

Volatile Components from Triolein Heated in Air¹

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ABSTRACT AND SUMMARY

In a continuing study to identify volatile odor constituents and their precursors from heated soybean oil, the following model triglycerides were heated to 192 C in air for 10 min: (a) pure triolein, (b) a mixture of triolein (25%)-tristearin, and (c) a randomly esterified triglyceride composed of oleic (25%) and stearic acids. Each model system produced the same major compounds which were identified as heptane, octane, heptanal, octanal, nonanal, 2-decenal, and 2-undecenal. These seven compounds apparently are unique to the oxidation of the oleate fatty acid in each triglyceride sample. Minor volatile compounds from oxidized triolein included saturated and unsaturated aldehydes and *n*-hydrocarbons and saturated primary alcohols, methyl ketones, gamma lactones, and monobasic acids. Incorporation of stearic acid in the triglycerides noticeably increased the amounts of saturated minor compounds and the range of their carbon chain lengths. Decomposition products characteristic of the oxidation of stearate were apparent among decomposition products associated with the oxidation of oleate.

INTRODUCTION

Oxidation of oleic acid and its ester derivatives has been under investigation for many years. Up until the mid 1940s, those investigations focused on the mechanism(s) of oxygen addition to the monounsaturated molecules and on the primary oxidation products—hydroperoxides (1). Thereafter, the investigations shifted to hydroperoxide decomposition and the secondary oxidation products formed. Although the secondary decomposition products included many classes of compounds, the studies covered mainly aldehydes probably because they are major odor and flavor constituents of oxidized fats, and because aldehydes are easily characterized via their 2,4-dinitrophenylhydrazine (DNPH) derivatives. The major carbonyl compounds predicted from the decomposition of the four oleate isomeric hydroperoxides, where the OOH substituent is located at the 8, 9, 10, and 11 carbon atom position, are octanal, nonanal, 2-decenal, and 2-undecenal (2a,2b). The presence of those four aldehydes in oxidized lipids containing the oleate unsaturation has been well documented (2-11). Aliphatic aldehydes identified but not expected from the oxidation of oleic acid and its ester derivatives are C 2-7 alkanals and C 6-9 2-alkenals (2-5,7-11). The "unexpected" alkanals may be attributed to oxidation-decomposition of higher to lower molecular weight aldehydes (2c,10,12-15), but no experimental evidence has been reported which might indicate the immediate precursors of the C 6-9 2-alkenals.

In addition to aldehydes, other volatiles identified from oxidized oleate include: mono- and dibasic acids (9,16,18), methyl ketones (9,19), fatty acid esters (7,9,10), *n*-alcohols (4,9,10), gamma and delta lactones (9,17), and hydrocarbons (4,9,10,19). Many of these compounds plus the alkanals and 2-alkenals are suspected of contributing odors and flavors to oxidized lipids (2,8). Even though seven classes of compounds have been identified from oxidized oleate, most of the studies were limited to the identifica-

tion of volatiles in only one or two classes of compounds. Relative odor and flavor significance of each oleate volatile could be better assayed if their relative proportions were known, i.e., all the volatiles collected, separated, and identified during one analysis.

This paper is part of a continuing study to characterize volatile compounds (room odors) which develop when soybean oil (SBO) is heated to cooking oil temperature (20). To pursue that objective, each major fatty acid of SBO, as its pure and mixed triglyceride, is heated to cooking oil temperature and the resulting volatiles are collected and identified. This approach of volatile analysis using individual pure compounds intensifies the less concentrated SBO volatile compounds—thus aiding in their identification—and may possibly establish each volatile's fatty acid precursor(s). A previous report described the identification and quantitation of volatiles from heated tristearin (21). This study covers the identification of volatiles from heated pure triolein, randomly esterified oleo-stearin and a mixture of triolein-tristearin. The synthesized and mixed triglycerides were prepared to determine if both triglyceride systems quantitatively and qualitatively produced the same volatiles. The oleic content in the mixed and synthesized triglycerides was chosen to be comparable to that found in SBO, so that in parallel experiments involving oleic and other major SBO fatty acids the level of the oleate volatiles may be anticipated.

