

XLV.—*Isomeric Salts containing Quinquevalent Nitrogen. Part VII. Benzylhydrindamine Bromocamphorsulphonates.*

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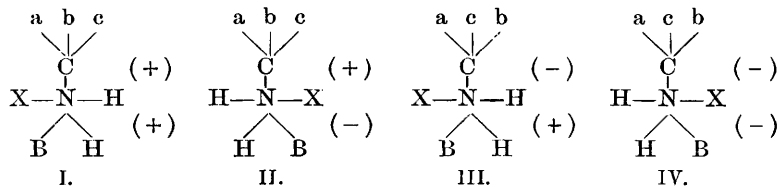
BENZYLHYDRINDAMINE, a base prepared by treating *dl*-hydrindamine with benzyl chloride, combines with α -bromocamphorsulphonic acid, forming a salt which, on fractional crystallisation, is resolved into isomerides of the composition $C_{16}H_{17}N, C_{10}H_{14}BrO \cdot SO_3H$.

The more sparingly soluble α -compound differs from the more readily soluble β -compound in appearance, melting point, and other ordinary properties, and although the specific rotations are practically the same in alcoholic they become dissimilar in chloroform solution.

When the two isomerides are separately decomposed with barium hydroxide, they both give an optically inactive benzylhydrindamine, and the ammonium bromocamphorsulphonate obtained from the solution of the barium salt is, in both cases, identical in ordinary and in optical properties with ammonium *d*-bromocamphorsulphonate; consequently the two isomerides consist of the same base and the same acid.

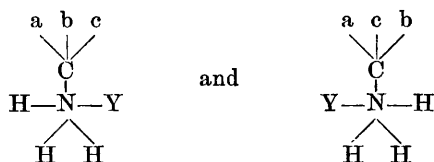
Judging by analogy, the isomerism of these two salts is of the same peculiar character as that of the hydrindamine bromo- and chloro-camphorsulphonates and *cis*- π -camphanates (Kipping, *Trans.*, 1900, 77, 861), but whereas in the latter the nitrogen atom is united with only *three* different atoms or groups, the benzylhydrindamine salts contain a nitrogen atom directly combined with the radicles H, C_9H_9 , C_7H_7 , and $C_{10}H_{14}BrO \cdot SO_3$.

Now the presence of four different groups attached to nitrogen might determine the existence of enantiomorphously related optically active forms, and since benzylhydrindamine contains an asymmetric carbon group, if the arrangement of the groups around the nitrogen atom is really such as to give rise independently to further optical isomerism, the following four hydrochlorides of benzylhydrindamine would, theoretically, be capable of existence:



These four isomerides might therefore be expected to unite in pairs (I and IV, II and III) to form two externally compensated or racemic salts differing from one another in ordinary properties.

If, however, the chlorine atom, X, in the above compounds be displaced by the ion of *d*-bromocamphorsulphonic acid, the forms I and IV, II and III are no longer enantiomorphously related, and the formation of externally compensated salts is therefore impossible; on the other hand, two partially externally compensated salts might be formed, just as in the case of many of the salts of hydrindamine, and for the same reasons. Whether the observed isomerism of the benzyhydrindamine bromocamphorsulphonates should be attributed to the existence of four optically active ammonium bases, enantiomorphously related in pairs, as indicated by the above formulæ, or whether it should be considered to be analogous to that of the hydrindamine bromocamphorsulphonates, there is no means of deciding with certainty from the facts at disposal; there is, indeed, no considerable difference between the two views in question, except that in the case of the hydrindamine salts the enantiomorphous relationship of the forms



may be left open (*loc. cit.*, p. 869).

The fact that both salts afford an optically inactive benzyhydrindamine on decomposition is in accordance with either view, since when the base is liberated the nitrogen atom becomes tervalent.

The slight difference in the observed specific rotations of the salts in chloroform solution recalls the analogous observations made in the case of aqueous solutions of the hydrindamine compounds, but throws no light on their nature; if completely dissociated, they would probably both give the normal molecular rotation of the acid, but owing to their very slight solubility in water, their specific rotations in aqueous solution could not be determined.

