

Model Experiments about the Formation of Volatile Carbonyl Compounds¹

P. SCHIEBERLE and W. GROSCH, Deutsche Forschungsanstalt für Lebensmittelchemie, 8046 Garching, Germany

ABSTRACT

Autoxidation of linoleic acid, 9-hydroperoxy-10, 12-octadecadienoic acid (9-HPOD), 13-hydroperoxy-9, 11-octadecadienoic acid (13-HPOD), 2-octenal and 2,4-decadienal at 38 C were investigated with respect to the formation of volatile carbonyl compounds. The 13-HPOD and all compounds having a double bond in ω -6-position produce hexanal. After initiating by small amounts of alkoxy radicals, both hexanal and 2,4-decadienal autoxidize further. While, individually, hexanal reacts somewhat faster than 2,4-decadienal, forming the corresponding acid, in a mixture of the two aldehydes, hexanal is protected to a certain extent by the unsaturated aldehyde against autoxidation. This explains the predominance of hexanal among the volatile carbonyl compounds resulting from linoleic acid autoxidation. Small amounts of 2-octenal originate from both the 9-HPOD and the 2,4-decadienal as a result of oxidation of the ω -8-double bond of these compounds. Aside from its acid as main autoxidation product, 2-octenal yields heptanal and hexanal as volatile compounds.

INTRODUCTION

Although the volatile carbonyl compounds are only minor side products during autoxidation of fatty acids, they are of great significance for the aroma of foods because their threshold concentrations for odor and taste are very low (1).

The identified volatile carbonyl compounds arising from the autoxidative breakdown of linoleic acid at low and moderate temperatures are hexanal (66 mol %) as major, 2-octenal (18 mol %), 2-heptenal (6 mol %) and 2,4-decadienal (5 mol %) as minor components (2).

Initially, the autoxidation of linoleic acid or of its methyl ester results in 9-hydroperoxy-10, 12-octadecadienoic acid (9-HPOD) and 13-hydroperoxy-9, 11-octadecadienoic acid (13-HPOD), respectively, the corresponding methyl esters (3-6). It is generally accepted (7-10), that volatile carbonyl compounds stem from decomposition of these unsaturated fatty acid hydroperoxides via alkoxy radicals. Badings (11) proposed that β -scission of 13-HPOD leads to hexanal and of 9-HPOD to 2,4-decadienal (Fig. 1). He assumed formation of 2-octenal from the 11-hydroperoxide isomer, respectively, from decomposition of 2,4-decadienal.

Individual studies of the decomposition of the positional isomers of linoleate hydroperoxides to volatile aldehydes revealed that at temperatures above 100 C and in the absence of oxygen, both the 9- and 13-isomer gave rise to hexanal and 2,4-decadienal (12). To explain this phenomenon, it was assumed (12) that rearrangement of the hydroperoxy group is involved in the homolytic cleavage of the hydroperoxides. In contrast, at ambient temperature and in the presence of oxygen and ascorbic acid, hexanal resulted as the major volatile carbonyl compound in addition to traces of 2,4-decadienal from both the 9- and 13-HPOD (13).

Swoboda and Lea (14) explained the preferential formation of hexanal at moderate temperatures by a selective further oxidation of 2,4-decadienal. Taking 2,4-heptadienal and nonanal as examples, Lillard and Day (15) showed that 2,4-alcadienals oxidize more rapidly than a saturated alde-

hyde. Matthews et al. (16) identified hexanal as the main component in autoxidized 2,4-decadienal. In contrast, Michalski and Hammond (17) did not find labeled hexanal, but heptanal, after autoxidation of soybean oil containing [¹⁴C]-2,4-decadienal as additive. Loury (18) and Forney (19) found a stepwise breakdown of nonanal to C₆-C₈ homologs of aldehydes, alcohols, alkylformates and hydrocarbons.

Morita and Fujimaki (20) questioned the validity of the theory that carbonyl compounds are formed by the β -scission of monohydroperoxides because in the presence of cupric stearate and under degassed conditions, the unknown precursors of hexanal and 2,4-decadienal could be separated with the polar peroxide fraction.

