Monocarbonyl Compounds from Catalytic Decomposition of Autoxidized Unsaturated Fatty Acid Esters[1]

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ABSTRACT

Monocarbonyl compounds formed by the decomposition of autoxidized triolein, methyl linolenate, and methyl arachidonate were converted into their 2,4-dinitrophenylhydrazone derivatives and analyzed by thin layer and paper chromatographies. From decomposition of autoxidized triolein with acid-washed Fuller's earth alkanals were the only monocarbonyl products found, whereas, with metal catalysts or heat, 2-alkenals were the primary products. Autoxidized methyl linolenate and methyl arachidonate decomposed with metal catalysts or heat yielded 23-55% of 2,4-alkadienals but minor amounts with acid-washed Fuller's earth. The differences in distribution of monocarbonyl products were attributed to a selective course of scission of the hydroperoxides that depended upon the conditions of decomposition.

INTRODUCTION

Although monocarbonyl compounds are minor products from the decomposition of autoxidized fatty acids, they are important contributors to odors and flavors of lipid food products. Of the three principal classes of monocarbonyls, alkanals, 2-alkenals, and 2,4-alkadienals, the last are minor products from autoxidation of trilinolein, trilinolenin, and methyl arachidonate (1,2). The precursors of the 2,4-alkadienals from autoxidized methyl linoleate and methyl linolenate, the 9-linoleate and 12-linolenate hydroperoxides, have been reported to represent 50% (3) and 11% (4), respectively, of the hydroperoxide fractions.

In a previous investigation (5), arguments were presented that the destruction by oxidation was not the reason for the minor amounts of 2,4-decadienal obtained from autoxidized trilinolein. We reported (5) that from cupric stearate-catalyzed and thermal decomposition of autoxidized trilinolein, 2,4-decadienal represented at least 45% of the total monocarbonyls produced. From decomposition with acid-washed Fuller's earth, 2-nonenal represented 23-31% of total monocarbonyls, and 2,4-decadienal was negligible. We suggested that scission of the hydroperoxides was selective and that distribution of the monocarbonyls depended upon the conditions of decomposition.

Selective scission might explain the minor amounts of 2,4-dienals produced by decomposition of autoxidized polyunsaturated fatty acids. We, therefore, have investigated selectivity further by analysis of the monocarbonyl compounds resulting from catalytic decomposition of autoxidized triolein, methyl linolenate, and methyl arachidonate.

EXPERIMENTAL PROCEDURES

Highly purified triolein, methyl linolenate, and methyl arachidonate were obtained from the Hormel Foundation, Austin, Minn. Thin films of the esters were oxidized in beakers under diffused light at 22-25 C. Details of procedures have been described (5).

Autoxidized lipid decomposition was examined in sealed 15 x 150 mm tubes. In these experiments, 0.2-0.5 g autoxidized lipid was placed in the tube, cupric stearate (1-2.5%), ferrous stearate (2-2.5%) with o-phenanthroline (5%), or acid-washed Fuller's earth (10-15%) was added. After careful displacement of air with nitrogen, the tube was sealed and then heated in silicon oil at 85 (±2) C for 30 min. Autoxidized lipid in the sealed tube (neat) was heated in silicon oil at 200 C for 20 min, or at 165 C for 15 min. Analysis of the carbonyls was as described (5).

Autoxidized lipids also were treated with metal catalyst at 22-25 C. Samples (0.2-0.5 g) were dissolved in 10 ml carbonyl-free t-butyl alcohol and 2 ml H_2O in a 25 ml erlenmeyer flask, purged with N_2 for 3 min, treated with 0.3 g $FeCl_2$, or 0.017-0.050 g hemin (Nutritional Biochemicals Corp., Cleveland, Ohio) and 5 drops of 1 N NaOH or 5 drops of 1 N NaOH in 2 ml H_2O, purged with N_2 for 1 min, stoppered tightly, and agitated for 15-20 min at 22-25 C. Isolation and analysis of the carbonyls were as described (5).

