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LE SUEUR : DIHYDROXYSTEARIC ACID.

CXXXVIII.—The Products of the Action of Fused Potassium Hydroxide on Dihydroxystearic Acid.

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Two papers communicated to the Society by Dr. Crossley and the author (Trans., 1899, 75, 161; 1900, 76, 83) contain details of experiments made in order to devise a method by which the constitution of fatty acids might be determined. In this process, the fatty acid is first converted into an unsaturated acid with the double bond between the a- and β -carbon atoms and this acid is then oxidised with potassium permanganate in alkaline solution, whereby a dihydroxy-acid is produced,

$R \cdot CH: CH \cdot CO_2 H \longrightarrow R \cdot CH(OH) \cdot CH(OH) \cdot CO_2 H$,

which on further oxidation with potassium dichromate and dilute sulphuric acid is converted into a saturated acid containing two carbon atoms less than the original acid and oxalic acid or its oxidation products.

$\mathbf{R} \cdot \mathbf{CH}(\mathbf{OH}) \cdot \mathbf{CH}(\mathbf{OH}) \cdot \mathbf{CO}_{2}\mathbf{H} \rightarrow \mathbf{R} \cdot \mathbf{CO}_{2}\mathbf{H} + \mathbf{CO}_{2}\mathbf{H} \cdot \mathbf{CO}_{2}\mathbf{H} (\rightarrow \mathbf{CO}_{2} + \mathbf{H}_{2}\mathbf{O}).$

The final substance is not invariably an acid; for instance, if the original acid is of the type $R_2CH\cdot CH_2\cdot CO_2H$, the final oxidation product will be a ketone of the type R_2CO (Trans., 1899, 75, 164).

In this method, the second oxidation, that with potassium dichromate and dilute sulphuric acid, is carried out in an acid solution, and provided the dihydroxy-acid is soluble in such a solution, the method works well; if, however, it is insoluble, then the oxidation is very slow, and only a small part of the dihydroxy-acid is completely It was thought that in such cases fusion of the dihydroxyoxidised. acid with potassium hydroxide might serve the same purpose as the oxidation with potassium dichromate and dilute sulphuric acid, and the work described in this paper was undertaken in order to see whether this assumption was correct. Dihydroxystearic acid was chosen because it can be obtained fairly easily in large quantities and is insoluble in water; it was also hoped that the results obtained would furnish evidence from which the formula of dihydroxystearic acid and consequently that of oleic acid might be definitely established. For instance, using the generally accepted formula for the acid, oleic acid, CH₂·[CH₂]₇·CH:CH·[CH₂]₇·CO₂H, on oxidation with potassium permanganate, should give dihydroxystearic acid,

$$CH_3 \cdot [CH_2]_7 \cdot CH(OH) \cdot CH(OH) \cdot [CH_2]_7 \cdot CO_2H$$
,

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which, on fusion with potassium hydroxide, would be broken up, yielding molecular quantities of pelargonic acid, $CH_3 \cdot [CH_2]_7 \cdot CO_2H$, and azelaic acid, $CO_2H \cdot [CH_2]_7 \cdot CO_2H$, as the sole initial products. The pelargonic and azelaic acids might suffer further decomposition and the author has satisfied himself that such does actually happen in the case of the latter.

The results obtained were unexpected, for instead of the final product being an acid or acids containing fewer carbon atoms than the original substance, the main product was an acid containing the same number of carbon atoms, which clearly showed that, whatever may be the correct formula of dihydroxystearic acid, the main decomposition did not take place between the two carbon atoms to which the hydroxyl groups are attached. The result of the work described in this communication therefore apparently gives no clue to the constitution of dihydroxystearic acid; further investigation of the dibasic acid obtained may, however, furnish some evidence in this direction.

The fusion of dihydroxystearic acid with potassium hydroxide was first carried out at 270—275°, and the substances isolated from the product were found to consist mainly of an oil boiling at 280—300° under 50 mm. pressure, together with small quantities of pelargonic and azelaic acids. The effect of carrying out the fusion at a somewhat lower temperature was next tried, when, as is described below, the following substances were isolated : A dibasic acid, $C_{18}H_{84}O_5$, melting at $111-111\cdot5^\circ$; an acid, $C_{18}H_{34}O_3$, melting at $78\cdot5-79^\circ$; pelargonic acid; and azelaic acid. The first of these was obtained in a 58 per cent. yield of that theoretically obtainable and the other three only in small quantities.