For the same reason, namely, their slight solubility, it is not very easy to convert the isomerides into well-crystallised salts of some optically inactive acid. When, however, a solution of the β -salt is treated with a solution of picric acid, a precipitate of benzyhydrindamine picrate is obtained. This salt is identical in melting point and in crystalline character with the picrate obtained by precipitating a solution of benzyhydrindamine hydrochloride.

Now if the isomeric benzyhydrindamine bromocamphorsulphonates

represented salts derived from two different externally compensated bases, as formulated above, the β -salt might be expected to give a picrate different from that obtained from benzylhydrindamine hydrochloride, because whereas the latter would contain all four bases, the β -salt would contain only two of them, I and IV, or II and III; the fact, then, that the picrates are identical in outward properties, taken in conjunction with the apparent homogeneity of the hydrochloride of the base, seems to show that the original benzylhydrindamine has not been resolved into isomeric externally compensated bases, or, in other words, that the existence of its two bromocamphorsulphonates is not caused by optical isomerism of the groups united to nitrogen. The evidence, however, is not satisfactory, and the whole problem is of considerable complexity so, for the present at any rate, it seems preferable to regard the isomerism of the benzylhydrindamine salts as being analogous to that of the salts of hydrindamine.

Accepting the latter view, isomerism of this kind has now been observed in the case of the

Hydrindamine bromocamphorsulphonates (Trans., 1900, 77, 861)	
„ chlorocamphorsulphonates („)	
„ <i>cis</i> - π -camphanates, and („)	
Benzylhydrindamine bromocamphorsulphonates.	

The following compounds, however, namely :

Hydrindamine <i>d</i> -camphor- π -sulphonate (this vol., p. 370)	
„ <i>d</i> -mandelate „	
„ <i>d</i> -camphor- α -sulphonate (this paper)	
„ <i>d</i> -hydroxy- <i>cis</i> - π -camphanate („)	

do not afford any evidence of the existence of isomeric forms when they are fractionally crystallised.

It will be obvious from this summary that the nature of the isomerism in question is of a very peculiar character, inasmuch as with one and the same base, namely, *dl*-hydrindamine, acids which are very closely related to one another give different results: α -bromocamphor-sulphonic acid gives separable isomerides differing very considerably in ordinary properties, whilst its simple reduction product, camphor- π -sulphonic acid, gives an apparently homogeneous salt; again, *cis*- π -camphanic acid affords separable isomerides somewhat similar to one another in properties, whereas its hydroxy-derivative gives a salt which is apparently homogeneous.

These remarkable facts, and the discovery that ordinary *d*-bromocamphorsulphonic acid contains a small quantity of the corresponding *l*-acid (this vol., p. 370), raised misgiving as to whether the formation of these isomeric salts might not after all be caused by the presence of

some isomeride in the acids used, but a reconsideration of the facts and further experimental evidence show such a view to be untenable.

As previously stated (Trans., 1900, 77, 861), the more readily soluble β -salt can be partially converted into the α -salt in the case of the three pairs of isomerides already described; this fact has since been confirmed in the case of the *cis*- π -camphanates. It has also been shown that *some* ammonium bromocamphorsulphonate, identical in ordinary and in optical properties with the salt prepared from the α -isomeride, can be obtained from the more readily soluble β -salt; the further experiment described below proves that the *whole* of the acid in the β -salt consists of ordinary *d*-bromocamphorsulphonic acid.

Again, the hydrindamine *cis*- π -camphanates have (sometimes) widely different specific rotations in alcoholic solution, but give practically identical values when they are dissolved in water; this fact, and the partial conversion of the β - into the α -salt on evaporating with the *dl*-base, seemed to prove beyond doubt that the acids of the two isomerides were identical; in the course of further experiments with these remarkable salts, additional evidence, perhaps not wholly unnecessary in view of the origin and nature of the acid, has been obtained that this conclusion is correct.

