LV.—*Methylisobutylacetic acid*,
 $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{COOH}$.

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IN a recent paper on $\beta\beta$ -methylethylpropionic acid (this vol., 264), it was pointed out that the object of the work was to obtain by synthesis some of the fatty acids which had not been previously described, and to compare their properties with those of some fatty acids of unknown constitution derived from camphoric acid by fusion with potash. With this same object in view, we have prepared and investigated the properties of methylisobutylacetic acid under the direction of Dr. Perkin, the results of the investigation forming the subject of the present paper.

The acid was obtained from ethylic malonate in two ways, which however only differed in the order of insertion of the groups methyl and isobutyl. By one method, ethylic isobutylmalonate,

was prepared by the action of isobutylic bromide on ethylic sodio-malonate, and this was converted into ethylic methylisobutylmalonate, $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_3)(\text{COOEt})_2$, by treating its sodium derivative with methylic iodide. By the second method, ethylic sodio-methylmalonate was acted on by isobutylic bromide, the product being (as before) ethylic methylisobutylmalonate. Judging from the subsequent yield of acid, the former method seems to give rather better results.

Ethylic methylisobutylmalonate is an oil which boils at $230-235^\circ$, and, on hydrolysis, yields methylisobutylmalonic acid,

a solid, melting at 122° ; this, in its turn, is decomposed on distillation, losing carbon dioxide and yielding methylisobutylacetic acid, $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{COOH}$. The pure acid boils at $204-205^\circ$ under a pressure of 755 mm.

For the purpose of identification, the following derivatives of methylisobutylacetic acid have been prepared.

Ethylic salt, $\text{C}_6\text{H}_{13} \cdot \text{COOEt}$; an oil boiling at $165-166^\circ$ (769 mm.).

Acid chloride, $\text{C}_6\text{H}_{13} \cdot \text{COCl}$; a pungent-smelling liquid boiling at $152-153^\circ$ (745 mm.).

Amide, $\text{C}_6\text{H}_{13} \cdot \text{CO} \cdot \text{NH}_2$; a colourless solid crystallising from ether in needles melting at 90° .

Anilide, $\text{C}_6\text{H}_{13} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$; a colourless solid crystallising from

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high boiling, light petroleum in long, silky needles melting at 110—111°.

Paratoluidide, $C_6H_{13} \cdot CO \cdot NH \cdot C_7H_7$; a colourless solid separating from low boiling light petroleum in minute needles melting at 86°.

EXPERIMENTAL PART.

Methylisobutylmalonic acid, $CH(CH_3)_2 \cdot CH_2 \cdot C(CH_3)(COOH)_2$.

The details of the first method of preparation are as follows.

Isobutylic bromide (109 grams) was added to a mixture of ethylic malonate (127 grams) with a solution of sodium (18.5 grams) in alcohol (200 grams), and the whole heated on the water bath until the mixture was perfectly neutral. When cold, it was diluted with water, and the oil extracted with ether; the ethereal solution was then washed with water, dried with calcium chloride, and the ether distilled off on the water bath. The oily residue was fractionated, and the portion boiling at 224—226° (105 grams), and consisting of pure ethylic isobutylmalonate, was added to a solution of sodium (11.1 grams) in alcohol (150 grams), and treated with methylic iodide (70 grams). The mixture was heated on the water bath till neutral, and afterwards subjected to the same treatment as before, the final product being ethylic methylisobutylmalonate, $CH(CH_3)_2 \cdot CH_2 \cdot C(CH_3)(COOEt)_2$. It boils at 230—235°, and the yield was 86 grams.

This oil was not analysed, but at once saponified by boiling with an excess of alcoholic potash, the alcohol being afterwards removed by diluting with water and evaporating the liquid to dryness; the solid residue was then dissolved in water, acidified strongly, and repeatedly extracted with ether. After distilling off the ether, a viscous liquid remained, which solidified, however, on standing; it was placed in a vacuum over sulphuric acid for a day, then dried on a porous plate, and purified by recrystallisation from a small quantity of water.

0.1063 gave 0.2151 CO_2 and 0.0793 H_2O . $C = 55.19$; $H = 8.29$.

$C_8H_{14}O_4$ requires $C = 55.17$; $H = 8.05$ per cent.

Methylisobutylmalonic acid melts at 122°. It is extremely soluble in water, and can only be crystallised from very concentrated solutions; it can be dried at 100° without decomposition. The silver salt was prepared by precipitating a solution of its ammonium salt with silver nitrate; after washing and drying, it was analysed by ignition.

0.1737 gave 0.0972 Ag. $Ag = 55.95$.

$C_8H_{12}Ag_2O_2$ requires $Ag = 55.67$ per cent.

It was found that the silver salt could be heated to 135° without decomposition.

Methylisobutylacetic acid, $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{COOH}$.

