X.—*Organic Derivatives of Silicon. Part. IX.*
Experiments on the Resolution of dl-Benzylethyl-
propylisobutylsilicanesulphonic Acid.

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IN part III of these investigations (Trans., 1907, 91, 717) an account was given of the synthesis of *dl*-benzylmethylethylpropylsilicane, $\text{SiMeEtPr}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$, of the conversion of this silicohydrocarbon into its sulphonic derivative, $\text{SiMeEtPr}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, and of experiments on the resolution of this acid into its optically active components. Although in these experiments seven different salts, prepared from the *dl*-acid and an optically active base, were submitted to systematic fractional crystallisation, the results were negative and, except in one instance, which is referred to below, not the slightest indication of a resolution of the acid was obtained. As this might be due to the close similarity of the three alkyl radicles in the asymmetric silicon group, it seemed advisable to prepare and to examine a *dl*-sulphonic acid of the same type but containing three radicles less closely related than are the three normal homologous alkyls in benzyl-

* Mr. W. E. Bullock, B.Sc., took part in the earlier stages of this work, and before leaving to undertake other duties, he had prepared and analysed the silicohydrocarbon, its sulphonic derivative, and the menthylamine salt of the sulphonic acid. The investigation was continued from this stage in conjunction with Mr. H. Davies.

methylethylpropylsilicanesulphonic acid. The results of this work are recorded below.

dl-Benzylethylpropylisobutylsilicane, $\text{SiEtPr}(\text{C}_4\text{H}_9) \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5$, was prepared by treating benzylethylpropylsilicyl chloride with magnesium isobutyl bromide; it is a colourless liquid having the character of a hydrocarbon, and boils at $282-283^\circ$ under atmospheric pressure.

dl-Benzylethylpropylisobutylsilicanesulphonic acid,
 $\text{SiEtPr}(\text{C}_4\text{H}_9) \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$,

was then obtained by sulphonating the silico-hydrocarbon with chloro-sulphonic acid under the conditions previously described in the case of the lower homologue (*loc. cit.*), and, having previous experience as a guide, little difficulty was met with in isolating this acid in the form of its *l*-menthylamine salt.

l-Menthylamine *dl*-benzylethylpropylisobutylsilicanesulphonate,

$\text{SiEtPr}(\text{C}_4\text{H}_9) \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H} \cdot \text{C}_{10}\text{H}_{21}\text{N} \cdot 2\text{H}_2\text{O}$,

crystallises well from moist light petroleum in glistening leaflets, and although it is readily soluble in the moist solvent, the anhydrous salt dissolves much more freely in absence of water; it is very similar in most respects, not only to its lower homologue, but also to the corresponding salt of benzylethyldipropylsilicanesulphonic acid (Marsden and Kipping, *Trans.*, 1908, **93**, 205), a fact which seems to show that the *dAlB* and *lAlB*-components of the salts formed from the two *dl*-acids are both very similar to the single salt of the dipropyl derivative, which contains no asymmetric silicon group.

The *l*-menthylamine salt of *dl*-benzylethylpropylisobutylsilicanesulphonic acid is not resolved into its components when it is systematically crystallised from moist light petroleum or from aqueous methyl alcohol; it is very useful, however, as a means of isolating the acid from the crude product of sulphonation of the silico-hydrocarbon, and also as a means of identifying the acid.

In the experiments on the resolution of the *dl*-acid, it was necessary to start from a preparation of known purity; for this reason the sodium salt of the *dl*-acid was always prepared from the pure *l*-menthylamine salt and then precipitated directly with the hydrochloride of the active base.

The *strychnine*, *brucine*, *cinchonidine*, *quinine*, and *cinchonine* salts were thus prepared, and from the last-named three compounds the corresponding alkaloidal *hydrogen* salts were also obtained by treating the normal salts with hydrochloric acid (compare *Trans.*, 1907, **91**, 233). These eight substances were separately and systematically crystallised from various solvents under different conditions, and the extreme fractions thus obtained were then examined. In all cases, except in that of the cinchonine hydrogen derivative, the melting or

decomposing points and specific rotations of these extreme fractions of a given salt were identical within the limits of probable experimental error.