The intent of our experiments was to clarify the discrepancies about the autoxidative breakdown of linoleic acid hydroperoxides to hexanal and 2,4-decadienal.

EXPERIMENTAL PROCEDURES

Materials

The following materials were obtained and purified where indicated: linoleic acid (Nu-Chek-Prep, Elysian, MN, 99%), hexanal (Merck, Darmstadt, Germany), distilled with a vigreux column (50 cm) at 35 C (45 mm Hg); 2-*trans*-octenal (California Aromatics and Flavors Inc., Belleville, NJ), 2-*trans*, 4-*trans*-decadienal (EGA, Steinheim, Germany); Silica Gel 60 (0.063-0.2 mm, Merck, Darmstadt, Germany) washed with concentrated HCl and adjusted to a water content of 7% (21); 95 g basic alumina, activity I, (Woelm, Eschwege, Germany) deactivated with 5 g water; Seasorb 43 (Fisher Scientific); 2,4-dinitrophenylhydrazine (Merck, Darmstadt, Germany), recrystallized from benzene. Cyclohexane and benzene were freed from carbonyl compounds as described (22) for *n*-hexane.

Preparation and Purification of Reagents

Di-*tert*-butyl peroxyoxalate (DBPO) was prepared from oxalyl chloride and *tert*-butyl hydroperoxide (23). Its concentration was measured by iodometric titration (23,24). 9-HPOD and 13-HPOD were prepared enzymatically using lipoxygenases from potatoes (13) and from soybeans (25), respectively, and purified by chromatography on 500- μ -thick plates of Silica Gel HF₂₅₄ containing 0.95% oxalic acid. After being developed twice with the solvent system heptane/diethyl ether (1:1, v/v), the hydroperoxides were located by UV, scraped off and eluted with methanol. The HPOD concentration was measured spectrophotometrically at 234 nm using 25,000 $\ell \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ (26) as molar extinction coefficient.

2-*trans*, 4-*trans*-Decadienal and 2-*trans*-octenal were purified by chromatography at 10 C on a column packed with Silica Gel 60 (25 x 1.8 cm) in pentane/diethyl ether (8:2, v/v). The sample (100 μ l) was dissolved in 0.5 ml of the same solvent mixture. In the effluent, 2,4-decadienal was monitored at 267 nm and 2-octenal at 219 nm. The concentrations were calculated using a molar extinction coefficient of 36,000 $\ell \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 267 nm (2,4-

¹These results were presented at the ISF/AOCS World Congress in New York (April 1980).

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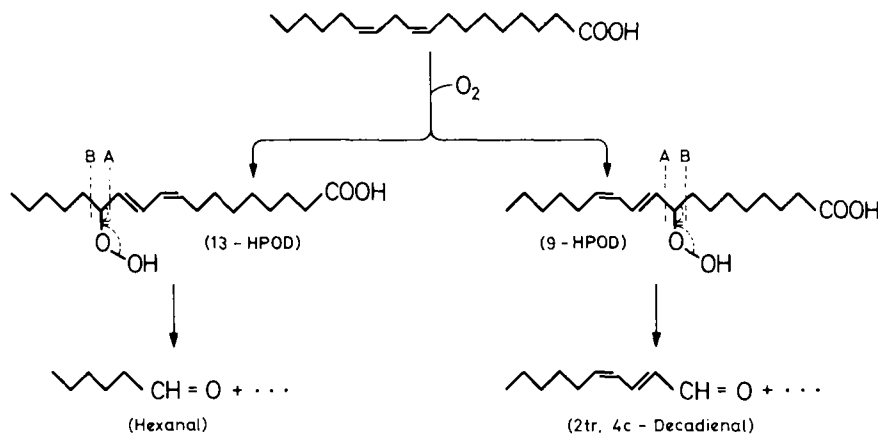


FIG. 1. Autoxidation of linoleic acid. Formation of hexanal and 2,4-decadienal (2).

decadienal) and $17,000 \ell \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 219 nm (2-octenal). These values were based on the analysis of aliquots of the aldehyde as 2,4-dinitrophenylhydrazine (2,4-DNPH) according to the procedure described next, using $38,000 \ell \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ as molar extinction coefficient at 390 nm (2,4-decadienal-DNPH) and $29,000 \ell \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 373 nm (2-octenal-DNPH) in chloroform.

