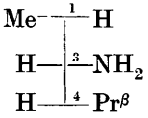
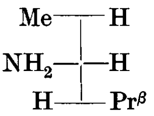
# CCCLXX.—*Researches in the Menthone Series. Part VIII. Further Characterisation of the Optically Active Menthylamines.*

By John Read and Ralph Alexander Storey.

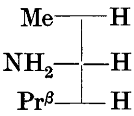
The relative molecular configurations (I to IV) which have been assigned to the stereoisomeric menthylamines were derived originally from a study of the interaction of these bases with nitrous acid (J., 1927, 2168; *Chemical Reviews*, 1930, 7, 27):



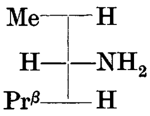
*l*(or *d*)-Menthylamine.
(I.)



*d*(or *l*)-*neo*-Menthylamine.
(II.)



*d*(or *l*)-*iso*-Menthylamine.
(III.)



*d*(or *l*)-*neoiso*-Menthylamine.
(IV.)

In interpreting the reactions concerned, the assumption was made that the main product in each case was formed through a direct replacement of $NH_2$ by OH, while the subsidiary product was regarded as the outcome of a Walden inversion. The molecular configurations deduced in this way appear to us to be sustained by the new physical and chemical evidence which we advance in this communication.

The *cis*-configuration has been allocated to *iso*menthone by Zeitschel and Schmidt (*Ber.*, 1926, 59, 2298) in conformity with the Auwers–Skita rule that density and refractive index are higher for the *cis*- than for the *trans*-isomeride; this conclusion is supported by the more recent observations of Hiraidzumi (Chikashige Anniv. Vol., Kyoto, 1930, 87). It is thus noteworthy that these constants (Table I) are markedly higher for *d*-*iso*- and *d*-*neoiso*-menthylamine, derived according to the above scheme from *iso*menthone, than for *l*- and *d*-*neo*-menthylamine, derived from menthone. It is also of interest that the values for the *d*-*neo*- or *d*-*neoiso*-base are in all instances slightly higher than for the *l*- or *d*-*iso*-base, respectively.

The optical rotatory powers of the free homogeneous bases lie between $[\alpha]_D^{25°}$ − 44·53° (*l*-) and + 28·96° (*d*-*iso*-). Some striking alterations in these numerical values occur when the bases are dissolved in chloroform: decreases of 14% and 42% are shown by the *l*- and the *d*-*neo*-base, respectively; while in the *iso*-series there are increases of 1·6% and 360% for the *d*-*iso*- and the *d*-*neoiso*-base, respectively.

A study of the optical rotatory powers of these four bases and a comprehensive series of their derivatives (Table II) has disclosed *inter alia* the following general relationships: (i) the four sets of values are generically related; (ii) the four bases fall into two well-defined families, depending upon their derivation from menthone or *iso*menthone; (iii) dextrorotatory *neoiso*menthylamine belongs configurationally to the *l*-series, which is characterised by the configurational unit $H|NH_2$; (iv) apart from the anomalous sense of rotation of the *d*-*neoiso*-base and its hydrochloride, and of β-naphthalenesulphonyl-*d*-*iso*menthylamine, the sign of the optical rotation is changed by reversing asymmetric centre (3), but not by reversing either of the remaining asymmetric centres, (1) or (4); (v) the lowest rotatory powers, considered numerically, are shown by substances of the *iso*- and *neoiso*-series, that is, by configurations having the most symmetrical distribution of like (H) or similar (Me and $Pr^\beta$) groups about a plane passing through the characteristic group (3) at right angles to the plane of the ring, the sequence being usually *l*>*l*-*neo*>*l*-*iso*>*d*-*neoiso*. The remarkable numerical relationships which are displayed by the optical rotatory powers of these four series of stereoisomeric substances, together with the bearing of the data upon the so-called principle of optical superposition, have been fully discussed elsewhere (*Chemical Reviews*, 1930, 7, 31; *Trans. Faraday Soc.*, 1930, **26**, 446).