So far, then, the facts established during the study of the salts described in these papers tend to bear out the theoretical views which have already been tentatively put forward to explain these cases of isomerism. The results of the investigation of the hydrindamine mandelates have shown, moreover, that *three* salts, which are optically different, namely, *dAdB*, *dAlB*, and *lAlB* may form a mixture which is not resolved into appreciably different fractions on crystallisation; it is therefore by no means improbable that, as already suggested, the product of the combination of an optically active acid with an externally compensated base may be a mixture of *four* optically different forms, which sometimes unite in pairs to form separable partially externally compensated salts, but sometimes give separable salts of the enantiomorphously related bases; from experience gained in working with various externally compensated acids and bases, it would seem that what has hitherto been generally regarded as the normal behaviour, namely, a separation of the optical antipodes, is in reality a somewhat exceptional result, and that in the majority of cases the two compounds unite to form a mixture of *dAdB* and *dAlB* or of *dAdB* and *lAdB*, as the case may be, which crystallises unchanged at the ordinary temperature.

The recently observed fact that tetrahydro- β -naphthylamine readily undergoes partial racemisation when liberated from its salts (Pope and Harvey, this vol., p. 74) might perhaps be thought to have some bearing on the question of the isomerism of the hydrindamine salts

considering the relationship between the two bases; and it might even be inferred that the α - and β -isomerides actually represent salts of the enantiomorphously related hydrindamines, which then at once undergo racemisation when set free from the acid. This possibility, however, has already been considered* and rejected (Kipping, *Trans.*, 1900, 77, 878, 909), and the further evidence arising from the study of the benzylhydrindamine salts seems to exclude the possibility of any separation of the enantiomorphously related bases having occurred.

Benzylhydrindamine.

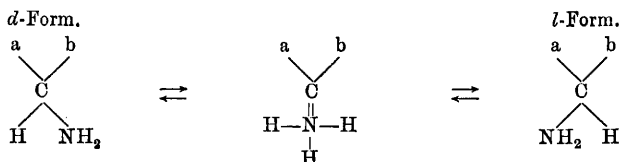
When benzyl chloride is added to an ethereal solution of hydrindamine, interaction occurs slowly at the ordinary temperature, crystals separate, and the change is completed by warming on the water-bath during some hours; after distilling off the ether and separating any unchanged benzyl chloride with a current of steam, the aqueous solution is evaporated to a small bulk, and the oily product which then separates is dissolved by the addition of a little alcohol; on cooling, benzylhydrindamine hydrochloride is deposited in almost colourless crystals and may be purified by recrystallisation from water or dilute alcohol.

For analysis, 0.2629 gram of a sample dried at 100° was dissolved in a large volume of boiling water, the solution acidified with dilute nitric acid and treated with silver nitrate: $\text{AgCl} = 0.1394$. $\text{Cl} = 13.4$.

$\text{C}_{16}\text{H}_{17}\text{N}, \text{HCl}$ requires $\text{Cl} = 13.6$ per cent.

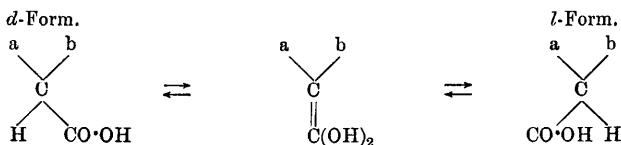
Benzylhydrindamine hydrochloride crystallises from water in very small prisms which melt at about 180—181° (corr.) when heated quickly,

* It was suggested that the mechanism of the change in such cases might be as follows.



This view has since been adopted by Pope and Harvey (*loc. cit.*), who apparently overlooked the fact that it had been previously advanced.

The readiness with which many substituted acids containing the asymmetric group in the α -position undergo racemisation may be accounted for in a similar manner:



but the melting point varies considerably with the experimental conditions and on continued heating even at about 175° the salt gradually liquefies; it is readily soluble in hot, but only sparingly so in cold water, and dissolves freely in cold alcohol.

The *base* is obtained as a colourless oil on treating a solution of the hydrochloride with an alkali; it is practically insoluble in cold water and has a neutral or only very feebly alkaline reaction to litmus; it volatilises in steam, but only slowly.