Autoxidation Experiments

The composition of the reaction systems and the incubation times are listed in the tables. Most of the autoxidation experiments were initiated by tert-butoxyradicals generated from the decay of the small amount of added DBPO. Only under these conditions were reproducible autoxidation rates obtained.

ANALYTICAL METHODS

Quantitation of HPOD and Linoleic Acid

From the reaction mixture, as described in Table I, an aliquot (14 ml) was freed from the solvent in a stream of nitrogen after addition of heptadecanoic acid (6 mg) as internal standard. The residue was taken up in 10 ml diethyl ether/methanol (8:2, v/v) and methylated with diazomethane (27). Half of the solution was chromatographed on Silica Gel HF₂₅₄ plates with hexane/diethyl ether (7:3, v/v) as solvent system. The HPOD was located on the plates by UV, scraped off, eluted with methanol, and measured spectrophotometrically at 234 nm using $25,000 \ell \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ (26) as molar extinction coefficient. Based

on experiments with known amounts of HPOD, a recovery of 70% was established. Therefore, the HPOD values presented are corrected for a loss of 30%.

The other half of the methyl ester solution was freed from solvent mixture, dissolved in 1 ml benzene and applied onto a column with a cooling jacket (12 x 1 cm) packed with Silica Gel 60 in pentane/diethyl ether (95:5, v/v). Methyl linoleate and the internal standard methyl heptadecanoate were eluted with 80 ml of the same solvent mixture, concentrated, and analyzed by gas liquid chromatography (GLC).

Analysis of the Volatile Carbonyl Compounds As 2,4-Dinitrophenylhydrazones (DNPH)

Isolation of carbonyl compounds. The solution of reactants and products in benzene was applied to a column (15 x 1 cm) packed with basic aluminium oxide (deactivated with 5% water) in pentane/methylene chloride (2:1, v/v) according to Heimann et al. (28). The column was maintained at 10 C by a cooling jacket. Elution was performed with 50 ml of the same solvent mixture. The total effluent from the column, including the benzene from the sample, was collected, diluted with 70 ml ethanol and after addition of 120 mg 2,4-dinitrophenylhydrazine, dissolved in 8 ml of 85% phosphoric acid, and then stored overnight at room temperature. After addition of 150 ml water and 100 ml methylene chloride, the organic layer was separated, washed 3 times with 100 ml of water and dried over anhydrous sodium sulfate. Celite (1.5 g) was suspended in the solution and the solvent removed in vacuum. The DNPH-Celite

TABLE I

Autoxidation of Linoleic Acid, HPOD and 2,4-Decadienal

Compound ^a	Linoleic acid	HPOD	After 24 hr at 38 C		
			2,4-Decadienal	Hexanal ^b	2-Octenal
(μmol)					
1. Linoleic acid	48	9	ND ^c	1.0 (1.1)	0.05
2. 13-HPOD	--	23	ND	4.6 (3.3)	0.15
3. 9-HPOD	--	23	ND	4.6 (3.3)	0.5
4. 2,4-Decadienal	--	--	20	6.7 (4.6)	2.0

^aThe substances (75 μmol) dissolved in 0.5 ml benzene containing 0.75 μmol DBPO were stored in a sealed vessel (vol: 10 ml) under an atmosphere of oxygen. After incubation (24 hr at 38 C) the reaction mixture was taken up in 25 ml benzene.

^bThe values in brackets are calculated on the basis of a 50% breakdown of the precursor linoleic acid, 9- or 13-HPOD and 2,4-decadienal.