EXPERIMENTAL PROCEDURES

Pure triolein was purchased from the Nu-Chek-Prep., Inc. (Elysian, MN), and deodorized at 1 mm pressure for 1.5 hr at 185-220 C prior to use. The randomly esterified triglyceride (oleo-stearin) was prepared from oleic acid (Hormel, Austin, MN), stearic acid (Matheson-Coleman and Bell, Norwood, OH), glycerine, and an esterification catalyst paratoluene sulfonic acid—according to Wheeler et al. (22). The synthesized triglyceride was purified by liquid-solid (Silica Gel) chromatography, then deodorized as above. The mixed triglyceride was prepared by adding triolein (Hormel) to tristearin (Anderson Clayton Foods, Jacksonville, IL) which was previously purified by crystallizing three times in acetone. This third model triglyceride was also deodorized as above.

Fatty acid compositions [by gas liquid chromatography (GLC)] of each of the three model triglycerides were as follows: pure triolein (Nu-Chek-Prep, Inc.)—98.9% oleic, 0.7% stearic, 0.1% palmitic, 0.1% linoleic, and 0.2% linolenic; esterified oleo-stearin—25.2% oleic, 72.5% stearic, and 2.3% palmitic; mixed triolein (Hormel)-tristearin—26.5% oleic, 66.2% stearic, and 7.3% palmitic. Double bond locations (by reductive ozonolysis) (23) were as follows: pure triolein—>99.5% at the delta 9 carbon position, a trace at the delta 12 position; both the esterified oleo-stearin and the mixed triolein-tristearin—100% at the delta 9 position. None of the three model triglycerides had any detectable isolated *trans* (by infrared—isolated *trans* absorption at 926 cm⁻¹), free fatty acids (by titration with NaOH), or mono- or diglycerides [by thin layer chromatography (TLC)-precoated-0.25 mm thick-Silica Gel TLC plates developed in petroleum ether-diethyl ether-acetic acid mixture 70:25:5].

Specific details of the volatile collection and analysis procedure have been reported (20,21). Briefly, 2 cc of each model triglyceride was heated at 192 C in a stainless-steel

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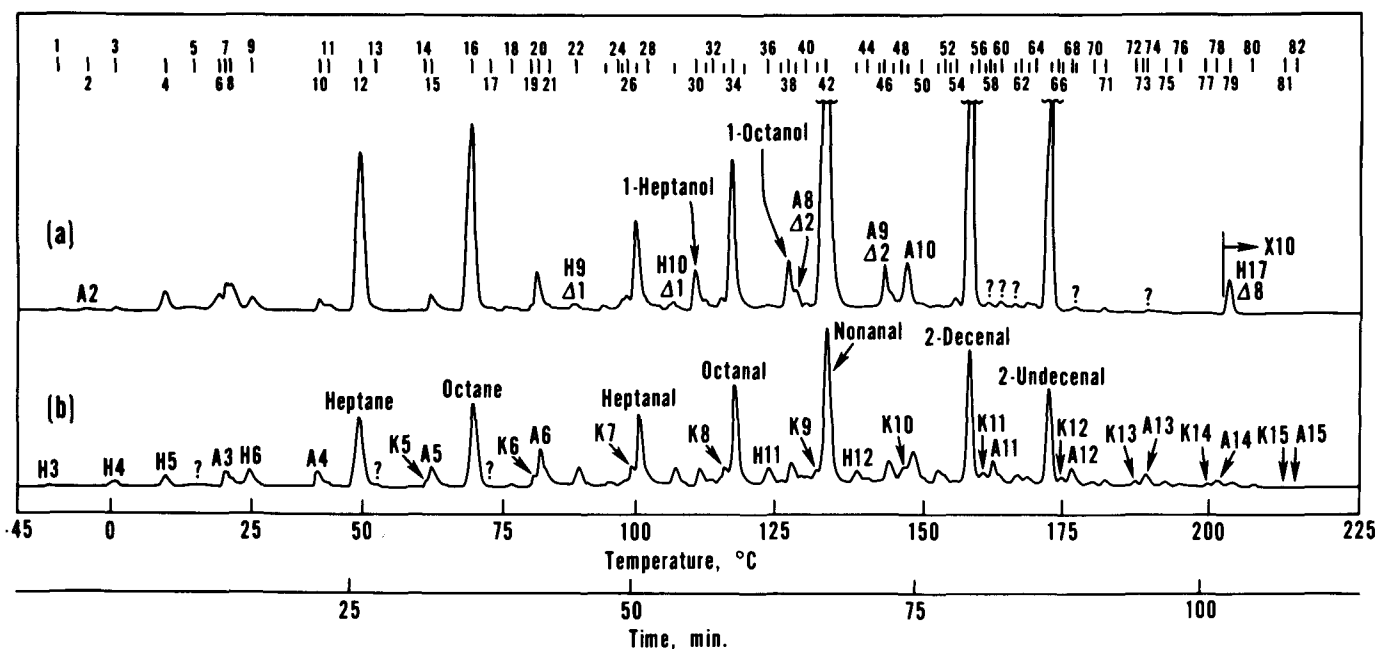


