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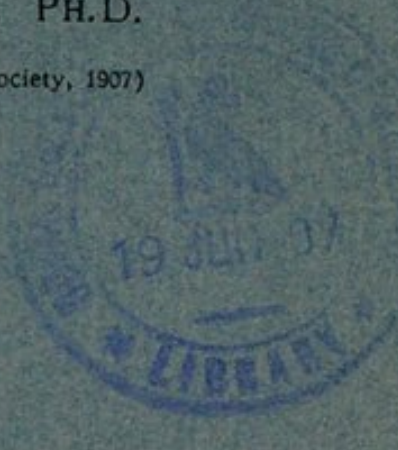
3.  
THE CONSTITUTION  
OF  
CHAULMOOGRIC AND HYDNOCARPIC ACIDS

BY  
MARMADUKE BARROWCLIFF, A.I.C.  
AND  
FREDERICK B. POWER, PH.D.

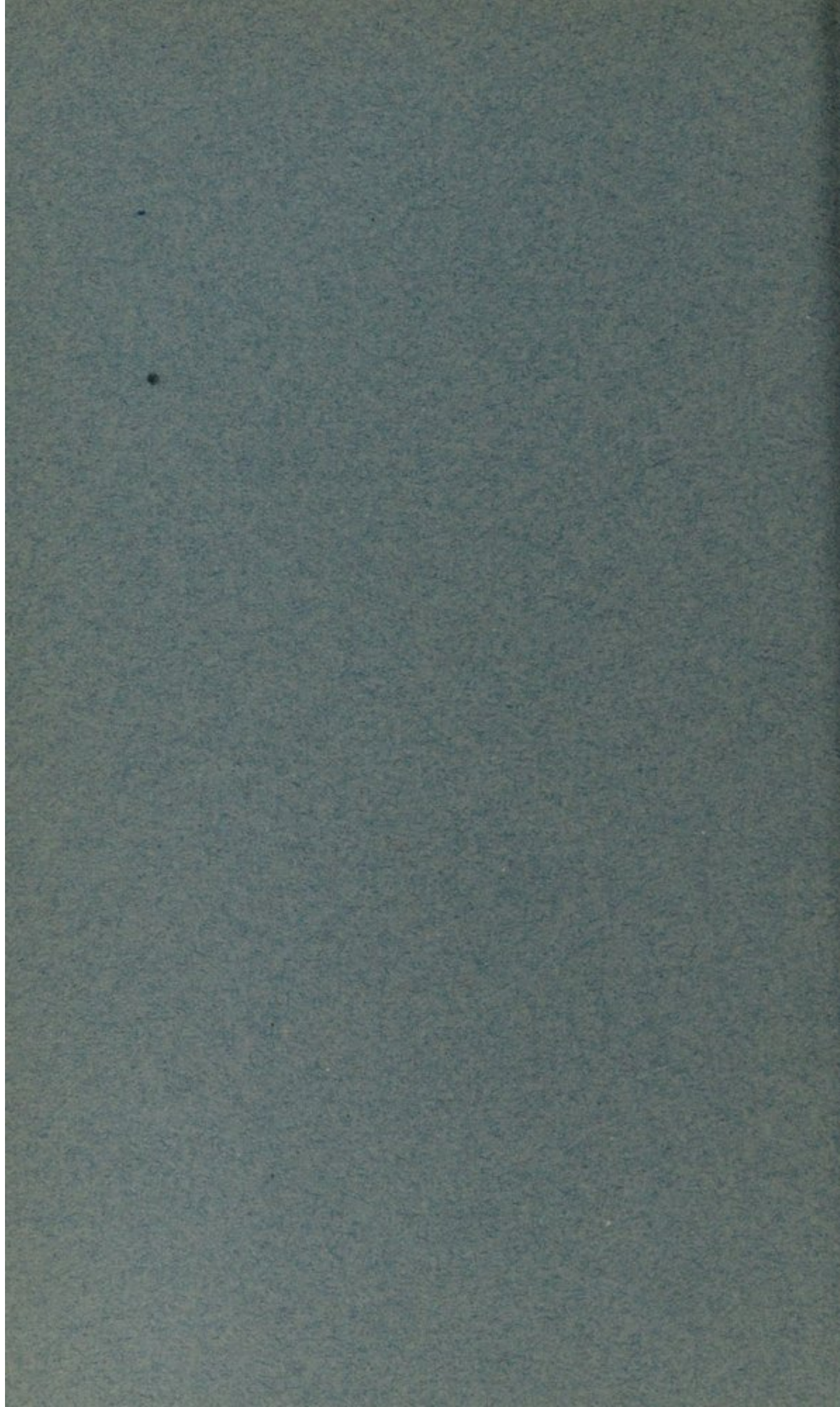
(From the Transactions of the Chemical Society, 1907)



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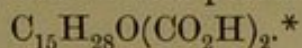
## LVII.—*The Constitution of Chaulmoogric and Hydno- carpic Acids.*

By MARMADUKE BARROWCLIFF and FREDERICK BELDING POWER.

IN a previous communication on "The Constituents of Chaulmoogra Seeds" (Power and Gornall, *Trans.*, 1904, **85**, 838) the isolation of a new, unsaturated, optically active acid was described. This acid, designated chaulmoogric acid, melted at  $68^{\circ}$ , had  $[\alpha]_D +56^{\circ}$ , and was shown to possess the formula  $C_{18}H_{32}O_2$ . Although isomeric with linolic acid, it combined with only two atomic proportions of bromine or iodine, and must, therefore, contain in its structure both a closed ring and an ethylenic linking.

In a subsequent communication, entitled "The Constitution of Chaulmoogric Acid, Part I" (*Trans.*, 1904, **85**, 851), several derivatives of this new acid were described. It was also shown that, for an unsaturated compound, it exhibited certain remarkable properties, since it was unattacked by fused alkalis, even at  $300^{\circ}$ , and when boiled with sodium and amyl alcohol the ethylenic linking was not reduced.

When oxidised in alkaline solution with potassium permanganate, dihydroxydihydrochaulmoogric acid,  $C_{18}H_{32}O_2(OH)_2$ , was obtained, together with formic acid, and an acid possessing the formula



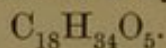
The authors have extended the study of chaulmoogric acid, more especially with regard to the products furnished by its oxidation with potassium permanganate. The present communication embodies the results obtained, and the conclusions which may be drawn from them respecting the constitution of this acid.

\* An ester, to which the formula  $C_{15}H_{28}(CO_2Et)_2$  was previously ascribed, has now been found to have consisted of impure ethyl dodecanedicarboxylate. No acid of the formula  $C_{15}H_{28}(CO_2H)_2$  is produced by the oxidation of chaulmoogric acid.

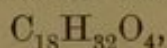


When a dilute aqueous solution of chaulmoogric acid in an excess of potassium hydroxide is treated at temperatures below  $10^{\circ}$  with an amount of potassium permanganate equivalent to one atomic proportion of oxygen, a considerable portion of the acid is recovered unchanged. This is due to the very sparing solubility of the potassium salt in water at low temperatures. If, however, an amount of permanganate equivalent to 2—3 atomic proportions of oxygen is employed at a temperature of  $18-20^{\circ}$ , two isomeric dihydroxydihydrochaulmoogric acids having the formula  $C_{18}H_{32}O_2(OH)_2$  can be isolated, whilst formic acid is also produced. The acid to which the name  *$\alpha$ -dihydroxydihydrochaulmoogric acid* may be applied melts at  $105^{\circ}$ , and has  $[\alpha]_D + 11.6^{\circ}$ . It is identical with the dihydroxy-acid previously described (Power and Gornall, *loc. cit.*). The isomeric acid, designated as  *$\beta$ -dihydroxydihydrochaulmoogric acid*, melts at  $93^{\circ}$ , and has  $[\alpha]_D - 14.2^{\circ}$ .

On repeating the oxidation with the use of an amount of permanganate equivalent to four atomic proportions of oxygen, an acid of the formula  $C_{18}H_{32}O_4$  was produced. This was isolated in the form of its methyl ester, which had the composition  $C_{19}H_{34}O_4$ , melted at  $64^{\circ}$ , and gave a semicarbazone melting at  $110^{\circ}$ . It thus appears that this is the methyl ester of a *hydroxyketodihydrochaulmoogric acid*. On hydrolysis with alcoholic sodium hydroxide this ester neutralised two equivalents of the alkali, notwithstanding the fact that it is derived from a monocarboxylic acid. This property is probably due to the opening of the ring by the hydrolysis of the grouping  $\cdot CH(OH) \cdot CO \cdot$ , with the formation of the sodium salt of a hydroxydicarboxylic acid,



The acid liberated from this salt was found to have the formula



but it did not again yield the original ester, and would therefore appear to be a lactonic acid, formed by the elimination of a molecule of water.

