

Formation of Eight-Carbon and Ten-Carbon Components in Mushrooms (*Agaricus campestris*)

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The formation of volatile C₈ components and less volatile C₁₀ (C₁₁) oxo and hydroxy acids was investigated in fresh mushrooms (*Agaricus campestris*). The components were isolated from the mushrooms by distillation-extraction and liquid-liquid extraction and analyzed by capillary gas chromatography-mass spectrometry. Further characterization was made by infrared spectroscopy, ¹H NMR spectroscopy, chemical reactions, and Me₃Si derivatizations. After addition of linoleic and linolenic acids, the following components were identified for the first time in mushrooms: (*Z*)-2-octenal, (*Z*)-1,5-octadien-3-one, (*Z*)-1,5-octadien-3-ol, (*Z,Z*)-2,5-octadienal, and (*Z,Z*)-2,5-octadien-1-ol (partly showing intensive mushroom-like odors). 10-Oxodecanoic acid, 10-hydroxydecanoic acid, 10-oxoundecanoic acid, 10-hydroxyundecanoic acid, 10-oxo-8-decenoic acid, 10-hydroxy-8-decenoic acid, 9-oxodecanoic acid, and 9-hydroxydecanoic acid were characterized as enzymatic products from linoleic acid.

Edible mushrooms like *Agaricus bisporus* (Cronin and Ward, 1971; Picardi and Issenberg, 1973), *Lentinus edodes* Sing (Kameoka and Higuchi, 1976), and *Boletus edulis* (Pyysalo, 1976) produce 1-octen-3-ol, 3-octanol, 2-octen-1-ol, and 1-octanol as volatile constituents. The major component 1-octen-3-ol possesses a mushroom-like aroma and is known as "mushroom alcohol". Dijkstra and Wiken (1976) showed that the natural (-) form of 1-octen-3-ol has a stronger flavor than the (+) form with a threshold in water at 0.46 ppb. The levorotatory form first determined by Freytag and Ney (1968) indicates a biosynthetic formation in mushrooms. The racemic alcohol is known as a product of autoxidized linoleate in cereals and vegetables. 1-Octen-3-one, 3-octanone, (*E*)-2-octenal, 1-octen-3-yl acetate, and 1-octen-3-yl propionate were characterized in aroma concentrates from *B. edulis* and *A. bisporus* (Pyysalo, 1976). The formation of C₈ components seems to be a common principle of basidiomycetes and some fungi like *Penicillium* and *Aspergillus* (Kaminski et al., 1974). Lumen et al. (1978) demonstrated a lipooxygenase system (in mushrooms) catalyzing the conversion of linoleic acid into 1-octen-3-ol during blending of fresh mushrooms. In the present work, we demonstrate the enzymic conversion of linoleic and linolenic acids into C₈ and C₁₀ components. Five C₈ and eight C₁₀ (C₁₁) components were identified for the first time as enzymic breakdown products of linoleic and linolenic acids.

EXPERIMENTAL SECTION

Fresh mushrooms (*Agaricus campestris*) were obtained by air freight from The Netherlands and stored at 4 °C until being analyzed (12-24 h).

Isolation of Volatile Aroma Extract. Three-hundred grams of fresh mushrooms was homogenized with 750 mL of phosphate buffer (0.1 M; pH 6.8) for 5 min. The slurry was cleared by filtration with a Hafico tincture press at 400 atm. The volatiles were isolated from the filtrate by means of distillation-extraction using fresh distilled pentane-ether (2:1) for 2 h (Teranishi et al., 1977). The aroma extract was dried over Na₂SO₄ and concentrated to a volume of 0.3 mL by using a Vigreux column. This sample preparation was repeated 10 times. Under the same conditions, two further experiments were carried out by

adding 100 mg of linoleic acid and 100 mg of linolenic acid, respectively, to the buffer solution before homogenizing the mushrooms.

