CXXVI.—*The Resolution of Externally Compensated Tetrahydro-β-naphthaquinaldine into its Optically Active Components.*

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Some time ago Professor W. J. Pope suggested to one of us that it would be well to undertake the stereochemical investigation of the reduced naphthaquinaldines, as it appeared that these compounds would yield easily crystallisable salts, and that their resolution might be of interest.

Pope and Read (T., 1910, **97**, 987) have pointed out that three kinds of behaviour must be distinguished when an externally compensated base (or acid) is crystallised with an optically active acid (or base), and that in the first case when the two salts *d*A*d*B and *l*A*d*B (or *d*A*d*B and *d*A*l*B) crystallise separately with no tendency to form solid solutions one in the other, the resolution by crystallisation or by Pope and Peachey's method proceeds with comparative ease. Thus, Pope and Peachey (T., 1893, **73**, 893) found that on crystallising Goldschmiedt's "tetrahydropapaverine" or pavine (Pyman, T., 1909, **95**, 1610) with *d*-α-bromocamphor-π-sulphonic acid, the salt *l*B*d*A separated in crystalline needles mechanically admixed with the gummy salt *d*B*d*A; and in applying the equilibrium method to the resolution of the same compound, Pope and Gibson (T., 1910, **97**, 2207) found that pavine is resolved with great ease.

In the present example, Pope and Peachey's equilibrium method

has been applied under slightly varying conditions. In the first experiment, two equivalents of the *dl*-tetrahydro-β-naphthaquinaldine were treated with one equivalent each of hydrochloric acid and ammonium *d*-α-bromocamphor-π-sulphonate, and in the second experiment sulphuric acid was substituted for hydrochloric acid. The object was to isolate what was eventually found to be the *d*A*d*B salt in a pure state, and then to obtain the hydrochloride of the *l*-base pure by fractional crystallisation. This was found to be an unsatisfactory method, but it was proved that the resolution of the base can be accomplished in either of the above ways. In the third experiment two equivalents of the base were treated in an excess of sulphuric acid solution, in which it is soluble, with one equivalent of ammonium *d*-α-bromocamphor-π-sulphonate. It was hoped that the *d*A*d*B salt would then crystallise out in an almost pure state, leaving the crude *l*-base dissolved in excess of sulphuric acid. It was soon found that the precipitated salt consisted of a mechanical mixture of crystals of the *d*A*d*B salt and the *d*A*l*B salt, which had different crystalline forms. Although fractional crystallisation was successful in yielding the *d*A*d*B salt pure, we could not succeed in obtaining the pure *d*A*l*B salt by this method. We obtained the *l*A*l*B salt by using ammonium *l*-α-bromocamphor-π-sulphonate in the second part of the third experiment, and this was again proved to contain crystals of the *l*A*d*B salt. The *d*A*l*B salt was then prepared indirectly from the *l*A*l*B salt and *d*-acid, and it was found, as was expected, to crystallise well, and to be only slightly more soluble than either the *d*A*d*B salt or the *l*A*l*B salt. It is thus seen that whilst the application of the equilibrium method to the resolution of *dl*-tetrahydro-β-naphthaquinaldine leads to a successful resolution of the base, large quantities of the pure salts could not be obtained, as the two salts *d*A*d*B and *d*A*l*B (or *l*A*l*B and *l*A*d*B) are crystalline in the presence of each other, and possess only slightly differing solubilities.

Since Pope and Read (T., 1909, **95**, 171; 1913, **103**, 444) have conclusively shown that hydroxymethylenecamphor may be employed in the resolution of externally compensated primary and secondary amines, experiments on the resolution of *dl*-tetrahydro-β-naphthaquinaldine by this method were carried out. *d*-Hydroxymethylenecamphor was condensed with the inactive base, and the product, which crystallised readily, was submitted to long fractionation. No trace of a resolution could be detected, and only one condensation product, namely, *dl*-tetrahydro-β-naphthaquinaldino-*d*-methylenecamphor was obtained. The hydrobromide obtained from the first fraction of the condensation product was

inactive. Obviously, although an externally compensated primary or secondary amine is theoretically capable of yielding two condensation products with *d*-(or *l*-)hydroxymethylenecamphor, it appears possible that one partly racemic condensation product may be formed, and the resolution of the base by this method is then impossible. From the present work it may be pointed out that although *d*-(or *l*-)hydroxymethylenecamphor may only yield one condensation product with a particular primary or secondary amine, since the product may be partly racemic, it by no means follows that the base in question is not externally compensated. It is not unlikely that Kipping and Salway's (T., 1904, **85**, 438) method for distinguishing between externally compensated and potentially inactive primary and secondary amines may have a similar limitation.

