The Occurrence of *n*-Decanoic Acid in Mutton Fat

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(*Received* 5 *August* 1952)

A number of fatty acid composition analyses have been made on animal body fats (see Hilditch, 1947), but the trace fatty acid constituents of these fats have not been fully investigated. The analyses reported by Hilditch (1947) show that most animal body fats, including those of sheep (Hilditch & Pedelty, 1941) contain saturated fatty acids ranging from C_{14} to C_{18} together with trace amounts of C_{12} acids. Although *n*-decanoic (capric) acid has been reported to be present in milk fats (Chevreul, 1823; Dhingra, 1933, 1934; Hilditch & Paul, 1936; Hilditch, 1947), in coconut and other palm-kernel oils (Görgey, 1848; McKinney & Jamieson, 1938), in the seed fats of a number of plants, including the elm (Schuette & Lunde, 1936), in the head oil of sperm whales (Hilditch & Lovern, 1928), and in wool grease (Weitkamp, 1945), it has not formerly been isolated from the animal body fats of animals receiving a natural diet. Evidence indicating its presence as a minor constituent of the body fats of pigs which had been fed a diet of only buttermilk, was, however, submitted by de la Mare and Shorland (1946). These authors considered that small amounts of low-molecular-weight saturated acids were assimilated from the buttermilk diet and deposited unchanged in the body tissue. Similarly, Longenecker & Hilditch (1938) reported trace amounts of both capric and lauric acids in the depot fats of rats which had been fed wholly on a diet of cows' milk, and Hilditch, Sime & Maddison (1942) identified 2·1 mol. % capric acid and 1·5 mol. % lauric acid in the fat of a lion. The C_{10} and C_{12} acids in this case were considered to have been derived from coconut cake which had been eaten by animals whose flesh had been fed to the lion.

Recent investigations on the external fatty tissues of old ewes have revealed that the fat contains, in addition to the known straight-chain acids, trace amounts of methyl branched-chain saturated acids (Hansen, Shorland & Cooke, 1952*a*, *b*). The present paper reports the further examination of the trace components of mutton fat and the isolation from it of *n*-decanoic acid.

EXPERIMENTAL

Details of the preliminary preparation of bulk material for this investigation were reported earlier (Hansen *et al.* 1952*a*, *b*). The procedure was briefly as follows. From the external fatty tissues of old overweight ewes the fat was extracted by mincing and steam-rendering. The extracted glycerides (saponification equiv. 286·9, I_2 value 46·6, unsaponifiable matter 0·56 %, and free fatty acids 0·4 %) after being converted to methyl esters (7·69 kg.) and hydrogenated were repeatedly crystallized from acetone at −30° yielding 332·6 g. 'liquids' (I_2 value 7·0). Fractional distillation at about 0·2 mm. in a 22-plate Vigreux column resulted in a series of thirteen fractions and a residue (see Table 1, Hansen *et al.* 1952*a*). In this present paper, the first fraction only of this series, HL1 (wt. 17·0 g., saponification equiv. 234·9, I_2 value 1·7) has been submitted to detailed investigation. Fraction HL1 was distilled *in vacuo* (column E, Shorland, 1952), and yielded ten fractions and a residue (see Table 1).

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

(Wt. 15·9 g., saponification equiv. 234·9, I_2 value 1·7.)

Fraction	Wt. (g.)	Saponification equiv.	Iodine value (Wijs)
HL1L1	1·06	180·1	Nil
HL1L2	1·16	192·3	3·0
HL1L3	1·15	201·5	0·5
HL1L4	1·42	209·8	3·6
HL1L5	0·64	220·3	4·7
HL1L6	1·01	219·8	3·7
HL1L7	1·54	228·5	1·5
HL1L8	1·78	239·5	1·5
HL1L9	1·97	242·4	1·3
HL1L10	2·83	240·4	0·9
HL1LR*	0·77	258·7	24·0

* Residue excluding unsaponifiable matter. Saponification equiv. 233·6 (acid).

