Food Chemistry **39** (1991) 59–72

Breakdown of the Flavour Compound 2(E)-Hexenal in Different Solvents

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(Received 27 November 1989; revised version received and accepted 15 January 1990)

ABSTRACT

The influence of the solvents 20 per cent (v/v) aqueous ethanol (pH 3·5, Et) and triacetin (Tr) on the rate and on the products of the breaksown of 2(E)-hexenal at 38°C has been investigated. The rate constants ($\times 10^{-3}\,h^{-1}$*), which were determined for hexanal (7·65 Et, 8·04 Tr), 2(E)-hexenal (3·8 Et, 9·8 Tr), 3(Z)-hexenal (20·08 Et, 26·35 Tr) and some* C_7*-aldehydes, indicated that 2(E)-hexenal was more stable in Et than in Tr. In Tr, autoxidation of 2(E)-hexenal to the corresponding acid was the major reaction and the minor product, butanoic acid, was the most important odour compound. In Et, the flavour potential of 2(E)-hexenal was lowered by the formation of 3-hydroxyhexanal and 3-ethoxyhexanal. Isomerisation of the 2(E)-double bond into 2(Z)-, 3(E)- and 3(Z)-double bonds also took place, affording among other compounds, 3(Z)-hexenal which, on the basis of its low odour threshold, predominated in the overall aroma.*

INTRODUCTION

2(E)-Hexenal is an important aroma compound of many fruits and vegetables (Van Straten & Maarse, 1983), and it is used as flavouring substance for 'green' notes in fruit flavours (Bauer *et al.*, 1988).

2(E)-Hexenal is not stable and its concentration decreases quite rapidly during the storage of apple juice (Emberger, 1981), kiwifruit extract (Takeoka *et al.*, 1986) and tomato juice (Crouzet *et al.*, 1983). The aroma defects arising in these foods are not caused only by the loss of 2(E)-hexenal

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but, also, by aroma compounds resulting from the breakdown of 2(E)-hexenal.

In an earlier communication (Fischer & Grosch, 1988) about model experiments concerning the degradation of 2(E)-hexenal, the breakdown products formed in 20 per cent (v/v) aqueous ethanol (pH 6·5) were analysed. Thirty volatiles were detected, and among these, 3(Z)-hexenal, butanoic acid, pentanoic acid, 2(E)- and 3(E)-hexenoic acid had the highest odour units (ratio of the concentration to the odour threshold).

The aim of the following study is to show the influence of solvents such as 20 per cent (v/v) aqueous ethanol at pH 3·5 and triacetin, on the rate and on the products of the breakdown of 2(E)-hexenal. The pH of 3·5 was selected, since it lies in a range occurring in many fruits (Ulrich, 1970). Among the products of 2(E)-hexenal, those showing high odour units (ratio of the concentration to the odour threshold) were detected by an aroma extract dilution analysis (AEDA, Schmid & Grosch, 1986; Ullrich & Grosch, 1987).

MATERIALS AND METHODS

Materials

In addition to the chemicals earlier reported (Fischer & Grosch, 1988), the following were used in the present study: pentanal, 2(E)-pentenal, 1-penten-3-ol, 2(E/Z)-pentenol, 2(E)-pentenol, 3(E)-hexenol, heptanal, 2(E)-heptenal and octanal were from Aldrich (Steinheim, FRG); 4(Z)-heptenal was a gift of Haarmann & Reimer, Holzminden and 3(Z)-hexenoic acid was a gift from Dr Berger, Institute of Food Technology and Analytical Chemistry, TU-Weihenstephan, FRG.

The solvents were purified (Fischer & Grosch, 1988); silica gel 60 (Merck, Darmstadt, FRG) was treated with HCl and deactivated with 7 per cent (w/w) water according to Esterbauer (1968). 3(E)-Hexenal was prepared by oxidation of 3(E)-hexenol (Kajiwara *et al.*, 1975). The aldehydes were purified by distillation *in vacuo* and then stored at −60°C until use (Fischer & Grosch, 1988). Twenty per cent EtOH, pH 3·5: sodium citrate buffer (0·2 M, pH 3·5) was diluted with ethanol to a final concentration of 20 per cent (v/v).

