

Identification and Quantitation of Volatile Compounds in Two Heated Model Compounds, Trilinolein and Linoleic Acid Esterified Propoxylated Glycerol

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Static headspace (HS) and capillary gas chromatography/infrared spectroscopy–mass spectrometry (GC/IR–MS) were used to collect, separate, identify, and quantitate the oxidative and thermal decomposition products in two heated model compounds, linoleic acid esterified propoxylated glycerol (EPG-08 linoleate) and trilinoleylglycerol, both without added antioxidants. Approximately 4 L of EPG-08 linoleate or trilinoleylglycerol was heated in a deep-fat fryer at 192 ± 8 °C for 12 h each day until the oil sample contained $\geq 20\%$ polymeric material, which occurred after 24 h of heating. The major volatile compounds both in heated EPG-08 linoleate and in heated trilinoleylglycerol were pentane, hexanal, 2-heptenal, 1-octen-3-ol, 2-pentylfuran, 2-octenal, and 2,4-decadienal. The identified volatile compounds from heated EPG-08 linoleate are those generally expected from the oxidative and thermal decomposition of fats and oils containing linoleic acid, except acetoxyacetone (1-acetoxy-2-propanone). Acetoxyacetone was found at 2.1, 3, and 2.4 ppm in the unheated, 12 h heated, and 24 h heated samples, respectively.

Keywords: *Volatile oxidation products; trilinoleylglycerol; linoleic acid esterified propoxylated glycerol; fat substitutes*

INTRODUCTION

Concern over health and nutrition has increased the public's desire for low-fat and low-calorie foods (Babayán, 1974; Rekha et al., 1991). Consequently, consumers have become concerned about how much fat they consume, as evidenced by the size and continued growth of the market for low-calorie foods (Rekha et al., 1991; Katz, 1998). Fats and oils do have numerous desirable functions; they act as carriers of fat-soluble vitamins A, D, E, and K and supply linoleic acid, an essential fatty acid (Shukla, 1992; Akoh, 1998). As many Americans seek to reduce their caloric intake for medical or health reasons, food technologists continue to explore ways to produce food substances that provide the same functional and sensory properties as fats and oils but without the calories. The major fat substitute categories include protein-based substitutes, carbohydrate-based substitutes, reduced-calorie fats, and fat-based fat substitutes, such as Olestra, Sorbestrin, and fatty acid esterified propoxylated glycerols (EPGs) (Haumann, 1986; Dziezak, 1989; Thayer, 1992; Akoh, 1998). EPGs are very low caloric, heat stable fat substitutes. To form EPGs, glycerol is propoxylated with propylene oxide to form a polyether polyol, which is then esterified with fatty acids (Gillis, 1988; White and Pollard, 1989; Cooper, 1990a,b). EPGs are metabolized much less than regular fats/oils due to the polyol chain between the

glycerol backbone and the fatty acids, which prevents lipase cleavage (Thayer, 1992).

Linoleic acid is one of the key precursors for fried flavor compounds (Pokorny, 1989). During frying the ratio of linoleic to oleic continually decreases, which alters the relative amount and concentration of the key flavor volatiles in the oil as a function of time (Yoon et al., 1987).

Oxidation occurs readily in unsaturated lipids, because proton abstraction from a carbon adjacent to a double bond is favored due to the formation of a stable allylic radical (Frankel, 1984; Kanner et al., 1987; Kubow, 1992). The hydroperoxides formed and subsequent decomposition products will differ, depending upon the conditions of oxidation. Temperature, pressure, oxygen concentration, and the presence of pro- or antioxidants will affect the rate of autoxidation, as well as the concentration and composition of the products formed. Whereas the autoxidation of oleate is initiated by the abstraction of hydrogen from the 8- and 11-positions, linoleate autoxidation is initiated by the abstraction of hydrogen from the doubly allylic methylene group on carbon 11 (Frankel, 1980; 1984). The result is a stable, delocalized pentadienyl radical from linoleate. Chan and Levett (1977) separated a series of linoleate hydroperoxide isomers based on double-bond position and geometric configuration. It was later reported that the rearrangement of linoleate hydroperoxide isomers was nonstereoselective on the basis of the isomers separated from an equilibrium mixture (Chan and Levett, 1977), although the distribution of these geometric hydroperoxide isomers can be influenced by temperature (Chan et al., 1975, 1979), which influences the volatiles formed upon decomposition of the hydro-

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peroxides. Although fatty acid hydroperoxides are generally tasteless and odorless, their decomposition products greatly impact flavor. Some volatile aldehydes, such as *trans*-4-heptenal, 2,7-decadienal, 2,6-heptadienal, and 3-hexenal, are extremely potent and can affect the flavor of vegetable oils at relatively low concentrations (Frankel, 1983). The volatile compounds formed from oxidized linoleate have been investigated in depth and are reported elsewhere (Frankel et al., 1981; Neff and Selke, 1993).

