Odor Significance of Undesirable Degradation Compounds in Heated Triolein and Trilinolein[1]

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ABSTRACT: To better understand production of undesirable or negative odors such as fruity, plastic, and waxy that are characteristic of higher oleic acid-containing oils, model heated oil systems of triolein and trilinolein were studied. Identification of the odor significance of volatile compounds produced by fractionated and nonfractionated triolein and trilinolein was done by purge and trap–gas chromatography–ion trap mass spectrometry–olfactometry. The predominant odors of the triolein heated 1, 3, and 6 h at 190°C were fruity and plastic, with other negative odors of acrid and grassy. Some of the volatile compounds that produced negative odors in heated triolein, in order of increasing concentration, were hexanal (grassy), octanal (fruity), (*E*)-2-decenal (plastic), nonanal (fruity), and (*E*)-2-undecenal (plastic). Some of the negative odor compounds in trilinolein heated for 1, 3 and 6 h, in order of increasing concentration, included (*E*)-2-nonenal (plastic), pentanal (grassy), and hexanal (grassy). However, the amount of volatile compounds produced and the intensity levels of the odors were lower in trilinolein than in triolein. Formation of many of the volatiles was explained after identification of the volatile precursors, including epoxy, keto, and dimer oxidation products that were produced during heating.

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KEY WORDS: Frying oil, heated oil, nonvolatile, odor, olfactometry, oxidation product, trilinolein, triolein, undesirable odor, volatile.

Studies of higher oleic vegetable oils, such as moderate to high-oleic sunflower and high-oleic corn and canola oils, as frying oils have shown that these oils had improved frying stability compared to the commodity oils (1–5). However, the desirable fried food odor and flavor associated with higher levels of linoleic acid was diminished in foods fried in higher oleic oils (1–5). Along with diminished fried food odor and flavor, negative odors such as fruity, plastic, acrid, and waxy were characteristic of higher-oleic oils during frying or heating (1–5).

Frying oils are exposed to extreme environmental conditions resulting in partial degradation of the frying oil triglycerides by oxidation, polymerization, isomerization, cyclization, and hydrolysis reactions (6–8). These reactions affect the flavor quality of foods fried in the oils. Frying alters oils to complex mixtures of unaltered triglycerides, triglycerides with conjugated diene and *trans* fatty acids, volatile compounds such as aldehydes, triglyceride oxidation products such as alkoxy, epoxy, keto monomeric compounds, higher molecular weight oxidation products, thermal degradation products such as oligomeric triglycerides and triglycerides with cyclized fatty acids and hydrolysis products such as diglycerides (8). Also, frying oils, that have cooled to room temperature contain triglyceride monohydroperoxides, which are only fleetingly present at frying oil temperatures (8). A large number of the oxidation products have not been identified (8).

Many of the triglyceride oxidation products formed, would be expected to be decomposed to volatile compounds during frying or heating (8). Although major quantities of the volatiles are steam-distilled out of the frying oil, some quantities remain in the oil and in the fried foods to affect flavor and odor of the food. For better control of the production of undesirable flavor and odors, the respective volatile precursors or the molecular markers for the undesired volatiles need to be identified.

Owing to the complexity of the vegetable oil mixture of oxidation products, model frying or heating oil systems of a single triglyceride such as triolein and trilinolein have been studied to obtain a simpler mixture of oxidation products or potential volatile precursors (9–16). One objective of this work with triolein and trilinolein was to better understand the production of negative odors in modified composition oils such as high-oleic-containing oils. Some nonvolatile or volatile precursor products of heated triolein and trilinolein have been reported (9–16). The nonvolatile products are not directly amenable to gas chromatographic analysis, and some are not amenable to normal liquid chromatographic techniques. Generally, the nonvolatile products, which may serve as volatile precursors, fall into two categories: (i) dimers plus other polymerization products and (ii) oxidized products. Nonvolatile decomposition products have been analyzed using thin-layer chromatography (TLC), size exclusion chromatography (SEC), and, more recently, supercritical fluid chromatography. Unfortunately, polymerized products do not produce distinctly resolved chromatographic peaks using

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SEC. Also, oxidized compounds are believed to coelute with normal triglycerides or elute just before them during SEC. A common approach to analysis of the complex mixture produced by heated oils, as demonstrated by Chang, Peterson, and Ho (9), among others, is the conversion of the fatty acids in the oil to methyl or ethyl esters by transesterification and then treatment with urea to produce urea-adduct-forming esters and non-urea-adduct-forming esters. The non-urea-adduct-forming esters are then fractionated by silica liquid chromatography.The fractions thus separated are cleaved using acid to break up polymers and then are further separated using TLC. This was a labor-intensive, time-consuming approach, but because of the complexity of the original mixture, few options were available.

These labor-intensive methods proved effective at identifying numerous decomposition products from a variety of oil samples. However, it is desirable to identify these nonvolatile decomposition products in a single chromatographic run without the need for fractionation, derivatization, and other chemical treatment. We recently demonstrated the utility of atmospheric pressure chemical ionization-mass spectrometry (APCI-MS) for identification of numerous autoxidation products formed from triacylglycerol standards of triolein, trilinolein, and trilinolenin (17). These autoxidation products consisted of hydroperoxides, bishydroperoxides, epoxides and bisepoxides, as well as hydroxy, epidioxy and other compounds. All of these autoxidation products were more polar than the starting triglycerides, so chromatographic separation was focused on components eluted before the starting triglycerides. In the case of decomposition products formed under model heating conditions, dimers and other compounds, which were less polar than the starting triolein, were expected. Thus, a chromatographic separation was necessary that would provide separation of polar oxidation products such as those produced by oxidation, as well as nonpolar products such as oligomers with longer retention times than the unreacted triglyceride. We recently developed, using a model system of heated triolein, a high-performance liquid chromatography (HPLC) system coupled with APCI-MS for on-line identification of the numerous degradation products (16).

In this work, we identified the negative odors and corresponding volatile odor compounds produced from heated triolein and trilinolein, isolated the identified nonvolatile oxidation products from the heated triolein and trilinolein, and thermally decomposed these isolated oxidation products to define their role as volatile precursors or molecular markers for undesirable odors in triolein and trilinolein with application to high-oleic acid oils.

EXPERIMENTAL PROCEDURES

Materials. Triolein and trilinolein (99+% purity) were purchased from Nu-Chek-Prep, Inc. (Elysian, MN). These triglycerides were checked for the presence of non-triglyceride products by peroxide value, polar phase TLC with ultraviolet detection of any conjugated oxidized linoleic acid and visualization of unsaturated nontriglycerides by iodine vapor, polar component analysis, and detection of oligomer, mono- and diglycerides, and free fatty acid by size exclusion HPLC (SEC) coupled with an evaporative light scattering detector (ELSD). Fatty acid purity was checked by gas chromatography (GC) of the transmethylated triglyceride, and triglyceride purity by reversed-phase HPLC (RP-HPLC) coupled with an ELSD. The triolein and trilinolein were used without further purification. Acetonitrile (ACN; EM Science, Gibbstown, NJ) and dichloromethane (DCM; Fisher, Fair Lawn, NJ) were HPLC grade and were used without further purification.

Model heating oil system. Six test tubes (2 × 12.5 cm), each containing 5 g triglyceride and 3.14 cm^2 exposed oil surface, were heated to 190°C by submersion in a temperature-controlled silicone oil bath. Two percent water (100 uL) was added each hour through a capillary submerged to the bottom of each test tube, to simulate the moisture introduced by frying a food product. One sample was removed each hour for analysis. The samples were frozen neat under argon and stored in the freezer at −15°C until analysis. The heating reaction gave the desired polar component fraction of approximately 15% at 3 h and 30% at 6 h heating time. The heating reactions were performed in duplicate. Reproducibility of the model heating oil system was confirmed by similar polar component, SEC, and RP-HPLC coupled with an ELSD for degradation product quantitation and degradation product identification and by RP-HPLC coupled with APCI-MS for each model heating oil system experiment.

