V.—*Researches in the Menthone Series. Part VI. The Crystallisation of Menthylamines with Optically Active Acids.*

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IT has been shown (J., 1926, 2209; 1927, 2168) that *l*-, *d*-*neo*-, *d*-*iso*-, and *d*-*neoiso*-menthylamine may be prepared easily from *l*-piperitone, and the externally compensated forms of the first three of these stereoisomeric bases from *dl*-piperitone (J., 1926, 2223). So far, however, no convenient method of obtaining the enantiomerides of the above active forms has been described; for although *d*-piperitone and *d*-menthol might serve for the purpose (J., 1926, 2214; *J. Soc. Chem. Ind.*, 1927, **46**, 871), these substances may be secured only with considerable difficulty and in small amounts.

As a result of an examination of possible methods for the optical resolution of *dl*-, *dl*-*neo*-, and *dl*-*iso*-menthylamine with the aid of optically active acids, we are now able to describe satisfactory processes for the preparation in quantity of *d*-menthylamine and *l*-*neo*-menthylamine. The first of these results may be regarded as particularly important, since it not only furnishes a new optically active base of unusual interest but also opens up a new route to *d*-menthol, which may be obtained by the interaction of *d*-menthylamine with nitrous acid.

dl-Menthylamine and *dl*-*neo*-menthylamine were resolved by fractionally crystallising the hydrogen *d*-tartrates in the usual way; in each instance the salt containing the desired form of the base (*d*A*d*B and *d*A*l*B, respectively) was fortunately the less soluble of the two diastereoisomerides. *dl-iso*-Menthylamine was not resolved when treated in a similar way. Altogether, four methods of resolution were applied to each of the three externally compensated bases under consideration, the salts examined being the *d*(or *l*)-α-bromocamphor-π-sulphonates, *d*(or *l*)-camphor-10-sulphonates, and the normal and hydrogen *d*-tartrates. Complete resolution was achieved only in the two instances noted, but a study of the behaviour of the other salts concerned has disclosed results of considerable general interest. The appended table contains a summary of the molecular rotatory powers in dilute aqueous solution of the optically pure salts, prepared in the majority of instances by mixing equivalent weights of the optically active acid and base and recrystallising the product. The values of $[M]_D$ for the acidic and basic ions in dilute aqueous solution are taken as follows: α-bromocamphor-π-sulphonic acid ± 279° (J., 1910, **97**, 2201), camphor-10-sulphonic acid ± 50° (J., 1910, **97**, 2214), *d*-tartaric acid + 42° for the acid salts (Meyer und Jacobson, "Lehrbuch der organischen Chemie," 1913, I, ii, 666), *l*-menthylamine — 70°, *d-neo*-menthylamine + 41°, and *d-iso*-menthylamine + 45° (J., 1927, 2169). The observed value for each salt is stated immediately below the value calculated for it from the data just quoted.

TABLE I.

Values of $[M]_D$, *calculated and observed, for salts of certain menthylamines with optically active acids in dilute aqueous solution.*

Acid.	*l*-Base.	*d-neo*-Base.	*d-iso*-Base.
d-α-Bromocamphor-π-sulphonic, calc.	+209°	+320°	+324°
obs.	+207	+341	+396
l-α-Bromocamphor-π-sulphonic, calc.	−349	−238	−234
obs.	−348	−230	−249
d-Camphor-10-sulphonic, calc.	− 20	+ 91	+ 95
obs.	−20·5*	+ 93	+ 95
l-Camphor-10-sulphonic, calc.	−120	− 9	− 5
obs.	−112	± 0	± 0
d-Tartaric (acid salt), calc.	− 28	+ 83	+ 87
obs.	− 25	+ 84	+ 98

	d-Base.	*l-neo*-Base.
d-Tartaric (acid salt), calc.	+112	+ 1
obs.	+113	± 0

* Tutin and Kipping, J., 1904, **85**, 70.

As it might be unjustifiable to assume practically complete ionisation on the part of the normal tartrates, the values for these salts have not been included. No marked divergence from the calculated values is apparent in this list except among the α-bromocamphor-π-sulphonates, and here the most pronounced discrepancies are shown by salts of the type *d*A*d*B; similar instances of abnormalities when the constituent ions are of the same sign of rotatory power have been pointed out by Pope and Read (J., 1912, **101**, 775).

