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☼ Volatile Components from Trilinolein Heated in Air

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ABSTRACT

Pure trilinolein and mixtures of trilinolein-tristearin, trilinolein-triolein, and trilinolein-triolein-tristearin were heated to 192 C in air. Volatiles were collected, separated, and identified by gas chromatography-mass spectrometry. Major volatiles observed from each heated sample produced compounds unique to the autoxidation-decomposition of the trilinolein component and included: pentane, acrolein, pentanal, 1-pentanol, hexanal, 2- and/or 3-hexenal, 2-heptenal, 2-octenal, 2,4-decadienal, and 4,5-epoxydec-2-enal. When samples containing both trilinolein and triolein were heated, volatiles were produced that could be ascribed to each triglyceride. However, heated mixtures containing tristearin produced no observable volatiles that could be related to the oxidized saturated triglyceride. Minor volatiles identified from the heated trilinolein and its mixtures included; aliphatic acids, saturated and unsaturated aldehydes, primary and secondary alcohols, gamma lactones, furans, hydrocarbons, and methyl ketones.

INTRODUCTION

Soybean oil, which has linoleic acid as its major constituent (51-55%), is an important source for cooking oils in domestic markets. However, the oil is less important in foreign markets where differences in culture backgrounds result in objections to its use. These objections arise from volatile compounds and resulting unfamiliar odors produced by heated soybean oil which we are currently investigating.

Linoleic acid and its esters have been examined extensively as oxidizable substrates to form hydroperoxides (1-4) and as precursors of volatile decomposition products (5-23). The emphasis on linoleic acid may be attributed to its relatively high susceptibility to oxidation, 10-100 times greater than that of monoene or saturated isologues (1,7,24), and to its greater abundance in edible fats and oils than the more reactive triene isologue (25). In the majority of the volatile decomposition studies, either a single class of compounds was isolated and analyzed or investigations centered on those volatiles (aldehydes and ketones) that formed 2,4-dinitrophenylhydrazine (DNPH) derivatives.

In contrast to prior approaches, excepting that of Thompson et al. (18), our research involves the collection and identification of *all* classes of volatiles that develop when soybean oil is heated to cooking oil temperature (185-200 C). To avoid the complications in results that would arise from a mixture of the unsaturated fatty acids in soybean oil, pure triglycerides of each of the major fatty acids of SBO are used for our heated oil-volatile compound study. Previously, we characterized volatiles from heated tristearin (26), triolein (27), and thermally decomposed methyl oleate hydroperoxides (28). This paper reports our results with trilinolein and various triglyceride mixtures containing trilinolein when heated to 192 C in air.

EXPERIMENTAL PROCEDURES

Trilinolein and triolein were purchased from the Nu-Check-Prep., Inc. (Elysian, MN). Thin layer chromatography (TLC), described below, indicated a slight impurity in the trilinolein but none in the triolein. The trilinolein was purified by liquid chromatography (Silica gel.— hexane solvent), whereupon the purified material had only a single spot on further TLC analysis. Triolein was deodorized at 1 mm pressure for 1.5 hr at 185-220 C prior to use. Tristearin was purchased from Anderson Claton Foods, Jacksonville, IL, purified by three recrystallizations from acetone, and deodorized as above.

Fatty acid compositions [by gas liquid chromatography (GC) of methyl esters prepared from the triglycerides] of each of the three model triglycerides were: purified trilinolein — 99.8% linoleic, 0.03% palmitic, 0.06% oleic, and 0.1% linolenic; triolein — 98.9% oleic, 0.7% stearic, 0.1% palmitic, 0.1% linoleic, and 0.2% linolenic; tristearin — 88.9% stearic and 11.1% palmitic. Neither trilinolein nor triolein had UV absorption at 233 mm (conjugated diene); however, trilinolein had 0.18% conjugated triene, calculated from absorption at 268 nm (29). None of the three model triglycerides contained isolated *trans* double bonds (no infrared isolated *trans* absorption at 962 cm^{-1} from prepared methyl esters), free fatty acids (by titration with NaOH), or mono- or diglycerides (by TLC, Kieselgel 60 F-254 precoated-0.25 mm thick-Silica Gel TLC plates developed in petroleum ether/diethyl ether/acetic acid mixture, 70:25:5).

