Volatile Compounds in Heated Oleic Acid-Esterified Propoxylated Glycerol

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ABSTRACT: Static headspace and capillary gas chromatography, in combination with infrared and mass spectrometry, were used to collect, separate, identify, and quantitate the oxidative and thermal decomposition products in two heated model compound triacylglycerols, oleic acid-esterified propoxylated glycerol (EPG-08 oleate) and triolein. The EPG-08 oleate and triolein were each heated in a deep-fat fryer at 192 ± 8°C for 12 h each day until the oil contained ≥20% polymeric material. Most of the volatile compounds identified in heated triolein and EPG-08 oleate were associated with the oxidative and thermal decomposition of oleates, such as short-chain alkanes, aldehydes, and alcohols. The major volatile compounds (concentration >20 ppm) in heated EPG-08 oleate and triolein were heptane, octane, heptanal, octanal, *trans*-2-decenal, nonanal, and *trans*-2-undecenal. However, a few minor volatile compounds, not previously found in heated fats and oils, were identified in the heated EPG-08 oleate samples. These compounds included 1,2-propanediol, 1-hydroxy-2-propanone (hydroxyacetone), 1-acetoxy-2-propanone (acetoxyacetone), 2-ethyl-4-methyl-1,3-dioxolane, 2,2,4-trimethyl-1,3-dioxolane, 2-heptyl-4-methyl-1,3-dioxolane, and 4-methyl-2-octyl-1,3-dioxolane. Alkyl-substituted dioxolanes have been found in heated methyl linoleate. *JAOCS 75,* 683–690 (1998).

KEY WORDS: Capillary gas chromatography, fatty acid-esterified propoxylated glycerol, infrared spectroscopy, mass spectrometry, static headspace analysis, triolein, volatile oxidation products.

Fat and caloric reduction in food products has become a topic of considerable interest to consumers, and therefore, the food processing industry (1). Because fats and oils contribute 9 kcal per gram, compared to the 4 kcal per gram provided by proteins or carbohydrates, they are a primary target in efforts to reduce the caloric content of food (2,3). Fatty acid-esterified propoxylated glycerols (EPG) are expected to have many of the desirable fat-like properties of regular fats and oils because they are derived from naturally occurring fats and oils and are closely related structurally to naturally occurring fats and oils. EPG are made by reacting glycerol with propylene oxide to form a polyether polyol, which is then esterified with fatty acids (4–8). EPG are metabolized to a much smaller degree than naturally occurring fats or oils due to the altered EPG molecular structure; a small polyether extension, placed between the glycerol backbone and the fatty acid, substantially reduces lipolytic activity (1). For a variety of reasons (flavor development, regulatory considerations, relative stability), it is important to determine whether EPG undergo the same oxidative and thermal decomposition reactions as naturally occurring fats and oils.

Most of the volatile compounds identified in heated triolein and EPG-08 oleate were associated with the oxidative and thermal decomposition of oleic acid, such as short-chain alkanes, aldehydes, and alcohols. Upon oxidation of oleic acid, hydrogen will be removed from the allylic methylene groups (adjacent to the double bond) at either C_8 or C_{11} to produce two possible allylic radicals in which electrons are delocalized among three carbons. Each of these radicals then reacts with oxygen to produce one of four hydroperoxides, 8-hydroperoxide (–OOH), 9-OOH, 10-OOH, and 11-OOH (9–11).

The hydroperoxides formed from the oxidation of oleic acid are unstable at temperatures above 100°C and will rapidly decompose to form a variety of secondary oxidation products. The first step of hydroperoxide decomposition involves cleavage of the oxygen-oxygen bond in the hydroperoxide group to produce a hydroxy radical and an alkoxy radical (9,10,12). Next, the carbon-carbon bond on one side of the alkoxy group is cleaved. Cleavage on the carboxyl side (or ester side, if attached to a triglyceride) of oleic acid will produce an aldehyde and an acid (or ester), whereas cleavage on the hydrocarbon side will produce a hydrocarbon and an oxoacid (or oxoester). When a vinylic radical is produced, however, an aldehyde will be formed. For example, decomposition of 8-OOH from methyl oleate results in the production of 2-undecenal and methyl-heptanoate when cleaved on the acid side, and decanal and methyl-8-oxooctanoate when cleaved on the hydrocarbon side. The 9-, 10-, and 11-hydroperoxides associated with methyl oleate undergo similar cleavage reactions. Unsaturated products can undergo further decomposition to produce additional oxidation products.

