210. *Long-chain Carbon Compounds.* n-*Tetratriacontanoic and* n-*Hexatetracontanoic Acids and their Derivatives.*

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THE crystal spacings of the synthetic higher *n*-fatty acids and many of their derivatives, together with the heats of crystallisation of a series of their ethyl esters, have been examined in these laboratories (for the former, see *Proc. Roy. Soc.*, 1930, *A*, **128**, 24; 1937, *A*, **158**, 691; and for the latter, J., 1934, 1449; 1936, 1372). For this purpose, preparations of the highest attainable degree of purity were necessary.

The pure *n*-aliphatic acids dissolve in concentrated sulphuric acid at 70°, giving colourless solutions; on the other hand, the purest specimens of myristic, palmitic and stearic acids obtained from Schering–Kahlbaum all give dark solutions owing to the presence of unsaturated material, which may be oleic acid. Myristic acid can be completely freed from this impurity by two crystallisations from glacial acetic acid, palmitic acid by four, but after this operation has been repeated six times, stearic acid still shows the presence of oleic acid. The most satisfactory method of eliminating this substance from palmitic and stearic acids consists in a preliminary crystallisation from concentrated sulphuric acid, the temperature of which must not be raised above 70°, followed by three from acetic acid. For this purpose, it is essential that anhydrous acetic acid should be used.

Each of the three acids then contains quantities of the order of 1% of, presumably, lower or higher homologues, and the final purification is effected by converting them into their ethyl esters, fractionating these in a vacuum, and reconverting the middle fraction into the acids, which are then recrystallised from acetic acid until their respective setting points are constant to within ± 0·01°. The m. p. determined in a capillary tube by the ordinary method is of very much less value as a criterion of purity, although a more accurate observation can be made, and a better judgment formed of the purity of the specimen, by using the apparatus previously described (J., 1936, 137). In this, the temperature at which resolidification takes place has never been found to differ by more than ± 0·2° from the setting point.

If an alcoholic solution of an alkali is used for the saponification of the esters, it is advisable in all cases to remove the alcohol before the soaps are decomposed by a mineral acid, for experience has shown that there is a possibility of the resulting organic acids being contaminated with re-formed esters unless this precaution is taken.

The acids of even, and in some cases, odd, carbon content higher than 22 were obtained from behenic acid, which can be prepared from erucic acid in an exceptionally pure condition. The synthesis of the acids of *even* carbon content, commencing with 110 g. of behenic acid, can be continued up to *tetratriacontanoic acid*, but an insufficient amount (4—5 g.) of that acid is obtained for further progress. The following well-known methods were employed : reduction of the ethyl esters to the corresponding alcohols, the conversion of these into iodides, and then into malonic ester derivatives, and the decomposition by heat of the dicarboxylic acids. Acids with an *odd* number of carbon atoms were prepared from the iodides by interaction with potassium cyanide and the hydrolysis of the resulting nitriles.

In the various operations, loss of material is due mainly to the precautions necessary for the purification of all the intermediate derivatives. For instance, one must fractionate the esters in a high vacuum before proceeding to the synthesis of the next higher acid, or determining their heats of crystallisation, or converting them into acids for crystallographic work. This procedure has also to be followed in the case of alcohols, prepared by the reduction of the esters by the Bouveault–Blanc method, for these derivatives cannot be freed from small quantities of sodium salts by crystallisation alone. Dicarboxylic acids cannot be completely decomposed into monocarboxylic acids unless quantities not greater than 6 g. are taken, and they must be maintained in a fused condition for long periods in a high vacuum. Finally, the sharpness of the melting points of the respective α- and β-modifications of the iodides containing 22 to 30 carbon atoms constitutes a valuable criterion of their purity. Beyond C_{30} these derivatives appear to exist in the α-form only.