Although these facts might seem to be sufficient to show that the *dl*-acid had not been resolved in any of these experiments, it was not impossible that the salts of the *d*- and *l*-acids, like many of those of *d*- and *l*-sulphobenzylethylpropylsilicyl oxides (Trans., 1908, **93**, 457), might be so similar in melting point and in specific rotation as to be practically indistinguishable; for this reason it was thought advisable, in many cases, to convert the two samples of the alkaloidal salt separately into the *l*-menthylamine derivative and to compare the two specimens of the latter with the original *l*-menthylamine salt of the *dl*-acid; this test also failed to afford any evidence of the resolution of the acid.

The one salt which showed an exceptional behaviour was the cinchonine hydrogen derivative. On crystallising this compound systematically from aqueous alcohol and then recrystallising the two extreme fractions once from ethyl acetate (containing a little methyl alcohol), two colourless samples were obtained; these, when dried at 100°, showed a difference in melting point of about 5°, to which, however, little importance could be attached, as the 'most soluble' fraction melted at the lower temperature and might contain traces of impurity. When examined polarimetrically in methyl-alcoholic solution, however, a difference, which could not be due to experimental error, was observed, the 'most readily soluble' fraction giving $[\alpha]_D + 61.6^\circ$, the other $[\alpha]_D + 72.7^\circ$. After one recrystallisation from ethyl acetate (and methyl alcohol) these values became $+57.1^\circ$ and 73.8° respectively and the decomposing points of the two fractions were then identical (220—223°).

These specimens having been placed aside, the next 'most readily soluble' fraction of the salt was examined; this gave $[\alpha]_D + 62.5^\circ$ and decomposed at the same temperature (220—223°) as the other portions.

These results seemed to show that the *dl*-acid had been resolved, but unfortunately the further examination of these fractions failed to establish this inference; when separately converted into the *l*-menthylamine salt and also into the normal cinchonidine salt, the two extreme fractions gave, in both cases, products which, so far as could be ascertained, were identical with one another, and also with the corresponding salts of the original *dl*-acid.

The observed difference in specific rotation of the fractions of this cinchonine hydrogen salt has not yet been accounted for. The compound was prepared from a sample of the normal cinchonine salt, and as the latter had been obtained originally by converting the pure *l*-menthyl-

amine salt into the sodium salt and precipitating with cinchonine hydrochloride, it could hardly have been impure; further, the purity of the normal cinchonine salt, and at the same time that of the base contained in it, had been established by the fact that the two extreme fractions resulting from the systematic crystallisation of the preparation were identical in melting point and in specific rotation. It seemed, therefore, that the only possible impurity in the cinchonine hydrogen derivative might be some unchanged normal cinchonine salt; but the latter has a high specific rotation, $[\alpha]_D +110^\circ$, and if present would doubtless pass into the mother liquors and thus raise the specific rotation of the more soluble fractions of the hydrogen salt, so that the low values obtained for the latter could not be explained on this basis.

Even, in spite of these considerations, if the results of the crystallisation of the cinchonine hydrogen salt had stood alone, they might possibly have been passed over and attributed to some undiscovered source of error, but as a matter of fact very similar and quite independent observations were made some time ago by one of us during the examination of the corresponding salt of benzylmethylethylpropylsilicanesulphonic acid (Kipping, *Trans.*, 1907, **91**, 717). The cinchonine hydrogen salt of this acid, systematically crystallised from aqueous alcohol and then from anhydrous acetone containing a trace of water, gave extreme fractions of almost identical melting point, but in methyl-alcoholic solution the specific rotation of the 'most readily soluble' fraction was $+75.1^\circ$, and that of the 'most sparingly soluble' fraction $+64.9^\circ$; after further crystallisation, two corresponding fractions having $[\alpha]_D +77.4^\circ$ and $+65.3^\circ$ respectively were obtained. The difference is of the same order as that observed in the case of the *isobutyl* compound, but in these experiments the more soluble fractions have the higher rotation. The 'most readily soluble' fraction, having $[\alpha]_D +77.4^\circ$ (see above), was converted into the sodium, and then into the *l*-menthylamine salt, and the latter was recrystallised from moist light petroleum in order to separate traces of cinchonine; it melted at $116-122^\circ$, and seemed, therefore, to be a slightly impure specimen of the salt of the *dl*-acid which melts at $122-123^\circ$.