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Oxidation of oleic acid produces both volatile and nonvolatile decomposition products. The volatile oxidation products are important because they affect the odor and taste of lipids. The volatile products associated with oleic acid have been studied extensively (12–18).

The major volatile components of methyl oleate are octanal, nonanal, 2-decenal, and 2-undecenal. 2-Undecenal is derived from 8-OOH. 9-OOH produces 2-decenal and nonanal. Nonanal can also be formed upon decomposition of 10-OOH. Octanal is a decomposition product from 11-OOH (12).

Results of studies on the oxidation of fat-based fat substitutes have only recently been published. In one study on olestra and its thermal oxidation products, it was reported that the fatty acids in olestra undergo chemical reactions similar to the fatty acids in triacylglycerols under frying conditions (19).

The objective was to collect, separate, identify, and quantitate the volatile oxidative and thermal decomposition products in EPG produced during heating at deep-fat frying temperatures and compare the volatile compounds to those in another heated model compound, triolein. Because the flavor of deep-fat fried food is due primarily to volatile decomposition products (20), it is important to identify similarities, as well as differences, between the volatile compounds formed by fat-based fat substitutes, such as EPG, and naturally occurring fats and oils.

EXPERIMENTAL PROCEDURES

Materials. Two model compounds were used, trioleylglycerol (triolein) and EPG-08 oleate. Triolein (approximately 3.8 L) was synthesized from oleic acid (>99%) and glycerol, and EPG-08 oleate (approximately 3.8 L) was synthesized from oleic acid (>99%) and propoxylated glycerol by ARCO Chemical Co. (Newtown Square, PA). The "08" in EPG-08 oleate refers to the initial mole ratio of propylene oxide to glycerol during propoxylation. Samples of triolein and EPG-08 oleate with added pure, distilled α-tocopherol (Henkel Corp., Cincinnati, OH) and samples of triolein and EPG-08 oleate without added α-tocopherol were used. α-Tocopherol (1,000 ppm by weight) was added immediately after oil sample synthesis. The oil samples were purged with nitrogen for at least 30 min immediately prior to the addition of α-tocopherol. The α-tocopherol was added with stirring, and the samples were transferred to a dark brown bottle to exclude light, purged with nitrogen for 15 min, and then sealed. After arrival at the University of Illinois, all samples were held at approximately −20°C until used. A small electric deep-fat fryer (model F175A; Intedge Industries Inc., Whippany, NJ) was used for heating each oil. The oil samples were heated without frying any food. The capacity of the fryer was 5.58 kg, and the surface area of the oil was approximately 610 cm^2 (20.2 × 30.2 cm). Samples of each oil were heated at 192 ± 8°C for 12 h/day until each oil contained ≥20% polymeric material. After each 12-h heating period, the oil was cooled to approximately 95°C. A sample (approximately 100 mL) was removed, placed in an amber glass bottle with a Teflon-lined cap, blanketed with nitrogen, and stored in the dark at approximately 5°C until the following day for analysis. This heating process was repeated each day until the oil contained at least 20% polymeric material (20–23).

High-performance size-exclusion chromatography (HPSEC) analysis. The amount of polymeric material was determined by HPSEC (23,24), according to the method of Hansen *et al.* (23) with an evaporative light-scattering detector, ELSD II (Alltech Associates, Burtonsville, MD).

Volatile analysis. A static headspace sampler HS-40 (Perkin-Elmer, Norwalk, CT) with a heated 150-cm transfer line was used to transfer the volatile compounds to the head of the GC capillary column (25–27). The column was in a 5890 series II capillary GC, connected to an infrared detector (IRD 5965B) and a mass-selective detector (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 system. Teflon/silicone vial septa, secured by aluminum caps, were used to seal the sample vials. Prior to use, the septa were held at 55°C under vacuum for ≥2 days to ensure complete removal of any contaminating volatile compounds. 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 kg/m^2 (32 psi). Then, the volatile compounds were transferred for 5 min and simultaneously collected at the head of the capillary column by cryofocusing (−50°C). The column was held at −50°C for an additional 1 min after sample transfer was completed. Next, the column was temperature-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 (HP-5, 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 B (IRD 5965B detector and transfer line) temperature was 250°C. Each sample was analyzed in triplicate. Compound identification was based on infrared spectra, mass spectra, and, for compounds where standards were available, retention times.

