

# 4-Hydroxy-2-alkenals and Other Products Formed by Water-Mediated Oxidative Decomposition of $\alpha,\beta$ -Unsaturated Aldehydes<sup>†</sup>

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Water-mediated (pH 6.5) model experiments were carried out with (*E*)-2-hexenal (1), (*E*)-2-octenal (2), and (*E,E*)-2,4-decadienal (3) under oxygen atmosphere. After complete degradation of the  $\alpha,\beta$ -unsaturated aldehydes 1-3 and solvent extraction of the products formed, separation into neutral and acid fractions was performed by bicarbonate treatment. Subsequent HRGC, HRGC-MS, and HRGC-FTIR analyses revealed predominant formation of acids from 1 and 2, while for 3 the neutral fraction prevailed. In the neutral fractions 3-hydroxyhexanal was the major product formed from 1 and 1-hydroxy-2-heptanone and hexanal were found to be the major products formed from 2; the dienal 3 predominantly yielded hexanal and hexanoic acid. As minor products the toxicologically relevant compounds 4-hydroxy-(*E*)-2-hexenal, 4-hydroxy-(*E*)-2-octenal, and 4-hydroxy-(*E*)-2-nonenal arising from 1-3, respectively, were detected.

## INTRODUCTION

Alkenals and alkadienals, including (*E*)-2-hexenal (1), (*E*)-2-octenal (2), and (*E,E*)-2,4-decadienal (3), are formed by oxidative processes from unsaturated fatty acids (Grosch, 1987, 1989). They are considered to contribute desirably to the aroma of a variety of foods, but they are also frequently associated with undesirable flavors as well (Grosch, 1982; Boelens and Van Gemert, 1987; Ho et al., 1987; Grosch, 1989; Gasser and Grosch, 1990; Schieberle and Grosch, 1991). In addition, due to their chemical reactivity, these compounds are known to be susceptible to further degradations *via* autoxidation (Fischer and Grosch, 1988), hydration (Fischer and Grosch, 1991), and retro-aldol condensation reactions (Josephson and Lindsay, 1987; Josephson and Glinka, 1989).

The purpose of this research was to study the water-mediated oxidative degradation of 1-3 to elucidate novel structures including those exhibiting potential toxicological relevance.

## EXPERIMENTAL PROCEDURES

**General.** All commercial chemicals used, including 1-3 (Aldrich), were of analytical grade quality. They were stored under nitrogen at -30 °C. All solvents employed were of high purity at purchase and were redistilled before use.

**Model Degradation Studies.** Using a 100-mL two-neck flask, the educt (1 mmol each of 1-3) was added to 50 mL of distilled water (pH 6.5). After solubilization by sonification for 20 min, the flask was fitted with a balloon cap and the mixture was magnetically stirred under oxygen at room temperature until >90% of the educt was decomposed (HRGC control).

**Isolation of Products.** The oxidized mixture was treated with 50 mL of saturated bicarbonate solution and extracted three times with 50 mL of diethyl ether. After organic phase was thoroughly washed with diluted HCl and distilled water, dried over sodium sulfate, and filtered and an external standard was added (400  $\mu$ g each of cyclohexanol, 1-octanol, and 2-decanol for HRGC analysis of 1, 2, and 3, respectively), the mixture was carefully concentrated to 0.5 mL using a Vigreux column (45 °C). The aqueous phase was adjusted with 0.5 N HCl to pH 2 and extracted three times with 50 mL of diethyl ether. After the extract was thoroughly washed with distilled water, it was treated

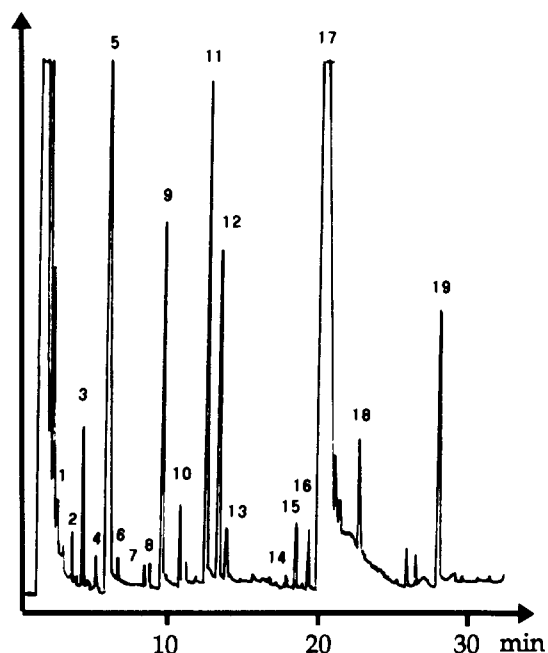
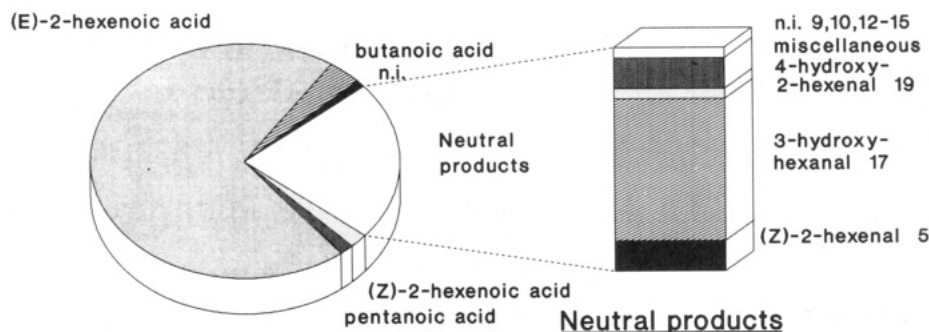