Details of preparation, isolation, and identification of the 2,4-dinitrophenylhydrazone (2,4-DNPH) derivatives of the carbonyl compounds have been described (5). Briefly, in the isolation procedure, the carbonyl compounds were converted to 2,4-DNPH derivatives by passage through a H_3PO_4-2,4-dinitrophenylhydrazine-celite column (6). The carbonyls 2,4-DNPH were separated on a hydrated alumina column; the less polar (monocarbonyls) were eluted with benzene-hexane and the more polar with $CHCl_3$. The latter compounds were believed to be aldo- and keto-glycerides (or methyl esters) and will be referred to as polar carbonyls. Reference to these compounds in this article will be summarized in statements in the text, and no data will be presented. The monocarbonyls 2,4-DNPH were separated into classes by paper chromatography; the resolved classes then were separated into individual compounds by thin layer chromatography (TLC) with Silica Gel G as adsorbant and 3:1 benzene-hexane as elutent. Homologues with carbon chain length greater than C_7 were separated further with the paper-vaseline chromatographic method (7). Optical density values were converted to μm/10 g for the alkanals, 2-alkenals, and 2,4-alkadienals. Percentage values reported for these compounds were mean values. The standard deviation of the mean was calculated from the normalized difference by the standard formula:

$$\text{standard deviation} = \pm \sqrt{\frac{\Sigma d^2}{n-1}}$$

Concentrations of all other carbonyl derivatives referred to in this article will be expressed in optical density values.

RESULTS AND DISCUSSION

Triolein

Autoxidized triolein was decomposed completely by all of the methods used, and the yields of monocarbonyls, as percentage of peroxide value that was converted to monocarbonyl compounds, varied from 4-75% (Table I). Higher temperature (200 C) than the 165 C used previously (5)

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[2] Retired.

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TABLE I

Monocarbonyl From Autoxidized Triolein[a]

	Treatment in sealed tubes			Treatment in t-BuOH
Monocarbonyl	Fuller's earth (acid washed)	Cupric stearate	200 C (neat)	$FeCl_2$
PV[b] Initial	45-150[c]	45-150[c]	45-150[c]	45-150[c]
After reaction	0	0	0	0
Total[d] µm/10 g	169-494	11-31	33-88	46-130
Percentage PV conversion	66-75%	4-5%	10-16%	16-20%
Alkanals, %				
C_8	24 ± 2	9 ± .8	4 ± 1.3	5 ± 1.9
C_9	43	23 ± 2.7	12 ± 1	9 ± 1.3
C_{10}	33 ± 2	1 ± 1	1 ±.6	1 ±.6
2-Alkenals, %				
C_{10}	---	32 ±.8	39 ± 1.3	39 ± 2.1
C_{11}	---	35 ± 2	44 ± 2.5	46 ± 3.5

[a] 2,4-DNPH derivatives; mean values and standard deviation of the mean.

[b] Peroxide value, meq/1,000 g.

[c] Peroxide values, 45, 55, 75, and 150.

[d] Total for alkanals and 2-alkenals.

was needed to decompose autoxidized triolein completely by heat. Alkanals were the only monocarbonyls found with acid-washed Fuller's earth, whereas 2-alkenals were the primary products with cupric stearate, ferrous chloride, and heat. Polar carbonyls, with a maximum of 365 nm in CCl_4 and believed to be conjugated unsaturated keto-glycerides, were the primary products from the decomposition of autoxidized triolein with cupric stearate. The polar carbonyl-to-monocarbonyl ratios (optical density values) were 7.6 with cupric stearate, 1.8 with ferrous chloride or after heating at 200 C, and 0.8 with acid-washed Fuller's earth.

Methyl Linolenate

Autoxidized methyl linolenate was decomposed completely by all of the methods, except sodium hydroxide (Table II), and the yields of monocarbonyls varied from 6-11%. Metal catalyzed and thermal decomposition of autoxidized methyl linolenate resulted in the formation primarily of propanal and 2,4-heptadienal, whereas, with acid-washed Fuller's earth, the primary products were propanal, 2-hexenal, and what was believed to be 2,6-nonadienal. With paper chromatography, the last compound separated with the 2-enals, although moving slightly more slowly than the 2-enals but moving more rapidly than the 2,4-dienals. With TLC (Silica Gel G), the compound believed to be 2,6-nonadienal separated between 2-pentenal and 2-hexenal, whereas, on the paper-vaseline system (paper chromatography), this compound separated between 2-heptenal and 2-octenal (Table II). Hammond and Hill (8) found 2-*trans*-, 6-*cis*-nonadienal as a decomposition product of autoxidized trilinolenin.