Polar component analysis. Polar component composition of each heated oil sample was analyzed by column chromatography in duplicate using the American Oil Chemists' Society (AOCS) official method (18).

Liquid chromatography. SEC of the heated triolein mixtures was performed with four 25 cm × 4.6 mm, 7 mm particle size, Ultrastyragel columns (Waters Associates, Milford, MA) in series. Two 500 Å and two 100 Å columns were used. DCM at 0.5 mL/min was used as the isocratic solvent for SEC. The SEC ELSD was a Sedex Model 55 (Sedone, Altonville, France). The drift tube was set at 32°C. The gas flow was set at a pressure of 1.6 bars. The photomultiplier gain was times 5. High-purity N_2 was used as the nebulizer gas. SEC chromatogram peak identification was in reference to a standard of soybean oil oligomers (dimer, trimer, tetramer, etc.) and to a standard oleic series of tri-, di-, mono-olein and oleic acid.

The HPLC system used for semiquantitation of the heated triolein and trilinolein products was RP-HPLC performed with a Thermo Separation Products (Schaumburg, IL) Model SP 8800 ternary solvent system with two RP-HPLC columns with bonded silyl (CT8) ODS, Inertsil ODS-80 Å (Keystone Scientific, Bellefonte Park, PA), 25 cm × 0.46 cm, 5 μm particle size with the columns in series. The elution gradient was as follows: 80% ACN/20% DCM to 20% ACN/80% DCM after 120 min. The flow rate was 0.6 mL/min throughout. A 250 μg sample was injected. The ELSD was operated as stated for SEC. Degradation product HPLC chromatogram peaks were identified based on earlier analyses of heated tri-

olein *via* RP-HPLC coupled with an APCI-MS (16).

To assist the study of the origin of volatiles in heated triolein and trilinolein, preparative reversed-phase separation was used for fractionation of the heated triglycerides. A Dynamax C_{18} column, 30 × 2.25 cm, 60 μm particle size (Rainin Instrument Co., Inc., Woburn, MA), was used with an isocratic flow of 40% ACN/60% DCM at 4.0 mL/min. A refractive index detector, Waters model 410 detector, with the cell at 50°C and a sensitivity of 128 was used for the preparative separation. To expedite collecting enough material for studies of volatiles, triolein and trilinolein, that had been heated for 6 h were fractionated by the polar component procedure to collect 1 g each of polar component. The polar components were then used for the RP-HPLC fractionation to collect manually the epoxy, keto, monohydroperoxide, and dimer fractions. Fifty micoliters of a 500-mg polar component/mL solution in DCM was injected. Enough material, 100 to 150 mg, for each fraction was collected by preparative RP-HPLC for purge and trap–GC–MS–olfactory analysis of the respective fractions to determine the nonodor volatile and odor volatiles that can be produced. Functional purity of the HPLC fractions was confirmed by performing analytical RP-HPLC-ELSD and comparing the chromatogram with the identified components of the RP-HPLC APCI-MS chromatogram.

The data output from the ELSD or refractive index detector was processed or integrated by a Star Chromatography Workstation with version 4.0 software (Varian Associates, Inc., Walnut Creek, CA). The amounts of products are expressed in chromatogram peak area percentage, since suitable standards were not available for detector calibration. Hence, the reported results are semiquantitative, because most of the analyses are of mixtures of components with various functional groups, which give different detector responses.

The HPLC system used for RP-HPLC APCI-MS contained a model LDC 4100 MS (Thermo Separation Products), quaternary pump with membrane degasser. The same HPLC columns were used as described for RP-HPLC-ELSD. The gradient used for separation of the heated triolein and trilinolein components was as follows: initial conditions, 75% ACN/25% DCM; linear from 0 to 20 min to 70% ACN/30% DCM, then linear from 20 to 50 min to 30% ACN/70% DCM, held until 85 min; the column was recycled to starting conditions linearly from 85 to 99 min. The flow rate was 0.8 mL/min throughout. Flow was split using a tee so that ~680 μL/min went to an ELSD and ~120 μL/min went to the mass spectrometer. A Varex MKIII ELSD detector (Alltech Associates, Deerfield, IL) was used as an auxiliary detector for RP-HPLC APCI-MS. The drift tube was set to 140°C, the gas flow was 2.0 standard liters per minute. High-purity N_2 was used as the nebulizer gas. ELSD output was simultaneously directed to a stand-alone data system with 24-bit resolution (EZ-Chrome Elite; Scientific Software, Inc., Pleasanton, CA). Injections of 10 μL were made using a Hewlett-Packard Series 1050 autosampler, (Wilmington, DE).

MS A Finnigan MAT TSQ700 (San Jose, CA) mass spectrometer operating in Q1 low-mass mode was used for acquisition of APCI-MS data. The APCI-MS vaporizer was operated at 400°C, the capillary heater was operated at 265°C, the corona voltage was set to 6.0 mA. Sheath and auxiliary gases were set to 35 psi and 5 mL/min, respectively. Spectra were obtained from 100 to 2,000 amu with a scan time of 2 s.

Volatile compound analysis. Volatile compound analysis was conducted with a dynamic purge and trap apparatus equipped with a test tube adapter (Tekmar model 3000; Tekmar-Dohrmann Company, Cincinnati, OH) coupled with a Star model 3400 (Varian, Inc.) gas chromatograph equipped with an olfactory or sniffing port attachment and a Saturn model 3 ion trap mass spectrometer (Varian, Inc.). A 50-mg sample was introduced into the test tube (1.9 × 7.6 cm) and heated at 100°C for 9 min preheat time. The volatiles were trapped on a 30.5 cm Tenax #1 trap (Tekmar), sample purge time 10 min, desorb temperature 170°C for 6 min, moisture control system desorb temperature 180°C, GC transfer line and valve temperature 160°C. The volatiles were thus introduced into a GC column (DB 1701,1 μm film thickness, 30 m × 0.32 mm; J&W Scientific, (Folsom, CA). The column was programmed at −20°C (2 min), then heated from −20 to 233°C at 3°C /min. The column helium flow rate was 2 mL/min with 28 mL/min injector split vent flow. The GC injector was set at 240°C, and the line to the mass spectrometer was set at 230°C. At the end of the GC column a vitreous silica outlet splitter (Varian, Inc.) divided the flow between the mass spectrometer and the sniffing port, with 10 parts gas volume to the sniffing port and 1 part to the mass spectrometer. The sniffing port allowed volatile odor identification and intensity level determination by trained oil panelists according to procedures previously published (19,20). The ion trap MS operated in the electron ionization mode with mass scan range 23 to 400 *m/z* scanned three times over 0.8 s. Filament emission current was 25 microamps, axial modulation was 2.1 volts, the manifold heater was set at 160°C, and the filament/multiplier delay was 2.5 min. Compound structural identifications were made from spectral comparisons with the NIST 92 mass spectrometry library (Varian, Inc.) and from retention time comparisons with standard compounds. Quantitation of volatiles in area percentage is semiquantitative. For selected volatiles for which suitable standards were available, the quantitation amount is quantitative, based on the external standard method, and is expressed in parts per million (ppm).

