

165. Long-chain Acids containing a Quaternary Carbon Atom. Part II.

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The provisional formulation of phthioic acid as ethyl-*n*-decyl-*n*-dodecylacetic acid (Stenhagen and Ställberg, *J. Biol. Chem.*, 1941, **139**, 345) has been proved incorrect by the synthesis of the substance. For this purpose the method of Hudson and Hauser (*J. Amer. Chem. Soc.*, 1940, **62**, 2457; 1941, **63**, 3156) has been employed. A discussion of the present state of the problem is included and our conclusion, in which we believe Dr. Stenhagen concurs, is that the chain must be longer than thought possible heretofore on the X-ray evidence. It seems that any structure with two long chains of comparable length will be found inconsistent with the small area of the compressed films of phthioic acid. Hence there is probably only one long chain and the smaller apparent length is due to considerable tilting of the molecules.

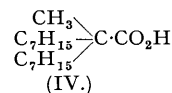
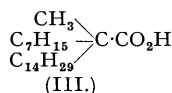
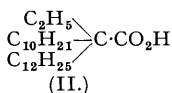
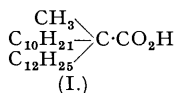
THE present investigation was undertaken in connexion with the study of the structure of phthioic acid, C₂₆H₅₂O₂, which was isolated from the lipid fraction of tubercle bacilli by Anderson and his associates (*Physiol. Rev.*, 1932, **12**, 166; *J. Biol. Chem.*, 1936, **112**, 759; and other papers) and has aroused considerable interest because of its ability to produce lesions similar to those characteristic of tuberculosis.

Methods of chemical degradation have thrown little clear light on the structure of phthioic acid, but from a study of monolayers on water and from examination of barium phthioate multilayers by X-ray reflection, Stenhagen and Ställberg (*loc. cit.*) concluded that phthioic acid is a trisubstituted acetic acid with one short hydrocarbon chain and two long chains of unequal length as expressed by the annexed formula, where *x* and *y* are 8—13, *z* = 0 or 1, and *x* + *y* + *z* = 21. These authors suggested that the concept of phthioic as a methylated long-chain fatty acid, which was derived by Spielman and Anderson (*J. Biol. Chem.*, 1936, **112**, 759), partly by analogy with tuberculostearic acid, did not appear compatible with the physical evidence.

Recently, Schneider and Spielman (*J. Biol. Chem.*, 1942, **142**, 345) have expressed the view that the chemical evidence is consistent with the above formula except for the isolation, by Anderson and Spielman, of an oxidation product, a steam-volatile C₁₁-acid, not identical with undecic acid. Furthermore, azelaic acid was found by Wagner-Jauregg (*Z. physiol. Chem.*, 1937, **247**, 135) among the oxidation products of phthioic acid. Schneider and Spielman point out, however, that these facts can be accommodated if the above formula is modified so that at least one of the long chains is methylated or otherwise branched.

In Part I (Birch and Robinson, *J.*, 1942, 488) a survey was made of the methods applicable to the synthesis of long-chain acids containing a quaternary carbon atom. We have now obtained further trisubstituted acetic acids by use of the valuable method of Hudson and Hauser (*loc. cit.*), which depends on the α-alkylation of esters with sodium triphenylmethyl and alkyl halides in ethereal solution.

For the preparation of methyl-*n*-decyl-*n*-dodecylacetic acid (I) and ethyl-*n*-decyl-*n*-dodecylacetic acid (II), methyl *n*-decyl-*n*-dodecylacetate was employed, and its sodium-enolate brought into reaction with methyl iodide and ethyl iodide respectively. Methyl-*n*-heptyl-*n*-tetradecylacetic acid (III) and methyl-di-*n*-heptylacetic acid (IV) were obtained in the same way from methyl *n*-heptyl-*n*-tetradecylacetate and methyl di-*n*-heptylacetate by interaction with sodium triphenylmethyl and methyl iodide.



In all cases sodium triphenylmethyl was used in excess and the average yields of the product were 70—80% if the ester was allowed to react with sodium triphenylmethyl for about 3—4 hours. This yield was considerably

decreased when the reaction mixture was kept overnight, presumably as the result of self-condensation of the ester. Still smaller yields were obtained by repetition of the processes.

