LXXXVII.—*Isomeric Partially Racemic Salts containing Quinquevalent Nitrogen. Part IX. Resolution of the β -Modification of dl-Hydrindamine d-Bromocamphorsulphonate.*

By FREDERIC STANLEY KIPPING.

ACCORDING to the view briefly summarised in the preceding paper, the partially racemic β -salt, obtained from *dl*-hydrindamine and *d*-bromocamphorsulphonic acid, should consist of a mixture of two isomerides, one derived from the *d*-, the other from the *l*-base, and these salts should be different from the *ad*- and *al*-components of the partially racemic α -salt. In the expectation that the β -salt, like the α -salt, might be resolved by crystallising it at a temperature above its transition point, experiments were carried out in hot ethyl acetate solution, and after several unsuccessful attempts, the resolution was accomplished, but only with very great difficulty.

The first product of this resolution, namely, that precipitated from the hot solution, resembles the *ad*-isomeride (p. 878) very closely in properties, and is a mixture of two salts, one identical with the *ad*-isomeride, the other doubtless identical with the βd -component of the regenerated *ad*-salt; it was not found possible, however, to separate completely these two isomerides, and the βd -modification has not yet been obtained free from the *ad*-salt.

The second product of this resolution of the partially racemic β -salt, namely, that obtained from the ethyl acetate mother liquors, is also a mixture of two isomerides, one being identical with the *al*-component of the partially racemic α -salt (p. 879), the other with the βl -modification contained in the regenerated *al*-salt (p. 888); these two isomerides have been separated and obtained in a pure condition.

These results seem to show that the explanation of the formation of the partially racemic α - and β -salts originally given by the author (Trans., 1900, 77, 861) is substantially correct, and only requires modifying in one unimportant detail, namely, that the β -salt, instead of being composed of only two isomerides, which differ from the com-

ponents of the α -salt, is really a compound formed by the crystallographic union of two new isomerides with the two components of the α -salt.

The β -salt, therefore, consists of

This β -salt represents a new type of crystalline compounds which may be classed as *partially di-racemic*, since they may be regarded as formed by the crystallographic union of two partially racemic salts; as will be shown later, the d -bromocamphorsulphonate of dl -methylhydrindamine (this vol., p. 922) and the partially racemic β -salt of d -chlorocamphorsulphonic acid and dl -hydrindamine (this vol., p. 902) also belong to this class of interesting substances.

These partially di-racemic β -salts are not merely mixtures of their four components, but differ from the latter in crystalline form, and also, as a rule, in containing water of crystallisation, the components being generally anhydrous. They form well-defined, or fairly well-defined, crystals of considerable size, and under ordinary treatment, such as crystallisation from warm water, aqueous alcohol, moist ethyl acetate, and so on, they behave as if composed of only one substance.

It is obvious, therefore, that failure to resolve a compound by fractional crystallisation of its salts affords very little evidence as to whether such a compound is or is not composed of enantiomorphously related components; in the case of dl -hydrindamine, five different optically active acids were tried before the experiments were successful. Although these partially di-racemic salts appear to be so unchangeable, it seems possible that the relative proportions of the four components may vary within certain limits according to the temperature at which the salt is deposited and the nature of the solvent; the αd - and βd -forms being apparently capable of forming mixed crystals, and the αl - and βl -modifications being probably closely related to one another in crystalline form, the removal of a portion of the two α -isomerides, as partially racemic α -salt, might have little effect on the crystalline structure of the residual partially di-racemic salt, but would, of course, alter its specific rotation (since the α - have very different specific rotatory powers from those of the β -modifications), and probably also its melting point. If such a variation in composition be possible, the fact would afford an explanation of the somewhat discordant results obtained in the determination of the specific rotation of the partially di-racemic hydrindamine d -bromo- and d -chlorocamphorsulphonates (Trans., 1900, 77, pp. 885, 897); the samples,

having doubtless been crystallised under slightly different conditions, were possibly not identical as regards the relative proportions of their four component isomerides. Direct observations pointing to the same conclusion have been made in the course of this work, inasmuch as samples of the partially di-racemic bromo-salt, which seemed to be free from the α -isomeride, on repeated crystallisation under different conditions, have sometimes afforded a small quantity of the partially racemic α -salt; long continued crystallisation, therefore, is always necessary before a sample of the β -salt can be regarded as pure.