The tartrates and camphor-10-sulphonates noted above gave essentially constant optical rotatory powers in dilute aqueous solution, but with the α-bromocamphor-π-sulphonates considerable fluctuations were observed in the optical activity. Sensibly identical values for two consecutive preparations were rarely observed, and changes occurred upon evaporating or recrystallising particular specimens of these salts. This behaviour is probably to be referred to the occurrence of dynamic isomerism on the part of the acid, similar observations having been made by Kipping and his collaborators in studying its salts with hydrindamine (J., 1900, **77**, 872), benzylhydrindamine (J., 1901, **79**, 435), β-methylhydrindamine (J., 1903, **83**, 922), and *l*-menthylamine (J., 1904, **85**, 68; see also J., 1905, **87**, 632); salts of *d*-α-bromocamphor-10-sulphonic acid also have been shown to display corresponding changes in rotatory power (Pope and Read, J., 1914, **105**, 800). Such behaviour appears to be most noticeable when the acid is combined with a strong primary base, and the optical resolution of such bases is therefore liable to be complicated by the formation of α- and β-salts.

Upon fractional crystallisation of the salts of the three abovementioned externally compensated menthylamines with *d*-α-bromocamphor-π-sulphonic acid, the rotatory powers of successive fractions oscillated irregularly and afforded no satisfactory indication of the rotatory power of the contained base (compare Table II*a*); in none of these instances was it possible to achieve more than a partial resolution of the base. This result was to be anticipated, and an explanation may be found on the lines indicated above.

Unexpectedly, however, the *d*-camphor-10-sulphonates prepared from these externally compensated bases exhibited very similar irregularities in their optical rotations (compare Table II*b*), and it was not found possible to resolve any of the bases with the help of this acid. Since the *d*- and *l*-camphor-10-sulphonates of the pure optically active bases gave constant and normal optical rotations (Table I), it does not appear possible in this case to ascribe the observed variations to tautomerism of the acid; moreover, no change in the rotatory power of a particular specimen of such a salt was noticed upon evaporating its aqueous solution to dryness. Further experiments showed also that the optically active menthylamines do not undergo optical inversion when liberated from their salts. The explanation advanced above thus appears inadequate to account for the abnormal rotatory powers of the mixed diastereoisomeric salts obtained by combining *d*-camphor-10-sulphonic acid with a specific externally compensated menthylamine.

For the present, the abnormal behaviour described in this paper has prevented the complete optical resolution of any of the externally compensated menthylamines with the aid of camphor-10-sulphonic acid or α-bromocamphor-π-sulphonic acid; possibly, however, more favourable results may attend fractional crystallisation of the respective pairs of these diastereoisomeric salts from hot solutions, or from solutions containing small amounts of free acid or alkali.

EXPERIMENTAL.

Salts of Menthylamines.

1. *α-Bromocamphor-π-sulphonates.*—Equimolecular amounts of *l*-menthylamine hydrochloride and ammonium *l*-α-bromocamphor-π-sulphonate were dissolved in about ten times their weight of hot water, to which a little alcohol was added. On cooling, the solution deposited *l*-menthylamine *l*-α-bromocamphor-π-sulphonate in small prisms; after two recrystallisations from dilute alcohol, the salt * had m. p. 183—184°, $[\alpha]_D$ −74·7°, $[M]_D$ −348°. The rotatory power was practically unaffected by evaporating an aqueous solution of the salt to dryness. The salt dissolved readily in alcohol, chloroform, or acetone.

l-Menthylamine *d*-α-bromocamphor-π-sulphonate, prepared similarly, had m. p. 225°, $[\alpha]_D$ +44·4°, $[M]_D$ +207° (compare J., 1904, **85**, 69, 71).

When *dl*-menthylamine hydrochloride (J., 1926, 2226) was mixed in the same way with ammonium *d*-α-bromocamphor-π-sulphonate (1 mol.), a first fraction of the separation, forming about one-quarter of the total quantity possible, had $[M]_D$ +275°. Repeated crystallisation of this product yielded further fractions having values of $[M]_D$ which fluctuated irregularly between + 223° and + 324°. Similar values were exhibited by a large number of fractions deposited from the various mother-liquors. Results of the same general character were obtained when ethyl acetate was used as the solvent. The following values (Table II*a*) were found upon regenerating menthylamine hydrochloride from a series of these fractions.

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* Unless otherwise stated, the following conditions hold for all optical rotatory powers quoted in this paper: the dry, anhydrous salt (*w* g.) was dissolved in water to form a solution having a concentration of approximately 1%, and the observation was made in a 2-dcm. tube at the ordinary temperature (about 15°). In order to economise space, the observed values of *a* are only quoted, as a rule, when they fall below 0·2°. The respective values of *M* for menthylamine *a*-bromocamphor-*π*-sulphonate, camphor-10-sulphonate, normal tartrate, and hydrogen tartrate are 466, 387, 460, and 305.