FIG. 1. Gas chromatogram of volatile compounds from thermally oxidized triolein (curve a) and randomly esterified oleo-stearin (curve b). Numbers 1-82 relate to GC peaks in both curves. H = hydrocarbons; A = aldehydes; K = methyl ketones; numbers adjacent to letters indicate number of carbon atoms in compound. $\Delta 1$ = unsaturated in the 1 position, etc. The following GC peaks were the result of unresolved but identified compounds: Curve "a," peak 34—octanal and hexanoic acid; curve "b," peaks 22—nonane and 1-nonene; 29—decane, and 1-decene; 34—octanal and hexanoic acid; and 79—heptadecane and heptadecene.

container for 10 min. During each of the 10-min heating periods, volatiles generated from the hot oils were continually swept out of the container with air and collected directly on a gas chromatograph (GC) column (glass—14 ft X 4 mm ID column, packed with 10% OV-17 on Chromosorb G) cooled to -60 C. Subsequently, the volatiles were separated by temperature programming (nonlinear from -60 C to 0 C then 2 C/min to 250 C) and as they eluted off the GC column they were simultaneously monitored by a flame ionization detector, by smelling at the GC exit port and by a mass spectrometer (MS) (nuclide 12-90 double focusing-magnetic scanning) set to scan from m/e 10 to 450 every 9 sec. Output of the MS was fed to a computer for later processing. Volatiles were identified from their mass spectra and the identifications confirmed by comparing GC elution temperatures of the volatiles with those of authentic compounds. Elution temperatures were experimentally determined for each volatile except where noted. In those cases elution data was ascertained by extrapolating data of homologous compounds.

The above computer processing of MS data has recently been modified; therefore, a more in depth description of that procedure will be given. After each completed GC/MS analysis, the stored MS data is processed by the computer to give a total ionization (TI) curve. That curve is obtained by summing all the m/e peak intensities in each MS scan and plotting that total intensity value against its scan number. Since the TI curve closely resembles the volatile GC, each 9-sec scan can be directly associated with its corresponding position on the volatile GC curve. Therefore, inspecting the TI curve will reveal which MS scans contain spectra of any particular volatile (GC peak) of interest. To identify a volatile, its mass spectrum is displayed on an oscilloscope screen by selecting the proper MS scan number (from TI curve) and entering that number in a computer program. Visual inspection of the spectrum will indicate if subtraction of background (mass spectra of water, air, or GC column bleed-off) or mass spectra of prior eluted volatiles would enhance the quality of the displayed spectrum. The unknown spectrum is then compared (by computer) to over 35,000 known spectra and up to 13

favorable comparisons (names of compounds), along with 13 similarity indexes, can be listed on a print-out sheet. The similarity index indicates how well the unknown spectrum matches a particular known spectrum. The unknown's mass spectrum is then manually inspected and compared against the mass spectra of those compounds listed on the print-out sheet for positive identification. At times none of the listed compounds correspond to the unknown and at other times no compounds are even listed on the print-out sheet; under those circumstances, manual interpretation of the unknown spectrum is attempted. Fortunately, standard mass spectra were available in our library of standard spectra as well as in the literature for each of the identified compounds, except in one instance.