Isolation of Less Volatile Oxo and Hydroxy Acids from Mushrooms. Three-hundred grams of fresh mushrooms was homogenized with 500 mL of phosphate buffer (0.1 M; pH 6.8; containing 300 mg of potassium linoleate) for 5 min. The slurry was cleared by filtration with a Hafico tincture press at 400 atm, obtaining 600 mL of filtrate. The procedure was repeated 10 times to get 6 L of extract (from 3000 g of mushrooms; 3 g of linoleate). The filtrate was first extracted with 5 L of fresh distilled ether-pentane (1:2) at pH 6.8 (to isolate neutral components) and then adjusted to pH 2.5 and extracted by liquid-liquid extraction with ether for 24 h. After being dried over Na₂SO₄ the extract was concentrated, methylated with diazomethane, and concentrated to a volume of 3 mL.

Adsorption Chromatography. The aroma concentrate of the volatiles was separated by liquid-solid chromatography (LSC) according to the polarity of components as described previously (Tressl et al., 1977). The fractions were concentrated and further investigated by preparative gas chromatography and capillary gas chromatography-mass spectrometry. The extract containing methylated oxo and hydroxy acids was separated into five fractions by using a water-cooled column (100 × 1.4 cm i.d.) filled with silica gel 60 (Merck 7734; activity II-III), and the fractions were eluted with 250 mL of (I) P-MC (pentane-methylene chloride) (2:1), (II) P-MC (1:1), (III) P-ether (4:1), (IV) P-ether (1:1), and (V) ether.

Gas Chromatography. Packed-Column GLC-Infrared Spectral (IR) Analysis. Alcohols and carbonyls were separated from the LSC fractions by using a 3 m long × 4 mm i.d. glass column packed with 60-mesh Chromosorb WAW coated with 15% FFAP (column A). The column was programmed at 4 °C/min from 60 to 250 °C. At the outlet of the column, the samples were split 1:20 (1 part FID) and collected in dry ice cooled Pyrex tubes (3 mm × 15 cm long). The IR spectra were measured as thin films between salt plates or as a solution in CCl₄ by using an ultramicro cavity cell and a beam condenser with a Perkin-Elmer Model 357 instrument.

Capillary GLC-Mass Spectrometry. The main capillary GLC-MS analyses were carried out using a 50 m glass capillary column (0.32 mm i.d.) coated with Carbowax 20M (column B). Conditions were as follows: temperature program 70-190 °C; 2 °C/min in a Carlo Erba Fractovap 2101 connected with a double-focusing mass spectrometer

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Table I. Formation of Volatiles in Mushrooms (*A. campestris*)

component	I_K^b FFAP	M_r	mass spectra		concn, ppm			identification
			fragmentation		I ^c	II ^d	III ^e	
1, hexanal	1032	100	44, 41, 27, 29, 43, 39, 28, 55		0.23	0.56	0.09	R_t , MS
2, 1-octanol	1480	130	41, 56, 55, 43, 70, 29, 69, 42		+	+	+	R_t , MS
3, 3-octanone	1192	128	43, 57, 29, 71, 72, 99, 27, 41		8.65	7.8	5.5	R_t , MS
4, 3-octanol	1310	130	59, 55, 83, 41, 29, 31, 27, 43		1.5	2.0	1.25	R_t , MS
5, 1-octen-3-one	1238	126	70, 55, 43, 97, 27, 29, 39, 41		0.7	2.2	1.1	R_t , MS
6, 1-octen-3-ol	1369	128	57, 43, 41, 72, 85, 99, 55, 71		30.1	61.0	25.1	R_t , MS
7, (Z)-2-octenal ^a	1379	126	55, 70, 29, 57, 83, 41, 82, 69		1.8	7.5	1.9	R_t , MS, IR
8, (Z)-2-octen-1-ol	1547	128	57, 41, 55, 68, 43, 67, 54, 81		4.8	17.4	5.0	R_t , MS, IR
9, (Z)-1,5-octadien-3-one ^a	1254	124	55, 69, 95, 109, 56, 67, 81, 83		+	+	0.33	R_t , MS, IR
10, (Z)-1,5-octadien-3-ol ^a	1400	126	57, 70, 55, 41, 69, 42, 29, 27		+	+	27.5	R_t , MS, IR
11, (Z,Z)-2,5-octadienal ^a	1425	124	81, 124, 59, 67		-	-	+	R_t , MS
12, (Z,Z)-2,5-octadien-1-ol ^a	1600	126	79, 67, 41, 55, 93, 108, 70, 77		+	+	17.9	R_t , MS, IR
13, benzaldehyde	1479	106	77, 106, 105, 41, 40, 78, 42, 39		15.8	11.7	10.8	R_t , MS

^a First identified in mushrooms. ^b Kovats indices; column D. ^c Control experiment with fresh mushrooms. ^d Addition of linoleic acid to the mushrooms. ^e Addition of linolenic acid to the mushrooms.