^cND: not detectable.

mixture was applied onto a column (5 x 2 cm) packed with neutral aluminium oxide (activity grade III) in cyclohexane. From the crude DNPH mixture of the column the monocarbonyl DNPH was separated through elution with 100 ml benzene/cyclohexane (1:1, v/v). The solvent mixture was removed in vacuum and the remaining residue dissolved in chloroform. The concentration of the monocarbonyl DNPH were calculated from the absorbance at 360 nm using $23,000 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ as molar extinction coefficient.

Separation of monocarbonyl DNPH into classes. The procedures described by Schwartz et al. (29) were modified as follows. A column (internal diameter 1 cm) was prepared using a slurry of 1 g activated (150 C for 24 hr) Celite 545 and 1 g activated (400 C for 24 hr) Sea Sorb 43 in chloroform. The solvent was drained to a height of 0.5 cm over the top of the bed. A layer of 0.5 ml ethyl acetate containing 0.3 to 1.5 μmol DNPH was carefully added. After adsorption of the DNPH, the sides of the tube were rinsed successively with 1 ml and 2 ml ethyl acetate. The DNPH classes were eluted with the following sequence of solvents: alkanal-DNPH with chloroform, 2-alkenal-DNPH with 2% methanol in chloroform and 2,4-alkadienal-DNPH with 10% methanol in chloroform. The classes were established on the basis of their absorption maxima (2,30). The DNPH derivatives were evaporated to dryness, pooled according to class, dissolved in a known volume of chloroform and their concentration determined spectrophotometrically (30).

Qualitative analysis. Separation and identification of individual compounds within a class was performed as described earlier (31). Mass spectra of the monocarbonyl-DNPH were obtained with a Varian Mat mass spectrometer CH 7 provided with a direct insertion probe (70 eV; temperature of the ion source 200 C, temperature of the sample 90-145 C).

Quantitation of individual compounds within a DNPH class. After separation by thin layer chromatography (TLC) on Kieselgur plates impregnated with carbowax 400 and with cyclohexane as solvent (30,32), the DNPH occurring in each class were quantitated by densitometric measurements of the plates at 370 nm (alkanal-DNPH), 390 nm (2-alkenal-DNPH) and 405 nm (2,4-alkadienal-DNPH) using the Chromatogram Spectrophotometer (C. Zeiss, Oberkochen, Germany). Analysis of carbonyl compounds was standardized with authentic compounds.

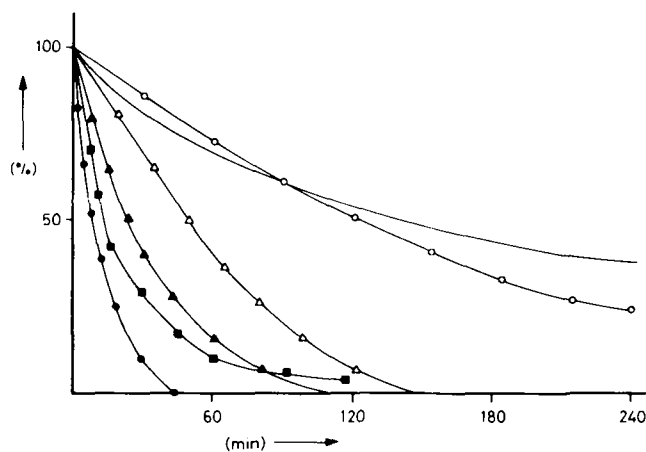


FIG. 2. Samples (75 μmol) prepared with and without DBPO (0.75 μmol) as detailed in the footnotes of Table II were oxidized in an atmosphere of oxygen at 38 C: methyl linoleate with DBPO (---●); hexanal without (o---o) and with DBPO (---●); 2,4-decadienal without (Δ --- Δ) and with DBPO (Δ --- Δ); 2-octenal with DBPO (■---■).