That mixtures of the four isomerides, in proportions very different from those existing in the partially di-racemic salt, may enter into crystallographic union, forming an apparently homogeneous substance, is shown in this paper. The crude βd -salt (containing the αd -isomeride) and the pure βl -salt, when mixed in equal quantities and crystallised, give a hydrated compound which is indistinguishable from the ordinary partially di-racemic β -salt by inspection, but which, nevertheless, differs from it in melting point and specific rotation.

EXPERIMENTAL.

The separation of the components of the partially racemic β -salt of hydrindamine and d -bromocamphorsulphonic acid is a far more troublesome process than the resolution of the α -salt, partly because of the smaller quantities of this isomeride which are available, but principally because of its more complex character; as shown below, it consists of four components.

The β -salt, freed from the α -isomeride by repeated crystallisation from water and dilute alcohol, is dried in the air and dissolved in a small quantity of ethyl acetate, in which the hydrated crystals are readily soluble. The solution is then placed in a beaker covered with a clock-glass, and left on the water-bath for some hours, when the syrupy residue thus obtained usually begins to deposit minute crystals; a little more dry ethyl acetate is then added, and the heating continued, whereupon a small proportion of the salt is slowly deposited in silky needles; this deposit (a) is rapidly separated from the hot solution and washed thoroughly with boiling ethyl acetate, in which it is only very sparingly soluble.

If the operation has been successful, this precipitate (a), on recrystallisation from water, will give long, slender needles, and will be practically free from any partially racemic β -salt; if, however, precipitation has been carried too far, the substance deposited from the aqueous solution may consist almost entirely of unchanged β -salt, which separates in rosettes of hydrated prisms.

The ethyl acetate filtrate and washings from the original deposits,

when concentrated on the water-bath, may or may not give a second deposit of silky needles, according to the manner in which the first operation has been conducted; if no precipitate forms, the addition of light petroleum (b. p. 80—90°) and further heating may cause a second separation from the hot solution; the petroleum, however, must be added very cautiously, otherwise the solution separates into two layers and the lower one then solidifies to a mass of unresolved salt. When it is found that no further resolution occurs on continued heating, the ethyl acetate solution is mixed with a few drops of water and left at the ordinary temperature until most of the solvent has evaporated; the deposit, which consists of the hydrated, partially racemic β -salt, is separated and submitted again to the original treatment; the filtrate is evaporated to dryness, the residue dissolved in a considerable quantity of cold water, and after some time the cold solution (*b*) is filtered from traces of resinous matter and concentrated.

The original β -salt is thus resolved by repeated treatment into the substance (*a*) melting at about 215°, and the substance or substances in the aqueous solution (*b*).

Examination of the Precipitate (a).

The substance which separates from the hot ethyl acetate solution of the β -salt crystallises from water in long, silky needles, but from hot saturated solutions it is deposited as an oil. When freed from partially racemic salt by one or two crystallisations from water, it melts, not quite sharply, between 213° and 216°, generally at about 215°, and is indistinguishable in outward properties from the *ad*-salt (p. 878).

As this preparation was conceivably one of the two salts of which the partially racemic β -compound was supposed to consist, a sample was dried at 100° and examined optically, with the following results:

Substance.	Solvent.	Vol. of solution.	Length of tube.	α_D .	$[\alpha]_D$.
0.5010	Water	25 c.c.	200 mm.	+2.33°	+58.25°
0.4078	Chloroform	„	„	+0.98	+30.0

These values agree very closely with those of the *ad*-salt, namely, +61° in aqueous and +30° in chloroform solution; further, the melting point of this new substance is not very different from that of the *ad*-salt.

Now the sample of β -salt from which this substance had been prepared was repeatedly crystallised before submitting it to resolution, and it seemed quite impossible that the above substance could be

derived from some partially racemic α -salt which had escaped detection; nevertheless, a fresh sample of β -salt was purified even more carefully than before, and this preparation was then resolved. The deposit (α), as before, crystallised from water in long needles melting at 215–216° fairly sharply, and when mixed with ad -salt it gave a mixture melting at 218°. Its specific rotation was determined with the following results:

Substance.	Solvent.	Vol. of solution.	Length of tube.	α_D .	$[\alpha]_D$.
0.5436	Water	25 c.c.	200 mm.	2.44°	56.3°
0.5436	Chloroform	„	„	1.25	28.7

A third sample, prepared from a different specimen of the β -salt, also melted at 214–216°, and its melting point did not change appreciably after three crystallisations from water; its specific rotation was determined in aqueous solution and found to be $[\alpha]_D + 58.7^\circ$, a value which agreed closely with that of the first preparation.