CH 5 DF (Varian MAT, Germany). Mass spectra were recorded at 70 eV with a resolution of 1500–2000 (10% Tal).

For column C, a 50-m glass capillary (0.32 i.d.) coated with OV-101, programmed at 2 °C/min from 100 to 250 °C, was used.

For column D, a 50-m glass capillary (0.32 i.d.) coated with FFAP, programmed at 2 °C/min from 70 to 220 °C, was used.

Nuclear Magnetic Resonance Spectroscopy (¹H NMR). Spectra were obtained in CDCl₃ at 270 MHz by using a Bruker WH 270 instrument.

RESULTS AND DISCUSSION

Fresh mushrooms were homogenized with phosphate buffer solution, and the volatiles were concentrated by distillation-extraction. Under the same conditions, experiments were carried out by adding linoleic acid and linolenic acid as precursors. The aroma extracts were concentrated and investigated by capillary gas chromatography-mass spectrometry. Individual constituents were isolated, purified by preparative gas chromatography, and further characterized by infrared spectroscopy. The less volatile oxo and hydroxy acids were isolated by means of liquid-liquid extraction with ether, methylated with CH₂N₂, separated by liquid-solid chromatography, and investigated by GC-MS. Individual constituents were further purified by preparative gas chromatography and characterized by infrared spectroscopy. ¹H NMR spectroscopy, chemical reactions, and Me₃Si derivatives. Eleven components containing eight carbon atoms were identified in the aroma concentrates of *A. campestris*. Major components were 1-octen-3-ol ("mushroom alcohol"), 3-octanone, (Z)-2-octen-1-ol, (Z)-2-octenal, 3-octanol, and 1-octen-3-one. With the addition of linoleic acid during blending of fresh mushrooms, the concentration of these components increased considerably. Therefore, linoleic acid is considered as their (natural) precursor. Five C₈ components containing two double bonds were characterized for the first time. They increase considerably with the addition of linolenic acid which is suggested as a precursor. When the enzymes were inhibited by addition of 60% methanol or heating the mushrooms (Tressl and Drawert, 1973), both precursors were not transformed into C₈ components.

Identification of C₈ Components (Table I). The components 1–6 were identified by comparison of retention data and mass spectra of the mushroom components with synthesized samples (commercially available or gifts).

(Z)-2-Octenal was characterized for the first time in mushrooms. The mass spectrum is identical with that of

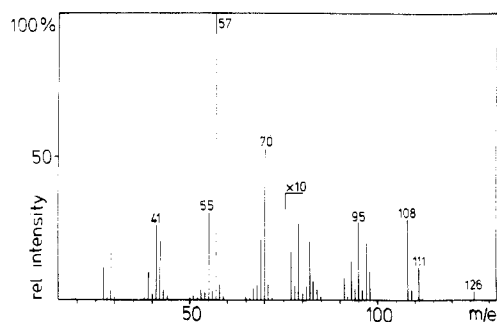


Figure 1. Mass spectrum of (Z)-1,5-octadien-3-ol.

(E)-2-octenal which has been identified by Pyysalo (1976) in *B. edulis* and *A. bisporus*. The configuration of the double bond was confirmed by infrared spectroscopy of the purified component: IR 970 not detectable, 3020, 2720, 1695, 1635 cm⁻¹ (—CH=CHC=O). After reduction with NaBH₄ it showed the retention and mass spectrum of (Z)-2-octen-1-ol: MS m/e (rel intensity) 126 (M^+), 55 (100), 70 (96), 29 (75), 57 (69), 83 (68), 41 (54), 82 (48), 69 (45), 67 (37).

