Naturally occurring n-tridecanoic acid was first isolated from coconut oil (Jantzen & Witgert, 1939; Nobori, 1942), while the branched-chain C₁₃ acid (±)-10-methylldodecanoic acid) was first found in degras (Weitkamp, 1945) and later in mutton fat (Hansen, Shorland & Cooke, 1954b). In the present paper the occurrence in animal fats of n-tridecanoic and 11-methylldodecanoic acids is established for the first time. (±)-10-Methylldodecanoic 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 (10-1 g., sapon. 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).

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Wt. (g.)</th>
<th>Sap. equiv.</th>
<th>M.p. (°)</th>
<th>α₁₀⁰⁰°</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₅, 1</td>
<td>0-70</td>
<td>228-8</td>
<td>-6°0 to -5°5</td>
<td>0-00°</td>
</tr>
<tr>
<td>K₅, 2</td>
<td>1-50</td>
<td>229-8</td>
<td>-15°8 to -15°3</td>
<td>+0-34</td>
</tr>
<tr>
<td>K₅, 3</td>
<td>1-65</td>
<td>227-2</td>
<td>-23°0 to -22°5</td>
<td>+0-54</td>
</tr>
<tr>
<td>K₅, 4</td>
<td>1-45</td>
<td>227-2</td>
<td>-15°8 to -15°3</td>
<td>+0-74</td>
</tr>
<tr>
<td>K₅, R</td>
<td>4-30</td>
<td>227-2</td>
<td>-1°2 to -0°7</td>
<td>+0-14</td>
</tr>
</tbody>
</table>

Fraction 4 (1550 g., sapon. 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., sapon. equiv. 227-0, iodine value 10-0, m.p. -12°0 to -11°5, α₁₀°⁰₅ = 0-64°), L₆ (3-80 g., sapon. equiv. 226-7, iodine value 9-6, m.p. -4°0 to -3°0, α₁₀°⁰₅ = 0-54°), and LR (3-32 g., sapon. equiv. 235-4, iodine value 10-6, m.p. 3°0-3°9, α₁₀°⁰₅ = 0°00°) 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 A₁₃ (m.p. 41°-41°9°) and a soluble portion A₃ (0-47 g., m.p. 37°-38°5°). A₁₃, on admixture with an equal quantity of synthetic n-tridecanoic acid (Eastman-Kodak), m.p. 41°3°, showed no depression of m.p.

(±)-10-Methylldodecanoic acid

The soluble portion A₅, 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 combined with BS₆-10, and with B₁₁₀ 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°; [α]₁₀°⁰₅ = 5°5° in CHCl₃. It was therefore presumed to be the ante-isoo acid.
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 F11 (m.p. 45.5-45.8°). The soluble fraction FS1 (10.72 g.) was crystallized twice from 20 vol. of ethanol at −70°C and then 3 times from 20 vol. of acetone at the same temperature. F16 (8.50 g. acids) was converted into methyl esters of which 4.19 g., denoted G, were recrystallized 7 times to 25 vol. of methanol at −40°C. The soluble fractions GS1-7 (3.17 g.), denoted H, were combined and crystallized 4 times from 25 vol. of methanol at −40°C. 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°C and then 7 times from 80 vol. of light petroleum at −40°C, giving finally 0.38 g. of precipitate 111 (m.p. 39.4-40.0°C). The melting point of 111 was depressed to 35-7°C when mixed with an equal weight of the normal acid.

This fraction was therefore presumed to consist of 11-methyldodecanoic acid.

Table 2. Chemical and physical properties of fractions

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Wt. (g.)</th>
<th>Sap. equiv.</th>
<th>nD 25</th>
<th>M. p. (°C)</th>
<th>Combustion analysis (%)*</th>
<th>X-ray long spacing</th>
</tr>
</thead>
<tbody>
<tr>
<td>A13</td>
<td>2.90</td>
<td>214.0</td>
<td>1-4288</td>
<td>41-6-41.9</td>
<td>73-1</td>
<td>29-7†</td>
</tr>
<tr>
<td>ES4</td>
<td>0.95</td>
<td>214-3</td>
<td>1-4444§</td>
<td>6-2-6.5</td>
<td>72-7</td>
<td>34-6‡</td>
</tr>
<tr>
<td>111</td>
<td>0.38</td>
<td>214-8</td>
<td>1-4293</td>
<td>39-4-40.0</td>
<td>73-0</td>
<td>26-3†</td>
</tr>
</tbody>
</table>

* Calc. for C13H26O2: C, 72.9; H, 12.2%.
† Crystallized from benzene.
‡ Determined at 25°.

The X-ray long spacings were determined with a Philips Geiger X-ray spectrometer, iron-filtered Kα 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 A13 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 29-7Å for remelted material and 34-6Å for specimens recrystallized from benzene. These agree with 30-0 and 35-3Å for the C and A modifications respectively, found by Francis, Piper & Malkin (1930). Slagle & Ott (1933) reported a value of 34-92Å for the A modification. On crystallizing from the melt and cooling to room temperature, we obtained the C form (29-7Å) whereas, under similar conditions, Von Sydow (1954) obtained the A form. Fraction 111 differs from n-tridecanoic acid by the long spacing of 26-3Å. This agrees with 26-2Å found by Arosenius, Ställberg, Stenhagen & Tagström-Eketorp (1949), and 26-8Å reported by Velick (1947) for the C14 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° found, when odd-numbered normal and iso-acids are mixed (cf. Hansen, Shortland & Cooke, 1954). These data, together with the melting point of 40-0°, show that 111 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 [α]D 15 in chloroform was found to be +5-5°, as compared with the value of +5-88° found by Milburn & Truter (1954). Thus, the three fractions described above are identified as n-tridecanoic acid (A13), 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 C14 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.
REFERENCES