The methyl esters of fraction HL1L2, denoted H57, (wt. 1·16 g., saponification equiv. 192·3, I_2 value 3·0; m.p. (acids) 28·5°) were then submitted to chromatographic separation by elution with light petroleum (b.p. 50–60°) through a column packed with alumina (see Table 2).

On the basis of their having almost identical refractive indices (see Table 2) methyl ester fractions H57*b*, H57*c*, H57*d* and H57*e* were bulked and denoted H65 (wt. 0·62 g., saponification equiv. 190·8, m.p. −11·7°). Further purification of fraction H65 was effected by means of repeated low-temperature crystallization of its fatty acids (wt. 0·52 g., m.p. 29·0°) from light petroleum (b.p. 50–60°) and from methanol, yielding fraction H65S2LL (wt. 0·34 g., saponification equiv. 171·9, m.p. 31·2°). (See Table 3).

The chemical and physical characteristics of fraction H65S2LL are recorded in Table 4.

Two further fractions HL1L1SLS (0·21 g., m.p. 30·5°) and HL1L1LSSL (0·23 g., m.p. 30·2°) were independently derived from HL1L1 (Table 1) by low-temperature fractional crystallization.

Table 2. *Chromatographic separation of the methyl esters of fraction H57*

(Wt. 1·16 g., saponification equiv. 192·3, I_2 value 3·0.)

Fraction	Eluent (Light petroleum b.p. 50–60°) (ml.)	Wt. (g.)	Refractive index $n_D^{20°}$
H57*a*	25	0·07	1·4298
H57*b*	25	0·42	1·4254
H57*c*	25	0·12	1·4253
H57*d*	25	0·05	1·4252
H57*e*	25	0·03	1·4252
H57*f*	50	0·03	1·4282
H57*g*	50	0·01	—

The long crystal spacing reported in this paper was determined by means of a Philips Geiger X-ray spectrometer using Kα-radiation from an iron target tube with a Mn filter. Samples were melted on a glass slide and quickly cooled.

All melting points were determined in closed capillaries and are uncorrected.

DISCUSSION

Fraction H65S2LL possessed a melting point of 31·2° in close agreement with reported values for *n*-decanoic acid, namely 31·3° (Deffet, 1931), 31·19° (Meyer & Reid, 1933) and 30·9° (Weitkamp, 1945). Saturation of the fraction is indicated by the zero iodine value. Evidence of molecular weight is furnished by saponification equivalent (171·9) and combustion analyses (C, 69·9; H, 11·5%) both agreeing closely with the requirements for a saturated fatty acid $C_{10}H_{20}O_2$ (saponification equiv. 172·3; C, 69·7, H, 11·7%). The X-ray long spacing of fraction H65S2LL (22·8 A.) agrees within experimental error (± 0·5 A.) with the value of 23·02 A. recorded by Slagle & Ott (1933) for a melted specimen of *n*-decanoic acid. This figure distinguishes it from *n*-undecanoic acid (25·32 A.) and from *n*-dodecanoic acid (27·18 A.). When admixed with an equal quantity of authentic capric acid (m.p. 30·0°) fraction H65S2LL gave a mixed melting point of 30·0°. The chemical and physical data presented above are consistent with the fraction isolated in this work being *n*-decanoic acid.

The occurrence of capric acid in the back fat of pigs which had been fed solely on buttermilk, was attributed by de la Mare & Shorland (1946) to assimilation from the diet and direct deposition. On this hypothesis it is not surprising that as capric acid is present in the milk fat of sheep (Dhingra, 1933), it is also present in trace amounts in their body fats. (In this investigation capric acid was estimated to be present to the extent of about 0·1% of the total fatty acids.) It would be expected to occur in even greater quantities in the depot fats of lambs as well as in the young of certain other mammals, such as goats, horses, camels, buffaloes and humans (Hilditch, 1947), of whose milk fats it is a component.

The storage of dietary fatty acids below C_{16} has already been indicated, but the evidence suggests that, possibly owing to more rapid oxidation, the

Table 3. *Purification of fatty acids (H65) by means of fractional crystallization*

(Wt. 0·52 g., m.p. 29·0°, saponification equiv. of methyl esters 190·8.)