2-Octen-1-ol, component 8, was characterized in mushroom extracts and in the linoleic acid experiment as (Z)-2-octen-1-ol: MS m/e (rel intensity) 128 (M^+), 57 (100), 41 (58), 55 (50), 68 (41), 43 (38), 67 (38), 54 (37), 81 (36), 82 (27), 110 (18); IR no absorption at 970, 3450, 3020, 1020, 730 cm⁻¹ (—CH₂CH=CHCH₂OH) showed the Z configuration.

(Z)-2-Octen-1-ol was characterized by Wasowicz (1973) in *A. bisporus*. Pyysalo (1976) demonstrated the E isomer in *B. edulis* and *A. bisporus*.

(Z)-1,5-Octadien-3-one was identified as a potent lipid oxidation product in butterfat. Its threshold in water was determined at 10¹² ppb with a metallic, fungal odor quality (Swoboda and Peers, 1977). The Z configuration of the ω₃ double bond was proved by infrared spectroscopy (no absorption at 970 cm⁻¹).

(Z)-1,5-Octadien-3-ol was characterized as a contributing constituent in mushrooms for the first time. The mass spectrum is shown in Figure 1. Typical peaks are formed by an allylic fragmentation. The Z configuration of the ω₃ bond was confirmed by infrared spectroscopy of the purified sample: IR 3450, 1120 [—CH(OH)], 3080, 990, 920 (—CHCH=CH₂), 3020, 675–730 cm⁻¹ (—CH=CH—), no absorption at 975 cm⁻¹; showed Z configuration. The component possessed an intensive mushroom-like odor with an earthy odor quality.

(Z,Z)-2,5-Octadien-1-ol was isolated from the linolenic acid experiment and purified by preparative gas chroma-

Table II. Formation of Oxo and Hydroxy Acids in Mushrooms

component	I_K , FFAP	I_K , OV- 101	mass spectra		concn, mg/g ^b	identification
			M_r	fragmentation		
I, methyl 10-oxodecanoate	2091	1484	200	74, 55, 87, 125, 157, 169, 172, 150	9.4	R_t , MS, IR, ¹ H NMR
II, methyl 10-hydroxydecanoate	2338	1567	202	74, 55, 87, 69, 84, 98, 110, 172	96.7	R_t , MS, IR, ¹ H NMR
II, ^a methyl 10-hydroxydecanoate trimethylsilyl ether		1657	274	227, 73, 69, 55, 75, 89, 103, 259		
III, methyl 10-oxoundecanoate	2200	1572	214	43, 125, 55, 58, 97, 83, 87, 157	4.1	R_t , MS, IR
IV, methyl 10-hydroxyundecanoate	2220	1592	216	55, 74, 43, 45, 87, 129, 125, 172	0.42	
IV, ^a methyl 10-hydroxyundecanoate trimethylsilyl ether		1689	288	117, 73, 75, 159, 241, 244, 159, 273		
V, methyl 10-oxo-8-decenoate	2190	1592	198	74, 98, 55, 69, 83, 41, 138, 166	5.8	R_t , MS, IR
VI, methyl 10-hydroxy-8-decenoate	2283	1587	200	74, 41, 55, 87, 43, 81, 108, 150	2.3	R_t , MS, IR
VI, ^a methyl 10-hydroxy-8-decenoate trimethylsilyl ether		1620	272	73, 129, 75, 225, 257, 143, 150, 271		
VII, methyl 9-oxodecanoate	2053	1429	200	43, 55, 74, 58, 111, 83, 143, 152	1.0	R_t , MS
VIII, methyl 9-hydroxydecanoate	2083	1494	202	45, 74, 55, 87, 109, 152, 157, 185	1.0	R_t , MS

^a Silylated compounds. ^b Linoleic acid.

