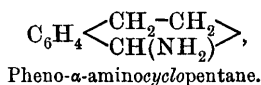
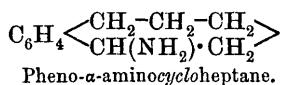


LXI.—*The Resolution of Pheno- $\alpha$ -aminocycloheptane into its Optical Isomerides. Tartrates of Pheno- $\alpha$ -aminocycloheptane and of Hydrindamine.*

By FREDERIC STANLEY KIPPING and ALBERT EDWARD HUNTER.

PHENO- $\alpha$ -AMINOCYCLOHEPTANE (Kipping and Hunter, Trans., 1901, 79, 602) and pheno- $\alpha$ -aminocyclopentane ( $\alpha$ -hydrindamine), being very similar in constitution, especially with regard to the nature and position in the molecule of the asymmetric carbon group, as shown in the following formulæ,



it seemed possible that the two bases would behave in a similar manner towards a given optically active acid; if this actually proved to be the case, the study of the compounds of pheno- $\alpha$ -aminocycloheptane might throw some light on the nature of those hydrindamine salts which have recently been investigated (Kipping, Trans., 1900, 77, 861; 1901, 79, 430) and appear to be altogether abnormal.

The experiments which have so far been made with the *cycloheptane* derivative have shown, however, that the two bases behave quite differently; whereas *dl*-hydrindamine hydrogen tartrate is not changed by fractional crystallisation from water, the corresponding compound of *dl*-pheno- $\alpha$ -aminocycloheptane with *d*-tartaric acid is readily resolved into the salts of its enantiomorphously related components.

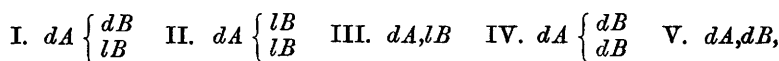
Of these two salts, the more sparingly soluble is that of the *l*-base, which is thus easily isolated; it is almost optically inactive, owing to the molecular rotation of the base being approximately equal to that of the acid, but of opposite sign.

The active base does not show the least tendency to undergo racemisation, and when liberated from its salts or when submitted to

distillation in steam, its optical properties seem to remain absolutely unchanged; further, when treated with benzoyl chloride and sodium hydroxide, it yields an optically active benzoyl derivative, and although the sign of rotation is changed, there is no evidence of even partial racemisation having occurred.

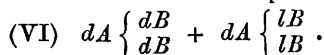
These observations might be quoted in support of the view that the existence of the hydrindamine salts already referred to cannot be explained by assuming that the optically active hydrindamines immediately undergo complete racemisation when liberated from their salts (Trans., 1900, 77, 878, 909); but considering that in the case of other bases, almost as closely related to pheno- $\alpha$ -aminocycloheptane in constitution, as, for example, in that of tetrahydro- $\beta$ -naphthylamine (Pope and Harvey, Trans., 1901, 79, 74), partial racemisation occurs when the base is set free from its salts and when it is benzoylated by the Schotten-Baumann method, it would seem that arguments based on analogy have little, if any, value as regards such reactions. It would follow, therefore, that even if racemisation of amino-compounds, in which the amino-group is directly united with the asymmetric carbon atom, is due to tautomeric changes,  $>\text{CH}\cdot\text{NH}_2 \rightleftharpoons >\text{C}\cdot\text{NH}_2$ , as previously suggested, such changes are not necessarily intermediate steps in the formation of salts or in the production of alkyl derivatives.

The relationship between the various salts which have been obtained from *dl*-pheno- $\alpha$ -aminocycloheptane and *d*-tartaric acid is not without interest, and of the five (or six) compounds which might be prepared, namely,



all have been isolated and studied.

The first of these compounds, a normal salt, is deposited from neutral and also from acid solutions; it may be regarded as a partially compensated compound, but may possibly be more complex in character and consist of a partially racemic compound of the two salts,



The normal salt of the *l*-base (II) cannot be obtained directly by crystallising solutions of the *dl*-base in aqueous tartaric acid, but was prepared from the pure *l*-base; it is more readily soluble in water than the normal salt (I) of the *dl*-base, and also more readily soluble than the hydrogen salt (III).