Experimental.

dl-*Tetrahydro-β-naphthaquinaldine*, $C_{10}H_6<\begin{matrix}NH-CHMe\\ CH_2\cdot CH_2\end{matrix}$.

This compound was prepared according to the description of Doebner and v. Miller (*Ber.*, 1884, **17**, 1711), who obtained β-naphthaquinaldine, and Bamberger and Müller (*Ber.*, 1891, **24**, 2646), who obtained the reduced base. We found that the base is an almost colourless oil, boiling at 215—216°/15 mm. and 205—207°/5 mm. It possesses a remarkable blue fluorescence, which is best observed in benzene or alcoholic solution. On crystallising twice from methyl alcohol, it was obtained in massive, colourless prisms, melting at 49—50°, and the same melting point was obtained with a specimen liberated from the three times recrystallised hydrochloride; the above authors give 51—52° (Found, C = 85·0; H = 7·9. Calc., C = 85·3; H = 7·6 per cent.). The platinichloride compound was obtained in minute, orange-red crystals, which decomposed at a high temperature without melting (Found, Pt = 24·55. Calc., Pt = 24·27 per cent.).

dl-*Tetrahydro-β-naphthaquinaldine Picrate*, $C_{14}H_{15}N,C_6H_2(OH)(NO_2)_3,2H_2O$.

This compound, which does not appear to have been previously prepared, separated on mixing alcoholic solutions of equivalent quantities of the base and the acid. It was crystallised from dilute alcohol, and obtained in glistening, yellow needles containing two molecules of water of crystallisation. It melts at 100—101°:

0·1796 gave 0·3443 CO_2 and 0·0784 H_2O. C = 52·3; H = 4·8.

$C_{26}H_{18}O_7N_4,2H_2O$ requires C = 51·9; H = 4·8 per cent.

Resolution of dl-*Tetrahydro-β-naphthaquinaldine.*

In the first experiment two equivalents (36 grams) of the hydrochloride of the base were treated with one equivalent (25·3 grams) of ammonium *d*-α-bromocamphor-π-sulphonate, and the whole brought into solution with 200 c.c. of boiling aqueous alcohol. A precipitate quickly formed, and this, after being collected and dried, weighed 50 grams. This was recrystallised from aqueous alcohol until its rotatory power was constant. Four crystallisations were necessary, and the values of the specific rotatory powers obtained in ethyl alcoholic solutions were $[\alpha] + 93{\cdot}1°$, $+104{\cdot}3°$, $+119{\cdot}6°$, $+133{\cdot}7°$, for the mercury-green line. The *benzoyl* derivative prepared from the pure salt had $[\alpha]_{5461} - 590{\cdot}6°$ in ethyl-alcoholic solution. The mother liquor obtained from the separation of the *d*-acid salt was treated with sodium hydroxide, and the free base extracted with benzene. That was then converted into its hydrochloride, and this submitted to fractional crystallisation from alcohol. The most insoluble fraction was obtained in colourless plates, and had $[\alpha]_{5461} - 116{\cdot}5°$ in ethyl alcohol. It was identified as the platinichloride derivative (Found, Pt = 24·1. Calc., Pt = 24·3 per cent.). This hydrochloride was converted into the benzoyl derivative, which had $[\alpha]_{5461} + 587{\cdot}6°$ in ethyl alcohol. It thus appears that the base was resolved by this method, but the method could not be considered satisfactory, as only small quantities of the pure optically active salts were obtained.

