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Effect of Oleic and Linoleic Acids on the Production of Deep-Fried Odor in Heated Triolein and Trilinolein

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To determine sources of desirable deep-fried flavor in frying oils, degradation products from heated triolein and trilinolein with 5–31% polar compounds representing low to high deterioration were evaluated by purge-trap gas chromatography–mass spectrometry–olfactometry. (*E,E*)-2,4-Decadienal, 2-heptenal, 2-octenal, 2,4-nonadienal, and 2,4-octadienal produced deep-fried odor at moderate–strong intensities in heated trilinolein. However, unexpected aldehydes—2,4-decadienal, 2,4-undecadienal, 2,4-nonadienal, and 2-octenal (all <15 ppm)—were produced in triolein heated for 6 h. These dienals possibly were produced by hydroperoxidation and/or hydroxylation followed by dehydration of 2-alkenals. The 2-alkenals were produced from thermal decomposition of hydroperoxides, epoxides, and keto and dimeric compounds produced during the heating of triolein. These aldehydes produced low intensities of deep-fried odor in triolein. This information helps to explain sources of the deep-fried flavor that is characteristic of high linoleic frying oils but which is only at low intensity levels in high oleic frying oils.

Keywords: Fried odor; frying oil; mass spectrometry; nonvolatile; odor; olfactometry; oxidation; trilinolein; triolein; volatile compound

INTRODUCTION

Foods are deep-fat-fried to develop the desirable characteristic flavors imparted from frying. However, frying degrades oils by various chemical processes including oxidation, polymerization, isomerization, cyclization, and hydrolysis that affect the flavor quality—both positively and negatively—of foods fried in the oils. Numerous research studies have described the negative odors and flavors from heated oils (1–3). Dobbs et al. (3) reported characteristic odors of buttery, sulfur, fishy, and painty in heated canola oil, whereas Mounts et al. (2) found that heated soybean oil had burnt, acrid, fishy, and doughy odors. Many of these odors are characteristic of oils containing linolenic and linoleic acids. Other researchers have analyzed the volatile and nonvolatile decomposition products in frying oils to better understand the source of these characteristic odors and flavors. Chang and co-workers studied volatile compounds from heated corn and cottonseed oils (4, 5) and reported that the higher linoleic acid containing oils produced the most pleasant odors but also had the most volatile compounds. In addition, Perkins (6) found that the higher linoleic acid containing cottonseed oil had more nonvolatile compound formation than lower linoleic acid containing tallow. During the past 15 years, plant geneticists have developed a wide variety of vegetable oils with modified fatty acid compositions

based on previous research that showed that oils with fewer polyunsaturates as well as more oleic acid and saturates produced more stable oils. For example, low linolenic acid canola oils had the same odors as regular canola oil but the modified oil was more acceptable (7). In addition, heated low linolenic acid soybean oils had odors similar to those of regular soybean oil but at significantly weaker intensities (2). Studies of higher oleic acid vegetable oils such as high-oleic sunflower, high-oleic canola, and mid-oleic corn oils as frying oils have shown that these oils had improved frying stability compared to commodity sunflower, canola, and corn oils (8–11). However, not only was the desirable fried odor and flavor associated with higher levels of linoleic acid diminished in foods fried in higher oleic oils but the oil also had increased intensities of negative odors such as fruity, plastic, acrid, and waxy that were characteristic of higher oleic oils during frying or heating (10–13). To manufacture oils with improved oil quality and stability, it is important for food researchers to understand what odor and flavor characteristics that specific fatty acids impart to oils and foods. This information would also be essential in recommending fatty acid compositions for plant breeders to develop better oilseeds. However, it is difficult to understand the roles that various fatty acids play in the development of positive and negative odors/flavors in frying oils because of the mixture of fatty acids and the influence of minor oil constituents in the oils. To help solve this problem, some researchers have studied pure triacylglycerols such as triolein and trilinolein. Chang and co-workers found that more volatile compounds were produced during simulated frying of trilinolein (LLL) than in triolein (OOO) (4, 14–16). Selke et al. (17, 18) found similar results. The purpose of our current research was to learn more about the effect that the various degradation products in

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heated LLL and OOO have on the positive deep-fried odor and flavor in frying oils. In the 20 years since the works of Chang, Selke, and Perkins were published, many improvements have been made in instrumentation to analyze volatile and nonvolatile decomposition products including capillary chromatography, gas chromatography–mass spectrometry, and liquid chromatography–mass spectrometry. In addition to measuring the volatile and nonvolatile decomposition products of heated LLL and OOO, we also analyzed the odors of the volatile compounds by olfactometry to determine odor types and intensities characteristic of various peaks and analyzed the precursors of the these volatile degradation products by high-performance liquid chromatography (HPLC) to determine the sources of deep-fried odor.