By the oxidation of chaulmoogric acid in alkaline solution with an excess of permanganate, an amount of the latter equivalent to 6—7 atomic proportions of oxygen was consumed. A *tricarboxylic acid* (m. p.  $68^{\circ}$ ), having the formula  $C_{18}H_{32}O_6$ , was thus obtained, together with *n*-dodecanedicarboxylic acid,  $[CH_2]_{12}(CO_2H)_2$ , a smaller quantity of *n*-undecanedicarboxylic acid,  $[CH_2]_{11}(CO_2H)_2$ , and still smaller quantities of oxalic and malonic acids. The tricarboxylic acid is a very stable compound, and the numerous attempts to obtain from it such degradation products as would throw light on its constitution were unsuccessful.

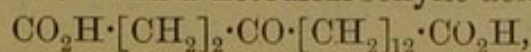
In order to ascertain whether the same products would be obtained under different conditions, an oxidation of chaulmoogric acid was conducted in acetic acid solution. The *n*-dodecanedicarboxylic acid and the



tricarboxylic acid,  $C_{18}H_{32}O_6$ , were again produced, and, in addition to these, a keto-dicarboxylic acid,  $C_{17}H_{30}O_5$  (m. p.  $128^\circ$ ), identical with the acid of this formula described in the previous communication (*loc. cit.*). When this keto-acid is oxidised in alkaline solution with an amount of potassium permanganate equivalent to three atomic proportions of oxygen, the principal product is *n*-dodecanedicarboxylic acid, which is apparently associated with a small quantity of *n*-undecanedicarboxylic acid. The constitution of this keto-acid may therefore be represented by the formula  $CO_2H \cdot [CH_2]_2 \cdots CO \cdot [CH_2]_{12} \cdot CO_2H$ , oxidation taking place principally at the place indicated by the dotted line with the production of *n*-dodecanedicarboxylic and malonic acids, and also, to a much less extent, at the other side of the carbonyl group, yielding *n*-undecanedicarboxylic and succinic acids. The amount of succinic acid formed was not sufficient to permit of its identification, but malonic acid, as already stated, has been identified as a product of the oxidation of chaulmoogric acid with an excess of permanganate. The extreme ease with which this keto-acid is broken down by alkaline permanganate doubtless accounts for the fact that no appreciable amount of it could be isolated from the products afforded by the oxidation of chaulmoogric acid with this reagent.

By the addition of hydrogen bromide to ethyl chaulmoograte, *ethyl bromodihydrochaulmoograte* is formed, which is optically active, having  $[\alpha]_D + 3.88^\circ$ . When the latter ester is reduced with zinc dust and acetic acid it gives *ethyl dihydrochaulmoograte*,  $C_{17}H_{33} \cdot CO_2Et$  (m. p.  $17^\circ$ ), which is optically inactive. It would therefore appear that the asymmetry of the chaulmoogric acid molecule is destroyed when the ethylenic linking is resolved by the addition of two atoms of hydrogen. When the elements of hydrogen bromide are split off from ethyl bromodihydrochaulmoograte the original ester is not regenerated, but a product is obtained which has a rotatory power of about  $+7.30'$  in a 1-dm. tube. The latter ester, on hydrolysis, afforded a mixture of acids, from which, on oxidation with permanganate, a *ketodicarboxylic acid*,  $C_{18}H_{32}O_5$  (m. p.  $126^\circ$ ), was obtained.

A consideration of the results recorded in this communication renders it evident that the constitution of chaulmoogric acid cannot be represented by any single formula. In the first place, by its limited oxidation, it yields two dihydroxy-acids, and, furthermore, when more completely oxidised, two series of products are obtained. These products are, on the one hand, a stable tricarboxylic acid,  $C_{18}H_{32}O_6$ , and, on the other, formic acid and a ketodicarboxylic acid,



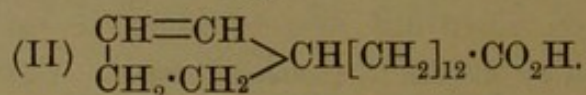
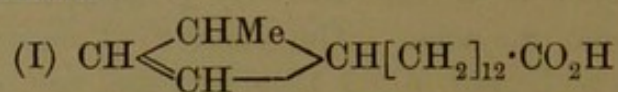
the latter, by further oxidation, yielding *n*-dodecane and *n*-undecanedicarboxylic acids.



The formation of a tricarboxylic acid,  $C_{18}H_{32}O_6$ , possessing the same number of carbon atoms as chaulmoogric acid, shows that the ethylenic linking is contained in the ring, and not in an allylic grouping, as was previously supposed.

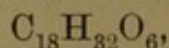
The carbon chain  $\cdot[CH_2]_{12}\cdot CO_2H$  contained in the keto-acid must be present in the original chaulmoogric acid molecule, and it therefore follows that the ring contained in the latter can consist of not more than five carbon atoms.

As chaulmoogric acid, from the nature of its oxidation products, cannot be a trimethylene compound, it must contain either a methylcyclobutene or a cyclopentene ring. The formation of the tricarboxylic acid would then be explained by assigning to chaulmoogric acid one of the following formulæ :

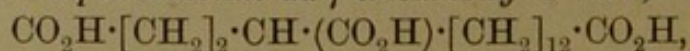


The product formed by the addition of hydrogen bromide to ethyl chaulmoograte is, as stated above, optically active, but on reducing this product with zinc dust and acetic acid the resulting ethyl dihydrochaulmoograte is inactive. It is inconceivable, however, that racemisation could be effected by a simple process of reduction when it is not brought about by treatment with hydrogen bromide or even by distilling the resulting product. From these considerations it seems highly probable that dihydrochaulmoogric acid no longer contains an asymmetric carbon atom, whereas if derived from formula I it would contain two such carbon atoms. Moreover, the ketodicarboxylic acid,  $C_{17}H_{30}O_5$ , if derived from a methylcyclobutene compound, would have the constitution  $CO_2H \cdot CHMe \cdot CO[CH_2]_{12} \cdot CO_2H$ , and would give on oxidation *n*-dodecanedicarboxylic and acetic acids, whereas it has been shown that malonic acid is formed and not acetic acid.

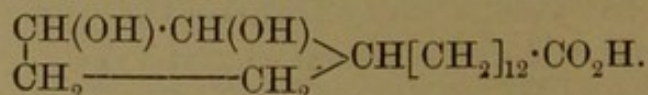
From these considerations it follows that formula II may correctly be assigned to chaulmoogric acid. The tricarboxylic acid,



will therefore be *n*-pentadecane- $\alpha\alpha'\gamma$ -tricarboxylic acid,



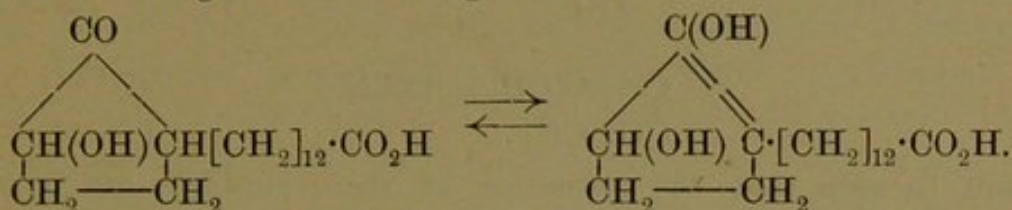
and the constitution of the dihydroxydihydrochaulmoogric acid, which by its oxidation yields this tricarboxylic acid, may be represented by the formula :



The tricarboxylic acid, although optically inactive, still contains an asymmetric carbon atom. The racemisation probably takes place in



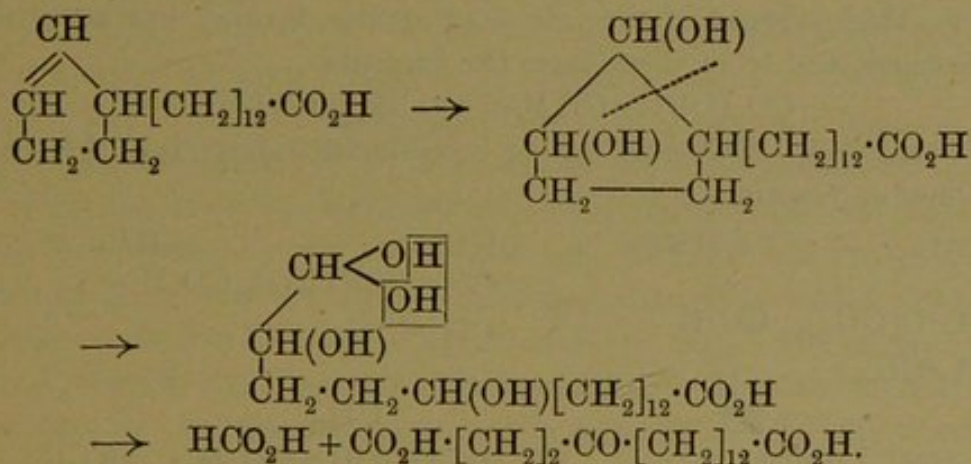
the hydroxyketo-acid, and may be attributed to keto-enolic tautomerism occurring in the following manner :



The optically inactive hydroxyketo-acid obtained is therefore probably represented by the above formula.