RESULTS AND DISCUSSION

Characterization of heated triolein and trilinolein. Triolein had an inital peroxide value of 0.4 meq peroxide/ Kg sample and 0.1% polar component. However, no nontriglyceride products were detected by TLC. Trilinolein had an inital peroxide value of 0.9 meq with 0.5% polar component. However, no nontriglyceride products were detected by TLC. Triolein was analyzed at 100% oleic acid and 100% triolein. Trilinolein was analyzed at 99.9% linoleic and 0.1% oleic acid and 99.8% trilinolein and 0.2% dilinoleoyloleoylglycerol. No oligomer, monoglyceride, diglyceride, or free fatty acids were

TABLE 1
Polar Components (total weight %)[a] Obtained in 0 to 6 h Heating of Triolein and Trilinolein[b]

Heating (h)	Polar triolein (%)	Polar trilinolein (%)
0	0	1
1	5	5
2	—	8
3	16	17
4	—	18
5	—	21
6	31	25

[a]The polar component contained all degradation products except unreacted triglyceride that had been produced each heating hour for heated triolein and trilinolein. The polar component analysis was conducted according to the silicic acid column chromatography method, Official Method Cd 20-91 of the American Oil Chemists' Society (18).
[b]See Experimental Procedures section for heating conditions.

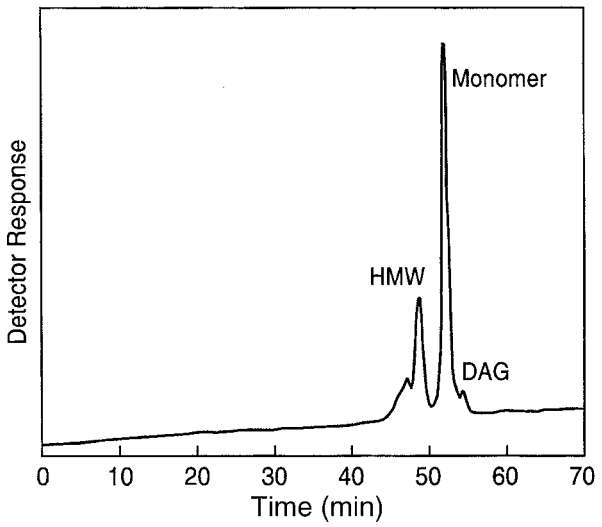

FIG. 1. Representative size exclusion chromatogram (SEC) for heated triolein and trilinolein. HMW are high molecular weight compounds, which represent dimers and higher oligomers and triglycerides with a fatty acid moiety attached *via* an ether linkage to one of the fatty acids. Monomers include unreacted triglycerides plus triglyceride oxidation products. DAG are diglycerides or hydrolysis products of the triglycerides. See the Experimental Procedures section for SEC analytical conditions.

detected by SEC in either triolein or trilinolein. The oils were heated until the polar components reached 25–31% by 6 h of heating. The percentages of polar component formed in triolein and trilinolein with heating time are shown in Table 1. The percent polar component data indicated that, although trilinolein contained more double bond unsaturation and might be expected to produce a greater amount of degradation or oxidation products per hour than triolein, the amount of polar component formation was apparently about the same for both triglycerides. This may be because of oxygen limitation due to a blanket of steam above the heated oil surface (8).

Further characterization of the model frying oil systems was performed by SEC analysis. Figure 1 is a representative SEC chromatogram for heated triolein or trilinolein. For heated triolein and trilinolein, those decomposition products, semiquantitated by SEC-ELSD, are shown for higher molecular weight (HMW) compounds, monomeric triglyceride (unreacted triglyceride plus monomeric triglyceride oxidation products), and diglyceride present in the samples as a function of heating time in Table 2. No monoglyceride and free fatty acids were detected for either triolein or trilinolein. Presumably these latter components steam-distilled out of the reaction samples (8). For triolein, diglyceride was detectable by 3 h and increased slightly, but was still less than 1% by 6 h. HMW compound formation (dimer plus chain addition products of the triglyceride; 16) increased from 0% at time zero to 16% at 6 h heating. HMW compound formation increased, while monomeric compounds decreased with heating time. For trilinolein, diglyceride was detected by 4 h and increased slightly, but remained less than 1% by 6 h of heating. HMW compound formation increased slightly faster for trilinolein than for triolein, from 0% at time zero to 19% at 6 h of heating. Therefore, although trilinolein, with an increased number of sites of unsaturation, might be expected to degrade more rapidly than triolein, the degree of trilinolein degradation was only slightly more than for triolein.

TABLE 2
Higher Molecular Weight Compounds (HMW), Monomer (unreacted triglyceride + triglyceride oxidation products), and Diglyceride (DAG)[a] as a Percentage[a] Obtained in 0 to 6 h Heating of Triolein (OOO) and Trilinolein (LLL)[b]

		Hours of heating at 190°C						
		0	1	2	3	4	5	6
HMW	OOO	0.0	3.6	6.6	9.7	13.1	14.9	15.9
	LLL	0.0	3.8	7.8	12.0	13.4	16.3	18.8
Monomer	OOO	100.0	96.4	93.4	90.3	86.8	85.0	83.9
	LLL	100.0	96.2	92.2	88.0	86.5	83.6	80.6
DAG	OOO	0.0	0.0	0.0	0.1	0.1	0.1	0.2
	LLL	0.0	0.0	0.0	0.0	0.1	0.1	0.6

[a]Degradation products determined semiquantitatively by size exclusion chromatography coupled with evaporative light scattering detector (see Fig. 1). See the Experimental Procedures section for analysis conditions.
[b]See the Experimental Procedures section for complete heating conditions.

TABLE 3
Odors and Volatile Compounds in Fractionated[a] and Unfractionated Triolein After Heating up to 6 h at 190¡C[b]