Figure 1. HRGC-MS separation on a J&W DB-Wax fused silica capillary column (30 m  $\times$  0.25 mm i.d.; film thickness 0.25  $\mu$ m) of neutral products formed from 1 by water-mediated (pH 6.5) oxidation.

in the same manner as the neutral fraction, but using 2,2-dimethylpentanoic acid (1 mg) as external standard for 1-3. The two organic phases obtained were then subjected to HRGC, HRGC-MS, and HRGC-FTIR analysis.

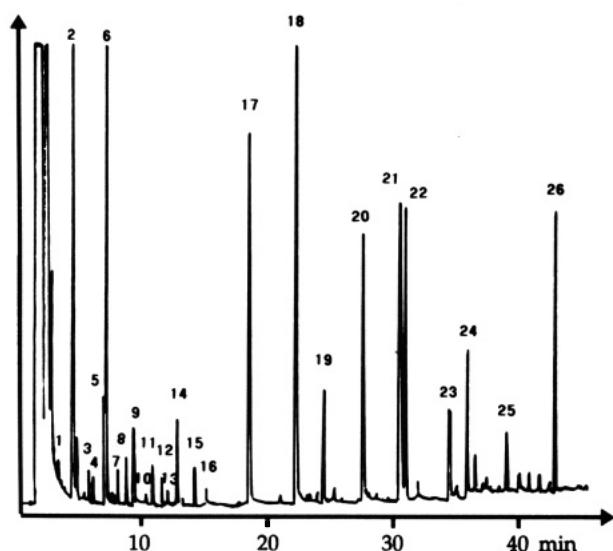
**Preparative Separation and Purification of Products 14, 15, and 17.** After diethyl ether extraction of the mixtures obtained by complete oxidative degradation of 2 and 3 (3 mmol each), respectively, the products were subjected to liquid chromatographic separation on silica gel (0.2-0.5 mm, Merck; 20  $\times$  400 mm glass column) using 200-mL fractions of a pentane-diethyl ether gradient [9 + 1 (A); 8 + 2 (B); 7 + 3 (C); 5 + 5 (D); 2 + 8 (E)]. Fractions C, D, and E, containing 17, 15, and 14, respectively, were concentrated under vacuum (rotavapor) to 2 mL and were further separated by flash chromatography (Still et al., 1978) using a 10  $\times$  300 mm glass column filled with silica gel (0.032-0.063 mm; Merck). Elution (10 mL/min) with a pentane-diethyl ether gradient [9 + 1 (I); 7 + 3 (II); 5 + 5 (III); 4 + 6 (IV)] under N<sub>2</sub> pressure (1 bar) led to separation of 40 10-mL fractions (I/1-10 to IV/1-10). For subsequent HPLC

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### Total distribution of products

**Figure 2.** Quantitative distribution of products formed from 1 by water-mediated (pH 6.5) oxidation. Miscellaneous neutral compounds: 1, pentanal; 2, 2-pentanol; 3, (*E*)-2-pentenal; 4, (*Z*)-3-hexenal; 6, educt 1; 7, 5-oxo-(*E*)-2-hexenal; 8, (*E*)-2-penten-1-ol; 11, standard; 16, 2-hydroxyhexanal; 18, 5-ethyl-2(5*H*)-furanone. n.i., not identified, peaks 9, 10, 12–15. The numbers correspond to the peak numbers in Figure 1.



**Figure 3.** HRGC-MS separation on a J&W DB-Wax fused silica capillary column (30 m × 0.25 mm i.d.; film thickness 0.25 μm) of neutral products formed from 2 by water-mediated (pH 6.5) oxidation.

purification of 17, 15, and 14, fractions II/6–8, III/5–7, and IV/3–5, respectively, were each combined and concentrated *in vacuo* to 1 mL. Preparative HPLC was performed using a 16 × 250 mm SiO<sub>2</sub> Lichrospher 60 column (5 μm; Knauer, Berlin). Elution was carried out with diethyl ether (10 mL/min) monitored at 220 nm.

