

LXXXVIII.—*Isomeric Partially Racemic Salts containing Quinquevalent Nitrogen. Part X. The Four Isomeric Hydrindamine d-Chlorocamphorsulphonates*  
 $\text{NR}_1\text{R}_2\text{H}_3$ .

By FREDERIC STANLEY KIPPING.

THE further investigation of the partially racemic  $\alpha$ - and  $\beta$ -salts derived from *dl*-hydrindamine and *d*-chlorocamphorsulphonic acid (Kipping, *Trans.*, 1900, 77, 889) was a natural consequence of the results described in the preceding papers, and it was expected, from the close relationship between corresponding salts of the two acids, that the methods used for the resolution of the bromo-compounds would be equally successful in the case of the chloro-derivatives; these expectations, however, were not realised; it was not found possible to resolve either of the partially racemic salts of the chloro-acid by crystallising from boiling ethyl acetate, with or without the addition of light petroleum.

Fortunately, an alternative method was available for the isolation of the four isomerides, the existence of which had been premised, namely, to combine the optically active bases obtained from the bromo-salts with the chloro-acid, and then to submit the products to fractional crystallisation; the results of these experiments may be summarised as follows.

*d*-Hydrindamine, prepared from the pure  $\alpha d$ -component of the

partially racemic bromo-salt, combines with *d*-chlorocamphorsulphonic acid, giving two isomeric salts in very unequal quantities.

The principal product, which corresponds with the *αd*-bromo-salt, and which is therefore distinguished as the *α*-isomeride, is easily obtained in a pure condition. It separates from water in well-defined, compact, hydrated crystals, melts at 208—209° when dehydrated, and has a specific rotation  $[\alpha]_D + 46^\circ$  in aqueous and  $[\alpha]_D + 15.5^\circ$  in chloroform solution. It is very different in ordinary properties from the corresponding *αd*-bromo-salt, and also from all the other three isomeric chloro-salts.

The second product, which corresponds with the *βd*-bromo-salt, is formed in relatively very small quantities, but can nevertheless be isolated in what seems to be a pure condition. This *βd*-isomeride crystallises from water in long, hydrated needles and melts at 202—203° when dehydrated; its specific rotation is  $[\alpha]_D + 59^\circ$  in aqueous and  $[\alpha]_D + 50.0^\circ$  in chloroform solution.

The great difference in outward characters between these isomerides is very noteworthy considering the great similarity which seems to exist between the corresponding *αd*- and *βd*-forms of the bromo-camphorsulphonate; it is also interesting to note that in spite of these differences the isolation of the *βd*-isomeride is exceedingly troublesome, this modification retaining small quantities of the *αd*-compound with great tenacity.

That these two chloro-salts are really produced from identical components was proved by decomposing the pure *αd*-form and regenerating the salt from the same acid and the same base; the product consists of a mixture of the *αd*- and *βd*-isomerides.

As the *βd*-chloro-salt has a much higher specific rotation than the *αd*-isomeride, it is obvious that its formation cannot be attributed to racemisation of the chloro-acid.

*l*-Hydrindamine, prepared from the pure *αl*-modification of the bromo-salt, also combines with *d*-chlorocamphorsulphonic acid, giving rise to a mixture of very unequal quantities of two isomerides.

The principal product, the *αl*-modification, corresponding with the *αl*-bromo-salt, separates from water in long, anhydrous needles, indistinguishable by inspection from those of the *αl*-bromo-compound; it melts at 118—119° and has a specific rotation  $[\alpha]_D + 44^\circ$  in aqueous, and  $[\alpha]_D + 45.5^\circ$  in chloroform solution.

The subsidiary product, namely, the *βl*-isomeride, is formed in relatively very small quantities, and its separation from the *αl*-salt is a most troublesome operation; nevertheless, it can be isolated in a pure condition, and then crystallises from water in long, anhydrous needles melting very indefinitely at about 140°. Its specific rotation is  $[\alpha]_D + 57.5^\circ$  in aqueous and  $[\alpha]_D + 60.5^\circ$  in chloroform solution. This

$\beta$ -chloro-salt closely resembles the corresponding bromo-isomeride in nearly all respects, and like the latter seems to be dimorphous.

The pure  $\alpha$ -form of the chloro-acid, when decomposed and regenerated from the same acid and the same base, gives rise to both the  $\alpha$ - and  $\beta$ -modifications, so that the isomerism of the two compounds is of the same type as that of the  $\alpha$ - and  $\beta$ -salts. Here, again, since the subsidiary product has a higher specific rotation than its isomeride, its formation cannot be attributed to racemisation of the chloro-acid.