			Unfractionated			Fractionated from triolein heated 6 h			
Volatile[b]	ID[e]	Odor[c]	1 h	3 h	6 h	OOH	Keto	Epoxy	Dimer
Pentanal	RT,MS[n]	Grassy	0	34.2 (2)[d]	81.6 (1)	23.6 (2)	9.9 (1)	9.9 (1)	105.2 (2)
2-Propylfuran	MS*	Fruity	0	1.0 (0)	1.0 (0)	0.1 (1)	0	0	0
1,4-Pentadien-3 ol	MS*	Plastic	0	1.1 (5)	1.5 (2)	0.7 (6)	0.1	0.1 (8)	0.1
(*E* or *Z*)-2 Octene	MS*	Plastic	0	1.0 (0)	10.6 (8)	2.0 (2)	1.3 (8)	1.4 (8)	2.9 (2)
3-Hexanone	RT,MS	Musty	0	0.7 (2)	2.4 (3)	0.8 (0)	0.6 (2)	1.2 (2)	8.7 (0)
Hexanal	RT,MS	Grassy	49.8 (5)	68.1 (5)	15.4 (8)	122.3 (7)	45.3 (8)	44.0 (7)	40.6 (6)
3 Hexanol	RT,MS	Grassy	0	0.9 (1)	3.0 (2)	0.3 (0)	0.1 (0)	0.2 (0)	0.6 (0)
2-Butyl-tetrahydrofuran	MS*	Citrus	0	7.1 (2)	9.5 (2)	1.7 (4)	0.6 (0)	0.6 (1)	0.3 (1)
4-Nonyne	MS*	Fruity	0	0.7 (1)	1.0 (3)	0.3 (2)	0.2 (0)	0.1 (0)	0
(*E*)-2 Hexenal	RT,MS	Grassy	1.8 (5)	2.7 (5)	5.9 (5)	1.6 (3)	0.4 (3)	0.3 (4)	0
Heptanal	RT,MS	Fruity	261.0 (8)	227.1 (5)	441.2 (8)	152.3 (3)	73.7 (4)	73.3 (1)	77.5 (6)
2-Heptanol	RT,MS	Putty	0.3 (3)	109.1 (4)	1.8 (3)	0.3 (1)	0.1 (0)	0.0 (0)	0.1 (0)
Tetrahydro-2-methyl-2 furanol	MS*	Mint	0	12.3 (0)	14.6 (2)	0.9 (0)	0.5 (0)	0	0.8 (0)
2-Pentylfuran	RT,MS	Fruity	12.0 (2)	11.1 (3)	22.9 (3)	6.7 (1)	0.8 (0)	1.0 (0)	2.9 (0)
4-Octen-3-one	RT,MS	Mushroom	0	0.4 (6)	0.7 (8)	0.5 (6)	0.0 (6)	0.1 (6)	0.3 (5)
Octanal	RT,MS	Fruity	399.1 (10)	379.0 (9)	583.0 (9)	194.7 (8)	118.9 (6)	109.6 (7)	103.8 (6)
1 Octanol	RT,MS	Mushroom	44.1 (8)	8.1 (6)	88.7 (5)	15.7 (5)	1.6 (6)	1.2 (5)	1.2 (9)
(*E*)-4-Nonenal	MS*	Grassy	0.8 (3)	1.3 (2)	1.6 (9)	0.5 (2)	0.2 (0)	0.1 (1)	0
Nonanal	RT,MS	Fruity	766.8 (10)	606.4 (10)	734.1 (8)	248.3 (6)	121.2 (7)	129.6 (7)	116.8 (8)
(*Z*)-2-Nonenal	RT,MS	Plastic	0.4 (5)	0.4 (5)	2.1 (7)	0.7 (5)	0.1 (7)	0	0
5-Ethyl-dihydro-2(3H)-furanone	MS*	Leather	0	3.5 (0)	18.3 (4)	3.8 (2)	0.6 (1)	0	0
(*E*)-2-Nonenal	RT,MS	Plastic	34.9 (8)	33.0 (10)	60.3 (9)	10.6 (6)	6.4 (9)	6.4 (8)	1.5 (1)
2-Decanone	RT,MS	Plastic	3.1 (5)	3.1 (8)	7.9 (3)	.4 (3)	0.1 (2)	1.0 (6)	1.2 (5)
1-Methyl-2-(4-methylpentyl)-cyclopentene	MS*	Buttery	0	20.0 (5)	22.1 (6)	0.1 (2)	0.5 (1)	0.1 (4)	0
Decanal	RT,MS	Minty	0.4 (6)	10.6 (4)	7.0 (4)	3.9 (3)	1.7 (2)	1.1 (1)	0.4 (1)
2-Decyn-1-ol	MS*	Plastic	0.9 (3)	1.3 (2)	1.1 (3)	0.1 (0)	0.2 (1)	0	0
(*Z*)-2-Decenal	RT,MS	Acrid	1.5 (5)	2.0 (6)	5.5 (6)	0.3 (4)	0.1 (5)	0	0
5-Propyl-dihydro-2(3H)-furanone	MS*	Minty	0	2.0 (0)	8.5 (3)	1.6 (0)	0.3 (0)	0.4 (3)	0.3 (0)
(*E*)-2-Decenal	RT,MS	Plastic	253.4 (6)	74.0 (8)	292.2 (10)	27.4 (1)	29.1 (1)	16.9 (2)	9.3 (1)
(*E*)-2-Undecenal	RT,MS	Coconut	137.8 (5)	49.3 (0)	178.9 (3)	21.8 (2)	9.2 (0)	4.6 (1)	3.5 (1)

[a]OOH, keto, epoxy, dimer = triolein monohydroperoxides, ketoenes, epoxyanes and enes, and dimers.
[b]See the Experimental Procedures section for purge and trap volatile analysis, heated triolein preparation, and preparation of OOH, keto, epoxy, dimer fractions. Values are mass spectrometric total ionization area counts × 10^3.
[c]Odor description at 6 h (19).
[d]Intensity of odor (0 = none; 10 = strong).
[e]ID = identification of compounds (RT = gas chromatographic retention time based on reference standard, and MS = mass spectral identification with NIST92 library: Varian, Inc.). *Tentative identification.

Volatile compounds in heated triolein and trilinolein; odor importance. To determine the odor importance of volatiles generated in heated triolein and trilinolein at frying temperatures, purge and trap–GC–MS–olfactometry (PTO) was utilized. A PTO profile (compound GC retention time and peak area and mass spectral identification with respect to standard compounds and mass spectral library search) was obtained for the triglycerides heated 1, 3, and 6 h with the identities of the odor volatiles shown in Tables 3 and 4 for heated triolein and trilinolein, respectively. Some of the volatile compounds listed in Tables 3 and 4 for heated triolein and trilinolein have been reported previously (21–27).

To determine the origin of odor volatiles in heated triolein and trilinolein, volatile profiles were also obtained and shown in Tables 3 and 4 for the respective potential volatile precursors, that formed in the model triolein and trilinolein frying systems: the epoxy, keto, dimer, and monohydroperoxide fractions of the 6-h heated triolein and trilinolein. Volatiles which had earlier GC retention times than pentanal had little odor importance. Thus, odor identification was started just before the GC elution of pentanal and was continued to the GC elution of undecadienal.

For the triolein samples heated 1, 3, and 6 h, some of the negative odor volatiles (odor description) shown in Table 3 were: hexanal (grassy), heptanal (fruity), and octanol (mushroom), (*Z*)-2-decenal (acrid) and (*E*)-2-decenal (plastic).

TABLE 4
Odors and Volatile Compounds in Fractionated[a] and Unfractionated Trilinolein After Heating up to 6 h at 190¡C[b]

			Unfractionated			Fractionated from triolein heated 6 h			
Volatile[b]	ID[e]	Odor[c]	1 h	3 h	6 h	OOH	Keto	Epoxy	Dimer
Pentanal	RT,MS	Grassy	69.9 (4)	42.1 (1)	87.2 (3)	307.2 (1)[d]	319.7 (1)	243.4 (4)	396.7 (5)
1,4-Pentadien-3-ol	MS*	Plastic	0	1.0 (0)	1.0 (0)	0.1 (1)	0	0	0
Hexanal	RT,MS	Grassy	224.8 (6)	188.8 (8)	335.6 (9)	2096.9 (10)	1767.3 (10)	1300.9 (10)	1913.4
(10)									
(Z)-2-Hexenal	RT,MS	Unknown	4.6 (5)	0	7.7 (1)	4.3 (7)	4.6 (3)	0	1.6 (6)
(*E*)-2-Hexenal	RT,MS	Unknown	33 (0)	20.0 (3)	39.0 (0)	55.2 (4)	0	47.6 (4)	0
(Z)-4-Heptenal	MS*	Fruity	12.2 (3)	5.9 92)	9.8 (2)	0	0	7.5 (3)	7.5 (5)
Heptanal	RT,MS	Fruity	10.4 (4)	11.8 (0)	22.8 (3)	67.2 (7)	79.5 (6)	47.3 (4)	29.0 (8)
(*E*)-4-Heptenal	MS*	Fruity	0	0.5 (0)	0.4 (2)	7.3 (5)	1.7 (3)	0	0
2-Pentyl furan	RT,MS	Fruity	96.5 (2)	113.1 (2)	169.5 (4)	115.3 (2)	74.3 (2)	74.5 (3)	79.3 (3)
4-Octen-3-one	RT,MS	Mushroom	6.3 (5)	2.8 (5)	41.6 (5)	5.8 (8)	5.1 (7)	6.1 (7)	6.3 (8)
Octanal	RT,MS	Fruity	0	1.5 (4)	3.0 (4)	47.0 (5)	175.5 (10)	5.7 (7)	4.6 (6)
(*Z*)-2-Octenal	RT,MS	Plastic	0	6.5 (3)	9.2 (2)	16.0 (4)	13.8 (5)	11.3 (3)	9.7 (5)
(*E*)-6-Dodecene	MS*	Plastic	1.1 (3)	2.2 (6)	4.0 (5)	0.3 (4)	0.5 (8)	0.4 (3)	0.5 (4)
Nonanal	RT,MS	Fruity	0	0	1.9 (6)	113.1 (4)	363.3 (10)	14.1 (4)	3.8 (6)
(*Z*)-2-Methyl-4-hexen-3-ol	MS*	Fruity	1.1 (6)	16.8 (8)	11.5 (6)	41.9 (5)	46.0 (7)	30.5 (5)	61.1 (7)
(*E*)-2-Methyl-4-hexen-3-ol	MS*	Fruity	0	3.7 (4)	5.7 (7)	5.4 92)	6.5 (5)	4.4 (4)	10.9 (8)
(*Z*)-2-Nonenal	RT,MS	Plastic	0	2.2 (5)	2.1 (5)	2.6 (4)	3.9 (6)	1.8 (6)	0.6 (4)
(*E*)-2-Nonenal	RT,MS	Plastic	2.5 (5)	5.2 (9)	12.0 (8)	4.5 (7)	8.8 (8)	4.5 (8)	2.7 (9)