A previous study (27) indicated that similar volatile profiles are obtained from the same fatty acid composition whether they are in the form of randomly esterified triglycerides or in the form of mixed pure triglycerides. Therefore, mixtures used in this study were prepared by mixing pure triglycerides in the following proportions: 1.15 g trilinolein (55%)-0.96 g tristearin (45%), 0.90 g trilinolein (55%)-0.75 g triolein (45%), and 1.36 g trilinolein (55%)-0.58 g triolein (23%)-0.54 g tristearin (22%).

Specific details of the volatile collection and analysis procedure have been reported (26,27). Briefly, 2 cc of trilinolein or each triglyceride mixture was heated to 192 C in a stainless steel container, frequently called a microroom or micro-fry-pan. During the subsequent 10 min heating period, volatiles generated from the hot oils were continuously swept out of the container with air and collected directly on a 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). As they eluted from the GC column, they were simultaneously monitored by a flame ionization detector, by smalling 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. The GC was coupled to the MS via a silicone rubber membrane separator. Output from the MS was stored in a computer system for later processing. Mass spectrometric identifications of volatile compounds, matched by computer with those of library reference compounds, were confirmed by GC retention data. Areas under GC peaks were integrated by a computer system which has been described previously (26).

RESULTS

Trilinolein

A total of 54 — 17 major and 37 minor — volatile compounds were collected from trilinolein oxidized at 192 C in air. The following is the composition of the volatiles by compound classes (numbers in parentheses show number of compounds in each chemical class):

Aliphatic acids	(6)	1.8%	2,4-Alkadienals	(4)	17.8%
Primary alcohols	(4)	3.5%	Furans	(2)	1.1%
Secondary alcohol	(1)	1.5%	Gamma lactones	(3)	0.5%
Alkanals	(5)	19.3%	Hydrocarbons	(3)	11.2%
2-Alkenals	(8)	23.4%	Methyl ketone	(1)	<0.1%
Epoxy-2-enal	(1)	3.8%	Unidentified	(16)	16.1%

The 17 major volatile compounds (Table I) accounted for 88% of the total integrated area of the gas chromatogram (Fig. 1a). Because of unresolved compounds, the chromatogram revealed only 13 main GC peaks (nos. 2, 5, 14, 18, 19, 24, 26, 30, 37, 56, 57, 61, and 62). For the most part, the major compounds are the same major

TABLE I

Major Volatiles Derived from Heated (192 C) Model Triglycerides[a,b]

GC peak No. in Figs. 1 and 2	Compound	TriLo (pure)		TriLo and TriSt		TriLo and TriOl		TriLo and TriOl and TriSt	
		Area	Rel.	Area	Rel.	Area	Rel.	Area	Rel.
				Percent					
A. Trilinolein Volatiles									
2	Pentane	10.5	12.0	11.9	13.1	11.1	15.2	15.5	19.7
5	Acrolein	4.2	4.8	3.5	3.8	3.2	4.4	2.6	3.3
5	Propanal	0.6	0.7	0.5	0.6	0.5	0.7	0.4	0.5
14	Pentanal	3.2	3.6	3.3	3.6	2.6	3.6	2.0	2.5
18	Pentanol	3.0	3.4	2.3	2.5	1.9	2.6	1.5	1.9
19	Hexanal	15.1	17.2	14.4	15.8	13.3	18.2	15.0	19.1
23,24[c]	2/3-Hexenal	1.6	1.8	1.1	1.2	1.2	1.6	1.0	1.3
26	Unk. & Heptanal	7.2	8.2	6.5	7.1	5.2	7.1	5.1	6.5
29,30[c]	2-Heptenal	13.5	15.3	13.8	15.2	12.3	16.7	11.9	15.1
30	1-Octen-3-ol	1.5	1.7	1.6	1.8	1.4	1.9	1.3	1.7
30	2-Pentyl Furan	0.7	0.8	0.8	0.9	0.7	1.0	0.7	0.9
35,37[c]	2-Octenal	3.9	4.4	2.8	3.1	3.0	4.1	3.3	4.2
56,57[c]	2,4-Decadienal	16.7	19.0	21.8	23.9	13.2	18.0	13.5	17.2
61	Unk. MW = 156	2.5	2.8	2.4	2.5	1.3	1.8	1.5	1.9
62	4,5-epoxydec-2-enal	3.8	4.3	4.5	4.8	2.3	3.1	3.3	4.2
	Subtotal	88.0	100.0	91.2	100.0	73.2	100.0	78.6	100.0
B. Triolein Volatiles									
11	Heptane	—	—	—	—	1.3	8.0	0.6	6.8
16	Octane	—	—	—	—	1.9	11.7	0.7	8.0
28	1-Heptanol	—	—	—	—	0.4	2.5	Trace	Trace
36	1-Octanol	—	—	—	—	0.4	2.5	Trace	Trace
31	Octanal	—	—	—	—	1.7	10.5	1.0	11.4
40	Nonanal	—	—	—	—	4.6	28.4	2.6	29.5
52	2-Decenal	—	—	—	—	3.1	19.1	2.0	22.7
59	2-Undecenal	—	—	—	—	2.8	17.3	1.9	21.6
	Subtotal					16.2	100.0	8.8	100.0
	Total major volatiles	88.0	100.0	91.2	100.0	89.4	100.0	87.4	100.0