That the acid $C_{18}H_{34}O_5$ (m. p. 111–111.5°) is dibasic is clearly shown from the analysis of its salts, its titration with standard alkali, the determination of the molecular weight of its ethyl ester by the freezing point method, and also from its capability of forming an amic acid and a diamide. That it is also a monohydroxy-acid is shown from the fact that it yields a monoacetyl derivative on treatment with acetic anhydride or acetyl chloride. No mention could be found of the previous existence of this acid.

Analyses of the acid $C_{18}H_{34}O_3$ (m. p. 78.5-79°) and of its sodium salt gave numbers which agree closely with the calculated values for the formulæ assigned to them. The acid may be regarded as an internal anhydride, formed by the elimination of one molecule of water from a molecule of dihydroxystearic acid:

$$\mathrm{CO}_{2}\mathrm{H} \cdot \mathrm{C}_{15}\mathrm{H}_{31} < \overset{\mathrm{CH} \cdot \mathrm{OH}}{\operatorname{CH} \cdot \mathrm{OH}} \quad \longrightarrow \quad \mathrm{CO}_{2}\mathrm{H} \cdot \mathrm{C}_{15}\mathrm{H}_{31} < \overset{\mathrm{CH}}{\operatorname{CH}} > \mathrm{O}.$$

It was thought that such an acid would be reconverted into dihydr-

oxystearic acid by boiling with dilute acids or alkalis, but experiments carried out in this direction have so far proved unsuccessful.

By the distillation of dihydroxystearic acid under reduced pressure, Saytzeff (J. pr. Chem., 1886, [ii], 33, 313) obtained an acid melting at 77-79° and solidifying at 69-70°, to which he assigned the formula $C_{18}H_{34}O_3$. He regarded it as an anhydride of dihydroxystearic acid formed as described above. But this acid must have been impure, because the numbers which Saytzeff obtained on analysis do not agree at all closely with those calculated for the formula $C_{18}H_{34}O_8$, the mean of four analyses giving 70.91 per cent. of carbon, whereas the calculated amount is 72.49 per cent. It must, however, be stated that the sodium and silver salts on analysis gave numbers which agree well with those calculated for a monobasic acid of the formula $C_{18}H_{34}O_8$.

Albitzky (J. Russ. Phys. Chem. Soc., 1899, 31, 76) has described glycidic acids of similar composition, obtained by the action of barium hydroxide on the chlorohydroxystearic acids.

The formation of a monohydroxydicarboxylic acid from a dihydroxymonocarboxylic acid is not easy to explain, unless it is assumed that the acid $C_{18}H_{34}O_3$ is first formed and that this is immediately oxidised to the acid $C_{18}H_{34}O_5$. Thus

CH_3	CH_3	$CO_{2}H$
$(\dot{C}H_2)_m$	$(\dot{C}H_2)_m$	$(\dot{\mathbf{C}}\mathbf{H}_2)_m$
ĊН•ОН	$\rightarrow \dot{C}H_{>0}$	→ ĊH·OH
¦с́н∙он	́ Ċн	$\dot{\mathbf{CH}}_{2}$
$(\dot{C}H_2)_n$	$(\dot{\mathbf{C}}\mathbf{H}_2)_n$	$(\dot{\mathrm{CH}}_2)_n$
ĊО ₂ Н	$\dot{C}O_2H$	$\dot{\mathrm{CO}}_{2}\mathrm{H}$

EXPERIMENTAL.

