

XXXIX.—*The Separation of β -Crotonic Acid from α -Crotonic Acid.*

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THE separation of β -crotonic acid from α -crotonic acid is effected, according to Michael and Schulthess (*J. pr. Chem.*, 1892, [ii], 46, 245), by means of the different solubilities of the sodium salts in alcohol. One part of sodium α -crotonate dissolves in 340 parts of alcohol (98—99 per cent.) at 15°, whilst at the same temperature, one part of sodium β -crotonate requires 12·7 parts of alcohol of the same strength; the more soluble β -crotonate is then decomposed by hydrochloric acid, and the free acid purified by distillation *in vacuo*. β -Crotonic acid, obtained by Michael's method or by the method described by Fittig and Kochs (*Annalen*, 1892, 268, 15), is stated by J. Wislicenus (*Chem. Centr.*, 1897, ii, 259) to contain α -crotonic acid, in spite of Michael's acid giving no precipitate in alcoholic precipitate on neutralisation

with alcoholic sodium hydroxide. The pure acid has been obtained (J. Wislicenus, *loc. cit.*) by transforming liquid β -crotonic acid, dissolved in alcohol, into its sodium salt, and by removing the sodium α -crotonate by concentrating the solution and precipitating the last traces of the salt by the addition of an equal volume of ether; the sodium β -crotonate left in solution is decomposed by hydrochloric acid, and the acid, which is purified by recrystallisation from pentane, crystallises in needles or prisms melting at $15.45\text{--}15.5^\circ$; the yield must be small, and the method of preparation seems tedious.

In a paper by one of us (Morrell and Hanson, *Trans.*, 1904, 85, 197), the optically active constituents of $\alpha\beta$ -dihydroxybutyric acid, prepared from α -crotonic acid, were described, and it was stated that the optically active constituents of a second $\alpha\beta$ -dihydroxybutyric acid were under investigation.

The oxidation of "*isocrotonic*" acid, supplied by Kahlbaum, gave an acid the brucine and quinine salts of which were virtually identical with those of symmetrical $\alpha\beta$ -dihydroxybutyric acid, so that it was necessary to devise a method of separation of the two isomeric acids, and to prepare salts of β -crotonic acid, which are less soluble than the corresponding α -crotonates. The brucine salts of the two acids were found to have different solubilities, and the β -acid yielded the less soluble salt, but unfortunately these salts are very soluble in all ordinary solvents. The quinine salts, however, are sparingly soluble in water, and the salt of the β -acid is much less soluble than that of the α -acid; it is therefore quite easy to separate the two salts by crystallisation from water, and the quinine β -crotonate can be recrystallised from that solvent without undergoing any change in melting point. From the quinine salt, the barium β -crotonate has been prepared, and this has given the pure acid by treatment with dilute sulphuric acid in the presence of pure ether. The melting point agrees with that given by Wislicenus, namely, 15° . Determinations of the density, molecular weight, and molecular refraction have been made. The molecular weight in glacial acetic acid solution corresponds with the formula $\text{C}_4\text{H}_6\text{O}_2$, and there seems no justification for the double formula proposed by Wislicenus (*Chem. Centr.*, 1897, ii, 259).

Michael and Schulthess (*loc. cit.*) state that the purity of β -crotonic acid can be shown by neutralising its alcoholic solution with 10 per cent. caustic soda solution; sodium β -crotonate is very soluble in alcohol, and, under the experimental conditions, no precipitate ought to be formed on neutralisation. We have tested the β -crotonic acid prepared from the quinine salt, following Michael's directions, and have found that no insoluble sodium crotonate was formed; moreover, the determination of the solubility of sodium β -crotonate gave values agreeing with those obtained by Michael.

EXPERIMENTAL.

Brucine α -Crotonate.—This salt, which was prepared by neutralising a boiling aqueous solution of α -crotonic acid with brucine, is exceedingly soluble in water, alcohol, or benzene; 5 grams dissolve in 7 c.c. of hot benzene, and the salt slowly crystallises out in hexagonal prisms, which soften at 90° and melt at 125° .

Quinine α -Crotonate.—This salt crystallises from a hot aqueous solution in aggregates of slender needles, which melt at 136° without decomposition; a solubility determination at 17° showed that 0.3203 gram was dissolved in 13.7 grams of solution, hence the solubility of the salt in water at 17° is 2.4.