[a]TriLo = trilinolein; TriSt = tristearin; TriOl = triolein.

[b]Data in pure TriLo and TriLo-TriSt columns are from Figure 1, and data in TriLo-TriOl and TriLo-TriOl-TriSt columns are from Figure 2.

[c]GC peak sets 23 and 24: 29 and 30; 35 and 37; plus 56 and 57 appear to be the result of geometrical isomers.

volatiles observed by Thompson et al. (18) that were recovered from trilinolein heated to 185 C and periodically injected with steam. Excluding the cis isomers of hexenal, heptenal, and octenal (see below for explanation), the identified minor volatiles from trilinolein are listed in Table II and are grouped into classes of chemical compounds. Some of the compound classes (viz., acids, alcohols, and lactones) represent homologous series; e.g., C_1-C_9 alkanoic acids. Other than hexanoic acid (1.2%), all GC peak areas of minor compounds ranged from 0.9% down to trace levels. Some of the volatiles have only tentative identifications because of limited concentrations.

Except for acrolein, 2-nonenal, and 4,5-epoxydec-2-enal, the unsaturated aldehydes gave two GC peaks that may be the result of GC column separation of cis and trans isomers. Each pair is characterized by a preceding peak followed by a larger one. According to Badings (7), oxidation of oleate produces predominantly trans isomers of 2-alkenals. Hoffman and Keppler (20) separated the less concentrated trans-cis 2,4-decadienal, which on their GC column eluted first, from the abundant trans-trans isomer, both of which were isolated from oxidized linoleic acid. Consequently, the small preceding peaks are probably due to the cis and trans-cis isomers, and the large peaks are the results of the trans and trans-trans isomers. Components from GC peaks No. 23 and No. 24 were identified as hexenals (Table I), but because the mass spectra of the 2- and 3-positional isomers are quite similar, we were not able to distinguish if just one or both positional isomers were present. In Tables I and II, each pair of aldehyde isomers is listed as a single entity, and the GC area contributions are combined and listed as a single value.

Acrolein and propanal eluted at the same time (TC peak No. 5). However, they were sufficiently fractionated to permit identification from their mass spectra. Both aldehydes have intense parent ions in their mass spectra (acrolein = 56, propanal = 58), each of which is free from interference from the others' mass spectra; therefore, the total GC peak area was apportioned according to the ratios of their parent ions. Just as these two aldehydes were partially resolved so also were the two compounds associated with GC peak No. 26, an unknown and heptanal (Table I). The unknown's MW could not be determined from its mass spectrum; the only information gathered
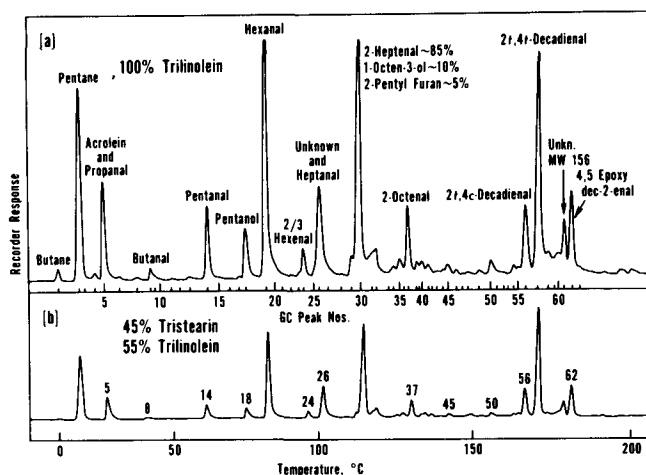