It was found that the trisubstituted acetic acids obtained on hydrolysis of the products contained unchanged disubstituted acetic acids and full purification was tedious and difficult. Except in the case of ethyldecyldodecylacetic acid, which is discussed later, all attempts to remove the disubstituted acid by partial esterification, by partial hydrolysis of the esters, by conversion into lead salts, or by renewed treatment of the ester with sodium triphenylmethyl and alkyl iodide proved unsuccessful. Finally, the pure acids were obtained by fractional crystallisation of their amides. The trisubstituted acetamides were much more readily soluble than the disubstituted acetamides and had lower melting points; e.g., methyldecyldodecylacetamide has m. p. 42° and decyldodecylacetamide has m. p. 112.5°. The pure amides readily furnished the corresponding acids by treatment with sodium nitrite and sulphuric acid.

In the case of ethyldecyldodecylacetic acid a separation from admixed decyldodecylacetic acid could be effected by partial hydrolysis of the ester, the trisubstituted ester remaining practically unchanged after boiling for 5 hours with excess of 25% alcoholic potassium hydroxide, whereas the disubstituted ester was all hydrolysed under these conditions.

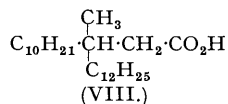
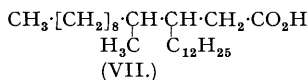
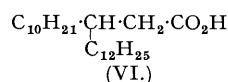
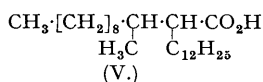
The m. p.'s given below are those which were found immediately after the preparations, because in several cases the m. p. rose on keeping. The phenomenon may be due to polymorphism but suggests imperfect orientation of the molecule in the newly formed crystals and a slow process of better marshalling of the long chains in the solid state.

		M.p.	M.p. of amide.
Methyldecyldodecylacetic acid	C ₂₅ H ₅₀ O ₂	41°	42°
Ethyldecyldodecylacetic acid	C ₂₆ H ₅₂ O ₂	27—28	Liquid
Methylheptyltetradecylacetic acid	C ₂₄ H ₄₈ O ₂	44	30—31
Methyldiheptylacetic acid	C ₁₇ H ₃₄ O ₂	Liquid	Liquid
Phthioic acid	C ₂₆ H ₅₂ O ₂	20—21	45

No close relation of the synthetic acids with phthioic acid can be deduced from these figures. Methyldecyldodecylacetic acid forms an amide^a with m. p. similar to that of phthioic amide but has a much higher melting point than phthioic acid. Ethyldecyldodecylacetic acid forms a liquid amide and differs from phthioic acid in the fact that its ester is difficult to hydrolyse.

A characteristic property of phthioic acid according to Stenhagen and Stållberg (*loc. cit.*) is that it forms unimolecular layers collapsing on compression at an area of about 38 Å.². Film measurements with the above synthetic acids showed, however, that their monolayers cannot be compressed below about 65 Å.² without collapse, and in this respect behave in nearly the same way as the disubstituted acetic acids. The same result was obtained with monolayer films of methyl-n-nonyl-n-dodecylcarbinol (prepared from methyl nonyl ketone and dodecylmagnesium bromide). These and other film measurements will be described in detail in a later communication. Phthioic acid is optically active, and this fact introduces some dubiety into the comparisons. Unfortunately we have been unable to resolve methyldecyldodecylacetic acid and the study of the film properties of an optically active member of this series is still desirable.

Branched-chain acids of the disubstituted-acetic acid and of the di- and tri-substituted-propionic acid types have also been synthesised in order to examine their properties in films.



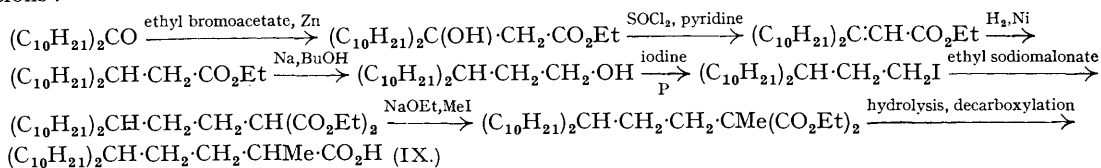
3-Methyl-2-n-dodecyl-lauric acid (V) was obtained by alkylation of ethyl malonate, *sec.*-undecyl bromide and n-dodecyl bromide being used.