The isolation of these four isomeric hydrindamine chlorocamphorsulphonates affords strong support to the author's views as to the nature of the isomeric partially racemic salts, but a discussion of their properties from this standpoint is postponed until the isomeric derivatives of methylhydrindamine have been described (p. 918).

#### EXPERIMENTAL.

##### *Attempts to Resolve the partially Racemic $\alpha$ - and $\beta$ -Salts.*

It has already been mentioned that the resolution of the partially racemic hydrindamine chlorocamphorsulphonates (Trans., 1900, *loc. cit.*) has not yet been accomplished, and the difference in behaviour between these salts and those of the bromo-acid is certainly noteworthy.

The partially racemic  $\alpha$ -salt was dissolved in a very small quantity of alcohol, the solution evaporated to a syrup, and hot ethyl acetate added, together, in some cases, with a slight amount of light petroleum (b. p. 80—90°); on allowing the solution to simmer on the water-bath, very slender needles were slowly deposited, just as in the case of the bromo-salt, and it seemed that a partial resolution had occurred; when, however, this precipitate was separated and dissolved in water, the solution gave deposits of the bulky, opaque masses of the partially racemic  $\alpha$ -salt. Fractional crystallisation of the original deposit from boiling ethyl acetate was also tried, the operations being continued until only a very small quantity of salt remained, but even this preparation seemed to consist of approximately equal quantities of the  $\alpha$ - and  $\beta$ -components, as when crystallised from water it gave the hydrated partially racemic salt.

The partially racemic  $\beta$ -salt was examined in a somewhat similar manner, but it could not be made to crystallise from the hot solutions, and, on cooling, crystals of the original  $\beta$ -salt were slowly deposited.

##### *Formation and Separation of the $\alpha$ - and $\beta$ -Isomerides.*

The pure  $\alpha$ -modification of hydrindamine bromocamphorsulphonate (this vol., p. 878) was decomposed with barium hydroxide solution, the

base distilled in steam, and the distillate neutralised with *d*-chloro-camphorsulphonic acid, prepared from the carefully purified ammonium salt (Kipping and Pope, Trans., 1895, 67, 354); after having been concentrated, the solution, on cooling, deposited a large quantity of salt in long, opaque bundles or bands of small prisms; this salt was removed, the solution concentrated, and the first and successive deposits repeatedly and systematically crystallised from water and aqueous alcohol.

The salt was thus separated into seven fractions, each of which, excepting the last, had been crystallised about six times, the mother liquors from the first (fraction I) being used to dissolve the next, and so on; fraction VII was obtained by evaporating the final mother liquors to a small bulk and then separating the whole of the deposit from the cold solution.

All the fractions thus obtained seemed to be identical, and consisted of broad, opaque bands of characteristic appearance; melting point determinations indicated the presence of water of crystallisation, the several fractions partly liquefying at about 140°, then gradually solidifying and melting again at 203–208°.

When dried at 100°, fraction I melted sharply at 208–209°; fraction VII sintered at 203–204°, and melted at 206–207°.

The specific rotations\* of these two fractions (dried at 100°) were determined in chloroform and in aqueous solutions, with the following results:

	Substance.	Solvent.	Vol. of solution.	$\alpha_D$ .	$[\alpha]_D$ .
Fraction I	0.5	Chloroform	25 c.c.	+0.62°	+15.5°
„ VII	0.5	„	„	1.52	38.0
„ I	0.5	Water	„	1.84	46.0
„ VII	0.5	„	„	2.10	52.5

Obviously, in spite of their similarity in appearance and melting point, these two fractions contained salts having very different specific rotations, especially in chloroform solution, and the presence of isomerides was distinctly indicated.

In order to ascertain to what extent the fractional crystallisation had effected a separation of these isomerides, fractions II and VI were also dried at 100° and examined in the polarimeter:

	Substance.	Solvent.	Vol. of solution.	$\alpha_D$ .	$[\alpha]_D$ .
Fraction II	0.5	Chloroform	25 c.c.	+0.59°	+14.7°
„ VI	0.5	„	„	0.80	20.0
„ II	0.5	Water	„	1.86	46.5
„ VI	0.5	„	„	1.86	46.5

\* A 200 mm. tube was employed in all these polarimetric determinations.

These results indicated that fractions I to V probably consisted of the *ad*-salt only, whilst fraction VI contained a small amount, and fraction VII a larger proportion of the *βd*-isomeride.