A further quantity of tetratriacontanoic acid was prepared by following the method used by Mrs. G. M. Robinson for the synthesis of triacontanoic acid (J., 1934, 1544). Both the acid and its *ethyl* ester were identical in all respects with those obtained stepwise from behenic acid; this is a valuable confirmation of the purity of the acid, since the possible impurities would not be identical in both preparations.

From the acid containing 34 carbon atoms, those with 36 and 38 were prepared, but the most interesting was that with 46 atoms synthesised by the Robinson method. Also, from the first of these acids small quantities of the *α-hydroxy-acid*, and the *hydrocarbons* containing 66 and 67 carbon atoms, were obtained, although in insufficient amount to effect satisfactory purification. The crystal spacing of the former hydrocarbon varied by + 0·5%, and the latter by + 1·0% from the *A* values calculated by extrapolation from those of lower carbon content. These two hydrocarbons, the acids mentioned above, and the α-hydroxy-acid contain a larger number of carbon atoms than any whose spacings have yet been determined.

Crystals of acids containing an even number of carbon atoms obtained by deposition from such non-polar solvents as acetone or benzene show the *B* crystal spacings, whereas from acetic acid they give the *C* spacing only. On the other hand, the crystals of acids containing an odd number of carbon atoms show the *B* spacings irrespective of the solvent used in their preparation.

When both the *B* and the *C* spacings are plotted against the carbon content of the even-membered acids, straight lines are obtained on which lie with striking accuracy the spacings of all such acids up to that containing 46 atoms. A similar relationship is shown by the ethyl esters, alcohols, iodides, and dicarboxylic acids, and by the acids of odd carbon content.

The heats of crystallisation of the methyl and ethyl esters of many of these acids have been described previously and that of ethyl tetratriacontanoate is given in this communication.

EXPERIMENTAL.

n-*Tetratriacontanoic Acid.*—This was prepared in the first instance by following in detail the method used by Mrs. G. M. Robinson (*loc. cit.*) to synthesise the acid containing 30 carbon atoms.

The most suitable method for the preparation of behenoyl chloride consists in the action of oxalyl chloride on a benzene solution of behenic acid. It is purified by distillation in a vacuum of 10^{-5} mm., melts at 40°, is very soluble in ether or benzene, and rapidly hydrolysed when exposed to the air (Found : Cl, 9·6. Calc. for $C_{22}H_{43}OCl$: Cl, 9·9%).

This chloride was allowed to react with ethyl sodio-α-acetylbrassylate, ether being used as a medium in some preparations and benzene in others without affecting the final yield. The product, ethyl α-acetyl-α-behenoylbrassylate, was saponified in three stages, (1) shaking with cold 3% aqueous caustic soda, (2) boiling with 5% sulphuric acid, and (3) refluxing with 8% aqueous soda. The final yield of 13-ketotetratriacontanoic acid was unaffected if treatment (2) was omitted, or if the final saponification was carried out at a lower temperature, or with a higher or lower concentration of alkali. The products of the saponification formed an insoluble cake consisting of the sodium salts of behenic acid with much smaller quantities of 13-ketotetratriacontanoic acid, and some 12-acetyl-lauric acid. The mixture was converted into the free acids, which were repeatedly ground with small quantities of alcohol to remove the 12-acetyl-lauric acid and some behenic acid, and the residual acids were esterified with ethyl alcohol. The crystalline esters were repeatedly washed with large quantities of cold ether, in which ethyl behenate alone was soluble, and the residual keto-ester purified by several crystallisations from benzene.

From six preparations, some of which were carried out by Dr. F. J. E. Collins, a total amount of 50 g. of the pure keto-ester was obtained. This represents an average yield of 14%, and the behenic acid recovered, 70%, calculated on the behenic acid used as behenoyl chloride in the synthesis.

Considerable quantities of 12-acetyl-lauric acid were isolated both from the alkaline solutions used in the saponification and during the operations mentioned above.