TABLE II.

Molecular rotatory powers of salts derived from mixtures of l- *and* d-*menthylamine.*

$[M]_D$ of fraction.	$[M]_D$ of basic ion: Calc. (from salt).	$[M]_D$ of basic ion: Found (for hydrochloride).
(a) d-*a-Bromocamphor-π-sulphonates.*		
+205°	−73°	−14°
+235	−43	−10
+260	−18	± 0
+324	+46	+29
+312	+34	+35
(b) d-*Camphor-*10-*sulphonates.*		
+43	− 7	± 0
+31	−19	± 0
+33	−17	− 6
+50	± 0	− 9
+38	−12	± 0
(c) *Hydrogen* d-*tartrates.*		
+38	− 4	− 4
+35	− 7	− 6
+18	−24	−25
± 0	−42	−43

2. *Camphor*-10-*sulphonates.*—Equimolecular proportions of ammonium *l*-camphor-10-sulphonate and *l*-menthylamine hydrochloride were dissolved in about eleven times their weight of hot water; the crystalline separation of l-*menthylamine* l-*camphor*-10-*sulphonate*, which formed as the liquid cooled, was recrystallised from hot water, after which it had $[\alpha]_D$ − 28·9°, $[M]_D$ − 112°. The salt preserved this rotatory power when again recrystallised. It dissolved in alcohol and chloroform, and less readily in acetone, benzene, and ethyl acetate (Found: C, 61·4; H, 9·3. $C_{20}H_{37}O_4NS$ requires C, 62·0; H, 9·6%).

The salt formed by *dl*-menthylamine with *d*-camphor-10-sulphonic acid was prepared and fractionally crystallised from water in the manner outlined under (1) above. The first fraction had $[M]_D$ + 48°, and as a result of repeated fractional crystallisation specimens of salt were obtained with values of $[M]_D$ fluctuating irregularly between + 31° and + 60°. Similar fractions were deposited from the mother-liquors. Fractionation from ethyl acetate yielded equally indefinite results. The values observed on regenerating the base from a number of these fractions are summarised above (Table IIb).

3. *Normal Tartrates.*—*l*-Menthylamine (2 mols.) dissolved in ether was mixed with *d*-tartaric acid (1 mol.) dissolved in warm alcohol. A crystalline deposit of *l*-menthylamine *d*-tartrate separ-

ated as the solution cooled. It was readily soluble in water or alcohol, and slightly soluble in acetone or ethyl acetate; but recrystallisation was impracticable, owing to the tendency of the salt to pass into a syrup. In dilute aqueous solution it gave $[\alpha]_D - 24{\cdot}6°$, $[M]_D - 113°$.

When *dl*-menthylamine (2 mols.) was mixed with *d*-tartaric acid (1 mol.) in warm alcohol, a gummy salt was formed. This became crystalline when treated with small quantities of dry acetone, but efficient fractional crystallisation was impracticable. The purest fraction isolated had $[\alpha]_D + 13{\cdot}0°$, $[M]_D + 60°$, and this yielded optically impure *d*-menthylamine hydrochloride with $[M]_D + 15°$ (w 0·1990 g., $\alpha + 0{\cdot}16°$).

4. *Hydrogen Tartrates.*—A crystalline salt was readily obtained on mixing equimolecular proportions of *l*-menthylamine and *d*-tartaric acid in hot alcohol. After recrystallisation from hot water, *l*-menthylamine hydrogen *d*-tartrate had $[\alpha]_D - 8{\cdot}0°$, $[M]_D - 25°$ (w 0·1990 g., $\alpha - 0{\cdot}16°$); it dissolved in alcohol, but not in acetone, chloroform, benzene, or ethyl acetate.