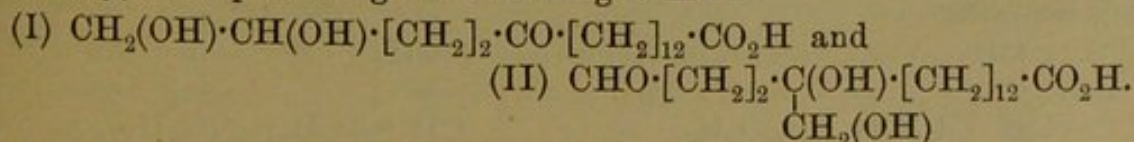
The formation of the ketodicarboxylic acid,  $\text{C}_{17}\text{H}_{30}\text{O}_5$ , remains to be considered. That it cannot have been formed by the further oxidation of the tricarboxylic acid is shown by the great stability of this compound towards alkaline permanganate solution. Moreover, as this keto-acid is the only acid obtained which possesses but one atom of carbon less than chaulmoogric acid, its formation is probably accompanied by the production of the formic acid which occurs amongst the products of oxidation.

The formation of these two acids from the formula deduced above for chaulmoogric acid could only be explained in the following manner :



Experience has shown, however, that in every instance of the oxidation of a compound possessing a ring containing a double linking, the ring opens at that point alone, so that this explanation must be considered improbable.

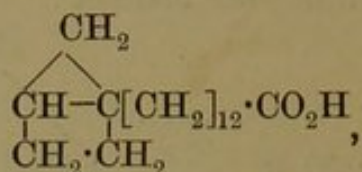
There are two hypothetical acids from which the above mentioned keto-acid and formic acid could have been formed by further oxidation, namely, those possessing the following formulæ :



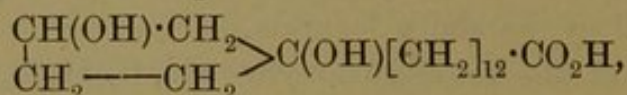
These two hypothetical acids could, however, not be produced from an acid of the formula deduced above for chaulmoogric acid. If, on the



other hand, the constitution of chaulmoogric acid were to be represented by the formula :

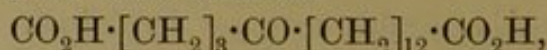


it will be seen that the formation of these products can readily be explained. The second dihydroxydihydrochaulmoogric acid will then have the following structure,

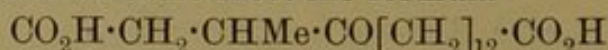


and on further oxidation could yield the hypothetical compounds represented above, and, consequently, the ketodicarboxylic acid,  $\text{C}_{17}\text{H}_{30}\text{O}_5$ , and formic acid.

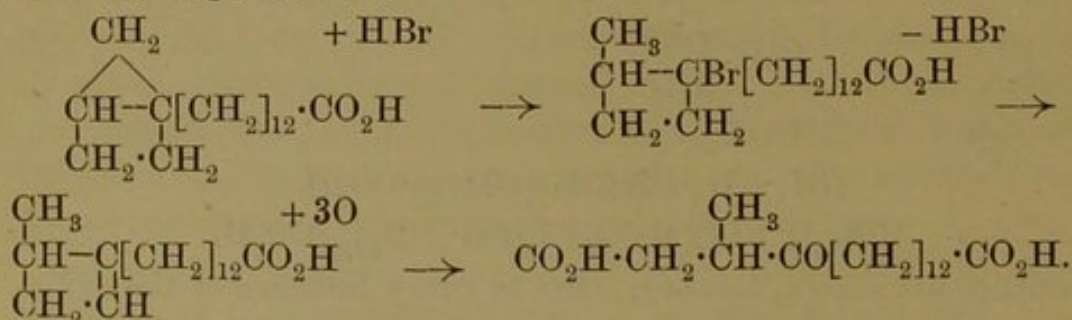
The ketodicarboxylic acid,  $\text{C}_{18}\text{H}_{32}\text{O}_5$ , obtained by the oxidation of the acids produced by removing the elements of hydrogen bromide from ethyl bromodihydrochaulmoograte, was at first thought to have been derived from the *cyclopentene* structure deduced for chaulmoogric acid, and therefore to have the formula



which would give succinic acid on further oxidation. It was found, however, that, instead of succinic acid, oxalic, formic, and acetic acids were formed, and from these facts the formula

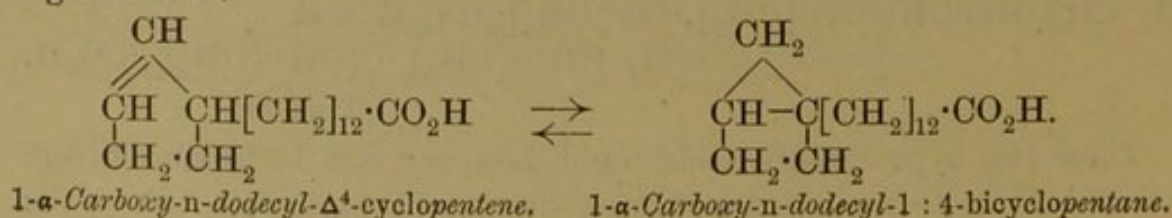


may be deduced. This acid can be considered to have been formed by the following reactions :



Dihydrochaulmoogric acid may therefore be considered a mixture of *α-carboxy-n-dodecylcyclopentane* and *1-α-carboxy-n-dodecyl-2-methylcyclobutane*.

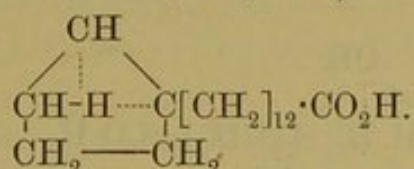
From the foregoing considerations it is seen that the behaviour of chaulmoogric acid can be explained by assigning to it both the following formulæ :





Chaulmoogric acid has, however, all the properties of an individual substance. It has, moreover, been obtained from the seeds of three botanically distinct species of plants, and in all cases it possesses identical properties. In addition to this, a homologue of it, hydnocarpic acid,  $C_{16}H_{28}O_2$ , has been isolated (Trans., 1905, 87, 888), which shows an analogous behaviour on oxidation, and, like chaulmoogric acid, has all the characters of an individual substance. For these reasons it cannot be considered possible that chaulmoogric acid is a mixture of stable isomerides, and it must therefore be regarded as being in a state of tautomerism between the two formulæ represented above, or at all events existing in such a state as to undergo chemical change in accordance with both these formulæ.

This conclusion respecting the constitution of chaulmoogric acid may also be expressed by a formula analogous to that proposed by Thorpe for glutaconic acid (Trans., 1905, 87, 1669) as follows:



In this formula the dotted lines represent a state of equilibrium between the hydrogen atom and two carbon atoms.

The results obtained by Sir W. H. Perkin for the molecular magnetic rotation of ethyl chaulmoograte, as previously recorded (Trans., 1904, 85, 851), are quite in harmony with the above conclusion. The average value found at  $14^\circ$  (21.02) lies between that calculated for the ester if it possessed the pentene structure (21.31) and that for the bicyclic structure (19.51). Sir W. H. Perkin has now kindly determined the rotation of ethyl chaulmoograte at a higher temperature, when for a rise of  $68.6^\circ$  a diminution of 0.231 in the molecular magnetic rotation was observed, but as a small reduction with rise of temperature is usual amongst such compounds no deduction can be drawn from this observation.

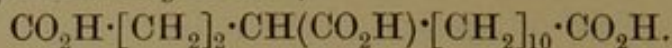
A determination of the molecular magnetic rotation of chaulmoogric acid at  $84^\circ$  gave a result analogous to that obtained for its ethyl ester, inasmuch as the value found (19.031) lies between the numbers calculated for the two formulæ suggested for this acid.

Hydnocarpic acid,  $C_{16}H_{28}O_2$  (m. p.  $60^\circ$ ;  $[\alpha]_D + 68^\circ$ ), the isolation of which has previously been described (Trans., 1905, 87, 884), is a homologue of chaulmoogric acid, and is associated with the latter in the three fatty oils from which it has been obtained. The two acids are in every respect similar in their properties, and are evidently of closely analogous constitution.

