Branched-Chain Fatty Acids of Butterfat

7. INVESTIGATION OF THE C₁₃ ACIDS*

By F. B. SHORLAND, T. GERSON AND R. P. HANSEN

*Fats Research Laboratory, Department of Scientific and Industrial Research,
Wellington, New Zealand*

(Received 31 May 1955)

Naturally occurring *n*-tridecanoic acid was first isolated from coconut oil (Jantzen & Witgert, 1939; Nobori, 1942), while the branched-chain C₁₃ acid ((+)-10-methyldodecanoic acid) was first found in degreas (Weitkamp, 1945) and later in mutton fat (Hansen, Shorland & Cooke, 1954*b*). In the present paper the occurrence in animal fats of *n*-tridecanoic and 11-methyldodecanoic acids is established for the first time. (+)-10-Methyldodecanoic acid has also been isolated.

In Part 6 of this series Shorland, Gerson & Hansen (1955) reported the isolation of (+)-12-methyltetradecanoic, 13-methyltetradecanoic and *n*-pentadecanoic acids by the combined processes of ester fractionation and low-temperature crystallization. The C₁₃ acids were isolated from the same sample of butterfat by the use of similar procedures.

EXPERIMENTAL

By fractional distillation of V3 (cf. Shorland *et al.* 1955) there was obtained a series of fractions of which the second, V3, 2 (411.4 g., saponification equiv. 215.2, iodine value 5.5) was selected to concentrate the methyl esters of C₁₃ acids by fractionation, giving finally a fraction K5 (10.11 g., sap. equiv. 229.8, iodine value 4.8, m.p. -13.0° to -12.2°). K5 on refractionation in column E (Shorland, 1952) was shown to consist of methyl esters of C₁₃ acids (see Table 1).

m.p. -4.0° to -3.0°, $\alpha_D^{18} + 0.54^\circ$), and LR (3.52 g., sap. equiv. 235.4, iodine value 10.6, m.p. 3.0-3.9°, $\alpha_D^{18} 0.00^\circ$) were used for the isolation of C₁₃ acids.

In agreement with previous experience with the methyl esters of the C₁₃ acids (cf. Shorland *et al.* 1955) it was found that the later fractions of methyl esters of C₁₃ acids had relatively high melting points and low optical rotations, suggesting that the methyl ester of the *n*-acid was the main constituent (see Table 1).

n-Tridecanoic acid

To isolate the *n*-acid, fractions K5, R and LR were combined and the corresponding acids denoted A. Crystallization of A (6.56 g., m.p. 32.7-33.3°) 3 times from 40 vol. of light petroleum (b.p. 50-60°) at -40° gave 2.80 g. of precipitate AI3 (m.p. 41.6-41.9°) and a soluble portion AS3 (0.47 g., m.p. 37.7-38.5°). AI3, on admixture with an equal quantity of synthetic *n*-tridecanoic acid (Eastman-Kodak), m.p. 41.3°, showed no depression of m.p.

(+)-10-Methyldodecanoic acid

The soluble portion AS1, and the remaining fractions of methyl esters of C₁₃ acids, K5 (1-4), L5, and L6 after conversion into fatty acids, were bulked, and denoted B, giving a total weight of 14.76 g. B was crystallized 10 times from 40 vol. of light petroleum (b.p. 50-60°) at -70° and the soluble fractions BS1 to 5 (4.15 g.) were combined and recrystallized three times from 10 vol. of light petroleum at -70°. The solids denoted C (1.91 g., m.p. 23.3°) were

Table 1. Fractionation of methyl esters of C₁₃ acids (fraction K5)

Fraction	Wt. (g.)	Sap. equiv.	M.p. (°)	α_D^{18}
K5, 1	0.70	228.8	-6.0 to -5.5	0.00°
K5, 2	1.50	229.8	-15.8 to -15.3	+0.34
K5, 3	1.65	227.2	-23.0 to -22.5	+0.54
K5, 4	1.45	227.2	-15.8 to -15.3	+0.74
K5, R	4.30	227.2	-1.2 to -0.7	+0.14
	9.60	—	—	—

Fraction 4 (1550 g., sap. equiv. 225.4, iodine value 8.1), obtained during the course of fractionation of (V1+V2) referred to previously (Shorland *et al.* 1955), was similarly resolved into seven fractions. Of these, L5 (7.64 g., sap. equiv. 227.0, iodine value 10.0, m.p. -12.0° to -11.5°, $\alpha_D^{18} + 0.64^\circ$), L6 (3.80 g., sap. equiv. 226.7, iodine value 9.6,

combined with BS6-10, and with BI10 giving 12.4 g. of acids denoted D. D was crystallized 9 times from 20 vol. of light petroleum at -70°, and the soluble fractions DS1-5 (1.57 g.), denoted E, were recrystallized from light petroleum using 20 vol. at -70°, 10 vol. at the same temp. and 50 vol. twice at -40°. The soluble fraction ES4 had m.p. 6.2-6.5°; $[\alpha]_D^{18} + 5.5^\circ$ in CHCl₃. It was therefore presumed to be the *ante-iso* acid.

* Part 6: Shorland, Gerson & Hansen (1955).