Preparation of Dihydroxystearic Acid.—The acid was prepared by the oxidation of oleic acid with potassium permanganate in alkaline solution, as recommended by Saytzeff (*loc. cit.*). Eighty-four grams of oleic acid (Kahlbaum's pure acid) were dissolved in 1500 c.c. of water containing 33 grams of potassium hydroxide, the solution was cooled to 0° , and a cold solution of 84 grams of potassium permanganate in 1500 c.c. of water gradually added, the mixture being well stirred by means of a turbine and its temperature maintained below 10° . The whole was allowed to remain overnight, filtered from the separated manganese dioxide, and acidified with dilute sulphuric acid, when a very voluminous, white precipitate of dihydroxystearic acid separated out. This was filtered off, dried on a porous plate, and extracted with

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a small volume of ether in order to remove any unoxidised oleic acid. The residue (insoluble in ether) was recrystallised from rectified spirit until its melting point was constant, when 45 grams of pure dihydroxystearic acid were obtained, the yield amounting to 48 per cent. of that theoretically possible.

Melting Point of Dihydroxystearic Acid.—Various temperatures have been given as the correct melting point of pure dihydroxystearic acid. Saytzeff (loc. cit.), Hazura (Monatsh., 1888, 9, 186), and others, state that the acid melts at 136.5° ; Edmed (Trans., 1898, 73, 629) gives 134° as the melting point, Gröger (Ber., 1889, 22, 620) gives $130.5-131.5^{\circ}$, and lastly, Freundler (Bull. Soc. Chim., 1885, [iii], 13, 1052), who separated the acid into its optical isomerides, states that it melts at 131° . In view of these conflicting statements, it was deemed advisable to make every effort to ascertain the true melting point of the pure acid. The dihydroxystearic acid, obtained as described above, after two recrystallisations from rectified spirit melted at $130.5-131^{\circ}$ (uncorr.), and after three further recrystallisations still melted at this temperature. On analysis :

0.1500 gave 0.3754 CO₂ and 0.1536 H₂O. C = 68.25; H = 11.38. C₁₈H₃₆O₄ requires C = 68.35; H = 11.39 per cent.

The acid was then boiled with a large volume of water, in which it is insoluble, whereas the higher hydroxylated acids, such as sativic acid (tetrahydroxystearic acid), are somewhat soluble, and again recrystallised from rectified spirit, when it still melted at $130\cdot5-131^{\circ}$ (uncorr.). It was next boiled with ether, in which it is slightly soluble, and the ethereal solution filtered off from the undissolved portion. Both this undissolved residue and the acid obtained by evaporation of the ethereal solution melted at exactly the same temperature, namely, $130\cdot5-131^{\circ}$. The dihydroxystearic acid, which was obtained by the author from the oxidation of the unsaturated acids of the oil of *Carthamus tinctorius*, also melted at this temperature (*J. Soc. Chem. Ind.*, 1900, 19, 104). On applying the usual method for correcting the melting point of a substance, $131\cdot5-132^{\circ}$ is obtained as the corrected melting point of pure dihydroxystearic acid.

Calcium Salt of Dihydroxystearic Acid.—Saytzeff (loc. cit.) states that calcium dihydroxystearate, after drying in a desiccator, contains 1 mol. of water of crystallisation; Edmed (loc. cit.), on the other hand, states that the dried salt contains 3 mols., but from the following results it will be seen that the air-dried salt contains only 1 mol. of water of crystallisation. The salt was prepared by adding an aqueous solution of the potassium salt of the acid to an aqueous solution of calcium chloride. On analysis;

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Fusion of Dihydroxystearic Acid with Potassium Hydroxide.-Five grams of dihydroxystearic acid, 25 grams of pure potassium hydroxide, and sufficient water to form a thick paste, were well mixed together in a nickel crucible and heated in a metal bath. At 200°, the mass completely liquefied, and at 250° it turned slightly brown in colour and evolved a small amount of hydrogen. The temperature was then raised to 270-275° and maintained at this point until the rapid evolution of hydrogen which at first took place had ceased. The product was then cooled, dissolved in water, acidified with dilute sulphuric acid, and subjected to steam distillation. The distillate contained pelargonic acid, which was identified by the melting point of its crystalline zinc The residue in the flask contained a dark oil, which was filtered salt. off (filtrate = A) from the mother liquor, dried in a vacuum desiccator, treated with ether, and the ethereal solution (filtered from a small amount of insoluble residue) evaporated, when 1.2 grams of an oil which distilled without decomposition at 280-300° under 50 mm. pressure were obtained. Azelaic acid was isolated from the aqueous filtrate A and identified by its melting point (106°) and analysis.

