XIX.—*Determination of the Constitution of Fatty Acids. Part I.*

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SOME short time ago one of us, in conjunction with Professor Perkin (Trans., 1898, 73, 1), described an investigation of a complicated mixture of fatty acids derived from the fusion of camphoric acid with alkalis; as the difficulties encountered in identifying some of the fatty acids were very great, it was considered desirable to try and devise a method for the determination of the constitution of such acids, and the object of this paper is to give a short account of experiments which have been carried out in this direction.

So far as our present experiments go, we think they may be described as satisfactory, and although the method may not be an infallible one, it seems likely to prove of considerable importance as a means of establishing the constitution of organic acids.

The method of procedure which was suggested to us by Professor Perkin is the following. Starting with a fatty acid, $X \cdot CH_2 \cdot CH_2 \cdot COOH$, this is first converted into the ethylic salt of the monobromo-derivative by Volhard's process (*Annalen*, 1887, 242, 61); from the work of

* The experiment referred to was made on the methylic tartrates, but this would not materially alter the result as stated above.

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Auwers and Bernhardt (*Ber.*, 1891, 24, 2209) and others, there can be no doubt that, under these conditions, the bromine atom takes up the α -position, yielding the substance $X \cdot CH_2 \cdot CHBr \cdot COOEt$. The brom-etheral salt is then treated with quinoline or diethylaniline (compare Weinig, *Annalen*, 1894, 280, 253), whereby the elements of hydrobromic acid are removed, and the ethylic salt of an unsaturated acid of the acrylic series, $X \cdot CH : CH \cdot COOEt$, is produced. The free acid obtained from this salt by hydrolysis is then oxidised, first with potassium permanganate, giving rise to the corresponding dihydroxy-acid, $X \cdot CH(OH) \cdot CH(OH) \cdot COOH$, and then with chromic acid, when the molecule is broken down at the position occupied by the double bond in the unsaturated acid, giving $X \cdot COOH$ and $COOH \cdot COOH$.

The result is, therefore, the production of oxalic acid and a fatty acid (or *ketone*) containing two carbon atoms less than the original acid, and as the number of isomerides decreases greatly with loss of two carbon atoms, the possibility of identification is much enhanced.

We have carried out this process with three acids, namely, valeric, *iso*-valeric, and *iso*-butylacetic acids, as we considered that the oxidation products of the acids of the acrylic series corresponding with these fatty acids would be typical examples of what might be expected to be met with in actual determinations. Thus valeric acid gives ethylacrylic acid, and this, on oxidation, propionic acid (*normal acid*); *iso*-valeric acid gives dimethylacrylic acid, which then yields acetone (*ketone*); and *iso*-butylacetic acid gives *iso*-propylacrylic acid, and, on oxidation, *iso*-butyric acid (*iso-acid*).

With the three acids mentioned, the method works well. In all cases we have been careful to note the yields of substances obtained in the various stages, and there is here appended a tabulated list of results. The numbers express the percentage yields, and are referred, in the case of the unsaturated ethereal salt and acid, to the amounts theoretically obtainable from the brom-etheral salt employed; and in the case of the "acid or ketone produced on oxidation," to the amounts theoretically obtainable from the unsaturated acid used.

Acid employed.	Brom-etheral salt.	Unsaturated ethereal salt.	Unsaturated acid.	Acid or ketone produced on oxidation.
Valeric acid.....	97.5	52.0	41.0	53.0
<i>iso</i> -Valeric acid.....	—	80.0	55—60	47.0
<i>iso</i> -Butylacetic acid.	93.0	70.0	61.0	50.0

The poor yield of unsaturated ethereal salt obtained from ethylic bromovalerate is accounted for by the fact that there is also pro-

duced a considerable quantity of some substance of higher boiling point, which is at present under investigation ; and the comparatively small amount of the solid dimethylacrylic acid obtained from its ethylic salt is due to the fact that an oily substance is produced at the same time (see page 164). In no case was oxalic acid identified in the products of the reaction, nor could it be expected to resist the action of the strong oxidising agents employed.