Quantitative analysis. External standards, rather than internal standards, were used for quantitation (25–27). This was done to eliminate the possibility of contamination from the internal standard and the possibility of misidentification of an internal standard component or degradation product as derived from the oil sample. A calibration curve of total ion chromatogram (TIC) peak area vs. concentration was plotted (28). The data from the calibration curves were used to quantitate the volatile compounds in each oil sample. 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-hep-

TABLE 1
External Standards Used to Quantitate the Volatile Compounds in Triolein and EPG-08 Oleate

Compound quantitated	Standard used
Hexane	Hexane
Heptane, 1-heptene, propyl acetate	Heptane
2,2,4-Trimethyl-1,3-dioxolane	Heptane
2-Ethyl-4-methyl-1,3-dioxolane, octane, 1-octene	Octane
Nonane, 1-nonene	Nonane
2-Octanone/1-decene	Decane
Propanal, acetone, 2-propenal	Propanal
Butanal, formic acid, ethyl formate, methyl acetate	Butanal
Acetic acid, hydroxyacetone, pentanal	Pentanal
1,2-Propanediol	Hexanal
Heptanal, 1-heptanol	Heptanal
Acetoxyacetone	Heptanal
Butylcyclopentane/propylcyclohexane	Heptanal
Methyl 3-oxobutanoate	Heptanal
Octanal, 1-octanol	Octanal
Nonanal, *trans*-2-nonenal, nonyl formate	Nonanal
2-Decanone/octanoic acid, heptanoic acid	Decanal
trans-2-Decenal, *trans*-2-undecenal	Decanal
8-Heptadecene	2,4-Decadienal

tene and heptane concentrations (ppm) in triolein and in EPG-08 oleate samples. Table 1 lists the standards used for quantitation of each of the volatile compounds in the oil samples. The external standards selected for quantitation were chosen based on their availability and volatility. Standards were used for quantitation of those sample compounds that eluted relatively close to the standard because the volatility of the standard and the sample compounds would therefore be similar.

p-Anisidine value (p-AV). The *p*-AV of the oil samples were determined in triplicate by the Official Method Cd 18-90 of the AOCS (29).

RESULTS AND DISCUSSION

The concentration of the volatile compounds (≥0.1 ppm) in heated EPG-08 oleate and in heated triolein with added α-tocopherol are shown in Tables 2–5. The smaller concentration of volatile compounds in the unheated triolein sample with added tocopherols, as compared to the unheated triolein without added tocopherols, suggests that the added tocopherols protected the triolein from autoxidation prior to heating (Tables 3,5). There were also five additional volatile compounds found in the EPG-08 oleate sample without added tocopherols (Table 4), as compared to the EPG-08 oleate sample with added tocopherols (Table 2). The unheated EPG-08 oleate with added tocopherols had a smaller concentration of total volatile aldehydes than the unheated EPG-08 oleate without added tocopherols, as would be expected due to the protective effect of tocopherols (30). The heated EPG-08 oleate with added tocopherols had significantly higher concentrations of total volatile aldehydes, which suggests that the tocopherols were not effective at frying temperatures, as expected (31). The aldehydes were found in greater concentrations than other classes of volatile compounds. The total volatile aldehyde concentration increased substantially after a 12-h heating period for both EPG-08 oleate samples and the triolein sample with added tocopherols. Upon further heating, there was a general decrease of the total volatile aldehydes in EPG-08 oleate and triolein, as shown in Tables 6–9. The observed increase in volatile aldehyde concentration on heating the EPG-08 oleate and triolein for 12 h may be due to the rapid decomposition of hydroperoxides at temperatures exceeding 100°C (32). After more than 12 h of heating, the rate of evaporation of volatile aldehydes is greater than the rate of formation of the volatile aldehydes, accounting for the decrease in concentration of total volatile aldehydes after 24-h and 36-h heating periods.

The increase in total volatile aldehydes after a 12-h heating period was accompanied by a large increase in the *p*-AV for EPG-08 oleate and triolein (Tables 6–9). The increase in *p*-AV in the heated triolein was an indication of an increase in the nonvolatile aldehyde content of the heated oil. As heptane and octane are formed, 11-oxo-9-undecenoate and 10-oxo-8-decenoate are also formed and remain attached to the rest of the triacylglycerol (32). 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 *p*-AV, despite a decrease in the concentration of the total volatile aldehydes. Whereas evaporation will prevent buildup of volatile compounds in the oil, the nonvolatile compounds will increase during heating as a result of dimer and polymer formation (21,22,33). Further oxidation and thermal decomposition would be the only mechanism of nonvolatile compound loss.