β-n-Decyl-β-n-dodecylpropionic acid (VI) was obtained from decyldodecylacetic acid by the homologation reaction of Arndt and Eistert (*Ber.*, 1935, 68, 200; 1936, 69, 1074). 4-Methyl-3-n-dodecyltridecoic acid (VII) and β-methyl-β-n-decyl-β-n-dodecylpropionic acid (VIII) were prepared in the same way from 3-methyl-2-dodecyl-lauric acid (V) and methyldecyldodecylacetic acid (I). Monolayer films of these acids had collapse areas similar to those of the trisubstituted acetic acids.

The failure to obtain, with any of the above acids, surface areas similar to those occupied by films of phthioic acid suggested the desirability of investigating branched-chain acids with a long-chain substituent further removed from the carboxyl group. It was thought possible that an acid of the type CHR₁R₂[CH₂]_xCO₂H might form monolayer films compressible to a smaller area.

Taking into consideration the X-ray results of Stenhagen, which indicated a chain-length of about 15 carbon atoms for phthioic acid, and also the relatively high molecular rotation of phthioic acid, suggesting, as pointed out by Spielman and Anderson (*loc. cit.*), an asymmetric carbon atom near the carboxyl group, the

preparation of 2-methyl-5-n-decylpentadecic acid was undertaken. It was obtained by the following sequence of reactions :



Monolayer films of 2-methyl-5-decylpentadecic acid (IX) showed similar properties to those of the acids previously described; they could not be compressed without collapse below an area of about 64 Å.²

Our conclusions may be summarised by the statement that monolayer films of branched-chain acids containing two long chains cannot be compressed below an area of about 60 Å.² no matter where the second chain may be in relation to the carboxyl group, and whether they contain a quaternary carbon atom or not. This difference from the behaviour of films of phthioic acid as reported by Stenhagen and Ställberg (*loc. cit.*) seems to rule out the possibility that the phthioic acid molecule has an overall length corresponding to a 15 carbon atom chain, the remaining carbon atoms being mainly arranged in a second long chain.

The alternative view that phthioic acid is a long-chain acid containing several short branches (methyl groups), as originally suggested by Spielman and Anderson, is not easily reconciled with the results obtained by Stenhagen and Ställberg by X-ray examination of barium phthioate. These authors also point out that 3 : 7 : 11 : 15-tetramethylhexadecic acid (phytanic acid) forms films behaving differently from those of phthioic acid.

From a recent communication of Stenhagen and Ställberg (*J. Biol. Chem.*, 1943, **148**, 685) it appears, however, that in the case of branched-chain acids the long crystal spacings, as determined by X-rays, are considerably shorter than in the case of the normal acids, the values found being 40·5, 51·0, and 56·0 Å. for the 2-methyl-substituted C₂₁-, C₂₅-, and C₂₇-acids respectively, and 45·7 Å. for the 10-methyl-substituted C₂₄-acid, compared with values of 56·3, 66·0, and 70·8 Å. for the normal C₂₀-, C₂₄-, and C₂₆-acids. These authors point out that the long chains in these branched-chain acids are tilted, thus differing from normal-chain acids, which crystallise with vertical chains. It is, therefore, doubtful whether the long spacings of 35 Å. found by the same authors for phthioic acid do necessarily require an assignment of a chain length of about 15 carbon atoms.

The film properties of C₂₆-acids with several short branches (CH₃) are unknown, no such acid having yet been synthesised. They might be quite different from those of lower homologues, such as phytanic acid, which, as mentioned above, forms films differing from those of phthioic acid.

No definite conclusions are possible until such C₂₆-acids with a number of short branches have been examined and work with this object in view will be undertaken when opportunity offers.

According to Wagner-Jauregg (*loc. cit.*), tuberculostearic acid, with two methyl groups, gives 1·4CMe in the Kuhn-Roth estimation and phthioic acid gives 2·4CMe. Hence we may surmise that phthioic acid contains at least three methyl groups and certainly not more than four. Analogy suggests a dimethyl-*n*-tetracosic acid with one methyl group in the same position relative to carboxyl as in tuberculostearic acid.

EXPERIMENTAL.