From Table II it is seen that the melting points of derivatives of the *d*-*neo*- and *l*-bases (menthone series) are usually higher than those of the corresponding derivatives of the *d*-*neoiso*- and *d*-*iso*-base (*iso*menthone series). Further, in each of the series the *neo*-derivatives have the higher melting point, the general sequence being *d*-*neo*>*l*>*d*-*neoiso*>*d*-*iso*. Hence, in general, configurations having the most symmetrical distribution of like or similar groups, as indicated above, possess the lowest melting points.

An inspection of configurations (II) and (I) suggests that the amino-group of *d-neo*menthylamine should react with greater ease than that of *l*-menthylamine, since this group is situated in the *cis*-position to a hydrogen atom and an *iso*propyl group, respectively. Similarly, *d-neoiso*menthylamine (IV) should react more readily than *d-iso*menthylamine (III). Chemical evidence bearing upon the relative molecular configurations of these stereoisomerides was therefore sought by allowing equimolecular mixtures of pairs of these bases to react competitively in solution with insufficient quantities of various acid anhydrides, acid chlorides, and aldehydes. Distinct evidence was obtained in this way of the following comparative rates of reaction: *d-neo*menthylamine>*l*-menthylamine; *d-iso*>*l*; *d-neoiso*>*l*; *d-neo*>*d-iso*; *d-neoiso*>*d-iso*. These results are in accordance with the relative molecular configurations, (I) to (IV), which have been assigned to the four series of stereoisomerides.

As an extension of these experiments, some preliminary observations have been made on the comparative rates of reaction of the *d*- and *l*-forms of menthylamine, *neo*menthylamine, and *iso*menthylamine with *d*- or *l*-camphor-10-sulphonyl chloride. In all three instances the reaction was distinctly more rapid between a dextrorotatory molecule of one reagent and a lævorotatory molecule of the other than between a dextrorotatory or a lævorotatory molecule of each kind. From a series of similar observations made in these laboratories, it appears that, in general, when an optically active molecule has equal opportunities of reacting with either of two antimeric molecules there is usually a preference in favour of reaction occurring with the form of the second molecule which displays the opposite sense of rotation. A detailed treatment of this interesting theme is reserved for later publication. It may be added that some of the pairs of diastereoisomeric camphor-10-sulphonylmenthylamines prepared in the course of this work appear to form partial racemates.

## EXPERIMENTAL.

*Physical Properties of Optically Active Menthylamines.*—The *l*-menthylamine was prepared by reducing *l*-menthoneoxime (*Annalen*, 1893, **276**, 360; J., 1926, 2221); it was liberated from a specimen of the hydrochloride having $[\alpha]_D^{25^\circ}$ − 36·1° (*c* 2·0 water). All four of the stereoisomeric bases were dried over solid potassium hydroxide before being distilled under diminished pressure in an atmosphere free from carbon dioxide. *d-neo*Menthylamine was obtained from a carefully purified specimen of the hydrochloride (J., 1926, 2218) having $[\alpha]_D^{25^\circ}$ + 20·9° (*c* 2·0, water); and *d-iso*menthylamine (J., 1926, 2221) and *d-neoiso*menthylamine (J., 1927, 2172) from recrystallised hydrochlorides having, respectively, $[\alpha]_D^{25^\circ}$ + 23·2° and + 20·3° (*c*, 2·0, water). The four stereoisomeric bases are closely similar in appearance, odour, and physical properties; chemically, they are all strong bases, which absorb carbon dioxide eagerly from the air, forming solid crystalline deposits.

TABLE I.