MATERIALS AND METHODS

Triacylglycerols. OOO and LLL were purchased from NuCheck Prep, Inc. (Elysian, MN) and were screened before use for oxidation, for purity, and for non-triglyceride products by peroxide value, polar phase thin-layer chromatography (TLC) with ultraviolet detection of conjugated oxidized linoleic acid and visualization of unsaturated non-triglycerides by iodine vapor, polar component analysis, and detection of oligomer, monoacylglycerols, diacylglycerols, and free fatty acid by size exclusion (SEC) HPLC coupled with evaporative light scattering detection (ELSD). Fatty acid purity was checked by gas chromatographic (GC) analysis of the transmethylated triacylglycerol and triacylglycerol purity by reversed-phase HPLC (RP-HPLC) coupled with ELSD. OOO and LLL were used without further purification. Acetonitrile (ACN) (EM Science, Gibbstown, NJ) and dichloromethane (DCM) (Fisher, Fair Lawn, NJ) were of HPLC grade and were used without further purification.

Heating Protocol. Six test tubes (2×12.5 cm), each containing 5 g of triacylglycerol, with 3.14 cm^2 exposed oil surface, were heated to 190°C by submersion in a temperature-controlled silicone oil bath. Two percent water ($100 \mu\text{L}$) was added each hour to each tube through a capillary submerged at the bottom of each tube to simulate moisture from frying. One sample tube was removed from the bath each hour for analysis. The samples were frozen neat under argon and stored at -15°C . This heating process was done in duplicate. Reproducibility of the heating protocol was confirmed by similar results for polar components, SEC and RP-HPLC-ELSD product quantitation, and identification by RP-HPLC–mass spectrometry (MS)–atmospheric pressure chemical ionization (APCI).

Total Polar Compound Analysis. Amounts of polar compounds were analyzed in duplicate according to the AOCS (19) column chromatography method.

Measurement of Nonvolatile Compounds by Liquid Chromatography. SEC of heated LLL and OOO was done using four $25 \text{ cm} \times 4.6 \text{ mm}$, $7 \mu\text{m}$ particle size, Ultrastaygel columns (Waters Associates, Milford, MA) in series. Two 500 \AA and two 100 \AA columns used DCM at 0.5 mL/min 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 , and gas flow was set at a pressure of 1.6 bar. 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-, and mono-olein and oleic acid. Semiquantitation of the heated OOO and LLL decomposition products was done by RP-HPLC with a Thermo Separation Products model SP 8800 ternary solvent system (Schaumburg, IL) with two RP-HPLC columns with bonded silyl (CT8) ODS, Inertsil ODS-80A (Keystone Scientific, Bellefonte Park, PA), 25 cm , 4.6 mm , $5 \mu\text{m}$ packing particle size with the columns in series. Gradient elution was $80\% \text{ ACN}$, $20\% \text{ DCM}$ to $20\% \text{ ACN}$, $80\% \text{ DCM}$ after 120 min. The flow rate was 0.6 mL/min .

Ten microliters of 25 mg of solute/ mL DCM was injected. The ELSD was operated as described for SEC. Peaks in the HPLC chromatograms were identified based on earlier analyses of heated OOO by RP-HPLC/APCI-MS (20).

Preparative RP separation was used to fractionate heated OOO and LLL. A Dynamax C_{18} column, $30 \times 2.25 \text{ cm}$, $60 \mu\text{m}$ particle size (Rainin Instrument Co., Inc., Woburn, MA), was used with an isocratic flow of $40\% \text{ ACN}$, $60\% \text{ DCM}$ 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 preparative separation. To collect enough material for volatile compound analyses, LLL and OOO heated for 6 h were used for fractionation after the polar compound procedure. Polar compounds were then used for the RP-HPLC fractionation to manually collect the epoxy, keto, monohydroperoxide (OOH), and dimer fractions. Fifty microliters of a 500 mg of polar component/ mL solution in DCM was injected; 100 – 150 mg for each fraction was collected by preparative RP-HPLC for purge and trap GC-MS analysis of the respective fractions for measuring volatile compounds and for olfactometry analysis. 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 HPLC system used for RP-HPLC/APCI-MS contained an LDC 4100 MS (Thermo Separation Products) with a quaternary pump with membrane degasser. The same HPLC columns were used as for RP-HPLC-ELSD. The gradient for separation of the heated OOO and LLL components was as follows: initial conditions, $75\% \text{ ACN}$, $25\% \text{ DCM}$; linear from 0 to 20 min to $70\% \text{ ACN}$, $30\% \text{ DCM}$, then linear from 20 to 50 min to $30\% \text{ ACN}$, $70\% \text{ DCM}$, 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 $\sim 680 \mu\text{L/min}$ went to an ELSD and $\sim 120 \mu\text{L/min}$ went to the mass spectrometer. A Vorex 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 , and the gas flow was 2.0 standard L/min . Nebulizer gas was high-purity N_2 . 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 $10 \mu\text{L}$ were made using a series 1050 autosampler (Hewlett-Packard, Wilmington, DE).