*Regeneration of the ad-Salt.*

The first five fractions, which constituted about 85 per cent. of the whole, were next decomposed with barium hydroxide solution, the base distilled in steam and again neutralised with the chloro-acid, which was recovered from the solution of the barium salt. The solution was then concentrated, and the *regenerated* salt systematically crystallised from water and aqueous alcohol as before; it was thus separated into eight fractions, all of which except the last (VIIIa) had been crystallised about eight times.

Fractions Ia and VIIIa were dried at 100°; they then melted at 207° and 200° respectively, and gave the following values when examined optically:

Fraction	Substance.	Solvent.	Vol. of solution.	$\alpha_D$ .	$[\alpha]_D$ .
Ia	0.5	Chloroform	25 c.c.	+0.63°	+15.75°
„ VIIIa	„	„	„	0.72	18.0
„ Ia	„	Water	„	1.83	45.7

These results seem to show that the regenerated salt was homogeneous, but as this could hardly be the case, fraction VIIa (the last but one), which differed somewhat from the others in appearance, was also examined, and as the following data show, an impure preparation of the missing *βd*-isomeride was thus discovered.

Fraction VIIa	0.5 gram	Chloroform	25 c.c.	+1.39°	+34.8°
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This experiment emphasises the importance of examining such salts for the presence of isomerides, and shows also that even when one of the compounds is produced in relatively very small proportion it does not necessarily pass into the final mother liquors when the crude product is systematically crystallised; similar observations have been made in the case of the other salts examined.

Having proved that the chloro-salt regenerated from the pure *ad*-compound contains an isomeride, attempts were made to isolate the latter.

The two fractions, VII and VIIa, of the crude preparation were therefore mixed together and crystallised two or three times from water at the ordinary temperature; a salt was then deposited in opaque, bulky masses of slender needles, barely distinguishable from the partially racemic  $\alpha$ -salt, and some of the mother liquors gave a similar deposit, containing, however, a few much larger prisms, which were

obviously crystals of the *ad*-isomeride. The latter were separated mechanically, the crystallisation from water being repeated several times (without fractionating) until the deposits seemed to be free from the *ad*-compound; the salt was then crystallised twice from water and once from ethyl acetate containing a small quantity of methyl alcohol, the most sparingly soluble portion being separated each time.

A preparation was thus obtained in small, lustrous, anhydrous prisms; it melted sharply at 195—196°, and appeared to be a pure compound.

An optical examination of this preparation (IX), dried at 100°, gave the following results:

	Substance.	Solvent.	$\alpha_D$ .	$[\alpha]_D$ .
Fraction IX	0.5	Chloroform	+1.39°	+34.7°
"	"	Water	2.18	54.5

From the moderately close agreement between these values and those previously obtained with fraction VII (p. 905), which had not been by any means so exhaustively treated, it seemed that the isolation of the pure  $\beta d$ -isomeride had been accomplished. As a matter of fact, however, in spite of appearances to the contrary, the sample (fraction IX) just examined still contained relatively large quantities of the *ad*-isomeride. As this preparation separated from warm concentrated aqueous solutions as an oil, and its purity on that account seemed doubtful, it was again fractionally crystallised from water and thus resolved into 8 or 10 very small portions, some of which, when repeatedly crystallised at the ordinary temperature, occasionally gave one or two prisms of the *ad*-modification; these crystals were separated mechanically, and the residual salt was then further treated, the most sparingly and the most readily soluble portions being rejected; it was finally precipitated from its concentrated solution in hot methyl alcohol by the addition of ethyl acetate, and separated into two fractions, X and XI; the mother liquors from the last fraction (XI) seemed to be free from *ad*-salt, as when evaporated to dryness and the residue crystallised from water no prisms of this isomeride could be observed in the deposit.

These two fractions were dried at 100° and examined optically:

	Substance.	Solvent.	Vol. of solution.	$\alpha_D$ .	$[\alpha]_D$ .
Fraction X	0.5	Water	25 c c.	+2.21°	+55.2°
" XI	"	"	"	"	55.2
„X+XI	"	Chloroform	"	1.39	34.8

These two samples melted sharply and simultaneously at 195—196°, showing no signs of sintering even at 194°; when crystallised slowly from water or aqueous methyl alcohol, they were deposited in long,

concentrically grouped needles of some size, and the deposits seemed to be homogeneous. From hot solutions, however, the salt still separated as an oil, and it was this behaviour alone which led to its further purification.