The dibasic acid was heated in a retort to $195\text{--}215^{\circ}$ when it decomposed into carbon dioxide and a fatty acid, and this acid, after repeated fractionation, was found to boil constantly at $204\text{--}205^{\circ}$. A second sample of the acid was prepared from ethylic malonate by introducing first the methyl group, and afterwards the isobutyl group, the details of the processes being practically the same as those given for the other method. The fatty acid obtained boiled at exactly the same temperature as did the other sample, namely, $204\text{--}205^{\circ}$, under a pressure of 755 mm.; the penetrating odour and general properties of this acid are similar to those of the higher fatty acids.

0.1034 gave 0.2440 CO_2 and 0.0994 H_2O . $\text{C} = 64.36$; $\text{H} = 10.68$.

$\text{C}_7\text{H}_{14}\text{O}_2$ requires $\text{C} = 64.61$; $\text{H} = 10.77$ per cent.

Ethylic methylisobutylacetate, $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{COOC}_2\text{H}_5$.—This was prepared by saturating a solution of the acid in pure ethylic alcohol with dry hydrogen chloride, and allowing the mixture to remain for some time; water was then added, and the oil which separated extracted with ether. The ethereal solution, after being washed first with sodium carbonate, and then with water, was dried with calcium chloride, and the ether evaporated. An oil remained behind which, on fractionation, was observed to boil constantly at $165\text{--}166^{\circ}$ (769 mm.).

Found..... $\text{C} = 68.37$; $\text{H} = 11.44$ per cent.

Theory for $\text{C}_9\text{H}_{18}\text{O}_2$.. $\text{C} = 68.35$; $\text{H} = 11.39$..

Methylisobutylacetyl chloride, $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{COCl}$.—This compound was prepared by heating 11 grams of the acid with 4 grams of phosphorus trichloride for 10 minutes in a reflux apparatus; after decanting from the heavier phosphorous acid, the liquid was fractionated. The acid chloride boils at $152\text{--}153^{\circ}$ (745 mm.), and possesses the pungent and disagreeable odour characteristic of the higher acid chlorides. Analysis.

Found..... $\text{Cl} = 24.05$ per cent.

Theory for $\text{C}_6\text{H}_{13}\text{COCl}$.. $\text{Cl} = 23.90$..

Methylisobutylacetamide, $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{CONH}_2$.—This substance was obtained from the ethylic salt and also from the acid chloride.

The ethylic salt was heated with concentrated aqueous ammonia in a sealed tube at 180° for 10 hours, and the product repeatedly

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extracted with ether; the ethereal solution was dried with calcium chloride, the ether removed by evaporation, and the residue poured into a basin to solidify. The solid was then recrystallised first from ether and subsequently from light petroleum of high boiling point.

The acid chloride was slowly added to concentrated aqueous ammonia, the mixture extracted with ether several times, and the ethereal solution dried with calcium chloride. The amide was then extracted and purified as in the previous case. Both samples melted at 90° (a low melting point for an amide of a higher fatty acid), and crystallised from both petroleum and ether in needles.

Found..... N = 10.70 per cent.

Theory for $C_6H_{13}\cdot CO\cdot NH_2$.. N = 10.85 ,,

This amide is extremely soluble in alcohol and chloroform, rather less so in ether, and sparingly in ethylic acetate, benzene, and light petroleum of low boiling point; it is insoluble in cold water.

Methylisobutylacetanilide, $CH(CH_3)_2\cdot CH_2\cdot CH(CH_3)\cdot CO\cdot NH\cdot C_6H_5$.—This anilide was prepared by boiling the acid with twice its weight of aniline for 24 hours in a reflux apparatus; the solid product was dissolved in ether, the ethereal solution washed with hydrochloric acid, then with sodium carbonate solution, and finally with water. After drying with calcium chloride, the ether was distilled off, and the dark-coloured residue purified by repeated crystallisation from petroleum (b. p. 100 — 120°), from which it separates in beautiful, long, silky needles melting at 110 — 111° .

Found..... N = 7.10 per cent.

Theory for $C_6H_{13}\cdot CO\cdot NH\cdot C_6H_5$.. N = 6.83 ,,

This anilide is very soluble in ether, chloroform, benzene, ethylenic chloride, ethylic acetate, and alcohol; water precipitates it from a concentrated alcoholic solution, and it can be conveniently recrystallised from dilute alcohol. It is sparingly soluble in cold petroleum, but it dissolves readily in hot petroleum; it is insoluble in cold water.

Methylisobutylacetoparatoluidide,

—The preparation and purification of this substance only differed from those of the anilide in two points; the mixture of acid with $2\frac{1}{2}$ times its weight of paratoluidine was heated for a shorter period (15 hours) on account of the higher boiling point of paratoluidine, and the crude product was recrystallised from light petroleum of low boiling point. It crystallises in minute needles melting at 86° .

Found..... N = 6.19 per cent.

Theory for $C_6H_{13}\cdot CO\cdot NH\cdot C_7H_7$.. N = 6.39 ,,

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This toluidide is very soluble in alcohol, chloroform, ether, benzene, and ethylic acetate; it is sparingly soluble in cold, but readily in hot light petroleum; it is insoluble in cold water.

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