[a]OOH, keto, epoxy, dimer = triolein monohydroperoxides, ketoenes, epoxyanes and enes, and dimers.
[b,c,d,e]See Table 3. *Tentative identification.

These odor volatiles had odor intensities of 5 or greater. Odor intensities for hexanal, (*E*)-2-decenal, and 4-octen-3-one increased between 1 and 6 h heating. Trilinolein heated for 1, 3, or 6 h produced the following negative odors: hexanal (grassy), 4-octen-3-one (mushroom), (*E*)-6-dodecene (plastic), nonanal (fruity), and (*Z* and *E*)-2-nonenal (plastic). These odor volatiles had odor intensities of 5 or greater. The odor intensity for hexanal increased and the other volatiles just named remained at a high intensity level during 1 to 6 h of heating.

The total mass spectrometric ion current area counts shown in Tables 3 and 4 are useful for showing increase or decrease in individual odor volatiles of the same type with heating time. However, for valid comparison of the amount of one volatile type with another, calibration is required due to differences in mass spectrometeric ionization response with compound type (28). Calibration of the volatiles is also necessary, because there is an inherent discrimination by the purge and trap method that emphasizes HMW such as nonanal compared to lower molecular weight compounds such as hexanal (29). The calibration in this work to obtain appropriate response factors will overcome the purge and trap method discrimination. For example, it can be correctly stated that heated trilinolein produced more *E*-2-heptenal than hexanal. The mass spectrometric ionization area counts were converted by the external standard method to concentrations as ppm or micrograms volatile per gram of oil for those volatiles for which standards were available (28). These data are shown for the volatiles produced from heated triolein and trilinolein with respect to the heating time of these triglycerides (Table 5). In triolein, the abundance of the predicted aldehydes octanal, nonanal, 2-decenal, and 2-undecenal decreased from 1 to 3 h followed by an increase through 6 h. Other nonoleic hydroperoxide volatiles such as pentanal, hexanal, and 2-nonenal increased with heating time. However, nonoleic-type volatiles remained at lower levels than volatiles derived directly from oleic hydroperoxides. Nonoleic hydroperoxide-derived volatiles were produced from oleic products such as the oleic hydroperoxides, ketoenes, epoxyenes, epoxyanes and dimers, which were detected by RP-HPLC APCI-MS of the heated triolein. The non-oleic volatile 2-nonenal was not detected in the epoxy fraction. For heated trilinolein, the ppm data showed that the negative odor volatiles 2-pentylfuran and hexanal, which were expected from oxidized linoleic acid, increased with heating time. Unlike triolein, which produced linoleic-type volatiles such as hexanal, oleic-type volatiles such as octanal, nonanal, 2-decenal, and undecenal were detected by RP-HPLC APCI-MS in trilinolein in amounts too small for quantitation. Volatiles such as 2-hexenal, 2-pentylfuran, and 2-nonenal, which were not predicted directly from decomposition of linoleic hydroperoxides (25), remained at low concentrations although they increased throughout the heating period.

The ppm data are shown in Table 6 for the respective hydroperoxy, keto, epoxy, and dimer fractions obtained by preparative HPLC of the triolein and trilinolein heated for 6 h. For most volatiles, these fractions upon thermal decomposition produced more of the same volatiles than the respective unfractionated triolein and trilinolein after 6 h of heating. Also, predicted volatiles were more abundant than those volatiles that would not be expected from the oxidized fatty acids of the respective triglyceride. For most of the volatiles there were differences in the amounts of the same volatiles

TABLE 5
Volatile Compounds (ppm) by External Standard Procedure for Purge and Trap Headspace-Gas Chromatography Ion Trap Mass Spectrometry of OOO and LLL Heated 1,3, and 6 h at 190¡C[a]

	Heating time (h)					
	One		Three		Six	
Volatile[b]	OOO	LLL	OOO	LLL	OOO	LLL
Pentanal[d]	15.9	42.5	24.4	28.5	48.9	50.8
Hexanal	17.2	58.0	22.3	50.4	45.4	82.5
2-Heptanol	2.1	ND	1.8	ND	4.0	ND
2-Pentylfuran	ND[c]	28.2	ND	33.0	ND	40.7
4-Octen-3-one[d]	0.4	1.4	1.3	1.1	0.8	4.4
E-2-Heptenal (heptanol)	(19.2)	98.6	(7.4)	80.0	(27.5)	127.3
E-2-Nonenal	9.0	1.3	14.7	2.0	44.7	5.2
E-2-Hexenal	ND	11.3	1.9	6.9	1.9	13.5
Octanal	42.2	ND	38.5	ND	53.8	ND
1-Octanol	103.4	0.0	28.1	ND	168.4	ND
Nonanal	485.1	0.0	348.0	ND	403.0	ND
E-2-Decenal	418.5	0.0	152.0	ND	197.8	ND
E-2-Undecenal[d]	624.2	0.0	233.5	ND	737.2	ND

[a]See the Experimental Procedures section for purge and trap volatile analysis and heated triolein and trilinolein preparation.
[b]Mean concentration, $n = 2$.
[c]ND = not detected at minimum fit threshold (1–1000) with peak threshold of 1%.
[d]SD in ppm of 4-octen-3-one: OOO ± 0.8 (1 h), ± 0.2 (3 h), ± 0.3 (6 h) and LLL ± 0.2 (1 h), ± 0.4 (3 h), ± 1.0 (6 h). SD in ppm of pentanal: OOO ± 2.7 (1 h), ± 1.0 (3 h), 13.0 (6 h) and LLL ± 2.5 (1 h), ± 2.0 (3 h), ± 10.0 (6 h). SD in ppm *E*-2-undecenal: OOO ± 23.0 (1 h), ± 40.0 (3 h), ± 18.0 (6 h). For abbreviations see Table 2.

among the hydroperoxy, keto, epoxy, and dimer fractions.