Benzylhydrindamine Bromocamphorsulphonates.

The base, liberated from the pure hydrochloride and separated by extracting with ether or distilling in steam, is treated with a slight excess of *d*-bromocamphorsulphonic acid in aqueous alcohol, and the solution evaporated if necessary; on cooling, crystals are deposited and by repeated fractional crystallisation of the first and subsequent deposits from boiling water or dilute methyl alcohol, two salts are obtained in a state of purity.

α -Salt.—The more sparingly soluble, or α -salt, separates from water in flat, thin, transparent plates melting sharply at 210 – 211° (corr.); it is almost insoluble in ether, and only very sparingly soluble in ethyl acetate or cold water, but dissolves comparatively easily in hot alcohol or cold chloroform. It is usually obtained in microscopic plates or fern-like masses, which, however, under the microscope, are easily distinguished from the crystals of the β -isomeride. The salt is anhydrous.

0.2 gave 0.0707 AgBr. Br = 15.0.

$C_{16}H_{17}N, C_{10}H_{14}BrO \cdot SO_3H$ requires Br = 14.9 per cent.

Determinations of the specific rotation of the α -salt gave the following results:

0.25 gram was dissolved in 96 per cent. ethyl alcohol, the solution diluted to 25 c.c. and examined in a 200 mm. tube: $\alpha_D = +1^{\circ}0'$, whence $[\alpha]_D = +50^{\circ}$ and $[M]_D = +267^{\circ}$.

0.2 gram dissolved in chloroform, all other conditions as before, gave $\alpha_D = +40'$, whence $[\alpha]_D = +41.6^{\circ}$.

0.4 gram dissolved in chloroform, all other conditions unchanged, gave $\alpha_D = +1^{\circ}16'$, whence $[\alpha]_D = +39.7^{\circ}$.

The base obtained from the α -salt is optically inactive: 1 gram of the salt decomposed with potash in the cold and the base extracted with ether gave an ethereal extract (about 20 c.c.) which showed no optical activity when examined in a 200 mm. tube.

In order to prove that the salt is derived from ordinary *d*-bromocamphorsulphonic acid, a sample was decomposed by warming it with a

solution of the calculated quantity of barium hydroxide; after cooling and extracting the base with ether (the extract was optically inactive), the aqueous solution of the barium salt was precipitated with ammonium carbonate, the filtered solution evaporated to dryness, and the residue heated on the water-bath until all ammonium carbonate had been expelled; the residual ammonium bromocamphorsulphonate was finally recrystallised from a very small quantity of water, dried, and its specific rotation determined in aqueous solution. The value obtained agreed with that of ammonium *d*-bromocamphorsulphonate.

β-Salt.—The more readily soluble, or *β*-salt, melts at 192–194° (corr.), and also differs from the *α*-isomeride in outward properties, being usually obtained in aggregates of poorly defined, microscopic prisms; it is anhydrous and its behaviour towards solvents is similar to that of the *α*-salt.

0.2 gave 0.0702 AgBr. Br = 14.9.

$C_{16}H_{17}N, C_{10}H_{14}BrO \cdot SO_3H$ requires Br = 14.9 per cent.

The specific rotation of this salt was determined in alcoholic and in chloroform solution:

0.25 gram was dissolved in 96 per cent. ethyl alcohol, the solution diluted to 25 c.c. and examined in a 200 mm. tube: $\alpha_D = +1^{\circ}2'$, whence $[\alpha]_D = +51.5^{\circ}$ and $[M]_D = +275^{\circ}$.

Under the same conditions, but using chloroform as solvent:

0.2 gram gave $\alpha = +44'$: $[\alpha]_D = +45.8^{\circ}$.

0.4 „ „ $\alpha = +1^{\circ}22'$: $[\alpha]_D = +42.8^{\circ}$.