METHODS

Storage experiments

For the determination of rate constants, a solution (40 ml) of the aldehyde (2 mg/ml) was stirred in an atmosphere of pure oxygen at 38°C using the apparatus reported earlier (Fischer & Grosch, 1988). To identify the products, the initial concentration of the 2(E)-hexenal was increased to 8 mg/ml.

Quantification of the aldehydes

In the kinetic experiments, the determination of the aldehydes was performed by gas chromatography (aldehydes in 20 per cent EtOH, pH 3·5) and after derivatisation with 2,4-dinitrophenylhydrazine (aldehydes in triacetin), by HPLC (Fischer & Grosch, 1988). *n*-Octanol, instead of *n*-heptanal, was used as internal standard in the latter procedure.

Analysis of the breakdown products of 2(E)-hexenal

The products formed in 20 per cent EtOH, pH 3·5, were isolated and analysed as detailed earlier (Fischer & Grosch, 1988). In the case of the reaction mixture dissolved in triacetin, two methods, designated (a) and (b), were used for the analysis of the products:

(a) The solvent and the peroxides formed were separated from the other products by chromatography on water-cooled columns (35 cm × 2 cm) packed with a slurry of silica gel 60 in pentane. The reaction mixture, in portions of 5 ml per run, was applied on the column and the elution was performed with pentane (50 ml), pentane/diethyl ether (95:5, v/v, 100 ml), pentane/diethyl ether (9:1, v/v, 100 ml), pentane/diethyl ether (85:15, v/v, 100 ml) and finally pentane/diethyl ether (80:20, v/v, 100 ml). The effluent (flow rate: 1·5 ml/min) was collected in fractions of 50 ml. The last two fractions, in which the peroxides were detected by TLC, were omitted, and the other fractions were combined, concentrated by distillation of the solvent, and finally analysed by high resolution gas chromatography (HRGC) on capillary OV-1/FFAP.

(b) Analysis of the neutral fraction: the reaction mixture (20 ml) was extracted with pentane (2 × 30 ml) to separate the products from the triacetin. The pentane solutions were combined and washed successively with 0·5 M sodium carbonate (2 × 30 ml) (since most of the peroxides were peracids, they were removed by this step) and brine (50 ml). The pentane solution of the neutral compounds was dried over sodium sulphate, concentrated by distillation of the solvent, and finally analysed by HRGC on capillary SE-54.

High-resolution gas chromatography

HRGC of the combined solutions of the neutral and acid reaction products was performed on capillary OV-1/FFAP using the conditions earlier reported (Fischer & Grosch, 1988).

The neutral reaction products were analysed on capillary SE-54 (30 m × 0·32 mm, film thickness, 0·3 μm). The AR-glass capillary was deactivated and coated according to Grob (1986). The flow of the carrier gas helium was 2·0 ml/min. The samples were applied by the on-column injection technique at 35°C. After 4 min, the temperature of the oven was quickly raised (40°C/min) to 50°C, held for 2 min, again raised at a rate of 6°C/min to 280°C, and finally held at 280°C for 5 min.

Retention data of the compounds are presented as retention indices (RI) calculated according to Halang *et al.* (1978).

Preparative GC

The SE-54 column [3 m × 2 mm stainless steel column packed with SE-54 (15 per cent, w/w) on Chromosorb W-AW DMCS, 100–120 mesh] was used with the following temperature program: after 2 min at 80°C, the temperature was raised by 4°C/min to 180°C and then kept at 140°C for 8 min. Helium was used as carrier gas (30 ml/min). The GC column effluent was split in a ratio of 1:12 (v/v) to an FID and a cooling trap (U-shaped glass capillary cooled with liquid nitrogen).

Mass spectrometry (MS)

HRGC–MS analyses were performed using an MS-8230 (Finnigan MAT, Bremen, FRG) in tandem with an OV-1/FFAP or an SE-54 capillary. The conditions for the HRGC were the same as described above. The electron impact mass spectra MS(EI) were generated at 70 eV and the chemical ionization spectra MS(CI) were obtained at 125 eV with isobutane as reagent gas.