Now from the results of the experiments with the regenerated ad -salt, the component of the β -salt, namely, βd , has a specific rotation less than $[\alpha]_D + 50^\circ$ in aqueous solution; it seemed, therefore, that the substance actually obtained from the β -salt could not consist of the pure βd -modification.

A considerable quantity of the mixture of the three different preparations obtained from the partially racemic β -salt was next submitted to a systematic fractional crystallisation from water, and thus resolved into eight portions, each of which had been crystallised 8–10 times; the most sparingly soluble (fraction I) and the most readily soluble (fraction VIII) were then examined; they melted at 217–219° and at 208–212° respectively, and had the following specific rotations in aqueous solution:

	Substance.	Vol. of solution.	Length of tube.	α_D .	$[\alpha]_D$.
Fraction I	0.502	25 c.c.	200 mm.	+ 2.42°	+ 59.9°
Fraction VIII...	0.4955	„	„	2.18	55.0

It thus appeared that the product from the β -salt is not a single substance; fraction I seemed to be identical with the ad -salt, fraction VIII with the mixture of ad - and βd -salts obtained from the regenerated ad -isomeride (p. 884); as, however, fraction VIII might conceivably have contained traces of the partially racemic β -salt, it was thrice crystallised from water, and again examined optically; its specific rotation in aqueous solution was then $[\alpha]_D + 56.2^\circ$.

Fractional crystallisation was therefore continued, aqueous methyl alcohol being used instead of water, and after many operations the melting point of the most sparingly soluble portion rose to 222–223°,

which is identical with that of the *ad*-salt; its specific rotation in aqueous solution was also identical with that of this isomeride.

The most readily soluble portions now melted almost sharply at 213–214°, and, when examined polarimetrically, gave the following values:

Substance.	Solvent.	Vol. of solution.	Length of tube.	α_D .	$[\alpha]_D$.
0.5	Water	25 c.c.	200 mm.	+2.23°	+55.75°
0.5	Chloroform	„	„	1.25	31.0

These results prove that the precipitate (α) obtained in the resolution of the pure partially racemic β -salt is a mixture of isomerides, one of which is identical with the *ad*-isomeride, the other being doubtless identical with the βd -modification, the existence of which has already been shown to be probable.

Many attempts have been made to obtain the βd -isomeride in a pure condition; the most readily soluble portions of the salt referred to above were mixed with the most readily soluble fractions of the regenerated *ad*-salt (p. 885), and the mixture systematically crystallised from water and dilute alcohol until all the more sparingly soluble substances had been separated. About 1.5 grams remained, representing the most soluble portion obtained from about 50 grams of salt; this melted at 200–203°, and had a specific rotation $[\alpha]_D +51^\circ$ in aqueous solution. It was crystallised twice from water, the more sparingly soluble portions (about half) being rejected; the mother liquors were then evaporated and the deposit crystallised from ethyl acetate and a little methyl alcohol. The substance finally obtained melted at 207–208°, and had a specific rotation of $[\alpha]_D +49.2^\circ$ in aqueous solution; this sample represents the most concentrated form of the βd -isomeride which has yet been prepared.

It is very doubtful whether it would be possible to obtain the βd -salt quite free from its *ad*-isomeride; the two substances are obviously very similar in properties and form mixed crystals.

The impure βd -salt of specific rotation $[\alpha]_D +49.2^\circ$ differs from the *ad*-isomeride principally in the manner in which it crystallises from cold water and from aqueous alcohol; from the former, it is deposited in large, opaque tufts of concentrically grouped, slender needles, from the latter in bunches of ill-defined prisms, whereas the *ad*-salt gives a transparent deposit of separately-formed, coarse needles and of massive, well-defined prisms respectively.

Although these differences may appear to be unimportant, there is not the least doubt as to the existence of the βd -isomeride; the very fact that there is so much difficulty in separating the two components of the deposit (α) is almost conclusive evidence that they are very closely

related and that the lower melting point and specific rotation of the more soluble portions of this substance are not due to the presence of any ordinary impurity. If these results stood alone, they might possibly still leave an impression of doubt; fortunately, they are confirmed in every respect by the experiments described later, especially by the results of the investigation of the corresponding salts of *d*-chloro-camphorsulphonic acid, as in this case the isolation of the pure β *l*-isomeride was accomplished.