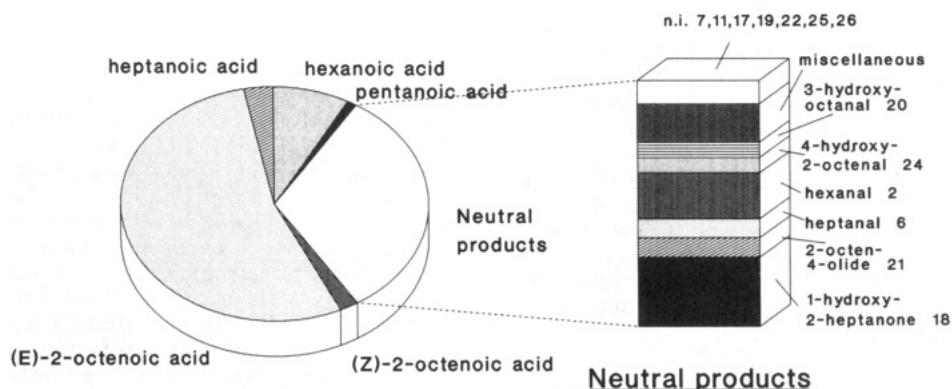
**Capillary Gas Chromatography (HRGC).** For HRGC a Carlo Erba Fractovap 4160 gas chromatograph equipped with a

J&W fused silica DB-Wax capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm) was used. Split injection (1:30) was employed. The temperature program was 3 min isothermal at 50 °C, ramped to 240 °C at 4 °C/min. The flow rates were 1.6 mL/min of He for the carrier gas, 30 mL/min of N<sub>2</sub> for the makeup gas, and 30 mL/min of H<sub>2</sub> and 300 mL/min of air for the detector gases. The injector temperature was kept at 220 °C and the detector temperature at 250 °C. Linear retention index (*R*<sub>i</sub>) was based on a series of hydrocarbons.

**Capillary Gas Chromatography–Mass Spectrometry (HRGC–MS).** A Varian 3300 gas chromatograph equipped with a split injector (1:20) was combined by direct coupling to a Finnigan MAT 44 mass spectrometer with a PCDS data system. The same type of column and the same temperature program as mentioned above for HRGC analysis were used. The temperature of the ion source and of all connection parts was 220 °C, electron energy was 70 eV, and cathodic current was 0.7 mA.

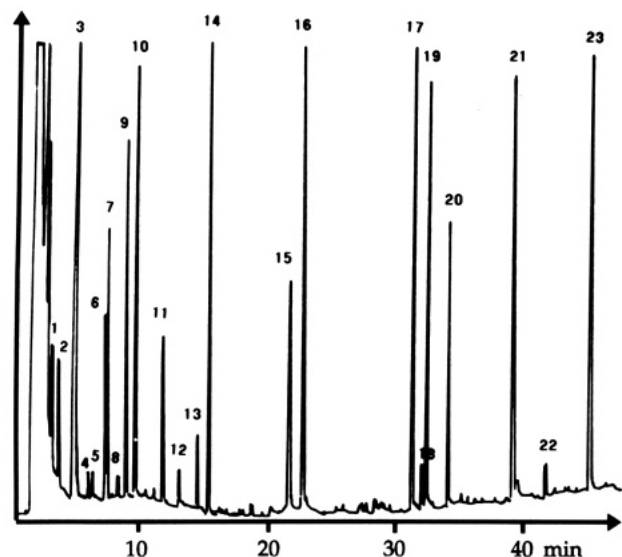
Results of qualitative analyses were verified by comparison of HRGC retention (*R*<sub>i</sub>) and mass spectral data with those of authentic reference substances. Quantitative HRGC determinations were carried out by means of external standards added without evaluation of response factors (*F* = 1.0).

**Capillary Gas Chromatography–Fourier Transform Infrared Spectroscopy (HRGC–FTIR).** HRGC–FTIR analysis was carried out with a Nicolet 20 SXB system interfaced with a Dani 6500 gas chromatograph equipped with flame ionization detector. The same type of column as mentioned above for HRGC analysis was used. Total sample injection mode employing programmed temperature vaporization (PTV) (40–240 °C, 0.1 min) was performed. Temperature program, gases, and flow rates were the same as described above for HRGC. Light pipe and transfer line were held at 250 °C. Vapor-phase FTIR spectra were recorded from 400 to 4000 cm<sup>-1</sup> with a resolution of 8 cm<sup>-1</sup>.



### Total distribution of products

**Figure 4.** Quantitative distribution of products formed from 2 by water-mediated (pH 6.5) oxidation. Miscellaneous neutral compounds: 1, 2-pentanone; 3, 2-butyrfuran; 4, 1-butanol; 5, 2-heptanone; 8, (*Z*)-4-heptenal; 9, 1-pentanol; 10, 2-octanone; 12, (*E*)-2-heptenal; 13, 1-hepten-3-ol; 14, 1-hexanol; 15, (*Z*)-2-octenal; 16, educt 2; 23, 7-pentadecanone. n.i., not identified, peaks 7, 11, 17, 19, 22, 25, and 26. The numbers correspond to the peak numbers in Figure 3.