NaOH and hematin (in NaOH solution hemin, is con-

TABLE II

Monocarbonyl from Autoxidized Methyl Linolenate[a]

	Treatment in sealed tubes			Treatment in t-BuOH		
Monocarbonyl	Fuller's earth (acid washed)	Cupric stearate	165 C (neat)	$FeCl_2$	Hematin (hemin-NaOH)	NaOH
PV[b] Initial	70-375[c]	70-375[c]	70-375[c]	70-375[c]	170,220	170,220
After reaction	0	0	0	0	0	100
Total[d] µm/10 g	32-151	28-106	32-135	22-109	67-70	50-66
Percentage PV conversion	8-11%	6-8%	7-9%	6-7%	6-8%	---
Alkanals, %						
C_2	3.9 ± .1	6.0 ± 1.1	5.7 ± 1.1	4.5 ± .5	2.8 ± .4	5.1 ± 1.8
C_3	48.0 ± 2.8	45.0 ± 4.2	49.0 ± 1.4	31.4 ± 3.4	34.5 ± 1.3	68.4 ± .4
C_4	3.7 ± .5	1.5 ± .8	3.4 ± .4	6.1 ± 1.5	1.5 ± 1.4	2.6 ± .4
2-Alkenals, %						
C_4	1.4 ± .5	2.3 ± 1.1	3.2 ± .5	2.1 ± 1.5	---	---
C_5	6.5 ± 1.1	7.4 ± 1.3	5.9 ± 1.9	9.7 ± .9	4.8 ± .3	6.1 ± 1.1
C_6	17.3 ± 1.2	1.3 ± .4	1.4 ± .5	1.9 ± .4	---	---
C_7-C_8	16.8 ± 2.2	---	---	---	---	---
C_9	---	---	1.1 ± .3	---	2.5 ± .6	4.4 ± 1.1
2,4-alkadienals, %						
C_7	2.4 ± .4	36.5 ± 3.0	30.3 ± 3.2	44.3 ± 4.1	53.9 ± .4	13.4 ± .4
Trienals[e] (?)	3 ± .7%(382)	12 ± 1.5%(390)	4 ± .8%(382)	13 ± 2.3%(389)	12 ± 7%(382)	32 ± 1.2%(394)

[a] 2,4-DNPH derivatives; mean values and standard deviation of the mean.

[b] Peroxide value, meq/1,000 g.

[c] Peroxide values, 70, 120, 130, and 375.

[d] Total for the alkanals, 2-alkenals, and 2,4-alkadienals.

[e] Percentage of total monocarbonyls in optical density values; () maximum, nm in CCl_4.

TABLE III

Monocarbonyl From Autoxidized Methyl Arachidonate[a]