These results were not recorded in describing the experiments on the crystallisation of cinchonine hydrogen benzylmethylethylpropylsilicanesulphonate (*loc. cit.*) because, on trying to confirm them with a totally different preparation, the two extreme fractions of the salt were found to have the same specific rotations within the limits of experimental error. The matter, however, has now assumed another aspect; the observed differences in specific rotation are in both cases so large as to exclude any possibility of their being due to error in the

polarimetric readings, and the melting or decomposing points of the fractions of different specific rotation are so nearly identical that it is difficult to believe that they contain impurity. On the whole, it seems possible that the cinchonine hydrogen salts are really resolved under certain conditions, but that the enantiomorphous relationship of the two optically active acids is even more difficult to establish than in the case of the *d*- and *l*-forms of sulphobenzylethylpropylsilicyl oxide (*loc. cit.*). This possibility will be further examined as soon as a fresh supply of one of the *dl*-acids has been obtained.

EXPERIMENTAL.

Benzylethylpropylisobutylsilicane, $\text{SiEtPr}(\text{C}_4\text{H}_9)\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$.

In preparing this silico-hydrocarbon, benzylethylpropylsilicyl chloride (Trans., 1907, 91, 722) was treated with an ethereal solution of magnesium isobutyl bromide, and as no reaction seemed to occur at the ordinary temperature, the ether was evaporated and the residue heated at about 140° during three hours. After cooling, and adding water, the crude product was separated and distilled under diminished pressure. The principal fraction was then heated with sodium until no further action occurred, and was finally submitted to fractional distillation under atmospheric pressure; it was thus obtained as a colourless, mobile, refractive liquid boiling at $282\text{--}283^\circ$, the yield of the pure compound being about 60 per cent. of the theoretical:

0.1596 gave 0.4503 CO_2 and 0.1654 H_2O . $\text{C} = 77.0$; $\text{H} = 11.5$

0.2617 „ 0.7443 CO_2 „ 0.2740 H_2O . $\text{C} = 77.1$; $\text{H} = 11.5$.

$\text{C}_{16}\text{H}_{28}\text{Si}$ requires $\text{C} = 77.4$; $\text{H} = 11.3$ per cent.

Sulphonation of the Silico-hydrocarbon.—The behaviour of benzylethylpropylisobutylsilicane towards concentrated sulphuric acid was not investigated, as it seemed probable that the sulphonic derivative would be obtained far more easily with the aid of chlorosulphonic acid (compare Trans., 1907, 91, 739); employing this reagent, and proceeding just as described in the case of benzylmethylethylpropylsilicane, sulphonation is accomplished without difficulty, and a clear, slightly fluorescent, aqueous solution of the crude ammonium salt is ultimately obtained.

The acid is most conveniently isolated in the form of its *l*-menthylamine salt, which is precipitated as an oil on adding excess of menthylamine hydrochloride to the solution of the ammonium salt. The precipitate slowly solidifies to a pasty mass, which is first pressed on porous earthenware, and then fractionally crystallised from light petroleum (b. p. $40\text{--}50^\circ$) to which a few drops of water are added; after many crystallisations, the pure salt was obtained in colourless

plates, but a considerable proportion of the crude product remained in the mother liquors as an oil, which has not yet been investigated. The yield of the pure compound is poor compared with that obtained in the sulphonation of benzylmethylethylpropylsilicane.

l-Menthylamine *dl*-Benzylethylpropylisobutylsilicanesulphonate,
 $\text{SiEtPr}(\text{C}_4\text{H}_9)\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}, \text{C}_{10}\text{H}_{21}\text{N}.$

This salt is indistinguishable in appearance from that of its lower homologue, which it resembles in every respect, so that a detailed description is unnecessary. It crystallises well from moist light petroleum, but does not separate even from very highly concentrated solutions in absence of water; the hydrated crystals liquefy far below 100° , the anhydrous salt melting at $127\text{--}128^\circ$:

3.196, of air-dried salt, lost 0.2238 at 100° . $\text{H}_2\text{O} = 7.0$.