The hydrogen salt of the *l*-base (III) is obtained by crystallising a solution of the *dl*-base in a large excess of aqueous *d*-tartaric acid, and is consequently more sparingly soluble than the corresponding salt of the *d*-base (V); it contains 3 mols.  $\text{H}_2\text{O}$ . The normal salt of the

## 576 KIPPING AND HUNTER: THE RESOLUTION OF PHENO-

*d*-base (IV) can be isolated from the mother liquors obtained in the crystallisation of the preceding compound; it is anhydrous. The hydrogen salt of the *d*-base (V) was obtained by crystallising the normal salt from aqueous tartaric acid.

The tartrates of *dl*-hydrindamine behave differently from the corresponding salts of the *cycloheptane* base. The hydrogen tartrate is easily obtained in crystals from a solution of the base (1 mol.) in aqueous *d*-tartaric acid (1 mol.); it is readily soluble in water, and is unchanged on repeated fractional crystallisation. The normal tartrate is still more readily soluble, and does not yield salts of enantiomorphously related bases when fractionally crystallised.

The bromocamphorsulphonates of pheno- $\alpha$ -aminocycloheptane and of hydrindamine, like the tartrates, fail to show the similarity in properties which might have been expected; whereas the salt of *dl*-hydrindamine crystallises very readily and can be resolved into unequal quantities of the isomerides already described (Kipping, *loc. cit.*); that of the *dl*-cycloheptane base is usually deposited as an oil which solidifies very slowly and does not lend itself to fractional crystallisation. The bromocamphorsulphonate of the *l*-base, on the other hand, crystallises with great facility even at about 100°, so that the opposite behaviour of the *dl*-salt is obviously due to the fact that it is a mixture.

The examples afforded by the above salts may be employed to give precision to the term 'partial racemism' or 'partially racemic' which, first used by E. Fischer (compare Ladenburg, *Ber.*, 1898, 31, 938), has come to be employed rather in a wide sense to denote salts of a *d*- or *l*-acid with a *dl*-base, or of a *d*- or *l*-base with a *dl*-acid, which may be very different in character.

According to Ladenburg (*loc. cit.*), a partially racemic compound is "eine Verbindung zweier Körper, die nur theilweise Spiegelbilder sind, so dass also durch die Verbindung nur eine theilweise Aufhebung der optischen Activität stattfindet und der racemische Körper noch optische Activität besitzt," and he applies this definition more particularly to the salt of *dl*-methylglutaric acid with quinine and to the salt of *dl*-tartaric acid with strychnine (*Ber.*, 1898, 31, 1969); these salts, however, he seems to regard as derivatives of racemic acids, for he says further that the quinine salt "kein Gemisch der Salze von *d*- und *l*-Säure, sondern ein einheitliches Salz ist, also nur das Salz der racemischen Säure sein kann," and he also represents the strychnine salt by the formula  $rC_4H_6O_6 \cdot 2C_{21}H_{22}O_2N_2 \cdot 6\frac{1}{2}H_2O$ .

Now it is rather difficult to understand Ladenburg's point of view in this matter, since a racemic acid is merely a crystalline combination of the *d*- and *l*-isomerides, and has no existence except in such a form; when combined with a base, a racemic acid ceases to exist, and there are

formed salts of the *d*- and *l*-acids, which may behave in various ways.

Considering this point more generally, an externally compensated dibasic acid and an optically active mon-acid base may unite in solution to form two normal salts, namely,  $dA \left\{ \begin{smallmatrix} dB \\ dB' \end{smallmatrix} \right.$  and  $lA \left\{ \begin{smallmatrix} dB \\ dB' \end{smallmatrix} \right.$  analogous compounds being produced, namely,  $dA, dB$ , and  $lA, dB$ , if the acid be monobasic or if, being dibasic, the hydrogen salts are formed.