Quantitation of the Volatile Acids by GLC

At the end of an incubation experiment, 3 ml diethyl ether containing 3.5 mg decanoic acid as internal standard was injected through the septum of the Erlenmeyer flask. After addition of 100 μl methanol, the acids were methylated with diazomethane according to the method of Schlenk and Gellerman (27). The solution was concentrated to 0.5 ml in a stream of nitrogen at -18 C . GLC was performed on a 3 m x 3.2 mm stainless steel column of 15% diethyleneglycol succinate on Varaport 30 (80-100 mesh). After 4 min at 70 C, the temperature was programmed from 70-170 C at 4 C/min. Analysis was standardized by treating a mixture of fatty acids (equal amounts C_6 - C_{16}) in the same way.

Mass spectrometry in tandem with GLC (ion source: 180 C; energy: 70 eV) was employed for identification of the volatile compounds. The spectra obtained were compared with those of authentic samples.

Peroxides

Peroxides were quantitated with the FE test (33). The absorbances measured were referred to a calibration curve obtained with linoleic acid hydroperoxides.

RESULTS

Autoxidation of Linoleic Acid and HPOD

During the reaction time of 24 hr, 45% of linoleic acid and 70% of both 9- and 13-HPOD were oxidized (Table I). In the fraction of volatile carbonyl compounds, hexanal and 2-octenal were identified by mass spectrometry of the DNPH and by comparison with the spectra of the authentic samples. 2,4-Decadienal was not detected in any of the experiments. Its absence in experiment 1 does not contradict the results of Badings already mentioned (2), because he autoxidized a 50-fold higher amount of linoleic acid and therefore the yield of the minor volatile carbonyl compounds was considerably higher in his experiments.

For a better comparison of the individual experiments, the amounts of hexanal formed were based on a 50% autoxidation of the precursors (Table I). The values show that more hexanal was formed in the breakdown of HPOD than in that of linoleic acid. In contrast to hexanal which arose in equal amounts from the two HPOD, 2-octenal arose primarily from the 9-HPOD.

In the subsequent experiments, the solvent benzene was omitted to accelerate the autoxidation. A comparison of the 2,4-decadienal breakdown in Tables I and IV demonstrates the difference.

Autoxidation Rate of Aldehydes

The autoxidation rates of those aldehydes described in the literature (2) as major volatile products of the autoxidative breakdown of linoleic acid were measured (Fig. 2). Hexanal, 2-octenal and 2,4-decadienal autoxidized with similar velocities when alkoxy radicals to initiate the reaction were added, yet significantly faster than methyl linoleate.

The autoxidation of hexanal and 2,4-decadienal was also performed without addition of DBPO. As shown in Figure 2, hexanal degraded significantly slower than the unsaturated aldehyde. This result parallels that with 2,4-heptadienal and nonanal (15).

Autoxidation Products from Aldehydes

Autoxidation of hexanal, octanal and 2-octenal afforded the corresponding fatty acid as main product (Table II), and the 2-octenal also yielded low amounts of hexanal and heptanal. In contrast, the corresponding acid was absent in the experiments with 2,4-decadienal where hexanal pre-

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TABLE II

Autoxidation of Volatile Compounds: Products Identified by Mass Spectrometry

Compound	DBPO (μmol)	Reaction time ^c (min)	Autoxidation (%)	Products ^d (μmol)
Hexanal ^a	0.75	120	99	Hexanoic acid (58)
Hexanal ^a	--	240	76	Hexanoic acid (46)
Octanal ^a	0.75	120	97.5	Octanoic acid (53)
2-Octenal ^b	0.75	120	97	2-Octenoic acid (31), heptanal (2.5) Hexanal (1.6)
2,4-Decadienal ^b	0.75	120	99	Hexanal (9.9), 2-octenal (1.1) Hexanoic acid (2.0)
2,4-Decadienal ^b	--	180	98	Hexanal (8.9), 2-octenal (1.7), Hexanoic acid (2.5)

^aThe aldehyde (75 μmol) was injected by means of a syringe through the septum of a 100-ml Erlenmeyer flask containing DBPO and oxygen.