Identification of Nonvolatile Compounds by MS-LC. 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 , and the corona voltage was set to $6.0 \mu\text{A}$. Sheath and auxiliary gases were set to 35 psi and 5 mL/min , respectively. Spectra were obtained from 100 to 2000 atomic mass units (amu) with a scan time of 2 s.

Volatile Compound Analysis by MS–Olfactometry. Volatile compounds were analyzed with a purge and trap apparatus equipped with a test tube adapter (Tekmar model 3000, Tekmar-Dohrmann Co., Cincinnati, OH) coupled with a model 3400 GC equipped with olfactometry (sniffing port attachment) and a Saturn model 3 ion trap mass spectrometer (Varian, Inc., Walnut Creek, CA). A 50 mg sample was placed in the $1.9 \times 7.6 \text{ cm}$ test tube and heated at 100°C for 9 min of preheat time. Volatile compounds were trapped on a 30.5 cm Tenax No. 1 trap, with 10 min of sample purge time, 170°C for 6 min of desorption time, 180°C MCS desorb temperature, and 160°C GC transfer line and valve temperature. Volatile compounds were introduced into a GC column, DB-1701, $1 \mu\text{m}$ film thickness, $30 \text{ m} \times 0.32 \text{ mm}$ (J&W Scientific, Folsom, CA). The column was programmed at -20°C (2 min) and then heated from -20 to 233°C at 3°C/min . The column helium flow rate was 2 mL/min with a 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 VSIS splitter (Varian, Inc.) divided the flow between the mass spectrometer and the sniffing port with 10 parts of gas volume to the sniffing port for odor analysis and

Table 1. Percent Total Polar Compounds, Higher Molecular Weight Compounds, Monomeric Compounds (Unreacted Triacylglycerol and Triacylglycerol Oxidation Products) in OOO and LLL Heated for 0, 1, 3, and 6 h at 190 °C

degradation product	lipid	hours at 190 °C			
		0	1	3	6
total polar compounds	OOO	0	5	16	31
	LLL	1	5	17	25
higher molecular weight products	OOO	0.0	3.6	9.7	15.9
	LLL	0.0	3.8	12.0	18.8
monomer	OOO	100.0	96.4	90.3	83.9
	LLL	100.0	96.2	88.0	80.6
diacylglycerol	OOO	0.0	0.0	0.1	0.2
	LLL	0.0	0.0	0.0	0.6

1 part to the mass spectrometer for volatile compound identification. Odor types and intensities were determined by three trained sensory judges experienced in evaluating heated oil odors and deep-fried odor/flavor. Judges were trained and experienced in perceiving the positive, desirable deep-fried food odor/flavor by evaluating unaged, fresh potato chips fried in fresh cottonseed oil. Any peak with detectable odor was described as to odor attribute and rated on a 0–10 intensity scale with 0 = none and 10 = strong. Judges had experience and training in rating the intensity of the odors by evaluating fresh and aged potato chips with weak, moderate, and strong levels of deep-fried flavor intensity. The ion trap MS operated in the EI mode with a mass scan range from m/z 23 to 400 over 0.8 s. Filament emission current was 25 μ A, axial modulation was 2.1 V, manifold heater was set at 160 °C, and filament/multiplier delay was 2.5 min. Compound structural identifications were made both from spectral comparisons with the NIST 92 mass spectrometry library (Varian, Inc.) and from retention time comparisons with standard compounds.

RESULTS AND DISCUSSION

Chemical Analysis of Heated Triacylglycerols.