The two salts thus produced (1) may be different in physical properties and may be separable by fractional crystallisation as is frequently, if not usually, the case; (2) they may unite crystallographically when deposited from solution, giving a substance differing in crystalline form and in other physical properties from one or from both its components; (3) they may possibly be deposited from solution side by side in equal quantities forming a mere mixture; (4) they may possibly form a crystalline intercalation, somewhat similar to a pseudoracemic substance (Kipping and Pope, *Trans.*, 1897, 71, 989) as regards its crystallographic relationship to its components.

An optically active dibasic acid and an externally compensated base may unite in solution to form three normal salts, namely, (a)  $dA \left\{ \begin{smallmatrix} dB \\ lB' \end{smallmatrix} \right.$  (b)  $dA \left\{ \begin{smallmatrix} dB \\ dB' \end{smallmatrix} \right.$  and (c)  $dA \left\{ \begin{smallmatrix} lB \\ lB' \end{smallmatrix} \right.$ ; on crystallising, the salt containing both bases in one molecule may alone be deposited as a definite compound, but if not, the mixture of the two salts (b) and (c) may possibly behave in any one of the four ways already enumerated.

Corresponding possibilities are of course to be expected when, in any of the above cases, the dibasic acid and mon-acid base are exchanged for a di-acid base and a monobasic acid.

Now in all the above cases, except in that in which a separation occurs on fractional crystallisation and in that in which only one kind of molecule (a) is produced, the salt conforms to Ladenburg's definition unless the meaning of 'Verbindung' be interpreted as a crystallographic union, the result of which is to give a product differing from at least one of its components in crystalline form, and consequently in other properties; if this limitation be not made, the term 'partially racemic' would include a number of salts of different types in much the same way as did at one time the term racemic (Kipping and Pope, *loc. cit.*)

Before classing a salt as a partially racemic compound, it is necessary therefore to compare its behaviour with that of its component salts in much the same way as is necessary in characterising a racemic compound; according to Roozeboom (*Zeit. physikal. Chem.*, 28, 1899, 494), the method based on solubility determinations with mixtures of equal

and of unequal quantities of the two component salts may be made use of, but no experiments of this kind seem to have been made.

Returning to the tartrates described above, it would seem that the partially racemic hydrogen salt of pheno- $\alpha$ -aminocycloheptane does not exist, as the mixture of the two components  $dA, dB, dA, lB$ , shows the behaviour noted under (1). The normal tartrate of the  $dl$ -base, which differs crystallographically from the normal salt of the  $l$ -base, may be either a partially racemic salt or consist of identical molecules  $dA \begin{Bmatrix} dB \\ lB \end{Bmatrix}$ ; to class a compound of the latter type as partially racemic would be obviously incorrect, and opposed to the whole meaning of the word racemic as now used; as, therefore, there are no means of distinguishing between the two possibilities, the salt may, for the present, be classed as a partially compensated substance.

The existence of partially externally compensated salts which are mere mixtures of equal quantities of their components, and which, nevertheless, cannot be resolved by fractional crystallisation, seems to be doubtful, although, possibly,  $dl$ -hydrindamine  $d$ -mandelate is an example of such a substance (Kipping and Hall, Trans., 1901, 79, 442).

#### EXPERIMENTAL.

##### *dl*-Pheno- $\alpha$ -aminocycloheptane Tartrate.

When  $dl$ -pheno- $\alpha$ -aminocycloheptane, partly dissolved and partly suspended in water, as obtained by distilling in steam, is neutralised with  $d$ -tartaric acid and the solution then concentrated and allowed to cool, a salt separates in highly lustrous needles or prisms, and further quantities of the same compound are obtained on again concentrating the mother liquors.

This salt has a neutral reaction to litmus, and is the normal salt of the  $dl$ -base; it has the composition  $C_4H_6O_6, 2C_{11}H_{15}N$ . It is only sparingly soluble in cold water, but dissolves fairly easily on boiling; it melts and decomposes at about  $235^\circ$ , but the rate of heating influences the result very considerably, temperatures ranging from  $230^\circ$  to  $240^\circ$  being observed, according as the salt is slowly or rapidly heated.

