335. *A Synthesis of Certain Higher Aliphatic Compounds. Part IV. Synthesis of* n-*Triacontanoic Acid from Stearic Acid.*

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THE method of extension of the carbon chains of carboxylic acids which was developed in Part III (J., 1930, 745) enables us to pass up the homologous series by a number of methylene groups at a time which is limited only by the inaccessibility of the higher ω-bromo-*n*-fatty acids. It happens that the acid of this type with the longest chain and which is also readily available is ω-bromoundecoic acid and the use of this acid enables an extension of twelve methylene groups to be made in one series of operations.

By a fortunate chance, this should allow of the synthesis of *n*-triacontanoic acid from stearic acid and we thus directly connect two chain-lengths of importance in the chemistry of natural products.

As stearic acid has been so closely studied that the purity of the starting point can be guaranteed, the synthetical scheme offered the opportunity of establishing a standard of reference in a group which is characterised by a very confused literature.

Ethyl α-acetylbrassylate, $CO_2Et\cdot[CH_2]_{10}\cdot CH(COMe)\cdot CO_2Et$, was prepared from ethyl ω-bromoundecoate and ethyl sodioacetoacetate, and its sodio-derivative condensed with stearoyl chloride to ethyl α-acetyl-α-stearoylbrassylate, which on hydrolysis in stages afforded 13-*keto*-n-*triacontanoic acid*, $CH_3\cdot[CH_2]_{16}\cdot CO\cdot[CH_2]_{11}\cdot CO_2H$. This keto-acid on reduction by Clemmensen's method (*Ber.*, 1913, **46**, 1837) yields *n*-triacontanoic acid, m. p. 93·5—94°. The acid has already been compared and identified by Chibnall, Latner, Williams, and Ayre (*Biochem. J.*, 1934, **28**, 321) with one obtained by them as a product of hydrolysis of coccerin. Professor A. C. Chibnall has also kindly sent me a specimen of a triacontanol isolated by him from lucerne; also the triacontanoic acid obtained from it on oxidation. These products are identical with *n*-triacontanol and *n*-triacontanoic acid synthesised by the above method. The alcohol was obtained from the acid by the Bouveault-reduction of ethyl *n*-triacontanoate.

Starting with *n*-triacontanoic acid, it has been found possible to obtain 13-*ketodotetracontanoic acid*, $CH_3\cdot[CH_2]_{28}\cdot CO\cdot[CH_2]_{11}\cdot CO_2H$, but the separations necessary become very difficult to effect and the preparation of quantities adequate for a study of the related normal acid has not yet been possible.

EXPERIMENTAL.

Ethyl α-Acetylbrassylate.—Working in the usual manner in boiling alcoholic solution, ethyl 11-bromoundecoate (52·5 g.) and ethyl sodioacetoacetate (30 g. of the ester) gave *ethyl α-acetylbrassylate* (40 g.), b. p. 202°/0·5 mm. (Found: C, 66·5; H, 9·9. $C_{19}H_{34}O_5$ requires C, 66·7; H, 9·9%). An attempt to condense the sodio-derivative of this ester with *n*-hexoyl chloride, followed by hydrolysis and reduction to stearic acid, gave, instead, myristic acid. In this case it appears that the hexoyl group was preferentially removed in the hydrolysis. The intermediate keto-acid was, of course, obtainable from ethyl acetylbrassylate itself. The ester (5 g.) was refluxed with acetic acid (100 c.c.), sulphuric acid (20 c.c.), and water (100 c.c.) for 2 hours; the 13-*ketomyristic acid* (2·8 g.) produced crystallised from light petroleum in colourless plates, m. p. 75° (Found: C, 69·6; H, 10·6. $C_{14}H_{26}O_3$ requires C, 69·7; H, 10·7%). On reduction by Clemmensen's method, myristic acid was produced, colourless plates from light petroleum–benzene, m. p. 53·5—54° (Found: C, 73·7; H, 12·1. Calc. for $C_{14}H_{28}O_2$: C, 73·7; H, 12·1%).

13-*Keto*-n-*triacontanoic Acid.*—A solution of ethyl α-acetylbrassylate (38 g.) in dry ether (100 c.c.) was added to a suspension of finely granulated sodium (2·6 g.) in ether (100 c.c.), and the formation of the sodio-derivative completed by heating on a steam-bath. Stearoyl chloride (from 31·7 g. of stearic acid * by the action of thionyl chloride) in ether (250 c.c.) was gradually introduced with cooling and next day the mixture was refluxed for 1 hour. After removal of the solvent the product was shaken in the cold with aqueous sodium hydroxide (150 c.c. of 3%) for 8 hours, isolated, and treated with boiling dilute sulphuric acid (1750 c.c. of 5%) for 12 hours. The greater part of the product solidified on cooling. The whole was collected by means of ether and refluxed with aqueous sodium hydroxide (750 c.c. of 8%) for 3 hours. The acid obtained on acidification (25 g., m. p. 93°) was washed with boiling light petroleum; it crystallised from acetone and ether, in both of which it was sparingly soluble, in colourless, rectangular plates, m. p. 104° (Found: C, 76·9; H, 12·2. $C_{30}H_{58}O_3$ requires C, 77·2; H, 12·4%).