^bThe aldehyde (75 μmol) dissolved in a suitable solvent and 0.75 μmol DBPO dissolved in pentane was pipetted into a 100-ml Erlenmeyer flask. The substances were freed from the solvents in a stream of oxygen at -18°C . The flask was sealed hermetically with a septum.

^cAfter oxidation at 38°C , the reaction mixture was taken up in benzene injected with a syringe through the septum.

^dThe results of quantitative analysis are given in brackets (μmol).

TABLE III

Time Course of the Autoxidation of Hexanal, 2-Octenal and 2,4-Decadienal: Formation of Products

<u>Hexanal^a</u>					
Reaction time (min)	Autoxidation (%)	Products (μmol)			Peroxides ^b
		Hexanoic acid			
0	0	0			0
15	69	36			0.5
30	93	52			0.7
60	99	58			0.4

<u>2-Octenal^a</u>					
Reaction time (min)	Autoxidation (%)	2-Octenoic acid	Products (μmol)		Peroxides ^b
			Heptanal	Hexanal	
0	0	0	0	0	2.0
15	56	15	1.6	1.3	11.3
30	71	21	2.9	1.8	14.2
45	82	NA ^c	2.8	1.6	10.5
60	90	26	2.7	1.7	7.9
90	94	NA	2.5	1.5	7.1
120	97	31	2.5	1.6	6.4
180	100	37	2.6	1.5	6.2

<u>2,4-Decadienal^a</u>						
Reaction time (min)	Autoxidation (%)	Hexanal	2-Octenal	Products (μmol)		Peroxides ^b
				Hexanoic acid		
0	0	0	0	NA		1.5
15	32	2.0	0	NA		9.2
30	57	3.6	0.9	NA		9.8
45	72	4.8	1.4	NA		12.1
60	83	6.2	1.3	NA		10.2
90	94	8.9	1.4	NA		8.2
120	99	9.9	1.1	2.0		7.0
180	100	10.2	0.7	NA		5.4

^aPreparation of the samples and reaction conditions are described in the footnotes of Table II.

^bThe peroxide value caused by DBPO was subtracted.

^cNA: not analyzed.

TABLE IV

Autoxidation of Aldehyde Mixtures

No.	Reaction system ^a (μmol)			Autoxidation (%) ^a		Volatile products ^b (μmol)		
	Octanal	2,4-Decadienal	DBPO	Octanal	2,4-Decadienal	Hexanal	Hexanoic acid	Octanoic acid
1	75	--	0.75	98	--	0	0	53
2	--	75	0.75	--	99	10.2	2	0
3	75	75	1.5	60	92	9.8	2.8	14.3
4	75	150	2.25	46	90	17.3	2.8	7.0
5	150	75	2.25	65	95	12.0	5.6	37.0

^aReaction systems were prepared as detailed in the footnotes of Table II.

^bAfter 2 hr at 38 C.

dominated among the identified compounds and minor quantities of 2-octenal and hexanoic acid were found. Except for an acceleration of the reaction, the addition of DBPO did not influence the product spectrum of 2,4-decadienal. The identified products agree with the findings of Michalski and Hammond (17).

In comparison to linoleic acid, 9- and 13-HPOD, 2,4-decadienal was the most efficient precursor of hexanal (experiment 4, Table I.)

The time course of product formation was monitored during autoxidation of hexanal, 2-octenal and 2,4-decadienal (Table III). As opposed to hexanal, the two unsaturated aldehydes yielded relatively high levels of peroxides which are labile because their concentrations went through a transient maximum. Whether these intermediates are involved in the formation of carbonyl compounds shall be investigated. During 2,4-decadienal autoxidation (Table III), a linear increase of the concentration of hexanal was observed. In contrast, hexanal and heptanal very soon reached a low level plateau during the breakdown of 2-octenal.