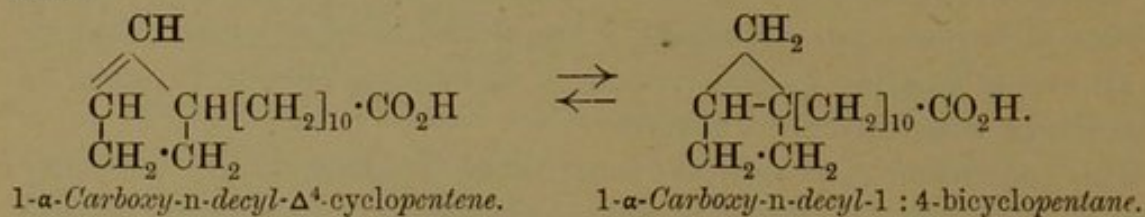
From a consideration of the constitutional formulæ assigned to chaulmoogric acid it was to be expected that hydnocarpic acid would



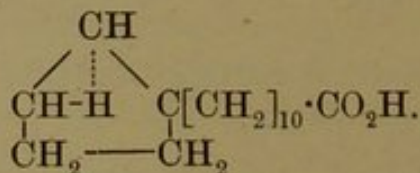
possess essentially the same structure, the only difference being in the length of the side chain. This proved to be the case, for, on oxidation in alkaline solution with an excess of potassium permanganate, hydnocarpic acid yielded *n*-decanedicarboxylic acid,  $[\text{CH}_2]_{10} \cdot (\text{CO}_2\text{H})_2$ , and a tricarboxylic acid,  $\text{C}_{16}\text{H}_{28}\text{O}_6$  (m. p.  $60^\circ$ ), which is considered to be *n*-tridecane- $\alpha\alpha'\gamma$ -tricarboxylic acid,



The following formulæ may therefore be ascribed to hydnocarpic acid :



These may be expressed, as in the case of chaulmoogric acid, by one formula, as follows :



## EXPERIMENTAL.

### I. *Chaulmoogric Acid*, $\text{C}_{18}\text{H}_{32}\text{O}_2$ .

The chaulmoogric acid employed in this investigation was prepared from genuine chaulmoogra oil (from the seeds of *Taraktogenos Kurzii*, King). The oil was hydrolysed with alcoholic potash, the acids liberated, fractionally crystallised from alcohol, and the chaulmoogric acid finally purified by distillation under diminished pressure and recrystallisation from alcohol (compare Trans., 1904, 85, 846). It was then obtained in colourless, glistening leaflets, and, when freshly distilled, melted at  $68.5^\circ$ , and had  $[\alpha]_D + 62.1^\circ$  in chloroform solution. After keeping for some time the optical rotatory power of the acid becomes somewhat diminished and it acquires a slightly yellow colour. If it be then again distilled, a dark brown substance is left in the distilling flask, which is probably formed by polymerisation.

*Oxidation of Chaulmoogric Acid in Alkaline Solution with Potassium Permanganate* ( $\text{O} = 2\text{—}3$  Atomic Equivalents).—One hundred grams of chaulmoogric acid were dissolved in a solution of 50 grams of potassium hydroxide in 5 litres of water, and to this were added 5 litres of a 2 per cent. solution of permanganate, the temperature being kept between  $16^\circ$  and  $20^\circ$ . The whole of the permanganate was instantly reduced. After filtering, the liquid was made nearly neutral with sulphuric acid, and concentrated to a small bulk. The acids were then liberated, and



steam passed through the liquid in order to remove any volatile acid. The distillate was found to contain a small amount of formic acid, which was identified by the usual tests and by the analysis of its barium salt:

0.3002 gave 0.3060  $\text{BaSO}_4$ . Ba = 60.0.

$(\text{CO}_2\text{H})_2\text{Ba}$  requires Ba = 60.4 per cent.

This acid was evidently produced by the further oxidation of one of the dihydroxydihydrochaulmoogric acids subsequently described.

The non-volatile acids remaining in the distilling flask were extracted, and converted into their methyl esters by treatment with methyl alcohol and sulphuric acid. The product was then distilled under a pressure of 16 mm., when the following fractions were collected: 200—220°; 220—245°; 245—260°; 260—275°; 275—290°/16 mm. There then remained in the flask a quantity (22 grams) of an undistillable oil, which apparently consisted of condensation products.

*Fraction 200—220°/16 mm.*—This was analysed with the following result:

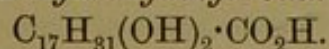
0.1030 gave 0.2519  $\text{CO}_2$  and 0.0964  $\text{H}_2\text{O}$ . C = 66.7; H = 10.4.

$\text{C}_{16}\text{H}_{30}\text{O}_4$  requires C = 67.1; H = 10.5 per cent.

It evidently consisted chiefly of the methyl ester of *n*-dodecanedicarboxylic acid,  $\text{C}_{16}\text{H}_{30}\text{O}_4$ , which was obtained in larger quantity by the oxidation of chaulmoogric acid with an excess of permanganate, and its identity established.

*Fractions 220—245° and 245—260°/16 mm.*—These were small in amount, and were found to consist of mixtures of the constituents of the fractions of lower and higher boiling point.

#### *Isolation of Two Dihydroxydihydrochaulmoogric Acids,*



*Fraction 260—275°/16 mm.*—This was the largest fraction obtained. On cooling, it deposited a considerable quantity of a solid substance, which was brought on a porous plate to remove adhering oil, after which it melted at 60—68°:

0.0933 gave 0.2366  $\text{CO}_2$  and 0.0910  $\text{H}_2\text{O}$ . C = 69.2; H = 10.8.

$\text{C}_{19}\text{H}_{36}\text{O}_4$  requires C = 69.5; H = 11.0 per cent.

This substance agreed in composition with a methyl ester of dihydroxydihydrochaulmoogric acid. After several crystallisations from methyl alcohol it yielded an ester crystallising in long, glistening needles, which melted at 75—76°, and this melting point was not changed by further crystallisation:

0.1056 gave 0.2669  $\text{CO}_2$  and 0.1045  $\text{H}_2\text{O}$ . C = 68.9; H = 11.0.

$\text{C}_{17}\text{H}_{31}(\text{OH})_2\cdot\text{CO}_2\text{Me}$  requires C = 69.5; H = 11.0 per cent.



0.3360 gram in 100 c.c. of chloroform gave  $\alpha_D + 0^\circ 5'$  in a 2-dcm. tube, whence  $[\alpha]_D + 12.4^\circ$ .

The ester was hydrolysed and the acid extracted and crystallised from ethyl acetate, in which it was readily soluble. It separated in clusters of small, silky needles, melting at  $105^\circ$ :

0.0944 gave 0.2368  $\text{CO}_2$  and 0.0922  $\text{H}_2\text{O}$ .  $\text{C} = 68.4$ ;  $\text{H} = 10.8$ .

$\text{C}_{18}\text{H}_{34}\text{O}_4$  requires  $\text{C} = 68.8$ ;  $\text{H} = 10.8$  per cent.

0.5008 gram in 100 c.c. of absolute alcohol gave  $\alpha_D + 0^\circ 7'$  in a 2-dcm. tube, whence  $[\alpha]_D + 11.6^\circ$ .

This acid is thus shown to be a dihydroxydihydrochaulmoogric acid, and was found to be identical with the acid of the same composition described in the previous communication, the melting point of which was given as  $102^\circ$  (Trans., 1904, 85, 860).

The mother liquors from the crystallisation of the ester melting at  $75$ — $76^\circ$  were found to be laevorotatory, and from them an ester was isolated which, after several crystallisations, melted at  $68$ — $69^\circ$ . This ester crystallised in silky needles, and was much more soluble in methyl alcohol than the one of higher melting point which was previously isolated:

0.8420 gram in 100 c.c. of chloroform gave  $\alpha_D - 0^\circ 16'$  in a 2-dcm. tube, whence  $[\alpha]_D - 15.8^\circ$ .

On hydrolysing this ester an acid was obtained which, after two crystallisations from ethyl acetate, melted at  $92$ — $93^\circ$ :

0.1004 gave 0.2520  $\text{CO}_2$  and 0.0986  $\text{H}_2\text{O}$ .  $\text{C} = 68.5$ ;  $\text{H} = 10.9$ .

$\text{C}_{18}\text{H}_{32}\text{O}_2(\text{OH})_2$  requires  $\text{C} = 68.8$ ;  $\text{H} = 10.8$  per cent.

0.2936 gram in 25 c.c. of absolute alcohol gave  $\alpha_D - 0^\circ 20'$  in a 2-dcm. tube, whence  $[\alpha]_D - 14.2^\circ$ .

This acid is therefore an isomeride of that melting at  $105^\circ$ , but it is much more sparingly soluble in ethyl acetate than the latter. Both these acids yield sodium salts which are only sparingly soluble in cold water.

*Fraction 275—290°/16 mm.*—This evidently also contained some of the two dihydroxydihydrochaulmoogric acids which were isolated from the preceding fraction.

*Oxidation of Chaulmoogric Acid in Alkaline Solution with Potassium Permanganate* ( $\text{O} = 4$  Atomic Equivalents).—One hundred grams of chaulmoogric acid were dissolved in the same amount of solution of potassium hydroxide as in the preceding experiment, and to this was added a solution of 150 grams of potassium permanganate in 8 litres of water, the temperature of the mixture being kept at  $15$ — $18^\circ$ . The acids were extracted, converted into their methyl esters, and fractionally distilled under a pressure of 15 mm. Several fractions were



collected, of which those boiling at 265—275° and 275—285°/15 mm. solidified on cooling.