We have experimented with both quinoline and diethylaniline, using them as reagents for the elimination of the elements of hydrobromic acid, and find that, with the lower fatty acids, the one gives quite as good results as the other, but with the higher fatty acids diethylaniline is to be preferred. For example, in the case of ethylic bromisobutylacetate, the 42 per cent. yield of ethylic isopropyl acrylate, obtained when using quinoline, was increased to 70 per cent. by employing diethylaniline. Quinoline always gives rise to tarry products, which are not easy or agreeable to work with, whereas diethylaniline does not ; in the latter case, however, the substances require to be heated together for a much longer time, and it is very difficult to eliminate the last traces of hydrobromic acid. As, however, the unsaturated ethereal salts are subsequently heated with alcoholic potash, the latter objection is of no great moment.

We intend to further test the efficacy of the method by trying it on other acids, such as (a) stearic acid, and from preliminary experiments already made with this acid, it seems highly probable that the various reactions will take place as expected. The insolubility of the hydroxylated higher fatty acids in water may render the oxidation with chromic acid a difficult operation, in which case it will be of interest to see whether fusion with potash will serve a similar purpose.

(b) It will be noticed that, among the acids examined, none contain alkyl groups in the α -position. In such a case, as, for example, ethylisopropylacrylic acid, quite a new point is raised. This acid,

still contains one α -hydrogen atom, and should, therefore, yield an α -brom-ethereal salt in the usual manner ; but when the latter is treated with quinoline, there are two possible ways in which hydrobromic acid may be eliminated (compare Perkin, *Trans.*, 1896, 69, 1466), giving rise to

Methyl- α -isopropylacrylic acid.

or

Dimethyl- α -ethylacrylic acid.

The study of the oxidation products of the unsaturated acid or acids produced would, therefore, be of special importance.

(c) The method may also prove to be applicable in the case of di-basic acids, and we propose to try it on pimelic (isopropylsuccinic) acid.

EXPERIMENTAL.

Acetone from Isovaleric Acid.

Instead of starting with isovaleric acid, the ethylic salt of α -bromisovalerate supplied by Kahlbaum was employed, which, on distillation, boiled constantly at 185° — 186° , and a bromine determination gave the following numbers.

0.2514 gave 0.2275 AgBr. Br = 38.50.

$C_4H_8Br \cdot COOC_2H_5$ requires Br = 38.28 per cent.

Treatment of Ethylic α -Bromisovalerate with Quinoline.—Weinig (*Annalen*, 1894, 280, 253) has shown that diethylaniline may be used instead of alcoholic potash for the elimination of the elements of hydrobromic acid, and later Perkin and Goodwin (this Journal, 1896, 69, 1470) described experiments in which they employed quinoline for the preparation of dimethylacrylic acid from ethylic α -bromisovalerate. We have followed their instructions exactly, using 50 grams (1 mol.) of the brom-etheral salt and 70 grams (2 mols.) of freshly distilled coal-tar quinoline; on fractionating the product, it was found to distil between 153° and 155° as a colourless oil of penetrating odour. The yield is 80 per cent. of the theoretical.

This ethereal salt is readily saponified by alcoholic potash, and the dimethylacrylic acid formed boils constantly at a temperature of 114° under a pressure of 40 mm. On standing, the distillate solidifies almost completely to a mass of needle-shaped crystals, which, after being freed from the mother liquor by spreading on a porous plate and recrystallisation from light petroleum (b. p. 60° — 80°), melted at 68.5° — 69° , and gave the following results on analysis.

0.1047 gave 0.2296 CO_2 and 0.0744 H_2O . C = 59.80; H = 7.90.

$C_5H_8O_2$ requires C = 60.00; H = 8.00 per cent.