Ethyl 13-*ketotetratriacontanoate*, m. p. 80·9°, r. p. 80·2°, is only slightly soluble in boiling ether (Found : C, 78·4; H, 12·5. $C_{36}H_{70}O_3$ requires C, 78·5; H, 12·7%). The *acid* itself has m. p. 107·7° and gives a crystal spacing of 90·9 A. (Found : C, 78·2; H, 12·5. $C_{34}H_{66}O_3$ requires C, 78·1; H, 12·6%).

12-*Acetyl-lauric acid*, crystallised from acetone, has m. p. 73·5° and its crystal spacing is 39·63 A. (Found : C, 69·4; H, 10·7. $C_{14}H_{26}O_3$ requires C, 69·4; H, 10·7%). On oxidation with sodium hypobromite it gives a nearly quantitative yield of brassylic acid, m. p. 113·3° (Found : C, 63·8; H, 9·8. Calc. for $C_{13}H_{24}O_4$: C, 63·9; H, 9·8%).

n-*Tetratriacontanoic acid* was obtained in 80% yield by the reduction of the keto-acid by Clemmensen's method, the course of the reaction being followed by observations of the m. p. of the product, which fell during the operation from 107·7° to about 94°; after it had risen to 96·1°, the reduction was complete. The acid was purified by conversion into the ethyl ester, which was distilled in a vacuum of 10^{-5} mm. and on saponification gave the free acid, m. p. 98·2°, r. p. 97·8°, and s. p. 98·0°. The solubility of the acid in boiling ether or methyl alcohol is about 0·04% in each case (Found : C, 80·2; H, 13·6. $C_{34}H_{68}O_2$ requires C, 80·3; H, 13·4%). The potassium salt is almost insoluble in water or boiling benzene, and soluble to the extent of about 0·15% in boiling ethyl alcohol.

The *ethyl* ester of this acid has a setting point of 75·3°, m. p. 75·4°, r. p. 75·2° (Found : C, 80·5; H, 13·5. $C_{36}H_{72}O_2$ requires C, 80·6; H, 13·4%). The *anilide*, prepared by the interaction of tetratriacontanoyl chloride and aniline in benzene solution, has m. p. 114°, r. p. 113° (Found : N, 2·7. $C_{40}H_{73}ON$ requires N, 2·4%).

α-*Bromotetratriacontanoic acid* was prepared from the acid by Hell and Sadomsky's method (*Ber.*, 1891, **24**, 2388). It is soluble in ether and may be crystallised from benzene (Found : Br, 13·7. $C_{34}H_{67}O_2Br$ requires Br, 13·6%). This acid shows a type of dimorphism very similar to that observed in some of the higher *n*-aliphatic iodides. The β-modification is formed by allowing a specimen to remain at room temperature for some time. It melts at 89·1° and if the temperature is allowed to fall slowly it resolidifies at 87° and on again heating shows the same m. p. If the specimen in the capillary tube, however, is heated to 96° and then allowed to cool, resolidification takes place at 76·5° and if the temperature is raised at once, the α-modification formed under these conditions melts at 77·37°.

The corresponding *α-hydroxy-acid* was prepared from the bromo-derivative by the method described by Ashton, Robinson, and Smith (J., 1936, 285). When a solution in acetone, acetic acid or benzene is cooled rapidly, it separates as a gel, although ill-defined crystals can be obtained by slowly cooling a benzene solution. These crystals melt indefinitely at 109°, although after resolidification they re-melt at about 102°, and Dr. Piper found the crystal spacing to be 87·6 A., calculated from a poor photograph. This value falls on the extrapolation of the *A* graph connecting the spacings of the lower α-hydroxy-acids with their carbon content. Since the synthetic acids give the *B* spacings, Dr. Piper considered that the specimen was impure. An attempt was made to purify the small amount available by recrystallisation of its ethyl ester, which was afterwards converted into the barium salt of the acid. This salt was then extracted with boiling acetone, followed by benzene, to remove any inert material that might have been present. The acid recovered from the salt was similar in its behaviour to the original specimen. On crystallisation from benzene it fused indefinitely between 109° and 110°, but on resolidifying it remelted at about 104—105°. The crystal spacing, however, was now 77·0 A., calculated from a better photograph than the first, and this lies on the extrapolation of the *B* graph (Found: C, 77·5; H, 12·9. $C_{34}H_{68}O_3$ requires C, 77·8; H, 13·0%).