During the identification procedure, the technique of mass chromatography (MC) is frequently used to determine which GC peaks may be the result of unresolved compounds and which GC peaks may be the result of a homologous series of compounds. The MC technique utilizes the TI curve and superimposes upon it a plot of the intensity of any chosen m/e ion in each scan vs scan number. The superimposed MC curve can be thought of as a chromatogram from a unique GC detector which is sensitive only to one preselected m/e ion. Generally, the chosen m/e ion will be characteristic of a particular compound or class of compounds. For example, by choosing the m/e 44 ion, characteristic of aliphatic n -aldehydes, the presence and position in the gas chromatogram of those compounds which contain the aldehyde function can be ascertained. Comparable information is obtained for primary alcohols, methyl ketones, aliphatic acids, and gamma lactones by choosing m/e ions of 31, 58, 60, and 85, respectively. If two or more of the characteristic m/e ion plots show maxima under the same TI curve peak, then the TI peak (GC peak) may be the result of unresolved compounds. If any one of the characteristic m/e ions show maxima under more than one TI curve peak, than a homologous series of compounds may be present. Knowledge of unresolved compounds or of the presence of a homologous series of compounds can be an aid in the identification of unknown volatiles.

Volatile peak areas were integrated by our GC-computer system. Individual peak areas were then adjusted to compensate for the particular volatile's number of ionizable carbon atoms and its molecular weight. The combined corrected areas were subsequently normalized to give relative weight percent values. Details of the integration system and method of calculations has been described previously (21).

RESULTS AND DISCUSSION

Thermal oxidation of triolein produced 61 volatile compounds which consisted of saturated and unsaturated aldehydes and hydrocarbons, saturated primary alcohols, aliphatic acids, methyl ketones, gamma lactones, and 13 unidentified compounds. The gas chromatogram of those volatiles can be noted in Figure 1, chromatogram "a," and the identified compounds plus their relative GC peak areas are listed in Tables I-III. It is apparent from curve "a" that heating triolein to 192 C in air results in the formation of seven major volatile components which were identified from their mass spectra as heptane, octane, heptanal, octanal, nonanal, 2-decenal, and 2-undecenal. Those compounds, as shown in Table II, contributed 82% to the total GC peak area. Of these seven compounds, octanal, nonanal, 2-decenal, and 2-undecenal, have been previously noted as the principal decomposition products from oxidized oleic acid and its derivatives (2a,3-11), even when oxidation temperatures ranged from ambient to 200 C and decomposition was induced by heat, metals, and acids. In a number of the investigations, as in this study, the C-8, C-9, Δ^2 C-10, and Δ^2 C-11 aldehydes were found in different relative concentrations, generally C-9 > C-8 > Δ^2 C-10 > Δ^2 C-11, with nonanal almost exclusively being the dominant component.

Most of the oleate oxidation-volatile identification studies were limited to the analyses of aldehydes; very few studies included the identification of compounds in other compound classes, e.g., hydrocarbons. This probably was the consequence of more stringent methods required to analyze hydrocarbons; hydrocarbons contribute only a small portion to the total volatile fraction, and perhaps because of the questionable odor and flavor contributions, hydrocarbons—especially saturated *n*-hydrocarbons—impart to oxidized oils. Of the oleate-hydrocarbon formation studies reviewed (4,9,10,14,19), none included quantitative data on the hydrocarbons collected and identified nor suggested their immediate precursors. However, the studies did show that both heptane and octane were associated with the hydrocarbon fraction in the oleate volatiles. This latter information agrees with the results of this study which shows that in addition to the five major aldehydes, heptane and octane are also principal degradation products from oxidized oleate.