The specific rotation of the  $dl$ -salt was determined in aqueous solution with the following result:

0.25 gram of air-dried salt dissolved in water and the solution diluted to 25 c.c. gave in a 200 mm. tube  $\alpha + 0.26^\circ$ , whence  $[\alpha]_D 13^\circ$ .

The molecular rotation of the salt is therefore  $[M]_D + 60^\circ$ , a value which agrees fairly well with that calculated from the specific

rotations of the normal metallic tartrates, namely,  $[\text{M}]_D + 67^\circ$  (compare Landolt, *Das optische Drehungsvermögen*).

Fractional crystallisation of this normal tartrate from water does not seem to resolve it into salts of the *d*- and *l*-bases, and the salt may be regarded as a partially compensated compound having the composition  $dA \left\{ \begin{smallmatrix} dB \\ lB \end{smallmatrix} \right.$  or  $dA \left\{ \begin{smallmatrix} dB \\ dB \end{smallmatrix} \right. + dA \left\{ \begin{smallmatrix} lB \\ lB \end{smallmatrix} \right.$ ; the attempts to resolve it into different fractions by crystallisation were not carried beyond two or three operations, owing to the occurrence of hydrolytic dissociation and consequent loss of base.

### *Salts of l-Pheno- $\alpha$ -aminocycloheptane.*

*l-Pheno- $\alpha$ -aminocycloheptane Hydrogen Tartrate.*—The mother liquors remaining after the separation of several crops of crystals of the normal salt just described give, finally, deposits consisting of very slender needles, which form felted masses quite unlike the prisms of the normal salt; these very slender crystals consist of the hydrogen tartrate, as was proved by titrating a dried and weighed sample with sodium hydroxide solution. The presence of this salt is not due to excess of tartaric acid having been added, originally, but to the fact that the normal salt is partially dissociated, hydrolytically in aqueous solution, and on boiling or evaporating on the water-bath the base volatilises with the steam.

In order to prepare the hydrogen salt in larger quantities, the normal salt was mixed with one molecular proportion of *d*-tartaric acid and the mixture dissolved in a considerable quantity of hot water; on cooling, however, the normal salt was deposited unchanged and the mother liquors gave only small quantities of the hydrogen salt together with the tartaric acid which had been added, and most of which had remained uncombined. This rather unusual behaviour is doubtless due to the fact that in solutions containing the hydrogen salts of the *d*- and *l*-bases, the normal partially compensated compound is more sparingly soluble than either of the hydrogen tartrates, and on crystallising a change occurs which may be presented as follows,  $dA, dB + dA, lB = dA \left\{ \begin{smallmatrix} dB \\ lB \end{smallmatrix} \right. + dA$ .

On adding a considerable quantity of *d*-tartaric acid to a solution saturated with the normal *dl*-salt and containing a few crystals of the latter in suspension, the crystals slowly dissolve, but on concentrating the solution and allowing it to cool, the normal salt is again deposited in the first fractions, apparently in a pure condition; if, however, the proportion of *d*-tartaric acid present in solution be increased, the first fractions consist of a mixture of the normal *dl*-salt and of the hydrogen

salt, until at last, by using a very large excess of the acid, crystals of the hydrogen tartrate are deposited almost, but not quite, free from those of the normal salt.

The pheno- $\alpha$ -aminocycloheptane hydrogen tartrate which is thus obtained is the salt of the *l*-base; after one recrystallisation from water, it was obtained in needles melting at about  $175^{\circ}$  and having a specific rotation of about  $[\alpha]_D + 4^{\circ}$ . On repeated crystallisation, it seems to be completely separated from any normal salt and from the hydrogen salt of the *d*-base, and is thus obtained in lustrous needles or prisms very similar in appearance to the crystals of the normal *dl*-salt. It melts and decomposes at  $181$ – $182^{\circ}$ , the rate of heating having very little effect on the melting point.

Unlike the normal salt, it contains water of crystallisation:

0.1936 lost 0.0282  $H_2O$  at  $100^{\circ}$ .  $H_2O = 14.5$ .

0.2711 „ 0.0370  $H_2O$  over sulphuric acid and 0.0015 at  $100^{\circ}$ .  $H_2O = 14.2$ .