The yield of pure acid is from 55—60 per cent. of the theoretical obtainable from the brom-etheral salt employed. On extracting the porous plate just mentioned with ether, a small amount of an oily liquid was obtained which showed no signs of solidifying even after long standing, and which was not further investigated.

Perkin and Goodwin (*loc. cit.*) also mention this oily bye-product.

Treatment of Ethylic α -Bromisovalerate with Diethylaniline.—In using quinoline for the elimination of the elements of hydrobromic acid, there is always a considerable quantity of tarry matter formed, and in later experiments we found that diethylaniline could be used with

advantage instead of quinoline; the yield of unsaturated ethereal salt is considerably increased, and no tarry products are produced, although the mixture requires to be heated for a much longer period. The yield of ethylic dimethylacrylate as obtained in the experiments just described is good, but we thought it of sufficient interest to try the effect of diethylaniline on ethylic α -bromisovalerate. The process was carried out exactly as described on page 166.

There is, however, in this case, no particular advantage to be derived, for the yield of ethylic dimethylacrylate is no higher than when quinoline is employed.

Oxidation of Dimethylacrylic Acid with Potassium Permanganate.—Ten grams of dimethylacrylic acid were neutralised with potassium hydroxide and dissolved in 600 c.c. of water; the whole was stirred with a turbine, and maintained at 0° throughout the operation; a rapid current of carbonic anhydride was then passed in, and a cold solution of 12 grams of potassium permanganate in 400 c.c. of water gradually added from a tap funnel. After standing overnight, the liquid was filtered from precipitated manganese dioxide, and evaporated to a small bulk; no attempt was made to isolate the dihydroxy-acid produced, but the liquid was at once submitted to the process of:—

Oxidation with Potassium Dichromate and Sulphuric Acid.—For this purpose, the evaporated liquid was placed in a flask connected with a condenser, and, after warming to 70° on the water-bath, a solution of 30 grams of potassium dichromate in dilute sulphuric acid was slowly run in, the heating continued for eight hours, and the whole steam distilled. The distillate, which was slightly acid to litmus paper, was carefully neutralised with potassium hydroxide, and again steam distilled; on adding an alcoholic solution of parabromophenylhydrazine to the distillate, there was an immediate and copious precipitate, which was collected and dried on a porous plate. After recrystallisation from light petroleum (b. p. 80 — 100°), it was obtained as beautiful, shining scales melting at 94° . Bromine determinations gave the following results.

- I. 0.2886 gave 0.2314 AgBr. Br = 34.09.
 - II. 0.1226 „ 0.0998 AgBr. Br = 34.58.
- $(\text{CH}_3)_2\text{C}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}$ requires Br = 35.24 per cent.

Although the figures obtained are not so good as might be desired, there can be no doubt that this substance is the parabromophenylhydrazine compound of acetone (compare Neufeld, *Annalen*, 1888, 248, 96), the ease with which it undergoes decomposition accounting for the lowness of bromine found.

The parabromophenylhydrazine compound obtained weighed 10.7 grams, whereas the amount theoretically obtainable from 10 grams of

dimethylacrylic acid is 22.7 grams; this is a 47 per cent. yield of the substance.

The residue from the steam distillation was examined for oxalic acid, after removing the chromium by the use of sulphurous acid and then boiling with excess of sodium carbonate. No traces of the acid were found, nor is this to be wondered at, as, when produced, it would at once be further oxidised to carbonic anhydride and water, in presence of the strong oxidising agent employed. This remark also applies to the other oxidations mentioned in this paper; in no case was any oxalic acid detected.

Propionic Acid from Valeric Acid.

Preparation of Valeric Acid.—This acid was prepared by the condensation of ethylic sodiomalonate and normal propylic iodide, and, after saponification, heating the propylmalonic acid so formed. It boiled constantly between 184° and 185° (uncorr.).