Proton magnetic resonance spectra (^{1}H-NMR)

^{1}H-NMR was recorded with a Bruker AM 360 spectrometer operating at 360 MHz.

AEDA

AEDA was performed as reported by Fischer & Grosch (1988). Aromagrams (FD-factors of the odour compounds versus their RI values) were plotted according to Schieberle & Grosch (1988).

Peroxides

Peroxides were quantified with the Fe-test (Tsoukalas & Grosch, 1977). The absorbances measured were referred to a calibration curve obtained with linoleic acid hydroperoxides.

Thin-layer chromatography (TLC): HPTLC-plates (Merck, Darmstadt, FRG) coated with silica gel were developed in *n*-hexane/diethyl ether 6:4 (v/v). The peroxides were visualised by spraying the plate with solutions of potassium iodide and starch (Satoh *et al.*, 1976).

RESULTS AND DISCUSSION

Rate constant and half-life

2(E)-Hexenal, and other saturated and unsaturated aldehydes having 6 or 7 carbon atoms, were dissolved in 20 per cent EtOH, pH 3·5, and triacetin, and then stored at 38°C. As earlier shown (Fischer & Grosch, 1988), the breakdown of the aldehydes followed a pseudo-first-order rate law, since the reactants (oxygen, solvents) were present in a large excess.

The rate constants for the breakdown of the aldehydes were determined, and the half-lives were calculated. The data obtained are summarised in Table 1.

3(Z)-Hexenal was the most labile aldehyde in both solvents. Compared with 2(E)-hexenal it degraded five times faster in 20 per cent EtOH, pH 3·5, and 2·7 times faster in triacetin. The breakdown rates of the unsaturated aldehydes were affected by the nature of the solvent, and were higher in triacetin than in 20 per cent EtOH, pH 3·5. In contrast, the breakdown of the saturated aldehydes was almost independent of the solvent. Consequently, in 20 per cent EtOH, pH 3·5, the half-life of the 2(E)-hexenal was twice as

TABLE 1
Rate Constants for the Degradation of C_6- and C_7-Aldehydes at 38°C

Aldehyde	*Rate constant k and half-life* $t_{1/2}$			
	20 per cent EtOH, pH 3·5		*Triacetin*	
	$k(h^{-1})^a \times 10^3$	t 1/2 (h)	$k(h^{-1})^a \times 10^3$	$t_{1/2}$ (h)
Hexanal	7·65 ± 0·44	91	8·04 ± 0·51	86
2(E)-Hexenal	3·79 ± 0·26	183	9·81 ± 0·24	71
3(Z)-Hexenal	20·08 ± 0·79	36	26·35 ± 1·12	26
Heptanal	9·09 ± 0·42	76	9·45 ± 0·31	73
2(E)-Heptenal	5·06 ± 0·52	137	12·24 ± 1·28	57
4(Z)-Heptenal	3·98 ± 0·07	174	10·86 ± 0·62	64

[a] Values are mean of six replicates ± SD.

TABLE 2
Storage Experiments with a Mixture of Hexanal and 2(E)-Hexenal Dissolved in Triacetin

Aldehyde[a]	$k\ (h^{-1}) \times 10^3$ *at 38°C*[b]
Hexanal	48·65 ± 6·21
2(E)-Hexenal	5·56 ± 1·29

[a] The reaction mixture contained 2 mg of each aldehyde per ml of triacetin.
[b] Values are mean of three replicates ± SD.

high as that of hexanal, whereas the stability of 2(E)-hexenal in triacetin was lower than that of hexanal.

