxidative and thermal decomposition products in heated trilinolein. Trilinolein without added antioxidants was heated in a deep-fat fryer at 190°C for 12 h each day for a total of 24 h until the amount of polymeric material in the oil exceeded 20%. The concentration of the volatile compounds in trilinolein, as well as the *p*-anisidine values and polymer content, increased with an increase in heating time. After 24 h of heating, the concentrations of the major volatile compounds (>10 ppm) had increased as follows: pentane (33.4–398.7 ppm), pentanal (11.7–73.5 ppm), 1-pentanol (5.2–46.7 ppm), hexanal (67.6–346.1 ppm), (*E*)-2-hexenal (12.9–87.6 ppm), (*E*)-2-heptenal (309.6–894.1 ppm), 1-octen-3-ol (35.2–150.2 ppm), formic acid (0–18.7 ppm), hexanoic acid (0–83.8 ppm), heptanal (2.5–29.5 ppm), 2-pentylfuran (29.2–146.9 ppm), (*E*)-2-octenal (26.4–347.2 ppm), (*E*)-2-octenal (26.4–347.2 ppm), (*E*)-2-nonenal (31.6–163.2 ppm), (*E,Z*)-2,4-decadienal (15.0–320 ppm) and (*E,E*)-2,4-decadienal (43.1–1137.5 ppm).

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

The volatile compounds isolated from heated trilinolein have been reported by Thompson *et al.* (1) and Selke *et al.* (2). The volatile compounds isolated from heated methyl linoleate (3) have also been reported and were similar to those isolated from heated trilinolein. However, the changes in concentration of the volatile decomposition compounds contained in trilinolein that occurs during deep-fat frying have not been reported. The objective of the current research is to identify and quantitate the volatiles in heated trilinolein by static headspace (HS) and capillary gas chromatography/infrared spectroscopy–mass spectrometry (GC/IR–MS). Static HS–capillary GC has been reported as an excellent method for the analysis of volatile compounds in vegetable oils (4). The present work will enhance our understanding of the relationship between the concentration of volatiles in the oil and their formation during deep-fat frying.

EXPERIMENTAL PROCEDURES

Materials. Approximately 3.8 L of trilinolein synthesized from linoleic acid (99%) and glycerol (ARCO Chemical Co., Newtown Square, PA) was heated at 190°C for 12 h each day. The trilinolein did not contain any added antioxidants. An electric deep-fat fryer model F175A (Intedge Industries Inc., Whippany, NJ) was used for heating the oil. The capacity of the fryer was 5.58 kg, and the surface area of the oil was 610 cm^2 (20.2 × 30.2 cm). After each 12-h heating period, the oil was allowed to cool to <100°C. A 100-mL sample was removed, purged with nitrogen, sealed and stored at 5°C in the dark until the following day for analysis. This heating process was repeated until the oil contained at least 20% polymeric material (5).

HPSEC analysis. The amount of polymeric material was determined by high-performance size-exclusion chromatography (HPSEC) (5,6). The HPSEC system (Rainin Instruments, Woburn, MA) contained 2 size-exclusion columns in series (500 × 8 mm) with 5 μm i.d. particles. The packing (styrene divinylbenzene) in the first column had a pore size of 500 Å, and the second had a pore size of 100 Å. The detector was an evaporative light scattering detector, ELSD II (Varex, Burtonsville, MD).

p-*Anisidine value.* The *p*-anisidine values of the oil samples were determined in triplicate by the official method Cd 18-90 of the American Oil Chemists' Society (7).

Static HS-GC/IR-MS analysis. A static HS sampler HS-40 (Perkin-Elmer, Norwalk, CT) with a heated 150-cm transfer line was used to transfer the volatiles from the trilinolein sample in the vial to the GC capillary column. The column in a 5890 series II capillary GC was connected in series to an IRD 5965B and then to 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 22,500 kg/m^2 (32 psi) with helium. 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 an additional 1 min after the sample transfer was completed. 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 was used. The injector purge was off from 0 to 0.5 min, then continually on after 0.5 min. The detector (IRD 5965B) temperature was 250°C. Each sample was analyzed in triplicate.