OOO and LLL were analyzed to determine the purity of the compounds and the presence of trace amounts of any compounds by analyses of triacylglycerol structures and fatty acid compositions. OOO contained 100% oleic acid and 100% OOO, whereas LLL had 99.9% linoleic acid and 0.1% oleic acid and 99.8% LLL and 0.2% dilinoleoylglycerol. No oligomer, monoacylglycerol, diacylglycerol, or free fatty acids were detected by SEC in either unheated OOO or LLL (Table 1). OOO had an initial peroxide value of 0.4 mequiv/kg and 0.1% total polar compounds with no detectable non-triacylglycerol or triacylglycerol oxidation products. LLL had an initial peroxide value of 0.9 mequiv/kg and 0.5% total polar compounds and no detectable non-triacylglycerol or triacylglycerol oxidation products. The triacylglycerols were heated until the percent total polar compounds reached 25–31% (Table 1). The heating protocol was designed to produce low, moderate, and high levels of total polar compounds to represent these three levels of deterioration usually found in frying oils. After 1 and 3 h of heating, total polar compound levels were similar for OOO and LLL; however, after 6 h of heating, OOO had a significantly higher level than LLL. Decomposition products in heated OOO and LLL included higher molecular weight products, monomeric triacylglycerols (unreacted triacylglycerol plus monomeric triacylglycerol oxidation products), and diacylglycerol (Table 1). No monoacylglycerols or free fatty acids were detected, probably because of steam distillation (21). Diacylglycerol was detected in OOO by 3 h and increased slightly at 6 h. Higher molecular weight compounds [dimer plus chain addition products of the triglyceride (20)] in-

Table 2. Volatile Compounds (Parts per Million) Producing Deep-Fried Odor from OOO and LLL Heated for 1, 3, and 6 h at 190 °C

volatile compound	hours at 190 °C					
	1		3		6	
	OOO	LLL	OOO	LLL	OOO	LLL
(<i>E</i>)-2-heptenal	0.0	98.6	0.0	80.1	0.0	127.3
(<i>E</i>)-2-octenal	1.1	15.9	0.5	35.7	5.8	72.6
(<i>E,E</i>)-2,4-octadienal	0.0	0.2	0.0	0.4	0.0	0.6
(<i>E,Z</i>)-2,4-nonadienal	0.1	0.1	0.2	0.3	0.3	0.4
(<i>E,E</i>)-2,4-nonadienal	4.2	4.5	4.1	7.6	5.5	12.6
(<i>E,E</i>)-2,4-decadienal	12.6	221.1	10.7	423.7	14.1	632.9
(<i>Z,E,E,Z</i>)-2,4-decadienal	0.0	9.2	0.0	12.8	0.0	17.5
(<i>E,E</i>)-2,4-undecadienal	0.7	0.0	2.0	0.0	3.0	0.0

creased from 0% initially to 16% at 6 h of heating, whereas monomeric compounds (oxidized plus unreacted triacylglycerol) decreased with time. These results agree with those of the work of Hansen et al. (22) on heated triolein. Diacylglycerol was not detected in LLL until 6 h and was <1%. Higher molecular weight compound levels were higher for LLL than for OOO at all heating times.

Volatile Compounds Producing Fried Odor. Olfactometry was used to determine the odor attributes of each peak in the chromatograms. This paper reports only the volatile compounds that produced a deep-fried odor; Neff et al. (34) reported the volatile compounds that produced negative odors such as plastic, waxy, grassy, and fruity from the same samples of heated OOO and LLL. Volatile compounds that produced a deep-fried odor detected in olfactometry analyses for heated OOO and LLL are shown in Table 2. These eight volatile compounds, (*E,E*)-2,4-decadienal, (*E*)-2-heptenal, (*E*)-2-octenal, (*E,Z,Z,E*)-2,4-decadienal, (*E,E*)-2,4-nonadienal, and (*E,Z*)-2,4-nonadienal, have been reported previously in heated OOO and LLL (23–27); however, few researchers have conducted odor analyses to determine odor attributes and intensity levels of each attribute. As expected, the amounts of these compounds increased in almost all cases with heating time for both OOO and LLL. A deep-fried odor was produced by (*E,E*)-2,4-decadienal, (*E*)-2-heptenal, (*E*)-2-octenal, (*E,Z,Z,E*)-2,4-decadienal, (*E,E*)-2,4-nonadienal, (*E,Z*)-2,4-nonadienal, and (*E,E*)-2,4-octadienal in LLL. (*E,E*)-2,4-Decadienal and (*E*)-2-heptenal were present in the greatest amounts from heated trilinolein primarily because they were formed directly from the decomposition of linoleic acid compounds bearing hydroperoxy-containing carbons (21). In addition, 2-heptenal has been reported as a decomposition product of 2,4-decadienal (28). The (*E*)-2-octenal, (*E,E*)-2,4-nonadienal, (*E,Z*)-2,4-nonadienal, and (*E,E*)-2,4-octadienal found in LLL cannot be explained by the classical beta scission mechanism for linoleic hydroperoxide decomposition (24). These compounds were at low concentrations, although they increased throughout the heating period. (*E*)-2-Octenal may be produced from further oxidation at the methylene carbon between the carbonyl and olefinic group of the 3-nonenal produced from the decomposition of the linoleic 13-hydroperoxide (21, 24). 2,4-Nonadienal may be produced from hydroperoxidation at the allylic carbon five of 3-nonenal followed by loss of hydroperoxide to form the 2,4-diene system. A small amount of 2,4-nonadienal was observed from thermal decomposition of 3-nonenal in a GC injection port followed by GC-MS analysis (H. Gardner, unpublished work). By the same mechanism, 2,4-octadienal may be produced from 2-octenal. 2,4-Decadienal, 2-octenal, 2,4-nonadienal, and 2,4-