*Isolation of a Hydroxyketodihydrochaulmoogric Acid,*  
 $C_{17}H_{30}O(OH) \cdot CO_2H.$

*Fraction* 265—275°/15 mm.—This was the larger of the two fractions, and on analysis it gave the following result:

0.0961 gave 0.2410  $CO_2$  and 0.0882  $H_2O$ . C = 68.4; H = 10.2 per cent.

After being brought on a porous plate to remove adhering oil, the solid ester was crystallised several times from methyl alcohol, when it separated in needles melting at 64°, and this melting point was not altered by further crystallisation:

0.1051 gave 0.2697  $CO_2$  and 0.0986  $H_2O$ . C = 70.0; H = 10.4.

0.1003 „ 0.2577  $CO_2$  „ 0.0940  $H_2O$ . C = 70.1; H = 10.4.

$C_{19}H_{34}O_4$  requires C = 69.9; H = 10.4 per cent.

The solid which separated from the fraction 275—285°/15 mm. likewise consisted of the above-described ester.

The ester was hydrolysed, and the acid extracted and crystallised from alcohol, from which it separated in needles melting at 90°. It was very soluble in cold ethyl acetate, but less freely in alcohol:

0.1162 gave 0.2946  $CO_2$  and 0.1060  $H_2O$ . C = 69.1; H = 10.1.

0.1013 „ 0.2573  $CO_2$  „ 0.0920  $H_2O$ . C = 69.3; H = 10.1.

0.0984 „ 0.2477  $CO_2$  „ 0.0913  $H_2O$ . C = 68.8; H = 10.3.

$C_{18}H_{32}O_4$  requires C = 69.2; H = 10.3 per cent.

$C_{17}H_{30}O_4$  „ C = 68.4; H = 10.1 „

From these results it is evident that the acid has the formula  $C_{18}H_{32}O_4$ . Both acid and ester were optically inactive.

The methyl ester, when treated with semicarbazide hydrochloride and sodium acetate, yielded a semicarbazone which crystallised from alcohol in small needles melting at 110°. This shows the ester to be that of a hydroxyketodihydrochaulmoogric acid.

0.5108 of the ester required for hydrolysis 6.4 c.c.  $N/2$  NaOH, the calculated amount for  $C_{16}H_{28}O_2(CO_2Me)$  being 3.1 c.c.

The fact that this substance, although the ester of a monocarboxylic acid, when heated with an excess of alkali neutralises two equivalents of the latter, is probably due to hydrolysis of the grouping  $\cdot CH(OH) \cdot CO \cdot$  in the ring, with the formation of a dibasic hydroxy-acid,  $C_{18}H_{34}O_5$ , and the latter then apparently loses water, yielding a lactonic acid,  $C_{18}H_{32}O_4$ . This assumption receives support from the fact that no semicarbazone could be obtained from the acid furnished by the hydrolysis of the ester, and, on re-esterifying the acid, instead of the original ester, a fatty substance was obtained. The amount of material available was insufficient for its further investigation.



*Oxidation of Chaulmoogric Acid in Alkaline Solution with an Excess of Potassium Permanganate.*—One hundred grams of chaulmoogric acid were dissolved in an aqueous solution of 50 grams of potassium hydroxide, and the opalescent liquid diluted with water to the measure of 5 litres. This was allowed to flow slowly, with constant stirring, into 11 litres of a 3 per cent. solution of potassium permanganate, the temperature being kept below  $20^{\circ}$  by the addition of ice. After standing for some hours, the excess of permanganate was removed by sodium bisulphite. The liquid was then heated, filtered, the filtrate concentrated, acidified with sulphuric acid, and distilled with steam. The distillate contained an acid which was converted into its barium salt, and from this a silver salt was prepared and analysed:

0.3024 gave 0.1960 Ag.  $\text{Ag} = 64.8$ .

$\text{C}_2\text{H}_3\text{O}_2\text{Ag}$  requires  $\text{Ag} = 64.7$  per cent.

The volatile product was thus identified as acetic acid. From the results of an experiment subsequently described, this appears to have been produced by the decomposition of malonic acid, and not to have been a direct product of oxidation.

The non-volatile acids were then extracted and converted into their methyl esters. On distilling the product under 15 mm. pressure the following fractions were obtained: below  $220^{\circ}$  (45 grams);  $220\text{--}260^{\circ}$  (8 grams);  $260\text{--}270^{\circ}$  (55 grams);  $270\text{--}280^{\circ}/15$  mm. (5 grams). These fractions were all optically inactive, and were subsequently examined as follows.

#### *Isolation of n-Undecane and n-Dodecane Dicarboxylic Acids.*

*Fraction boiling below  $220^{\circ}/15$  mm.*—This was fractionally distilled under 15 mm. pressure, when it was further resolved into the following fractions: (a) below  $200^{\circ}$  (5 grams); (b)  $200\text{--}205^{\circ}$  (13 grams); (c)  $205\text{--}210^{\circ}$  (3 grams); (d)  $210\text{--}215^{\circ}/15$  mm. (13 grams).

Fraction (c) and (d), on standing, deposited a crystalline substance, which was collected and crystallised from methyl alcohol. It then separated in clusters of needles melting at  $41^{\circ}$ :

0.1335 gave 0.3272  $\text{CO}_2$  and 0.1256  $\text{H}_2\text{O}$ .  $\text{C} = 66.8$ ;  $\text{H} = 10.5$ .

0.1279 „ 0.3132  $\text{CO}_2$  „ 0.1204  $\text{H}_2\text{O}$ .  $\text{C} = 66.8$ ;  $\text{H} = 10.5$ .

$\text{C}_{16}\text{H}_{30}\text{O}_4$  requires  $\text{C} = 67.1$ ;  $\text{H} = 10.5$  per cent.

0.6876 required for hydrolysis 9.5 c.c.  $N/2$  NaOH, the calculated amount for  $\text{C}_{12}\text{H}_{24}(\text{CO}_2\text{Me})_2$  being 9.6 c.c.

By the hydrolysis of this ester an acid somewhat sparingly soluble in ether was obtained. It was crystallised from ethyl acetate, from which it separated in small, glistening leaflets melting sharply at  $124^{\circ}$ :



0.0935 gave 0.2234  $\text{CO}_2$  and 0.0859  $\text{H}_2\text{O}$ .  $\text{C} = 65.2$ ;  $\text{H} = 10.2$ .

0.1208 „ 0.2879  $\text{CO}_2$  and 0.1098  $\text{H}_2\text{O}$ .  $\text{C} = 65.0$ ;  $\text{H} = 10.1$ .

$\text{C}_{14}\text{H}_{26}\text{O}_4$  requires  $\text{C} = 65.1$ ;  $\text{H} = 10.1$  per cent.

This substance agrees in composition and melting point with *n*-dodecanedicarboxylic acid,  $[\text{CH}_2]_{12}(\text{CO}_2\text{H})_2$ , obtained by Brown and Walker by the electrolysis of potassium ethyl suberate (*Annalen*, 1891, 261, 123). In order to confirm its identity with the above-mentioned acid, its diethyl ester was prepared. This was found to have the same melting point ( $28^\circ$ ) as a specimen of the synthetic ester which was kindly supplied to us by Professor A. Crum Brown, and a mixture of the two esters showed no diminution in melting point. A mixture of the two acids likewise melted at the same temperature ( $124^\circ$ ) at which each separately fused.

The fraction (b), b. p.  $200\text{--}205^\circ/15$  mm., deposited no solid ester, even on long standing. It was therefore hydrolysed and the acids extracted. These melted indefinitely at  $93\text{--}105^\circ$ , but after several crystallisations from ethyl acetate an acid was obtained which separated in small, glistening needles, melting at  $112^\circ$ , and this melting point was not changed by further crystallisation:

0.1093 gave 0.2553  $\text{CO}_2$  and 0.0956  $\text{H}_2\text{O}$ .  $\text{C} = 63.7$ ;  $\text{H} = 9.7$ .

0.1158 „ 0.2700  $\text{CO}_2$  „ 0.1029  $\text{H}_2\text{O}$ .  $\text{C} = 63.6$ ;  $\text{H} = 9.9$ .

$\text{C}_{13}\text{H}_{24}\text{O}_4$  requires  $\text{C} = 63.9$ ;  $\text{H} = 9.8$  per cent.

This substance agrees in composition and melting point with the brassylic acid,  $\text{C}_{13}\text{H}_{24}\text{O}_4$  [regarded as *n*-undecanedicarboxylic acid,  $[\text{CH}_2]_{11}(\text{CO}_2\text{H})_2$ ], obtained by Grossmann by the oxidation of behenolic acid, and is undoubtedly identical with it (*Ber.*, 1893, 26, 645).

From the fraction of esters (a), boiling below  $200^\circ/15$  mm., of which after several oxidations further quantities were accumulated, adipic, *n*-pimelic, and suberic acids were isolated, whilst higher members of the same series were also found to be present. It was ascertained, however, by some other experiments that these acids were produced by the long continued action of permanganate on the above-mentioned *n*-undecane- and *n*-dodecane-dicarboxylic acids.