FIG. 1. Gas chromatograph of volatile compounds from thermally oxidized trilinolein (Curve "a") and from a mixture of 55% trilinolein and 45% tristearin (Curve "b"). Numbers 1-63 relate to GC peaks in Curves "a" and "b" of both Figures 1 and 2.

indicated that it may be an aldehyde (an intense m/e 44 ion) (30) and that its MW is greater than 71, which was the highest mass spectral ion of any significance in its spectrum. Because the unknown's mass spectrum was so much more intense than that of heptanal, undoubtedly the unknown was the main contributor to the peak (No. 26) area.

Originally, GC peak No. 30, a prominent peak in each GC curve in Figures 1 and 2, was thought to be solely associated with 2-heptenal. On subsequent volatile analyses, content of peak No. 30 were trapped and re-injected on a more polar column (14 ft x 4 mm ID glass column packed with 10% Silar 10 C). With temperature programming, three GC peaks appeared that were due to 2-pentyl furan (5%), 1-octen-3-ol (10%), and 2-heptenal (85%). Similar results were obtained by Hoffmann (5), who collected fractions (GC peaks) from oxidized soybean oil and methyl linoleate. The fractions contained 2-heptenal and had a pronounced mushroom odor. When he rechromatographed the trapped material on a different GC column, three subfractions appeared. The first (2-10%) was unidentified, but by MS was found to have a MW of 138, which also is the MW of

TABLE II

Minor Volatiles Derived from Heated (192 C) Model Triglycerides[a]

Compounds identified	Carbon chain lengths	TriLo (pure) Area %	TriLo & TriSt Area %	TriLo & TriOl Area %	TriLo, TriOl, & TriSt Area %
Acids	C 1,3,4,5,6,7	1.8	2.8	2.9[b]	5.6[b]
1-Alcohols	C 3,4,6*[c]	0.5	ND[d]	0.2	0.3
Alkanals	C 4	0.4	0.3	1.2[e]	0.9[e]
2-Alkenals	C 9	0.2	0.1	0.4	0.2
2,4-Alkadienals	C 9	1.1	0.8	0.7	0.9
Gamma lactones	C 4*,6*,9*	0.5	ND	0.5	0.5
n-Hydrocarbons	C 4,6*	0.7	0.4	0.2	0.6
Furan	C 4*	0.4	Trace	0.1	Trace
Methyl ketone	C 7*	Trace	Trace	0.2	Trace
Unknowns (15)		6.4	4.4	4.2[f]	3.6[f]
Subtotal minor compounds		12.0	8.8	10.6	12.6

[a]TriLo = trilinolein; TriSt = tristearin; TriOl = triolein.

[b]These GC peak areas include areas from C 2,8,9 alphatic acids derived from triolein.

[c]Compounds marked with * are only tentatively identified. Their GC elution temperatures correspond with those of authentic compounds; however, corroborating mass spectral data was not conclusive.

[d]None detected.

[e]The GC peak area includes the area from decanal derived from triolein.

[f]Only 14 unknowns are involved with these GC peak areas.

2-pentyl furan. Subfraction two (65-70%) was identified as trans-2-heptenal and the third peak (25-30%), which smelled of mushrooms, was identified as 1-octen-3-ol.