$\text{C}_{26}\text{H}_{49}\text{O}_3\text{NSSi}, 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 6.9$ per cent.

0.1848 gave $\text{C} = 64.2$; $\text{H} = 10.3$.*

0.1866 „ $\text{C} = 64.1$; $\text{H} = 10.4$.

0.1676 „ $\text{C} = 64.2$; $\text{H} = 10.4$.

$\text{C}_{26}\text{H}_{49}\text{O}_3\text{NSSi}$ requires $\text{C} = 64.6$; $\text{H} = 10.1$ per cent.

The equivalent of the anhydrous salt was determined by the method previously described (*loc. cit.*, p. 736) and was found to be 484, the calculated value being 483.

The molecular weight was also determined by the ebullioscopic method in methyl-alcoholic solution:

Substance.	Weight of solvent.	<i>E</i> .	M. W.
0.469	20.2	0.080	243
0.666	20.2	0.105	264
0.328	16.0	0.070	280
0.894	16.0	0.160	294
1.419	16.0	0.235	316

Although the isolation of this menthylamine salt necessitates repeated fractional crystallisation from moist light petroleum, the compound is not thereby resolved into its optically active components; this statement is based on the very close resemblance between this salt and the corresponding derivative of its lower homologue, and also on the fact that the aqueous solution of the sodium salt prepared from it shows no visible optical activity.

Metallic Salts of dl-Benzylethylpropylisobutylsilicanesulphonic Acid.—The solution of the sodium salt, prepared from the pure *l*-menthylamine derivative by adding a very slight excess of sodium carbonate and then distilling the menthylamine in a current of steam, has a very

* Mr. Bullock's rough note-book, in which the weights of the CO_2 and H_2O respectively were recorded, has been mislaid; the above data were supplied to me at the time the combustions were made.—F. S. K.

soapy nature and froths in a very troublesome manner during the steam distillation. When neutralised with acetic acid and evaporated, the sodium salt separates as a soapy mass which, after several days, becomes flaky and apparently crystalline; on filtering, however, the salt remains as a paste which, under the microscope, is seen to consist of oily globules. Although readily soluble in water, the salt is precipitated on addition of other salts, such as sodium carbonate, to its concentrated aqueous solution.

The solution of the *ammonium* salt of the sulphonic acid, prepared by decomposing some of the alkaloidal salts with ammonia, is very similar to that of the sodium salt.

The *barium* salt is precipitated in flocculent masses from a solution of the sodium salt, and is only very sparingly soluble in cold water, but dissolves freely in warm aqueous alcohol.

Cinchonidine dl-Benzylethylpropylisobutylsilicanesulphonate.

This salt was prepared by treating the neutral aqueous solution of the sodium salt with excess of a solution of cinchonidine hydrochloride; the oily precipitate, which soon solidified, was washed well with water and fractionally crystallised from aqueous alcohol; after six crystallisations the two extreme fractions melted simultaneously at 184°.

These two fractions were then recrystallised once from ethyl acetate, dried at 100°, and examined polarimetrically in methyl-alcoholic solution.

'*Most soluble*' fraction.—0.573, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 3.18^\circ$; whence $[\alpha]_D - 69.4^\circ$.

'*Least soluble*' fraction.—0.599, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 3.28^\circ$; whence $[\alpha]_D - 68.6^\circ$.

The cinchonidine salt is very readily soluble in the common alcohols, and in chloroform; it crystallises well, in lustrous needles or prisms, from acetone, ethyl acetate, benzene, or ether; it is only very sparingly soluble in hot water.