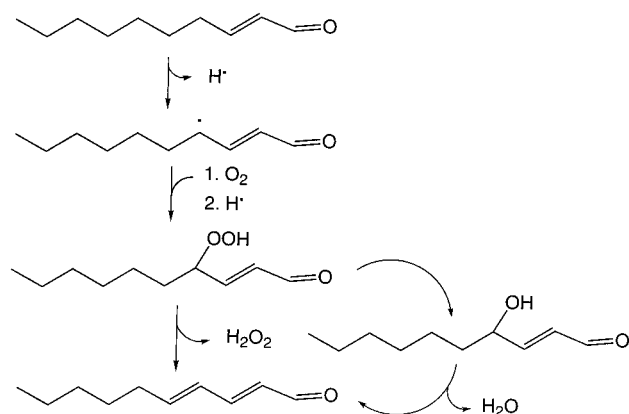


Figure 1. Proposed mechanism for formation of 2,4-dienals in heated triolein by hydroperoxidation with water/peroxide elimination reaction of 2-enals produced from decomposition of oleic hydroperoxides.

undecadienal produced deep-fried odor in heated OOO; however, these compounds were not formed directly from oleic acid hydroperoxides. These compounds were generated at significantly lower amounts than volatile compounds derived directly from oleic hydroperoxides. The compounds may have been formed by the hydroperoxidation or hydroxylation of the allylic methylene carbon hydrogen followed by loss of hydrogen peroxide or water from 2-alkenals produced from decomposition of oleic hydroperoxides (Figure 1). The scheme shows a possible mechanism for the production of 2,4-decadienal in heated OOO from 2-decenal. 2-Decenal would be expected by the classical beta scission of oleic 10-hydroperoxide (24) and may undergo a hydroperoxidation by classical free radical chemistry at the 2-decenal allylic methylene carbon to form a hydroperoxide group at that site. Further loss of hydrogen peroxide would produce a double bond between carbons 4 and 5 to produce 2,4-decadienal. Also, at 190 °C, the hydroperoxide group may decompose to form the hydroxy group or the allylic methylene carbon may react with hydroxy radical to form a hydroxy group at the methylene carbon. Dehydration of this hydroxy compound may also produce 2,4-decadienal. Following the same scheme, 2-undecenal produced from the oleic 11-hydroperoxide may produce 2,4-undecadienal. In addition, the scheme could account for the formation of 2,4-nonadienal from 2-nonenal, which is not expected from oleic hydroperoxides; however, 2-nonenal may be a decomposition cleavage oxidation product of 2-undecenal.

2,4-Decadienal and 2-heptenal, which derived directly from linoleic acid decomposition, are assumed to contribute the most to the deep-fried odor because of the high parts per million levels produced. The effect that these compounds when produced indirectly and at low levels have on the deep-fried flavor in foods is not fully understood, although foods fried in high-oleic oils have low intensities of deep-fried flavor (12, 29). Results of previous studies on the development of deep-fried flavor in potato chips prepared in high-oleic sunflower oil or cottonseed oil showed that chips fried in high-oleic sunflower oil had weak deep-fried flavor intensity initially, but the flavor increased with increased heating/frying time of the oil (12). On the other hand, the high linoleic acid containing cottonseed oil produced chips with moderate to strong deep-fried flavor in the early stages of frying in the same study.

Of the eight volatile compounds that produced a deep-fried odor in olfactometry analyses of OOO and LLL, this odor was detected in seven peaks [except (*E,E*)-2,4-undecadienal] in LLL and in four [2-octenal, (*E,E*)-2,4-nonadienal, (*E,E*)-2,4-decadienal, and (*E,E*)-2,4-undecadienal] in OOO. All intensities were <5 (weak to moderate odor intensity) in OOO but primarily in the moderate to strong (4–10) intensity range for LLL (Figure 2). This information helps to explain why higher linoleic acid containing oils such as sunflower and cottonseed produce fried foods with high levels of deep-fried flavor, whereas oils with higher amounts of oleic acid have diminished levels of this flavor. Odors and flavors such as fruity, waxy, and plastic are more prevalent in high-oleic oils (12). Neff et al. (34) explained this on the basis of high levels of volatile compounds found in heated OOO such as 2-nonenal and 2-decenal that produced plastic and fruity odors. Other researchers have reported odors in oxidized lipids. Belitz and Grosch (30) and Badings (31) reported frying odor only from (*E,E*)-2,4-decadienal, (*E,Z*)-2,4-decadienal, and (*E,Z*)-2,4-heptadienal. Belitz and Grosch (30) reported odors described as fatty from (*E*)-2-heptenal, (*E*)-2-octenal, and (*E,E*)-2,4-nonadienal with no reports on the other compounds identified as having a deep-fried odor in this study. Badings (31) reported a cardboard odor from (*E,E*)-2,4-octadienal. The discrepancies from the studies could be attributed to the lack of familiarity with frying odors or perhaps to differences in experiences and/or training.

