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The Occurrence of Optically Active 3-Methyl-dodecanoic Acid in Sperm Oil

PER KOCH CHRISTENSEN and RUDOLF A. GEHE

Institutt for treforedlingskjemi, Norges tekniske högskole, Trondheim, Norway

The main part of a liquid impurity in technical dodecanoic acid produced from hydrogenated sperm oil fatty acids has been isolated and characterized. The substance is optically active and by means of IR, NMR and mass spectrometric analyses it has been identified as (+)3-methyl-dodecanoic acid.

In connection with the industrial production of technical dodecanoic acid from hydrogenated sperm oil fatty acids, the problem of too low titer (m.p.) arose. Compared with n-C_{12} fatty acids from coconut oil the titer value was found to be 1—2°C too low. The observation was made, however, that a liquid sweated out from the distilled saturated sperm n-C_{12} fatty acid fraction if this was left to stand.

From the crude product it was possible to press out a liquid in a hydraulic press leaving a main fraction with increased titer value. IR-Spectrophotometry then indicated that the liquid fraction contained, in addition to unbranched fatty acids, a compound most probably a branched chain fatty acid as judged from the CH_3-absorption band and from the optical activity of the material.

The production process is outlined in Fig. 1. The liquid fraction product after pressing represents the raw material for this investigation.

Branched chain fatty acids have been reported found in a variety of natural sources, mostly as small percentage impurities in fatty materials where the bulk of the fatty acids is made up of regular unbranched fatty acids. Wool fat contains, however, more than 50 % branched chain acids,[1] and fats from a variety of animals contain small amounts of this type of fatty acid. The first record of branched chain fatty acids in nature was made in 1929—30 by Anderson and Chargaff[2] who reported such compounds in tubercle bacilli. The literature up to 1960 regarding the chemistry of the branched chain fatty acids has been covered most thoroughly by the book of Abrahamsson, Ställberg-Stenhagen and Stenhagen, "The Higher Saturated Branched Chain Fatty Acids".[3] The natural occurrence of these substances has also been covered in reviews.[5,6]

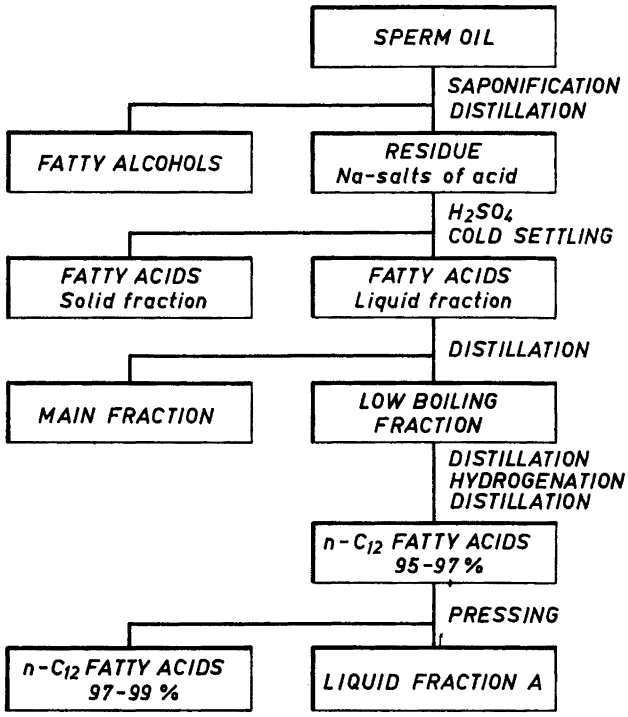

Fig. 1. Production of fatty acids. Liquid fraction A is raw material for this investigation.

Preliminary investigations of the product were done using IR-absorption data to follow the purity of the mixture of compounds following urea inclusions.