The fractions X and XI, having been mixed together, were submitted to another long series of crystallisations from water and aqueous methyl alcohol; in these operations, traces of the  $\alpha d$ -salt were repeatedly met with, especially when a deposit, which had been formed very slowly, was treated with a very slight amount of methyl alcohol, the solution rapidly decanted, and the residue crystallised from water; combining this method with fractional crystallisation, the pure  $\beta d$ -isomeride was ultimately obtained in a crystalline form very different from that of the impure salt; its properties are described on p. 909.

It is very difficult to give even an approximate estimate of the relative proportions of the  $\alpha d$ - and  $\beta d$ -isomerides in the original chloro-salt, owing to the large number of crystallisations required to effect their separation and to the fact that a portion of the  $\beta d$ -salt cannot be isolated; roughly speaking, the quantity of pure  $\beta d$ -isomeride actually obtained amounted only to about 5 per cent.

*$\alpha d$ -Hydrindamine d-Chlorocamphorsulphonate.*

This isomeride, as already indicated, is obtained in a pure condition without any difficulty by repeatedly crystallising the crude salt from hot water.

The crystals thus obtained consist of very large, white, fern-like masses of small, ill-defined, hydrated prisms; from cold solutions in water or aqueous alcohol, the salt is deposited in well-defined, six-sided, transparent crystals, but when they attain a considerable size they often have a rather curious appearance and consist of an opaque, white core surrounded by transparent parts.

Samples of the crystals from aqueous solution, which were dried in the air, and had apparently slightly effloresced, were heated at  $100^{\circ}$ .

1.139 lost 0.0435 at  $100^{\circ}$ ;  $H_2O = 3.8$  per cent. ( $1H_2O$  requires 4.3 per cent.)

From its solution in methyl alcohol, the salt is precipitated on adding ethyl acetate in the form of slender, well-defined, apparently anhydrous prisms indistinguishable by inspection from the crystals of the  $\beta d$ -isomeride obtained in a similar manner.

The  $\alpha d$ -salt is very readily soluble in boiling water, and does not separate as an oil from hot saturated solutions; it dissolves freely in cold chloroform. Its specific rotation in aqueous solution is  $[\alpha]_D + 46^{\circ}$ , and in chloroform  $[\alpha]_D + 15.5^{\circ}$ .

The great difference in appearance between the hydrated crystals

of this *ad*-salt and the anhydrous crystals of the corresponding bromo-salt (p. 878) is very noteworthy; the difference between this salt and its  $\beta d$ -isomeride is also remarkable considering the probable similarity between the *ad*- and  $\beta d$ -isomerides of the bromo-salt.

*$\beta d$ -Hydrindamine d-Chlorocamphorsulphonate.*

The pure salt separates from water in long, lustrous needles or prisms, absolutely different in appearance from the bulky, opaque masses which are formed when a small proportion of the *ad*-isomeride is present, and it does not separate as an oil even from hot saturated solutions. The crystals from aqueous solution are hydrated; when rapidly heated, they generally melt at  $100^{\circ}$  in their water of crystallisation.

0.5014 air-dried salt lost 0.0198 at  $100^{\circ}$ .  $H_2O = 3.9$ .

$C_{10}H_{14}OCl \cdot SO_3H, C_9H_{11}N, H_2O$  requires  $H_2O = 4.3$  per cent.

From a solution in methyl alcohol, ethyl acetate precipitates the  $\beta d$ -salt in small, transparent, apparently anhydrous prisms melting at  $202-203^{\circ}$ . It is very readily soluble in alcohol and chloroform, but only sparingly so in cold water.

Determinations of the specific rotation were made with a sample of the salt which seemed to be pure, and which was previously dried at  $100^{\circ}$ :

Substance.	Solvent.	Vol. of solution.	$\alpha_D$ .	$[\alpha]_D$ .
0.4816	Chloroform	25 c.c.	+1.9°	+49.3°
"	Water	"	2.27	58.8

The great difference between the value  $[\alpha]_D + 49.3^{\circ}$  and those ( $+38^{\circ}$ ,  $+34.7^{\circ}$ ,  $+34.8^{\circ}$ ) previously obtained in chloroform solution with samples of the impure salt, show that the latter must have contained a very large proportion of the *ad*-isomeride in spite of its apparent homogeneity. The value in aqueous solution is remarkably high, and corresponds with a molecular rotation  $[M]_D + 235^{\circ}$ ; since the basic ion has no appreciable optical activity in the *ad*-isomeride, and the molecular rotation of the acid is only  $[M]_D + 188^{\circ}$  (Trans., 1900, 77, 902), it may be inferred that the salt is only very partially dissociated.