The unpredicted dienals occurred at very low levels in OOO, and these compounds produced lower intensities of deep-fried odor in comparison to LLL. 2,4-Octadienal, 2,4-nonadienal, and 2,4-decadienals were produced in LLL, but no 2,4-undecadienal was detected. These dienals, except 2,4-decadienal, are unexpected from linoleic acid and trilinolein (23, 25). Thompson et al. (14) reported 133 volatile compounds in heated LLL including predominant aldehydes *trans*-2-heptenal, *trans*-2-octenal, (*E,E*)-2,4-nonadienal, and (*E,E*)-2,4-decadienal. Ninety-two volatile compounds were detected in heated OOO with predominant aldehydes *trans*-2-decenal and *trans*-2-undecenal by Chang et al. (4). Nawar (32) reported 2-decenal and *trans*-2-undecenal as primary aldehydes in olive oil with its higher levels of oleic acid.

Volatile Compound Precursors. Dimer, epoxy, keto, and OOH fractions obtained by preparative HPLC of OOO and LLL heated for 6 h were thermally decomposed, and volatile compounds were analyzed for peak size, odor attributes, and odor intensities. The nonvolatile degradation products (OOH, keto, epoxy, and dimeric triacylglycerol compounds) from OOO and LLL produced a total of six volatile compounds [(*E,E*)-2,4-decadienal, (*E*)-2-heptenal, (*E*)-2-octenal, (*E,E*)-2,4-nonadienal, (*E,E*)-2,4-octadienal, and (*E,E*)-2,4-undecadienal] described as having a deep-fried odor (Table 3). (*E*)-2-Heptenal and (*E,E*)-2,4-octadienal were not detected in any of the fractions of heated OOO. Amounts of volatile compounds differed slightly among the OOH, keto, epoxy, and dimer fractions. The same compounds that produced a deep-fried odor in the unfractionated samples were the same as in the four fractions; however, (*E,Z*)-2,4-decadienal and (*E,Z*)-2,4-nonadienal that had a deep-fried odor in OOO and LLL did not have a detectable odor in the fractions. Volatile compounds were also in higher concentrations, with the exception

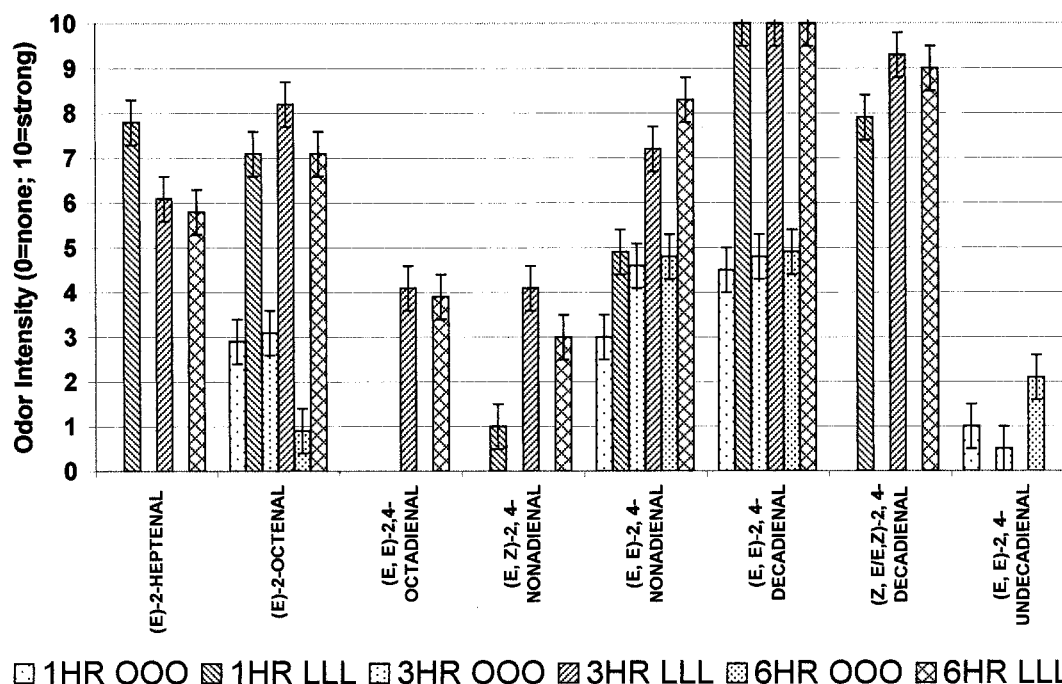


Figure 2. Intensity levels of deep-fried odor from alkenals and alkadienals in triolein (OOO) and trilinolein (LLL) heated for 1, 3, and 6 h at 190 °C.

