The Occurrence of *n*-Pentadecanoic Acid in Hydrogenated Mutton Fat

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When *n*-heptadecanoic acid (margaric acid) was isolated from hydrogenated mutton fat (Hansen, Shorland & Cooke, 1954*a*) it was anticipated that other fatty acids of high molecular weight and with an odd number of carbon atoms would also be present in this material. Further investigations have now been made and *n*-pentadecanoic acid has been found in the same hydrogenated sample of external carcass fat from old ewes.

n-Pentadecanoic acid has not hitherto been established as a component of natural fats, although unpublished evidence obtained by Morice & Shorland in this laboratory indicates that it is present in hydrogenated shark-liver oil. It has, however, been found (together with other fatty acids containing an odd number of carbon atoms) in synthetic fats manufactured from 'gatsch' (cf. Williams, 1947).

The sample of mutton fat used in this investigation was earlier shown to contain small quantities of *n*-decanoic acid (capric acid; Hansen & Cooke, 1953) together with the branched-chain acids 12-methyltetradecanoic acid, 13-methyltetradecanoic acid (Hansen, Shorland & Cooke, 1953), and 14-methylhexadecanoic acid (Hansen, Shorland & Cooke, 1952). *n*-Pentadecanoic acid is thus the third C_{15} acid to be identified from this source.

EXPERIMENTAL

As formerly reported (Hansen *et al.* 1952, 1953, 1954*a*; Hansen & Cooke, 1953) the fat used in this work (sap. equiv. 286·9, iodine val. 46·6, unsaponifiable matter 0·56%, and free fatty acids 0·4%) was extracted by steam-rendering the minced external fatty tissues cut from the carcasses of old overweight ewes. The glycerides were converted into methyl esters (7·69 kg.), which were hydrogenated at 180° using a Ni catalyst supported on kieselguhr, and then repeatedly crystallized from 10 vol. acetone at −30°. Fractional distillation of 6·45 kg. of the acetone-insoluble esters ('solids') was then carried out in a 490 × 3·8 cm. stainless-steel column packed with 3–4 mm. diameter single-turn glass helices. Of the 16 fractions and a large residue which resulted, the third (denoted OS3, wt. 40·0 g., sap. equiv. 253·6, iodine val. 0·5) was selected for this investigation. Part of fraction OS3 (34·76 g.) was refractionated *in vacuo* (0·1–0·5 mm.) in a 50 × 1·8 cm. column (column *E*, Shorland, 1952) to yield ten fractions (OS3S1 to OS3S10) and a residue as shown in Table 1.

Fractions OS3S6 (denoted O15, wt. 4·30 g., sap. equiv. 256·5, m.p. 17·8–18·2°; m.p. (acids) 49·6–50·4°) possessed characteristics similar to those of methyl pentadecanoate. Accordingly the acids of O15 were submitted to low-temperature crystallization from 40 vol. of the following solvents at −40°, the soluble fraction being removed after each crystallization: light petroleum (b.p. 50–60°) (3 crystallizations); methanol (6 crystallizations); ether (1 crystallization); and acetone (2 crystallizations). The resulting purified acid fraction O15S11S (wt. 2·39 g.) had the following physical and chemical properties: m.p. 52·8–53·1°; sap. equiv. 242·4; combustion analyses: C, 74·5; H, 12·5%; iodine val. 0·0; X-ray long spacing 35·5 Å; n_D^{60} 1·4328: methyl ester m.p. 18·4–19·0°; methyl ester n_D^{20} 1·4402. The acid fraction when mixed in equal proportions: (*a*) with the C_{15} *iso* acid from butterfat (K14S17LS3S, m.p. 52·0°, Hansen, Shorland & Cooke, 1954*b*) gave a mixed m.p. of 45·5–46·0°, (*b*) with the C_{15} *iso* acid synthesized by Arosenius, Ställberg, Stenhagen & Tägtström-Eketorp (1949), m.p. 51·7–51·8°, it gave a mixed m.p. of 44·5–45·2°.

Table 1. *Fractional distillation of methyl esters* (OS3)

Wt. 34·76 g., sap. equiv. 253·6, iodine val. 0·5.