It seems from these determinations that the isomerides have practically the same specific rotation in alcoholic solution, and that their molecular rotation in this solvent is the same as that of the fully dissociated salts of *d*-bromocamphorsulphonic acid; this might be a mere coincidence, but the experiments on the decomposition products of the isomerides show that the base of the salts is in both cases optically inactive, and that both salts contain *d*-bromocamphorsulphonic acid.

The specific rotation of the *β*-salt in chloroform solution seems to be rather higher than that of the *α*-isomeride, the above results having been obtained under exactly the same conditions in the two cases; the difference, however, is so small that it almost falls within the limits of experimental error, and in any case it is not of any great importance, as the values obtained for the specific rotation in such a solvent cannot throw any light on the nature of the salts.

That the base obtained from the *β*-salt is identical with that given by the *α*-isomeride was proved by decomposing the former with a

warm solution of the calculated quantity of barium hydroxide and then extracting with ether; the ethereal extract was optically inactive, and when shaken with hydrochloric acid it gave a benzylhydrindamine hydrochloride identical as regards melting point and outward properties with that obtained from the α -salt in a similar manner, and also with the hydrochloride of the original base. The solution of the barium bromocamphorsulphonate was precipitated with ammonium carbonate and the ammonium salt of the bromo-acid was purified as described in the case of the α -isomeride; the specific rotation of this ammonium salt was found to be identical, within the limits of experimental error, with that of ammonium *d*-bromocamphorsulphonate.

Benzylhydrindamine Picrate.

In order to obtain further evidence as to the nature of the base contained in the isomeric benzylhydrindamine salts, attempts were made to transfer the base directly from the bromocamphorsulphonic acid to some optically inactive acid; from an examination of the new salt, information might then be obtained as to whether the original base had or had not been resolved into different components.

Owing to the very slight solubility of the α -salt, which crystallises unchanged from moderately concentrated hydrochloric acid, the β -isomeride was employed, but even in this case the choice of methods is limited for a similar reason. Picric acid, however, precipitates the base from a solution of its bromocamphorsulphonate in very dilute methyl alcohol, in the form of a canary-yellow, somewhat sticky mass, which, on recrystallisation from aqueous methyl alcohol is deposited in slender, well-defined, transparent, yellow prisms or in more compact, poorly-defined crystals. This picrate, when heated slowly, sinters slightly at 159–160° and melts completely at 162–163°.

The picrate was also prepared from a sample of benzylhydrindamine hydrochloride in a similar manner and compared with that obtained from the β -salt; they melted simultaneously, appeared to be identical in crystalline character under the microscope, and, in short, no difference between them could be observed; a finely divided mixture of the salts from the two sources melted at the same temperature as its separate constituents.

dl-Hydrindamine Camphor- α -sulphonate.

The unsuccessful result of the attempts to isolate isomeric salts analogous to the hydrindamine bromocamphorsulphonates from the product of the combination of hydrindamine and camphor- π -sulphonic acid (Kipping, this vol., p. 370), led us to try and obtain such isomerides with the aid of Reyhler's camphorsulphonic acid.

On neutralising this acid with an aqueous alcoholic solution of hydrindamine and then evaporating, the salt is deposited from the cold solution in long prisms or needles, but as it is very readily soluble in water it is most conveniently crystallised from a mixture of alcohol and ethyl acetate; by making use of these solvents and crystallising in a systematic manner, part of the product was finally obtained as two extreme fractions, which, however, proved to be identical in ordinary and in optical properties.

Hydrindamine camphor- α -sulphonate crystallises from water in transparent prisms melting at $167\text{--}168^\circ$ (corr.) apparently without decomposing; it is very readily soluble in water, chloroform, or alcohol, less readily in ethyl acetate, and almost insoluble in ether; it separates in prisms from all solvents which were examined, and under the microscope no indication of the presence of different crystals is observed.

The salt is anhydrous, and a nitrogen estimation gave results agreeing with those required for the formula $\text{C}_9\text{H}_{11}\text{N}, \text{C}_{10}\text{H}_{15}\text{O} \cdot \text{SO}_3\text{H}$.