	Treatment in sealed tubes				Treatment in t-BuOH		
Monocarbonyl	Fuller's earth (acid washed)	Cupric stearate	Fe stearate-o-phenanthroline	165 C (neat)	Hematin (hemin-NaOH)	NaOH	$FeCl_2$
PV[b] Initial	380,600	380,600	380,600	380,600	250,340	250,340	250,340
After reaction	0	0	0	0	0	90	0
Total[c] μm/10g	183-203	130-169	164-217	167-239	115-140	156-204	129-170
Percentage PV conversion	7-10%	7%	7-9%	8-9%	8-9%	---	10%
Alkanals, %							
C_2	2.9 ± .4	7.2 ± .2	7.1 ± 2.5	10.1 ± 1.6	.4	.5 ± .2	.3 ± .1
C_3	1.5 ± .2	2.0	3.5 ± .4	2.2 ± .2	1.8 ± 1.3	.9 ± .5	1.3
C_6	69.4 ± 3.4	55.9 ± .5	50.6 ± 3.6	54.5 ± 1.6	55.7 ± .4	86.1 ± 1.8	60.9 ± .1
2-Alkenals, %							
C_7	2.1 ± .4	.8 ± .5	1.8	3.0 ± 1.0	.7 ± .4	.1 ± .1	.2 ± .2
C_8	4.1 ± .2	3.2 ± .6	2.4	4.1 ± .5	4.4 ± 1.3	1.7	5.7 ± .5
C_9	6.4 ± .9	.8	1.5 ± .2	1.6 ± .6	2.4 ± .4	.6 ± .2	2.5 ± .2
C_{11}	3.3 ± 1.0	.1 ± .1	1.2 ± .1	.4	.1 ± .1	.3 ± .3	---
2,4-Alkadienals, %							
C_7	.3 ± .3	1.8 ± .3	1.1 ± .1	1.0 ± .1	1.7 ± .6	1.8 ± 1.6	1.2
C_{10}	5.6 ± .5	28.2	30.8 ± .9	23.1 ± 2.2	32.8 ± 1.2	8.0 ± 2.5	27.9 ± .4
C_{11}-C_{12}	1.8 ± .3	---	---	---	---	---	---
C_{13}	2.6 ± 1.0	--	---	---	---	---	---
Trienals[d] (?)	5%(382)	7%(390)	6%(388)	3%(370)	15 ± 2.8%(392)	17 ± 3%(394)	8 ± 1.0%(392)

[a] 2,4-DNPH derivatives; mean values and standard deviation of the mean.

[b] Peroxide value, meq/1000 g.

[c] Total for alkanals, 2-alkenals, and 2,4-alkadienals.

[d] Percentage of total monocarbonyls in optical density values; () maximum, nm in CCl_4.

verted to hydroxyhemin or hematin) yielded similar total amounts of monocarbonyls but their distribution differed markedly, indicating that, in these systems, decomposition of autoxidized methyl linolenate to yield monocarbonyls was due primarily to hematin and not to NaOH. The monocarbonyls that separated (paper chromatography) between the origin and the 2,4-dienal band were believed to be trienals, which were found in appreciable amounts only with NaOH (Table II).

Methyl Arachidonate

Autoxidized methyl arachidonate was decomposed completely by the methods used, except that involving NaOH, and the yields of monocarbonyls varied from 7-10% (Table III). Hexanal and 2,4-decadienal were the principal monocarbonyls from metal catalyzed and thermal decomposition of autoxidized methyl arachidonate, whereas hexanal was the principal product with acid-washed Fuller's earth. The monocarbonyl that separated in the C_{11} enal region was believed to be an unconjugated dienal, 2,6-dodecadienal, and the products that separated in the C_7, between C_{11}-C_{12}, and C_{13} 2,4-dienal region were unidentified. Distribution of monocarbonyls differed markedly between NaOH and hematin (hemin + NaOH), indicating that hematin, rather than NaOH, was responsible. With paper chromatography, material that separated between the origin and the 2,4-dienal band was believed to be trienals (Table III); the products remaining at the origin constituted 4-12% of the total monocarbonyls (optical density values) with maxima of 365 to 387 nm in CCl_4 (data not shown).

Data from the present investigation of decomposition, by acid-washed Fuller's earth, of autoxidized triolein, methyl linolenate, and methyl arachidonate further support the suggested selective scission at the carbon linkage between the double bond and the hydroperoxide group to form monocarbonyl products. The course of scission of the hydroperoxides was less selective with metal catalysts and heat treatments at 165 C or 200 C; preference for scission of the carbon linkage was greater between the alkyl and hydroperoxide groups and apparently between the double bond and the hydroperoxide group, when the double bond was part of a trienyl or tetraenyl system.