*Physical Constants of Optically Active Menthylamines.*

| | *l*-. | *d-neo*-. | *d-iso*-. | *d-neoiso*-. |
|---|---|---|---|---|
| B. p. ............... | 81—82°/12 mm. | 84°/13 mm. | 87°/13·5 mm. | 89°/14·5 mm. |
| $d_{4^\circ}^{25^\circ}$ (corr.) ...... | 0·8525 | 0·8551 | 0·8632 | 0·8636 |
| $n_D^{25^\circ}$ ............... | 1·4600 | 1·4614 | 1·4659 | 1·4670 |
| $[R_L]_D$ ............ | 49·86 | 49·83 | 49·82 | 49·89 |
| $\alpha_D^{25^\circ}$ homogeneous | −37·97° | +12·93° | +25·00° | + 2·00° |
| $[\alpha]_D^{25^\circ}$ ,, | −44·53° | +15·12° | +28·96° | + 2·32° |
| $\alpha_{5461}^{25^\circ}$ ,, | −44·80° | +14·90° | +29·40° | + 2·30° |
| $[\alpha]_{5461}^{25^\circ}$ ,, | −53·21° | +17·42° | +34·06° | + 2·66° |
| $[\alpha]_D^{25^\circ}$ in $CHCl_3$ ... | −38·2° | + 8·7° | +29·4° | +10·7° |
| $[\alpha]_{5461}^{25^\circ}$ ,, ... | −45·3° | +10·0° | +34·6° | +12·4° |

The densities of the bases are reduced to vacuum standard. The calculated value for $[R_L]_D$ is 49·53. The values of $\alpha$ for the homogeneous bases were observed in a 1-dcm. tube; the chloroform solutions contained about 4 g. of the base in 100 c.c. Some of the values of $\alpha_D$ are higher than the maxima which have been recorded hitherto. The most marked difference is in the case of *d-neoiso*menthylamine, which has now been prepared in quantity for the first time; the recorded values for derivatives of this base remain unaltered (compare *Annalen*, 1893, **276**, 323; *Chemical Reviews*, 1930, **7**, 31; *Trans. Faraday Soc.*, 1930, **26**, 450).

*Physical Properties of Acyl Derivatives of Optically Active Menthylamines.*—The formyl, acetyl, benzoyl, and β-naphthalenesulphonyl derivatives have already been described (J., 1926, 2225; 1927, 2168). Each of the remaining derivatives included in Table II was prepared by warming a mixture of the appropriate free base (1 mol.) and acid chloride (1 mol.) in dry benzene; the product was shaken with dilute aqueous sodium hydroxide, added gradually, until the attainment of a permanent alkaline reaction. The derivative was isolated in the usual way, after the benzene solution had been washed thoroughly with dilute hydrochloric acid, followed by water. In making the propionyl derivatives, propionic anhydride was used in place of propionyl chloride. The solvents used in recrystallising the derivatives were aqueous alcohol, aqueous acetone, ethyl acetate, or light petroleum. All the crystalline derivatives formed colourless needles or prisms. The *n*-butyryl, *n*-hexoyl, and *n*-octoyl derivatives of the *iso*-base were obtained as viscid syrups; *n*-butyryl-*d*-*iso*menthylamine was originally isolated in a similar form, but it crystallised to a low-melting solid when kept in a sealed tube. The following representative derivatives were analysed: *bromoacetyl*-l-*menthylamine* (Found: C, 52·2; H, 8·1. $C_{12}H_{22}ONBr$ requires C, 52·2; H, 8·0%); iso*valeryl*-l-*menthylamine* (Found: C, 75·3; H, 11·8. $C_{15}H_{29}ON$ requires C, 75·3; H, 12·2%); *chloroacetyl*-d-neo*menthylamine* (Found: C, 62·1; H, 9·6. $C_{12}H_{22}ONCl$ requires C, 62·2; H, 9·6%); n-*hexoyl*-d-neo*menthylamine* (Found: C, 75·4; H, 12·4. $C_{16}H_{31}ON$ requires C, 75·8; H, 12·3%); iso*butyryl*-d-iso*menthylamine* (Found: C, 74·1; H, 12·0. $C_{14}H_{27}ON$ requires C, 74·6; H, 12·1%); n-*hexoyl*-d-iso*menthylamine* (Found: C, 75·8; H, 12·3. $C_{16}H_{31}ON$ requires C, 75·8; H, 12·3%); n-*octoyl*-d-iso*menthylamine* (Found: C, 76·9; H, 12·4. $C_{18}H_{35}ON$ requires C, 76·8; H, 12·5%); *phenylacetyl*-d-iso*menthylamine* (Found: C, 78·7; H, 9·8. $C_{18}H_{27}ON$ requires C, 79·1; H, 10·0%); *propionyl*-d-neoiso*menthylamine* (Found: C, 73·6; H, 12·0. $C_{13}H_{25}ON$ requires C, 73·9; H, 11·9%); n-*butyryl*-d-neoiso*menthylamine* (Found: C, 74·7; H, 12·1. $C_{14}H_{27}ON$ requires C, 74·6; H, 12·1%).