The detection in EPG-08 oleate of the alkyl-substituted 1,3-dioxolanes, 2-heptyl-4-methyl-1,3-dioxolane, and 4-methyl-2-octyl-1,3-dioxolane (Tables 2,4) can be accounted for by the condensation of 1,2-propanediol (or a similar compound) with octanal and nonanal, respectively. Aldehydes can undergo condensation with diols to form trioxanes and dioxolanes (34,35). Octanal and nonanal were found in relatively large concentrations in the heated EPG-08 oleate. The other dioxolanes identified, 2,2,4-trimethyl-1,3-dioxolane and 2-ethyl-4-methyl-1,3-dioxolane, can be formed by condensation of 1,2-propanediol with acetone and propanal, respectively. Both acetone and propanal were identified in heated EPG-08 oleate samples.

The volatile compound 8-heptadecene (Table 2) was detected in the 12-, 24-, and 36-h heated EPG-08 oleate with added tocopherols. The detection of 8-heptadecene in EPG-08 oleate was expected because the parent fatty acid is oleic acid. The alkene 8-heptadecene can be formed by the decarboxylation of oleic acid (36).

The other unique volatile compound identified was 1-acetoxy-2-propanone (acetoxyacetone) (Tables 2,4). The reaction of acetic acid with 1-hydroxy-2-propanone (hydroxyacetone) would account for the formation of 1-acetoxy-2-propanone. Both 1-hydroxy-2-propanone and acetic acid

TABLE 2
Volatile Compounds Formed by EPG-08 Oleate (with added tocopherols) During Heating

	Concentration (ppm)			
Volatile compound	0 h	12 h	24 h	36 h
Acetaldehyde	ND	ND	ND	ND
2-Propenal	ND	ND	ND	ND
Propanal/acetone	1.9 ± 0.0[a]	7.5 ± 1.2	20.3 ± 4.8	26.9 ± 0.5
Ethyl formate	ND	ND	ND	ND
Methyl acetate	ND	ND	ND	ND
Butanal	ND	32.5 ± 1.4	21.4 ± 1.2	7.5 ± 0.0
Formic acid	2.4 ± 0.0	18.5 ± 2.5	26.6 ± 0.0	39.6 ± 0.0
Pentanal	ND	ND	ND	ND
Acetic acid	3.8 ± 0.7	13.1 ± 3.3	12.6 ± 1.0	12.4 ± 1.0
Hexane	6.2 ± 0.6	25.7 ± 0.1	19.38 ± 0.0	11.81 ± 0.0
1-Heptene	1.0 ± 0.2	13.8 ± 1.5	9.11 ± 1.3	4.1 ± 0.0
Heptane	14.8 ± 0.9	197.4 ± 16.0	134.5 ± 22.6	235.6 ± 13.9
Propyl acetate	ND	ND	ND	ND
2,2,4-Trimethyl-1,3-dioxolane	ND	7.5 ± 0.7	7.7 ± 1.7	7.6 ± 0.0
2-Ethyl-4-methyl-1,3-dioxolane	1.0 ± 0.3	12.6 ± 1.2	10.7 ± 2.1	12.5 ± 1.8
1-Hydroxy-2-propanone	ND	ND	3.5 ± 0.1	11.4 ± 0.7
1-Octene	0.8 ± 0.0	8.5 ± 0.9	7.6 ± 2.0	7.8 ± 0.6
Octane	19.6 ± 3.1	218.3 ± 13.5	149.3 ± 9.4	164.0 ± 13.4
Acetoxyacetone	ND	17.0 ± 0.0	6.7 ± 0.0	6.3 ± 0.0
Heptanal	5.7 ± 0.2	40.5 ± 2.0	43.0 ± 2.7	39.0 ± 0.0
1,2-Propanediol	ND	12.4 ± 2.2	12.0 ± 0.0	ND
Butylcyclopentane/propylcyclohexane	2.1 ± 0.3	9.9 ± 1.5	14.0 ± 1.4	14.7 ± 1.9
1-Nonene	ND	16.2 ± 2.9	8.2 ± 1.6	3.0 ± 0.0
Nonyl acetate	ND	ND	ND	ND
Nonane	ND	4.8 ± 0.3	4.7 ± 0.6	2.3 ± 0.0
Methyl 3-oxobutanoate	4.6 ± 0.2	34.8 ± 2.1	21.8 ± 3.1	24.9 ± 1.3
1-Heptanol	2.0 ± 0.0	13.4 ± 2.5	13.0 ± 1.8	15.0 ± 2.0
2-Octanone/1-decene	ND	15.3 ± 0.1	13.5 ± 0.8	16.6 ± 2.9
Octanal	7.9 ± 0.4	69.7 ± 2.1	69.5 ± 8.6	72.8 ± 9.2
1-Octanol	1.7 ± 0.0	10.9 ± 1.6	9.2 ± 2.1	9.5 ± 0.2
Nonanal	36.8 ± 0.5	267.2 ± 5.3	200.7 ± 20.2	240.7 ± 21.4
Nonyl formate	ND	ND	ND	ND
trans-2-Nonenal	ND	14.0 ± 2.3	10.5 ± 2.8	19.7 ± 2.8
Heptanoic acid	ND	ND	ND	ND
trans-2-Decenal	63.0 ± 1.5	360.5 ± 5.5	236.5 ± 19.0	229.5 ± 5.5
trans-2-Undecenal	44.5 ± 3.0	195.0 ± 14.5	129.5 ± 3.0	131.0 ± 10.0
2-Decanone/octanoic	ND	11.5 ± 0.0	ND	59.0 ± 9.0
8-Heptadecene	ND	92.5 ± 10.0	85.0 ± 15.0	87.5 ± 8.8