Cinchonidine Hydrogen Salt.

This compound, prepared by treating the normal salt with excess of hydrochloric acid in alcoholic solution and then precipitating with water, was deposited as an oil which rapidly solidified; after having been washed with water it was crystallised seven times from aqueous alcohol. The extreme fractions, when dried at 100°, began to decompose at about 210°, liquefying simultaneously at about 218°; their specific rotations were determined in methyl-alcoholic solution.

'Most soluble' fraction.—0.866, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 3.17^\circ$; whence $[\alpha]_D - 45.8^\circ$.

'Least soluble' fraction.—0.920, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 3.33^\circ$; whence $[\alpha]_D - 45.2^\circ$.

The cinchonidine hydrogen salt crystallises well from aqueous alcohol and from aqueous acetone in lustrous plates. It is sparingly soluble in anhydrous acetone or ethyl acetate, much more readily so in presence of traces of water; it is very soluble in chloroform, but practically insoluble in benzene, ether, or petroleum.

Strychnine dl-Benzylethylpropylisobutylsilicanesulphonate.

The strychnine salt, obtained directly from the sodium salt as an oil, did not solidify even on keeping for some time; it was washed with very dilute alcohol, and the milky liquid decanted. In the course of twenty-four hours these washings deposited the salt in glistening plates, but on trying to crystallise the main portion of the salt from aqueous alcohols of different concentrations, it was invariably deposited as an oil; attempts to recrystallise a portion of the crystalline compound were equally unsuccessful, as, in spite of cooling and "seeding," the salt remained a liquid. The small sample of crystalline compound melted indefinitely from about $86-95^\circ$, owing to the presence of water of crystallisation, but after having been dried at 100° its melting point was $236-238^\circ$.

Although this compound, like so many of the alkaloidal salts of these silicanesulphonic acids, remains oily in presence of aqueous solvents, it crystallises well and readily from anhydrous acetone. It was therefore systematically treated with this solvent, and after eight operations the two extreme fractions were examined. The 'most soluble' one melted at $226-227^\circ$, the other at $237-238^\circ$, and their specific rotations, determined in methyl-alcoholic solution, were practically identical:

'Most soluble' fraction.—0.542, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 0.34^\circ$; whence $[\alpha]_D - 7.9^\circ$.

'Least soluble' fraction.—0.620, made up to 25 c.c. in a 2-dcm. tube gave $\alpha - 0.38^\circ$; whence $[\alpha]_D - 7.6^\circ$.

As their specific rotations were very low, and the experimental error might be large, the 'least soluble' fraction was decomposed with ammonia and converted into the *l*-menthylamine salt, which was then recrystallised from moist light petroleum; the melting point of this preparation was identical with that of the salt of the *dl*-acid, namely, $127-128^\circ$.

The low melting point of the 'most soluble' fraction was doubtless due to the presence of a trace of impurity formed by the decomposi-

tion of the salt during repeated crystallisation, as when recrystallised once its melting point rose to 235—237°.

Brucine dl-Benzylethylpropylisobutylsilicanesulphonate.

This salt was prepared by decomposing the cinchonidine hydrogen compound with ammonia and then precipitating the neutral solution of the ammonium salt with excess of brucine hydrochloride; the oily product, which soon solidified, was washed well with water, and systematically crystallised from aqueous alcohol, from which it separated in lustrous, very bulky masses of needles.

After nine operations, the extreme fractions were dried at 100°, and separately recrystallised from ethyl acetate; they then melted simultaneously at 163°, and had the same specific rotation in methyl-alcoholic solution within the limits of experimental error:

'Most soluble' fraction.—0.657, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 0.33^\circ$; whence $[\alpha]_D - 6.27^\circ$.

'Least soluble' fraction.—0.618, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 0.30^\circ$; whence $[\alpha]_D - 6.07^\circ$.