Freeman has reported a series of investigations on IR-absorption of methyl-branched fatty acids.[6] The region 1200—1400 cm^{-1} gives indications, at least to some extent, about the position of the branching methyl group. From this he concluded that if the branching occurs in the $\alpha, \beta, \gamma\delta$, or ε position, the absorption data will give a very good indication as to where branching occurs. The main differences in his spectra of these acids, compared with that of the normal acid, lie in the relative strengths and positions of the bands at approximately 7.78 and 8.10 microns (1298 and 1235 cm^{-1}), usually ascribed to the hydroxyl bending vibration of the carboxyl group which mostly is a doublet in long chain fatty acids. The shifts of the positions of these two bands correspond to the values of Freeman for methyl branching in position 3, while the relative intensities are a little out of line with his results. From Fig. 2 is seen that the main intensity difference of the IR-absorption bands lies in the much stronger band at 7.28 μ (1099 cm^{-1}) for the acid in question, compared with the normal C_{12} and C_{14} acids. This band is ascribed to the symmetrical C—H bending frequency of methyl groups. This agrees with a structure containing methyl branching. Integration of the methyl absorption bands of IR-spectra taken

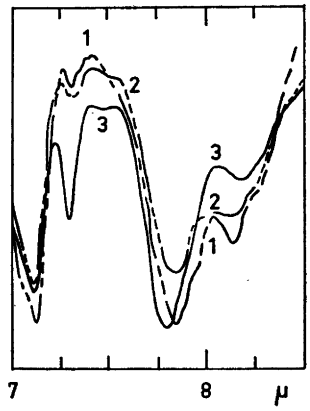

Fig. 2. Infrared spectra in CS_2. 1, dodecanoic acid; 2, tridecanoic acid; 3, 3-methyl-dodecanoic acid.

in CS_2-solutions gave values in the neighbourhood of both 2 and 3 methyl groups for the unknown acid. The integrations were done according to Freeman [6] and Ramsay,[7] respectively. Integration methods applied in cases like this cannot, however, be considered very accurate because of severe difficulties in an exact definition of the base line for the integration of the absorption band in question.

IR-absorption measurements were done on samples of free acid purified through complex formation with urea.[8,9] This will give residues enriched in branched chain fatty acids. Analytical gas-chromatography of the esterified samples was done with a silicone type filler and gave the following main components:

A	decanoic	acid	methyl	ester
B	dodecanoic	»	»	»
C	unknown fatty	»	»	»
D	tridecanoic	»	»	»
E	tetradecanoic	»	»	»

All components were saturated compounds as the product had been hydrogenated during processing according to Fig. 1. The main components were B and C with an estimate of 40—45 % B, 55—60 % C, and all other components less than 2 %.

A series of preparative gas-chromatograph runs then gave a pure optically active methyl ester with the following constants:

$[\alpha]_D^{20} = 5.13$ in $CHCl_3$, $n_D^{20} = 1.4333$

Nuclear magnetic resonance gave for the methyl esters the following values for methyl-hydrogen in the acid with the value for the hydrogens in $-OCH_3$ taken as 1.000:

dodecanoic	acid	methyl	ester	0.98	at	9.03 and	9.12 τ
unknown fatty	»	»	»	1.99	»	9.03 »	9.11 τ

It was thus shown that the unknown acid contained two methyl groups excluding the methoxy group.

The purified sample was analysed in a mass spectrometer giving the values for the most intense peaks as shown in Table 1. The values for the highest peaks of (+)methyl-3D-methyleicosanoate (II)[10] are given for comparison. The $m/e = 101$ is the number two intensity peak in both compounds and the m/e values for the ten most intense peaks are identical and give approximately the same pattern if plotted in a diagram (Fig. 3). The mass spectrometrically found molecular weight was 228, calculated for $C_{14}H_{28}O_2$:228.4.

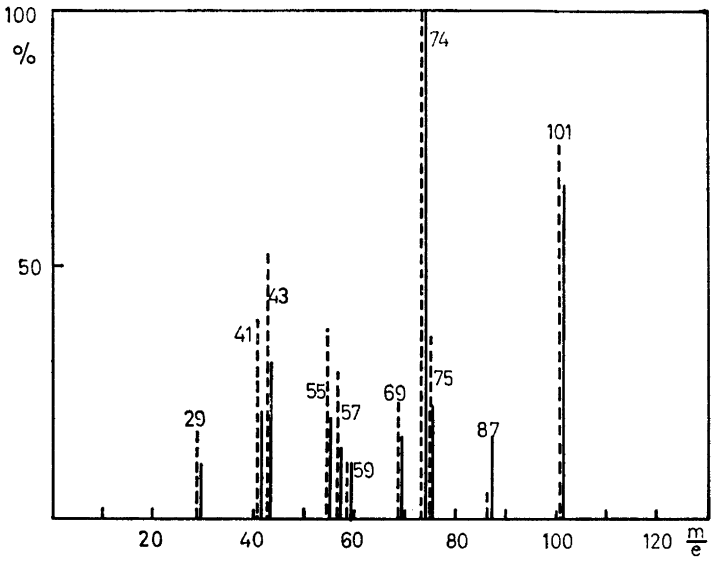

Fig. 3. Relative intensities of m/e for the 11 peaks of Table 1.
———— 3-methyl-dodecanoic acid methyl ester.
– – – – – – – 3-methyl-eicosanoic acid methyl ester.