An alternative and probably better method consists in esterifying the whole crude product (boiling 10% alcoholic sulphuric acid, 5 hours) and removing unchanged ethyl stearate by distillation at 0·5 mm. In this way the yield of keto-acid was found to be 48% and the substance was more readily purified than by direct crystallisation. The acid is moderately readily soluble in benzene.

n-*Triacontanoic Acid.*—A mixture of 13-ketotriacontanoic acid (5 g.), amalgamated zinc (100 g.), concentrated hydrochloric acid (100 c.c.), and acetic acid (20 c.c.) was heated so as to boil the acid gently for 4 days. Every 6 hours the mixture was cooled, the zinc and solid acid collected, fresh hydrochloric and acetic acids and zinc (10 g.) added, and the heating resumed. It was found best to allow some of the zinc to protrude above the surface of the liquid. The collection of the product was very difficult and it was necessary to extract the zinc 4 times with boiling acetic acid (150 c.c.). On dilution of the extracts with water, the acid was all precipitated; it was crystallised thrice from benzene (150 c.c. each time) and again from a large volume of acetone, forming colourless plates, m. p. 93·5—94° (Found: C, 79·6; H, 13·1. Calc. for $C_{30}H_{60}O_2$: C, 79·6; H, 13·3%). The substance is very sparingly soluble in ether and acetone and the dry powder is readily electrified by friction. Its melting point was not depressed on admixture with the acid obtained from the oxidation of the lucerne alcohol supplied by Professor Chibnall.

In June 1930, Dr. S. H. Piper kindly examined a specimen of the acid by *X*-rays. He obtained B spacings of 71·8 Å. and C spacings of 65·1 Å. The extrapolated values from the *n*-fatty acids then synthesised (C_{12}—C_{26}) should have given the respective values 73 Å. and 65·8 Å., so that it appears that the chain bends when it comprises 25—30 carbon atoms. Dr.

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* The purest stearic acid obtainable was thrice crystallised from ethyl alcohol, five times from benzene, and once from ether. The product had m. p. 71°.

Piper's data for the synthetic specimen have been, and certainly will continue to be, very useful for the more precise characterisation of this acid; Professor Chibnall has already made use of them, as well as of more recent determinations of the spacings (compare Chibnall *et alia, loc. cit.*), in connexion with his extensive researches on the constituents of waxes.

The *ethyl* ester was prepared by refluxing the acid (4 g.) with alcoholic sulphuric acid (50 c.c. of 10%) for 6 hours. The product was dissolved in benzene, agitated with aqueous barium hydroxide, and recovered from the filtered solution (yield, 3·7 g., crystallised from light petroleum). The ester crystallised particularly well from alcohol in colourless plates, m. p. 70·5° (Found : C, 79·9; H, 13·4. $C_{32}H_{64}O_2$ requires C, 80·0; H, 13·3%).

The methyl ester crystallised from light petroleum in colourless plates, m. p. 71·5°.

n-*Triacontanol.*—Sodium (25 g.) was used to reduce ethyl *n*-triacontanoate (4 g.) in alcohol (400 c.c.) or, better, *n*-butyl alcohol (200 c.c.), under the usual conditions of a Bouveault process (oil-bath at 150°). The triacontanol precipitated by water was dissolved in benzene and freed from triacontanoic acid by shaking with baryta solution. The crude alcohol (3 g.), m. p. 85°, obtained on removal of the solvent was crystallised successively from acetone, ethyl acetate, and benzene, finally forming lustrous plates, m. p. 86·5° (Found : C, 81·9; H, 13·8. Calc. for $C_{30}H_{62}O$; C, 82·2; H, 14·1%). The substance proved on direct comparison to be identical with Professor Chibnall's alcohol from lucerne; a mixture of the two specimens showed no depression of the melting point.

The *acetate*, prepared by means of acetic anhydride and sodium acetate, is freely soluble in ether and was crystallised thrice from light petroleum, forming plates, m. p. 69° (Found : C, 79·7; H, 13·5. $C_{32}H_{64}O_2$ requires C, 80·0; H, 13·3%).

n-*Triacontanyl Iodide.*—The alcohol was heated in a boiling brine-bath with red phosphorus, iodine, and a trace of water until no further reaction occurred. The product, after being washed in benzene solution with aqueous sodium bisulphite, crystallised from alcohol in colourless plates, m. p. 68·5° (Found : C, 65·5; H, 11·3; I, 23·2. $C_{30}H_{61}I$ requires C, 65·7; H, 11·1; I, 23·1%).

13-*Keto*-n-*dotetracontanoic Acid.*—The preparation followed in every detail that of 13-keto-*n*-triacontanoic acid, stearoyl chloride being replaced by an equivalent of *n*-triacontanoyl chloride (thionyl chloride on the acid). At the stage of hydrolysis with boiling aqueous sodium hydroxide the extremely sparing solubility of the sodium salt of the keto-acid was revealed. It was washed with over 2000 c.c. of boiling water and then decomposed with boiling dilute hydrochloric acid and thrice crystallised from benzene, once from ether, once from ethyl acetate, and again from a mixture of ether and benzene, forming colourless plates, m.p. 110° (contact with a nickel spatula considerably lowers the m. p.) (Found : C, 79·3; H, 13·0. $C_{42}H_{82}O_3$ requires C, 79·5; H, 12·9%). This substance will be further investigated at an early opportunity.

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[*Received, August 9th,* 1934.]