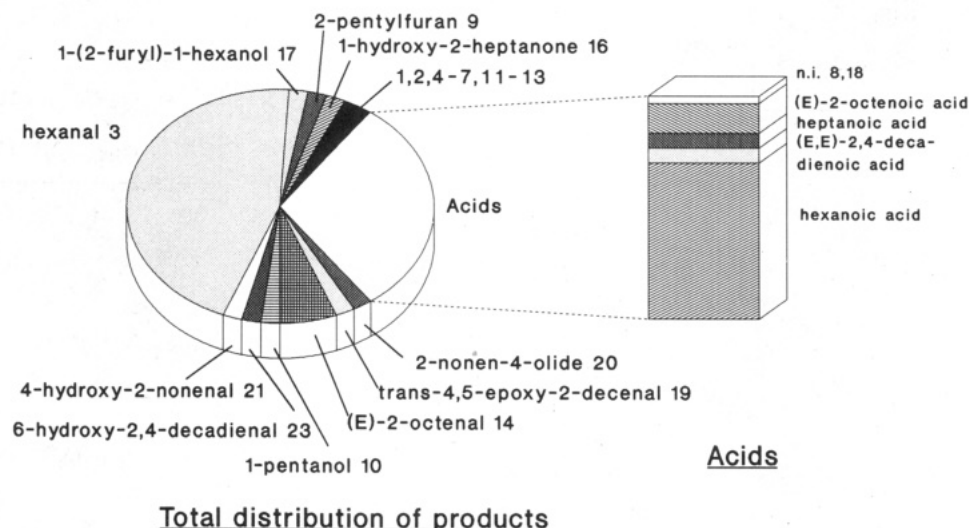
**Figure 5.** HRGC-MS separation on a J&W DB-Wax fused silica capillary column (30 m  $\times$  0.25 mm i.d.; film thickness 0.25  $\mu$ m) of neutral products formed from 3 by water-mediated (pH 6.5) oxidation).

**Nuclear Magnetic Resonance (NMR).**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AC 200 instrument with  $\text{CDCl}_3$  as solvent and  $\text{Me}_4\text{Si}$  as reference standard.

## RESULTS

The complete decomposition (>90% by HRGC) of (*E*)-2-hexenal (1), (*E*)-2-octenal (2), and (*E,E*)-2,4-decadienal (3) in the course of water-mediated (pH 6.5) oxidation was achieved after 64, 8, and 2 days, respectively. In the following, the results obtained are represented in relation to the  $\alpha,\beta$ -unsaturated aldehyde used.

**(*E*)-2-Hexenal (1).** In Figure 1, the HRGC-MS separation of neutral products formed from 1 is outlined. Their quantitative distribution is represented in Figure 2. The relation between acids and neutral products formed, also shown in Figure 2, was about 4:1. (*E*)-2-Hexenoic acid (4) and 3-hydroxyhexanal (7) predominated with about 66% and 16% (each of the total volatiles formed), respectively. Minor reaction products detected were butanoic acid (10) (4%), (*Z*)-2-hexenoic acid (2%), and pentanoic acid (1%)



**Figure 6.** Quantitative distribution of products formed from 3 by water-mediated (pH 6.5) oxidation. Miscellaneous neutral compounds: 1, pentanal; 2, 2-butanol; 4, 2-butyrfuran; 5, 1-butanol; 6, heptanal; 7, 2-heptanone; 11, (*E*)-2-heptenal; 12, 1-hexanol; 13, (*Z*)-2-octenal; 16, 2-butyl-(*E*)-2-octenal; 22, 3-hydroxy-4-decenal. n.i., not identified, peaks 8 and 18. The numbers correspond to the peak numbers in Figure 5.

as well as (*Z*)-2-hexenal (3%) and 4-hydroxy-(*E*)-2-hexenal (12) (0.8%).

**(*E*)-2-Octenal (2).** The HRGC-MS separation of neutral volatiles formed from 2 is shown in Figure 3. Their quantitative distribution is represented in Figure 4. The relation between acids and neutral volatiles produced was evaluated to be approximately 3:1 (Figure 4). In the acid fraction, with about 52% of the total volatiles, (*E*)-2-octenoic acid (5) distinctly predominated. In the neutral fraction, a quite uniform distribution of main products was observed; i.e., 1-hydroxy-2-heptanone (15) (9.5%), hexanal (9) (6%), heptanal (6) and 2-octen-4-olide (13) (each 2.5%, and 3-hydroxyoctanal (8) and 4-hydroxy-(*E*)-2-octenal (12) (each 1.8%) were found.