Methyl-n-decyl-n-dodecylacetic Acid (I).—Ethyl *n*-decylmalonate, b. p. 144—146°/0·15 mm., was obtained in 85% yield from ethyl malonate (144 g.), *n*-decyl bromide (62 g.), sodium (11 g.), a little sodium iodide, and alcohol (120 c.c.) by refluxing the mixture for 7 hours. It was converted into ethyl *n*-decyl-*n*-dodecylmalonate, b. p. 214—216°/0·25 mm., in 70% yield by refluxing its sodio-compound with *n*-dodecyl bromide (59·5 g.), a little sodium iodide, and alcohol (70 c.c.) for 12 hours; the recovered ethyl *n*-decylmalonate and *n*-dodecyl bromide, worked up in the same way, gave a further 10 g. of the ester (total yield, 80%). On hydrolysis with excess of 25% alcoholic potassium hydroxide and subsequent acidification *n*-decyl-*n*-dodecylmalonic acid was obtained in almost quantitative yield. This was partly decarboxylated by heating for 10 minutes at 100° under diminished pressure and then for 10 minutes at 100—105°/ < 1 mm. *n*-Decyl-*n*-dodecylacetic acid distilled, b. p. 224—226°/0·1 mm., as a colourless oil which quickly crystallised; m. p. 44—45° (Found: C, 78·8; H, 13·2. Calc. for C₂₄H₄₈O₂: C, 78·3; H, 13·0%). After crystallisation from acetone or acetic acid it had m. p. 47° (Stenhagen, *Trans. Faraday Soc.*, 1940, **36**, 597, gives the same m. p.). Its amide had m. p. 112·5°. This acid was converted into its methyl ester, b. p. 198—200°/0·25 mm., by refluxing for 5 hours with 10% methanolic sulphuric acid.

Methyl decyldodecylacetate (21 g., 0·055 mol.) was added to a freshly prepared solution of sodium triphenylmethyl (from 21 g., 0·075 mol., of triphenylchloromethane and 500 g. of 1% sodium amalgam) in dry ether (450 c.c.), the whole operation being conducted under pure nitrogen. The mixture was shaken and kept for 4 hours. Methyl iodide (30 g.) was then added and after 20 hours water was added, and the product isolated by means of ether and obtained as a pale yellow oil (16 g.), b. p. 196—200°/0·2 mm. It was refluxed for 5 hours with an excess of 25% alcoholic potassium hydroxide, the acid liberated and converted into its lead salt by solution in alcohol, neutralisation with alcoholic potassium hydroxide and precipitation with lead acetate. The lead salt was extracted with alcohol; it yielded on treatment with dilute nitric acid an acidic product, m. p. 34—35°, from acetone. This was converted into its amide by treatment with an excess of thionyl chloride and addition of the resulting acid chloride to concentrated aqueous ammonia. On fractional crystallisation from methanol or acetone two products were separated, namely, decyldodecylacetamide, m. p. 112·5°, and the more soluble methyldecyldodecylacetamide (about 8 g.), which after repeated crystallisations from acetone and finally from methanol had m. p. 42° (Found: C, 79·0; H, 13·4; N, 3·7. C₂₅H₅₁ON requires C, 78·7; H, 13·4; N, 3·7%). This amide was dissolved in 10 times its weight of concentrated sulphuric acid; an excess of 10% aqueous sodium nitrite was gradually added with cooling in ice. The mixture was kept overnight and diluted with water, and the resulting methyldecyldodecylacetic acid isolated by means of ether. After crystallisation from acetone it

had m. p. 41°. After 8 months the m. p. rose to 44.5° (Found : C, 78.4, 78.3; H, 12.9, 13.1; no N. $C_{25}H_{50}O_2$ requires C, 78.5; H, 13.1%).

A number of unsuccessful attempts were made to resolve this acid in order to investigate the film properties of the optically active trialkylacetic acid, which might perhaps differ from those of the *dl*-acid. No crystalline salts could be obtained with quinine, cinchonine, strychnine or brucine, and the acids from the oily products which separated showed no optical activity. In the case of *tert*-alcohols containing the hydroxyl group attached to the asymmetric carbon atom, Kenyon and Priston (J., 1925, 127, 1476) failed to effect any resolution.