The specific rotation of the salt was determined in aqueous solution, the two extreme fractions being employed:

First fraction: 0.6 gram was dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube: $\alpha_D = +39'$, whence $[\alpha]_D = +13.5^\circ$ and $[M]_D = +49.3^\circ$.

Last fraction: 0.6 gram under the same conditions gave $\alpha_D = +38'$, whence $[\alpha]_D = +13.2^\circ$ and $[M]_D = +48.2^\circ$.

The molecular rotation of this camphorsulphonic acid has been determined by Pope (Trans., 1900, 77, 1085), who found it to be $+51.7^\circ$; the above results accord fairly well with this value, and their close agreement with one another shows that no resolution of the salt has occurred, but whether it is a true partially racemic compound or a mere mixture, there is no evidence upon which to base a decision.

In alcoholic solution, the specific rotation is very much higher than in aqueous, as shown by the following determination:

0.5 gram dissolved in 96 per cent. ethyl alcohol, the solution diluted to 25 c.c. and examined in a 200 mm. tube, gave $\alpha_D = +1.2'$, whence $[\alpha]_D = +25.8^\circ$ and $[M]_D = +94^\circ$.

This great difference between the values obtained in these two solvents is rather noteworthy when contrasted with the comparatively small difference caused by the substitution of alcohol for water in the case of *dl*-hydrindamine camphor- π -sulphonate.

dl-Hydrindamine d-Hydroxy-cis- π -camphanate.

The fact that *cis*- π -camphanic acid yields separable isomeric salts with *dl*-hydrindamine rendered it probable that hydroxy-*cis*- π -camphanic acid (Kipping, *Trans.*, 1896, 69, 947) would do so likewise, but experiment showed this inference to be unfounded.

On treating hydroxy-*cis*- π -camphanic acid with an aqueous solution of the base in slight excess and then concentrating, the salt is deposited in long, transparent prisms; by systematic crystallisation from dilute methyl alcohol, the original preparation was separated into two extreme fractions which, however, proved to be identical.

Hydrindamine hydroxy-*cis*- π camphanate separates from dilute alcohol in prisms containing water of crystallisation.

0.5136 air-dried salt lost 0.0114 H_2O at 100° . $\text{H}_2\text{O} = 2.2$.

$\text{C}_9\text{H}_{11}\text{N}, \text{C}_{10}\text{H}_{14}\text{O}_{5.5}\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 2.5$ per cent.

The anhydrous compound melts at $206\text{--}207^\circ$ (corr.), sintering a little at about 202° ; it is readily soluble in cold alcohol or hot water, but the hydrated crystals are practically insoluble in chloroform, ether, or ethyl acetate. The specific rotation of the salt in aqueous solution was so low that it could not be determined with reasonable accuracy in dilute solutions, but a determination with a sample of the air-dried acid gave $[\alpha]_{\text{D}} = +10.8^\circ$ in 2 per cent. aqueous solution; the identity of the two extreme fractions of the salt in melting point and in all ordinary properties may be taken as satisfactory proof that the base has not been resolved into its enantiomorphously related constituents.

Aqueous solutions of hydrindamine hydroxy-*cis*- π -camphanate soon become acid to litmus when they are boiled, the base escaping with the steam. It is possible that this fact, which no doubt indicates hydrolytic dissociation, is accountable for the failure to isolate isomeric forms of the salt, since, as already pointed out, the isomeric *cis*- π -camphanates, which also undergo hydrolytic dissociation to some extent, are partially converted one into the other in aqueous solution.

Hydrindamine Bromocamphorsulphonate.

The difficulty of explaining satisfactorily the formation of the two hydrindamine bromocamphorsulphonates, when considered in the light of the recent discovery of the existence of isomeric bromocamphorsulphonic acids (this vol., p. 370), seemed to render desirable some further experimental evidence in support of the view that the isomerides are derived entirely from the same acid and the same base.