Along with the seven major compounds, 54 minor volatiles were also produced during thermal oxidation of triolein. Those 54 constituents consisted of 41 identified and 13 unidentified compounds. Names of the 41 identified compounds are listed in Table I along with their individual peak areas. In Table III those minor volatiles are grouped together in chemical compound classes and as shown are represented as homologous series in six classes: aldehydes, methyl ketones, hydrocarbons, primary alcohols, aliphatic acids, and gamma lactones. In both the major and minor compounds the aldehydes are the predominant class of volatiles. Among the minor volatiles, the primary alcohols are the second most abundant class of compounds. That is mainly due to the contributions of heptanol and octanol. As can be noted in Table I, heptanol and octanol contribute almost the entire amount (4.1%) to the total quantity (4.6%) of the triolein alcohols. A similar correlation exists

among the hydrocarbons where heptane and octane contribute 18.3% of the total (20%) triolein hydrocarbon fraction.

It may be just a coincidence that carbon chain lengths of predominant compounds in the hydrocarbon and alcohol fractions are the same, or perhaps there is some sort of a relationship between the four volatiles, e.g., their precursors and formation mechanism may be similar.

The 13 unknown minor volatiles—GC peaks 5, 13, 17, 24, 25, 32, 35, 50, 58, 60, 61, 69, and 74 in Figure 1—had insufficient concentrations to provide identifiable mass spectra; in addition, their low concentrations resulted in small GC peaks which, when combined, contributed less than 1% to the total integrated GC peak areas.

Two minor volatiles identified but not included in Table III are chloroform and 2-methyl pentane. Chloroform, GC peak 11 in Figure 1, an apparent contaminant, was found among volatiles from all three model triglycerides. Whereas, 2-methyl pentane, GC peak 6 in curve "a" of Figure 1, was found only among volatiles from heated triolein. Why the branched hydrocarbon was not also found among the volatiles from the other two oleate containing triglycerides is not known.

The triolein data in Table I show, with one exception—heptadecene, that the carbon chain lengths of the major or minor volatiles do not exceed 11 carbon atoms. This indicates that 192 C oxidation of triolein produces no apparent positional double bond movement beyond that due to the formation of the oleate 9 or 10 hydroperoxide (2a,2b). If positional isomerization had occurred, then in addition to the observed C-7 to C-9 2-alkenals, other 2-alkenals with carbon chain lengths of 12 or more carbon atoms would have been present. Since there is no reason to believe that oleate double bond isomerization would not occur equally in both directions from the original Δ^9 position, absence of 2-alkenals in either the 9 and less or the 12 and more carbon atom ranges preclude any isomerization at all. Therefore, the absence of C-12 and longer 2-alkenals suggests that no double bond isomerization occurred and that the observed C-6 to C-9 2-alkenals probably originated from secondary oxidation reactions (12,14). The only long carbon chain compound observed was heptadecene, tentatively identified as 8-heptadecene (peak 79 in Fig. 1). That compound may be formed by the decarboxylation of oleic acid formed by hydrolysis under our experimental conditions. Undoubtedly a parallel reaction occurs when stearic acid is incorporated in the triglyceride, since heptadecane was identified among the volatiles from the two stearate-containing triglycerides as well as from heated (192 C) tristearin (21).

Data in Tables I and II show 2-decenal and 2-undecenal are each associated with two sets of GC peaks in curves "a" and "b" of Figure 1. This is very likely the result of GC separation of the geometric isomers of the Δ^2 C-10 and C-11 aldehydes. Unpublished results demonstrated that our OV-17 pack GC column efficiently separates various geometric isomers of unsaturated aldehydes, e.g., *trans*-2, *cis*-4-decadienal from *trans*-2, *trans*-4-decadienal. According to Badings (8), oxidation of oleic acid and its ester derivatives produce predominantly the *trans* isomers of the C-10 and C-11 2-alkenals. Therefore, the small GC peaks 54 and 64 in curves "a" and "b" are probably due to the *cis* isomers of 2-decenal and 2-undecenal, and the large GC peaks 55 and 65 are probably due to the *trans* isomers of the two aldehydes.