During the crystallisation of this salt from aqueous alcohol and anhydrous ethyl acetate, it seemed that a resolution had occurred, as different fractions melted at different temperatures; it was found, however, that this behaviour was due to dimorphism. Samples of the salt, crystallised from aqueous alcohol and then dried at 100°, melted at 141—144°; but when such samples were crystallised two or three times from anhydrous ethyl acetate without removing any of the salt or leaving any appreciable quantity in solution, the melting point rose to 161—163° and became constant. On the other hand, when samples melting at 161—163° were recrystallised from aqueous alcohol they melted at 141—144°.

Quinine dl-Benzylethylpropylisobutylsilicanesulphonate.

For the preparation of this compound, a solution of the ammonium salt of the *dl*-acid, obtained by decomposing the strychnine salt, was employed, and excess of quinine hydrochloride. The product crystallised well from aqueous acetone in bulky masses of needles, but its solution in aqueous alcohol often gave oily deposits; it also crystallised well from a mixture of ethyl acetate and ether.

It was systematically crystallised from aqueous acetone; the two extreme fractions then melted simultaneously at 168—171°, and had practically the same specific rotation in methyl-alcoholic solution:

'Most soluble' fraction.—0.538, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 4.71^\circ$; whence $[\alpha]_D - 109.5^\circ$.

'Least soluble' fraction.—0.597, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 5.38^\circ$; whence $[\alpha]_D - 112.6^\circ$.

The salt is very readily soluble in the common alcohols, moist ethyl acetate, moist acetone, chloroform, or benzene, but practically insoluble in light petroleum.

Quinine Hydrogen Salt.

The decomposition of the normal salt with hydrochloric acid was carried out in the usual manner, and after washing well to remove quinine hydrochloride the product was systematically crystallised from aqueous acetone, from which it separated in bulky masses of needles; after many operations, the two extreme fractions were collected and dried at 100° . They both showed signs of decomposing at about 200° , and liquefied simultaneously at about 212° ; their specific rotations were determined in methyl-alcoholic solution:

'Most soluble' fraction.—0.531, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 3.60^\circ$; whence $[\alpha]_D - 84.7^\circ$.

'Least soluble' fraction.—0.466, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 3.09^\circ$; whence $[\alpha]_D - 82.9^\circ$.

This salt separates as an oil from aqueous alcohol unless the proportion of water is very large; it is practically insoluble in dry ethyl acetate or benzene, and only sparingly soluble in dry acetone, from which it separates in poorly-defined crystals. It dissolves freely in chloroform and in the common alcohols.

Cinchonine dl-Benzylethylpropylisobutylsilicanesulphonate.

This salt was prepared by treating a neutral solution of the pure sodium salt with excess of cinchonine hydrochloride; the oily precipitate soon solidified and was washed well with water. The salt was then systematically crystallised from aqueous methyl alcohol and the two extreme fractions were examined; they melted simultaneously and had the same specific rotation in methyl-alcoholic solution:

'Most soluble' fraction.—0.4785, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha + 4.19^\circ$; whence $[\alpha]_D + 109.4^\circ$.

'Least soluble' fraction.—0.445, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha + 3.94^\circ$; whence $[\alpha]_D + 110.7^\circ$.

This cinchonine salt separates from aqueous alcohol or aqueous acetone in silky needles; it is soluble in ethyl acetate and in anhydrous acetone, but it does not crystallise well from these solvents. The crystals deposited from aqueous solvents are hydrated and melt at about 70° , but the anhydrous salt melts at $139-141^\circ$.

Cinchonine Hydrogen Salt.

The normal cinchonine salt described above was treated with hydrochloric acid in alcoholic solution, and the hydrogen salt was then precipitated by adding water; the product quickly solidified and was washed with dilute hydrochloric acid and with warm water. It was then dissolved in alcohol and fractionally precipitated with water, these operations being repeated about six times in a systematic manner. The two extreme fractions were then separately dissolved in methyl alcohol, the solutions mixed with anhydrous ethyl acetate, and left to evaporate over sulphuric acid; the colourless deposits were finally separated and dried at 100° until constant.