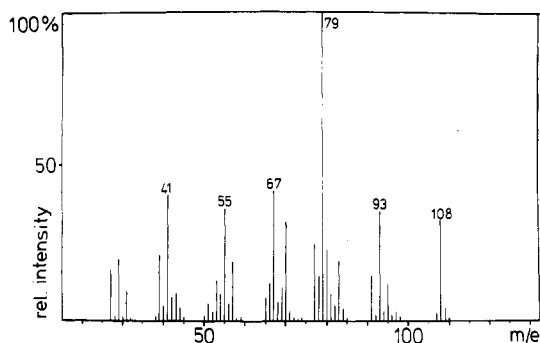


Figure 2. Mass spectrum of (Z,Z)-2,5-octadien-1-ol.

tography. The mass spectrum presented in Figure 2 is consistent with an octadien-1-ol: $M - 18$; $M - 31$; $M - (18 + 15)$; $M - (18 + 29)$ base peak. The position of the $\omega 3$ double bond was determined according to Tressl and Drawert (1971). The IR spectrum revealed a (Z,Z)-2,5-octadien-1-ol: IR 3450, 1020 ($=CHCH_2OH$), 3020, 675–730 cm^{-1} ($-CH=CH-$), no absorption at 970 cm^{-1} . (Z,Z)-2,5-Octadien-1-ol showed a mushroom-like odor with a green note.

2,5-Octadienal was detected by mass spectrometry. By $NaBH_4$ reduction it was transformed into the corresponding alcohol. The enzymic formation of C_8 components from linoleic and linolenic acids in mushroom homogenates is highly specific. All constituents contained Z configuration, and we observed no autoxidation products like hexanal, 2-hexenal, caprylic acid, 2,4-decadienals, or 2,4,7-decatrienals. Among the characterized components, 3-octanol, 1-octen-3-ol, and 1,5-octadien-3-ol are chiral substances. The stereospecificity was investigated by formation of diastereomeric esters and capillary GC-MS. All three alcohols were optically pure and levorotatory. These results and the methods used will be published in detail (Tressl and Engel, 1981).

Formation of Oxo and Hydroxy Acids in Mushrooms. In 1973 Tressl and Drawert demonstrated the enzymic splitting of linoleic acid into hexanal and 12-

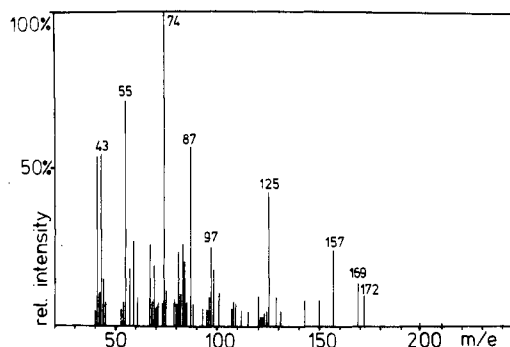


Figure 3. Mass spectrum of methyl 10-oxodecanoate.

oxo-(E)-10-dodecenoic acid (ripe bananas) and into (E)-2-nonenal and 9-oxononanoic acid (green bananas) by radiolabeling experiments. Hatanaka et al. (1977) showed the formation of (Z)-3-hexenal and 12-oxo-(E)-10-dodecenoic acid via 12-oxo-(Z)-9-dodecenoic acid from linolenic acid-1-¹⁴C in chloroplasts of *Thea sinensis*. Zimmerman and Coudron (1979) characterized 12-oxo-(E)-dodecenoic acid as the active component in the Wehnelt assay for wound hormones; they called it traumatin, which may be the precursor of traumatic acid. As demonstrated in Table I, linoleic acid and linolenic acid are split into C_8 components. Therefore, we looked for the corresponding C_{10} components. The results are shown in Table II. Three oxo acids and three hydroxy acids were characterized for the first time as enzymic products from linoleic and linolenic acids.

10-Oxodecanoic acid was isolated and purified by preparative gas chromatography. The mass spectrum is presented in Figure 3. The spectrum of component I shows the typical fragmentation of aldehyde esters (Noble and Nawar, 1971): $M - 18$ not detected; $M - 28$; $M - 31$ ($M - OCH_3$); $M - 32$ ($M - CH_3OH$), $M - 43$ [$M - (18 + 15)$]; $M - 44$; $M - 50$ (loss of $CH_3OH + H_2O$); methyl ester ions at m/e 59 ($-COOCH_3$), m/e 74, m/e 87, m/e 143. The IR spectrum is consistent with that of a saturated aldehyde ester: 2720 ($-CH=O$), 1730 ($-C=O$), 1435,