Examination of the Aqueous Solution (b).

The aqueous solution (b) obtained in treating the products of the resolution of the β -salt (p. 892), when crystallised slowly at the ordinary temperature, may give, first, either a deposit of partially racemic β -salt, in the form of yellow prisms or nodules, or white, bulky masses consisting of minute, concentrically grouped needles, which at first were thought to consist of partially racemic α -salt, so closely do they resemble the deposits of the latter. If the partially racemic β -salt separates first, crystallisation is continued until white specks appear, and the solution is then decanted and further evaporated. The bulky, white masses thus obtained melt somewhat indefinitely at about 122°, and when recrystallised from water are deposited apparently unchanged, except that their mother liquors often afford small quantities of the β -salt; on repeated fractional crystallisation, however, the deposits become more and more definite, and after about ten operations a relatively very small quantity of an apparently pure product is obtained.

This substance crystallised from water in long needles melting at about 130°; when separated into two fractions by crystallisation from water, the two fractions seemed to be homogeneous and identical. They were dried at 100° and examined optically in aqueous and in chloroform solution, with the following results:—

Fraction		Substance.	Solvent.	Vol. of solution.	Length of tube.	α_D .	$[\alpha]_D$.
I		0.5724	Water	25 c.c.	200 mm.	1.88°	41.1°
,,	II	0.4570	,,	,,	,,	1.63	44.6
,,	I	0.5724	Chloroform	,,	,,	1.85	40.4
,,	II	0.4570	,,	,,	,,	1.54	42.1

These values are very different from those given by the α *l*-salt under corresponding conditions, and the optical examination seems to show that this new substance is identical with the β *l*-isomeride obtained from the regenerated α *l*-salt (p. 888), but is not quite pure; on further investigation, these conclusions were fully confirmed and this substance is therefore referred to as the β *l*-salt.

The various aqueous filtrates resulting from the crystallisation of the βl -salt give, when evaporated at the ordinary temperature, deposits which generally contain three compounds, namely, the partially racemic β -salt, the opaque, white masses, and small rosettes of prisms; the latter crystals being of some size are distinctly yellow, and can thus be picked out from the deposits; when dissolved in hot water, they separate again, on cooling, in long needles which melt at about 130° and appear to be identical with the crystals of the βl -salt; if, however, they are mixed with some βl -salt, the mixture, when dissolved in hot water, gives an oily product, whereas the βl -isomeride separates in crystals even on the water-bath. When crystallised slowly, moreover, the solution of this mixture gives the opaque, white masses.

The rosettes of yellow prisms, therefore, are different from the crystals of the βl -isomeride, and this conclusion is confirmed by the results of polarimetric examination obtained with two different samples dried at 100° .

Substance.	Solvent.	Vol. of solution.	Length of tube.	α_D .	$[\alpha]_D$.
0.502	Water	25 c.c.	200 mm.	+2.36°	+58.7°
0.418	"	"	"	1.94	58.0

As the specific rotation of the αl -salt in aqueous solution is $[\alpha]_D + 60^{\circ}$, and as these samples (which, however, were not very carefully purified) have all the other properties of the αl -isomeride, there is no doubt that the latter is a component of the partially racemic β -salt.

The isolation of the βl -salt, which in any case is very troublesome, is best accomplished by the method previously described in the case of the regenerated αl -salt (p. 887); after repeatedly crystallising from cold dilute methyl alcohol (not fractionally) and picking out every time any crystals of the αl - or of the partially racemic β -salt which can be observed, the white, opaque masses are fractionally crystallised from warm water until the most sparingly soluble portion separates in distinct needles of some size. The mother liquors, again, give the white, opaque masses, which, having been separated from some βl -salt, when recrystallised from aqueous methyl alcohol furnish the rosettes of the αl -isomeride; these are removed and the operations continued.

In this way, the substance in the aqueous solution (b) is finally separated into αl -salt, crude βl -salt, and the partially racemic β -salt.