Tetratriacontanoyl chloride was obtained by the action of oxalyl chloride on the acid in benzene solution. Recrystallised from this solvent, it had m. p. 73·1°, r. p. 72·8°. It was slowly hydrolysed when exposed to the air in the crystalline condition (Found: Cl, 6·7. $C_{34}H_{67}OCl$ requires Cl, 6·7%).

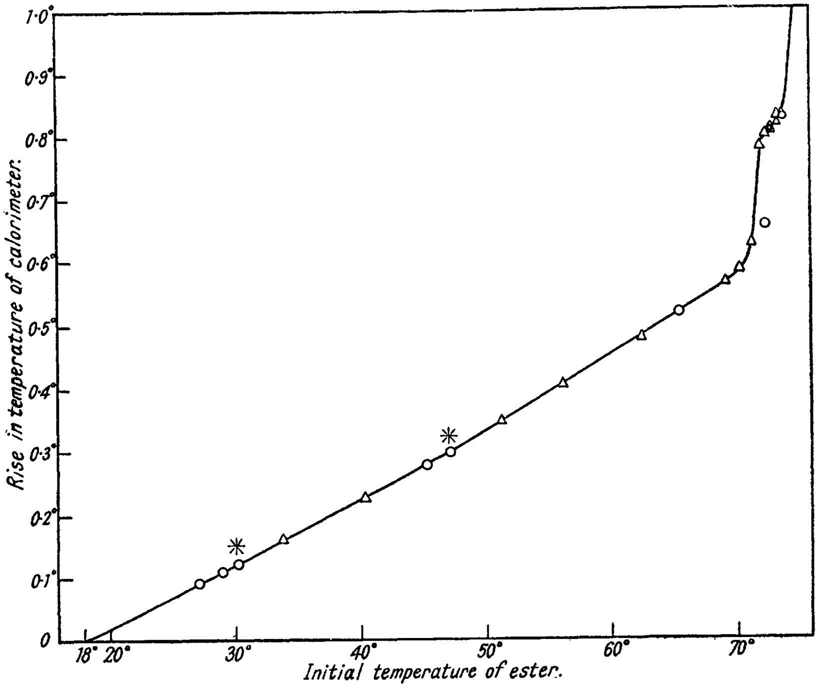
n-*Hexahexacontane*.—This *hydrocarbon* was prepared by the electrolysis of potassium tetratriacontanoate, but owing to its small solubility in aqueous alcohol at 70° it was only possible to deal with small quantities at a time. The products from several experiments were combined, the unchanged organic acid removed by boiling alcohol, and the hydrocarbon purified by repeated treatment with hot sulphuric acid until blackening no longer took place. It is insoluble in alcohol and may be recrystallised from benzene; m. p. 103·6°, r. p. 103·3°. The crystal spacing, 85·47 A., corresponds to the *A* form of the hydrocarbon, but this value shows that probably it was not pure (Found: C, 85·6; H, 14·3. $C_{66}H_{134}$ requires C, 85·5; H, 14·5%).

n-*Heptahexacontan*-34-*one* was prepared in small yield by the method described by Easterfield and Taylor (J., 1911, 99, 2298); m. p. 109—110° [Found: C, 84·2; H, 13·7. $(C_{33}H_{67})_2CO$ requires C, 84·3; H, 14·0%]. When this was reduced by Clemmensen's method, it gave *heptahexacontane*, which was purified as described above. It is insoluble in alcohol and may be recrystallised from benzene; m. p. 104·1°, r. p. 103·9°. Its crystal spacing, 87·84 A., calculated from a poor photograph, showed that the specimen was impure (Found: C, 85·3; H, 14·2. $C_{67}H_{136}$ requires C, 85·5; H, 14·5%).