Table 3. Volatile Compounds (Parts per Million) Producing Deep-Fried Odor from OOO and LLL Heated for 6 h at 190 °C and Fractionated

volatile compound	OOH		keto		epoxy		dimer	
	OOO	LLL	OOO	LLL	OOO	LLL	OOO	LLL
(<i>E</i>)-2-heptenal	0.0	155.7	0.0	144.8	0.0	126.8	0.0	133.7
(<i>E</i>)-2-octenal	0.5	83.2	0.1	73.5	0.1	67.1	0.1	87.9
(<i>E,E</i>)-2,4-octadienal	0.0	1.6	0.0	1.0	0.0	1.0	0.0	0.8
(<i>E,E</i>)-2,4-nonadienal	3.5	12.9	3.3	13.7	0.0	12.3	0.0	23.2
(<i>E,E</i>)-2,4-decadienal	9.2	487.7	0.7	334.6	6.4	317.3	5.7	126.2
(<i>E,E</i>)-2,4-undecadienal	0.1	0.0	0.2	0.0	0.1	0.0	0.1	0.0

of (*E,E*)-2,4-decadienal, in the fractions compared to the unfractionated samples. The fractions of LLL had greater amounts of volatile compounds producing a deep-fried odor than in the OOO fractions with the highest concentration from the OOH fraction for both OOO and LLL. Many of these aldehydes can be produced by beta scission about carbons of hydroperoxy, keto, and epoxy groups (21) or may be produced by a hyperoxidation mechanism (Figure 1). 2,4-Decadienal, which produced a deep-fried odor, was produced by each of the fractions, OOH, keto, epoxy, and dimer. Other volatiles, which produced deep-fried odor such as 2,4-nonadienal and 2,4-octadienal, were also produced in these same fractions of LLL. The epoxy, keto, and OOH fractions of LLL produced large parts per million levels of 2,4-decadienal, whereas only 126 ppm was produced by the dimer fraction. The OOH fraction produced the most volatiles from both OOO and LLL, and the amounts decreased in order with keto, epoxy, and dimer fractions from LLL. (*E,E*)-2,4-Nonadienal was not detected in the epoxy and dimer fractions of OOO (Table 3). 2,4-Undecadienal was not detected in the epoxy fraction of OOO after thermal decomposition.

The intensities of deep-fried odor detected in the volatile compounds produced from the four fractions varied significantly between OOO and LLL; however, significant differences were noted only for 2-octenal among fractions of LLL (Figure 3). Of the six volatile compounds listed in Figure 3, 2-heptenal and (*E,E*)-2,4-

octadienal did not produce any deep-fried odor from any fraction of OOO and (*E,E*)-2,4-undecadienal produced no deep-fried odor from any fraction of LLL. Nonvolatile compounds formed mainly from the oxidation of the triacylglycerol were the sources of the volatile compounds producing deep-fried odor in heated OOO and LLL. Proposed formation mechanisms of the major volatile compounds include thermal and acid-catalyzed decomposition of nonvolatile precursors by homolytic and heterolytic cleavage, respectively, of the initial 8-, 9-, and 11-monohydroperoxides of OOO and the 9-, 10-, 12-, and 13-monohydroperoxides of LLL, which exist briefly at frying oil temperature (21, 24). Also, these hydroperoxides decompose to secondary epoxy, keto, and dimer and other nonvolatile compounds at frying oil temperatures (23, 25). Many of these secondary products were identified on-line by RP-HPLC/APCI-MS of heated OOO (20) and LLL (Neff, unpublished work). The detection of OOH in the heated OOO and LLL might be unexpected because OOH should decompose upon formation at 190 °C to produce volatile compounds and more heat-stable compounds such as the epoxy, keto, hydroxy, aldehydic, and higher molecular weight compounds (21). The OOH were probably formed as the triacylglycerols cooled below 100 °C after heating, which is typical in intermittent frying rather than continuous frying (21, 33) and could help to explain why intermittent frying is more deleterious to the oil than continuous frying.