There is another method which sometimes gives the βl -salt in small quantities, but which is very uncertain; this is, to evaporate on the water-bath the ethyl acetate filtrate from the original deposit (α), when the oily residue gradually solidifies to a solid mass; if this is now repeatedly extracted with boiling ethyl acetate, the residue, when dissolved in water, gives the white, opaque masses of the mixture of αl - and βl -salts, the former being generally present in relatively

small proportion; from these deposits, the βl -salt is isolated by the method already described. The curious fact is here observed that, whereas the first deposit from the hot ethyl acetate solution of the partially racemic salt consists of the ad - and βd -isomerides, the most sparingly soluble portion of the residue just referred to is a mixture of the al - and βl -salts; this is doubtless because all the four components ad , al , βd , βl , are practically insoluble in boiling ethyl acetate when separated from the others, but are soluble in presence of the corresponding isomeride. In resolving the β -salt, it often happens that, although the original precipitate may appear to be a satisfactory resolution product and melt at a temperature far above the melting point of the partially racemic salt, yet when crystallised from water it gives a deposit consisting almost entirely of the latter; in such cases, therefore, the precipitate contains all the four isomerides.

Final Products of the Resolution of the β -Salt.

The following are the various products of the resolution of the partially racemic β -salt:

- (1) Pure ad -salt; m. p. 222—223°; $[\alpha]_D + 59.9^\circ$ in water.
- (2) Impure βd -salt; m. p. 207—208°; „ + 49.2 „
- (3) Pure al -salt; m. p. indefinite (130°); „ + 59.0 „
- (4) Pure βl -salt; m. p. „ (130°); „ + 39.4 „
- (5) Mixtures of the ad - and βd -salts in various proportions.

The quantities of (3) and (4) are approximately the same, and the sum of the weights of (1), (2), and (5) is approximately equal to that of the weights of (3) and (4); it may be concluded, therefore, that the partially racemic β -salt is composed of approximately equal quantities of the four isomerides, but it is impossible to make more than a rough estimate.

βl -Hydrindamine Bromocamphorsulphonate.

Various samples of the βl -salt obtained in the resolution of the partially racemic β -salt gave, when examined optically in aqueous solution, $[\alpha]_D + 40.4^\circ$, $+ 44.6^\circ$, and $+ 41.8^\circ$, whereas samples of the βl -salt, isolated from the regenerated al -modification (p. 888), gave $+ 41^\circ$ and $+ 39.5^\circ$ respectively; all these preparations crystallised in long needles, and were seemingly pure, but, nevertheless, most of them contained small quantities of the al -isomeride, of which $[\alpha]_D = + 60^\circ$.

A considerable quantity of this crude βl -salt having been prepared from the partially racemic β -compound, the whole was crystallised four times from water and aqueous methyl alcohol alternately, and the most sparingly soluble portion separated and dried at 100° (sample I).

Its specific rotation was then determined in chloroform and in aqueous solutions:

Sample	Substance.	Solvent.	Vol. of solution.	Length of tube.	α_D .	$[\alpha]_D$.
I	0.5	Chloroform	25 c.c.	200 mm.	1.47°	36.7°
„	II	0.5	„	„	1.46	36.5
„	III	0.5	„	„	1.47	36.7
„	I	0.5	Water	„	1.58	39.4

The two samples (II and III) were obtained in later preparations, and purified in a similar manner.

Further crystallisation failed to change the optical or other properties of this isomeride in any way, and the final value (+39.4°) obtained in aqueous solution agrees very closely with that of the pure sample of β l-salt isolated from the regenerated α l-modification; as the small quantity of the α l-isomeride present in the crude β l-salt becomes removed, the crystals of the latter gradually change from tufts of minute needles to distinct, lustrous prisms, and after some experience it is easy to tell by mere inspection when the β l-salt is free from its isomeride.

That the pure substance is identical with the β l-component of the regenerated α l-salt is proved by the identity in optical properties and in all other respects; samples from the two sources, when mixed and crystallised, behaved like a single substance.

Although several analyses of the partially racemic β -salt had been previously made (*loc. cit.*), and there could consequently be little doubt as to the composition of this β l-salt, a halogen determination was made with a pure sample dried at 100°:

0.306 gave 0.1285 AgBr. Br=17.9.

$C_{10}H_{14}OBr \cdot SO_3H, C_9H_{11}N$ requires Br=18.0 per cent.