*Fraction*  $220\text{--}260^\circ/15$  mm.—This was small in amount (8 grams), and consisted of a mixture of the constituents of the fraction boiling below  $220^\circ/15$  mm. and those of the fraction of higher boiling point.

*Isolation of a Tricarboxylic Acid*,  $\text{C}_{18}\text{H}_{32}\text{O}_6$  (*n*-Pentadecane- $\alpha\alpha'\gamma$ -tricarboxylic Acid).

*Fraction*  $260\text{--}270^\circ/15$  mm.—This fraction, which was the largest obtained, crystallised and became almost completely solid on standing. It was drained on a porous plate, to remove a small quantity of



adhering oil, and then dissolved in warm methyl alcohol, from which, on cooling, it separated in beautiful clusters of needles, melting at  $38.5^{\circ}$ . On further crystallisation the melting point remained unchanged. It distilled at  $260^{\circ}/15$  mm.:

0.1355	gave	0.3232 $\text{CO}_2$	and	0.1204 $\text{H}_2\text{O}$ .	$\text{C} = 65.0$ ; $\text{H} = 9.9$ .
0.1278	„	0.3046 $\text{CO}_2$	„	0.1153 $\text{H}_2\text{O}$ .	$\text{C} = 65.0$ ; $\text{H} = 10.0$ .
0.1064	„	0.2542 $\text{CO}_2$	„	0.0936 $\text{H}_2\text{O}$ .	$\text{C} = 65.1$ ; $\text{H} = 9.8$ .
$\text{C}_{14}\text{H}_{26}\text{O}_4$ requires $\text{C} = 65.1$ ; $\text{H} = 10.1$ per cent.					
$\text{C}_{17}\text{H}_{30}\text{O}_5$	„			$\text{C} = 65.0$ ; $\text{H} = 9.6$	„
$\text{C}_{21}\text{H}_{38}\text{O}_6$	„			$\text{C} = 65.3$ ; $\text{H} = 9.8$	„

2.3979 required for hydrolysis 36.4 c.c.  $N/2$  NaOH. The calculated amount for both  $\text{C}_{10}\text{H}_{20}(\text{CO}_2\text{Me})_2$  and  $\text{C}_{15}\text{H}_{29}(\text{CO}_2\text{Me})_3$  is 37.2 c.c., whereas  $\text{C}_{18}\text{H}_{24}\text{O}(\text{CO}_2\text{Me})_2$  would require only 30.5 c.c.

The ester was hydrolysed and the acid extracted with ether. After removing the solvent an oil was obtained which solidified to an amorphous, fatty looking mass, melting at  $61-63^{\circ}$ ; and difficulty was experienced in obtaining it crystalline. When, however, a portion was kept at  $62^{\circ}$  for some time it slowly solidified, and was seen to consist of small, slender needles. The main portion was then dissolved in an equal quantity of ethyl acetate, and the solution inoculated with the above-mentioned crystals, when the acid separated in hard aggregates of microscopic needles, which melted sharply at  $68^{\circ}$ . It was optically inactive:

0.1086	gave	0.2501 $\text{CO}_2$	and	0.0912 $\text{H}_2\text{O}$ .	$\text{C} = 62.8$ ; $\text{H} = 9.3$ .
0.1144	„	0.2630 $\text{CO}_2$	„	0.0967 $\text{H}_2\text{O}$ .	$\text{C} = 62.7$ ; $\text{H} = 9.4$ .
0.1229	„	0.2816 $\text{CO}_2$	„	0.1032 $\text{H}_2\text{O}$ .	$\text{C} = 62.5$ ; $\text{H} = 9.3$ .
$\text{C}_{12}\text{H}_{22}\text{O}_4$ requires $\text{C} = 62.6$ ; $\text{H} = 9.6$ per cent.					
$\text{C}_{18}\text{H}_{32}\text{O}_6$	„			$\text{C} = 62.8$ ; $\text{H} = 9.3$	„

Of these two formulæ the second seemed improbable, on account of the inference previously drawn from the magnetic rotation of chaulmoogric acid that it possessed an allylic grouping (Trans., 1904, 85, 855). On the other hand, the boiling point of the ester was much higher than would be expected had the acid the formula  $\text{C}_{12}\text{H}_{22}\text{O}_4$ . In order, therefore, to decide respecting the formula of the acid, molecular weight determinations were made of it and of its methyl and ethyl esters, and the propyl ester was also prepared and analysed:

0.9756	of the acid in 100 phenol	gave $\Delta t - 0.21^{\circ}$ .	M.W. = 343.
0.9902	„ „ 100 benzene „	$\Delta t - 0.15^{\circ}$ .	M.W. = 323.
$\text{C}_{18}\text{H}_{32}\text{O}_6$ requires M.W. = 344.			

*Methyl Ester.*—3.283 in 100 benzene gave  $\Delta t - 0.41^{\circ}$ . M.W. = 392.

$$\text{C}_{14}\text{H}_{26}\text{O}_4 = 258 ; \text{C}_{21}\text{H}_{38}\text{O}_6 = 386.$$

*Ethyl Ester.*—This was obtained as a colourless oil, which distilled at  $275^{\circ}/15$  mm.:



0.1151 gave 0.2835 CO<sub>2</sub> and 0.1065 H<sub>2</sub>O. C = 67.2; H = 10.3.

0.0955 „ 0.2358 CO<sub>2</sub> „ 0.0886 H<sub>2</sub>O. C = 67.3; H = 10.3.

1.3341 in 100 benzene gave  $\Delta t = 0.15^\circ$ . M.W. = 436.

C<sub>16</sub>H<sub>30</sub>O<sub>4</sub> requires C = 67.1; H = 10.5 per cent. M.W. = 286.

C<sub>24</sub>H<sub>44</sub>O<sub>6</sub> „ C = 67.3; H = 10.3 „ M.W. = 428.

*Propyl Ester*.—This was obtained as a viscid, colourless oil, which boiled at 302°/24 mm. :

0.1159 gave 0.2916 CO<sub>2</sub> and 0.1108 H<sub>2</sub>O. C = 68.6; H = 10.6.

0.1331 „ 0.3360 CO<sub>2</sub> „ 0.1278 H<sub>2</sub>O. C = 68.8; H = 10.7.

C<sub>18</sub>H<sub>34</sub>O<sub>4</sub> requires C = 68.8; H = 10.8 per cent.

C<sub>27</sub>H<sub>50</sub>O<sub>6</sub> „ C = 68.9; H = 10.6 „

From these results it is evident that the fraction boiling at 260—270°/15 mm. consists essentially of the trimethyl ester of a tricarboxylic acid having the formula C<sub>18</sub>H<sub>32</sub>O<sub>6</sub>, and, from considerations which are discussed in the introductory portion of this paper, it is seen that this acid is *n-pentadecane-aa'-γ-tricarboxylic acid*.

*n-Pentadecane-aa'-γ-tricarboxylic acid* is very soluble in alcohol, ether, chloroform, or ethyl acetate, moderately so in benzene, and insoluble in water. It is an exceedingly stable substance. When heated with concentrated nitric acid it dissolved, but separated unchanged on cooling. When warmed with an alkaline solution of permanganate it was only very slowly attacked at temperatures below 70°. When, however, it was treated at this temperature with an excess of permanganate, it yielded succinic acid. Attempts were made to obtain a hydroxy-acid or lactone by oxidising with limited quantities of permanganate, but most of the acid was recovered unchanged. It is unattacked by a chromic acid mixture, a fact which is probably due to the insolubility of the organic acid in water. When treated with chromic acid in acetic acid solution, the greater portion was recovered unchanged, and no other definite product could be isolated. An attempt was also made to obtain from the acid an unsaturated compound. For this purpose it was brominated by the Volhard method, and the elements of hydrogen bromide subsequently eliminated, but the results were of a negative character.

*Fraction 270—280°/15 mm.*—This was small in amount, and consisted to a large extent of the ester of the above-mentioned tricarboxylic acid.

For the more complete examination of the lower acids formed by the oxidation of chaulmoogric acid, another portion was treated in alkali solution with permanganate, as previously described. After removing the excess of permanganate, and filtering, the liquid was made neutral with sulphuric acid and evaporated to dryness. The mixture of



potassium salts thus obtained was powdered, thoroughly dried, suspended in absolute alcohol, and the acids esterified by passing dry hydrogen chloride through the boiling liquid for four hours. The mixture was then poured into water, the esters extracted with ether, and the ethereal solution washed with sodium carbonate and dried over sodium sulphate. After removing the ether, a quantity of alcohol distilled over, and, as this would contain the ester of any acetic acid produced by the oxidation, solid potash was added to it and the alcohol removed. The residue was then dissolved in water, the liquid acidified with sulphuric acid, and distilled with steam, but the distillate contained no acid. The ethyl esters, obtained as above described, were distilled under 30 mm. pressure, and the fraction boiling below  $190^{\circ}/30$  mm., which was small in amount, fractionated under the ordinary pressure. Fractions were collected at  $180-190^{\circ}$ ;  $190-200$ ;  $200-210^{\circ}$ , and  $210-220^{\circ}$ .