Speculations on Mechanisms

These results suggest that monocarbonyls from the decomposition of autoxidized unsaturated fatty acid esters are formed by different mechanisms, depending upon whether the hydroperoxide bond cleavage is heterolytic (ionic) or homolytic (radical). Figure 1 summarizes the mechanisms for these two reactions. The ionic reaction is catalyzed by strong acids and depends upon the ability of a migrating group to undergo a 1,2 shift from a carbon atom to an incipiently positive oxygen (9,10). Alkyl cannot compete with aryl migration for the ionic reaction, and the

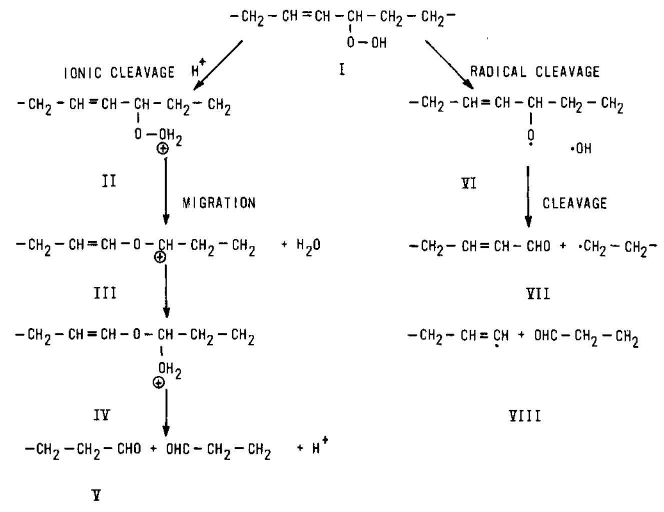

FIG. 1. Mechanisms for ionic and radical cleavage.

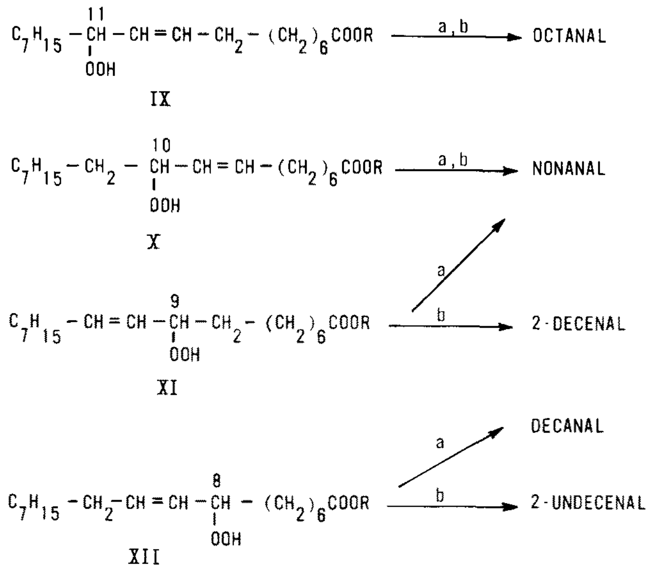

FIG. 2. Isomeric hydroperoxides and the monocarbonyl compounds expected from their decomposition by ionic and radical reactions. R is $(\text{oleate})CH_2\text{-}CH(\text{oleate})CH_2\text{-})$.

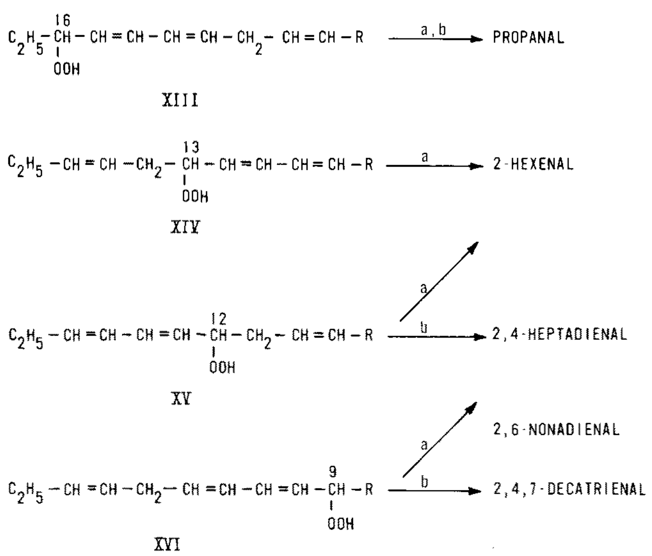

FIG. 3. Monocarbonyl products predicted from decomposition of hydroperoxides by ionic and radical reactions. R is $\text{-}(CH_2)_7COOCH_3)$.

mobility of vinyl apparently is similar to that of phenyl. Decomposition of hydroperoxides with heat or with metal catalysts (able to undergo 1-electron redox reaction) generates radicals of which two are alkoxy and alkylperoxy (11,12). For the formation of monocarbonyl compounds cleavage of the alkoxy radical (VI) will favor the stability of ejected radical and monocarbonyl product.