Optical Resolution of dl-*Menthylamine.*—*dl*-Menthylamine hydrochloride (18·4 g., 1 mol.) was decomposed with sodium hydroxide solution, and the free base, isolated by means of ether, was dissolved in warm alcohol containing *d*-tartaric acid (14·4 g., 1 mol.). When the salt obtained after removal of the alcohol was fractionally crystallised from boiling water, the first (10·7 g.) and second (4·8 g.) fractions had $[M]_D + 101°$ and $+ 80°$, respectively. Two further recrystallisations of these fractions sufficed to give 36% of the theoretical yield of pure d-*menthylamine hydrogen* d-*tartrate*, m. p. 168°, $[\alpha]_D + 37{\cdot}1°$, $[M]_D + 113°$, $[\alpha]_{5461} + 39{\cdot}1°$, $[M]_{5461} + 119°$ (Found : C, 54·5; H, 9·3. $C_{14}H_{27}O_6N$ requires C, 55·0; H, 8·7%). *d*-Menthylamine hydrochloride prepared from this salt had $[\alpha]_D + 36{\cdot}6°$, $[M]_D + 70°$. Salicylidene-*d*-menthylamine, m. p. 56—57°, $[\alpha]_D + 118°$ (c 0·75 in chloroform), showed the marked phototropic effect characteristic of salicylidene-*l*-menthylamine (J., 1926, 2234; 1927, 2174).

In conducting the above resolution it is advisable to seed the original solution with a crystal of pure *d*-menthylamine hydrogen *d*-tartrate. A final fraction obtained in the process displayed no appreciable optical activity when examined under the usual conditions; when decomposed, this yielded impure *l*-menthylamine hydrochloride having $[M]_D - 43°$. This and other specimens of the hydrochloride obtained from intermediate fractions displayed rotatory powers in approximate agreement with the calculated values (Table IIc).

Salts of neo*Menthylamines.*

1. *α-Bromocamphor-π-sulphonates.*—*d-neo*Menthylamine hydrochloride (J., 1926, 2217), having $[\alpha]_D + 21{\cdot}5°$ in 1% aqueous solution, was dissolved in hot water and mixed with ammonium *d*-α-bromocamphor-π-sulphonate (1 mol.); the resulting separation of colourless prisms consisted of *d-neo*menthylamine *d*-α-bromocamphor-π-sulphonate, m. p. 166·5°, $[\alpha]_D + 70{\cdot}8°$, $[M]_D + 330°$. A second preparation, made from the same specimens, had $[\alpha]_D + 73{\cdot}3°$, $[M]_D + 341°$. d-neo*Menthylamine* l-*α-bromocamphor-π-sulphonate*, prepared similarly, separated from water in long soft needles, m. p. 171°, $[\alpha]_D - 49{\cdot}3°$, $[M]_D - 230°$ (Found: C, 49·9; H, 7·4. $C_{20}H_{36}O_4NBrS$ requires C, 51·5; H, 7·8%).

The crystalline deposit obtained on mixing hot aqueous solutions of *dl-neo*menthylamine hydrochloride (2 mols.; J., 1926, 2227) and ammonium *d*-α-bromocamphor-π-sulphonate (1 mol.) had $[M]_D + 283°$; when the salt was recrystallised twice from dilute alcohol the molecular rotation changed through $[M]_D + 291°$ to $[M]_D + 318°$. The last fraction, m. p. 171°, when decomposed gave optically impure *l-neo*menthylamine hydrochloride having $[M]_D - 6°$. On adding a second molecular proportion of the ammonium salt to the original filtrate, a first fraction was deposited having $[M]_D + 287°$; the final fraction, having $[M]_D + 163°$, yielded optically impure *d-neo*menthylamine hydrochloride with $[M]_D + 9°$.

2. *Camphor*-10-*sulphonates.*—*d-neo*Menthylamine *d*-camphor-10-sulphonate, prepared by mixing equivalent weights of the acid and base in alcohol, separated from ether–light petroleum in clusters of small, transparent prisms, m. p. 180°, $[\alpha]_D + 24{\cdot}0°$, $[M]_D + 93°$. *d-neo*Menthylamine *l*-camphor-10-sulphonate crystallised from the same solvent in long prisms, m. p. 152°, $[M]_D \pm 0°$. No change was observed in these rotatory powers upon recrystallising the salts.

The salt obtained by mixing equimolecular weights of *d*-camphor-10-sulphonic acid and *dl-neo*menthylamine in warm alcohol was fractionally crystallised from ether–light petroleum. A series of fractions exhibited values of $[M]_D$ which fluctuated irregularly between $+ 75°$ and $+ 44°$; the specimens of *neo*menthylamine hydrochloride prepared from these two limiting fractions had $[M]_D + 4°$ and $\pm 0°$, respectively.

3. *Normal Tartrates.*—*d-neo*Menthylamine *d*-tartrate crystallised from acetone–methyl alcohol in clusters of colourless needles, m. p. 180°, $[\alpha]_D + 25{\cdot}0°$, $[M]_D + 115°$.