Table 1. Mass spectral data. Relative intensities of the most intense peaks.

m/e	Methyl ester of unknown acid Intensity in %	Methyl-3D-methyl eicosanoate of highest peak
29	11	17
41	21	39
43	31	52
55	20	37
57	14	29
59	11	11
69	16	23
74	100	100
75	22	36
87	16	5[a]
101	66	74

[a] This is not among the 10 most intense peaks.

It can be concluded that the unknown acid has a methyl branch in position 3 and is 3-methyl-dodecanoic acid (I).

As outlined in the flowsheet diagram in Fig. 1, the work so far had been performed on a hydrogenated sample of fatty acids. It was of interest to clarify the problem of whether this branched chain acid occurred as esterified 3-methyl-dodecanoic acid in the sperm oil, or as an esterified unsaturated acid which had been hydrogenated during processing. In the latter case the unsaturation could, of course, not have occurred as a methylene group or in the 2,3 or 3,4 position as long as the hydrogenated product was optically active.

Gas chromatography of an unhydrogenated distillation fraction comparable to the hydrogenated product revealed a shoulder on the dodecanoic acid methyl ester peak with retention value similar to that given by (I). Treatment of this mixture of acids *via* the urea adduct gave a residue enriched in branched chain acids. Analysed gas-chromatographically as methyl esters, the residue was identified as a mixture of C_{10}, C_{12}, and C_{14} normal acids together with the same branched chain acid as in the hydrogenated product. It was thus shown that the 3-methyl dodecanoic acid occurs as such in the sperm oil.

EXPERIMENTAL

Urea complex formation was done according to Ref. 9 by crystallization from methanol. Analytical gas chromatography was performed on Aerograph Hy-Fi Model 600 with a silicone SE 30 filling at 170°C. The relative retention times for the methyl esters were found to be:

decanoic	acid	methyl	ester	0.48
dodecanoic	»	»	»	1.000
tridecanoic	»	»	»	1.50
tetradecanoic	»	»	»	2.23
3-methyl-dodecanoic	»	»	»	1.18

Preparative gas chromatography was performed on Aerograph Hy-Fi Autoprep Model A-700 with helium as carrier gas.

IR-measurements were done as liquid film, in CS_2, and in $CHCl_3$ on a Perkin-Elmer Model 21 with NaCl optics.

Nuclear magnetic resonance spectra were done on an NMR Spectrometer Type RS 2 from Associated Electrical Industries Ltd., in tetramethylsilane for the methyl esters. The areas given for methyl groups, compared with the area of the $-OCH_3$ group, gave:

	dodecanoic	acid	methyl	ester	OCH_3 1.000; CH_3 0.98 at 9.03 and 9.12 τ
3-methyl-	»	»	»	»	OCH_3 1.000; CH_3 1.99 at 9.03 and 9.11 τ

Mass spectrometry was most kindly performed by E. Stenhagen and R. Ryhage of Karolinska Institutet, Stockholm, Sweden. The following *m/e* values were found to be stronger than 1 % relative to the strongest peak of compound (I).

m/e	%	*m/e*	%	*m/e*	%
229	6.7	115	3.5	70	3.1
228	7.2	111	1.5	69	16
213	3.6	109	1.7	68	1.9
209	1.0	102	5.8	67	2.6
208	1.4	101	66	59	11
207	6.5	99	1.8	57	14
199	1.4	98	2.9	56	5.7
198	1.4	97	5.1	55	20
197	9.6	96	1.3	54	1.2
185	5.8	95	2.4	53	1.6

171	4.2	88	3.6	45	1.0
167	1.1	87	17	44	1.5
157	4.2	85	3.9	43	31
155	1.2	84	1.7	42	6.4
154	3.4	83	6.5	41	21
152	1.3	76	1.3	39	3.8
143	4.9	75	22	29	11
141	1.0	74	100	28	1.8
139	1.1	73	5.5	27	5.0
129	2.4	71	6.1	15	3.4
125	1.4				

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