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

were volatile compounds identified in heated EPG-08 oleate with added tocopherols. The presence of 1-hydroxy-2-propanone may be due to the oxidation of 1,2-propanediol derivatives, which can produce 1-hydroxy-2-propanone (37).

Most of the volatile compounds found in the unheated EPG-08 oleate are those expected from the oxidative and thermal decomposition of oleates. Upon heating EPG-08 oleate, however, butylcyclopentane, 2-ethyl-4-methyl-1,3-dioxolane, and 2,2,4-trimethyl-1,3-dioxolane were detected. Although alkyl-substituted dioxolanes have been reported as volatile oxidative decomposition products of methyl linoleate (35,38), no report so far has indicated that alkyl-substituted dioxolanes can be formed by oleates. Thus, the 1,3-dioxolanes detected could be oxidative and thermal decomposition products that are unique to heated EPG-08 oleate, although EPG-08 oleate was not prepared with pure oleic acid (>99% by capillary GC), and the oil sample may have contained a small percentage (<0.5%) of linoleic acid.

The major volatile compounds were the same for both model compounds and have been found in other food or food oil samples. Most of the volatile compounds in EPG-08 oleate can be explained by the decomposition of the oleate 8-, 9-, 10-, and 11-hydroperoxides. Thus, EPG-08 oleate undergoes oxidative and thermal decomposition through a similar mechanism to other oleates. The protective effect of α-tocopherol was only noticeable in unheated oils, as expected.

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TABLE 3
Volatile Compounds Formed by Triolein (with added tocopherols) During Heating