This β l-salt seems to be more sparingly soluble in warm water than the α l-isomeride, but at the ordinary temperature their solubilities are the same, as was found experimentally; it separates from moderately concentrated warm solutions in long prisms or needles, from very concentrated hot solutions in felted masses which seem to be crystallographically different from the needles; even when its solutions are evaporated on the water-bath, the pure β l-salt separates in crystals, whereas the α l-isomeride under these conditions is often deposited as an oil. The β l-salt crystallises from aqueous methyl alcohol in fairly large, semi-transparent prisms, less well-defined than those of the α l-isomeride, which, however, it resembles very closely in most other respects. Like the latter, it does not melt definitely, a fact which adds to the difficulty of isolating a pure preparation; many melting point determinations have been made, but the behaviour of the salt

varies so much with the size of the crystals and with the rate of heating that concordant results are seldom obtained. The finely powdered salt sometimes melts almost completely at about 122° , but sometimes shows very little change until about 233° ; single crystals of moderate size sometimes melt almost entirely and fairly sharply at $128-130^{\circ}$, sometimes only partially even at 138° ; even if fusion, partial or complete, occurs at these relatively low temperatures, the salt generally solidifies again and melts for a second time at about 233° , decomposing slightly. It may be inferred that this behaviour is due to dimorphism; the form obtained from aqueous solutions has probably a melting or transition point of about 122° , at which temperature it passes more or less completely and rapidly, according to the conditions of the experiment, into a modification melting at a higher temperature; whether the second melting point or decomposition point (233°), which is fairly constant, is that of this second crystallographic modification or that of some compound of acid and salt has not been determined.

Synthesis of the partially Racemic β -salt (m. p. 130°).

The first results of the experiments on the resolution of the β -salt seemed to show that this substance was composed of *two* salts, namely, the component melting at about $215-216^{\circ}$, obtained from the deposit (a) (p. 892), and the component crystallising in tufts of needles melting at about 122° obtained from the aqueous solution (b) (p. 895); before it was known that each of these components is a mixture of isomerides, it seemed desirable to ascertain whether or not they were identical with the components of the partially racemic α -salt which respectively they resembled very closely. The best way of doing this seemed to be to mix the two β -products in equal quantities and crystallise the mixture from water; this experiment was therefore made.

The sample of the less fusible component which was used had been crystallised only once or twice from water to free it from partially racemic β -salt, and probably consisted, therefore, of the isomeric *ad*- and β *d*-salts in practically the same proportions as they occur in the partially racemic β -component; the sample of the more fusible component, however, had been fractionally crystallised from water, and probably contained a larger proportion of the β *l*-isomeride than the original mixture. Nevertheless, on crystallising the mixed salts from water, a substance was deposited in transparent, well-defined, hydrated prisms which were indistinguishable in appearance from the crystals of the ordinary partially racemic β -salt, and which, when dried, had the melting point of the latter. Crystallisation of this synthetical product failed to reveal the presence of any of the partially racemic α -salt.

This experiment proves that the ordinary partially racemic β -salt is really a mixture of four isomerides, and that the *ad*- and *al*-components which are obtained from it are not derived from the partially racemic α -salt present as impurity.

Synthesis of a New partially Racemic β -Salt.

Having found that the two components used in the preceding experiment were both mixtures of isomerides, and that the ordinary β -salt consists of four substances, it seemed interesting to ascertain the result of mixing the pure β l-salt with the (impure) β d-isomeride.

For this purpose, a sample of pure β l-salt having a specific rotation of $[\alpha]_D + 36.5^\circ$ in chloroform and $[\alpha]_D + 39.4^\circ$ in aqueous solution was mixed with an equal quantity of a sample of impure β d-salt having the values $[\alpha]_D + 31^\circ$ and $[\alpha]_D + 55.7^\circ$ under corresponding conditions.

The specific rotation of the mixture was then determined, with the following results :

Substance.	Solvent.	Vol. of solution.	Length of tube.	α_D .	$[\alpha]_D$.
0.5	Chloroform	25 c.c.	200 mm.	+1.64°	+41°
0.5	Water	„	„	1.93	48.5

On crystallising the mixture from water, a salt was deposited in rosettes of well-defined, transparent prisms, indistinguishable by inspection from the crystals of the ordinary partially racemic β -salt; these prisms, moreover, contained water of crystallisation, an air-dried sample losing 2.6 per cent. of water when heated at 100° during 7 hours, and 3.09 per cent. after heating during 13 hours; the ordinary β -salt contains 2.7 per cent. of water.