*Fraction 180—190°.*—A portion of this was shaken with concentrated aqueous ammonia, when an amide was formed which, when heated, decomposed without melting. The remainder of the fraction was hydrolysed in order to obtain the acid, which was identified as oxalic acid by its melting point and that of its methyl ester.

*Fraction 190—200°.*—This was analysed with the following result:

0.1213 gave 0.2321  $\text{CO}_2$  and 0.0808  $\text{H}_2\text{O}$ .  $\text{C} = 52.2$ ;  $\text{H} = 7.4$ .

$\text{CH}_2(\text{CO}_2\text{Et})_2$  requires  $\text{C} = 52.5$ ;  $\text{H} = 7.5$  per cent.

By the hydrolysis of this ester an acid was obtained which melted somewhat indefinitely at  $124-129^{\circ}$  with effervescence, and, when more strongly heated, developed a distinct odour of acetic acid. This product of oxidation was therefore identified as malonic acid, and is, without doubt, the source of the acetic acid previously obtained.

*Fractions 200—210° and 210—220°.*—These were small in amount. The latter fraction was examined for the presence of succinic acid, but with a negative result.

*Oxidation of Chaulmoogric Acid in Acetic Acid Solution with Potassium Permanganate.*—To a solution of potassium permanganate (200 grams) in 90 per cent. acetic acid (1500 c.c.) was added an acetic acid solution of chaulmoogric acid (50 grams), the temperature being kept below  $25^{\circ}$ . After standing for some hours, the excess of permanganate and the manganese dioxide were reduced with sulphur dioxide, the white precipitate of manganese salts removed by filtration, and the filtrate evaporated under slightly reduced pressure. The salts thus obtained were then decomposed with sulphuric acid, and the acids extracted and converted into their methyl esters. On distilling these under 15 mm. pressure the following fractions were obtained:



200—220°; 220—255°; 255—260°; 260—270°/15 mm. The first, third, and fourth of these fractions solidified on standing.

*Fraction* 200—220°/15 mm.—On analysis this gave the following result:

0.1301 gave 0.3185 CO<sub>2</sub> and 0.1223 H<sub>2</sub>O. C = 66.8; H = 10.5.

C<sub>16</sub>H<sub>30</sub>O<sub>4</sub> requires C = 67.1; H = 10.5 per cent.

This fraction evidently consisted of methyl *n*-dodecanedicarboxylate.

*Fraction* 220—255°/15 mm.—This was small in amount, and consisted of a mixture of the constituents of the preceding and succeeding fractions.

*Isolation of a Ketodicarboxylic acid, C<sub>17</sub>H<sub>30</sub>O<sub>5</sub> (γ-Keto-*n*-penta-decane-αα'-dicarboxylic Acid).*

*Fraction* 255—260° mm.—The crystalline solid which separated from this fraction was recrystallised from methyl alcohol, and was thus obtained in handsome plates, which melted sharply at 66°. On analysis:

0.1202 gave 0.2930 CO<sub>2</sub> and 0.1074 H<sub>2</sub>O. C = 66.5; H = 9.9.

C<sub>15</sub>H<sub>28</sub>O(CO<sub>2</sub>Me)<sub>2</sub> requires C = 66.7; H = 9.9 per cent.

By the hydrolysis of this ester an acid was obtained which was very sparingly soluble in ether. It was dried and crystallised from ethyl acetate, from which it separated in clusters of needles, melting at 128°. This acid was found to be identical with that of the same formula, C<sub>17</sub>H<sub>30</sub>O<sub>5</sub>, and melting point described in the previous communication (Trans., 1904, 85, 861). That it is a ketonic acid is shown by the following experiment.

One gram of the acid was dissolved in a dilute solution of potassium hydroxide, and to this was added a solution of 0.8 gram of hydroxylamine hydrochloride. The mixture was warmed for ten minutes, allowed to stand overnight, and then slightly acidified with sulphuric acid, when a substance separated which was soluble in an excess of acid. This was extracted with ether and crystallised from ethyl acetate, when it separated in small needles, melting at 83—84°:

0.1076 gave 0.2444 CO<sub>2</sub> and 0.0920 H<sub>2</sub>O. C = 61.9; H = 9.5.

C<sub>17</sub>H<sub>31</sub>O<sub>5</sub>N requires C = 62.0; H = 9.4 per cent.

*Oxidation of the Ketonic Acid, C<sub>14</sub>H<sub>28</sub>CO(CO<sub>2</sub>H)<sub>2</sub>.*—This acid was found to be very stable towards permanganate in the absence of alkali, but to undergo oxidation readily in alkaline solution.

About 6 grams of the acid were dissolved in an aqueous solution of potassium hydroxide (5 grams), and mixed with an amount of permanganate solution equivalent to three atomic proportions of oxygen



(6 grams  $\text{KMnO}_4$ ). Oxidation rapidly ensued with the development of heat, all the permanganate added being reduced. The acids were then extracted, converted into their methyl esters, and the latter distilled, when practically all passed over between  $200$  and  $210^\circ/15$  mm. This fraction was analysed:

$0.1396$  gave  $0.3394 \text{ CO}_2$  and  $0.1316 \text{ H}_2\text{O}$ .  $\text{C} = 66.3$ ;  $\text{H} = 10.5$ .

$\text{C}_{15}\text{H}_{28}\text{O}_4$  requires  $\text{C} = 66.2$ ;  $\text{H} = 10.3$  per cent.

$\text{C}_{16}\text{H}_{30}\text{O}_4$  „  $\text{C} = 67.1$ ;  $\text{H} = 10.5$  „

On standing, this fraction deposited a solid ester, which was collected and hydrolysed. The acid thus obtained, after several crystallisations, melted at  $124^\circ$ , and was identical with *n*-dodecanedicarboxylic acid,  $[\text{CH}_2]_{12}(\text{CO}_2\text{H})_2$ , which had previously been separated from the products of the direct oxidation of chaulmoogric acid. It was evident, however, from the analysis of the above fraction, that it also contained the ester of *n*-undecanedicarboxylic acid.

*Fraction 260—270°/15 mm.*—This was spread on a porous plate to remove a little adhering oil, and then crystallised from methyl alcohol. A further quantity of the ester of the ketonic acid, melting at  $66^\circ$ , was separated from it, but the greater portion melted at  $38^\circ$ , and this was analysed:

$0.1167$  gave  $0.2790 \text{ CO}_2$  and  $0.1033 \text{ H}_2\text{O}$ .  $\text{C} = 65.2$ ;  $\text{H} = 9.8$ .

$\text{C}_{21}\text{H}_{38}\text{O}_6$  requires  $\text{C} = 65.3$ ;  $\text{H} = 9.8$  per cent.

This ester thus agreed in composition and melting point with the methyl *n*-pentadecane- $\alpha\alpha'\gamma$ -tricarboxylate previously obtained, and a mixture of the two showed no diminution in melting point.

#### *Action of Hydrogen Bromide on Ethyl Chaulmoograte.*

One hundred grams of ethyl chaulmoograte were dissolved in 500 c.c. of light petroleum (b. p.  $40$ — $50^\circ$ ), and the solution, kept cool by means of ice, was saturated with dry hydrogen bromide. After remaining overnight, the solvent was removed by aspirating a current of dry air through the liquid under diminished pressure. The *ethyl bromodihydrochaulmoograte* thus obtained was a heavy, pale yellow liquid, having an agreeable odour. In moist air it slowly decomposed, evolving hydrogen bromide and becoming black. For the purpose of analysis a portion was repeatedly exposed to a gentle heat, and then placed in a vacuum desiccator containing paraffin wax and caustic potash.

$0.1047$  gave  $0.2367 \text{ CO}_2$  and  $0.0892 \text{ H}_2\text{O}$ .  $\text{C} = 61.7$ ;  $\text{H} = 9.5$ .

$\text{C}_{20}\text{H}_{37}\text{O}_2\text{Br}$  requires  $\text{C} = 61.7$ ;  $\text{H} = 9.5$  per cent.

$d_{20^\circ/20^\circ} = 1.0778$ .



2.8994 grams in 25 c.c. of chloroform gave  $\alpha_D + 0^\circ 54'$  in a 2-dcm. tube, whence  $[\alpha]_D + 3.88^\circ$ .

The same optical value was obtained from several different preparations, and it was not altered by their further treatment with hydrogen bromide.