The objective of this study was to collect, separate, identify, and quantitate the volatile oxidative and thermal decomposition products in a model compound, linoleic acid esterified propoxylated glycerol (EPG-08 linoleate), produced during heating at deep-fat frying temperatures. After the compounds in EPG linoleate had been identified, the next step was to compare the volatiles to those in another heated model compound, trilinolein. The flavor of deep-fat-fried food is due mainly to volatile decomposition products, particularly with respect to the volatile oxidation products of linoleic acid (White, 1991). Therefore, it is important to identify similarities, as well as differences, between the volatiles formed by fat-based fat substitutes, such as EPGs, and naturally occurring fats and oils containing linoleic acid. Volatile identification and quantitation will be done using a static headspace (HS) capillary gas chromatography/infrared spectroscopy–mass spectrometry (GC/IR–MS) system.

EXPERIMENTAL PROCEDURES

Frying Oil Samples and Conditions. Approximately 4 L each of EPG-08 linoleate and trilinolein was prepared by ARCO Chemical Co. (Newtown Square, PA). Capillary gas chromatographic analysis indicated the percentage of linoleic acid (as a percentage of the total fatty acids) in the trilinolein sample was 98.8 ± 0.0 wt %, and the percentage of linoleic acid in the EPG-08 linoleate sample was 92.1 ± 0.1 %. The "08" in EPG-08 linoleate refers to the mole ratio of propylene oxide to glycerol during propoxylation. Replicate samples were not synthesized and examined, so differences in product variability with respect to preparation conditions were not examined in this series of experiments. The samples were placed in brown bottles, the headspace was flushed with nitrogen, and the bottles were shipped to The University of Illinois. Neither sample contained added antioxidants. The samples were stored in the dark at -20 °C upon arrival. Within 1 week of arrival, the samples were heated neat, without added food samples, at 192 ± 8 °C for 12 h for 2 consecutive days. 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 ($20.2 \text{ cm} \times 30.2 \text{ cm}$). After each 12 h heating period, the oil was allowed to cool to <95 °C. A sample (~ 100 mL) was removed and placed in a brown glass bottle, the headspace was purged with nitrogen, and the sample was 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, which is an accepted end point (White and Wang, 1986; Husain et al., 1991).

High-Performance Size Exclusion Chromatography (HPSEC) Analysis. The amount of polymeric material was determined with HPSEC (White and Wang, 1986; Husain et al., 1991). A high performance liquid chromatography (HPLC) system (Rainin Instruments, Woburn, MA) with two size exclusion columns in series (each column was $500 \text{ mm} \times 8 \text{ mm}$) with a particle size of $5 \mu\text{m}$ was used for the HPSEC analysis. The packing in the first column had a pore size of 100 \AA , whereas the second had a pore size of 500 \AA . The detector was an evaporative light scattering detector, ELSD II (Varex, Burtonsville, MD).

Table 1. Standards Used To Quantitate the Volatile Compounds in Heated Trilinolein and in Heated EPG-08 Linoleate Containing Added Antioxidants

compounds found in EPG-08 linoleate	standard used
pentane	pentane
acetaldehyde	acetaldehyde
acrolein (2-propenal)	propanal
butanal, formic acid	butanal
pentanal, 1-pentanol	pentanal
heptanal, 2-heptanone	heptanal
3-octen-2-one	octanal
acetoxyacetone	heptanal
hexanal	hexanal
<i>trans</i> -2-hexenal	<i>trans</i> -2-hexenal
<i>trans</i> -2-heptenal, <i>cis</i> -2-heptenal	<i>trans</i> -2-heptenal
<i>trans</i> -2-octenal	<i>trans</i> -2-octenal
<i>trans</i> -2-nonenal	<i>trans</i> -2-nonenal
2-pentylfuran, 1-octen-3-ol, hexanoic acid	2-pentylfuran
<i>trans</i> , <i>cis</i> -2,4-decadienal, <i>trans</i> , <i>trans</i> -2,4-decadienal	<i>t,t</i> -2,4-decadienal