Bromination of Valeric Acid.—Forty-four grams of valeric acid were brominated with 135 grams of dry bromine and 4.5 grams of amorphous phosphorus in the usual manner, the product slowly poured into three times its volume of absolute alcohol, and the ethylic α -bromovalerate extracted with ether and distilled under diminished pressure. It boils constantly at a temperature of 110° (40 mm.), and is obtained in nearly theoretical amount (97.5 per cent.).

Treatment of Ethylic α -Bromovalerate with Diethylaniline.—Seventy-six grams (1 mol.) of the brom-etheral salt, and 115 grams (2 mols.) of diethylaniline, were heated in two portions in a flask attached to an air condenser and containing a thermometer, so that the temperature of reaction could be noted; this begins at about 175° , and the thermometer rises rapidly to 190 — 200° , at which temperature the whole was maintained for 6 hours. The product, when cold, was poured into excess of dilute hydrochloric acid, and extracted with ether, &c., but as it was found to contain bromine, it was again heated with diethylaniline (1 mol.) for 16 hours at 190 — 200° . After extracting in the manner just described, the ethereal solution was dried over calcium chloride, the ether distilled off, and the liquid residue fractionated; by this means, 24 grams of ethylic ethylacrylate were obtained boiling at 155 — 160° . This is only a 52 per cent. yield, which is accounted for by the fact that 12 grams of some substance of higher boiling point (270 — 280°) was also produced, the nature of which is at present under investigation.

Ethylic ethylacrylate is readily saponified by alcoholic potash, yielding *ethylacrylic acid* as a colourless, oily liquid, with pungent, characteristic odour, boiling at 195 — 197° under atmospheric pressure, and

showing no signs of solidification even when cooled to -14° . The yield of pure acid is 41 per cent. of the amount theoretically obtainable from the ethylic bromovalerate employed.

A portion of the acid was converted into the silver salt and analysed.

0.3510 gave 0.1834 Ag. $\text{Ag} = 52.25$.

$\text{C}_5\text{H}_7\text{O}_2\text{Ag}$ requires $\text{Ag} = 52.17$ per cent.

Oxidation of Ethylacrylic Acid.—Fourteen grams of the acid were oxidised exactly as described on page 165, firstly, with 16 grams of potassium permanganate, and then with a solution of 45 grams of potassium dichromate dissolved in dilute sulphuric acid; the mixture was distilled in a current of steam, and the distillate, after neutralisation with potassium hydroxide, was evaporated to complete dryness, finally on the water-bath. The fatty acids obtained on distilling the residue with concentrated sulphuric acid were dried by standing for some time in contact with concentrated sulphuric acid, and then fractionally distilled. Eventually, nearly the whole of the acids boiled between 137° and 143° , and a portion boiling at 140° was converted into the silver salt and analysed.

0.1914, on ignition, gave 0.1144 Ag. $\text{Ag} = 59.77$.

0.2386 gave 0.1744 CO_2 , 0.0640 H_2O , and 0.1420 Ag. $\text{C} = 19.92$;
 $\text{H} = 2.97$; $\text{Ag} = 59.51$.

$\text{C}_2\text{H}_5\text{COOAg}$ requires $\text{C} = 19.89$; $\text{H} = 2.76$; $\text{Ag} = 59.66$ per cent.

The fraction boiling between 137° and 143° was then converted into the anilide by heating for 24 hours with twice its volume of pure aniline, and the solid product was repeatedly crystallised from light petroleum (b. p. $80-100^{\circ}$), from which it separates in white, glistening plates melting at $102-103^{\circ}$ (compare Crossley and Perkin, *Trans.*, 1898, 73, 34).

0.1814 gave 15.2 c.c. moist nitrogen at 21° and 762 mm. $\text{N} = 9.56$.

$\text{C}_2\text{H}_5 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ requires $\text{N} = 9.39$ per cent.

These data prove conclusively that the acid produced by oxidising ethylacrylic acid in the manner described is propionic acid. The amount of propionic acid obtained was 5.5 grams, which corresponds with a 53 per cent. yield of the amount theoretically obtainable from the ethylacrylic acid used.