Obviously, however, this substance cannot be identical with the ordinary partially racemic β -salt, and as a matter of fact it differs from the latter in melting point; when previously dried at 100° , instead of melting at 130° (the melting point of ordinary β -salt), it fuses fairly sharply at 158 – 160° , probably undergoing some crystallographic change at lower temperatures, since it seems to melt partially at about 140° and then solidify again.

A consideration of the optical properties of this salt in different solvents affords insufficient evidence that it is different from the ordinary partially racemic β -salt. Calculating from the values of its components, its specific rotation in chloroform should be $[\alpha]_D + 33.7^\circ$ and in water $[\alpha]_D + 47.5^\circ$, those actually found being $[\alpha]_D + 41^\circ$ and $+48.5^\circ$ respectively; in chloroform, therefore, the observed is very different from the calculated value, whereas in aqueous solution the two values are practically the same, showing that in the latter case the

presence of the one isomeride does not seem to change appreciably the specific rotation of the other.

Now the specific rotation of the ordinary partially racemic β -salt was previously given as $+41.5^\circ$ in chloroform (one determination only), and from $+48.3^\circ$ to $+54.3^\circ$ in water; taking the lowest of these values in aqueous solution, the results agreed very closely with those obtained with the synthetical salt.

During the present investigation, a specimen of the ordinary partially racemic β -salt was obtained by crystallisation from aqueous alcohol in large, beautifully defined, flat prisms, all of which were obviously identical; as this sample seemed to represent a perfectly definite compound, it was dried in the air and examined optically, with the following results:

Substance.	Solvent.	Vol. of solution.	Length of tube.	α_D .	$[\alpha]_D$.
0.5	Chloroform	25 c.c.	200 mm.	$+1.82^\circ$	$+45.5^\circ$
0.5	Water	„	„	2.16	54.0

Calculating for the anhydrous substance, the values would be

$$\text{chloroform: } [\alpha]_D + 46.8^\circ, \quad \text{water: } [\alpha]_D + 55.5^\circ,$$

which are higher in both cases than any previously obtained.

From the results of these experiments, it would seem, therefore, that the four isomerides of the ordinary partially racemic β -salt may crystallise together in different proportions, giving products which are apparently homogeneous, and which have all the ordinary characteristics of a pure single substance; a change in the solvent or in the temperature at which crystallisation occurs probably causes a slight alteration in the proportions of the four components of the β -salt without appreciably altering the crystalline form, so that on fractionally crystallising under ordinary conditions, a number of slightly different substances may be obtained. In any case, on crystallising the original salt, obtained from *dl*-hydrindamine and *d*-bromocamphor-sulphonic acid, the whole of the βd - and βl -components remain in the deposits of partially racemic β -salt, since the two products of the resolution of the α -salt are homogeneous, and consist of the pure αd - and αl -isomerides respectively.

That the partially racemic α -salt is free from the βd - and βl -isomerides might be inferred from a consideration of the specific rotation of the salt itself and those of its components, the values in 2 per cent. aqueous solution being as follows:

$$\alpha\text{-Salt: } [\alpha]_D + 60.8^\circ; \quad \alpha d\text{-salt: } [\alpha]_D + 61^\circ; \quad \alpha l\text{-salt: } [\alpha]_D + 60^\circ.$$

Taking the values in 2 per cent. aqueous solution, the average for the partially racemic β -salt is about $[\alpha]_D + 51.0^\circ$; those of its components are as follows: αd -salt, $+61^\circ$; αl -salt, $+60^\circ$; βd -salt

(impure), $+50^{\circ}$; βl -salt, $+39^{\circ}$. Assuming that the ordinary partially racemic β -salt contains approximately equal quantities of all four components, its calculated specific rotation would be $[\alpha]_D + 52.5^{\circ}$.

It is an interesting question whether the ad - and al -isomerides and the βd - and βl -forms are actually produced in equal quantities on combining the dl -base with the acid, or whether a larger proportion of, say, the ad -salt is formed from d -base than of al -salt from the l -base; from theoretical considerations, equality is, perhaps, to be expected.

A comparison of the properties of the four isomeric hydrindamine bromocamphorsulphonates, described in this and in the preceding paper, with those of the corresponding d -chlorocamphorsulphonates (see below) and a discussion of their isomerism form the subject of a later communication (p. 937).

UNIVERSITY COLLEGE,
NOTTINGHAM.