$C_4H_6O_6, C_{11}H_{15}N, 3H_2O$  requires  $H_2O = 14.8$  per cent.

It seems to be rather more readily soluble in cold water than the normal partially compensated salt, but it is only sparingly soluble in this liquid and also in ethyl alcohol; it crystallises from water unchanged even in absence of tartaric acid.

As this salt is formed by the combination of a dextrorotatory acid with a levorotatory base, and as the two compounds have approximately the same molecular rotations, but of opposite signs, solutions of the salt are almost optically inactive.

Two different samples were examined with the following results:

0.4560 gram of dehydrated salt dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube, gave  $\alpha - 0.03^{\circ}$ ;  $[\alpha]_D - 0.8^{\circ}$ .

0.4974 gram of dehydrated salt under the same conditions gave  $\alpha - 0.10^{\circ}$ ;  $[\alpha]_D - 2.5^{\circ}$ .

The readings in these experiments being so small, the agreement may be considered as fairly satisfactory, and the molecular rotation, calculated from the mean value, may be taken as  $[M]_D = -5^{\circ}$ .

As the molecular rotation of *d*-tartaric acid in the metallic hydrogen tartrates is  $[M]_D + 42^{\circ}$ , that of the levorotatory base would be  $[\alpha]_D - 47^{\circ}$ , a value which agrees very well with that obtained from observations made with its hydrochloride.

*l*-Pheno- $\alpha$ -aminocycloheptane Tartrate.—On adding an alcoholic solution of *d*-tartaric acid to an ethereal solution of *l*-pheno- $\alpha$ -aminocycloheptane, keeping the base in excess, the normal tartrate is deposited in crystals which melt fairly sharply at  $215$ – $217^{\circ}$ , effervescing and turning slightly brown.



The salt thus obtained was quickly dissolved in hot water and the solution rendered alkaline with the *l*-base; from this solution it was deposited in flat, transparent, triangular plates, very different in appearance from the crystals of the partially compensated normal salt, and apparently anhydrous. It was comparatively easily soluble in hot water, much more so than the hydrogen tartrate, but its solution on boiling gave off half of the base, and on subsequently cooling the hydrogen tartrate (m. p. 181—182°) was deposited. On adding powdered tartaric acid to a cold saturated solution of this normal salt, a heavy precipitate of colourless needles of the hydrogen tartrate was produced.

*l*-Pheno- $\alpha$ -aminocycloheptane Hydrochloride.—This salt was prepared by decomposing the hydrogen tartrate of the *l*-base with sodium hydroxide, distilling in steam, and evaporating the distillate with excess of hydrochloric acid. It separates from water in lustrous, striated needles or prisms and shows no signs of melting when heated at 250°; it is moderately easily soluble in boiling water, sparingly so in cold water, and very sparingly so in ethyl alcohol.

In order to ascertain whether partial or complete racemisation had occurred in the formation of the hydrochloride from the hydrogen tartrate in the above manner, the halogen salt was fractionally crystallised from water and thus separated into two crystalline portions, leaving only a very small quantity in the mother liquors. The two fractions were then dried and examined optically.

*Fraction I.* 0.272 gram dissolved in water, the solution diluted to 25 c.c., and examined in a 200 mm. tube gave  $\alpha - 0.52^\circ$ , whence  $[\alpha]_D - 24^\circ$ .

*Fraction II.* 0.264 gram under the same conditions gave  $\alpha - 0.50^\circ$ , whence  $[\alpha]_D - 23.7^\circ$ .

It seems from these results that racemisation does not take place either on liberating the active base from its salts or on heating it at 100°, and this conclusion is confirmed by experiments described later.

Taking the mean of the above values, the molecular rotation of the base would be  $[M]_D - 47^\circ$ , a result which agrees very well with that deduced from the observations made with the hydrogen tartrate.

*Benzoyl-l-pheno- $\alpha$ -aminocycloheptane*,  $C_{11}H_{14}N \cdot CO \cdot C_6H_5$ .