Isobutyric Acid from Isobutylacetic Acid.

Preparation of Isobutylacetic Acid.—This acid was prepared by the condensation of ethylic sodiomalonate with isobutylic bromide, and

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subsequent distillation of the product, after saponification with alcoholic potash. The acid boiled at 198—200°.

Bromination of Isobutylacetic Acid.—Fifty-two grams of the acid, 4·8 grams of amorphous phosphorus, and 140 grams of dry bromine were treated in the usual manner. *Ethyl α-bromisobutylacetate* was obtained as a colourless, pleasant smelling liquid boiling at 115° under a pressure of 43 mm.

0·1530 gave 0·1295 AgBr. Br = 36·01.

$C_5H_{10}Br \cdot COOC_2H_5$ requires Br = 35·87 per cent.

The yield of the ethylic salt was 93 per cent. of the theoretical.

Treatment of Ethylic Bromisobutylacetate with Quinoline or Diethylaniline.—Eighty-five grams of the bromethylic salt were treated in two portions with quinoline exactly as described on page 164, and the unsaturated ethereal salt was distilled, when 22 grams were obtained boiling at 168—169° at the ordinary pressure. As this is only 42 per cent. of the amount theoretically obtainable, the effect of diethylaniline on the brom-ethereal salt was tried, when the yield was increased to 70 per cent. It was, however, found exceedingly difficult to get rid of the last traces of halogen; and even after a third treatment with diethylaniline, the substance did not give good results on analysis. Possibly this is due to the presence of traces of halogen.

I. 0·1040 gave 0·2526 CO_2 and 0·0966 H_2O . C = 66·23; H = 10·31.

II. 0·1570 „ 0·3820 CO_2 „ 0·1416 H_2O . C = 66·36; H = 10·02.

$C_5H_9 \cdot COOC_2H_5$ requires C = 67·60; H = 9·86 per cent.

Perkin and Goodwin (Trans., 1896, 69, 1471) found that ethylic dimethylacrylate, prepared in a similar manner, did not give good results on analysis, but no explanation of the fact is offered.

When hydrolysed with alcoholic potash, the oily, unpleasant smelling liquid boiling at 169° is converted into *isopropylacrylic acid*, which is a colourless, oily liquid of exceedingly unpleasant odour, boiling at 133° (50 mm.); it does not solidify when cooled to -15°. The yield is 61 per cent. of that theoretically obtainable.

The *silver salt* is a white, amorphous, insoluble precipitate. On analysis, it gave the following numbers.

0·2536 gave, on ignition, 0·1232 Ag. Ag = 48·58.

$C_6H_9O_2Ag$ requires Ag = 48·77 per cent.

Oxidation of Isopropylacrylic Acid.—Twenty grams of the acid were oxidised with 30 grams of potassium permanganate, and afterwards with 60 grams of potassium dichromate dissolved in dilute sulphuric acid, and worked up exactly as already described on page 165; after careful fractionation of the acid, the portion boiling at 153—154° was converted into the silver salt and analysed.

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0.2044, on ignition, gave 0.1134 Ag. Ag = 55.47.

0.2154 gave 0.1900 CO₂, 0.0682 H₂O, and 0.1198 Ag. C = 24.10 ;
H = 3.52 ; Ag = 55.61.

C₃H₇·COOAg requires C = 24.61 ; H = 3.59 ; Ag = 55.38 per cent.

The remainder of the acid (b. p. 152—158°) was converted into the anilide which crystallised from light petroleum (b. p. 80—100°) in glistening, feathery needles melting at 104—105° (compare Trans., 1898, 73, 34).

0.1296 gave 10 c.c. moist nitrogen at 20° and 762 mm. N = 8.84.

C₃H₇·CO·NH·C₆H₅ requires N = 8.59 per cent.

The acid (50 per cent. yield) produced by the oxidation of isopropyl-acrylic acid was, therefore, isobutyric acid, and the oxidation had taken place in the manner expected.

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