Static HS-GC/IRD-MSD Analysis. A static headspace 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 infrared detector (IRD 5965B) and mass spectrometer (MSD 5970) (Hewlett-Packard, Naperville, IL). Approximately 1 g of sample was weighed into each headspace vial, and the vial was placed in the HS-40. Teflon/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 days to ensure complete removal of contaminating volatiles. The oil sample was held at 150 °C for 10 min in the vial. The headspace injection needle was maintained at 170 °C while the transfer line temperature was 175 °C. The sample vial was pressurized for 7 min at $22\,500 \text{ kg/m}^2$ (32 psi). The volatiles were then 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. The column temperature was next programmed at 20 °C/min to 60 °C, then at 10 °C/min to 120 °C, and finally at 20 °C/min to 220 °C. Helium was used as the carrier gas. A fused silica capillary column (cross-linked 5% phenyl methyl silicone; $50 \text{ m} \times 0.32 \text{ mm}$, $d_f = 0.52 \text{ mm}$) (Hewlett-Packard) was used. The injection port temperature was 200 °C. A column head pressure of $17\,600 \text{ kg/m}^2$ (25 psi) with a volumetric flow rate of 10 mL/min was used. The injector purge was off from 0 to 0.5 min and then continually on after 0.5 min. The detector B (IRD 5965B) temperature was 250 °C. Each sample was analyzed in triplicate.

Quantitative Analysis. For the quantitative analysis, a series of external standards were used (Mahungu et al., 1994; Mahungu, 1994) (Table 1). A calibration curve of total ion chromatogram (TIC) peak area versus concentration was plotted (Kettrup et al., 1984). The data from the calibration curves were used to quantitate the volatiles in heated trilinolein and in the heated EPG-08 linoleate. For example, a linear plot of TIC peak area versus concentration (0 – 50 ppm) for 2-pentylfuran had a correlation coefficient of 0.99 and a slope of 0.0303. Thus, for 2-pentylfuran, its TIC peak area was divided by 0.0303 to determine the 2-pentylfuran concentration (parts per million) in the trilinolein and in the EPG-08 linoleate samples. Table 1 shows the standards used for quantitation of the volatiles in the stabilized trilinolein and stabilized EPG-08 linoleate samples.

***p*-Anisidine Value.** The *p*-anisidine values of the oil samples were determined in triplicate according to official method Cd 18-90 of the AOCS (1991).

RESULTS AND DISCUSSION

The major volatile compounds, pentane, hexanal, 2-heptenal, 1-octen-3-ol, 2-pentylfuran, 2-octenal, and 2,4-decadienal, remained the same throughout the

Table 2. Concentration of Dissolved Volatiles from Trilinolein before and after Heating at 192 ± 8 °C

volatile compound	concentration (ppm)		
	heated for 0 h	heated for 12 h	heated for 24 h
acrolein	4.4 ± 0.2 ^a	ND ^b	ND
pentane	33.4 ± 0.7	67.6 ± 2.3	398.7 ± 94.5
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 ± 10.0
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
<i>trans</i> -2-hexenal	12.9 ± 1.6	18.6 ± 0.5	87.6 ± 25.9
heptanal	2.5 ± 0.4	4.3 ± 0.3	29.5 ± 8.4
heptanone	ND	ND	5.2 ± 0.7
<i>trans</i> -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
<i>trans</i> -2-octenal	26.4 ± 0.0	36.0 ± 6.0	347.2 ± 83.2
<i>trans</i> -2-nonenal	31.6 ± 0.0	43.3 ± 2.0	163.2 ± 34.2
<i>trans,cis</i> -2,4-decadienal	15.0 ± 1.9	63.8 ± 11.2	320.0 ± 10.0
<i>trans,trans</i> -2,4-decadienal	43.1 ± 11.2	322.5 ± 45.0	1138 ± 140

^a Mean concentration ± standard deviation; *n* = 3. ^b ND, not detected.