The most striking difference between this  $\beta d$ -salt and its  $\beta l$ -isomeride is that the crystals of the latter are anhydrous, even when deposited from aqueous solution.

*Formation and Separation of the  $\alpha l$ - and  $\beta l$ -Isomerides.*

The *l*-base, obtained by decomposing the pure *al*-modification of hydrindamine bromocamphorsulphonate with barium hydroxide solution,



is neutralised with pure chlorocamphorsulphonic acid (prepared from its ammonium salt) and the solution concentrated; on cooling, the product is deposited in long, transparent needles, indistinguishable by inspection from those of the  $\alpha$ -form of hydrindamine bromocamphorsulphonate; the mother liquors are again evaporated, and the first and subsequent deposits systematically crystallised from water in the usual manner.

When the salt is thus separated into seven fractions, each of which except the last (VII), which is obtained from the final mother liquors, has been crystallised six times, there is no appreciable difference in appearance between them, and they all melt at about 117–119°, the last fraction, perhaps, not quite so sharply as the first.

The first fraction was now crystallised three times from water and three times from aqueous methyl alcohol, a considerable proportion being left in solution each time; it was then dried at 100° and examined in the polarimeter, with the following results:

	Substance.	Solvent.	Vol. of solution.	$\alpha_D$ .	$[\alpha]_D$ .
Fraction I	0.5	Water	25 c.c.	+1.77°	+44.25°
"	"	Chloroform	"	1.81	45.25

Only about 8 per cent. of the original salt remained when this preparation was finally crystallised three times from water, the optical properties of the final fraction being practically identical with those of Fraction I, as shown by the following data:

Substance.	Solvent.	Vol. of solution.	$\alpha_D$ .	$[\alpha]_D$ .
0.5	Water	25 c.c.	+1.77°	+44.25°
"	Chloroform	"	1.83	45.7

This preparation consists of the pure  $\alpha$ -isomeride, the properties of which are described later (p. 912).

The further examination of the salt contained in fractions II to VII at first failed to reveal the presence of an isomeride, but on separating the portions IV to VII into about ten fractions by crystallising from water, a slight difference in appearance between some of them might be observed, namely, that certain deposits contained tufts, which were composed of somewhat smaller needles than usual, and which consequently formed translucent, rather than transparent, aggregates. As it was not possible to separate these tufts from the confused crystalline mass by any mechanical process, those deposits which seemed to be similar were added together and this mixture again fractionally crystallised from water; some of the fractions thus obtained seemed to consist of pure  $\alpha$ -salt and were rejected, whilst others were richer in the translucent tufts and were collected separately; there was, however, no apparent connection between the appearance of a fraction

and its solubility, as when systematic crystallisation was again attempted, of six successive deposits, the second and fifth, for example, might give a considerable quantity of the tufts, but all the others yielded very little.

Guided, however, by the almost inappreciable difference in appearance (which is not readily described), samples, consisting largely of tufts, were ultimately obtained, and these, after several further crystallisations from water, gave deposits of small, transparent needles, indistinguishable in appearance from those of the  $\alpha$ -salt, but which always began to form at the bottom instead of at the surface of the solution; the melting point of these deposits now began to differ from that of the  $\alpha$ -isomeride, and to range from about  $120^{\circ}$  to  $130^{\circ}$ ; crystallisation from aqueous alcohol raised the melting point to  $135^{\circ}$ – $140^{\circ}$ .

A sample of the salt thus obtained in relatively very small quantities and having a melting point of about  $136^{\circ}$  was dried at  $100^{\circ}$  and examined in the polarimeter; as there was only 0.6 gram of this preparation, the salt recovered from the chloroform solution was used for the determination in water:

Substance.	Solvent.	Vol. of solution.	$\alpha_D$ .	$[\alpha]_D$ .
0.5	Chloroform	25 c.c.	+2.34°	+58.5°
„	Water	„	2.25	56.5

These values differ widely from those obtained with the samples of  $\alpha$ -salt (m. p.  $118^{\circ}$ – $119^{\circ}$ ), and prove the existence of the  $\beta$ -isomeride.

The final purification of this  $\beta$ -salt is a simple matter; after several recrystallisations from aqueous methyl alcohol, it is obtained in what is doubtless a state of purity, and its properties are described later (p. 912).