When a mixture of both aldehydes dissolved in triacetin was stored (Tables 1 and 2), the rate constant of hexanal increased strongly from $8 \times 10^{-3}\,h^{-1}$ to $49 \times 10^{-3}\,h^{-1}$, and that of 2(E)-hexenal decreased from

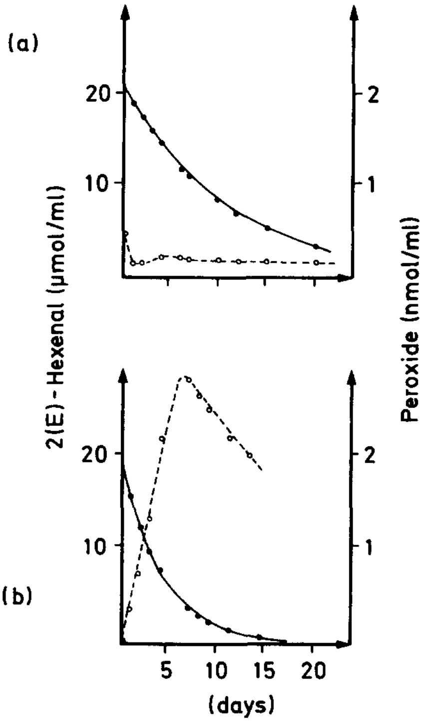


Fig. 1. Time course of the breakdown of 2(E)-hexenal and the formation of peroxides at 38°C depending on the solvent. (a) 20 per cent EtOH, pH 3·5; (b) triacetin. 2(E)-Hexenal (●), peroxides (○).

$10 \times 10^{-3} h^{-1}$ to $6 \times 10^{-3} h^{-1}$. This difference was not observed in the solvent 20 per cent EtOH, pH 3·5 (data not shown).

Formation of peroxides

As shown in Fig. 1, the nature of the solvent affected not only the rate of the breakdown of 2(E)-hexenal but, also, the peroxide concentration. In the case of 20 per cent EtOH, pH 3·5 (Fig. 1(a)), the concentration of peroxides was always very low, whereas, in triacetin (Fig. 1(b)) the peroxides increased over a period of 9 days to a maximum.

Products of 2(E)-hexenal in 20 per cent EtOH, pH 3·5

After degradation of approximately 85 per cent of the 2(E)-hexenal, the products formed were analysed by HRGC on capillary OV-1/FFAP, suitable for the separation of both the neutral and the acid compounds. As summarised in Table 3, 24 products appearing in very different amounts were detected. Eleven of them (Nos. 1–5, 11, 15, 18, 22–24) were identified by comparison of the HRGC and MS data with those of reference substances. The chemical structures of six products (Nos. 6, 8, 17, 19–21) were derived from the mass spectra, the major signals of which are reported in Table 4.

The main reaction products of 2(E)-hexenal (Nos. 10 and 16) were isolated by preparative GC, and then identified as 3-ethoxyhexanal (No. 10) and 3-hydroxyhexanal (No. 16) on the basis of the MS, IR and ^{1}H-NMR data drawn up in Tables 5 and 6.

The aromagram (Fig. 2) obtained by AEDA indicated that 3-ethoxyhexanal and 3-hydroxyhexanal belonged to the aroma-active compounds formed by the breakdown of 2(E)-hexenal. However, on the basis of its high FD factor, 3(Z)-hexenal was the most significant aroma compound, although it amounted only to 1·7 per cent (Table 3). The low odour threshold of 0·75 ng/litre (air) (Ullrich & Grosch, 1988) is one reason for the high odour activity of 3(Z)-hexenal.

Products of 2(E)-hexenal in triacetin

The peroxides, formed during storage of 2(E)-hexenal (Fig. 1(b)) and the solvent triacetin, inhibited the analysis of the non-peroxide products. Therefore the reaction mixture was chromatographed on a silica gel column which removed most of both the triacetin and the peroxides. In the parallel experiment involving analysis of the neutral extract, the peroxides, being peracids, were removed during the extraction of the acids.

The combined peroxide free fractions obtained by column chromatography, and in addition, the neutral fraction alone, were analysed by HRGC/MS, as reported for the products formed in the solvent 20 per cent EtOH, pH 3·5. The results are summarised in Table 7.

2(E)-Hexenoic acid (No. 11), present as 85 per cent of the overall products, was by far the major compound, followed by 2(E)-pentenol.