Table 3. Concentration of Dissolved Volatiles from EPG-08 Linoleate before and after Heating at 192 ± 8 °C

volatile compound	concentration (ppm)		
	heated for 0 h	heated for 12 h	heated for 24 h
acetaldehyde	2.7 ± 0.8 ^a	14.0 ± 0.0	10.5 ± 0.3
acrolein	9.6 ± 0.8	7.7 ± 0.6	5.0 ± 1.0
pentane	42.5 ± 3.5	75.7 ± 3.4	46.4 ± 2.3
butanal	16.9 ± 0.9	18.2 ± 0.0	5.5 ± 0.0
hexane	6.3 ± 1.2	6.4 ± 1.4	2.8 ± 0.0
formic acid	12.1 ± 3.3	16.9 ± 6.2	16.0 ± 0.7
acetic acid	5.1 ± 1.3	5.3 ± 0.1	4.9 ± 0.8
pentanal	17.1 ± 2.0	19.6 ± 2.7	18.0 ± 0.1
ethyl formate	0.9 ± 0.0	0.9 ± 0.0	ND ^b
1-pentanol	7.8 ± 0.5	13.0 ± 1.0	10.4 ± 1.1
hexanal	96.8 ± 4.1	102.4 ± 12.4	87.1 ± 2.1
<i>trans</i> -2-hexenal	4.9 ± 0.5	32.1 ± 2.4	20.3 ± 3.5
heptanal	3.9 ± 0.6	6.0 ± 0.1	5.6 ± 0.1
heptanone	ND	2.1 ± 0.3	1.8 ± 0.1
<i>cis</i> -2-heptenal	17.7 ± 1.1	12.3 ± 2.1	ND
<i>trans</i> -2-heptenal	436.9 ± 22.5	380.8 ± 28.9	267.4 ± 29.9
1-octen-3-ol	87.5 ± 8.3 ^c	82.8 ± 15.8	70.6 ± 1.3
2-pentyl furan	21.5 ± 3.0	20.5 ± 5.0	25.4 ± 5.0
<i>trans</i> -2-octenal	75.2 ± 14.4	108.0 ± 36.0	109.6 ± 8.8
<i>trans,cis</i> -2,4-decadienal	50.0 ± 11.3	87.5 ± 6.3	51.2 ± 10.0
<i>trans,trans</i> -2,4-decadienal	146.2 ± 17.5	343.8 ± 22.5	210.0 ± 20.0
acetoxyacetone	2.1 ± 0.3	3.0 ± 0.2	2.4 ± 0.2

^a Average concentration ± standard deviation; *n* = 3. ^b ND, not detected. ^c 1-Octen-3-ol + hexanoic acid.

entire heating period for both EPG-08 linoleate and trilinolein. The concentrations of the volatile compounds in trilinolein and in EPG-08 linoleate produced after 0, 12, and 24 h of heating are shown in Tables 2 and 3, respectively. There were differences in the concentrations of the volatiles found. In particular, the occurrence of over 160 ppm of 2-nonenal in trilinolein and the absence of 2-nonenal in EPG-08 linoleate were unexpected. It is not readily apparent why nonenal was not detected. The primary linoleate hydroperoxides formed should be the 9-hydroperoxide and the 13-hydroperoxide linoleate (Frankel, 1980). The primary volatile oxidation products from the decomposition of the 9-hydroperoxide

Table 4. Anisidine Values and Total Volatile Aldehydes in Heated Trilinolein

heating time (h)	anisidine value (absorbance units/g of oil)	total volatile aldehydes (ppm)
0	3.6 ± 0.1	524
12	291.4 ± 4.4	842
24	335.1 ± 2.9	3399

Table 5. Anisidine Values and Total Volatile Aldehydes in Heated EPG-08 Linoleate

heating time (h)	anisidine values (absorbance units/g of oil)	total volatile aldehydes (ppm)
0	3.1 ± 0.1	878
12	167.0 ± 2.2	1132
24	156.0 ± 1.5	790

linoleate should be nonenal and decadienal, whereas the primary volatile oxidation products upon the decomposition of the 13-hydroperoxide linoleate isomer will be hexanal and heptanal. The polyol backbone may have affected the decomposition of the 9-linoleate hydroperoxide, producing relatively lower amounts of *trans*-2-nonenal than normally occurs. A large amount of volatiles was found in the unheated sample, which emphasizes the poor stability characteristic of oils with very high percentages of polyunsaturated fatty acids unprotected with the appropriate antioxidants, even under good storage conditions.

Except for acetoxyacetone, the volatiles formed by EPG-08 linoleate are those expected and previously found upon the oxidative and thermal decomposition of linoleates (Selke et al., 1980; Frankel et al., 1981; Frankel, 1983). The observation that pentane, hexanal, 2-heptenal, 1-octen-3-ol, 2-pentylfuran, 2-octenal, and 2,4-decadienal are the major volatiles from both EPG-08 linoleate and trilinolein suggests that trilinolein and EPG-08 linoleate undergo thermal oxidation and decomposition via a similar mechanism, primarily the decomposition of the linoleate 9- and 13-hydroperoxides.