This compound was prepared by treating the *l*-base with benzoyl chloride by the Schotten-Baumann method. It was immediately precipitated in crystals, and the crude product, when merely washed with water and dried, melted at 174—175°. It crystallised from alcohol in long, lustrous needles, very similar in appearance to the crystals of the benzoyl derivative of the *dl*-base (Kipping and Hunter, *loc. cit.*); the



two compounds, however, differed in melting point, the derivative of the *l*-base melting at 175—176°, the optically inactive compound at 171—172°, and a mixture of the two from 160—166°.

The benzoyl derivative of the *l*-base is dextrorotatory in methyl alcoholic solution; it is insoluble in cold water, but moderately easily soluble in cold chloroform.

*Picrates of dl- and of l-Pheno- $\alpha$ -aminocycloheptane.*

The picrate of the *dl*-base is obtained as a precipitate, mixed, apparently with a little normal tartrate, on adding a hot aqueous solution of picric acid to a similar solution of the *dl*-tartrate; it crystallises from water in yellow prisms and decomposes at about 205°.

The picrate of the *l*-base, prepared from a solution of the hydrogen tartrate of the *l*-base in a similar manner, crystallises from water in well-defined, yellow prisms and decomposes at about 185°.

The decomposing points of both these picrates depend greatly on the rate of heating, and the compounds are consequently of little use for purposes of identification; they are both moderately easily soluble in methyl alcohol, but only very sparingly so in cold water.

*Salts of d-Pheno- $\alpha$ -aminocycloheptane.*

*d-Pheno- $\alpha$ -aminocycloheptane Tartrate.*—As a rule, it is not very easy to isolate both the bases by crystallising the product of the combination of a *dl*-base with an optically active acid, as, after separating the more sparingly soluble salt of one of the bases, there remains a mixture which usually does not lend itself to further fractional crystallisation. In the case of *dl*-pheno- $\alpha$ -aminocycloheptane, however, owing to the unusual behaviour of its tartrates, salts of both bases can be obtained in a pure condition by one series of crystallisations.

Starting with an aqueous solution of the *dl*-base in a large excess of tartaric acid, the hydrogen tartrate of the *l*-base is first isolated as already described; the mother liquors from this salt give, on evaporation, a deposit which seems to consist of a mixture of both the hydrogen tartrates with free tartaric acid, but on separating this deposit from the remaining aqueous solution of the acid and again dissolving in water, crystals of the normal salt of the *dl*-base are obtained, because the relative quantity of free acid in the solution has been diminished. If, now, the normal, partially compensated salt be separated as far as possible, the mother liquors yield, on evaporation, a mixture of tartaric acid and the normal or hydrogen tartrate of this *d*-base; this normal salt is finally obtained in a pure condition by further fractional crystallisation.

This salt crystallises from water in concentrically grouped needles

or prisms, has a neutral reaction to litmus, and is anhydrous; it melts and decomposes at about  $216-217^\circ$ , but unless carefully dried its melting point falls to about  $210^\circ$ . It is less readily soluble in water than the hydrogen salt of the *d*-base, and for this reason it is obtained, and can be crystallised, from solutions containing free tartaric acid; in this case, therefore, the behaviour is similar to that of the tartrate of the *dl*-base, and the formation of this normal salt, on crystallising such acid solutions, may be represented as follows:  $2 dA, dB = dA \left\{ \frac{dB}{dB} + dA \right.$

*d*-Pheno- $\alpha$ -aminocycloheptane Hydrogen Tartrate.—This salt is deposited when excess of tartaric acid is added to a hot solution of the normal salt of the *d*-base and the solution concentrated if necessary; it can also be obtained by boiling a solution of the normal salt, when hydrolytic dissociation occurs and half the base volatilises with the steam. It forms long, slender needles, melts and decomposes at  $205-206^\circ$ , and seems to be more readily soluble in cold water than the other salts, except, perhaps, the normal tartrate of the *l*-base.

*d*-Pheno- $\alpha$ -aminocycloheptane Hydrochloride.—That the two salts just described are really those of the *d*-base was proved by decomposing the normal salt with sodium hydroxide, distilling in steam, and evaporating the distillate with hydrochloric acid; the hydrochloride thus obtained was identical with that of the *l*-base in ordinary properties, but its solution in water was dextrorotatory.