When evaporated on the water-bath, an alcoholic solution of *dl-neo*menthylamine (2 mols.) and *d*-tartaric acid (1 mol.) yielded a crystalline mass, which was fractionally crystallised from acetone-methyl alcohol. After three recrystallisations, the molecular rotation changed from $[M]_D$ + 86° through + 136° to + 124°. The last fraction yielded optically impure *d-neo*menthylamine hydrochloride, with $[M]_D$ + 31°. A fraction having $[M]_D$ + 89° gave impure *l-neo*menthylamine hydrochloride, with $[M]_D$ − 18°.

4. *Hydrogen Tartrates.*—*d-neo*Menthylamine hydrogen *d*-tartrate crystallised from acetone-methyl alcohol in small, colourless prisms, m. p. 179°, $[\alpha]_D$ + 27·4°, $[M]_D$ + 84°.

Optical Resolution of dl-neo*Menthylamine.*—Hot alcoholic solutions of *dl-neo*menthylamine (1 mol.) and *d*-tartaric acid (1 mol.) were mixed, and the solvent was removed. Three recrystallisations of the resultant crystalline mass from acetone–methyl alcohol (1 : 1) furnished a pure specimen of *l-neo*menthylamine hydrogen *d*-tartrate, m. p. 188°; 0·2074 g. made up to 20 c.c. with water gave no appreciable optical rotation when examined in a 2-dcm. tube in sodium light. *l-neo*Menthylamine hydrochloride prepared from this salt had $[\alpha]_D$ − 20·2°, $[M]_D$ − 39°. Salicylidene-*l-neo*-menthylamine had m. p. 99°, $[\alpha]_D$ − 31·3° (*c* 0·33 in chloroform; compare J., 1926, 2219).

Pure *d-neo*menthylamine hydrogen *d*-tartrate could not be isolated, but an impure fraction from the mother-liquors, having $[M]_D$ + 67°, yielded a specimen of optically impure *d-neo*menthylamine hydrochloride with $[M]_D$ + 25°.

Salts of iso*Menthylamines.*

1. *α-Bromocamphor-π-sulphonates.*—A hot aqueous solution of a mixture of equimolecular amounts of *d-iso*menthylamine (J., 1926, 2221) and ammonium *d*-α-bromocamphor-π-sulphonate deposited upon cooling a mass of long slender needles of d-iso*menthylamine* d-*α-bromocamphor-π-sulphonate.* Repeated recrystallisation of this salt from boiling water yielded specimens for which the values of $[M]_D$ varied irregularly from + 396° to + 295° (Found : C, 51·1; H, 8·3. $C_{20}H_{36}O_4NBrS$ requires C, 51·5; H, 7·8%).

*d-iso*Menthylamine *l*-α-bromocamphor-π-sulphonate crystallised from boiling water in small prisms, m. p. 206° (decomp.). The values of $[M]_D$ for this salt showed variations similar to those observed for the diastereoisomeride, changing from − 201° through − 249° to − 212°.

Upon attempting the optical resolution of *dl-iso*menthylamine (J., 1925, **127**, 2782; 1926, 2230) with the aid of ammonium *d*-α-bromocamphor-π-sulphonate, in the manner described above for *dl-neo*menthylamine, fractions of salt were obtained with values of $[M]_D$ ranging from + 263° to + 290°; the specimens of *iso*-menthylamine hydrochloride prepared from these fractions were almost optically inactive, the highest rotatory power observed being $[M]_D$ + 9°, for a hydrochloride from a fraction of salt having $[M]_D$ + 268°.

2. *Camphor*-10-*sulphonates*.—*d*-*iso*Menthylamine *d*-camphor-10-sulphonate, prepared from the free acid and base, crystallised from ethyl acetate in clusters of hard prisms, m. p. 180°, $[\alpha]_D$ + 24·6°, $[M]_D$ + 95°. *d*-*iso*Menthylamine *l*-camphor-10-sulphonate crystallised from ethyl acetate in soft needles, m. p. 188°, $[M]_D$ ± 0°. The rotatory powers of both these salts remained unaltered on further crystallisation.

Equimolecular amounts of *dl*-*iso*menthylamine and *d*-camphor-10-sulphonic acid were mixed in hot alcohol and the solvent was removed. Upon fractionation of the resultant crystalline mass from ethyl acetate, the molecular rotatory powers of the various fractions oscillated in an irregular manner between + 32° and + 51°; all the specimens of *iso*menthylamine hydrochloride prepared from these fractions were optically inactive in aqueous solution (*c* 3·5).