Our OV-17 GC column did not resolve all the volatiles from the three heated model triglycerides as efficiently as it did the above mentioned isomeric 2-alkenals. In curve "a" of Figure 1, GC peak 34 was due to octanal and hexanoic acid, and in curve "b" unresolved volatiles were: nonane and 1-nonene—peak 22, decane and 1-decene—peak 29,

TABLE I

Compounds Identified in Collected Volatiles from Heated (192 C) Triolein, Esterified Olein-Stearin, and Tristearin (Weight %)

Peak no. in GLC (Fig. 1) ^a	No. carbon atoms	Triolein ^{b,c} pure	Esterified ^b olein-stearin	Tristearin (21) pure
<i>n</i> -Aldehydes				
2	2	0.2	Trace	ND
7	3	0.2	1.8	0.4
10	4	0.2	1.3	1.8
15	5	0.9	2.4	3.6
20	6	1.9	3.6	4.8
27	7	5.1	6.4	4.8
34	8	8.5	8.6	4.6
42	9	22.3	15.0	4.4
49	10	2.8	3.4	4.0
59	11	ND ^d	1.7	3.2
68	12	ND	1.3	2.1
73	13	ND	0.8	1.2
78	14	ND	0.5	0.7
82	15 ^e	ND	Trace	0.3
Subtotal		42.1	46.8	35.9
Δ 2-Aldehydes				
8	3	0.2	0.4	ND
31	7	0.1	0.4	ND
39	8	0.5	0.3	ND
46	9	2.1	1.4	ND
54	10- <i>cis</i> ?	0.4	0.1	ND
55	10- <i>trans</i> ?	16.1	9.4	ND
64	11- <i>cis</i> ?	Trace	0.1	ND
65	11- <i>trans</i> ?	11.1	6.5	ND
Subtotal		30.5	18.6	0.0
<i>n</i> -Hydrocarbons (anes and enes)				
1	3 ^e	Trace	0.1	ND
3	4 ^e	0.1	0.4	0.4
4	5	0.6	0.6	0.5
9	6	0.4	1.4	0.2
12	7	8.6	6.0	0.5
16	8	9.7	6.2	0.6
22	9	ND		0.9
22	9 Δ 1	0.2	1.1	ND
29	10	ND		0.9
29	10 Δ 1	0.3	1.2	ND
36	11	ND	1.0	0.6
43	12	ND	0.8	0.5
51	13	ND	0.8	0.6
62	14	ND	0.5	0.4
70	15	ND	0.1	0.4
75	16	ND	0.2	0.2
79	17	ND		2.1
79	17 Δ 8? ^f	0.1	0.3	
Subtotal		20.0	20.7	8.8
Primary <i>n</i> -alcohols				
18	5	0.1	Trace	0.2
23	6	0.3	0.2	0.3
30	7	1.6	1.6	0.3
38	8	2.5	1.6	0.4
45	9	0.1	0.1	0.5
53	10	ND	Trace	0.4
Subtotal		4.6	3.5	2.1
Methyl ketones				
14	5	ND	0.2	2.4
19	6	0.1	0.5	3.6
26	7	0.4	1.1	4.6
33	8	0.3	1.1	4.3
41	9	ND	0.7	4.9
48	10	ND	1.1	4.5
57	11	ND	0.6	3.8
67	12	ND	0.4	2.6
72	13	ND	0.2	1.5
77	14	ND	0.1	0.6
81	15 ^e	ND	Trace	0.2
Subtotal		0.8	6.0	33.0

TABLE I (continued)

Compounds Identified in Collected Volatiles from Heated (192 C) Triolein, Esterified Olein-Stearin, and Tristearin (Weight %)