11-Methyldodecanoic acid

AS2 and DI9 were combined and denoted F (11.05 g.). Crystallization of F from 65 vol. of acetone at -40° yielded 0.25 g. of precipitate FI1 (m.p. $45.3-45.8^\circ$). The soluble fraction FS1 (10.72 g.) was crystallized twice from 20 vol. of ethanol at -70° , and then 3 times from 20 vol. of acetone at the same temperature. FI6 (8.50 g. acids) was converted into methyl esters of which 4.19 g., denoted G, were recrystallized 7 times from 25 vol. of methanol at -40° . The soluble fractions GS1-7 (3.17 g.), denoted H, were combined and crystallized 4 times from 25 vol. of methanol at -40° . The soluble portions HS1-4, denoted I, were again combined (2.05 g.), reconverted into acids (1.83 g.), and crystallized 4 times from 75 vol. of acetone at -75° and then 7 times from 80 vol. of light petroleum at -40° , giving finally 0.38 g. of precipitate I11 (m.p. $39.4-40.0^\circ$). The melting point of I11 was depressed to 35.7° when mixed with an equal weight of the normal acid. This fraction was therefore presumed to consist of 11-methyldodecanoic acid.

conditions, Von Sydow (1954) obtained the A form. Fraction I11 differs from *n*-tridecanoic acid by the long spacing of 26.3 Å. This agrees with 26.2 Å found by Arosenius, Stållberg, Stenhagen & Tågström-Eketorp (1949), and 26.8 Å reported by Velick (1947) for the C₁₃ *iso*-acid. When mixed with an equal quantity of *n*-tridecanoic acid the melting point of the latter (41.3°) was depressed by 5.7° . This depression is in accord with depressions of $5-7^\circ$ found, when odd-numbered normal and *iso*-acids are mixed (cf. Hansen, Shorland & Cooke, 1954*a*). These data, together with the melting point of 40.0° , show that I11 is 11-methyldodecanoic acid.

The m.p. of ES4 (6.5°) agrees with that reported by Weitkamp (1945), (6.2°), by Nunn (1951), (5.6°), and by Milburn & Truter (1954), (5.8°), for (+)-10-methyldodecanoic acid. The value for $[\alpha]_D^{18}$ in chloroform was found to be $+5.5^\circ$, as compared

Table 2. Chemical and physical properties of fractions

Fraction	Wt. (g.)	Sap. equiv.	n_D^{60}	M.p. ($^\circ$)	Combustion analysis (%) [*]		$[\alpha]_D^{18}$	X-ray long spacing (Å)
					C	H		
AI3	2.80	214.0	1.4288	41.6-41.9	73.1	12.2	—	29.7† 34.6‡
ES4	0.95	214.3	1.4444§	6.2-6.5	72.7	11.6	$+5.5^\circ$	—
I11	0.38	214.8	1.4293	39.4-40.0	73.0	12.3	—	26.3†

* Calc. for C₁₃H₂₆O₂: C, 72.9; H, 12.2%.

† Crystallized from benzene.

‡ Melted and then quickly cooled.

§ Determined at 25° .

The X-ray long spacings were determined with a Philips Geiger X-ray spectrometer, iron-filtered $K\alpha$ radiation being used. Melting points were determined in closed capillaries and are uncorrected. The optical rotation was determined in 1 dm. cells on the pure fractions unless otherwise stated.

C and H analyses were by Drs G. Weiler and F. B. Strauss, Oxford.

DISCUSSION

The combustion analyses and saponification equivalents of the three fractions described (see Table 2) correspond to those of a saturated C₁₃ acid. Fraction AI3 is identified as *n*-tridecanoic acid, because it had m.p. 41.9° which was not depressed when mixed with pure *n*-tridecanoic acid. This melting point agrees with the value of 41.76° (Pool & Ralston, 1942). The X-ray long spacings found were 29.7 Å for remelted material and 34.6 Å for specimens recrystallized from benzene. These agree with 30.0 and 35.3 Å for the C and A modifications respectively, found by Francis, Piper & Malkin (1930). Slagle & Ott (1933) reported a value of 34.92 Å for the A modification. On crystallizing from the melt and cooling to room temperature, we obtained the C form (29.7 Å) whereas, under similar

with the value of $+5.88^\circ$ found by Milburn & Truter (1954). Thus, the three fractions described above are identified as *n*-tridecanoic acid (AI3), 11-methyldodecanoic acid (I11) and (+)-10-methyldodecanoic acid (ES4).

The amounts of the saturated C₁₃ acids are estimated at approximately 0.1 % of the total fatty acids, as compared with 1.6 % of the C₁₅ acids. Moreover, whereas the predominant constituent of the C₁₅ acids was *n*-pentadecanoic, in these C₁₃ acids the main constituent appeared to be the *iso*-acid, with somewhat smaller proportions of the normal acid and minor amounts of the *ante-iso* acid.

SUMMARY

(+)-10-Methyldodecanoic, 11-methyldodecanoic and *n*-tridecanoic acids have been identified in butterfat, in amounts corresponding respectively to approximately 0.01, 0.05 and 0.03 % of the total fatty acids.

We are indebted to Mr M. Fieldes, Soil Bureau, Department of Scientific and Industrial Research, Wellington, New Zealand, for the X-ray analyses reported in this paper.

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