Autoxidation of Aldehyde Mixtures

The result that, after initiation by DBPO, hexanal autoxidizes faster than 2,4-decadienal (Fig. 2) seems to contradict the findings that hexanal accumulates during autoxidation of

2,4-decadienal (Table III). To clarify this point, we autoxidized mixtures consisting of 2,4-decadienal plus octanal. Octanal was selected as the saturated aldehyde instead of hexanal because it does not interfere with the analysis of hexanal resulting from the 2,4-decadienal autoxidation.

Experiments 1 and 2 (Table IV) indicate that octanal and 2,4-decadienal were completely oxidized individually under the reaction conditions chosen. In the aldehyde mixtures, more than 90% of 2,4-decadienal was autoxidized but only 46 to 65% of octanal. The differences in octanal consumption in experiments 3 and 4 (Table IV) demonstrated that the amount of oxidized octanal decreased as the concentration of 2,4-decadienal in the reaction system increased. Clearly saturated aldehydes like octanal are protected to a certain extent against autoxidation in the presence of an unsaturated aldehyde.

DISCUSSION

In the experiments described here, 13-HPOD and, in addition, all compounds with a double bond in ω-6-position, such as 9-HPOD, 2-octenal and 2,4-decadienal, produce hexanal during autoxidation. In the latter case, hexanal is evidently formed via an oxidative cleavage of this double bond. In the reaction route suggested in Figure 3 for the breakdown

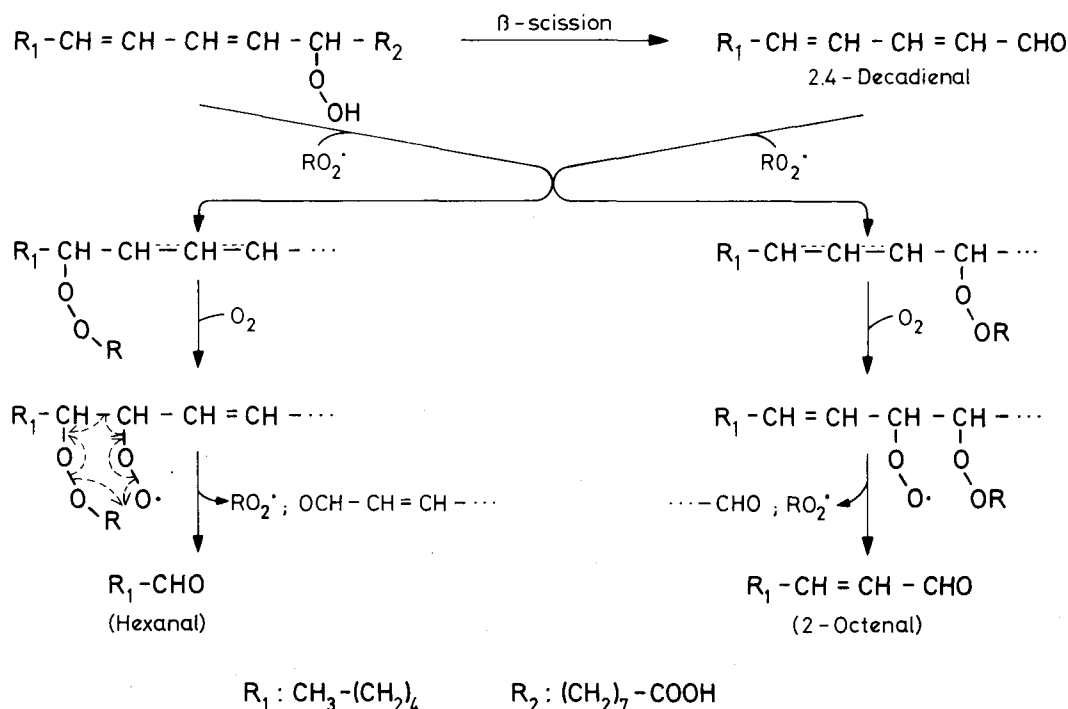


FIG. 3. Proposed pathway for the breakdown of 9-HPOD to hexanal and 2-octenal.