Ethyl-n-decyl-n-dodecylacetic Acid (II).—Methyl *n*-decyl-*n*-dodecylacetate (7 g., 0.018 mol.) was treated with an ethereal solution of sodium triphenylmethyl (from 7 g., 0.025 mol., of triphenylchloromethane and 170 g. of 1% sodium amalgam in 150 c.c. of dry ether). Ethyl iodide (10 g.) was added after 3½ hours, and the mixture worked up as already described for the lower homologue. The product (3.7 g.), b. p. 200—202°/0.2 mm., was refluxed for 5 hours with an excess of 25% alcoholic potassium hydroxide. Treatment of the free acid with lead acetate yielded only a small quantity (1 g.) of crude *n*-decyl-*n*-dodecylacetic acid giving an amide of m. p. 112.5°. The unhydrolysed ester (2.5 g.), which was recovered from the alcoholic filtrate from the lead salt, furnished, on refluxing for 7 hours with *n*-propyl-alcoholic potassium hydroxide, an oily acidic product. This was purified through its lead salt (1.9 g.) and converted into the amide by the usual method. Repeated crystallisation from acetone and methanol afforded a small quantity of *n*-decyl-*n*-dodecylacetamide, m. p. 112.5°. When the mother liquors were concentrated and cooled, a low-melting product crystallised, which liquefied at once on removal from the refrigerator. After repeated extractions with small quantities of chilled acetone, it was converted into the acid by treatment with sodium nitrite and sulphuric acid. On distillation under high vacuum, a viscous oil (0.8 g.) was obtained which slowly crystallised, m. p. 27—28°, from acetone. After some weeks it melted at 31° (Found : C, 78.5; H, 13.0. $C_{26}H_{52}O_2$ requires C, 78.8; H, 13.1%). The amide obtained from this specimen was a viscous oil (Found : C, 78.9; H, 13.2; N, 3.5. $C_{26}H_{53}ON$ requires C, 79.0; H, 13.4; N, 3.5%).

Methyl-n-heptyl-n-tetradecylacetic Acid (III).—The preparation of this acid was carried out like that of methyl-*n*-decyl-*n*-dodecylacetic acid. *n*-Heptyl-*n*-tetradecylacetic acid, which was obtained by the malonic ester method using *n*-heptyl bromide and *n*-tetradecyl bromide, had m. p. 42° (Found : C, 77.8; H, 12.9. $C_{23}H_{46}O_2$ requires C, 78.0; H, 13.0). The methyl ester of this acid gave, by interaction with sodium triphenylmethyl and methyl iodide and hydrolysis of the resulting ester, the crude trisubstituted acid (m. p. 39.5°), which was converted into the amide in order to separate it from some unchanged disubstituted acid. The amide, m. p. 30—31°, after repeated crystallisations from acetone and methanol, yielded by treatment with sodium nitrite and sulphuric acid methyl-*n*-heptyl-*n*-tetradecylacetic acid, m. p. 44° after recrystallisation from acetone (Found : C, 78.0; H, 13.2. $C_{23}H_{46}O_2$ requires C, 78.3; H, 13.0%).

Methyl-di-n-heptylacetic Acid (IV).—Di-*n*-heptylacetic acid, m. p. 26—27°, was prepared from *n*-heptyl bromide and malonic ester (Found : C, 74.9; H, 12.2. Calc. for $C_{16}H_{32}O_2$: C, 75.0; H, 12.5%). Its methyl ester (33 g.) furnished, by interaction with excess of sodium triphenylmethyl and methyl iodide, a colourless oil (27 g.), b. p. 132—136°/0.15 mm., which was hydrolysed with alcoholic potassium hydroxide. The product (22 g.) obtained on acidification, b. p. 162—168°/0.1 mm., was converted into the amide by means of thionyl chloride and ammonia. Repeated treatment with acetone separated a crystalline product, m. p. 107—108° (amide of unchanged disubstituted acid). The product remaining in solution furnished after repeated distillations methyl-*di-n*-heptylacetyl amide as a colourless, very viscous oil (9.8 g.), b. p. 181—182°/0.2 mm. (Found : C, 75.5; H, 12.9; N, 5.2. $C_{17}H_{35}ON$ requires C, 75.8; H, 13.0; N, 5.2%). It was converted into the acid by treatment with sodium nitrite and sulphuric acid. This was separated from some unchanged amide by converting it into its methyl ester, b. p. 172—173°/ca. 12 mm., and furnished on hydrolysis methyl-*di-n*-heptylacetic acid (5.4 g.), b. p. 171—171.5°/0.2 mm., as a viscous oil (Found : C, 76.1; H, 12.7. $C_{17}H_{34}O_2$ requires C, 75.5; H, 12.6%).