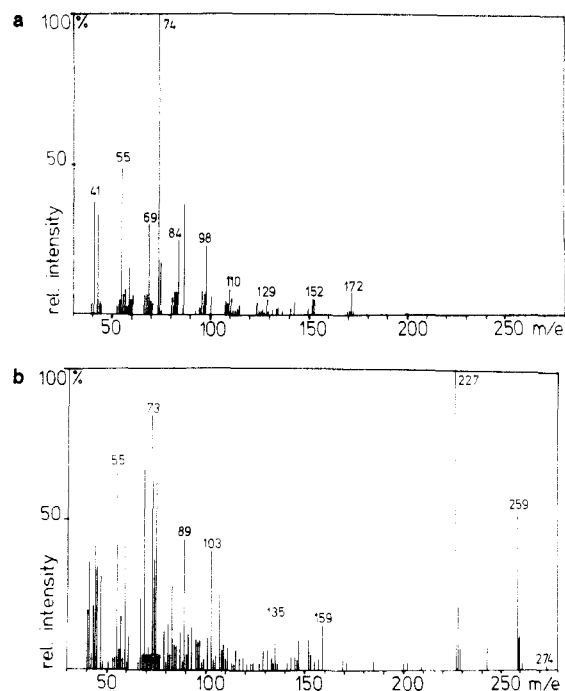


Figure 4. (a) Mass spectrum of methyl 10-hydroxydecanoate. (b) Mass spectrum of methyl 10-hydroxydecanoate trimethylsilyl ether.

1230 cm^{-1} ($-\text{OCH}_3$). The ^1H NMR spectrum was consistent with that of methyl 10-oxodecanoate (270 MHz, CDCl_3) (t = triplet; d = doublet; s = singlet): δ 9.70 (t, $J = 3$ Hz, 1 H, $-\text{CHO}$), 3.64 (s, 3 H, $-\text{COOCH}_3$), 2.43 (dt, $J = 8$ Hz resp. 3 Hz, 2 H, $-\text{CH}_2\text{CHO}$), 2.30 (t, $J = 8$ Hz, 2 H, $-\text{CH}_2\text{COOCH}_3$), 1.63 (m, 4 H, $-\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3 + -\text{CH}_2\text{CH}_2\text{CHO}$), 1.30 [m, 8–10 H, $-(\text{CH}_2)_n-$].

Methyl 10-oxodecanoate was characterized for the first time as an enzymatic breakdown product of linoleic acid.

Component II (Methyl 10-Hydroxydecanoate). The mass spectra of component II and of the Me_3Si derivative are shown in Figure 4. The fragmentation of hydroxy acids was investigated by Ryhage and Stenhagen (1960): M - 18 ($-\text{H}_2\text{O}$), not detected, M - 30 ($-\text{OCH}_3 + \text{H}$), M - 31 ($-\text{OCH}_3$), M - 49 ($-\text{OH} + \text{CH}_3\text{OH}$), M - 50 ($-\text{H}_2\text{O} + \text{CH}_3\text{OH}$), M - 59; m/e 74, 87, 59. The mass spectrum of the Me_3Si derivative is consistent with the fragmentation of ω -hydroxymethyl esters according to Eglington et al. (1968). Methyl 10-hydroxydecanoate trimethylsilyl ether: M = 274, M - 15 (CH_3), M - 47 ($-\text{CH}_3 + \text{CH}_3\text{OH}$). The peaks at m/e 159 and at m/e 146 are typical rearrangement fragments for ω -hydroxymethyl esters trimethylsilyl ethers. The IR spectrum showed absorption of a hydroxy group 1050 and 3450, 1735, 1435 and 1250 cm^{-1} (COOCH_3). The ^1H NMR spectrum is consistent with a ω -hydroxymethyl ester: δ 3.65 (s, 3 H, $-\text{COOCH}_3$), 3.62 (t, 2 H, $J = 7$ Hz, $-\text{CH}_2\text{OH}$), 2.30 (t, 2 H, $J = 7$ Hz, $-\text{CH}_2\text{CO}_2\text{CH}_3$), 1.58 (m, 5 H, $-\text{CH}_2\text{CH}_2\text{OH} + -\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$), 1.30 [m, 10–12 H, $-(\text{CH}_2)_n-$]; decoupling at 1.58 showed $-\text{CH}_2\text{OH}$.