In the second experiment two equivalents (31 grams) of the base were treated with one equivalent (25·4 grams) of *d*-α-bromocamphor-π-sulphonic acid and one equivalent (3·8 grams) of sulphuric acid. On boiling with 600 c.c. of aqueous alcohol a reddish-brown oil separated, which crystallised on cooling. This substance was the most insoluble, and it was separated at once. After being once recrystallised from aqueous alcohol, it showed $[\alpha]_{5461} + 131{\cdot}1°$ in ethyl alcohol, and when treated with benzoyl chloride and sodium hydroxide gave a benzoyl derivative, which had $[\alpha]_{5461} - 594{\cdot}0°$ in ethyl alcohol. The mother liquor yielded further quantities of the salt, which after three crystallisations had $[\alpha]_{5461} + 134{\cdot}5°$ in the same solvent. The mother liquors remaining were mixed, evaporated to small bulk, treated with baryta, and the base extracted with benzene. It was then noticed that a considerable quantity of *d*-α-bromocamphor-π-sulphonic acid was recovered as barium salt. The base was obtained from its benzene solution as hydrochloride, and this was submitted to fractional crystallisation from alcohol. After two crystallisations the hydrochloride in ethyl alcohol had $[\alpha]_{5461} - 44{\cdot}1°$, a value considerably less than that obtained in the

first experiment. It was, however, converted into the benzoyl derivative, and this compound after three crystallisations from ethyl alcohol had $[\alpha]_{5461}$ +572·0° in that solvent. This method of resolution, although successful, could not be considered satisfactory for the same reason as the above. The later fractions of the *d*-α-bromocamphor-π-sulphonate were always mixtures, but the possibility of separating easily a considerable quantity of the fairly pure *d*-α-bromocamphor-π-sulphonate as shown above indicated the conditions of the method finally adopted.

In the third experiment two equivalents (40 grams) of the base were dissolved in one and a-half equivalents (16·2 grams) of 2*N*-sulphuric acid; the base remained dissolved while the solution was hot. To the boiling solution was added one equivalent (33 grams) of ammonium *d*-α-bromocamphor-π-sulphonate, when an oil separated, which quickly crystallised on stirring. On fractional crystallisation the salt yielded seven fractions of specific rotatory powers varying from [α] +134·7° to +54·0° for the mercury-green line. The filtrate from the separation of the *d*-acid salt was treated with sodium hydroxide, and the base extracted with benzene. The benzene extract was well washed with water, dried with potassium hydroxide, filtered, and then shaken with 8·2 grams of sulphuric acid in 2*N*-solution, and the benzene separated. There was no precipitate. The sulphuric acid solution was heated almost to boiling, and a boiling aqueous solution of 28 grams of ammonium *l*-α-bromocamphor-π-sulphonate added. A bulky precipitate immediately formed, which after drying corresponded exactly with the theoretical amount of the salt expected, using the above weight of the ammonium lævo-salt. This salt was submitted to careful fractionation from aqueous alcohol, when nine fractions were obtained, having specific rotatory powers in ethyl-alcoholic solution varying from [α] −134·6° to −70·8° for the mercury-green line.

The pure salts obtained having been proved to be *d*A*d*B and *l*A*l*B, and the pure *d*A*l*B salt having been indirectly prepared, the nature of the further fractions was examined. They did not contain any sulphate, and those obtained in the separation of the *d*A*d*B salt were found to consist of crystals (plates) of the salt *d*A*d*B mixed with crystals (needles) of the *d*A*l*B salt, whilst those obtained in the separation of the *l*A*l*B salt consisted of crystals of the *l*A*l*B salt (plates) and *l*A*d*B salt (needles). The crystals could not be successfully sorted by hand, as they adhere to each other.

The rotatory powers of the fractions rapidly decreased in successive fractions as more and more of the salt *d*A*l*B (or *l*A*d*B) of low rotatory power accumulated in them until the lower fractions

contained more of this salt than of the *d*A*d*B salt (or *l*A*l*B salt). Thus in the separation of the *d*A*d*B salt of fraction (6):

0·1486, made up to 30·0 c.c. with alcohol and examined in a 4-dcm. tube at 29—30°, gave α_{5461} +1·07°, $[\alpha]_{5461}$ +54·0°, $[M]_{5461}$ +274·3°. The molecular rotatory power of the *d*A*d*B salt is $[M]_{5461}$ +683·8°, and of the *d*A*l*B salt is $[M]_{5461}$ +104·6° under the same conditions.

A further quantity was weighed, ground carefully with sodium hydroxide, extracted with benzene, the benzene extract thoroughly washed with water, dried with potassium hydroxide, and after filtering made up to 30·0 c.c.:

0·3963, treated as described, and the benzene solution obtained examined in a 4-dcm. tube at 29—30°, gave (for the base) α_{5461} −1·78°, $[\alpha]_{5461}$ −86·9°, $[M]_{5461}$ −171·2°.