TABLE 3

Products Formed during Storage of a Solution of 2(E)-Hexenal in 20 per cent EtOH, pH 3·5, at 38°C

No.	*Compound*[a]	*RI*		*Odour description*[c]	*Proportion (per cent)*[d]
		OV-1/FFAP	*SE-54*[b]		
1	Ethyl acetate[e]	665	646	—	<0·1
2	*n*-Pentanal[e]	731	695	—	<0·1
3	1,1-Diethoxyethane[e]	738	700	Fruity	<0·1
4	3(Z)-Hexenal[e]	858	821	Green, apple-like	1·7
5	3(E)-Hexenal[e]	870	833	Fruity	0·2
6	2(Z)-Hexenal[f]	903	852	Heavy	6·6
7	Unknown (M_r: 96)	948	905	—	0·2
8	3-Hexen-5-olide[f]	953	910	Musty, earthy	<0·1
9	Unknown (M_r: 84)	969	729	—	0·8
10	3-Ethoxyhexanal[g]	1 055	1 011	Fruity, pungent	35·2
11	Propionic acid[e]	1 095	—	—	<0·1
12	Unknown (M_r: 126)	1 101	1 090	—	<0·1
13	Unknown (M_r: 126)	1 106	1 105	—	1·8
14	5-Ethyl-2(5H)-furanone[h]	1 166	—	—	0·2
15	Butanoic acid[e]	1 175	—	Sweaty	<0·1
16	3-Hydroxyhexanal[g]	1 205	945	Fruity, pungent	37·8
17	1,1-Diethoxy-2(E)-hexene[f]	1 260	1 249	—	1·3
18	Pentanoic acid[e]	1 264	—	Rancid	<0·1
19	1-Ethoxy-1-hydroxy-2(E)-hexene[f]	1 325	1 263	—	6·1
20	4-Hexanolide[f]	1 350	—	—	<0·1
21	2(E)-Hexenoic acid[f]	1 380	—	—	<0·1
22	3(E)-Hexenoic acid[e]	1 430	—	Flowery	0·4
23	3(Z)-Hexenoic acid[e]	1 440	—	—	<0·1
24	2(E)-Hexenoic acid[e]	1 445	—	Musty	7·5

RI, retention index.

[a] The compounds were analysed after a breakdown of approximately 85 per cent of the 2(E)-hexenal.

[b] The fraction containing the neutral products was, in addition, analysed by HRGC on capillary SE-54.

[c] Odour description assigned in the sniffing port during HRGC on capillary OV-1/FFAP.

[d] Relative per cent composition based on integrated gas chromatographic peak areas (HRGC on capillary OV-1/FFAP).

[e] The compound was identified by comparing it with the reference substance on the basis of the following criteria: RI on the capillary OV-1/FFAP (in the case of the neutral substances also on capillary SE-54), mass spectrum (EI- and CI-mode) and odour quality.

[f] The structure was derived from the MS data reported in Table 4.

[g] The compound was isolated and identified on the basis of spectral data as detailed in the text.

[h] The MS agreed with the corresponding data reported for this compound by Takeoka *et al.* (1986).

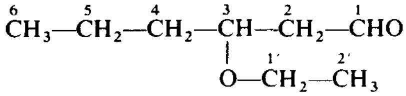
TABLE 4
MS-Data of Compounds Nos 6, 8, 17, 19, 20 and 21 Listed in Table 3