10-Hydroxydecanoic acid was characterized for the first time as an enzymatic splitting product of linoleic acid.

Component III (Methyl 10-Oxoundecanoate) (Figure 5). The mass spectrum of component III showed the typical fragmentation of ω -2-oxo acids according to Ryhage and Stenhagen (1960). M = 214, M - 15 (CH_3), M - 31 ($-\text{OCH}_3$), M - 57 [$\text{CH}_3\text{OC}(=\text{O})\text{CH}_2$]; M - (57 + 32), M - (57 + 32 + 18); m/e 58, 43, 71, 59, 74, 87. The IR spectrum of the isolated and purified component was consistent with a ω -2-oxo acid methyl ester: IR 1735, 1250, 1435 [$-\text{C}(=\text{O})\text{OCH}_3$]; 1720 cm^{-1} [$-\text{C}(=\text{O})\text{CH}_3$].

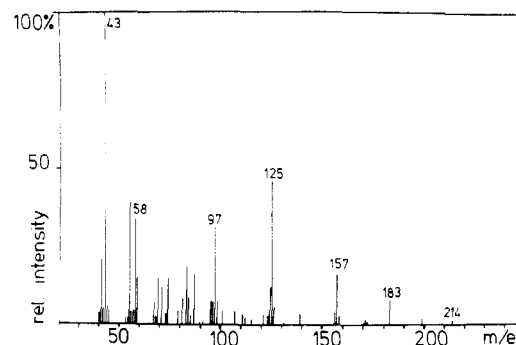


Figure 5. Mass spectrum of methyl 10-oxoundecanoate.

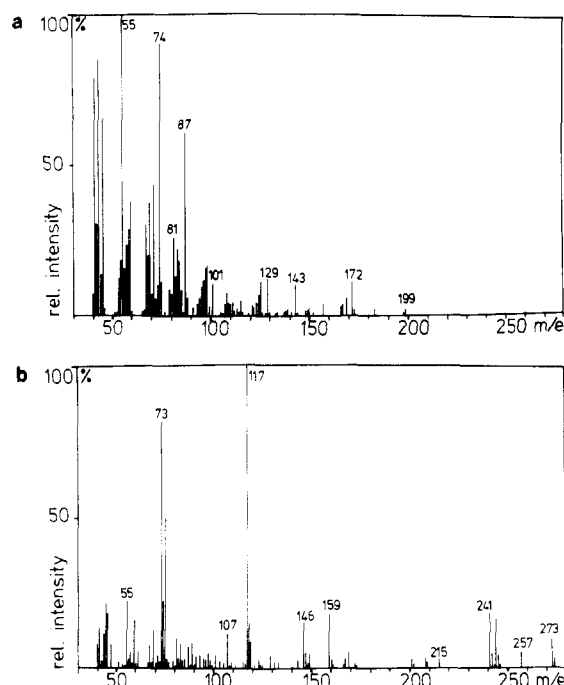


Figure 6. (a) Mass spectrum of methyl 10-hydroxyundecanoate. (b) Mass spectrum of methyl 10-hydroxyundecanoate trimethylsilyl ether.

By chemical reduction with NaBH_4 , component III was transformed into component IV. 9-Oxodecanoic acid was characterized as a minor product. This component is known as the queen substance (sex pheromone).

Component IV (Methyl 10-Hydroxyundecanoate) (Figure 6). The mass spectrum of component IV showed the typical fragmentation of ω -2-hydroxymethyl esters (Ryhage and Stenhagen, 1960): M - 44 [$\text{H}_3\text{COOC}(\text{CH}_2)_8 + \text{H}$], M - 49 ($-\text{OH} + \text{CH}_3\text{OH}$), M - 50 [$-\text{H}_2\text{O} + \text{CH}_3\text{OH}$]; m/e 45, 59, 74, 87, 143. The mass spectrum of the Me_3Si derivative showed the expected fragmentation of a ω -2-hydroxymethyl ester trimethylsilyl ether: M - 15, M - 47, M - 31; base peak at m/e 117 [$\text{CH}_3\text{CH}_2\text{OSi}(\text{CH}_3)_3$] and the typical rearrangement fragments of components containing a carbonyl and one Me_3Si group at m/e 146 and at m/e 159.