Precursors of the odor volatiles in heated triolein and trilinolein. Sources or molecular markers of the odor volatiles produced from the triolein and trilinolein were the nonvolatile compounds formed mainly from the oxidation of the triglyceride fatty acids (8,25). The formation of many of the detected volatiles can be explained by published mechanisms (21–25), including thermal and acid-catalyzed decomposition of the nonvolatile precursors by homo- and heterolytic cleavage of the initial 8-, 9-, 10-, and 11-monohydroperoxides of triolein and the 9-, 10-, 12-, and 13-monohydroperoxides of trilinolein, which exist fleetingly at frying oil temperature

TABLE 6
Volatile Compounds (ppm) by External Standard Procedure for Purge and Trap Headspace-Gas Chromatography-Ion Trap Mass Spectrometry of Heated (6 h at 190¡C) Triolein and Trilinolein Fractions[a]

	Triolein					Trilinolein			
Volatile	OOH	Keto	Epoxy	Dimer	Volatile	OOH	Keto	Epoxy	Dimer
					Pentane	768.6	680.3	557.5	124.9
					Propanal				
					2-Propenal	34.6	41.3	20.2	15.4
					Butanal	18.8	18.6	16.1	20.0
Pentanal	20.2	10.5	10.9	11.3	Pentanal	133.1	136.9	112.4	161.8
Hexanal	31.7	15.1	13.9	15.2	Hexanal	147.4	69.8	136.8	77.1
Heptanal	50.5	24.6	25.7	28.1	Heptanal	25.5	40.7	17.6	16.1
2-Heptanol	0.4	0.2	0.1	0.2					
E-2-Hexenal	1.6	0.6	0.9	ND	*E*-2-Hexenal	17.6	17.5	14.9	19.0
2-Pentylfuran	ND	ND	ND	ND	2-Pentylfuran	32.6	18.8	19.7	20.0
4-Octen-3-one	0.6	0.1	0.1	0.1	4-Octen-3-one	7.6	5.9	6.4	7.1
1-Heptanol	8.8	0.2	0.9	2.2					
					E-2-Heptenal	155.7	144.2	126.8	133.7
					1-Octen-3-ol	4.0	1.9	2.7	4.3
Octanal	33.5	21.6	20.1	19.9	Octanal	10.6	31.0	0.8	0.9
1-Octanol	42.2	11.4	11.1	12.2					
Nonanal	184.0	76.5	85.0	73.4	Nonanal	78.9	283.1	3.8	2.5
E-2-Nonenal	4.1	2.3	2.4	2.5	*E*-2-Nonenal	1.7	3.8	1.6	3.8
E-2-Decenal	67.9	63.6	39.8	22.3	*E*-2-Decenal	13.7	38.2	5.7	4.7
E-2-Undecenal	120.5	53.2	33.0	27.1					
					Hexadecane	38.8	193.5	79.0	29.1

[a]See the Experimental Procedures section for analysis details and fraction preparation. ND = not detected at minimum fit threshold (1-1000) with peak

TABLE 7
Suggested Mechanisms for Volatiles Formation by Heated Triolein Epoxides[a]

Epoxide/ double bond carbon location	Mechanism for epoxide formation[c]	Epoxide precursor monohydroperoxide[b]	Volatiles formed from epoxide decomposition[d]
9,8/10	OOH cyclization	8-OOH	2-Decenal
7,8/9			2-Undecenal
9,10/11	OOH cyclization	9-OOH	2-Nonenal
8,9/10			2-Decenal
9,10/7	OOH cyclization	10-OOH	Nonanal
			2-Decenal
10,11/8			Octanal
			2-Nonenal
11,12/9	OOH cyclization	11-OOH	Heptanal
			2-Octenal
10,11/8			Octanal
			2-Nonenal
9,10/Saturated	Epoxidation	Oleic Acid	Nonanal
			2-Decenal

[a]See the Experimental Procedures section for heating conditions, epoxide fraction isolation and identification (16), and volatile analysis conditions.
[b]Triolein monohydroperoxide identification by hydroperoxy carbon location.
[c]Reaction to form the epoxide from the monohydroperoxide (25,30,31).
[d]Volatiles produced by thermal decomposition of the triglyceride epoxide *via* β-scission (25,31,32).

(8,25). Also, these hydroperoxides decompose to secondary epoxy, keto, dimer and other nonvolatile compounds at frying oil temperatures (8,21–25). Many of these secondary products were identified online by RP-HPLC APCI-MS of the triolein (16) and trilinolein frying systems. This methodology assisted the determination of the molecular markers or volatile precursors for the odor volatiles discussed above. Thus, the heated triolein and trilinolein were fractionated by RP-HPLC with the eluant introduced into the APCI source attached to a quadrupole mass spectrometer to allow the identification of triglyceride degradation products online (without isolation and derivatization so as to avoid artifacts and decomposition), to allow identification of co-eluting HPLC components, and to detect minor degradation products. Several classes of oxidation products including hydroperoxides, epoxides, ketones, and dimers were confirmed for heated tri-

TABLE 8
Suggested Mechanisms for Volatiles Formation from Heated Trilinolein Epoxides[a]

Epoxide/ double bond carbon location	Mechanism for epoxide formation[c]	Epoxide precursor monohydroperoxide[b]	Volatiles formed from epoxide decomposition[d]
9,10/11,13	OOH cyclization	9-OOH	2,4-Decadienal
			2,4-Nonadienal
8,9/10,12			2,4-Decadienal
			2,4-Undecadienal
10,22/8,12	OOH cyclization	10-OOH	2,4-Nonadienal
			2-Octena[e]
9,10/8,11			2,4-Decadienal
			2-Nonenal
12,13/9,14	OOH cyclization	12-OOH	2,4-Heptadienal
			2-Hexenal
11,12/9,13			2,4-Octadienal
			2-heptenal
12,13/8,10	OOH cyclization	13-OOH	Hexanal
			2-Heptenal
13,14/9,11			Pentanal
			2-Hexenal
9,10/12	Epoxidation	Linoleic	2,4-Decadienal
			3-Nonenal
12,13/9	Epoxidation	Linoleic	Hexanal
			2-Heptenal

[a,b,c,d]See Table 7 footnotes.

TABLE 9
Volatile Precursor Fractions[a] (ELSD area%)[b] from Heated OOO and LLL Heated 1, 3, and 6 h at 190¡C

Volatile	1 h		3 h		6 h	
Precursors	OOO	LLL	OOO	LLL	OOO	LLL
OOH	20.8	39.4	19.7	21.8	16.3	3.1
Keto	24.7	9.1	10.5	9.4	7.8	10.2
Epoxy	21.9	6.1	20.4	7.8	21.1	10.2
Dimer	6.3	12.1	5.4	21.0	7.2	22.9
Total % monomer	67.4	54.6	50.7	39.0	45.2	23.5
Total % higher molecular weight products	32.6	45.4	49.3	61.0	54.8	76.5

[a]Compounds from heated OOO and LLL compounds identified by high-performance liquid chromatography (HPLC) coupled with atmospheric pressure chemical ionization mass spectrometry (16).
[b]Semiquantitation of heated OOO and LLL by reversed-phase HPLC with evaporative light-scattering detection (ELSD). Area % composition renormalized to exclude unreacted di- and triglycerides. For abbreviations see Table 2.

olein (16) and for heated trilinolein.

The presence of monohydroperoxides in heated triolein and trilinolein might be unexpected. Monohydroperoxides should decompose instantly upon formation at 190°C to produce volatiles and more heat-stable compounds such as the epoxy, keto, hydroxy, aldehydic and higher molecular weight compounds (8). Apparently, the monohydroperoxides were formed as the triglycerides were cooled below 100°C after heating (8,16). This process would occur in intermittent as opposed to continuous frying (6–8).