The molecular rotatory power of the pure base in benzene is $[M]_{5461}$ +309·3°. Obviously, fraction (6) obtained in the separation of the *d*A*d*B salt contained an excess of the *d*A*l*B salt.

In a similar manner fraction (8), obtained in the separation of the *l*A*l*B salt, was examined:

0·2162, made up to 30·0 c.c. with alcohol, gave, in a 4-dcm. tube at 29—30°, α_{5461} −2·04°, $[\alpha]_{5461}$ −70·6°, $[M]_{5461}$ −358·6°.

0·4627 of the same fraction, treated with sodium hydroxide and benzene as above, gave α_{5461} +0·57°, $[\alpha]_{5461}$ +23·82°, $[M]_{5461}$ +46·9°.

On comparing these figures with those given above it is again seen that fraction (8) obtained in the separation of the *l*A*l*B salt contained an excess of the *l*A*d*B salt, and from its rotatory power we find, as could be expected, that the rotation of the base is of the opposite sign, but not so large as that obtained from fraction (6) of the *d*A*d*B salt, which has a lower (and opposite) rotation.

Knowing the rotatory powers of the pure salts *d*A*l*B, *d*A*d*B, and *l*A*l*B, and also of the pure base, it will seem possible to calculate the percentage composition of the salt mixtures just described, and then to verify the rotatory powers of the salt mixtures observed. Since, however, the arithmetical law only applies to the salts when completely ionised, and also since the above salt mixtures may be contaminated with traces of the oxidised base, it is not considered advisable to make any deductions from the results of such calculations. At the same time, it is obvious that the above observations show the course taken by the resolution.

d-*Tetrahydro-β-naphthaquinaldine* d-*α-Bromocamphor-π-sulphonate*, $C_{14}H_{15}N,C_{10}H_{14}OBr\cdot SO_3H$.

As shown above, this salt is obtained in all the three methods of resolution. It is very sparingly soluble in water, and the salt undergoes noticeable hydrolysis. It is more readily soluble in alcohol, and crystallises from aqueous alcohol in colourless, thin plates. In solution the salt is strongly fluorescent. The substance begins to decompose at 233°, and melts completely at 240°:

0·1341 gave 0·2756 CO_2 and 0·0677 H_2O. C = 56·0; H = 5·6.
0·1109 „ 0·2282 CO_2 „ 0·0584 H_2O. C = 56·1; H = 5·8.
$C_{24}H_{30}O_4NBrS$ requires C = 56·69; H = 5·90 per cent.

The following rotatory-power determinations of the different specimens prepared were made in absolute ethyl-alcoholic solution at 29—30° in a 4-dcm. tube:

0·1577 gave α_{5461} + 2·83°, $[\alpha]_{5461}$ + 134·6°, $[M]_{5461}$ + 683·8°.
0·1389 „ α_{5461} + 2·49°, $[\alpha]_{5461}$ + 134·5°, $[M]_{5461}$ + 683·3°.
0·1531 „ α_{5461} + 2·75°, $[\alpha]_{5461}$ + 134·7°, $[M]_{5461}$ + 684·3°.

l-*Tetrahydro-β-naphthaquinaldine*-l-*α-bromocamphor-π-sulphonate*, $C_{14}H_{15}N,C_{10}H_{14}OBr\cdot SO_3H$.

As already explained, this salt was obtained from the mother liquor obtained in the third experiment after separating the *d*A*d*B salt mixtures, and treating this with sodium hydroxide, extracting the base with benzene, washing the benzene extract thoroughly with water, drying, filtering, and treating with an excess of sulphuric acid in 2*N*-solution. After separating the benzene, the sulphuric acid solution was heated to boiling and treated with ammonium *l*-*α*-bromocamphor-*π*-sulphonate. The salt which separated was purified by repeated crystallisation from aqueous alcohol until its rotatory power was constant. It was obtained in thin, colourless plates, which differed in appearance and behaviour on being heated in no way from its enantiomorph:

0·1630 gave 0·3372 CO_2 and 0·0802 H_2O. C = 56·4; H = 5·5.
$C_{24}H_{30}O_4NBrS$ requires C = 56·7; H = 5·9 per cent.