Component V [Methyl 10-Oxo-(E)-8-decenoate]. The mass spectrum of component V is shown in Figure 7. The fragmentation is consistent with that of the homologous methyl 12-oxo-(E)-10-decenoate (Zimmermann and Coudron 1979): M - 31, M - 32, M - 44, M - 49, M - 50, M - 59, M - 60 ($-\text{HCO}_2\text{CH}_3$). The IR spectrum of the purified component showed typical absorptions: IR 1735, 1250, 1435 [$-\text{C}(=\text{O})\text{OCH}_3$] and 2720, 1695, 1635, 970 cm^{-1} [$-\text{CH}=\text{CHCH}(=\text{O})$]. Therefore, the component is methyl 10-oxo-(E)-8-decenoate. By treatment with NaBH_4 , component V was transformed into component VI; by

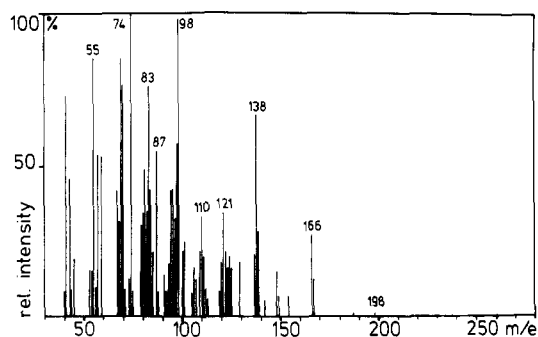


Figure 7. Mass spectrum of methyl 10-oxo-(E)-8-decenoate.

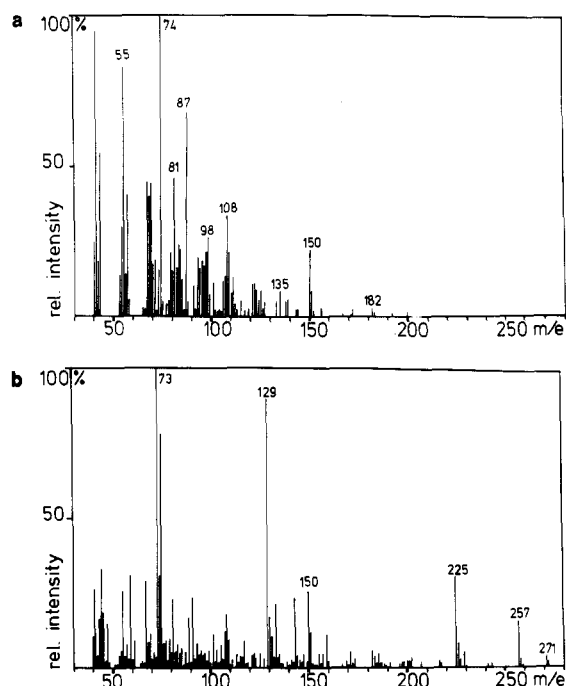


Figure 8. (a) Mass spectrum of methyl 10-hydroxy-8-decenoate. (b) Mass spectrum of methyl 10-hydroxy-8-decenoate trimethylsilyl ether.

reduction (of the $>C=C<$ bond) with Pt/H_2 , component I was formed.

Component VI (Methyl 10-Hydroxy-8-decenoate). Figure 8 presents the mass spectra of component VI and of the corresponding Me_3Si ether. The typical fragments are $M - 17$, $M - 18$, $M - 28$, $M - 50$, and $M - 49$. The

Me_3Si derivative shows the expected fragmentation of ω -hydroxymethyl esters: $M = 272$, $M - 1$, $M - 15$, $M - 47$; the base peak at m/e 129 [$(CH_3)_3SiOCH_2CH=CH_2$] indicates a unsaturated ω 2-hydroxy component.

Component VII and Component VIII. Methyl 9-oxodecanoate was detected as a minor constituent. The MS was consistent with that of ω 2-oxomethyl esters. The corresponding methyl 9-hydroxydecanoate showed the expected fragmentation.

All oxo and hydroxy acids were characterized for the first time as enzymic breakdown products from linoleic acid. Possible reaction schemes explaining the enzymic splitting and reduction of products will be presented (Tressl et al., 1981).

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