The compound associated with GC peak No. 62 is tentatively identified as 4,5-epoxydec-2-enal. Its identification is derived mainly from its mass spectrum, with some supportive nuclear magnetic resonance (NMR) and GC elution temperature evidence. Its mass spectrum includes the following characteristic m/e peaks (numbers in parentheses are normalized percent values): m/e 68(100), 43(31), 41(30), 55(27), 39(24), 99(23). 69(18), 84(16), 125(7), 139(5), and 168(<1). A computer search for a matching mass spectrum from our library of over 37,000 standard mass spectra failed to produce a single reasonable identification. During subsequent analysis of trilinolein volatiles, contents from GC peak No. 62 were trapped and subjected to NMR analysis. Results were similar to NMR data reported by Swoboda and Peers (31) for trans-4,5-epoxy-hepta-trans-2-enal. Because of weak NMR abosrptions, due to the small sample size, the data were considered only as suggestive. However, recently we received a mass spectrum of authentic 4,5-epoxydec-2-enal (data graciously supplied by Drs. P.A.T. Swoboda and K.E. Peers, both from the Agriculture Research Council, Food Research Institute, Norwich, England). Comparison between the mass spectra of their authentic compound and that of material from GC peak No. 62 strongly indicates the two compounds are identical. Although we lack authentic material to establish its GC elution temperature, our tentatively identified compound elutes 11 degrees higher than 2,4-decadienal (GC peak No. 57 in Figs. 1 and 2). The two compounds are comparable except at the 4-5 carbon atom positions where the dienal has a double bond and the other has an epoxy group. Miwa (32) has shown that an epoxyoctadecenoic acid elutes 1.0 equilvanent chain length higher than a corresponding conjugated octadecadienoic acid. Thus, the mass spectrometric, NMR, and elution data all support the proposed identification of 4,5-epoxydec-2-enal.

Oxidized lipids are precursors of epoxy compounds. Recently, Swoboda and Peers (31) oxidized butterfat and cod liver oil at 35 C in air and isolated and identified trans-4,5-epoxyhept-trans-2-enal as one of the major oxidation products. The authors postulated epoxyheptenal was formed via the 16-hydroperoxide of linolenic acid, some of which converts to 15,16-epoxy-12-hydroperoxy-9,13-octadecadienoic acid. Subsequent carbon chain cleavage between the 11-12 carbon atoms would yield the epoxyheptenal. Similarly, epoxydecenal can be derived from the oxidation of linoleic acid. Gardner et al. (33) isolated 12,13-epoxy-9-hydroperoxide-10-octadecenoic acid from the 13-hydroperoxide of linoleic acid. Degradation of the epoxy-9-hydroperoxy intermediate (carbon chain cleavage between the 8-9 carbon atom positions) would yield the 4,5-epoxydec-2-enal.

Examination of the mass spectrum from GC peak No. 61 led only to a tentative molecular weight assignment of 156. The spectrum has a series of fragment ions characteristic of a ketone or a hydrocarbon (m/e 29, 43, 57, 71, 85, 99). These and other distinctive mass peaks are listed with their normalized percent values in parentheses: m/e 56(100), 43(66), 85(43), 86(38), 99(37), 71(33), 55(29), 29(29), 109(26), 127(19), 112(9), 31(3), and 156(<1). This unknown plus the epoxydecenal may have a significant effect on odors and flavors from cooking oils, since both are prominent volatiles found in heated soybean oil (unpublished results).

Trilinolein-Tristearin

When tristearin was added to trilinolein to produce a 45:55 ratio mixture, respectively, the number of heated oil
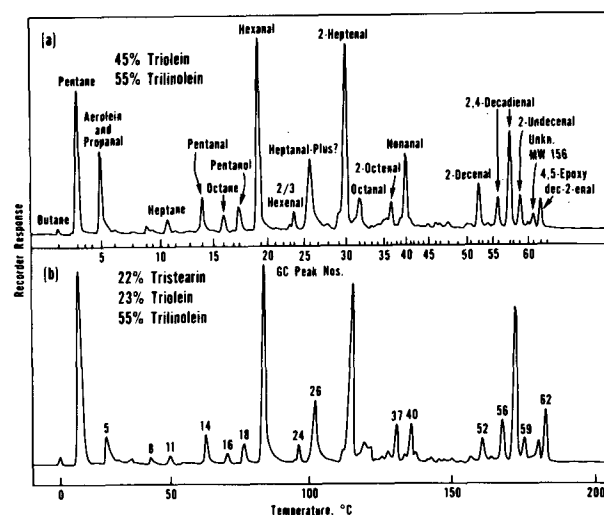

FIG. 2. Gas chromatograph of volatile compounds from a thermally oxidized mixture of 55% trilinolein and 45% triolein (Curve "a") and from a mixture of 55% trilinolein, 23% triolein, and 22% tristearin (Curve "b"). Numbers 1-63 relate to GC peaks in Curves "a" and "b" of both Figures 1 and 2.

volatiles decreased from 54 down to 45. The decrease, all among the minor compounds, was the consequence of diluting the trilinolein concentration, which in effect decreased the concentrations of various minor volatiles below their detection levels. In Figure 1b is the gas chromatograph of those volatiles from the heated mixture: in Tables I and II are listed the volatile identities and their relative GC peak areas.