The following rotatory-power determination was made in absolute ethyl-alcoholic solution at 29—30°:

0·1572, made up to 30·0 c.c. and examined in a 4-dcm. tube, gave α_{5461} − 2·82°, $[\alpha]_{5461}$ − 134·5°, $[M]_{5461}$ − 683·3°.

l-Tetrahydro-β-naphthaquinaldine-d-*α-bromocamphor-π-sulphonate*, $C_{14}H_{15}N,C_{10}H_{14}OBr\cdot SO_3H$.

This salt was prepared by isolating the base from the *l*-tetrahydro-β-naphthaquinaldine *l*-α-bromocamphor-π-sulphonate by means of alkali, washing this solidified base with water until free from any soluble substance, and treating in alcoholic solution with an equivalent quantity of *d*-α-bromocamphor-π-sulphonic acid. It is sparingly soluble in water, but much more readily so in ethyl alcohol. It was recrystallised from aqueous alcohol, and obtained in long, colourless needles, very different in appearance from the salts previously described. It shows a tendency to melt at a lower temperature than the above salts, but decomposition sets in, and melting is complete at 240°:

0·0949 gave 0·1982 CO_2 and 0·0529 H_2O. C = 56·9; H = 6·2.
$C_{24}H_{30}O_4NBrS$ requires C = 56·7; H = 5·9 per cent.

The following rotatory-power determination was made in absolute ethyl alcohol at 29—30°:

0·1825, made up to 30·0 c.c. and examined in a 4-dcm. tube, gave α_{5461} + 0·50°, $[\alpha]_{5461}$ + 20·6°, $[M]_{5461}$ + 104·6°.

d- *and* l-*Tetrahydro-β-naphthaquinaldine*, $C_{14}H_{15}N$.

The *d*- and *l*-bases were obtained by grinding the pure *d*-tetrahydro-β-naphthaquinaldine *d*-α-bromocamphor-π-sulphonate and the *l*-tetrahydro-β-naphthaquinaldine *l*-α-bromocamphor-π-sulphonate respectively with filtered sodium hydroxide solution. The products easily separated as oils, which crystallised on keeping, the crystallisation being hastened by cooling the mixture in ice and salt. They were collected, washed with water, dried, and recrystallised from methyl alcohol or light petroleum. The bases are very readily soluble in organic solvents, and yield massive, colourless prisms on spontaneous evaporation of the solvent. The melting points of the two bases were identical, namely, 54·6°, that is, higher than the melting point of the racemic base (m. p. 49—50°).

d-*Tetrahydro-β-naphthaquinaldine*.

0·1234 gave 0·3489 CO_2 and 0·0798 H_2O. C = 84·5; H = 7·2.
$C_{14}H_{15}N$ requires C = 85·3; H = 7·6 per cent.

l-*Tetrahydro-β-naphthaquinaldine*.

0·1072 gave 0·3340 CO_2 and 0·0709 H_2O. C = 85·0; H = 7·4.
0·1202 „ 0·3767 CO_2 „ 0·0835 H_2O. C = 85·5; H = 7·7.
$C_{14}H_{15}N$ requires C = 85·3; H = 7·6 per cent.

The following determinations of rotatory power were made at 29—30° in a 4-dcm. tube, the substances being made up to 30·0 c.c. with the solvent noted.

d-*Tetrahydro-β-naphthaquinaldine.*

0·2010, in absolute ethyl alcohol, gave α_{5461} +2·92°, $[\alpha]_{5461}$ +108·96°, $[M]_{5461}$ +214·4°.

0·1919, in the same solvent, gave α_{5461} +2·79°, $[\alpha]_{5461}$ +109·04°, $[M]_{5461}$ +214·8°.

0·1496, in benzene, gave α_{5461} +3·13°, $[\alpha]_{5461}$ +157·0°, $[M]_{5461}$ +309·3°.

l-*Tetrahydro-β-naphthaquinaldine.*

0·1942, in absolute alcohol, gave α_{5461} −2·81°, $[\alpha]_{5461}$ −108·5°, $[M]_{5461}$ −213·7°.

d-*Tetrahydro-β-naphthaquinaldine Platinichloride*, $(C_{14}H_{15}N)_2H_2PtCl_6$.