No.	*Compound*	*MS Data*	
6	2(Z)-Hexenal	MS(EI)	43 (100 per cent), 41 (68 per cent), 39 (61 per cent), 83 (46 per cent), 55 (45 per cent), 42 (38 per cent), 69 (22 per cent), 98 (12 per cent)
		MS(CI)	99 (100 per cent)
8	3-Hexen-5-olide	MS(EI)	43 (100 per cent), 41 (39 per cent), 55 (29 per cent), 42 (23 per cent), 83 (23 per cent), 69 (20 per cent), 112 (14 per cent)
		MS(CI)	113 (100 per cent), 81 (21 per cent), 99 (14 per cent)
17	1,1-Diethoxy-2(E)-hexene	MS(EI)	103 (100 per cent), 101 (66 per cent), 75 (47 per cent), 73 (46 per cent), 55 (40 per cent), 47 (38 per cent), 45 (33 per cent), 43 (32 per cent), 129 (22 per cent), 41 (18 per cent), 143 (10 per cent), 172 (2 per cent)
		MS(CI)	173 (100 per cent), 129 (38 per cent), 101 (14 per cent)
19	1-Ethoxy-1-hydroxy-2(E)-hexene	MS(EI)	103 (100 per cent), 73 (100 per cent), 45 (66 per cent), 47 (50 per cent), 75 (48 per cent), 43 (40 per cent), 55 (33 per cent), 101 (31 per cent), 145 (10 per cent)
		MS(CI)	145 (100 per cent)
20	4-Hexanolide	MS(EI)	60 (100 per cent), 73 (43 per cent), 41 (38 per cent), 43 (23 per cent), 87 (14 per cent), 114 (1 per cent)
		MS(CI)	115 (100 per cent)
21	2(Z)-Hexenoic acid	MS(EI)	41 (100 per cent), 99 (92 per cent), 39 (91 per cent), 42 (80 per cent), 73 (70 per cent), 55 (59 per cent), 114 (57 per cent)
		MS(CI)	115 (100 per cent)

TABLE 5

MS, IR and ^{1}H-NMR Data for 3-Ethoxyhexanal

MS(EI):	45 (100 per cent), 73 (85 per cent), 55 (74 per cent), 101 (M-43; 58 per cent), 70 (44 per cent), 43 (42 per cent)
MS(CI):	145 (M + 1; 100 per cent), 101 (88 per cent)
IR (cm^{-1}):	2895 and 2870 (Fermi resonance), 1738 (C=O), 1 100 (C—O—C)



$$\overset{6}{\mathrm{C}}\mathrm{H_3}—\overset{5}{\mathrm{C}}\mathrm{H_2}—\overset{4}{\mathrm{C}}\mathrm{H_2}—\underset{\mathrm{O—\overset{1'}{C}H_2—\overset{2'}{C}H_3}}{\overset{3}{\mathrm{C}}\mathrm{H}}—\overset{2}{\mathrm{C}}\mathrm{H_2}—\overset{1}{\mathrm{C}}\mathrm{HO}$$

^{1}H-NMR (CDCl$_3$), δ: 0·91 (*t*, J 7·0 Hz, H-6), 1·16 (*t*, J 7·0 Hz, H-2′), 1·39 (*m*, H-5), 1·48 (*dd*, J$_{2-1}$ 2·5 Hz, J$_{2-3}$ 6·0 Hz), 2·55 (*m*, H-4), 3·48 (*m*, H-3, H-1′), 9·80 (*t*, J$_{2-3}$ Hz, H-1)

TABLE 6

MS, IR and ^{1}H-NMR Data for 3-Hydroxyhexanal

MS(EI):	45 (100 per cent), 55 (72 per cent), 73 (60 per cent), 43 (50 per cent), 70 (48 per cent), 42 (40 per cent)
MS(CI):	117 (M + 1), 99 (55 per cent)

^{1}H-NMR (CDCl$_3$), δ: 0·92 (*t*, J7·0 Hz, H-6), 1·19 (*m*, H-5), 1·37 (*dd* J$_{2-1}$ 1·2 Hz, J$_{2-3}$ 6·7 Hz, H-2), 2·59 (*m*, H-4), 3·47 (*m*, H-3), 4·15 (*m*, OH), 9·83 (*t*, J$_{1-2}$ Hz, H-1).