*Reduction of Ethyl Bromodihydrochaulmoograte.*—A more convenient way of preparing dihydrochaulmoogric acid than that described in the previous communication (Trans., 1904, 85, 857) has been found to be by the reduction of ethyl bromodihydrochaulmoograte with zinc dust and acetic acid. The *ethyl dihydrochaulmoograte* thus obtained distils at  $230^\circ/22$  mm. When cooled, it solidifies to a mass of glistening needles, which melt at  $17^\circ$ . The dihydrochaulmoogric acid obtained by the hydrolysis of this ester melted at  $71^\circ$ , and is, as stated in the previous communication (*loc. cit.*), optically inactive. It is a very stable substance, and all attempts to prepare definite oxidation products from it resulted in its complete degradation.

*Elimination of Hydrogen Bromide from Ethyl Bromodihydrochaulmoograte.*—The bromo-ester was heated with an alcoholic solution of potassium hydroxide, when the elements of hydrogen bromide were eliminated with the simultaneous hydrolysis of the ester. The acid thus obtained was converted into the ethyl ester and the latter distilled. This had an optical rotation of  $+7^\circ 35'$  in a 1-dcm. tube. When the hydrogen bromide was eliminated, either by the distillation of the bromo-ester or by heating it with diethylaniline, products were obtained which had a rotatory power respectively of  $+7^\circ 40'$  and  $+7^\circ 20'$  in a 1-dcm. tube.

The acid obtained by the action of alcoholic potash on the bromo-ester, as above described, when fractionally crystallised was found to be a mixture, and no pure substance could be isolated from it.

*Formation of a Keto-dicarboxylic Acid,  $C_{15}H_{30}CO(CO_2H)_2$ .*—The above mixture of acids was treated in the cold with an excess of potassium permanganate in the presence of only a slight excess of alkali. The acids thus produced were converted into their methyl esters, and the latter fractionally distilled under 15 mm. pressure. A portion boiling between  $220$  and  $275^\circ/15$  mm. deposited a considerable quantity of a crystalline substance. This was collected and crystallised from methyl alcohol, from which it separated in beautiful plates, melting at  $64$ — $65^\circ$ . On analysis:

0.0966 gave 0.2389  $CO_2$  and 0.0877  $H_2O$ .  $C = 67.4$ ;  $H = 10.1$ .

$C_{20}H_{36}O_5$  requires  $C = 67.4$ ;  $H = 10.1$  per cent.

This ester, on hydrolysis, yielded an acid which was almost insoluble in ether. The acid was collected, dried, and dissolved in



hot ethyl acetate, from which, on cooling, it separated in small needles melting at  $126^{\circ}$ :

0.1128 gave 0.2716  $\text{CO}_2$  and 0.0988  $\text{H}_2\text{O}$ .  $\text{C} = 65.7$ ;  $\text{H} = 9.7$ .

$\text{C}_{18}\text{H}_{32}\text{O}_5$  requires  $\text{C} = 65.9$ ;  $\text{H} = 9.8$  per cent.

This was found to be a keto-acid, since it gave an *oxime* which, after crystallisation from ethyl acetate, melted at  $67-68^{\circ}$ .

Two-and-a-half grams of the acid were oxidised in alkaline solution with 3.8 grams of potassium permanganate. After removing the manganese dioxide, the liquid was concentrated, acidified with sulphuric acid, and distilled with steam. From the small amount of acid contained in the distillate a barium salt was prepared, which gave the reactions of formic and acetic acids.

The contents of the distillation flask were then diluted with water, and the insoluble acid separated by filtration. This was found to consist chiefly of *n*-dodecanedicarboxylic acid, which had previously been obtained by the direct oxidation of chaulmoogric acid. The filtrate was concentrated and extracted several times with ether, the ethereal solution dried with sodium sulphate, and the solvent removed, when a small quantity of a crystalline acid was obtained. This melted indefinitely between  $100^{\circ}$  and  $130^{\circ}$ , evolved gas at  $150-160^{\circ}$ , indicating the presence of some malonic acid, and at the latter temperature a substance sublimed in thin needles, which was identified as oxalic acid.

From considerations discussed in the introductory portion of the paper, it is seen that the above-described acid,  $\text{C}_{18}\text{H}_{32}\text{O}_5$ , is probably  *$\gamma$ -keto- $\beta$ -methyl-n-pentadecane- $\alpha\alpha'$ -dicarboxylic acid*.

## II. *Hydnocarpic Acid*, $\text{C}_{16}\text{H}_{28}\text{O}_2$ .

The hydnocarpic acid employed in this investigation was prepared from the oil of *Hydnocarpus Wightiana* (Blume) in the manner described by us in a previous communication (Trans., 1905, 87, 888). It crystallises in colourless, glistening leaflets, melting at  $60^{\circ}$ , and having  $[\alpha]_D + 68^{\circ}$  in chloroform solution. Like its higher homologue, chaulmoogric acid, it undergoes change on keeping, acquiring a yellow colour, which is attended with a lowering of the melting point. If it be then distilled under diminished pressure, a brown, resinous substance is left in the distilling flask. This change takes place more readily with hydnocarpic than with chaulmoogric acid.

*Oxidation of Hydnocarpic Acid in Alkaline Solution with an Excess of Potassium Permanganate.*—Sixty-five grams of hydnocarpic acid were dissolved in a solution of 18 grams of potassium hydroxide in 3 litres of water. To this was gradually added, with constant stirring,



a solution of 270 grams of potassium permanganate in 7 litres of water, the temperature during the oxidation being kept at 15—20°. After standing overnight, the excess of permanganate was removed with sodium bisulphite, and the liquid filtered. The acids were then liberated, extracted, and converted into their methyl esters. On distilling the latter under 18 mm. pressure the following fractions were obtained: 195—210°; 210—240°; 240—250°; 250—255°/18 mm. The first, third, and fourth of these fractions solidified almost completely on standing.

*Isolation of n-Decanedicarboxylic Acid.*

*Fraction 195—210°/18 mm.*—This was analysed with the following result:

0.1334 gave 0.3142 CO<sub>2</sub> and 0.1187 H<sub>2</sub>O. C = 64.2; H = 9.9.

C<sub>14</sub>H<sub>26</sub>O<sub>4</sub> requires C = 65.1; H = 10.1 per cent.

C<sub>13</sub>H<sub>24</sub>O<sub>4</sub> „ C = 63.9; H = 9.8 „ „

This ester was hydrolysed and the acids crystallised from ethyl acetate. An acid was thus obtained which crystallised in small needles, melting at 123°:

0.1020 gave 0.2345 CO<sub>2</sub> and 0.0887 H<sub>2</sub>O. C = 62.7; H = 9.7.

C<sub>12</sub>H<sub>22</sub>O<sub>4</sub> requires C = 62.6; H = 9.6 per cent.

This acid is evidently identical with the *n*-decamethylenedicarboxylic acid prepared synthetically by Nördlinger (*Ber.*, 1890, 23, 2357), who found it to melt at 124.5—125.5°.

*Fraction 210—240°/18 mm.*—This was very small in amount, and consisted of the constituents of the preceding and succeeding fractions.

*Isolation of a Tricarboxylic Acid, C<sub>16</sub>H<sub>28</sub>O<sub>6</sub> (n-Tridecane-αα'γ-tricarboxylic Acid).*

*Fractions 240—250° and 250—255°/18 mm.*—The former of these two fractions was the largest obtained, but they were found to consist essentially of the same substance. The solid which separated from them was spread on a porous plate, in order to remove a little adhering oil, and then twice crystallised from methyl alcohol, from which it separated in rosette-like clusters of fine needles, melting sharply at 28°. On distillation the ester passed over at 245/15 mm. as a colourless oil, which solidified on cooling:

0.1390 gave 0.3236 CO<sub>2</sub> and 0.1187 H<sub>2</sub>O. C = 63.5; H = 9.5.

0.1410 „ 0.3284 CO<sub>2</sub> „ 0.1208 H<sub>2</sub>O. C = 63.5; H = 9.5

C<sub>19</sub>H<sub>34</sub>O<sub>6</sub> requires C = 63.7; H = 9.5 per cent.



2.0986 required for hydrolysis 33.4 c.c.  $N/2$  NaOH, the calculated amount for  $C_{13}H_{25}(CO_2Me)_3$  being 35.1 c.c.

The hydrolysis of this ester yielded an acid which solidified in hard, warty masses, melting at 52—55°. The acid was subsequently dissolved in hot ethyl acetate, from which, on cooling, it separated in aggregates of fine needles, melting at 60°, and this melting point was not altered by further crystallisation. It is optically inactive:

0.1239 gave 0.2750  $CO_2$  and 0.0993  $H_2O$ . C = 60.5; H = 8.9.

0.1106 „ 0.2458  $CO_2$  „ 0.0876  $H_2O$ . C = 60.6; H = 8.8.

$C_{16}H_{28}O_6$  requires C = 60.8; H = 8.9 per cent.

This acid is a lower homologue of the tricarboxylic acid obtained by the oxidation of chaulmoogric acid, and, from considerations noted in the introductory portion of the paper, it is evidently *n-tridecane- $\alpha\alpha'\gamma$ -tricarboxylic acid*.

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