This compound was prepared by treating pure *d*-tetrahydro-β-naphthaquinaldine *d*-α-bromocamphor-π-sulphonate with platinic chloride. It is an orange-red, microcrystalline powder, almost insoluble in all organic solvents and in water. It was impossible to determine its rotatory power. It begins to decompose at about 200°, and does not melt:

0·2931 gave 0·0702 Pt. Pt = 23·95.
$(C_{14}H_{15}N)_2H_2PtCl_6$ requires Pt = 24·27 per cent.

d- *and* l-*Benzoyltetrahydro-β-naphthaquinaldines*, $C_{14}H_{14}NBz$.

Many specimens of the benzoyl derivatives of the active bases were obtained during the course of the work. One specimen of the *d*-benzoyl derivative was prepared from *d*-tetrahydro-β-naphthaquinaldine *d*-α-bromocamphor-π-sulphonate by treating it with sodium hydroxide and benzoyl chloride in the usual manner. After crystallisation from ethyl alcohol, it was obtained in colourless needles, which do not show any fluorescence in solution. It is moderately soluble in alcohol or acetone, and melts at 198—199°:

0·1302 gave 0·3996 CO_2 and 0·0766 H_2O. C = 83·7; H = 6·5.
$C_{21}H_{19}ON$ requires C = 83·7; H = 6·3 per cent.

0·1086, made up to 30·0 c.c. with absolute ethyl alcohol, and examined in a 4-dcm. tube at 29—30°, gave α_{5461} −8·50°, $[\alpha]_{5461}$ −587·0°, $[M]_{5461}$ −1767·0°.

It is unnecessary to detail all the preparations of the benzoyl

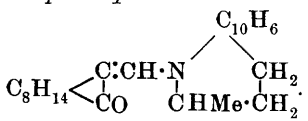
derivatives, and it will now suffice to quote the preparation of the l-*benzoyl* derivative made from the hydrochloride of the base obtained from the mother liquors after the separation of *d*-tetrahydro-β-naphthaquinaldine *d*-α-bromocamphor-π-sulphonate in the first resolution experiment. The hydrochloride having $[\alpha]_{5461}$ $-116{\cdot}5°$ in ethyl-alcoholic solution was treated as usual with sodium hydroxide and benzoyl chloride, and the product after recrystallisation from ethyl alcohol was obtained in colourless needles identical in appearance and general properties with the *d*-benzoyl derivative. It melted at 198—199°:

0·1115 gave 0·3404 CO_2 and 0·0608 H_2O. C = 83·3; H = 6·1.
$C_{21}H_{19}ON$ requires C = 83·7; H = 6·3 per cent.

0·1053, made up to 30·0 c.c. with absolute ethyl alcohol and examined in a 4-dcm. tube at 29—30°, gave α_{5461} +8·25°, $[\alpha]_{5461}$ +587·6°, $[M]_{5461}$ +1768·7°.

It is thus seen that the value of the rotation of the benzoyl derivative is considerable, and opposite in sign to that of the optically active base from which it is prepared; it is interesting to note that the same kind of change of sign of rotation is observed on benzoylating other optically active bases, many of which are quinaldines, for example, tetrahydroquinaldine (Pope and Peachey, T., 1899, **75**, 1066), tetrahydro-*p*-toluquinaldine (Pope and Rich, T., 1899, **75**, 1093), the 2 : 4-dimethyltetrahydroquinolines (Thomas, T., 1912, **101**, 725), and bornylamine (Forster, T., 1898, **73**, 386).

dl-*Tetrahydro-β-naphthaquinaldino*-d-*methylenecamphor*,



d-Hydroxymethylenecamphor was prepared from *d*-camphor according to the description given by Bishop, Claisen, and Sinclair (*Annalen*, 1894, **281**, 331). The condensation of this compound with *dl*-tetrahydro-β-naphthaquinaldine was carried out by mixing 7·5 grams of the former with 8·1 grams of the base in the presence of acetic acid. The mixture was heated for half an hour on the water-bath, when an almost quantitative amount of the crystallised product was obtained. Rather more than 15 grams of the product were prepared in two experiments. The compound, which is very easily obtained crystalline during its preparation, was recrystallised from alcohol, and formed thin, colourless plates, which do not show any fluorescence in solution. It melts at 182—183°. It

is sparingly soluble in cold alcohol, but dissolves fairly readily in the hot solvent. It is readily soluble in benzene or acetic acid, but less readily so in acetal:

0·1113 gave 0·3401 CO_2 and 0·0842 H_2O. C = 83·3; H = 8·4.
$C_{25}H_{29}ON$ requires C = 83·6; H = 8·1 per cent.