"isocrotonic" Acid.—The acid was obtained from Kahlbaum, who stated that it was prepared by heating β -hydroxybutyric acid, and freed from α -crotonic acid, as far as possible, by distillation *in vacuo* and by freezing out the last traces of the α -isomeride at -20° . Several analyses of the acid were made, but the percentages of carbon were invariably found to be too low (compare Michael and Schulthess, *loc. cit.*).

0.1845 gave 0.3732 CO_2 and 0.1145 H_2O . C = 55.16; H = 6.89.

0.1950 „ 0.3920 CO_2 „ 0.1243 H_2O . C = 54.82; H = 7.08.

$\text{C}_4\text{H}_6\text{O}_2$ requires C = 55.8; H = 6.97 per cent.

On distilling 100 grams of "*isocrotonic*" acid, about 40 grams boiled at 87° under 15–30 mm. pressure; the residue in the distilling flask became solid at the ordinary temperature, and the distillate was no purer than the original acid.

0.1773 gave 0.3515 CO_2 and 0.1190 H_2O . C = 54.06; H = 7.45.

The analysis showed that it was not possible to purify the acid by further distillation. The liquid β -crotonic acid passed slowly into α -crotonic acid and solidified completely.

Brucine β -Crotonate.—This salt is very soluble in water, alcohol, or benzene; from the last solvent, it crystallises out in prismatic needles, which melt between 98° and 100° without decomposition.

Quinine β -Crotonate.—The salt was prepared from the crude β -crotonic acid, and also from the acid which had been freshly distilled; the first crop of crystals melted at 147° , and on recrystallisation from water the fraction which separated first melted at 156 – 158° , the melting point being unchanged on repeated crystallisation from this solvent. The mother liquors, from the crystallisation of the fraction melting at 147° , gave crystals which melted at 134 – 136° . It would seem as if the two quinine salts crystallised together in about

equal quantities, and, on recrystallisation, separated into a less soluble form melting at 156—158° and a more soluble form melting at 134—136°.

β -Crotonic acid, which had been distilled *in vacuo* at 87°, gave a quinine salt which melted at 147°. Seventy grams of the quinine salt (m. p. 147°), obtained from 30 grams of redistilled β -crotonic acid, gave, on recrystallisation, 60 grams of salt melting at 156°. The mother liquors were found to contain the quinine α -crotonate (m. p. 132°). There is no evidence that quinine β -crotonate changes into the α -salt on crystallisation from water. The quinine β -crotonate crystallises in prismatic needles; an air-dried specimen of the crystals, on heating at 105°, does not lose in weight. A determination of the solubility of the salt gave the following numbers: 13.5930 grams of a saturated aqueous solution at 17° contained 0.1410 gram of the salt, hence its solubility in water at 17° is 1.04.

0.3045 gave 18 c.c. moist nitrogen at 16° and 757 mm. N=6.97.

0.1858 „ 0.4805 CO₂ and 0.1212 H₂O. C=70.5; H=7.24.

C₂₀H₂₄O₂N₂, C₄H₆O₂ requires C=70.24; H=7.31; N=6.83 per cent.

Barium β -Crotonate.—The quinine β -crotonate (m. p. 157°) was dissolved in hot water and decomposed by a slight excess of baryta water. The quinine was filtered off and a current of carbon dioxide passed through the filtrate in order to remove excess of baryta. The clear liquid was concentrated to a small bulk *in vacuo* at 50° and poured into alcohol; the barium salt was precipitated in large, lustrous, rhomboid plates, which contained a molecule of water of crystallisation.

0.9925 (air-dried) lost, at 110°, 0.0562 H₂O. H₂O=5.64.

0.2255 (dried at 110°) gave 0.1723 BaSO₄. Ba=44.85.

(C₄H₅O₂)₂Ba.H₂O requires H₂O=5.53. (C₄H₅O₂)₂Ba requires Ba=44.62 per cent.

β -Crotonic Acid.

The barium β -crotonate was covered with pure ether and a little water added; the calculated quantity of 10 per cent. sulphuric acid was added drop by drop, the mixture being thoroughly shaken; the barium sulphate was removed by filtration and the clear ethereal solution of β -crotonic acid was concentrated *in vacuo* at the ordinary temperature. On cooling, the liquid acid solidifies immediately in long needles melting at 15°. Wislicenus gives the melting point of the acid as 15.5°; the melting point with the thermometer in the solid is 14—15°.

0.1856 gave 0.3765 CO_2 and 0.1161 H_2O . $\text{C} = 55.32$; $\text{H} = 6.94$.