**(*E,E*)-2,4-Decadienal (3).** The HRGC-MS separation of neutral products formed from 3 and their quantitative distribution are represented in Figures 5 and 6, respectively. In contrast to the experiments carried out with 1 and 2, the oxidative decomposition of 3 yielded a higher amount of neutral products than acids (relation about 3:1). Prevailing products were hexanal (42%) and hexanoic acid (21%) (of the total volatiles formed). Minor products were (*E*)-2-octenal (2) (6%), (*E*)-2-octenoic acid (5) (4%), 1-(2'-furyl)hexan-1-ol (17) (2.5%), 6-hydroxy-(*E,E*)-2,4-decadienal (2.2%), *trans*-4,5-epoxy-(*E*)-2-decenal (16) (2%), 4-hydroxy-(*E*)-2-nonenal (14) (1.8%), and 1-pentanol and 2-nonen-4-olide (each 1.5%).

## DISCUSSION

As to the potential formation pathways of the products formed by water-mediated oxidative decomposition of 1-3, a few fundamental chemical reactions have to be considered: first of all, as shown in Figure 7, the oxidation of the carbonyl function *via* intermediate peroxy acid (A) leading both to acid (B) and, after decarboxylation, to aldehyde (C) (Schieberle and Grosch, 1981). In such a way, the formation of products 4-6 from 1 and 2, respectively, may be explained.

In addition, as outlined in Figure 8, the hydration of the double bond (D) and subsequent retro-aldol reaction (D1) as well as oxidation of the aldehyde formed (D2) have to be regarded (Josephson and Glinka, 1989; Fischer and Grosch, 1991). By these reactions, the generation of products 7-10 as well as 2 and 5 from 1 and 2 as well as 3, respectively, may be likely.

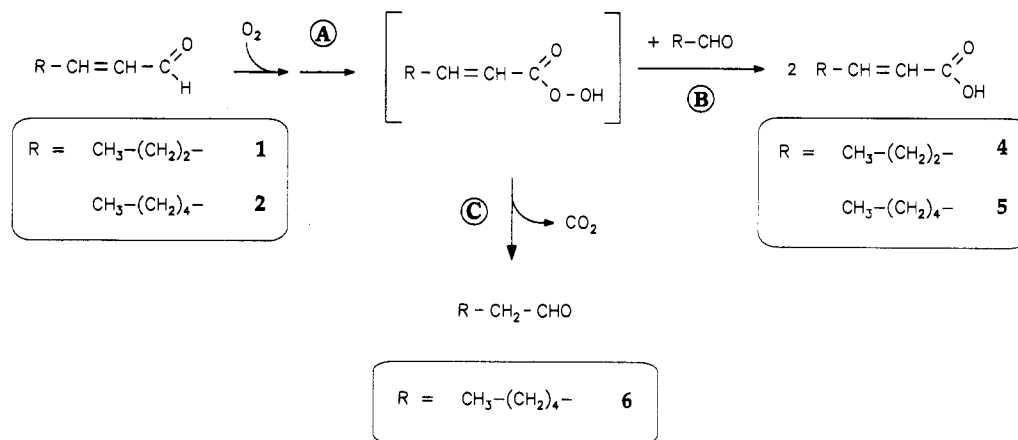


Figure 7. Postulated pathways for the formation of products 4-6 from 1 and 2, respectively.

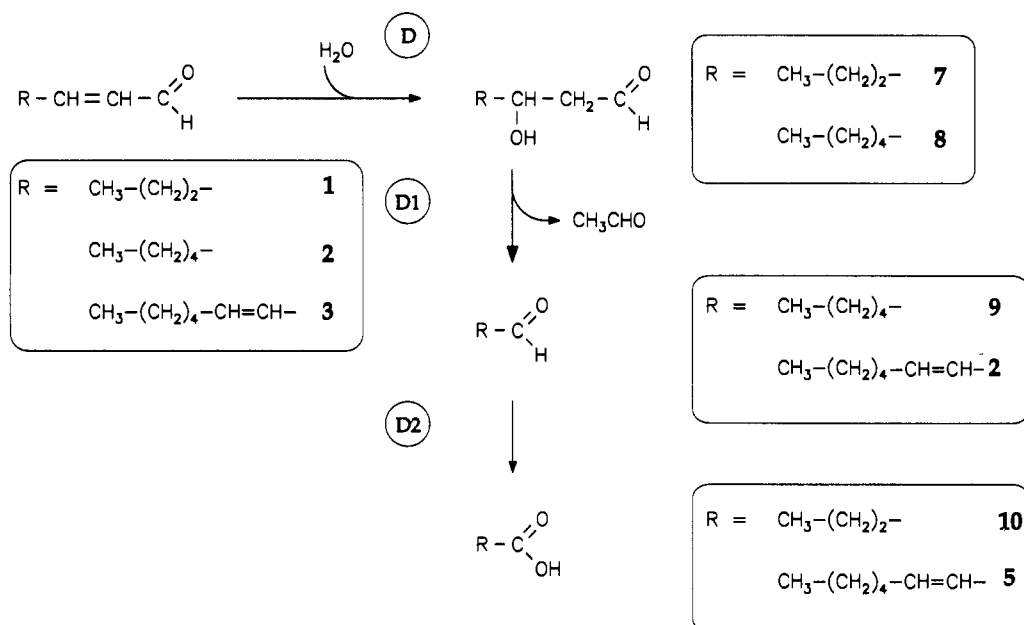


Figure 8. Postulated pathways for the formation of products 7-10 as well as 2 and 5 from 1 and 2 as well as 3, respectively.