Were it not for the decreased GC peak heights in Figure 1b, the two curves in Figure 1 could almost be superimposed. The strong resemblance between the two curves stems from the fact that only trilinolein-derived volatiles are present from the pure and mixed samples and that tristearin volatiles are absent (Tables I and II). This resemblance is in contrast to results from a previous model triglyceride study in which, compared to pure triolein, a heated mixture of triolein-tristearin resulted in an increased number of volatiles (27). The additional volatiles, all minor contributors to the total GC peak area, were due to oxidized-decomposed stearate. The disparity between the triolein and this study mirrors oxidation rate differences between the two triglycerides in each mixture, i.e., a 100:1 difference for linoleate-stearate but only a 10:1 difference for oleate-stearate (8,25).

Although the major peak areas of Figure 1a are considerably larger than those in Figure 1b upon normalization, corresponding peaks in each set, with one exception, have the same approximate relative percent values as shown in Table I. The exception is decadienal, whose GC peak area contribution substantially increased (17% to 22%) when derived from the heated linoleate-sterate mixture. Whether that increase is unique to the mixture or perhaps due to an undetected temperature change is not known.

Linoleate major volatiles from the linoleate-stearate mixture contributed 91% to the total GC peak area (Table I). Compared to corresponding area contribution (88%) from pure trilinolein, the slight increase in the mixture can be attributed to fewer minor compounds from the triglyceride mixture and to normalization of the remaining GC peak areas.

Trilinolein-Triolein

When tristearin is replaced by triolein to form a 55:45 trilinolein-triolein mixture, respectively, a modified trilin-

olein volatile profile is produced. The gas chromatogram of those volatiles from the trilinolein-triolein mixture is shown in Figure 2a, and volatile identifications and GC peak areas are listed in Tables I and II. These results show that, in addition to volatiles derived from oxidized trilinolein, there are also volatiles present that are unique to the oxidation-decomposition of triolein (Table I) (27). Although the linoleate-oleate mixture consisted of 45% triolein, its volatiles contributed only 16% to the total GC area. The low contribution is not surprising in light of the higher oxidation rate of linoleate compared to oleate (2,8,25).

Minor volatiles associated with the linoleate-oleate mixture are, with a few exceptions, the same as those from heated trilinolein (Table II). The additional minor volatiles, acetic, octanoic, nonanoic acids, and decanal, are products derived from oxidized oleate (27).

## Trilinolein-Triolein-Tristearin

Heating (192 C) the three component model system (55%-trilinolein, 23%-triolein, 22%-tristearin) produced a volatile profile (Fig. 2b) only slightly different from that of trilinolein-triolein (Fig. 2a). Volatile identities and their GC peak areas are listed in Tables I and II. The most obvious differences between Figure 2a and 2b are the less intense GC peaks of oleate's degradation products in "b," i.e., those GC peaks that are associated with heptane, octane, octanal, nonanal, 2-decenal and 2-undecenal. The decrease is a dilution effect. Thus, triolein-derived volatiles from the trilinolein-triolein mixture (triolein = 45%) accounted for 16.2% of the GC area; and when the triolein content was reduced to 23% as in the three component mixture, the summed oleate volatile peak areas decreased to 8.8% of the total. Tristearin again had no other effect than to act as a diluting solvent.
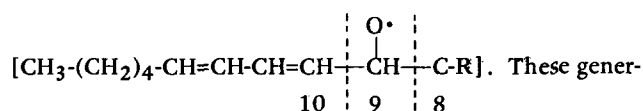
DISCUSSION

Autoxidation of linoleic results in the formation of primary oxidation products, which include equal amounts of conjugated 9- and 13-hydroperoxides (3,4). Theory predicts an additional nonconjugated 11-hydroperoxide (19), but no direct evidence for its existence has been found (4). Two major carbonyl compounds predicted and found from the decomposition of the 9-and 13-hydroperoxides are 2,4-decadienal (3,7,20) and hexanal (3,7,15), respectively. However, the relative quantities of the two aldehydes appear to be dependent on experimental conditions, e.g., temperature (10-12).