Heat of Crystallisation of Ethyl Tetratriacontanoate.—The measurements were carried out in identical apparatus and in an exactly similar manner to those described for the lower members of the series (King and Garner, J., 1936, 1372). As before, only the data essential for the calculation of the specific heats and heats of crystallisation are given (Table I), but the complete experimental data (below the setting point) are plotted in the figure, in which points marked △ again represent experiments in which the molten ester was allowed to crystallise in the thermostat at the temperature of the experiment, and those marked ⊙, experiments in which the ester was solid when it was placed in the thermostat. The water equivalent of the calorimeter was 338·8.

From the figure it appears that the curve for the tilted form may be divided into three straight portions, and that the breaks occur at 30° and 47° (*) corresponding to the transition temperatures of one tilted form into another, *i.e.*, $\beta_1 \longrightarrow \beta_2$ and $\beta_2 \longrightarrow \beta_3$ respectively. These transitions are reversible. The figure also shows that the transition from the vertical to the tilted form is completely reversible, confirming the view expressed by King and Garner (*loc. cit.*) that the vertical chains are more stable than the tilted chains at the melting point for compounds with very long chains. The transition temperature is approximately 3° below the setting point.

If the straight line drawn through the values of Q_V for the lower members of the series be extrapolated to C_{34}, a value of 21 kg.-cals./g.-mol. is obtained. Experimentally, Q_V was found to be abnormally low, *viz.*, 19·75 kg.-cals./g.-mol., a result which may be due either to the presence of impurity or to a factor which enters only into the crystallisation of the higher members of the series, causing divergence from the predicted values. A second abnormality occurs in the specific heat of the vertical form of the C_{34} ethyl ester, which is 1·24 cals./g., as compared with the mean value, 0·71 cal./g., for the members up to and including C_{30}. It must be pointed out, however, that, since the vertical form is only stable over a range of 3° below the setting point, the accuracy of measurement is not as great as in the lower members of the series where measurements of the vertical form may be carried out over a greater range of temperature.



Acids of Carbon Content higher than 34.—Dr. F. J. E. Collins prepared in these laboratories n-*hexatriacontanoic acid* from *n*-tetratriacontanoic acid, and n-*octatriacontanoic acid* from the former acid, by the methods previously mentioned. *n*-Hexatriacontanoic acid had m. p. 99·9°, r. p., 99·4° (Found : C, 80·4; H, 13·3. $C_{36}H_{72}O_2$ requires C, 80·6; H, 13·4%), its ethyl ester m. p. 78·6°, r. p. 78·3°, and the corresponding *alcohol* m. p. 92·9°, r. p. 92·1° (Found : C, 82·55; H, 14·1. $C_{36}H_{74}O$ requires C, 82·7; H, 14·2%). *n*-Octatriacontanoic acid had m. p. 101·6°, r. p. 100·1° (Found : C, 80·6; H, 13·4. $C_{38}H_{76}O_2$ requires C, 80·8; H, 13·5%), and its *ethyl* ester m. p. 80·55°, r. p. 80·3° (Found : C, 81·3; H, 13·4. $C_{40}H_{80}O_2$ requires C, 81·1; H, 13·5%). The corresponding *alcohol* was obtained in insufficient quantity to enable it to be purified satisfactorily. A condensate from the molecular still had m. p. 93·6° (Found : C, 82·6; H, 14·0. $C_{38}H_{78}O$ requires C, 82·9; H, 14·2%).

TABLE I.

Ethyl tetratriacontanoate (setting point = 75·19°).

(Wt. of ester, 5·0519 g.; glass, 5·6715 g.; platinum, 0·1428 g.)