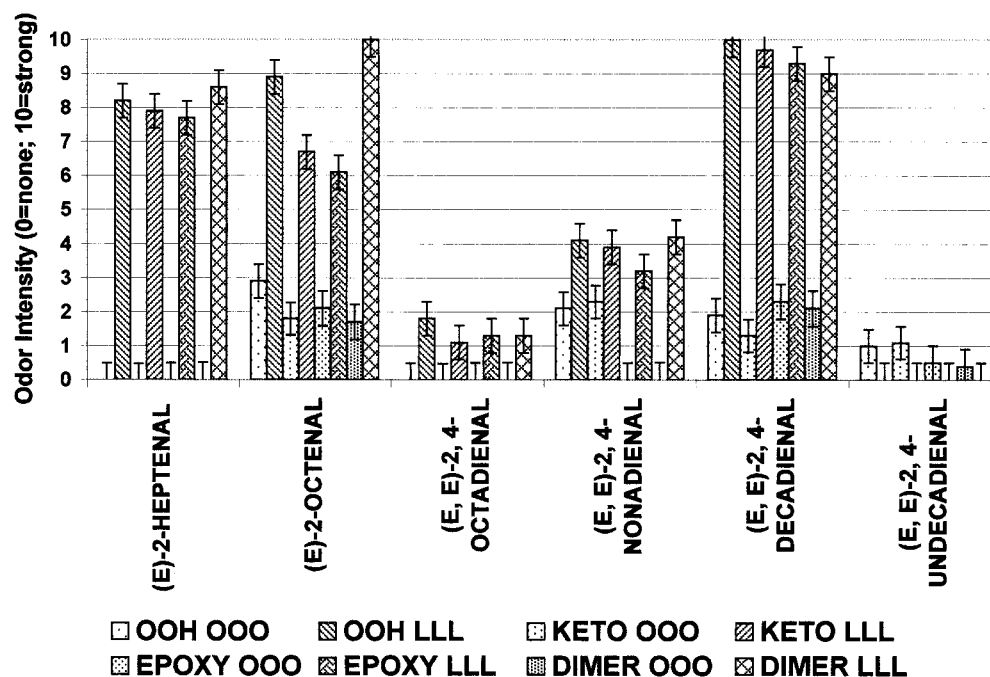


Figure 3. Intensity levels of deep-fried odor from alkenals and alkadienals in triolein (OOO) and trilinolein (LLL) heated for 6 h at 190 °C and fractionated.

Table 4. Volatile Precursor Compounds^a (ELSD Area Percent)^b from OOO and LLL after 1, 3, and 6 h of Heating at 190 °C

volatile precursor	hours at 190 °C					
	1		3		6	
	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 identified by HPLC coupled with MS-APCI.

^b Semiquantitation of heated triolein and trilinolein by RP-HPLC with ELSD.

Quantitation of Volatile Compound Precursors.

Amounts of nonvolatile decomposition products in OOO and LLL are shown in Table 4. Total monomeric products decreased and total high molecular weight products increased with heating time. By 6 h, the higher molecular weight products were the predominant source of volatile compounds. Monomeric OOH from OOO and LLL were in greatest amounts at 1 h but decreased with increasing time. However, the total secondary oxidation products increased with heating time, indicating that the OOH not only produced volatile compounds but also were a source of increasing amounts of secondary products with increased heating time. Monomeric keto products from OOO were at a high level at 1 h and decreased with time; however, the same fraction produced in LLL remained at the same low level at all times. Amounts of dimer and monomeric epoxy products from OOO were constant, but the same products from LLL increased slightly with time.

Conclusion. Seven volatile compounds, (*E,E*)-2,4-decadienal, (*E*)-2-heptenal, (*E*)-2-octenal, (*E,Z,Z,E*)-2,4-decadienal, (*E,E*)-2,4-octadienal, (*E,E*)-2,4-nonadienal, and (*E,Z*)-2,4-nonadienal, produced a deep-fried odor detected in olfactometry analyses for heated LLL;

however, the odor was detected only from four compounds, (*E,E*)-2,4-decadienal, (*E*)-2-octenal, (*E,E*)-2,4-nonadienal, and (*E,E*)-2,4-undecadienal, in heated OOO. 2,4-Decadienal and 2-heptenal were formed directly from the decomposition of linoleic acid and produced strong intensities of deep-fried odor, but the unpredicted aldehydes were possibly produced by hydroperoxidation and/or by hydroxylation followed by dehydration of 2-alkenals. The 2-alkenals were produced from thermal decomposition of hydroperoxides, epoxides, keto, and dimeric compounds produced during heating of OOO. These aldehydes produced low intensities of deep-fried odor in OOO. This information helps to explain sources of the deep-fried flavor that is characteristic of high-linoleic frying oils but which is at only low intensity levels in high-oleic frying oils.

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