	Concentration (ppm)			
Volatile compound	0 h	12 h	24 h	36 h
Acetaldehyde	ND	ND	ND	ND
2-Propenal	ND	ND	ND	ND
Acetone	ND	ND	ND	ND
Propanal	ND	ND	ND	ND
Ethyl formate	ND	ND	ND	ND
Methyl acetate	ND	ND	ND	ND
Butanal	ND	0.3 ± 0.0[a]	0.2 ± 0.0	0.1 ± 0.0
Formic acid	ND	ND	ND	ND
Pentanal	ND	ND	ND	ND
Acetic acid	ND	ND	ND	ND
Hexane	ND	0.5 ± 0.0	0.4 ± 0.0	0.4 ± 0.0
1-Heptene	ND	0.8 ± 0.0	0.5 ± 0.0	0.3 ± 0.0
Heptane	0.2 ± 0.0	29.9 ± 0.3	19.2 ± 2.0	10.6 ± 1.3
Propyl acetate	ND	ND	ND	ND
2,2,4-Trimethyl-1,3-dioxolane	ND	ND	ND	ND
2-Ethyl-4-methyl-1,3-dioxolane	ND	ND	ND	ND
1-Hydroxy-2-propanone	ND	ND	ND	ND
1-Octene	ND	0.6 ± 0.1	0.4 ± 0.1	0.1 ± 0.0
Octane	0.3 ± 0.1	36.0 ± 0.2	23.7 ± 2.7	13.0 ± 1.4
Acetoxyacetone	ND	ND	ND	ND
Heptanal	1.1 ± 0.3	4.9 ± 0.3	4.0 ± 0.7	2.9 ± 0.4
1,2-Propanediol	ND	ND	ND	ND
Butylcyclopentane/propylcyclohexane	ND	ND	ND	ND
1-Nonene	ND	0.5 ± 0.0	0.4 ± 0.0	ND
Nonyl acetate	ND	ND	ND	ND
Nonane	ND	1.1 ± 0.1	0.7 ± 0.1	0.3 ± 0.0
Methyl-3-oxobutanoate	ND	ND	ND	ND
1-Heptanol	ND	1.6 ± 0.1	0.7 ± 0.1	0.2 ± 0.0
Octanal	1.3 ± 0.2	8.5 ± 0.2	6.7 ± 1.2	5.1 ± 0.9
2-Octanone	ND	ND	ND	ND
1-Decene	ND	0.6 ± 0.1	0.2 ± 0.0	ND
1-Octanol	ND	1.3 ± 0.1	0.9 ± 0.2	0.1 ± 0.0
Nonanal	1.8 ± 0.5	31.4 ± 1.4	25.3 ± 3.5	18.6 ± 2.8
Nonyl formate	ND	ND	ND	ND
trans-2-Nonenal	ND	0.4 ± 0.0	ND	ND
Heptanoic acid	ND	ND	ND	ND
trans-2-Decenal	3.0 ± 0.5	65.0 ± 2.5	45.0 ± 6.0	19.5 ± 3.0
trans-2-Undecenal	1.5 ± 0.5	44.0 ± 3.5	31.0 ± 4.5	12.0 ± 2.5
2-Decanone	ND	ND	ND	ND
Octanoic acid	ND	ND	ND	ND
8-Heptadecene	ND	ND	ND	ND

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

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TABLE 4
Volatile Compounds Formed by EPG-08 Oleate (without added tocopherols) During Heating

	Concentration (ppm)			
Volatile compound	0 h	12 h	24 h	36 h
Acetaldehyde	12.1 ± 0.3[a]	12.3 ± 1.5	6.5 ± 1.1	5.5 ± 0.3