TABLE 7

Products Formed during Storage of a Solution of 2(E)-Hexenal in Triacetin at 38°C[a]

No.	*Compound*	*RI*		*Odour description*[c]	*Proportion (per cent)*[d]
		OV-1/FFAP	*SE-54*[b]		
1	*n*-Pentanal[e]	730	695	—	1·0
2	2(E)-Pentenal[e]	827	735	Fruity	<0·1
3	1-Penten-3-ol[e]	830	800	—	<0·1
4	2(Z)-Pentenol[e]	879	847	—	0·4
5	2(E)-Pentenol[e]	886	855	—	9·3
6	2(Z)-Hexenal[f]	903	865	Heavy	0·4
7	Unknown (M_r: 130)	1 081	935	—	0·4
8	Butanoic acid[e]	1 173	—	Sweaty	1·2
9	Pentanoic acid[e]	1 264	—	Rancid	0·4
10	2(Z)-Hexenoic acid[f]	1 378	—	Burning, sweaty	2·0
11	2(E)-Hexenoic acid[e]	1 442	—	Musty	85·0

RI, retention index.

[a,b,c,d,e,f] Footnotes refer to *a*, *b*, *c*, *d*, *e* and *f* in Table 3.

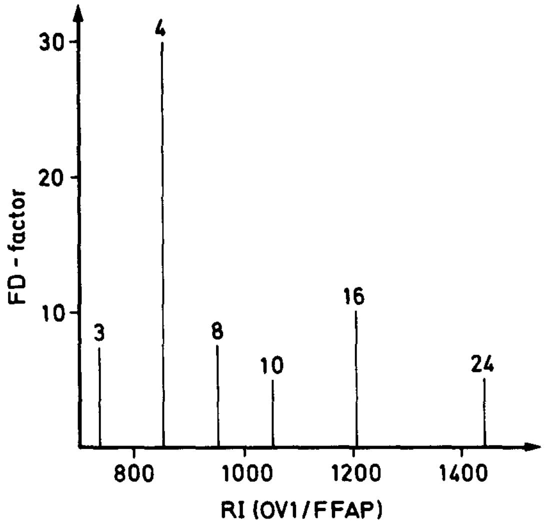


Fig. 2. Aromagram of the products formed by breakdown of 2(E)-hexenal dissolved in 20 per cent EtOH, pH 3·5. Numbering of the compounds as in Table 3.

Butanoic acid, whose presence amounted only to 1·2 per cent (Table 7), appeared as the main odour compound in the aromagram (Fig. 3). In spite of its higher proportion among the products, 2(E)-hexenoic acid had a lower FD-factor than butanoic acid, thus revealing a relatively high odour threshold.

The results indicate that the rate of the breakdown of 2(E)-hexenal, and the products formed, are strongly influenced by the two solvents.

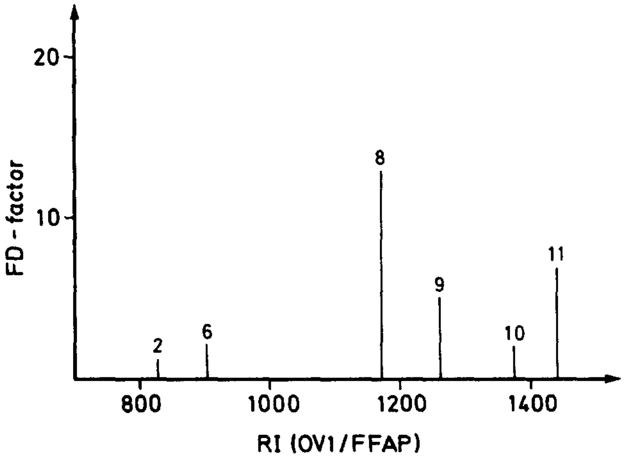


Fig. 3. Aromagram of the products formed by breakdown of 2(E)-hexenal dissolved in triacetin. Numbering of the compounds as in Table 7.

2(E)-Hexenal is more stable in the protophilic solvent ethanol/water than in the hydrophobic solvent triacetin. A comparison with earlier results (Fischer & Grosch, 1988) shows that the decrease in the pH from 6·5 to 3·5 in the solvent 20 per cent ethanol increases the reaction rate by 40 per cent, whereas a change from 20 per cent ethanol to triacetin accelerates the breakdown of 2(E)-hexenal 3·6-fold. This drastic increase in the reaction rate was also found for 2(E)- and 4(Z)-heptenal.