Methyl-n-nonyl-n-dodecylcarbinol.—Methyl nonyl ketone (25 g.) was gradually added to a Grignard solution, prepared from *n*-dodecyl bromide (37 g.) and magnesium (3.5 g.) in ether (40 c.c.), with stirring below 10°. The chief product was a colourless oil (21 g.), b. p. 200—204°/ca. 0.2 mm. (Found : C, 81.0; H, 14.0. $C_{23}H_{46}O$ requires C, 81.2; H, 14.1%).

3-Methyl-2-n-dodecyl-lauric Acid (V).—Ethyl *sec*-undecylmalonate, b. p. 180—182°/18 mm., was obtained in 70% yield from ethyl malonate (64 g.), *sec*-undecyl bromide (35 g.), sodium (5 g.), some sodium iodide, and alcohol (75 c.c.) by refluxing the mixture for 7 hours. This was converted into ethyl *sec*-undecyl-*n*-dodecylmalonate, b. p. 210—212°/0.16 mm., in 50% yield by refluxing its sodio-derivative with *n*-dodecyl bromide (17.5 g.) and some sodium iodide in xylene (30 c.c.) for 24 hours (Found : C, 74.6; H, 12.0. $C_{30}H_{58}O_4$ requires C, 74.7; H, 12.0%). It was hydrolysed by refluxing it repeatedly with *n*-propyl-alcoholic potassium hydroxide. The product obtained on acidification was decarboxylated under reduced pressure. On distillation, a colourless oil (9 g.), b. p. 228—230°/0.3 mm., was obtained, which crystallised on keeping (Found : C, 78.9; H, 13.1. $C_{25}H_{50}O_2$ requires C, 78.5; H, 13.1%). It melted at 67° after recrystallisation from acetone and furnished an amide, m. p. 102—103°.

β-*n*-Decyl-*β*-*n*-dodecylpropionic Acid (VI).—*n*-Decyl-*n*-dodecylacetic acid (6 g.) was converted by means of thionyl chloride into its chloride, and this treated with ethereal diazomethane. The diazo-ketone was obtained in yellow crystals after removal of the ether and excess of diazomethane under reduced pressure at room temperature. It was dissolved in warm methanol (50 c.c.), and the solution heated on a steam-bath while a methanolic suspension of silver oxide (from 2 g. of silver nitrate) was gradually added during about 1 hour; the mixture was then refluxed for 1 hour. The resulting methyl ester, b. p. 212—214°/0.25 mm., furnished by hydrolysis with alcoholic potassium hydroxide and subsequent acidification the required acid as a viscous oil (Found : C, 78.7; H, 13.1. $C_{25}H_{50}O_2$ requires C, 78.5; H, 13.1%). It solidified at 0°, but melted at room temperature. After several weeks it melted at 26.5°; amide, m. p. 55°.

4-Methyl-3-n-dodecyltridecoic Acid (VII).—3-Methyl-2-*n*-dodecyl-lauric acid (5 g.) was converted into its chloride, which was added to an ethereal solution of diazomethane. The resulting diazo-ketone yielded by treatment with silver oxide and ethyl alcohol the homologous ethyl ester. This was hydrolysed with alcoholic potassium hydroxide; the product obtained on acidification distilled as a colourless oil (3 g.), b. p. 209—210°/0.1 mm. (Found : C, 78.8; H, 13.1. $C_{26}H_{52}O_2$ requires C, 78.8; H, 13.2%). It deposited on standing traces of a crystalline material which seemed to be unchanged 3-methyl-2-dodecyl-lauric acid; its amide was a liquid.

β-Methyl-*β*-*n*-decyl-*β*-*n*-dodecylpropionic Acid (VIII).—Methyl-*n*-decyl-*n*-dodecylacetic acid was converted into its chloride, then into a diazoketone in the same way as described in the previous cases. The resulting diazo-ketone, m. p. 36° from methanol, yielded by treatment with methanol and silver oxide, methyl *β*-methyl-*β*-decyl-*β*-dodecylpropionate, b. p. 196—197°/0.2 mm. (Found : C, 79.6; H, 12.9. $C_{27}H_{54}O_2$ requires C, 79.0; H, 13.2%). On hydrolysis with alcoholic potassium hydroxide and subsequent acidification *β*-methyl-*β*-*n*-decyl-*β*-*n*-dodecylpropionic acid was obtained as a colourless viscous oil (Found : C, 78.9; H, 13.1. $C_{26}H_{52}O_2$ requires C, 78.8; H, 13.1%). It furnished a liquid amide (Found : C, 79.4; H, 12.9; N, 3.4. $C_{26}H_{53}ON$ requires C, 79.0; H, 13.4; N, 3.5%).