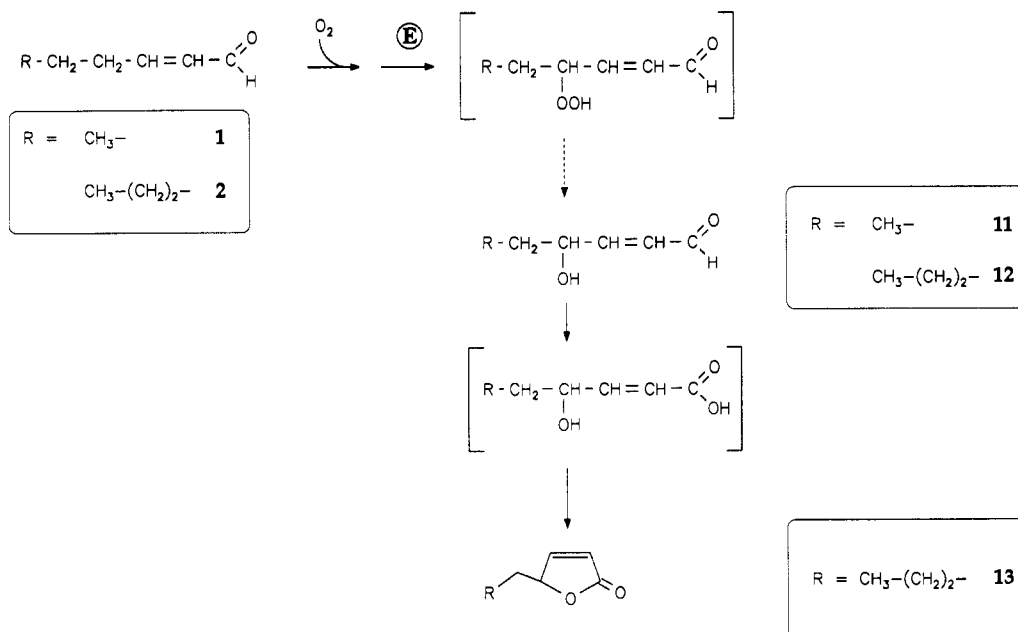
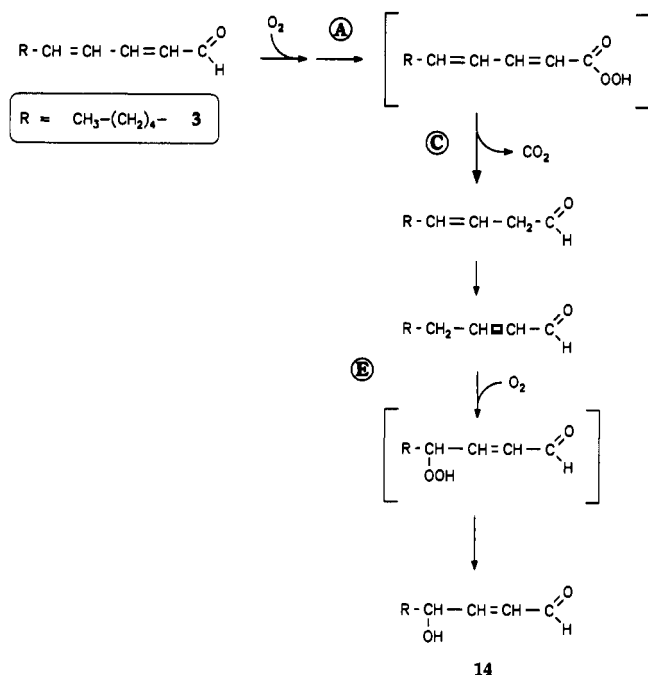


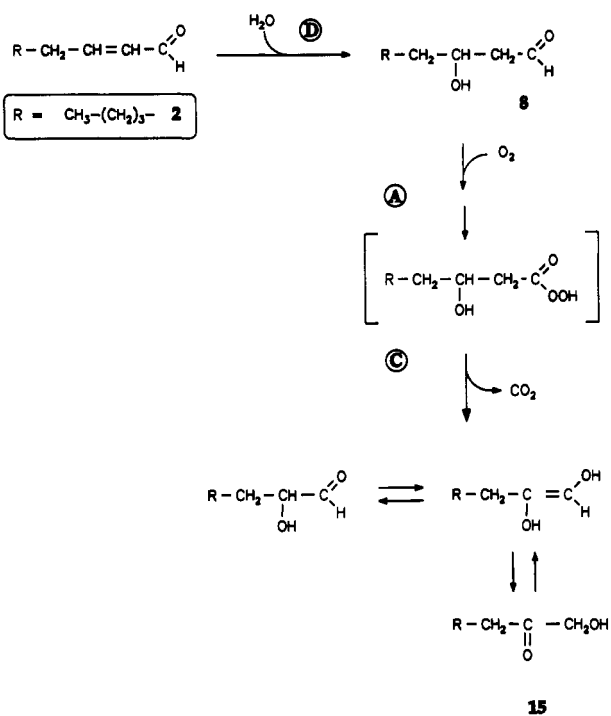
Figure 9. Postulated formation pathway of 4-oxygenated products 11, 12, and 14 via allylic hydroperoxidation.