Fraction	Conditions of crystallization	Soluble fraction	Wt. (g.)	M.p. (°)	Insoluble fraction	Wt. (g.)	M.p. (°)
H65	Light petroleum, 40 vol., −70°	H65L	0·06	10·4	H65S	0·45	31·2
H65S	Light petroleum, 40 vol., −70°	H65SL	0·02	16·0	H65SS	0·42	31·8
H65SS	Methanol, 40 vol., room temp.	H65S2L	0·41	—	H65S2S	Trace	—
H65S2L	Methanol, 40 vol., −60°	H65S2LL	0·34	31·2	H65S2LS	0·03	29·0

Table 4. *Characteristics of fatty acid fraction H65S2LL*

Fraction	Wt. (g.)	M.p. (°)	Saponification equiv.	X-ray long spacing	Combustion analysis*	Iodine value (Wijs)
H65S2LL	0·34	31·2	171·9	22·8 A.	C, 69·9% H, 11·5%	—
		(Value for *n*-decanoic acid 31·3)‡	(Calc. for $C_{10}H_{20}O_2$: 172·3)	(Value for *n*-decanoic acid 23·02 A)†	(Calc. for $C_{10}H_{20}O_2$: C, 69·7%; H, 11·7%)	Nil

* Analysis Weiler and Strauss, Oxford.
† Determination by Slagle & Ott (1933).
‡ Determination by Deffet (1931).

efficiency of storage diminishes with decreasing molecular weight (cf. Shorland & de la Mare, 1945) so that with the development of more refined techniques, it might be feasible to demonstrate that acids of molecular weight still lower than that of capric acid can occur in mutton tallow albeit in still smaller proportions. At the present time, however, the field of investigation relating to the trace constituents of fats remains relatively unexplored.

SUMMARY

n-Decanoic acid has been isolated in trace amounts from the external fatty tissue of sheep.

We are indebted to Dr F. B. Shorland, Director of this Laboratory, for his suggestions and co-operation, and to Mr M. Fieldes, Soil Bureau, Department of Scientific and Industrial Research, Wellington, New Zealand, for the X-ray analysis reported in this paper.

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The Biological Action of Substances Related to Thyroxine

4. THE THYROXINE-INHIBITORY PROPERTIES OF A SERIES OF 4-HYDROXY-3:5-DIIODOBENZOATES OF GLYCOLS

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(*Received* 9 *August* 1952)

During the course of a study of the physico-chemical properties of a series of *n*-alkyl 4-hydroxy-3:5-diiodobenzoates briefly reported by Maclagan, Sheahan & Wilkinson (1951), it was found that high antithyroxine activity was paralleled by oil:water partition coefficients relatively in favour of the water phase and by relatively rapid rates of alkaline hydrolysis. This work will be discussed later, but it appeared that suitable hydroxyalkyl esters might well show a greater affinity for the aqueous phase and might therefore be expected to exhibit enhanced antithyroxine activity. A number of such substances and several polyesters of certain glycols have been prepared and tested for thyroxine-inhibitory action.

Since *p*-hydroxybenzoic acid does not form the corresponding acid chloride with such reagents as phosphorus oxychloride or thionyl chloride, the required *p*-hydroxybenzoates could not conveniently be prepared directly from this acid. However, when the phenolic hydroxyl group was protected with an acyl group, acid chlorides were readily formed on treatment with thionyl chloride. Because of the ease with which it could subsequently be removed, the carbethoxyl group proved to be the most satisfactory protection for the hydroxyl group. The crude *p*-carbethoxyoxybenzoyl chloride reacted readily with 2 equivalents of the glycol to give the appropriate hydroxyalkyl *p*-carbethoxyoxybenzoate as principal product, or with 1 equivalent to form mainly the bis-ester. In each case the main product was contaminated to some extent with the alternative product; however, separation by fractional distillation presented no difficulty.