Peak no. in GLC (Fig. 1) ^a	No. carbon atoms	Triolein ^{b,c} pure	Esterified ^b olein-stearin	Tristearin (21) pure
<i>n</i> -Aliphatic acids				
21	4	Trace	0.1	2.4
28	5	Trace	0.2	2.4
34	6	0.1	0.5	2.5
40	7	0.1	0.5	1.1
47	8	0.3	0.6	0.7
56	9	0.6	0.3	0.3
66	10	0.1	Trace	0.1
Subtotal		1.2	2.2	9.5
Gamma lactones				
37	5	Trace	0.2	0.6
44	6	Trace	0.4	0.4
52	7 ^e	0.2	0.5	0.5
63	8	0.4	0.5	0.4
71	9 ^e	0.2	0.4	0.4
76	10	ND	0.1	0.3
80	11	ND	0.1	0.3
Subtotal		0.8	2.2	2.9
Total		100.0	100.0	92.2

^aApplicable only to volatiles derived from triolein and esterified olein-stearin. GLC = gas liquid chromatography.

^bGas chromatography (GC) peak no. 11 is HCCl_3 , a solvent used to clean the deodorization apparatus, and GC peak nos. 5, 13, 17, 24, 25, 32, 35, 50, 58, 60, 61, 69, and 74 are unknowns; all were present in volatiles derived from triolein, the esterified and the mixed triglycerides. Neither chloroform nor the unknown GC peak areas are included in the weight percent calculations.

^cGC peak no. 6 is 2-methyl pentane which was found only in volatiles from heated triolein. Its area is not included in the weight percent calculations.

^dND = none detected.

^eIdentification based on comparison of mass spectra with those of standards, but their GC elution temperatures were compared to retention data extrapolated from available homologous compounds.

^fNo 8-heptadecene standard mass spectrum available, tentative identification based on manual interpretation of its spectrum and on agreement of its elution temperature with those of extrapolated elution data.

TABLE II

Major Volatiles Derived from Heated (192 C) Model Triglycerides

Compounds identified	Peak no. in GLC (Fig. 1) ^a	Triolein pure		Olein-stearin randomly esterified		Triolein-tristearin mixed	
		Weight (%)	Relative (%)	Weight (%)	Relative (%)	Weight (%)	Relative (%)
Heptane	12	8.6	10.5	6.0	10.3	5.2	9.1
Octane	16	9.7	11.8	6.2	10.6	6.1	10.7
Heptanal	27	5.1	6.2	6.4	11.0	6.3	11.1
Octanal	34	8.5	10.4	8.6	14.8	8.9	15.6
Nonanal	42	22.3	27.3	15.0	25.7	14.3	25.1
2-Decenal ^b	54,55	16.5	20.2	9.5	16.3	9.8	17.2
2-Undecenal ^b	64,65	11.1	13.6	6.6	11.3	6.4	11.2
		81.8	100.0	58.3	100.0	57.0	100.0

^aApplicable only to volatiles derived from triolein and esterified olein-stearin. GLC = gas liquid chromatography.

^bPercent values calculated from the combined areas of the *cis*? (GC peaks 54, 64) and *trans*? (GC peaks 55, 65) isomers.

octanal and hexanoic acid—peak 34, and heptadecane and heptadecene—peak 79. Although these pairs of compounds eluted as single peaks, the compounds were identified from their mass spectra and confirmed by comparing their GC elution temperatures with those of authentic compounds by the procedure described in the Experimental Procedures section.

When stearic was included along with oleic acid in two of the model triglycerides, the number of heated oil volatiles increased from 61 (pure triolein) to 85 compounds. The increased number of volatiles, all among the minor constituents, undoubtedly are derived from the oxidation-decomposition of the stearate fraction in the glycerides. Of the 85 compounds, 72 have been identified (Tables I-III). The 13 unidentified compounds appear to be

the same ones encountered from heated triolein (same GC retention times). Here, too, they contributed less than 1% to the total integrated GC peak area.

The GC pattern of volatiles from the heated esterified olein-stearin sample can be noted in curve "b" of Figure 1. Resemblance between curves "a" and "b" is primarily due to the GC peaks of the seven major compounds derived from the oxidation of the oleate fraction in each model triglyceride. These seven GC peaks are noticeably larger in curve "a" than in curve "b" probably because of the different oleate concentrations in each sample—100% in curve "a" and 25% in curve "b." Although the seven GC peak areas are considerably larger in curve "a," upon normalization, corresponding peaks in each set have the same approximate relative percent value as shown in Table II.