The triglyceride epoxides detected by RP-HPLC APCI-MS in the heated triolein and trilinolein are listed in Tables 7 and 8, respectively. These epoxides were likely produced by two mechanisms. In the first, hydroperoxide cyclization (16,17,25,31), the hydroperoxide group forms an alkoxy radical through loss of a hydroxy radical. The alkoxy radical through cyclization with an adjacent carbon then forms an epoxide. If the adjacent carbon is part of a double-bond system, the double bond is shifted one carbon to result in epoxy group adjacent to a double bond. The cyclization mechanism produced triglyceride epoxides, such that the epoxy group was found to be distributed among oleic acid carbons 7 through 12 (16). The second likely epoxidation mechanism, hydroperoxidation, involved the reaction of the unsaturated fatty acid with a fatty acid hydroperoxide (16,17,25,31) to produce an epoxy group formed across the original oleic double bond. This reaction would produce only one oleic epoxide with the epoxide group across carbons 9 and 10 (16). Trilinolein produced similar epoxide isomers. The cyclization mechanism yielded the epoxy group distributed among linoleic carbons 8 through 14. For the hydroperoxidation mechanism, the epoxy group formed across the original linoleic double bonds produced two isomers with the epoxide group across carbons 9 and 10 for one isomer and carbons 12 and 13 for the other positional isomer.

The keto triolein fraction had the keto group on the previously hydroperoxy-containing carbons 8, 9, 10, and 11. Keto trilinolein had the keto groups at the previous hydroperoxy carbons 9 and 13. The chemistry for keto fatty acids at high temperature likely involved the initial decomposition of the monohydroperoxides to give the keto compounds (25,31).

Of particular interest were the HMW compounds detected by RP-HPLC APCI-MS in heated triolein (16) and trilinolein. One type of heated triolein HMW involved triolein units, which contained an aldehyde linked by one oxygen to an oleic acid of the triolein, molecular weight range 958 to 1014. These compounds represent ethers of butanal, pentanal, hexanal, heptanal, and octanal. These compounds were obviously from the reaction of triolein with aldehydic volatiles generated from degradation products during the frying or heating process. Also, HMW triolein products included nonpolar dimers with carbon-carbon and carbon-oxygen-carbon linkages, molecular weights 1768 and 1784, respectively. The corresponding dimers with one fatty acid containing a polar group such as keto and epoxy were found. Dimers with one fatty acid linked to a volatile aldehyde, molecular weight range 1870–1880, and dimers which have lost one fatty acid and a portion from another fatty acid were detected. Finally, with the longest HPLC retention time, dimers for which another fatty acid had attached to a dimer fatty acid, molecular weight range 1854–1862, were identified. Similar products in heated trilinolein were identified by the RP-HPLC APCI-MS method.

Although we have directly detected and identified on-line many species from heated triolein and trilinolein produced by the model frying oil systems, that previously would have required fractionation, derivatization and then analysis, we believe there are still other species present that have not been directly identified. Cyclic fatty acids are an example of a class of compounds that has been shown to be present in heated oils at very low levels but that we have not yet directly identified (8). However, one must keep in perspective the degree of information provided for the major components and classes observed here compared to previous methods of analysis and compared to labor-intensive classical chemical methods of analysis.

Quantitation of the volatile precursors of heated triolein and trilinolein. Semiquantitation of the identified triolein and trilinolein degradation products resolved by RP-HPLC-ELSD are shown in Table 9. RP-HPLC analysis gave much more information than SEC analysis on the amount of types of degra-

dation products produced with heating time from triolein and trilinolein. This table shows the semiquantitation of the fractions studied as volatile precursors and their formation during triglyceride heating with time. We were able to collect by preparative RP-HPLC only the epoxy, keto, dimer, and monohydroperoxide fractions previously identified by RP-HPLC APCI-MS. Therefore, semiquantitative data are shown for these fractions in Table 9. The epoxy fraction contained the triolein epoxides and epoxyenes and the trilinolein epoxyenes and epoxydienes shown in Tables 7 and 8, respectively. The dimer fraction contained two triglycerides, some with unoxidized fatty acids plus others with oxidized fatty acids. However, the dimer fraction did not contain the other HMW discussed above. Data in Table 8 show degradation product formation in the triolein and trilinolein with heating time. Total monomeric products decreased and total HMW products increased with heating time. Triolein and trilinolein monomeric hydroperoxy products decreased with heating time. By 6 h of heating, the HMW products may be the predominant source, mainly for trilinolein, of volatile compounds produced in the model frying systems. Triolein and trilinolein monomeric hydroperoxides were at high abundance at 1 h % heating but steadily decreased in abundance with heating time. However, the total secondary oxidation products increased with heating time. This likely meant that, although monohydroperoxides remained important for volatile production, they were also increasingly important for the formation of secondary products with heating time. Triolein monomeric keto products were present in relatively high abundance at 1 h % heating, but decreased with heating time. On the other hand, trilinolein monomeric keto products remained constant at relatively low abundance with heating time. Triolein momeric epoxy products were about constant and remained at relatively high abundance with heating time. Trilinolein monomeric epoxy products slightly increased with heating time. Triolein dimer products were about constant with heating time. Trilinolein dimer products increased with heating time. Total amount of HMW products, which include dimer compounds plus the other HMW discussed above, increased with heating time for the model heating oil systems.

Formation mechanisms of *volatiles from volatile precursors.* Proper identification of these fractions allowed us to focus on formation of volatiles in regard to volatile precursors with certain functional groups. The dimer, epoxy, keto, and hydroperoxide fractions isolated by preparative HPLC were subjected to thermal decomposition and the volatiles produced were analyzed by purge and trap–GC-olfactometry-MS. Actually, for the preparative HPLC fractions, all the triolein and trilinolein nonvolatile degradation products, the monomeric hydroperoxides, keto, epoxy, and dimeric triglyceride compounds, as expected, produced volatiles (21–25,30), which were investigated as odor and nonodor volatiles.

All of the preparative HPLC fractions from heated triolein, the monomeric hydroperoxy, keto, epoxy, and dimer fractions, as shown in Table 3, produced octanal, nonanal, 2-decenal, and 2-undecenal. These aldehydes were produced by thermal decomposition *via* homolytic cleavage about the oxidation functional group atoms (hydroperoxy, keto, epoxide, and dimer oxygen linkages) (16,17,25,30–32). By an acid heterolytic cleavage between an adjacent double bond and a carbon bearing a hydroperoxy group or by the action of both homolytic and heterolytic decomposition mechanisms (mixed mechanism), these aldehydes can be produced from hydroperoxy products under the conditions of our model frying systems (25,31). Many of the aldehydes can be produced from the triolein epoxides listed in Table 7 by homolytic cleavage, thermal decomposition, and acid-catalyzed epoxide chemistry (16,17,30–32). The above aldehydes are responsible for the grassy, plastic, and fruity odors in the heated triolein as shown in Table 3. Reference to Table 7 shows the epoxide structures that were identified by RP-HPLC APCI-MS for heated triolein and the volatiles that can be produced by homolytic cleavage or β-scission (25,30,31) and demonstrates that the epoxides possibly could produce many of the volatiles discussed above. The aldehydes such as pentanal and hexanal, usually expected from linoleic hydroperoxides (25), are produced in abundance in all the heated triolein HPLC fractions. Other compounds normally associated with oxidized linoleic acid such as 2-pentyl furan and 4-octen-3-one (25) were produced in heated triolein and the HPLC fractions, but in minor abundance compared to the expected oxidized oleic volatiles such as octanal and nonanal. The precursors of these nonoleic aldehyde volatiles were not uncovered during this work. However, these compounds may be produced from further oxidation of the volatile products such as 2-undecenal (25).

The preparative HPLC fractions from heated trilinolein, the monomeric hydroperoxy, keto, epoxy, and dimer fractions as shown in Table 4, all produced in abundance the aldehydes expected such as pentanal, hexanal, 2-heptenal, 2-nonenal, and 2,4-decadienal from the linoleic acid monohydroperoxides (25). These aldehydes are responsible for fruity, plastic, grassy, fried food odors in heated trilinolein. Reference to Table 8 shows that many of these aldehydes can be produced by β-scission and epoxy chemistry from epoxyenes and dienes detected by RP-HPLC-APCI-MS in heated trilinolein.