The effect of carrying out the fusion at a somewhat lower temperature was next tried, when it was found that no oil was produced, but that the acids left in the flask after steam distillation solidified to a hard mass, which at first was thought to be unchanged dihydroxy-This, however, was soon found not to be the case, as the stearic acid. substance is readily soluble in ether, in which dihydroxystearic acid is only slightly soluble, and on extracting the solid fractionally with chloroform two acids were obtained melting respectively at 111-111.5° and 78.5-79°. In order to obtain larger quantities of these two substances, 250 grams of dihydroxystearic acid were fused with potassium hydroxide in quantities of 40 grams at a time, the fusion being carried out as follows: 40 grams of dihydroxystearic acid, 200 grams of pure potassium hydroxide, and sufficient water to form a thick paste were well mixed in a nickel crucible and gradually heated in a metal bath, the mass being vigorously stirred the whole time. At 200°, the mass liquefied and there was much frothing; the temperature was then raised to 250° and maintained at this point until the frothing ceased, which took place after 20 minutes, during which time only traces of hydrogen were evolved. If the heating be continued, much hydrogen is evolved and the mass darkens. It is necessary that the fusion should be stopped the moment this second action sets in, otherwise the result-

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ing substances are those described on page 1317. The fused product was dissolved in water, acidified with dilute sulphuric acid, and the liberated acids separated from the mother liquor and washed with boiling water.

The whole of the mother liquor was extracted four times with a large volume of ether, when, on evaporation of the ethereal solution, 10 grams of a solid residue were obtained, which was readily soluble in hot water and crystallised out on cooling in large plates which melted at $105-106^{\circ}$ and had all the properties of azelaic acid. On analysis:

0.1550 gave 0.3272 CO₂ and 0.1182 H₂O. C = 57.57; H = 8.47. C₀H₁₆O₄ requires C = 57.44; H = 8.51 per cent.

On cooling, the acids liberated by sulphuric acid solidified to a hard mass, which was powdered, dried in a vacuum desiccator, and extracted with cold chloroform; the products soluble and insoluble in this solvent were then investigated.

Product Insoluble in Chloroform.

The portion insoluble in chloroform was recrystallised from acetic acid until its melting point was no longer changed $(111-111\cdot 5^{\circ})$.

Of the pure acid, 120 grams were obtained from 200 grams of dihydroxystearic acid, a yield which corresponds to 58 per cent. of that theoretically obtainable. On analysis:

0.1422 gave 0.3396 CO₂ and 0.1324 H₂O. C = 65.13; H = 10.34. 0.1340 , 0.3210 CO₂ , 0.1256 H₂O. C = 65.33; H = 10.41. C₁₈H₂₄O₅ requires C = 64.45; H = 10.30 per cent,

This acid is insoluble in cold water, but melts in boiling water. Its alcoholic solution gives a well-marked effervescence with a dilute solution of sodium carbonate or sodium hydrogen carbonate in the cold. It dissolves slowly in a cold solution of potassium hydroxide, and the solution thus produced does not affect potassium permanganate in the cold and reduces it only slightly on heating; it is without effect on Fehling's solution. The acid is somewhat readily soluble in alcohol, ether, ethyl acetate, or acetone in the cold, and also in hot acetic acid. It is insoluble in benzene, chloroform, or light petroleum in the cold, but dissolves readily in the former on heating. It crystallises from dilute alcohol or dilute acetic acid in aggregates of long, flat needles melting at $111-111.5^{\circ}$.

Titration of the Acid.—The acid was dissolved in alcohol which had been previously neutralised and the solution titrated with a decinormal solution of potassium hydroxide.

(ii). 0.5614 ,, 34.2 c.c. ,, litmus ,,

⁽i). 0.4172 required 25.23 c.c., using phenolphthalein as indicator,

One gram of the acid therefore requires (i) 60.5 c.c.; (ii) 60.9 c.c., the calculated amount for 1 gram of a dibasic acid, $C_{18}H_{34}O_5$, being 60.6 c.c.