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. The volatiles found in the trilinolein were quantitated with the external standard that

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TABLE 1

Standards Used to Quantitate the Volatile Compounds in Heated Trilinolein

Compounds found in trilinolein	Standard used
Pentane	Pentane
(*E*)-2-Octenal	(*E*)-2-Octenal
(*E*)-Nonenal	(*E*)-2-Nonenal
Ethanal	Ethanal
Acrolein (2-propenal)	Propanal
Butanal, formic acid	Butanal
Pentanal, 1-pentanol	Pentanal
Heptanal, 2-heptanone	Heptanal
Hexanal	Hexanal
(*E*)-2-Hexenal	(*E*)-2-Hexenal
(*E*)-2-Heptenal, (*Z*)-2-heptenal	(*E*)-2-Heptenal
2-Pentylfuran, 1-octen-3-ol, hexanoic acid	2-Pentylfuran
(*E,Z*)-2,4-Decadienal, (*E,E*)-2,4-decadienal	2,4-Decadienal

eluted closest to the compound of interest. In many cases, the external standard and the quantitated volatile component were identical. Table 1 lists the standards used for quantitation of the volatiles in trilinolein. Standard samples were prepared from soybean oil with no detectable volatiles as a solvent base. The standard samples were analyzed under the same conditions as the unknown. The HS sample vial contained approximately 1 g of soybean oil. A calibration curve of total ion chromatogram (TIC) peak area vs. concentration was plotted (8). The data from the calibration curves were used to quantitate the volatiles in the heated unstabilized trilinolein. For example, a linear plot of TIC peak area vs. concentration (0–50 ppm) for 2-pentylfuran had an R-squared value of 0.99 and a slope of 0.0303. Thus, for 2-pentylfuran, its TIC peak area from unstabilized trilinolein was divided by 0.0303 to determine the 2-pentylfuran concentration (ppm) in the oil.

RESULTS AND DISCUSSION

The trilinolein, without added antioxidants, contained ≥20% (21.2%) polymeric material after 24 h of heating. A polymeric material content of 20% corresponds to 27% polar material, which is the suggested maximum percentage of polar material recommended in frying oils (9). The major volatile compounds (>10 ppm) in the heated unstabilized trilinolein (Table 2) were identical to those reported by Selke *et al.* (2) in unstabilized trilinolein. The volatiles 1-octen-3-ol and 2-pentylfuran are characteristic volatile compounds formed from the thermal decomposition of trilinolein (10).

Pentane and hexanal are produced as a result of the decomposition of the 13-hydroperoxide (2), and both have been used with HS capillary GC for the determination of peroxidation of n-6 fatty acids (11). Acrolein co-eluted with pentane. Acrolein has been reported as a decomposition product of 2,4-decadienal (12). Thus, the presence of large amounts of 2,4-decadienal (Table 2) may account for the small amounts of acrolein in trilinolein.

The alkenals 2,4-decadienal and (*E*)-2-heptenal were found in large concentrations compared to other carbonyl compounds. The large concentrations of 2,4-decadienal and (*E*)-heptenal may be due to the high temperature (190°C) used during the heating period of the oil. The concentrations of both (*E*)-2-heptenal and 2,4-decadienal are reported to increase with an increase in heating temperature (13). (*E*)-2-Heptenal and 2,4-decadienal accounted for more than 50% of the carbonyl compounds dissolved in trilinolein. The trilinolein was heated at the high end of the temperature range normally used for frying oils.

During the deep-fat frying process, volatiles are formed rapidly until a balance is reached between their rate of formation and their decomposition and/or evaporation (14). However, during this study, all the volatile compounds increased with increasing heating time (Table 2). The trilinolein may not have reached equilibrium (rate of evaporation/decomposition vs. formation) in terms of volatiles production.

The anisidine values and total volatile aldehyde concentration for the heated trilinolein increased with an increase in heating time (Table 3). Initially, the unheated unstabilized trilinolein had a low anisidine value. The anisidine

TABLE 2

Effect of Heating on Concentration of Dissolved Individual Volatiles from Trilinolein