It is rather noteworthy that, although the isomeric  $\alpha$ - and  $\beta$ -chloro-salts differ in melting point by about  $20^{\circ}$ , their separation from one another is a far more difficult task than that of the corresponding bromo-isomerides, and is only equalled by the difficulty of isolating the  $\beta$ -modification of the chloro-salt; even after the experience gained in the cases just mentioned, it was some time before the  $\beta$ -salt was successfully isolated.

The quantity of the  $\beta$ -isomeride in the original salt probably does not amount to 10 per cent., and of this a considerable proportion cannot be separated from the  $\alpha$ -modification; the two compounds seem, in fact, to form mixed crystals which break up and become opaque when heated with water; this behaviour serves as a useful indication of the presence of the  $\beta$ -salt in the deposits.

*Regeneration of the  $\alpha$ -Salt.*

In order to obtain further quantities of the  $\beta$ -isomeride, and also to make certain that this substance is really composed of *l*-hydrindamine and a pure *d*-chloro-acid identical with that contained in the  $\alpha$ -salt, a considerable quantity of the latter, which had been exhaustively crystallised and which was doubtless free from  $\beta$ -isomeride, was decomposed with barium hydroxide solution; the chloro-salt was then regenerated from the base, which had been distilled in steam, and from the acid recovered from the barium salt.

This preparation, when fractionally crystallised, behaved in all respects like that previously examined, and the optical examination of a dried sample of the *crude*  $\beta$ -isomeride obtained from it gave the following result:

Substance.	Solvent.	Vol. of solution.	$\alpha_D$ .	$[\alpha]_D$ .
0.5	Chloroform	25 c.c.	+ 2.35°	+ 58.7°

 *$\alpha$ -Hydrindamine d-Chlorocamphorsulphonate.*

In appearance and in its behaviour towards solvents, there is a very close resemblance between the  $\alpha$ -salt of the chloro-acid and that of the corresponding derivative of the bromo-acid.

The  $\alpha$ -chloro-salt crystallises from water in long, slender, anhydrous needles, and from cold aqueous methyl alcohol in well-defined, compact prisms. It melts at 118—120° when in the form of moderately large crystals, but if these be crushed to a fine powder, the latter sinters distinctly at about 115°; as a rule, the large crystals melt completely below 121°, but the powder, after sintering, solidifies again, and then melts fairly sharply at 195—196° when heated quickly, without any appreciable charring. These observations seem to show that the salt is dimorphous, and that the ordinary form obtained from solutions is unstable at temperatures above about 115°; as in the case of the corresponding  $\alpha$ -bromo-salt, however, it is difficult to say whether or not this behaviour is due to partial loss of base.

The salt is very readily soluble in cold chloroform and dissolves freely in cold alcohol, but is only sparingly soluble in cold water.

Its specific rotation in a 2 per cent. aqueous solution is  $[\alpha]_D + 44.0^\circ$ , and in chloroform  $[\alpha]_D + 45.5^\circ$ .

 *$\beta$ -l-Hydrindamine d-Chlorocamphorsulphonate.*

The two preparations of *crude*  $\beta$ -salt, obtained as already described (p. 911 and above), were mixed and repeatedly crystallised from water

and aqueous methyl alcohol until their mother liquors gave homogeneous deposits; the pure compound was thus obtained in long needles.

A sample, dried at 100°, gave the following optical values:

Substance.	Solvent.	Vol. of solution.	$\alpha_D$ .	$[\alpha]_D$ .
0.5	Chloroform	25 c.c.	+ 2.42°	+ 60.5°
„	Water	„	2.30	57.5

Further crystallisation was not considered necessary, as the salt resembles the corresponding  $\beta$ l-bromo-compound so closely that its appearance was deemed to be sufficient evidence of its purity.

The  $\beta$ l-chloro-salt is readily soluble in methyl alcohol, from which it is deposited in coarse, ill-defined prisms; it seems to be less soluble in hot water than any of its isomerides, and from very concentrated hot solutions it crystallises in felted masses of very slender needles; it dissolves freely in cold chloroform.

Its melting point, like that of the  $\beta$ l-bromo-salt, is very indefinite and varies greatly with the size of the crystals; the coarse prisms obtained from cold solutions in methyl alcohol generally melt fairly sharply and completely at 145—146°, but when crushed to a fine powder the same preparation melts at 130—133°; occasionally the fused mass solidifies again when left in the hot bath and melts for a second time at about 232°, but these indications of dimorphism have not been very closely studied.

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UNIVERSITY COLLEGE,  
NOTTINGHAM.

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