The sodium salt was obtained as a hard mass of no very definite crystalline structure and could not be recrystallised from alcohol or water, owing to its great solubility. These remarks also apply to the neutral and acid potassium salts.

The *silver* salt was thrown down as a white, curdy precipitate when a solution of the sodium salt was poured into excess of a warm solution of silver nitrate. On analysis:

0.2310 gave 0.3360 CO₂, 0.1238 H_2O , and 0.0904 Ag. C = 39.66; H = 5.95; Ag = 39.13.

0.1344 gave 0.0534 Ag. Ag = 39.73.

 $C_{18}H_{32}O_5Ag_2$ requires C = 39.70; H = 5.88; Ag = 39.70 per cent.

The *barium* salt was obtained as a white precipitate on the addition of a solution of the sodium salt to a solution of barium chloride. The salt was dried at 100° and analysed :

0.2226 gave 0.1104 BaSO₄. Ba = 29.20. C₁₈H₃₂O₅Ba requires Ba = 29.52 per cent.

The calcium salt was obtained as a white, gelatinous precipitate on the addition of a solution of the sodium salt to a solution of calcium chloride. The amount of water present in the air-dried salt was found to vary in different samples. In one case, numbers were obtained which agreed with those required for a salt of the formula $C_{18}H_{32}O_5Ca,3H_2O$. The air-dried salt loses the greater part of its water in a vacuum, but the last traces are only expelled at 155°. The salt was therefore dried at 155°, until no further loss occurred, and analysed :

Precipitates were obtained on the addition of an aqueous solution of the sodium salt of the acid to solutions of salts of mercury, copper, lead, manganese, iron, zinc, magnesium, cobalt, or nickel.

Ethyl Ester, $C_{18}H_{32}O_5(C_2H_5)_2$.—The calculated quantity of ethyl iodide was added to the dry silver salt, which was covered with anhydrous ether in a flask attached to a reflux condenser and the whole heated on the water-bath for $2\frac{1}{4}$ hours. The resulting ethereal solution, which was of a bright yellow colour, due to finely divided silver iodide held in suspension, was evaporated, and the residual oil purified by distillation under reduced pressure. On analysis:

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0.1526 gave 0.3816 CO₂ and 0.1490 H₂O. C = 68.20; H = 10.85. C₂₂H₄₂O₅ requires C = 68.39; H = 10.88 per cent.

It was also prepared directly from the acid as follows. Fifty c.c. of concentrated sulphuric acid were gradually added to a solution of 10 grams of the acid in 100 c.c. of absolute alcohol and the mixture allowed to remain at the ordinary temperature for 4 days and then heated on the water-bath for 3 hours. The product was poured into water, extracted with ether, the ethereal solution well washed with water, and after evaporation of the solvent, the residual liquid was purified by fractional distillation under reduced pressure, when 7.2 grams, boiling at $268-274^{\circ}$ under 31 mm. pressure, were obtained. The ester thus produced had a slight acid reaction, due no doubt to the presence of a trace of free acid or acid ester.

The ester is a very faintly yellow, odourless oil boiling at $269-270^{\circ}$ under 30 mm. pressure, and shows no signs of solidifying when strongly cooled or kept for several months. It is insoluble in water, but dissolves readily in ether, benzene, or alcohol.

The molecular weight was determined by the freezing point method using benzene as solvent:

Wt. of ester.	Wt. of solvent.	Depression.	Mol. wt.
0·899 gram	20.83 grams	0.579°	$365 \cdot 2$
1.4752 "	20.83 "	0.937	37 0·3

The molecular weight of $C_{18}H_{32}O_5(C_2H_5)_2$ is 386.

The *methyl* ester, $C_{18}H_{32}O_5(CH_3)_2$, was prepared by the action of methyl iodide on the dry silver salt. On analysis:

0.1498 gave 0.3666 CO₂ and 0.1436 H₂O. C=66.74; H=10.65. C₂₀H₃₈O₅ requires C=67.04; H=10.61 per cent.

It is a colourless, oily liquid boiling at 258-259° under 30 mm. pressure and is insoluble in water, but dissolves readily in alcohol or ether.