As the β -salt is formed in such relatively small quantities, and as

this salt also gives a molecular rotation below the normal, it might be concluded that it contained a small proportion of the salt of *l*-bromocamphorsulphonic acid; such a conclusion, no doubt, would be difficult to reconcile with many of the facts already recorded, as, for example, the conversion of the β - into the α -isomeride on evaporating with the *dl*-base, and it is now shown to be quite untenable by the following experiment:

0.5 gram of a sample of the air-dried β -salt was dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube; the average reading was $\alpha_D = +2^\circ 3'$, whence $[\alpha]_D = +51.25^\circ$ and $[M]_D = +227.5^\circ$, a result which agrees well with previous determinations.

The whole of the solution was then carefully washed into a flask, treated with *N*/10 sodium hydroxide solution in slight excess of the quantity required to liberate the base, and boiled until the latter was completely expelled; after cooling and diluting to 25 c.c. again, the solution, when re-examined in a 200 mm. tube, gave $\alpha_D = +2^\circ 22'$, whence $[\alpha]_D = +59.25^\circ$ and $[M]_D = +263^\circ$. Taking the water of crystallisation in the original salt as being 2.8 per cent., the molecular rotation calculated for the anhydrous salt would be $[M]_D = +270^\circ$, a value which agrees exactly with that of *d*-bromocamphorsulphonic acid.

This result shows that the β -salt is free from the *l*-bromo-acid, and that its low molecular rotation is determined by the presence of hydrindamine; that the base contained in it is externally compensated seems to be a conclusion amply warranted by other facts already recorded.

Isomeric Hydrindamine cis- π -Camphanates.

The investigation of these interesting isomerides has been continued and, briefly stated, the results have only served to confirm those previously recorded; samples of the α -isomeride melting at 193° and having a specific rotation $[\alpha]_D = -8^\circ$, when repeatedly crystallised fractionally from alcohol, gradually change in specific rotation and become dextrorotatory, but without any alteration in melting point. The experimental results, however, are very irregular and uncertain, and sometimes two or three recrystallisations fail to bring about any noteworthy change in optical properties.

In the case of these isomerides, more attention has so far been paid to proving that they both contain externally compensated base (*Trans.*, 1900, 77, 909) than to establishing the identity of the acids contained in them, and although the fact that their molecular rotations are practically the same in aqueous solution, indicated the absence

of any isomeric acid, the evidence on this point was not altogether satisfactory. The partial conversion of the β - into the α -salt on evaporating with *dl*-base is a much stronger argument in support of the identity of the acids, but here again the experimental results are very irregular and uncertain; in working with moderate quantities (1–2 grams) of the β -salt, the solution may be evaporated with base as many as 10 times without any change in melting point of the salt being observed, but on persevering a favourable result is ultimately obtained, and after about 20 operations the melting point of the deposit has usually risen considerably.

The fact that *cis*- π -camphanic acid is formed by the distillation of π -hydroxycamphoric acid at a high temperature (Trans., 1896, 69, 944) and that consequently the acid used in these experiments might be a mixture of the *d*- and *l*-isomerides owing to partial racemisation having occurred, was a possibility which has not hitherto been discussed, although it has been shown that the acid from the α -salt is identical in melting point and appearance with that of the β -salt; this fact does not exclude the possibility just mentioned because *dl-cis*- π -camphanic acid is a mere mixture of the isomerides, and its melting point is practically the same as that of its separate components.

In order to obtain conclusive evidence on this point, samples of the α - and β -salts melting at 193° and 173° respectively were separately decomposed with a solution of hydrogen chloride in aqueous methyl alcohol; the precipitated acids were filtered off, washed well, and dried. Their specific rotations were then determined with the following results:

Acid from α -salt: 0.367 gram was dissolved in water and a few drops of ammonia, the solution diluted to 25 c.c. and examined in a 200 mm. tube: $\alpha_D = -38'$, whence $[\alpha]_D = -21.6^{\circ}$.

Acid from β -salt: 0.367 gram under exactly the same conditions gave $\alpha_D = -39'$, whence $[\alpha]_D = -22.1^{\circ}$.

These results show that the salts contain the same acid and thus confirm the conclusion arrived at from the consideration of the data already recorded.

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