0.1895 „ 0.3845 CO_2 „ 0.1180 H_2O . $\text{C} = 55.33$; $\text{H} = 6.91$.

$\text{C}_4\text{H}_6\text{O}_2$ requires $\text{C} = 55.8$; $\text{H} = 6.97$ per cent.

A molecular weight determination in glacial acetic acid gave the following numbers:

0.3903 in 16.7390 glacial acetic acid gave $\Delta t = 1.062^\circ$. $\text{M. W.} = 85.6$.

$\text{C}_4\text{H}_6\text{O}_2$ requires $\text{M. W.} = 86$ per cent.

The density of the acid was found to be $D_4^{12.5} = 1.0342$; Wislicenus (*loc. cit.*) obtained $D_4^{15} = 1.0312$.

Mr. Gold, of St. John's College, was kind enough to determine the refractive index of the acid for sodium light: $\mu_D^{14} = 1.4483$, molecular refraction = 37.27. The molecular refraction for α -crotonic acid is 36.94 (Kannonikoff, *J. pr. Chem.*, 1885, [ii], 31, 347).

In order to test the purity of the β -crotonic acid obtained from the quinine salt, the following experiments were performed:

(a) 0.5 gram of the acid was dissolved in 7.5 c.c. of absolute alcohol and neutralised by a 10 per cent. absolute alcoholic solution of sodium hydroxide. The solution remained quite clear, which showed that the acid was free from α -crotonic acid.

(b) Two grams of the acid were dissolved in 29.5 c.c. of absolute alcohol and the solution carefully neutralised by the alcoholic sodium hydroxide solution. An exceedingly slight precipitate formed, which was found to contain sodium carbonate. After filtration, the solution was evaporated to dryness, and the solid residue was extracted with 50 c.c. of absolute alcohol; the solid dissolved completely. From the alcoholic solution, the sodium β -crotonate was obtained, analysed, and its solubility in the solvent was determined.

0.255, dried at 100° , gave 0.1657 Na_2SO_4 . $\text{Na} = 21$.

$\text{C}_4\text{H}_5\text{O}_2\text{Na}$ requires $\text{Na} = 21.3$ per cent.

4.759 grams of a saturated 99 per cent. alcoholic solution of sodium β -crotonate at 15° contained 0.3295 gram of the salt, therefore 1 part of the salt dissolves in 14.4 parts of 99 per cent. alcohol. Michael and Schulthess found that one part of the sodium β -crotonate dissolves in 16.7 parts of 99.5 per cent. alcohol at 11° , and in 12.7 parts of 98—99 per cent. alcohol at 15° .

The Oxidation of Liquid β -Crotonic Acid.

“*isoCrotonic*” acid, obtained from Kahlbaum, was oxidised by barium permanganate according to the directions given by Fittig and Kochs (*Annalen*, 1892, 268, 16). The $\alpha\beta$ -dihydroxybutyric acid was obtained as a syrup, although in one preparation some crystals appeared

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in the form of long prisms with domed shaped ends, identical in appearance with those described by Fittig and Kochs (*loc. cit.*) as characteristic of $\alpha\beta$ -dihydroxybutyric acid prepared from α -crotonic acid. The yield of the syrup was the same as in the case of the oxidation of α -crotonic acid. The brucine salt of this $\alpha\beta$ -dihydroxybutyric acid is identical in melting point, specific rotatory power, and solubility with the $\alpha\beta$ -dihydroxybutyric acid described in a former paper. Fractional crystallisation of the brucine salt gave a product melting at 285° , which amounted to more than 50 per cent. of the total weight of the salt taken. The "*isocrotonic*" acid contained so much of the α -crotonic acid that it was found impossible to confirm Fittig and Koch's results. Investigation of the quinine salt gave the same results as in the case of the brucine salt. The proportion of quinine *cis*- $\alpha\beta$ -dihydroxybutyrate was at least 90 per cent. of the weight of the unrecrystallised quinine salt. The silver salt of this $\alpha\beta$ -dihydroxybutyric acid was prepared, and its solubility compared with that of the silver *cis*- $\alpha\beta$ -dihydroxybutyrate. The solubilities at 17° were practically the same, being 3.2 and 3.1; the solubilities of the two $\alpha\beta$ -dihydroxybutyrates at 15° and 13° are 1.45 and 5.1 respectively (Fittig and Kochs, *loc. cit.*).