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REFERENCES

1. Warner, K., and T.L. Mounts, Frying Stability of Soybean and Canola Oils with Modified Fatty Acid Compositions, *J. Am. Oil Chem. Soc. 70*:983–988 (1993).
2. Warner, K., P. Orr, L. Parrott, and M. Glynn, Effects of Frying Oil Composition on Potato Chip Stability, *Ibid. 71*:1117–1121 (1994).
3. Warner, K., Property Enhanced Oils, in *Proceedings Australian Oilseed Federation Oilseed Forum*, 1996, pp.1–8.
4. Warner, K., P. Orr, and P. Glynn, Effect of Fatty Acid Composition of Oils on Flavor and Stability of Fried Foods, *J. Am. Oil Chem. Soc. 74*:347–356 (1997).
5. Warner, K., and S. Knowlton, Frying Quality and Oxidative Sta-

bility of High-Oleic Corn Oils, *Ibid. 74*:1317–1322 (1997).
6. Getz, C., Chemical Changes of Oils and Fats at Elevated Temperatures, in *Proceedings of the 21st World Congress of the International Society for Fat Research (ISF)*, The Hague, P J Barnes and Associates, Bridgwater, England, 1995, pp. 577–582.
7. Warner, K., Chemistry of Frying Fats, in *Food: Chemistry, Nutrition, and Biotechnology*, edited by C.C. Akoh and D.B. Min, Marcel Dekker, New York, 1998, pp. 167–180.
8. Frankel, E.N., Frying Fats, in *Lipid Oxidation*, The Oily Press, Dundee, Scotland, 1998, pp. 227–248.
9. Chang, S.S., R.J. Peterson, and C.-T. Ho, Chemical Reactions Involved in the Deep-Fat Frying of Foods, *J. Am. Oil Chem. Soc. 55*:718–727 (1978).
10. Paulose, M.M, and S.S. Chang, Chemical Reactions Involved in the Deep-Fat Frying of Foods: VIII. Characterization of Nonvolatile Decomposition Products of Triolein, *Ibid. 55*:375–380 (1978).
11. Gardner, D.R., R.A. Sanders, D.E. Henry, D.H. Tallmadge, and H.W. Wharton, Characterization of Used Frying Oils. Part 1: Isolation and Identification of Compound Classes, *Ibid. 69*:499–508(1992).
12. Hansen, S.L., M.R. Myers, and W.E. Artz, Nonvolatile Components Produced in Triolein During Deep-Fat Frying, *Ibid. 71*:1239–1243 (1994).
13. Dobson, G., W.W. Christie, and M.C. Dobarganes, Changes in Molecular Species of Triacylglycerols During Frying, Fats and Oils, *Grasas Aceites 47*:34–37 (1996).
14. Artz, W.E., S.L. Hansen, and M.R. Myers, Heated Fat-Based Oil Substitutes, Oleic and Linoleic Acid-Esterified Propoxylated Glycerol, *J. Am. Oil Chem. Soc. 74*:367–374 (1997).
15. Hansen, S.L., W.J. Kruegar, L.B. Dunn, Jr., and W.E. Artz, Nuclear Magnetic Resonance and Gas Chromatography/Mass Spectroscopy Analysis of the Nonvolatile Components Produced During Heating of Oleic Acid Esterified Propoxylated Glycerol, a Fat Substitute Model Compound, and Trioleylglycerol, *J. Agric. Food Chem. 45*:4730–4739 (1997).
16. Byrdwell, W.C., and W.E. Neff, Non-volatile Products of Triolein Produced at Frying Temperatures Characterized Using Liquid Chromatography with Online Mass Spectrometric Detection, *J. Chromatogr. A 852*:417–432 (1999).
17. Neff, W.E., and W.C. Byrdwell, Characterization of Model Triacylglycerol (triolein, trilinolein and trilinolenin) Autoxidation Products *via* High-Performance Liquid Chromatography Coupled with Atmospheric Pressure Chemical Ionization Mass Spectrometry, *Ibid. 818*:169–186 (1998).
18. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 4th ed., American Oil Chemists' Society, Champaign, 1989, Method Cd 20-91.
19. Warner, K., Flavors and Sensory Evaluation, in *Bailey's Industrial Oil and Fat Products*, 5th edn., Vol. 1, Edible Oil and Fat Products, General Applications, edited by Y.H. Hui, John Wiley & Sons, Inc., New York, 1996, pp. 105–143.
20. Frankel, E.N., Methods to Determine Extent of Oxidation, in *Lipid Oxidation*, The Oily Press, Dundee, Scotland, 1998, pp. 79–98.
21. Frankel, E.N., Chemistry of Autoxidation: Mechanism, Products and Flavor Significance, in *Flavor Chemistry of Fats and Oils*, edited by D.B. Min and T.H. Smouse, American Oil Chemists' Society, Champaign, 1985, pp.1–37.
22. Grosch, W., Reactions of Hydroperoxides—Products of Low Molecular Weight, in *Autoxidation of Unsaturated Lipids*, edited by H.W.-S. Chan, Academic Press, London, 1987, pp. 95–139.
23. Frankel, E.N., Review: Recent Advances in Lipid Oxidation, *J. Sci. Food Agric. 54*:495–511 (1991).
24. Przbylski, R., and N.A.M. Eskin, Methods to Measure Volatile Compounds and The Flavor Significance of Volatile Compounds, in *Methods to Assess Quality and Stability of Oils and Fat-Containing Foods*, edited by K. Warner and N.A.M. Eskin, AOCS Press, Champaign, 1995, pp. 107–145.
25. Frankel, E.N., Hydroperoxide Decomposition, in *Lipid Oxidation*, The Oily Press, Dundee, Scotland, 1998, pp. 55–77.
26. Mahungu, S.M., S.L. Hansen, and W.E. Artz, Quantitation of Volatile Compounds in Heated Triolein by Static Headspace Capillary Gas Chromatography/Infrared Spectroscopy–Mass Spectrometry, *J. Am. Oil Chem. Soc. 71*:453–455 (1994).
27. Mahungu, S.M., S.L. Hanson, and W.E. Artz, Identification and Quantitation of Volatile Compounds in Two Heated Model Compounds, Trilinolein and Linoleic Acid Esterified Propoxylated Glycerol, *J. Agric. Food Chem. 47*:690–694 (1999).
28. Debbrecht, F.J., Quantitative Analysis, in *Modern Practice of Gas Chromatography*, edited by R.L. Grob, John Wiley & Sons, New York, 1997, pp. 166–210.
29. Snyder, J.M., E.N. Frankel, E. Selke, and K. Warner, Comparison of Gas Chromatographic Methods for Volatile Lipid Oxidation Compounds in Soybean Oil, *J. Am. Oil Chem. Soc. 65*:1617–1620 (1988).
30. Gardner, H.W., and E. Selke, Volatiles from Thermal Decomposition of Isomeric Methyl (12*S*,13*S*)-(*E*)-12,13-Epoxy-9-hydroperoxy-10-octadecenoates, *Lipids 19*:375–380 (1984).
31. Gardner, H.W., Oxygen Radical Chemistry of Polyunsaturated Fatty Acids, *Free Radical Biol. Med. 7*:65–86 (1989).
32. Neff, W.E., and W.C. Byrdwell, Triacylglycerol Analysis by High Performance Liquid Chromatography-Atmospheric Pressure Chemical Ionization Mass Spectrometry: *Crepis alpina* and *Vernonia galamensis* Seed Oils, *J. Liq. Chromatogr. 18*:4165–4181 (1995).

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