Expt. No.	Initial temp. of ester.	Fall in temp.	Rise in temp.	Expt. No.	Initial temp. of ester.	Fall in temp.	Rise in temp.
1	29·11°	11·64°	$0{\cdot}113_8$	21	47·26°	29·22°	$0{\cdot}295_1$°
29	72·61	54·89	$0{\cdot}800_7$	27	65·64	48·13	$0{\cdot}524_3$
31	73·96	55·95	$0{\cdot}827_7$	24—26	95·73	78·09	$1{\cdot}648_8$
5	30·34	12·69	$0{\cdot}123_1$	20, 22, 23	80·43	62·80	$1{\cdot}468_3$
14	45·35	27·60	$0{\cdot}277_9$				

$\sigma_{ST_1} = 0{\cdot}4344$ cal./g.; $\sigma_{ST_2} = 0{\cdot}4709$ cal./g.; $\sigma_{ST_3} = 0{\cdot}5860$ cal./g.
$\sigma_{SV} = 1{\cdot}242$ cal./g.; $\sigma_L = 0{\cdot}5520$ cal./g.
$Q_{T_1} = 30{\cdot}48$ kg.-cals./g.-mol. $Q_V = 19{\cdot}75$ kg.-cals./g.-mol.
Heat of transition $V \longrightarrow T_1 = 10{\cdot}73$ kg.-cals./g.-mol.

13-*Ketohexatetracontanoic Acid.*—This was prepared by the Robinson method. Tetratriacontanoyl chloride (15 g.) was allowed to react in ethereal solution in an atmosphere of nitrogen with a slight excess of ethyl sodio-α-acetylbrassylate. The resulting derivative, extracted in the usual manner, was shaken for 10 hours with a cold aqueous solution of potassium hydroxide. When the insoluble material was dissolved in ether, 4 g. of potassium tetratriacontanoate, probably due to the incomplete interaction of the acid chloride and the sodio-derivative, remained behind. The ethereal solution was evaporated and left 11·8 g., which were recrystallised from alcohol, and although an indefinite m. p. of 68—90° showed that it was not pure, the analytical data are close to those required for *ethyl α-acetyl-α-tetratriacontanoylbrassylate* (Found : C, 76·6; H, 12·0. $C_{53}H_{100}O_6$ requires C, 76·4; H, 12·0%). This derivative was unaffected by boiling with 8% aqueous potassium hydroxide, and saponification was effected in alcoholic solution. The solid potassium salts that separated were washed with water to remove potassium 12-acetyllaurate, converted into acids, and esterified with ethyl alcohol. The mixture of esters was distilled in a vacuum of 10^{-5} mm.; the distillate, constituting the main bulk of the product, was ethyl tetratriacontanoate, s. p. 75·30°. The residue in the flask was nearly pure *ethyl* 13-*ketohexatetracontanoate*, m. p. 91·7°. After several recrystallisations from benzene, the m. p. was 93·76° (Found : C, 80·05; H, 13·1. $C_{48}H_{94}O_3$ requires C, 80·2; H, 13·1%). The amount of pure ester was 1·5 g.; the yield, calculated as before, was equivalent to about one half of that obtained in the synthesis of the corresponding ketone containing 34 carbon atoms. It could not be raised by carrying out the saponification with barium hydroxide in place of potassium hydroxide. After several preparations, about 4 g. were finally obtained. The *acid* itself, m. p. 115°, had a crystal spacing of 124·0 A. (Found : C, 80·0; H, 12·9. $C_{46}H_{90}O_3$ requires C, 80·0; H, 13·0%).

Hexatetracontanoic acid was prepared in 86% yield by the reduction of the keto-acid by Clemmensen's method; m. p. 107·1° (Found : C, 81·6; H, 13·7. $C_{46}H_{92}O_2$ requires C, 81·7; H, 13·6%). The *ethyl* ester had m. p. 90·5°, r. p. 90·3°; the purity of the preparation was tested by taking two condensates in the molecular still, the first with the bath at 130° and the second at 150°. Both the original specimen and the first and second fractions all melted at the same temperature, *viz.*, that given above (Found : C, 81·6; H, 13·6. $C_{48}H_{96}O_2$ requires C, 81·8; H, 13·6%).

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