TABLE III
Minor Volatiles Derived from Heated (192 C) Model Triglycerides

Compounds identified	Triolein pure		Olein-stearin randomly esterified		Triolein-tristearin mixed	
	Carbon chain lengths	Weight (%)	Carbon chain lengths	Weight (%)	Carbon chain lengths	Weight (%)
Alkanals	C 2-6, 10	6.2	C 2-6, 10-15	16.8	C 2-6, 10-15	19.1
2-Alkenals	C 3, 7-11 ^a	3.4	C 3, 7-11	2.7	C 3, 7-11	2.9
Methyl ketones	C 6-8	0.8	C 5-15	6.0	C 5-15	7.5
Hydrocarbons						
anes	C 3-6	1.1	C 3-6, 9-17		C 3-6, 9-17	6.3
enes	C 9, 10, 17	0.6	C 9, 10, 17	8.5	C 9, 10, 17	
1-Alcohols	C 5-9	4.6	C 5-10	3.5	C 5-10	3.7
Aliphatic acids	C 4-10	1.2	C 4-10	2.2	C 4-10	1.8
Gamma-lactones	C 5-9	0.8	C 5-11	2.2	C 5-11	1.9
		18.7		41.9		43.2

^a2-Decenal and 2-undecenal, GC peaks 54 and 61 in chromatogram "a" and "b" of Figure 1 are probably the *cis* isomers.

The slightly higher weight and relative percent values for heptanal and octanal in the esterified data are attributed to perceptible amounts of heptanal and octanal produced from oxidized stearate. Aldehydes in the C 6-11 carbon atom range are the principal compounds produced from heated tristearin (21) (see last column in Table I). Decreases in the weight % values for heptane, octane, 2-decenal, and 2-undecenal reflect the increasing contributions of the minor volatiles to the total integrated area. Note in Table II that the seven major compounds contribute 82% of the total area of the triolein volatiles and only 58% of the total area of volatiles from the esterified or mixed model triglycerides.

Besides the obvious changes in the GC peak heights of the major volatiles, there are also qualitative differences between the two curves in Figure 1. Those differences involve the minor components (small GC peaks) and are more readily apparent in Table I and III than in Figure 1. Volatile compound listings in these tables show the stearate-oleate triglycerides produce not only minor volatiles common to triolein, but also new compounds as well. Most of these new compounds (aldehydes, methyl ketones, and *n*-hydrocarbons) have carbon chain lengths which range from C-11 to C-17 carbon atoms. These classes of compounds are the same as those which are the most abundant volatiles derived from heated tristearin (21) (see last column in Table I).

The heated mixed triolein-tristearin volatile GC curve is omitted from Figure 1 because the esterified and the mixed GC curves were nearly identical. This claim can be substantiated by noting the agreement in the data (Tables II and III) for the two model triglycerides. The correspondence between the esterified and mixed glyceride data exhibits the degree to which we are able to duplicate our results from one analysis to another. Similar agreement between volatile data was noted from duplicate analysis of heated tristearin volatiles (21). In addition, the correspondence between the two sets of data indicates that in future parallel studies there will be no need to follow the time-consuming esterification process to obtain model triglycerides composed of stearic and the unsaturated fatty acid under study. Simple mixing of model triglycerides, as was done with the triolein-tristearin sample, will be sufficient.

This study shows that triolein oxidizes at 192 C in air and produces volatiles consonant with those predicted from

the decomposition of the oleate 8, 9, 10, and 11 hydroperoxides; that major and minor volatiles are present which are not directly associated with the theoretical decomposition mechanism of the oleate 8, 9, 10, and 11 hydroperoxides; that under our experimental conditions stearate in a monoene-stearate glycerol system also produces volatiles along with those derived from oxidized oleate; that both the esterified and mixed model triglycerides oxidize and produce the same number, kind, and quantities of volatiles; and that we have close agreement of results from duplicate volatile analyses.

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