Fraction	Wt. (g.)	M.p. (°)	Saponification equiv.	Designation for further work
OS3S1	3·33	18·7–19·2	244·7	—
OS3S2	2·73	18·5–18·7	242·8	—
OS3S3	3·74	17·2–17·5	244·2	—
OS3S4	3·89	8·8– 9·2	251·3	O17
OS3S5	4·54	13·0–13·8	256·6	
OS3S6	4·30	17·8–18·2	256·5	O15
OS3S7	1·37	16·4–17·5	256·7	O16
OS3S8	4·02	17·4–18·1	256·7	
OS3S9	2·37	22·9–23·8	264·6	O18
OS3S10	1·29	26·8–29·1	268·0	—
OS3SR	2·85	—	280·2	—

By similar processes of low-temperature crystallization of the fatty acids, other fractions reported in Table 1, namely OS3S4 and OS3S5 (combined and denoted O17), OS3S7 and OS3S8 (combined and denoted O16), and OS3S9 (denoted O18), yielded varying amounts of purified acid. The largest of these fractions was O16S7S (wt. 4·19 g.) which possessed the following characteristics: m.p. 52·7–53·2°; sap. equiv. 242·3; combustion analyses: C, 74·6; H, 12·7%; iodine val. 0·0; X-ray long spacing 36·1 Å; n_D^{60} 1·4328.

The X-ray measurements reported in this paper were made with a Philips Geiger X-ray spectrometer using manganese-filtered Fe $K\alpha$ radiation. Combustion analyses were made by Drs G. Weiler and F. B. Strauss, Oxford. Melting points were determined in closed capillaries and are uncorrected.

DISCUSSION

A study of the following chemical and physical properties of fractions O15S11S and O16S7S respectively, establishes the presence in hydrogenated mutton fat of the C_{15} saturated straight-chain fatty acid *n*-pentadecanoic acid: saponification equivalents 242·4 and 242·3 (calc. for $C_{15}H_{30}O_2$: 242·4); combustion analyses: C, 74·5; H, 12·5 and C, 74·6; H, 12·7% (calc. for $C_{15}H_{30}O_2$: C, 74·4, H, 12·5%); iodine values 0·0 for O15S11S and O16S7S; m.p.'s 52·8–53·1° and 52·7–53·2°; values from the literature are as follows: Francis, Piper & Malkin (1930) 52·1°; Levene & West (1914) 53·0°; Links & de Groot (1953) 52·3–53·3°; Coops quoted by Links & de Groot 54·4°; Weitkamp (1945) 52·4°; Meyer & Reid (1933) 52·26°. X-ray long spacing 35·5 and 36·1 Å (Francis *et al.* (1930) 35·8 Å; Slagle & Ott (1933) 35·75 Å); refractive index for both fractions n_D^{60} 1·4328 (Dorinson, McCorkle & Ralston (1942), n_D^{60} 1·4329).

In his paper on the acidic constituents of degras, Weitkamp (1945) stated that all the *iso* acids with an even number of carbon atoms, when mixed with their corresponding normal acids, showed a depression of 10–15° in melting point. Investigations made in this laboratory indicate that in the case of *iso* acids with an odd number of carbons the depression appears to be smaller. The normal C_{15} acid reported in this paper (m.p. 52·8–53·1°) when mixed in equal proportions with the C_{15} *iso* acid from butterfat (K14S17LS3S, m.p. 52·0°, Hansen *et al.* 1954*b*) gave a mixed melting point of 45·5–46·0° (depression, 7–8°). Similarly, our normal C_{15} acid when admixed with the C_{15} *iso* 13-methyltetradecanoic acid (m.p. 51·7–51·8°) kindly supplied by Professor E. Stenhagen (Arosenius *et al.* 1949) gave a mixed melting point of 44·5–45·2° (depression, 7–8°).

In the sample of hydrogenated mutton fat examined, *n*-pentadecanoic acid is present to the extent of approximately 0·15% of the total fatty acids.

SUMMARY

Hydrogenated mutton fat has been found to contain approximately 0·15% of *n*-pentadecanoic acid.

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