The optical rotatory powers recorded in Table II were observed in chloroform solution at 25° ($c = 1{\cdot}0$ approximately; $l = 2$).

*Competitive Reaction of Binary Mixtures of Optically Active Menthylamines with Various Symmetric Reagents.*—The hydrochlorides of the optically active menthylamines used in these experiments were prepared in the usual way and possessed optical rotatory powers sensibly identical with those which have been recorded for the purified substances (J., 1927, 2169). In each experiment equal weights of the two bases were allowed to compete in solution for an insufficient weight of an acid anhydride, acid chloride, or aldehyde. The reagents used were acetic and propionic anhydrides, benzoyl chloride, benzaldehyde, and salicylaldehyde. In each instance the composition of the mixed product was calculated from its optical rotatory power in chloroform solution (compare Table II above; also *Trans. Faraday Soc.*, 1930, **26**, 444), and the result was checked by a further determination of the rotatory power, in aqueous solution, of the hydrochloride prepared from the recovered mixture of unchanged bases.

(1) *Mixture of* l-*menthylamine and* d-neo*menthylamine.* To a dry benzene solution containing equal weights of the two bases was added 60% of the calculated amount of the reagent, dissolved in a standard quantity of benzene. The solution was heated to incipient boiling on the water-bath, and dilute sodium hydroxide solution