Undoubtedly, oxidized linoleate and its degradation products decompose by other unknown mechanisms or are involved in chemical reations, because pentane, 2-octenal, and especially 2-heptenal are also formed in considerable quantities. Other unusual volatiles derived from oxidized linoleate, but in minor amounts, include hydrocarbons (12,18,21), alcohols (6,18,22), acids (18,23), and aldehydes (6,7,10,15,18).

Pentane, and as mentioned above, hexanal, and 2,4-decadienal (peaks 2, 19, and 57, Fig. 1a) were observed from the actual decomposition of linoleate's 13- and 9-hydroperoxides (34,35). Pentane and hexanal are derived from the 13-hydroperoxide. Carbon-carbon cleavage occurs on either side of the peroxy carbon atom to form either the C-5 hydrocarbon or the C-6 aldehyde
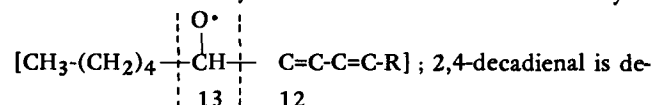
$$[CH_3\text{-}(CH_2)_4 \underset{13}{+} \overset{\overset{O\cdot}{|}}{CH} + \underset{12}{C=C\text{-}C=C\text{-}R}]$$; 2,4-decadienal is de-

rived from the 9-hydroperoxide where cleavage occurs between the 8 and 9 carbon atoms

$$[CH_3\text{-}(CH_2)_4\text{-}CH=CH\text{-}CH=CH \underset{10}{+} \underset{9}{\overset{\overset{O\cdot}{|}}{CH}} + \underset{8}{C\text{-}R}]$$. These gener-

ally accepted mechanisms can be used to account for the three compounds, but the precursor and formation mechanism(s) of 2-heptenal (peak No. 30) have eluded investigators and are unknown. Previously, 2-heptenal was attributed to a linoleate 12-hydroperoxide (5,22), but no evidence has been found for the latter's existence (4). Oxidation of 2,4-decadienal produces 2-heptenal but only at a low (0.2%) level (36). Formation of 2-heptenal and decadienal appear to be temperature dependent. Results from linoleate and trilinolein oxidation studies of Gaddis et al. (9), Swoboda and Lea (12), and Kimoto and Gaddis (15) showed increased 2-heptenal concentrations with increasing sample decomposition temperatures (165 C-210 C). In those studies, temperature dependency was even more dramatic for the formation of 2,4-decadienal. At temperatures below 75 C, 1-2% of the total carbonyl fraction was attributed to the dienal; however, at 85-210 C 2,4-decadienal contributions ranged from 43-72%.

In the present study, trilinolein was heated to 192 C to produce nearly equal amounts of 2-heptenal, hexanal, and 2,4-decadienal in addition to slightly lesser amounts of pentane (Table I). Given that pentane and hexanal primarily originate from 13-hydroperoxide and 2,4-decadienal from 9-hydroperoxide and that equal amounts of the two hydroperoxides are formed, as reported by Frankel et al. (4), then at 192 C either the 13-hydroperoxide is preferentially decomposed (pentane + hexanal = 11% + 15% = 26% vs. decadienal = 17%) or the 9-hydroperoxide decomposition products are less stable. The latter part of the above statement is based on the fact that no compound corresponding to pentane is observed that might have originated from the degradation of the 9-hydroperoxide, i.e., carbon-carbon cleavage between the 9-10 carbon atoms to yield an unsaturated C-9 compound. Obviously, further studies are required to elucidate compound precursors and decomposition mechanisms.

Results from this study show that (a) trilinolein is oxidized at 192 C in air to produce volatiles athat are predicted from the decomposition of linoleate's 9- and 13-hydroperoxides; (b) the oxidized diene produces 4,5-epoxydec-2-enal, which has not been previously identified among linoleic acid volatiles; (c) major and minor volatiles are present that are not directly associated with the theoretical decomposition of the 9- and 13-hydroperoxides; (d) a heated trilinolein-triolein mixture forms volatiles that are derived from oxidized oleate, but not in proportion to the triolein concentration; and (e) tristearin acts merely as a diluting solvent when mixed with trilinolein or a mixture of trilinolein-triolein.

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