2-Propenal	3.2 ± 0.7	1.5 ± 0.0	0.7 ± 0.0	0.6 ± 0.1
Acetone	4.2 ± 0.6	12.9 ± 0.6	11.9 ± 1.0	8.0 ± 0.3
Propanal	1.5 ± 0.0	9.5 ± 0.3	7.5 ± 1.0	6.3 ± 0.6
Ethyl formate	0.9 ± 0.0	0.5 ± 0.0	0.6 ± 0.3	ND
Methyl acetate	1.7 ± 0.8	0.8 ± 0.0	3.2 ± 0.7	ND
Butanal	7.6 ± 1.8	5.0 ± 0.9	9.1 ± 1.0	8.8 ± 1.4
Formic acid	30.1 ± 5.3	13.7 ± 1.6	10.1 ± 1.2	4.7 ± 0.0
Pentanal	ND	ND	ND	ND
Acetic acid	26.0 ± 1.5	15.5 ± 4.2	12.5 ± 1.0	15.0 ± 0.2
Hexane	6.3 ± 1.2	4.1 ± 1.2	7.2 ± 0.1	7.4 ± 0.1
1-Heptene	ND	ND	ND	ND
Heptane	18.0 ± 0.4	45.9 ± 3.9	28.5 ± 1.2	22.0 ± 1.7
Propyl acetate	0.9 ± 0.4	1.1 ± 0.3	1.9 ± 0.3	0.7 ± 0.1
2,2,4-TriMe-1,3-dioxolane	ND	3.1 ± 0.4	2.4 ± 0.3	2.4 ± 0.3
2-Et-4-Me-1,3-dioxolane	ND	3.8 ± 0.4	2.8 ± 0.3	2.0 ± 0.1
1-Hydroxy-2-propanone	ND	ND	ND	ND
1-Octene	ND	1.6 ± 0.5	1.2 ± 0.2	1.2 ± 0.3
Octane	23.9 ± 1.5	59.5 ± 0.9	36.9 ± 0.2	29.4 ± 2.7
Acetoxyacetone	6.7 ± 0.0	9.3 ± 0.1	6.8 ± 1.3	7.2 ± 1.3
Heptanal	13.9 ± 2.5	15.9 ± 3.8	11.9 ± 0.8	13.7 ± 0.3
1,2-Propandiol	ND	ND	ND	ND
Butylcyclopentane	ND	5.0 ± 0.8	3.2 ± 0.3	2.4 ± 0.1
Propylcyclohexane	ND	ND	ND	ND
1-Nonene	1.8 ± 0.3	3.3 ± 0.6	1.9 ± 0.3	1.8 ± 0.5
Nonyl acetate	ND	1.9 ± 0.0	3.6 ± 0.4	1.9 ± 0.1
Nonane	ND	ND	ND	ND
Methyl 3-oxo-butanoate	18.4 ± 2.5	13.6 ± 3.0	11.9 ± 0.3	13.7 ± 2.1
1-Heptanol	4.6 ± 1.5	5.6 ± 0.5	6.3 ± 1.6	7.2 ± 2.8
1-Decene	2.1 ± 0.4	3.9 ± 1.1	1.9 ± 0.3	2.4 ± 0.7
2-Octanone	ND	ND	ND	ND
Octanal	21.4 ± 0.7	36.6 ± 3.5	20.7 ± 1.1	24.6 ± 0.1
1-Octanol	5.7 ± 0.5	8.0 ± 0.7	5.5 ± 1.3	6.8 ± 1.8
Nonanal	55.3 ± 4.7	88.4 ± 18.4	65.8 ± 5.4	73.7 ± 1.0
Nonyl formate	ND	4.4 ± 1.0	3.9 ± 0.9	4.2 ± 0.7
trans-2-Nonenal	3.2 ± 1.4	9.3 ± 1.4	6.3 ± 1.8	7.7 ± 2.5
Heptanoic acid	ND	19.5 ± 6.0	22.0 ± 6.5	12.5 ± 0.5
trans-2-Decenal	99.0 ± 0.5	107.0 ± 4.0	66.0 ± 6.5	87.5 ± 17.5
trans-2-Undecenal	70.0 ± 16.0	57.0 ± 3.0	24.0 ± 2.0	36.0 ± 0.5
2-Decanone	ND	ND	ND	ND
Octanoic acid	ND	ND	ND	ND
8-Heptadecene	ND	ND	ND	ND