The corresponding acid was the predominating reaction product of the breakdown of 2(E)-hexenal dissolved in triacetin. This suggests that autoxidation of 2(E)-hexenal is the major reaction under these conditions. The autoxidation of an aldehyde proceeds via the corresponding peracid (Engler & Wild, 1897; Bayer & Villinger, 1900) which indeed increases to a maximum in triacetin, whereas only traces are detectable in 20 per cent EtOH, pH 3·5.

The number of products arising from 2(E)-hexenal dissolved in 20 per cent EtOH, pH 3·5, was higher, compared with triacetin as the solvent, due to an isomerisation of the 2(E)-double bond into 2(Z)-, 3(E)- and 3(Z)-double bonds, most likely catalysed by protons. Among the isomerisation products identified, 3(Z)-hexenal predominated in the aromagram.

The lower concentration of both peroxides and 2(E)-hexenoic acid reveals that autoxidation reactions were of minor importance for the 2(E)-hexenal/20 per cent EtOH, pH 3·5 reaction system. Under these conditions, the major products were identified as 3-hydroxyhexanal and 3-ethoxyhexanal.

The addition of water to 2-alkenals C_4, C_8–C_{10}, at room temperature and pH 4·0, was studied by Gracey *et al.* (1985). They found that the proportion of the 3-hydroxyalkenal formed increases with increasing chain length of the aldehyde.

As shown in Fig. 4, the mechanism proposed by Gracey *et al.* (1985) for the addition of water to 2-alkenals can be used to explain the formation of 3-hydroxyhexanal and 3-ethoxyhexenal.

3-Hydroxyalkanals can be split by a retro-aldol reaction (Gracey *at al.*, 1985; Josephson & Lindsay, 1987). However, it has been shown by Gracey *et al.* (1985) that the retro-aldol reaction, at room temperature and pH 4·0, occurs at a much slower rate than the hydration of the 2-alkenal. According to the mechanism discussed by Josephson and Lindsay (1987), a retro-aldol degradation of 3-hydroxyhexanal would yield butanal and acetaldehyde. Therefore, it is debatable whether the small amount of butanoic acid, identified in the 20 per cent EtOH, pH 3·5 reaction system, is formed by oxidation of butanal originating from a cleavage of the 3-hydroxyhexanal. The formation of butanoic acid, when triacetin is used as solvent, cannot be explained via this pathway. In this case, it is most likely formed by an oxidative split of the Δ^2-double bond of 2-hexenal.

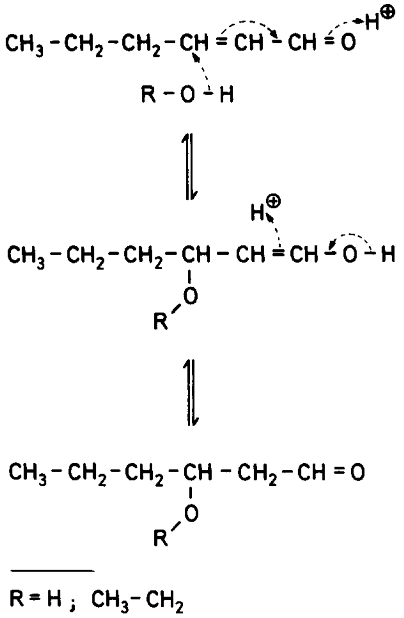


Fig. 4. Reaction of 2(E)-hexenal with water and ethanol (according to Gracey *et al.*, 1985).

Gracey *et al.* (1985) have suggested that hydration enhances significantly the flavour thresholds of 2-alkenals. Our results confirm this suggestion, since 3-hydroxyhexanal was a major product of the 2(E)-hexenal/20 per cent EtOH, pH 3·5 reaction system and showed only a relatively low FD factor in the aromagram. The same result was found for the second major product, 3-ethoxyhexanal.

ACKNOWLEDGEMENT

The work was supported by the AIF (Koeln) and the Forschungskreis der Ernaehrungsindustrie (Hannover).

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