Finally, allylic hydroperoxidation (Takeoka et al., 1986) has to be taken into account to explain the formation of

4-oxygenated reaction products 11-13 (Figure 9). Whereas the generation of 4-hydroxyalkenals 11 and 12 from 1 and



**Figure 10.** Postulated formation pathway of 14 from 3 via peroxo acid (A), retro-aldol reaction (C), and allylic hydroperoxidation (E).



**Figure 11.** Postulated formation pathway of 15 from 2 via hydration (D), peroxo acid (A), retro-aldol reaction (C), and subsequent rearrangement.

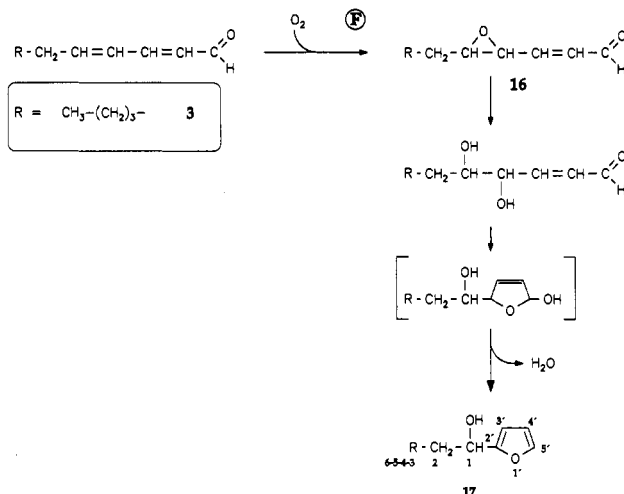
2, respectively, may be understood according to pathway E (Figure 9), the formation of 4-hydroxy-(*E*)-2-nonenal (14) might be explained by a cascade of reactions, in which the pathways A/C and E are involved (Figure 10). The importance of allylic hydroperoxidation is also obvious by the formation of 6-hydroxy-(*E,E*)-2,4-decadienal from 3 (cf. Figure 6).

For the generation of 1-hydroxy-2-heptanone (15) from 2 a pathway may be operative in which the initial product 8 undergoes oxidation via peroxo acid (A), retro-aldol reaction (C), and subsequent rearrangement (Figure 11). Many years ago, 15 was detected as minor component

**Table I. Chromatographic and Spectroscopic Data of 1-Hydroxy-2-heptanone (15)**

HRGC, <sup>a</sup> <i>R</i> <sub>i</sub>	1645
MS, <sup>b</sup> <i>m/z</i> (%)	43 (100), 99 (38), 71 (29), 41 (23), 55 (11), 42 (9), 100 (3), 56 (3)
vapor phase	
FTIR, $\nu$ (cm <sup>-1</sup> )	3533, 2942, 1730, 1412, 1283, 1054
<sup>1</sup> H NMR, <sup>c</sup> $\delta$	4.24 (br s, 2H, H-1), 2.40 (t, 2H, <i>J</i> = 7.2 Hz, H-3), 1.61 (s, OH), 1.2-1.3 (m, 6H, H-4, H-5, H-6), 0.90 (t, 3H, H-7)

<sup>a</sup> DB-Wax. <sup>b</sup> The eight most intense peaks are represented. <sup>c</sup> 200 MHz, CDCl<sub>3</sub>,  $\delta$  relative to Me<sub>4</sub>Si.



**Figure 12.** Postulated formation pathway of 17 from 3 via 4,5-epoxidation (F), opening to the 4,5-diol, acetalization, and dehydration.

**Table II. Chromatographic and Spectroscopic Data of 1-(2'-Furyl)hexan-1-ol (17)**

HRGC, <sup>a</sup> <i>R</i> <sub>i</sub>	1950
MS, <sup>b</sup> <i>m/z</i> (%)	97 (100), 94 (36), 107 (33), 79 (22), 150 (20), 77 (18), 41 (14), 168 (7)
vapor phase	
FTIR, $\nu$ (cm <sup>-1</sup> )	3646, 3124, 2940, 2875, 1151, 1012, 734
<sup>1</sup> H NMR, <sup>c</sup> $\delta$	7.37 (dd, 1H, <i>J</i> <sub>1</sub> = 1.8 Hz, <i>J</i> <sub>2</sub> = 0.8 Hz, H-5'), 6.33 (dd, 1H, <i>J</i> <sub>1</sub> = 3.2 Hz, <i>J</i> <sub>2</sub> = 1.8 Hz, H-4'), 6.23 (br d, 1H, <i>J</i> = 3.2 Hz, H-3'), 4.64 (t, 1H, <i>J</i> = 6.8 Hz, H-1), 1.83 (m, 2H, H-2), 1.2-1.4 (m, gH, H-3, H-4, H-5), 0.90 (t, 3H, H-6)
<sup>13</sup> C NMR, <sup>d</sup> $\delta$	142.7, 110.9, 106.5, 68.6, 36.2, 32.2, 25.8, 23.1, 14.6, signal for C-2' not discernible