Amides.—Henry (Compt. rend., 1885, 100, 944) has shown that the diamides of the dibasic acids (succinic, adipic, &c.) are more easily prepared from the methyl than from the ethyl ester by the action of an aqueous solution of ammonia. Experiments made with the ethyl ester showed that this statement also applies to the acid $C_{18}H_{34}O_5$, and the amides were consequently prepared from the methyl ester. Four grams of the methyl ester and 25 c.c. of an aqueous solution of ammonia, saturated at 0°, were heated together in a sealed tube at 185° for 12 hours. At the end of this time, the whole of the ester had disappeared, and a small amount of solid was present, which was filtered off (filtrate=A), dried on a porous plate, and purified by recrystallisation from rectified spirit. On analysis:

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0.1202 gave 8.9 c.c. moist nitrogen at 14° and 760 mm. N = 8.71. $C_{18}H_{36}O_3N_2$ requires N = 8.54 per cent.

The *diamide* is insoluble in water, ether, chloroform, or light petroleum, but readily dissolves in boiling acetone or alcohol, from the latter of which it separates in aggregates of fine needles melting sharply at 141°. It is insoluble in an aqueous solution of potassium hydroxide. The yield was small, only 0.7 gram being obtained from 11 grams of methyl ester.

The Amic Acid.—The filtrate (A) from the diamide was diluted with water and acidified with dilute hydrochloric acid, when the oil which separated out immediately solidified. It was filtered off, dried on a porous plate, and purified by recrystallisation from dilute alcohol. On analysis:

The amic acid crystallises from rectified spirit in aggregates of colourless needles melting at 136°. It is insoluble in water, ether, chloroform, or light petroleum, but dissolves slowly in a solution of potassium hydroxide in the cold and readily on warming. Its alcoholic solution is acid to litmus paper and gives a marked effervescence with a solution of sodium hydrogen carbonate in the cold.

Silver Salt of the Amic Acid.—The amic acid was dissolved in dilute alcohol, neutralised with ammonia and the warm solution of the ammonium salt poured into an excess of a solution of silver nitrate, when the silver salt separated out as a somewhat sticky, white precipitate, which soon became hard and granular. The whole was heated nearly to boiling, filtered, and the precipitate washed with water and alcohol, dried, and analysed:

0.1476 gave 0.0368 Ag. Ag = 24.93. $C_{18}H_{34}O_4NAg$ requires Ag = 24.77 per cent.

Action of Acetic Anhydride on the Acid.—Ten grams of the acid and 40 grams of acetic anhydride were boiled together for 3 hours in a flask attached to a reflux condenser. The acid readily dissolved in the anhydride on heating. On distilling the liquid product under 90 mm. pressure, the excess of acetic anhydride passed over below 90° , and the last traces of this substance were removed by raising the temperature to 130° for a short time and passing a slow current of dry air through the liquid. The acetylated product was then allowed to remain over solid potassium hydroxide in a vacuum for 4 days and analysed. The analytical results indicate that the substance is the

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monoacetylated anhydride, $C_{18}H_{31}O_4 \cdot CO \cdot CH_3$, and not the monoacetylated acid, $C_{18}H_{33}O_5 \cdot CO \cdot CH_3$.

2.1208 grams of the acetylated product were boiled for 5 hours with an excess of an alcoholic solution of potassium hydroxide. The alcohol was then evaporated off and the liquid acidified with dilute sulphuric acid and distilled with steam. The distillate required 50.17c.c. of decinormal potassium hydroxide for neutralisation; the acetic acid from 1 gram of the acetylated product would therefore require 23.65 c.c.

In a second experiment, the acetylated product, after removal of the excess of acetic anhydride by distillation in a vacuum, was repeatedly boiled with water to remove the last traces of this impurity; it was then filtered at 100° and dried in a vacuum over potassium hydroxide and sulphuric acid for 5 days. 1.9954 grams of this product were hydrolysed in the manner just described. The distillate required 41.9 c.c. of decinormal potassium hydroxide for neutralisation, whence 1 gram of the acetyl derivative would require 21.0 c.c.