The 'most soluble' fraction decomposed at $215-218^{\circ}$, the other at $220-223^{\circ}$, and their specific rotations in methyl-alcoholic solution were very different:

'Most soluble' fraction.—0.481, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha + 2.35^{\circ}$; whence $[\alpha]_D + 61.6^{\circ}$.

'Least soluble' fraction.—0.523, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha + 3.04^{\circ}$; whence $[\alpha]_D + 72.7^{\circ}$.

The 'most soluble' fraction was next recrystallised once from a mixture of methyl alcohol and ethyl acetate, leaving a fair proportion of the salt in the mother liquors: this specimen was dried at 100° until constant; it then decomposed at $220-223^{\circ}$, and had a lower specific rotation than the sample from which it had been prepared:

0.3192, made up to 16 c.c. in a 2-dcm. tube gave, $\alpha + 2.28^{\circ}$; whence $[\alpha]_D + 57.1^{\circ}$.

The 'least soluble' fraction was fractionally precipitated from its alcoholic solution by adding water, and after several operations the 'least soluble' portion was collected, recrystallised from a mixture of methyl alcohol and ethyl acetate, and dried at 100° ; it decomposed at $220-223^{\circ}$:

0.5095, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha + 3.01^{\circ}$; whence $[\alpha]_D + 73.8^{\circ}$.

The melting point of the 'most soluble' fraction being identical with that of the very highly purified 'least soluble' fraction, almost excluded the possibility that the low specific rotation of the former might be due to impurity, but as a further precaution a sample of the salt, next in order to the 'most soluble' fraction, was recrystallised once from methyl alcohol and ethyl acetate, and dried at 100° ; this specimen decomposed at $220-223^{\circ}$, and its specific rotation was almost as low as the 'most soluble' portion.

0.532 made up to 25 c.c. in a 2-dcm. tube, gave $\alpha + 2.66^{\circ}$; whence $[\alpha]_D + 62.5^{\circ}$.

It is perhaps unnecessary to add that, as the specific rotation of these salts might vary considerably in different samples of methyl alcohol containing variable proportions of water, the same sample of methyl alcohol was employed in all these determinations.

The above results could only be explained by assuming that the *dl*-acid had been resolved into its optical isomerides; in order, if possible, to obtain further evidence in favour of this conclusion, the samples of the cinchonine hydrogen salt having the specific rotations $+73.8^\circ$ and $+62.5^\circ$ respectively were separately decomposed with ammonia, and the cinchonine was separated by filtration. The solution from the salt $[\alpha]_D +62.5^\circ$ was examined in the polarimeter, but instead of being laevorotatory, as it might possibly have been, it was very feebly dextrorotatory, owing to the incomplete separation of the cinchonine; this difficulty occurs in the case of many of these salts, and the whole of the alkaloid is not removed without some trouble. For this reason, the neutral solutions of the ammonium salts were separately precipitated with *l*-menthylamine hydrochloride, and the *l*-menthylamine salts were then recrystallised from moist light petroleum; after dehydration, the salt obtained from the fraction $[\alpha]_D +73.8^\circ$ melted at $125-126^\circ$; that from the fraction $[\alpha]_D +62.5^\circ$ at $126-127.5^\circ$; a mixture of these two salts melted at $125-126^\circ$.

As the *l*-menthylamine salts of the *d*- and *l*-acids might have the same melting point, the two preparations, corresponding with the samples of cinchonine hydrogen salt $[\alpha]_D +73.8^\circ$ and $[\alpha]_D +62.5^\circ$ respectively, were separately decomposed with sodium carbonate and the menthylamine distilled in a current of steam; the neutral solutions of the sodium salts were then precipitated with cinchonidine hydrochloride, and the two samples of cinchonidine salt recrystallised first from aqueous alcohol and then from acetone containing a trace of water.

These two preparations melted simultaneously at 184° and had the same specific rotation ($[\alpha]_D -67.6^\circ$ and $[\alpha]_D -68.0^\circ$ respectively) in methyl-alcoholic solution.

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