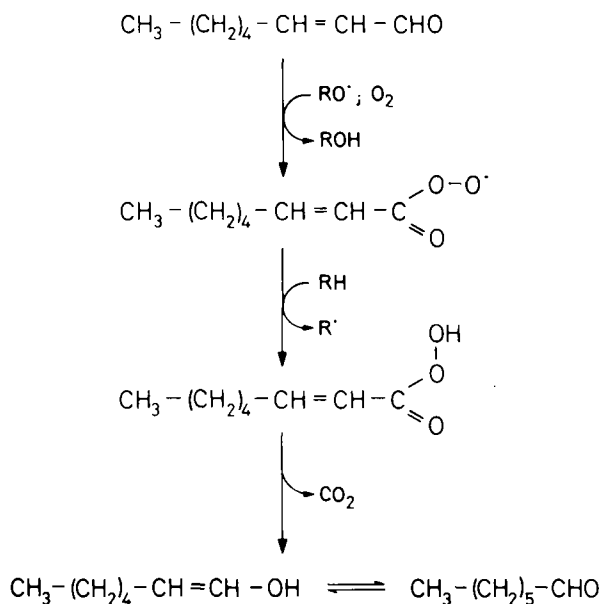


FIG. 4. Proposed pathway for the formation of heptanal from 2-octenal.

of 9-HPOD, free peroxy radicals attack the double bond systems of the hexanal precursors, causing peroxy peroxides to be formed. We assume that these polar peroxides are more labile than the primary hydroperoxides which result from the oxidation of unsaturated fatty acids. Therefore, they decompose easily to hexanal and to compounds of unknown structures.

The results and the pathways proposed in Figures 1 and 3 explain why hexanal predominates among the volatile aldehydes arising from the autoxidation of linoleic acid. It is the only aldehyde that arises both from the two initially formed hydroperoxides (9- and 13-HPOD) as well as from some of the unsaturated aldehydes. For this reason alone, the yield of 2,4-decadienal must be smaller than that of hexanal, as the 2,4-decadienal can only arise through β -scission of the 9-HPOD. Furthermore, in the reaction mixture containing both saturated and unsaturated aldehydes, 2,4-decadienal autoxidizes faster, resulting in additional amounts of hexanal.

A rearrangement of the hydroperoxy group as suggested by Chan et al. (12) was observed for the breakdown of 13-HPOD initiated by DBPO in the presence of oxygen (25). However, the composition of the volatile aldehydes cannot reflect this rearrangement because the results described here show that autoxidation of 9-HPOD, 13-HPOD and 2,4-decadienal all yield hexanal. Only in the absence of oxygen were relatively high amounts of 2,4-decadienal and hexanal obtained from the decomposition of 9- and 13-HPOD (12). Under these conditions, the composition of the aldehyde fraction indeed indicates that a rearrangement of the 9- and 13-HPOD isomers has occurred.

The results demonstrate that 2-octenal, which has been detected by several authors as a product of linoleic acid autoxidation (2,34), originates from the 9-HPOD and from 2,4-decadienal. Obviously, the ω -8-double bond is oxidized in these precursors (Fig. 3). The assumption that 2-octenal results from decomposition of the 11-hydroperoxide isomer (11) is dubious, because this hydroperoxide has never been detected among the products resulting from the autoxidation of methyl linoleate (3-6).

In contrast to hexanal, 2-octenal is more sensitive to autoxidation and forms heptanal and other compounds. Badings (2) has identified heptanal as a minor volatile component of linoleic acid autoxidation. Our results identify the precursor from which heptanal may be formed. The proposed pathway (Fig. 4) assumes that autoxidation of an aldehyde to an acid occurs via the corresponding peracid as intermediate (35). We suggest that in a side reaction, the peracid decomposes, eliminating carbon dioxide and an enol which rearranges to heptanal.

Oxoacids arise from the breakdown of 9- and 13-HPOD by β -scission (8). The formation of these acids was not studied in our experiments.

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