The calculated amount for 1 gram of the monoacetylated anhydride, $C_{2\theta}H_{84}O_5$, is 28.24 c.c. and for 1 gram of the monoacetylated acid, $C_{2\theta}H_{86}O_6$, 26.8 c.c.

These results are not in close agreement with the calculated values for the acetylated anhydride or acid, but they undoubtedly show that a monoacetylated derivative is formed by the action of acetic anhydride on the acid.

The oil left in the steam distillation flask solidified to a hard mass on cooling and after one recrystallisation from dilute alcohol melted at 110°, which shows that the original acid is obtained on hydrolysis of the acetylated product.

The acetylated anhydride is a very viscous, light yellow liquid, which shows no signs of solidification on long standing. It is readily soluble in alcohol or ether and dissolves slowly in aqueous potassium hydroxide.

Action of Acetyl Chloride on the Acid.—Five grams of the acid and 25 grams of acetyl chloride were boiled together for 1 hour in a flask attached to a reflux condenser, when the acid slowly dissolved. The product was treated in a similar manner to that obtained by the action of acetic anhydride. On analysis:

0.1810 gave 0.4446
$$CO_2$$
 and 0.1570 H_2O . $C = 67.00$; $H = 9.64$.
 $C_{20}H_{34}O_5$ requires $C = 67.79$; $H = 9.60$ per cent.

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1.7238 grams of this acetylated compound were hydrolysed and treated in a similar manner to the product obtained by the action of acetic anhydride as described above. The distillate required 44.0 c.c. of decinormal potassium hydroxide for neutralisation; the acetic acid obtained from 1 gram would therefore require 25.5 c.c.

The monoacetylated anhydride obtained by the action of acetyl chloride possesses the same properties as that obtained by the action of acetic anhydride.

Product Soluble in Chloroform.

The chloroform extract of the mixed acids (see p. 1318) on evaporation, left 37 grams of a residue which became semi-solid on standing. It was subjected to steam distillation until the distillate was only faintly acid. From this distillate, ether extracted 4.5 grams of a liquid which had a strong odour of pelargonic acid and from this 1.8 grams boiling at $249-255^{\circ}$ were obtained, and identified as pelargonic acid by analysis of the silver salt (Ag = 40.41 per cent.) and preparation of the zinc salt which melted at 130°.

 $Acid C_{18}H_{34}O_5$.—The oil which remained in the distillation flask partially solidified on cooling, and after spreading on a porous plate, yielded 16 grams of a solid material, which was then fractionally recrystallised from dilute alcohol until a substance of constant melting point was obtained. The amount of pure substance thus isolated was small, only about 6 grams being obtained from 200 grams of dihydroxystearic acid. On analysis:

The acid is sparingly soluble in cold light petroleum, but dissolves readily on heating. It is very readily soluble in chloroform, ether, ethyl acetate, or acetone in the cold, or in hot alcohol, and separates out from dilute alcohol in small but well formed plates, melting at $78.5-79^{\circ}$, and resolidifying at $76.5-77^{\circ}$.

The sodium salt was prepared by neutralising the acid with a warm solution of pure sodium hydroxide. A small quantity of alcohol was added to the solution, when, on cooling, the sodium salt separated out. It was recrystallised from dilute alcohol, from which it separated in glistening leaflets, which were dried at 100° and analysed.

0.2064 gave 0.0458 Na_2SO_4 . Na = 7.19. $C_{18}H_{33}O_8Na$ requires Na = 7.19 per cent.

The sodium salt is sparingly soluble in cold water, but dissolves

readily on heating. It is sparingly soluble in alcohol and insoluble in acetone.

The following attempts were made to reconvert the acid $C_{18}H_{34}O_{3}$ into dihydroxystearic acid, but in all three cases it was recovered unchanged: (1) boiling the acid with a 2 per cent. solution of potassium hydroxide for 11 hours; (2) boiling the acid with 10 per cent. sulphuric acid for 12 hours; (3) heating 0.5 gram of the acid, 30 c.c. of water, and 2 grams of barium hydroxide in a sealed tube at 143° for 8 hours. The investigation of this acid is being continued.

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