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

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TABLE 5
Volatile Compounds Formed by Triolein (without added tocopherols) During Heating

	Concentration (ppm)				Concentration (ppm)		
Volatile compound	0 h	12 h	24 h	Volatile compound	0 h	12 h	24 h
Acetaldehyde	ND	ND	ND	Acetaldehyde	ND	ND	ND
2-Propenal	ND	ND	ND	2-Propenal	ND	ND	ND
Acetone	ND	ND	ND	Acetone	ND	ND	ND
Propanal	0.1 ± 0.0[a]	0.3 ± 0.0	ND	Propanal	0.1 ± 0.0	ND	0.3 ± 0.2
Ethyl formate	ND	ND	ND	Ethyl formate	ND	ND	ND
Methyl acetate	ND	ND	ND	Methyl acetate	ND	ND	ND
Butanal	ND	ND	ND	Butanal	ND	ND	ND
Formic acid	ND	ND	ND	Formic acid	ND	ND	ND
Pentanal	ND	3.1 ± 0.4	2.7 ± 0.2	Pentanal	12.0 ± 0.3	2.7 ± 0.0	1.2 ± 0.3
Acetic acid	2.0 ± 0.7	ND	ND	Acetic acid	ND	ND	ND
Hexane	ND	ND	ND	Hexane	ND	ND	ND
1-Heptene	1.0 ± 0.0	1.0 ± 0.2	0.7 ± 0.2	1-Heptene	0.4 ± 0.0	ND	ND
Heptane	16.4 ± 2.0	30.2 ± 1.2	26.1 ± 1.0	Heptane	13.2 ± 0.8	10.6 ± 0.2	5.2 ± 1.0
Propyl acetate	ND	ND	ND	Propyl acetate	ND	ND	ND
2,2,4-Trimethyl-1,3-dioxolane	ND	ND	ND	2,2,4-Trimethyl-1,3-dioxolane	ND	ND	ND
2-Ethyl-4-methyl-1,3-dioxolane	ND	ND	ND	2-Ethyl-4-methyl-1,3-dioxolane	ND	ND	ND
1-Hydroxy-2-propanone	ND	ND	ND	1-Hydroxy-2-propanone	ND	ND	ND
1-Octene	1.1 ± 0.1	ND	ND	1-Octene	ND	ND	ND
Octane	24.5 ± 0.2	40.8 ± 1.7	33.9 ± 0.9	Octane	18.0 ± 1.1	15.1 ± 0.2	4.4 ± 1.1
Acetoxyacetone	ND	ND	ND	Acetoxyacetone	ND	ND	ND
Butylcyclopentane	ND	ND	ND	Butylcyclopentane	ND	ND	ND
Propylcyclohexane	ND	ND	ND	Propylcyclohexane	ND	ND	ND
1-Nonene	ND	ND	ND	1-Nonene	ND	ND	ND
Heptanal	21.9 ± 1.5	9.1 ± 4.0	7.5 ± 1.4	Heptanal	9.0 ± 0.8	11.5 ± 1.2	5.4 ± 0.8
Nonyl acetate	ND	ND	ND	Nonyl acetate	ND	ND	ND
Nonane	ND	1.9 ± 0.1	1.2 ± 0.1	Nonane	0.8 ± 0.0	ND	ND
Methyl-3-oxobutanoate	ND	ND	ND	Methyl-3-oxobutanoate	ND	ND	ND
1-Heptanol	7.8 ± 1.3	4.0 ± 0.0	2.7 ± 0.0	1-Heptanol	3.4 ± 0.1	5.2 ± 0.1	1.1 ± 0.3
Octanal	35.5 ± 2.1	36.6 ± 0.5	13.2 ± 1.8	Octanal	15.2 ± 0.4	18.2 ± 2.2	7.0 ± 2.3
2-Octanone	ND	ND	ND	2-Octanone	ND	ND	ND
1-Decene	ND	ND	ND	1-Decene	ND	ND	ND
1-Octanol	6.9 ± 0.3	4.9 ± 0.0	3.7 ± 0.4	1-Octanol	3.8 ± 0.4	4.7 ± 0.6	1.9 ± 0.7
Nonanal	69.0 ± 2.8	43.2 ± 4.7	41.2 ± 4.0	Nonanal	40.5 ± 0.0	49.5 ± 6.3	18.1 ± 6.1
Nonyl formate	ND	ND	ND	Nonyl formate	ND	ND	ND
trans-2-Nonenal	2.3 ± 1.4	ND	ND	*trans*-2-Nonenal	4.7 ± 0.0	6.8 ± 2.1	0.6 ± 0.0
Heptanoic acid	ND	ND	ND	Heptanoic acid	ND	ND	ND
trans-2-Decenal	135.0 ± 8.0	89.0 ± 13.0	74.5 ± 7.0	*trans*-2-Decenal	65.0 ± 7.0	89.0 ± 10.5	12.5 ± 0.5
trans-2-Undecenal	88.5 ± 4.0	61.0 ± 11.0	50.0 ± 7.5	*trans*-2-Undecenal	45.5 ± 3.6	79.0 ± 13.0	6.0 ± 2.6
2-Decanone	ND	ND	ND	2-Decanone	ND	ND	ND
Octanoic acid	ND	ND	ND	Octanoic acid	ND	ND	ND
8-Heptadecene	ND	ND	ND	8-Heptadecene	ND	ND	ND

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

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TABLE 6
Anisidine Values and Total Volatile Aldehydes in Heated EPG-08 Oleate with Added Tocopherols

Heating time (h)	Anisidine values	Total volatile aldehydes (ppm)
0	7.1 ± 0.1	159.9
12	58.4 ± 2.3	1077.9
24	72.5 ± 5.9	731.4
36	80.1 ± 1.5	767.1

TABLE 7
Anisidine Values and Total Volatile Aldehydes in Heated EPG-08 Oleate Without Added Tocopherols

Heating time (h)	Anisidine values	Total volatile aldehydes (ppm)
0	2.8 ± 0.4	287.1
12	54.8 ± 1.0	342.7
24	65.4 ± 4.4	218.6
36	67.7 ± 0.7	264.4

TABLE 8
Anisidine Values and Total Volatile Aldehydes in Heated Triolein with Added Tocopherols

Heating time (h)	Anisidine values	Total volatile aldehydes (ppm)
0	2.6 ± 0.7	8.6
12	29.5 ± 1.4	154.4
24	88.2 ± 0.4	112.1
36	87.6 ± 1.6	58.2

TABLE 9
Anisidine Values and Total Volatile Aldehydes in Heated Triolein Without Added Tocopherols

Heating time (h)	Anisidine values	Total volatile aldehydes (ppm)
0	2.1 ± 0.4	352.3
12	48.3 ± 0.3	242.3
24	72.8 ± 0.4	189.1
36	87.9 ± 1.5	192.0
48	97.9 ± 2.4	256.7
60	98.3 ± 2.2	51.1

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