0.241 gram dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube, gave  $\alpha + 0.42^\circ$ , whence  $[\alpha]_D + 21.8^\circ$ .

Considering the unavoidable experimental errors in dealing with such low specific rotations, this result agrees satisfactorily with that obtained in the case of the corresponding salt of the *l*-base.

#### *Tartrates of dl-Hydrindamine.*

The tartrates of *dl*-hydrindamine, as already stated, show little, if any, analogy with those of pheno- $\alpha$ -aminocycloheptane. The hydrogen tartrate is easily obtained by mixing the base with an aqueous solution of one molecular proportion of the acid and then evaporating; it forms masses of small needles or prisms, and is moderately soluble in cold water but only sparingly so in cold alcohol:

1.5285 lost 0.0905  $H_2O$  at  $100^\circ$ .  $H_2O = 5.9$ .

$C_9H_{11}N, C_4H_6O_6, H_2O$  requires  $H_2O = 5.98$  per cent.

The anhydrous salt melts and decomposes at  $168-169^\circ$ .

The principal points of difference between this salt and the corresponding derivative of pheno- $\alpha$ -aminocycloheptane are, firstly, that this

compound crystallises unchanged in absence of tartaric acid, whereas the mixture of *d*- and *l*-pheno- $\alpha$ -aminocycloheptane salts gives the normal salt of the *dl*-base, and, secondly, that fractional crystallisation fails to resolve the *dl*-hydrindamine salt into its components. A considerable quantity of the hydrogen salt was crystallised from water a great number of times, and the two end fractions were then examined; they were identical in melting point and in outward properties, and on examination in the polarimeter were also found to be identical optically.

0.3955 gram of air-dried salt dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube, gave  $\alpha +0.44^\circ$ , whence  $[\alpha]_D +13.9^\circ$ .

The molecular rotation, calculated for the anhydrous salt, is therefore  $[M]_D +42^\circ$ , and as that of *d*-tartaric acid is  $[M]_D 42^\circ$  in the hydrogen metallic tartrates, it is obvious that the salt contains equal quantities of the *d*- and *l*-bases.

The normal tartrate of *dl*-hydrindamine, prepared by neutralising an aqueous solution of the acid with the base, and allowing this solution to evaporate spontaneously, crystallises in plates and melts at about  $200^\circ$ ; it is much more readily soluble than the hydrogen salt and does not crystallise very well. When its aqueous solution is boiled, hydrindamine volatilises, and subsequently the hydrogen salt is deposited.

#### *l*-Pheno- $\alpha$ -aminocycloheptane Bromocamphorsulphonate.

Since it is with *d*-bromocamphorsulphonic acid that *dl*-hydrindamine forms two well-defined partially externally compensated salts, it seemed possible that the cycloheptane base would yield analogous isomerides. On neutralising an aqueous solution of the acid with *dl*-base and allowing the solution to crystallise spontaneously, the deposits were always of an oily consistency, and only very partially solidified, even in cold weather. Such solutions were therefore not examined further, but a separation of the bases with the aid of tartaric acid having been obtained, the *l*-base was combined with bromocamphorsulphonic acid.

The compound thus obtained crystallised with great facility from aqueous solutions, even on the water-bath, and was deposited in highly lustrous, striated prisms melting at  $216-217^\circ$ ; it was only sparingly soluble in cold water, but readily soluble in alcohol.

The specific rotation was determined by dissolving 0.45 gram in water, diluting the solution to 25 c.c., and examining it in a 200 mm. tube;  $\alpha +1.72^\circ$ , whence  $[\alpha]_D +47.8^\circ$ . The molecular rotation is therefore  $[M]_D +225.6^\circ$ ; taking that of the bromo-acid to be  $+270^\circ$ , the molecular rotation of the base is  $[M]_D -44.4^\circ$ . This result confirms those

previously obtained, and affords additional evidence of the stability of the base as regards racemisation; fractional crystallisation of the bromocamphorsulphonate failed to reveal the presence of any isomeride.

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