A unique (for frying oils) volatile compound identified was acetoxyacetone or 1-acetoxy-2-propanone. Acetoxyacetone was identified from its mass spectrum, infrared spectrum (figures not shown), and gas chromatographic retention time. The mass spectrum for acetoxyacetone had fragments at *m/z* 116 (C₅H₈O₃⁺) as the molecular ion, 86 (C₄H₆O₂⁺), 73 (C₃H₅O₂⁺), 43 (C₂H₃O⁺ 100% relative abundance), 27, and 15. The infrared spectrum for acetoxyacetone had a weak IR absorption band at 2942 cm⁻¹, which is associated with CH₂ antisymmetric stretch and CH stretch from CH₃, a strong band at 1766 cm⁻¹ associated with the C=O stretch for an ester, a medium doublet band at 1375 cm⁻¹ associated with the symmetric CH₃ deformations, and a very strong IR band at 1223 cm⁻¹ associated with a C—O—C antisymmetric stretch of an aliphatic ester (Lambert et al., 1987). Acetoxyacetone has been identified in other food products: as an aroma component in coffee (Reymon and Egli, 1965) and as a probable precursor to an important flavor constituent of bread (Wiseblatt and Zoumut, 1963).

The *p*-anisidine values for trilinolein and EPG-08 linoleate generally increased with an increase in heating time (Tables 4 and 5). Although both the unheated EPG-08 linoleate and trilinolein had low *p*-anisidine values, the change in *p*-anisidine values after heating indicated a substantial increase in aldehyde concentration due to heating. The major contributing factor to the increase in anisidine values is probably the formation of non-

volatile oxo compounds. For example, upon decomposition of the 9-hydroperoxide of methyl linoleate, one of the products formed will be methyl 9-oxononanoate (Frankel et al., 1981). With respect to the heated sample of trilinolein, 9-oxononanoate would remain attached to the rest of the triacylglycerol. Thus, the formation and accumulation of nonvolatile oxo compounds in the heated EPG-08 linoleate and trilinolein samples during heating could account for the high *p*-anisidine values.

Results from this study show that when EPG-08 linoleate is heated at ~195 °C, the volatile compounds produced are those predicted from the decomposition of the 9- and 13-hydroperoxides of linoleate. The absence of unusual volatiles from the oxidative decomposition of EPG-08 linoleate (except for relatively low concentrations of acetoxyacetone) suggests that the high rate of reactivity of linoleate may limit the participation of the EPG polyol backbone in volatile compound formation in EPG oil samples that contain even modest amounts of linoleic or more unsaturated fatty acids. Linoleates are known to decrease the volatile compound formation from oleates when trilinolein and triolein are mixed and oxidized at deep-fat-frying temperatures (Selke et al., 1980). The volatile compounds (except acetoxyacetone) formed by oxidized EPG-08 linoleate have been previously reported as volatile decomposition products of linoleates. Thus, EPG-08 linoleate is very similar to other linoleates in terms of volatile formation.

Triacylglycerols containing only linoleate would be expected to very susceptible to oxidation, particularly at frying temperatures, and, therefore, very unstable. Very large concentrations of aldehydes in each oil, although not expected, are not particularly surprising, given the highly unstable characteristics of linoleic acid in air at frying temperatures. The final synthesis step for each oil was done at relatively high temperature under partial vacuum. The delay between the synthesis and the heating experiments and the absence of anti-oxidants could explain the large concentration of volatiles in the unheated oil samples.

Under slightly different conditions of preparation and heating, differences in the relative amounts of the various volatiles formed are likely. However, large differences in the specific volatiles formed are unlikely, given the large susceptibility of linoleic acid to oxidation as well as its susceptibility to oxidation at a limited number of sites on the molecule (Frankel et al., 1981; Frankel, 1983).

It is also doubtful that the differences in volatile concentrations or the differences in *p*-anisidine values reflect any substantial difference in stability between the two oil samples. Although the *p*-anisidine and volatile data in this study suggest trilinolein may be less stable than EPG-08 linoleate, the free fatty acid values, food oil sensor values, and percent polymer reported by Artz et al. (1997) suggest that trilinolein is more stable than EPG-08 linoleate.

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