Privett and Nickell (13) reported the presence of ca. equal proportions of the four isomeric hydroperoxides from autoxidized methyl oleate which were predicted by Farmer's theory (14). These isomeric hydroperoxides and the monocarbonyl compounds that would be expected from their decomposition by the ionic (a) and radical (b) reactions are shown in Figure 2.

Frankel, et al., (4) reported the presence, exclusively, of the four conjugated hydroperoxides from the hydroperoxide fraction of autoxidized methyl linolenate. Monocarbonyl products predicted from the decomposition of these hydroperoxides by the ionic (a) and radical (b) reactions are shown in Figure 3. The prediction of monocarbonyl products for the ionic reaction is based upon several assumptions: alkyl cannot compete with trienyl migration (XIII and XVI); allyl cannot compete with dienyl migration (XIV and XV); and double bond will migrate for 2-hexenal (XIV and XV) and 2,6-nonadienal (XVI) formation. A double bond migration similar to that for 2,6-nonadienal apparently occurred for the formation of 2-nonenal from the decomposition of autoxidized trilinolein with acid-washed Fuller's earth (5), which was believed to be by the ionic reaction. No direct evidence is available to indicate that the double bond will migrate for 2-hexenal formation under the present experimental conditions. Prediction of the principal monocarbonyl products that would be expected from decomposition of autoxidized methyl arachidonate, by the ionic and radical reactions, would require support similar to that used for linolenate hydroperoxides (Fig. 3).

Migration is the main feature of the ionic reaction for the formation of monocarbonyl compounds, and the migrational aptitude of vinyl is much greater than that of alkyl (10). Results of the present and a previous investigation (5) indicate that selective scission of hydroperoxides was at the carbon linkage between the double bond and the hydroperoxide group to form monocarbonyls by the acid washed Fuller's earth catalyzed decomposition of autoxidized fatty acid esters. These results can be interpreted by the ionic reaction if the migrational aptitudes of conjugated and unconjugated vinyl homologues (from autoxidized linoleate, linolenate, and arachidonate), like vinyl (from autoxidized oleate) are greater than that of alkyl. 1,2 Alkyl migrations are rare for free radical reactions, but 1,2 aryl migrations are known to occur (15), and mobility of vinyl and vinyl homologues may be similar to that of aryl. The minor yield of decanal (Table I) from autoxidized triolein, 2- or 3-nonenal from the previously investigated autoxidized trilinolein (5), and 2,6-nonadienal or 2-hexenal (Table II) and apparently of the corresponding unconjugated 3,6-nonadienal or 3-hexenal from autoxidized methyl linolenate indicates that migration was not a factor for the metal catalyzed and thermal decompositions (radical reaction). Cleavage of the alkoxy radical is the main feature of the radical reaction for the formation of monocarbonyl compounds; cleavage will depend upon many factors (16,17), two of which are stability of ejected radical and monocarbonyl product. Dependence on these factors may be the reason for the lesser selectivity shown for the scission of hydroperoxides to form monocarbonyls for the radical reaction as compared to that for the ionic reaction.

The preceding discussion suggests the following tentative conclusions: formation of 2,4-heptadienal and 2,4-decadienal by the decomposition of the 12-linolenate and 11-arachidonate hydroperoxides, respectively, by the radical reaction should be favorable because of the elimination of allylic radicals. However, the minor proportions of the 12-linolenate and apparently of the 11-arachidonate hydroperoxides present, respectively, in the hydroperoxide fractions of autoxidized methyl linolenate and methyl arachidonate might explain the minor amounts of 2,4-dienals that were found in autoxidized trilinolenin and methyl arachidonate.

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