3. *Normal Tartrates*.—Hot alcoholic solutions of *d*-*iso*menthylamine (2 mols.) and *d*-tartaric acid (1 mol.) were mixed and evaporated to dryness on the water-bath. The remaining *d*-*iso*menthylamine *d*-tartrate separated from boiling water in large glistening plates, m. p. 204°, $[\alpha]_D$ + 32·9°, $[M]_D$ + 151°.

Upon replacing the *d*-base by the *dl*-base in the above experiment and crystallising the product from acetone–methyl alcohol, three successive fractions were obtained with $[M]_D$ + 108°, + 56°, and + 55°, respectively. The rotatory power of the first fraction remained practically unaltered upon recrystallisation, even when the sterile solution was seeded with a crystal of pure *d*-*iso*menthylamine *d*-tartrate; when decomposed, it yielded optically impure *d*-*iso*menthylamine hydrochloride with $[M]_D$ + 15°. A fraction of the original salt with $[M]_D$ + 51° yielded optically inactive *iso*menthylamine hydrochloride.

4. *Hydrogen Tartrates*.—*d*-*iso*Menthylamine hydrogen *d*-tartrate, prepared from the free acid and base, crystallised from acetone–methyl alcohol in fine needles, m. p. 190°, $[M]_D$ + 98°.

When mixed in equimolecular proportion in hot aqueous solution, *dl*-*iso*menthylamine and *d*-tartaric acid yielded a crystalline salt having $[M]_D$ + 45°, and this value remained practically unaltered upon fractionating the salt from the same solvent, even when the saturated solution was seeded with pure *d*-*iso*menthylamine hydrogen *d*-tartrate. Specimens of *iso*menthylamine hydrochloride prepared from these fractions were invariably optically inactive. As the molecular rotatory power in dilute aqueous solution of the hydrogen *d*-tartrate ion is about + 42°, it would appear that these separations all consisted of *dl*-*iso*menthylamine hydrogen *d*-tartrate; whether this salt forms a partial racemate, or merely a conglomerate whose components cannot be separated owing to their similar solubilities, remains undecided.

Effect of Evaporation on the Rotatory Powers of Menthylamine Salts in Aqueous Solution.

1. A specimen of *l*-menthylamine hydrochloride having $[\alpha]_D$ $-$ 35·3° (0·5040 g. in 20 c.c. of water gave α_D $-$ 1·78°) showed no alteration in rotatory power after evaporation to dryness in aqueous solution. The base was liberated with sodium hydroxide, extracted with ether, and reconverted into hydrochloride; the crude dry salt had $[\alpha]_D$ $-$ 35·2° in aqueous solution (0·6114 g. in 25 c.c. gave α_D $-$ 1·72°).

2. *Salts with* d-*α-Bromocamphor-π-sulphonic Acid.*—A specimen of the salt with *d-neo*menthylamine having $[M]_D$ + 341° (0·1160 g. in 20 c.c. gave α_D + 0·85°, $[\alpha]_D$ + 73·3°) was dissolved in water and evaporated to dryness on the water-bath; the dry recovered salt had $[M]_D$ + 310° (0·1082 g. in 20 c.c. gave α_D + 0·72°, $[\alpha]_D$ + 66·5°). The corresponding values for a specimen of the salt with *dl-neo*menthylamine were $[M]_D$ + 301° originally (0·1104 g. in 25 c.c. gave α_D + 0·57°, $[\alpha]_D$ + 64·5°), and $[M]_D$ + 264° after evaporation (0·1184 g. in 20 c.c. gave α_D + 0·67°, $[\alpha]_D$ + 56·6°). In a similar experiment the value of $[M]_D$ rose from + 282° to + 334° after evaporation in the presence of a small quantity of ammonia.

3. *Salts with* d-*Camphor-*10*-sulphonic Acid.*—The differences in rotatory power observed on applying similar treatment to salts of this acid with *d-neo-* and *dl-neo*-menthylamine were so slight as to be indistinguishable from possible experimental errors in making the polarimetric observations.

4. *Salts with* d-*Tartaric Acid.*—The normal *d*-tartrate of *d-neo*-menthylamine and the normal and hydrogen *d*-tartrates of *dl-neo*-menthylamine yielded results similar to those just indicated under (3).

In all these experiments the hydrochloride of the base was prepared from the original salt and from the specimen remaining after evaporation; in no instance, however, was any appreciable difference in rotatory power observed between the two specimens of the hydrochloride.

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