Volatile compound	Concentration (ppm) 0 h	12 h	24 h
Pentane	33.4 ± 0.7[a]	67.6 ± 2.3	398.7 ± 94.5
Acrolein	4.4 ± 0.2	ND[b]	ND
Butanal	1.7 ± 0.1	2.3 ± 0.3	ND
Formic acid	ND	2.2 ± 0.0	18.7 ± 0.0
Pentanal	11.7 ± 2.1	11.9 ± 0.6	73.5 ± 0.6
1-Pentanol	5.2 ± 0.1	7.3 ± 0.6	46.7 ± 10.0
Hexanal	67.6 ± 2.2	70.8 ± 2.5	346.1 ± 91.4
(*E*)-2-Hexenal	12.9 ± 1.6	18.6 ± 0.5	87.6 ± 25.9
Heptanal	2.5 ± 0.5	4.3 ± 0.3	29.5 ± 8.4
2-Heptanone	ND	ND	5.2 ± 0.7
(*E*)-2-Heptenal	309.6 ± 24.9	268.7 ± 19.3	894.1 ± 106.4
1-Octen-3-ol	35.2 ± 2.0	31.2 ± 0.5	150.2 ± 33.3
Hexanoic acid	ND	ND	83.8 ± 27.1
2-Pentylfuran	29.2 ± 2.0	15.4 ± 0.5	146.9 ± 37.6
(*E*)-2-Octenal	26.4 ± 0.0	36.0 ± 6.0	347.2 ± 83.2
(*E*)-2-Nonenal	31.6 ± 0.0	43.4 ± 2.0	163.2 ± 34.2
(*E,Z*)-2,4-Decadienal	15.0 ± 1.9	63.8 ± 11.3	320.0 ± 10.0
(*E,E*)-2,4-Decadienal	43.1 ± 11.3	322.5 ± 45.0	1137.5 ± 140.0

[a] Average concentration ± standard deviation; n = 3.
[b] ND = Not detected.

TABLE 3

Anisidine Values and Total Aldehydes in Heated Trilinolein

Heating time (h)	Anisidine values	Total volatile aldehydes (ppm)
0	3.6 ± 0.1[a]	522.1 ± 44.6
12	291.4 ± 4.4	842.3 ± 87.8
24	335.1 ± 2.9	3398.7 ± 500.1

[a] Average concentration ± standard deviation; n = 3.

values increased after each heating interval, which indicated an increase in aldehyde concentration with an increase in heating time. This agrees well with the observed increase of volatile aldehyde concentration with an increase in heating time. The other contributing factor to the increase in anisidine values may be the formation of oxo-compounds. As pentane is formed from 13-hydroperoxide, 13-oxo-9,11-tridecadienoate is formed (15); while the formation of 9-nonadiene radical would be accompanied by the formation of 9-oxononanoate. Both 13-oxo-9,11-tridecadienoate and 9-oxononanoate contain aldehyde groups and remain attached to the rest of the triacylglycerol. Thus, the formation of nonvolatile oxo-compounds in conjunction with an increase of volatile aldehydes in the heated trilinolein sample would account for the large *p*-anisidine values.

ACKNOWLEDGMENTS

This research was funded in part by the University of Illinois Agricultural Research Experiment Station, HATCH Project 50-314, the University of Illinois Campus Research Board, ARCO Chemical Co. and Best Foods, A division of CPC International, Inc.

REFERENCES

1. Thompson, J.A., W.A. May, M.M. Paulose and R.J. Peterson, *J. Am. Oil Chem. Soc. 55*:897 (1978).
2. Selke, E., W.K. Rohwedder and J.J. Dutton, *Ibid. 57*:25 (1980).
3. Frankel, E.N., W.E. Neff and E. Selke, *Lipids 16*:279 (1981).
4. Snyder, J.M., E.N. Frankel and E. Selke, *J. Am. Oil Chem. Soc. 65*:1617 (1988).
5. Husain, S., G.S. Sastry and N.P. Raju, *Ibid. 68*:822 (1991).
6. White, P.J., and Y-C. Wang, *Ibid. 63*:914 (1986).
7. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, Vol. 1, 4th edn., American Oil Chemists' Society, Champaign, 1989.
8. Kettrup, A., H. Stenner, J. Heicel and W. Lorek, *Applied Headspace Gas Chromatography*, edited by B. Klob, John Wiley & Sons, New York, 1984.
9. Paradis, A.J., and W.W. Nawar, *J. Am. Oil Chem. Soc. 58*:635 (1981).
10. Frankel, E.N., *Prog. Lipid Res. 22*:1 (1983).
11. Frankel, E.N., and A.L. Tappel, *Lipids 26*:479 (1991).
12. Matthews, R.F., R.A. Scanlan and L.M. Libey, *J. Am. Oil Chem. Soc. 48*:745 (1971).
13. Kimoto, W.I., and A.M. Gaddis, *Ibid. 46*:403 (1969).
14. Kubow, S., *Free Radical Biology and Medicine 12*:63 (1992).
15. Frankel, E.N., W.E. Neff and E. Selke, *Lipids 16*:279 (1981).

[Received January 11, 1994; accepted May 19, 1994]