2-Methyl-5-n-decylpentadecic Acid (IX).—A mixture of di-*n*-decyl ketone (40 g., prepared by pyrogenic decomposition of lead undecolate), zinc filings (8 g.), ethyl bromoacetate (22.5 g.), dry ether (75 c.c.), and benzene (75 c.c.) was heated on a steam-bath with stirring. After about 3 hours further quantities of zinc (6 g.) and ethyl bromoacetate (12 g.) were introduced, and the heating continued for a further 3 hours. The solution was then decanted from unreacted zinc into a mixture of ice and water containing a small quantity of acetic acid. The benzene-ether layer was repeatedly

washed with 10% aqueous acetic acid, some dilute aqueous ammonia, and water, and dried with sodium sulphate. Since in a preliminary experiment the product was found to decompose on distillation with formation of didecyl ketone, it was not isolated. The above benzene-ether solution was concentrated under reduced pressure, pyridine (32 g.) added, and thionyl chloride (34 g.) gradually introduced while the ice-cold mixture was stirred. It was kept overnight, then poured slowly into ice-water, and the product washed with dilute hydrochloric acid, dried, and distilled. *Ethyl 3-decyl- Δ^2 -tridecenoate* (36 g.) was obtained as a slightly coloured oil, b. p. 192—196°/0.4 mm., n_D^{19} 1.4600 (Found: C, 78.6; H, 12.0. $C_{25}H_{48}O_2$ requires C, 78.9; H, 12.6%).

Before hydrogenation, the above ester, dissolved in light petroleum (120 c.c., b. p. 60—80°), was filtered through a column of charcoal and, after removal of the solvent, refluxed in alcoholic solution with Raney nickel in order to remove any catalyst poisons. It was hydrogenated in alcoholic solution with Raney nickel at 40—60°/60 atm. *Ethyl 3-decyl-tridecoate* (29.5 g.) was obtained as a colourless oil, b. p. 179—181°/0.2 mm., n_D^{19} 1.4539 (Found: C, 78.6; H, 12.8. $C_{25}H_{50}O_2$ requires C, 78.5; H, 13.1 g.).

The reduction of this ester to the corresponding alcohol was effected by the method of Bleyberg and Ulrich (*Ber.*, 1931, **64**, 2504), light petroleum (260 c.c., b. p. 60—80°), sodium (35 g.), and butyl alcohol (160 c.c.) being used. A considerable quantity of high-boiling product was formed, presumably owing to self-condensation of the ester. *3-Decyl-tridecanol* (8 g.) was obtained as a viscous oil, b. p. 163—165°/0.15 mm., n_D^{21} 1.4608 (Found: C, 81.3; H, 13.7. $C_{23}H_{48}O$ requires C, 81.2; H, 14.1%). 7 G. of 3-decyltridecoic acid were recovered.

The above alcohol (8 g.) was converted into its iodide by heating with red phosphorus (0.26 g.) and iodine (3 g.) at 180° for 1½ hours. This was kept overnight with a solution of ethyl sodiomalonate (from 12 g. of malonic ester and 0.81 g. of sodium) in alcohol (10 c.c.); the mixture was then refluxed with stirring for 4 hours. *Ethyl (3-decyltridecyl)-malonate* (6 g.), b. p. 221—224°/0.45 mm., n_D^{20} 1.4540, was obtained as a colourless oil (Found: C, 74.7; H, 12.0. $C_{30}H_{58}O_4$ requires C, 74.7; H, 12.0%).

The above alkylated malonic ester was converted into its sodio-derivative by means of sodium (0.28 g.) in alcohol (15 c.c.); excess of methyl iodide was then added, and the mixture refluxed for 3 hours with stirring while further small quantities of methyl iodide were introduced at intervals. The product was hydrolysed with alcoholic potassium hydroxide. On acidification, followed by decarboxylation, *2-methyl-5-decylpentadecoic acid* (2.4 g.) was obtained as a viscous oil, n_D^{20} 1.4579, becoming turbid on cooling with ice (Found: C, 78.3; H, 13.1. $C_{26}H_{52}O_2$ requires C, 78.8; H, 13.1%).

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