The compound was submitted to most careful fractional crystallisation from alcohol, when from 15·3 grams four fractions, the total weight of which was 15·0 grams, were obtained, and they each had the same melting point.

The following rotatory determinations were made by making up the dissolved substance with absolute ethyl alcohol to 30·0 c.c. and examining the solution in a 4-dcm. tube at 29—30°:

Fraction (1), 0·1532 gave α_{5461} + 8·43°, $[\alpha]_{5461}$ + 412·7°, $[M]_{5461}$ + 1481·6°.

Fraction (3), 0·1492 gave α_{5461} + 8·22°, $[\alpha]_{5461}$ + 413·2°, $[M]_{5461}$ + 1483·4°.

These rotatory powers show that no resolution has taken place. The substance did not exhibit any mutarotation, showing no alteration after forty-six hours.

No alteration having been effected in the melting point and rotatory powers by further fractionation from acetone and from benzene it was concluded that the substance is partly racemic. The following further determinations of the rotatory powers were made by making up the substance at 29—30° to 30·0 c.c. with the solvent noted and examining in a 4-dcm. tube:

0·1544, in benzene, gave α_{5461} + 7·23°, $[\alpha]_{5461}$ + 351·2°, $[M]_{5461}$ + 1260·6°.

No mutarotation was observed during a space of twenty-four hours:

0·1562, in glacial acetic acid, gave the following values for α: after forty-five minutes, α + 9·02°; after fifty-five minutes, α + 8·91°; after sixty-five minutes, α + 8·84°; after eighty minutes, α + 8·73°; after ninety-five minutes, α + 8·71°; after one hundred and eighty-five minutes, α 8·65°; after twenty-four hours, α 8·65°, for the mercury-green line. Hence the constant values are α_{5461} + 8·65°, $[\alpha]_{5461}$ 415·3°, $[M]_{5461}$ + 1491·0°.

It is interesting to note that whilst the substance now described exhibits no mutarotation in benzene and in alcohol solution, it shows a mutarotation to a minimum value in acetic acid. *l*-Hydroxyhydrindamino-*d*-methylenecamphor, on the other hand (Pope and Read, T., 1913, **103**, 448), exhibits mutarotation in benzene, alcohol, and in glacial acetic acid solutions; in the two former the

mutarotation is to a maximum, and in the last-named solvent it is to be a minimum value.

dl-*Tetrahydro-β-naphthaquinaldine Hydrobromide*, $C_{14}H_{15}N,HBr$.

This salt was obtained by the action of bromine and alcohol on *dl*-tetrahydro-β-naphthaquinaldino-*d*-methylenecamphor according to the method described by Pope and Read (*loc. cit.*, p. 445). On keeping, the *hydrobromide* slowly crystallises out, and the filtrate when evaporated yields a brown, pasty mass of *d*-bromo-oxymethylenecamphor, which has already been investigated by Pope and Read. Four grams of the first fraction of *dl*-tetrahydro-β-naphthaquinaldino-*d*-methylenecamphor yielded 2·2 grams of the purified hydrobromide (theoretical = 2·9 grams). The salt was recrystallised from aqueous alcohol and from ethyl acetate:

0·1482 gave 0·1011 AgBr. Br = 29·0.

$C_{14}H_{15}N,HBr$ requires Br = 28·8 per cent.

It resembles the hydrochloride of the inactive base in solubility and in appearance. Its solutions are also fluorescent. It does not melt at 245°. On polarimetric observation in alcoholic solution it was found to be optically inactive.

Thus, there is no doubt that *dl*-tetrahydro-β-naphthaquinaldine has not been resolved by means of *d*-hydroxymethylenecamphor, and further experiments are in progress to determine how far the formation of such partly racemic compounds such as is described above is common; and, in cases where the externally compensated base can be resolved by crystallisation of its salts, a comparison of the partly racemic compound with the compound of the resolved base will be made.

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