<sup>a</sup> DB-Wax. <sup>b</sup> The eight most intense peaks are represented. <sup>c</sup> 200 MHz, CDCl<sub>3</sub>,  $\delta$  relative to Me<sub>4</sub>Si. <sup>d</sup> 50.3 MHz, CDCl<sub>3</sub>,  $\delta$  relative to Me<sub>4</sub>Si.

among the water-mediated oxidative decomposition products of methyl linoleate (Esterbauer and Schauenstein, 1967). In our study, 15 was identified by <sup>1</sup>H NMR spectroscopy after its preparative separation and purification from the product mixture obtained from 2. The chromatographic and spectroscopic data of 15 are outlined in Table I.

*trans*-4,5-Epoxy-(*E*)-2-decenal was detected among the reaction products of 3 (Figure 6). Recently, this compound has been found as an effective aroma substance in wheat bread (Schieberle, 1990) and also as a trace compound responsible for the "reversion flavor" of soybean oil (Guth and Grosch, 1990) and the "warmed-over-flavor" of boiled beef (Konopka and Grosch, 1991). The importance of epoxidation for the breakdown of 3 is also demonstrated for the generation of 1-(2'-furyl)hexan-1-ol (17) (Figure 12). By initial epoxidation (F), subsequent diol formation, cyclization, and dehydration, the formation of 17 from 3

**Table III. Chromatographic and Spectroscopic Data of 4-Hydroxy-(E)-2-nonenal (14)**

HRGC, <sup>a</sup> $R_i$	2287
MS, <sup>b</sup> $m/z$ (%)	57 (100), 43 (86), 41 (42), 55 (32), 86 (30), 71 (27), 81 (22), 99 (20)
vapor phase	
FTIR, $\nu$ (cm <sup>-1</sup> )	3650, 2939, 2872, 2807, 2720, 1715, 1636, 977
<sup>1</sup> H NMR, <sup>c</sup> $\delta$	9.58 (d, 1H, $J_1 = 7.8$ Hz, H-1), 6.82 (dd, 1H, $J_1 = 15.6$ Hz, $J_2 = 4.7$ Hz, H-3), 6.31 (ddd, 1H, $J_1 = 15.6$ Hz, $J_2 = 7.8$ Hz, $J_3 = 1.5$ Hz, H-2), 4.44 (m, 1H, H-4), 1.82 (m, OH), 1.7-1.2 (m, 8H, H-5, H-6), H-7, H-8), 0.90 (t, 3H, H-9)
<sup>13</sup> C NMR, <sup>d</sup> $\delta$	193.4, 158.7, 130.7, 71.1, 36.5, 31.6, 24.8, 22.5, 13.9
<sup>a</sup> DB-Wax. <sup>b</sup> The eight most intense peaks are represented. <sup>c</sup> 200 MHz, CDCl <sub>3</sub> , $\delta$ relative to Me <sub>4</sub> Si. <sup>d</sup> 50.3 MHz, CDCl <sub>3</sub> , $\delta$ relative to Me <sub>4</sub> Si.	

might be explained. 2-Furylcarbinols including 17 have been proven to be versatile building blocks in the synthesis of monosaccharides and other natural products (Kobayashi et al., 1988; Waldmann, 1989; Gawronski et al., 1990). In the food chemistry area, however, 17 has not been described to date. Its chromatographic and spectroscopic data are summarized in Table II.

The 4-hydroxyalkenals 11 and 12 were identified by comparison of  $R_i$  and MS data with those of reference substances [11:  $R_i$  1942;  $m/z$  43 (100), 57 (55), 58 (22), 55 (20), 41 (19), 71 (11), 69 (11), 42 (8). 12:  $R_i$  2140;  $m/z$  57 (100), 41 (37), 85 (31), 55 (15), 43 (14), 81 (11), 95 (11), 69 (5)]. Structural evaluation of 14 was performed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy after its preparative isolation and purification from the product mixture obtained from 3. The chromatographic and spectroscopic data of 14 are summarized in Table III.

The products 11, 12, and 14 are of particular importance due to their cytotoxic and mutagenic properties (Brambilla et al., 1986; Spitz et al., 1990; Selley et al., 1991). Their role as products of lipid peroxidation has been known for many years (Esterbauer, 1982). With our present studies, the  $\alpha,\beta$ -unsaturated aldehydes 1-3 were demonstrated as their potential immediate precursors for the first time. However, to confirm the postulated formation pathways (cf. Figures 1-6), labeling studies will be necessary.

#### ACKNOWLEDGMENT

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