## TABLE II.

*Physical Constants of Acyl Derivatives of Optically Active Menthylamines.*

| Derivative. | M. p. | $[\alpha]_D^{25^\circ}$. | $[\alpha]_{5461}^{25^\circ}$. | M. p. | $[\alpha]_D^{25^\circ}$. | $[\alpha]_{5461}^{25^\circ}$. |
|---|---|---|---|---|---|---|
| | l-*Menthylamine.* | | | d-neo*Menthylamine.* | | |
| Formyl ............ | 102—103° | −83·8° | — | 117—118° | +53·8° | — |
| Acetyl ............ | 145 | 81·7 | — | 169—170 | 53·0 | — |
| Propionyl ......... | 88 | 76·6 | −89·6° | 149 | 48·3 | +56·6° |
| *n*-Butyryl ...... | 73 | 70·9 | 79·4 | 104 | 46·8 | 53·5 |
| *iso*Butyryl ...... | 128 | 66·5 | 75·0 | 160—161 | 47·5 | 54·7 |
| *iso*Valeryl ...... | 110 | 64·7 | 76·7 | 132 | 42·8 | 51·3 |
| *n*-Hexoyl ......... | 60 | 60·0 | 71·2 | 65 | 40·0 | 45·0 |
| *n*-Octoyl ......... | 57 | 53·2 | 63·8 | 78 | 36·7 | 42·4 |
| Chloroacetyl ... | 76 | 71·9 | 86·6 | 150 | 50·7 | 57·7 |
| Bromoacetyl ... | 103 | 61·6 | 73·1 | 160 | 40·9 | 46·2 |
| Benzoyl ......... | 157 | 62·8 | — | 121·5 | 22·7 | — |
| Phenylacetyl ... | 106 | 60·4 | 72·1 | 120 | 34·5 | 41·0 |
| β-Naphthalene-sulphonyl ...... | 135 | 53·3 | — | 208 | 43·7 | — |
| Anisoyl ............ | 183 | 57·7 | 69·0 | 130 | 21·1 | 24·0 |
| | d-iso*Menthylamine.* | | | d-neoiso*Menthylamine.* | | |
| Formyl ............ | 45—46 | +31·3 | — | — | −3·9 | — |
| Acetyl ............ | 77—79 | 30·7 | — | 99—100 | 2·6 | — |
| Propionyl ......... | 83 | 27·7 | +32·1 | 103 | 0 | −1·0 |
| *n*-Butyryl ...... | — | 23·9 | 27·7 | — | 1·0 | 2·0 |
| *iso*Butyryl ...... | 116 | 22·8 | 25·9 | 128 | 3·7 | 5·4 |
| *iso*Valeryl ...... | 82 | 27·0 | 29·1 | 99 | 4·1 | 6·5 |
| *n*-Hexoyl ......... | — | 24·9 | 27·5 | 50 | 0 | 1·7 |
| *n*-Octoyl ......... | — | 23·3 | 26·0 | 55 | 1·2 | 2·9 |
| Chloroacetyl ... | 82 | 30·0 | 35·0 | 80 | 9·8 | 13·0 |
| Bromoacetyl ... | 80 | 30·3 | 37·1 | 100 | 7·5 | 10·3 |
| Benzoyl ......... | 97—98 | 18·3 | — | 151 | 10·4 | — |
| Phenylacetyl ... | 103 | 33·3 | 38·4 | 109 | 3·4 | 5·1 |
| β-Naphthalene-sulphonyl ...... | 80—81 | −2·8 | — | 120 | 10·7 | — |
| Anisoyl ............ | 121 | 25·3 | 30·7 | 156 | 9·5 | 11·8 |

was added gradually until the mixture remained faintly alkaline after repeated shaking. The cold solution was washed twice with water, then with sufficient dilute hydrochloric acid to render the mixture faintly acid, and finally again with water. The mixed derivative was recovered from the washed and dried benzene, and the mixed hydrochlorides of the unchanged bases from the hydrochloric acid washing. In the reactions with aldehydes no sodium hydroxide was added.

In the reaction with acetic anhydride, the crude dry mixture of acetyl derivatives (2·2 g.) had $\alpha_D$ − 0·27°, $[\alpha]_D$ − 6·6° (*c* 2·0455), and thus consisted of about 56% of acetyl-*d-neo-* and 44% of acetyl-*l*-menthylamine; the recovered hydrochloride (3·3 g.) had $\alpha_D$ − 0·29°, $[\alpha]_D$ − 9·6° (*c* 1·5105), and contained about 46% and 54% of *d-neo-* and *l*-menthylamine hydrochloride, respectively.

The mixed propionyl derivatives (3·5 g.) had $\alpha_D$ − 0·14°, $[\alpha]_D$

— 4·0° (*c* 1·7525), corresponding to 58% of propionyl-*d*-*neo*- and 42% of propionyl-*l*-menthylamine; the recovered hydrochloride (2·1 g.) had $\alpha_D$ — 0·41°, $[\alpha]_D$ — 15·6° (*c* 1·3140), thus containing 36% and 64% of *d*-*neo*- and *l*-menthylamine hydrochloride, respectively.

The mixed benzoyl derivatives had $\alpha_D$ — 0·44°, $[\alpha]_D$ — 14·8° (*c* 1·4845), and therefore contained 56% of benzoyl-*d*-*neo*menthylamine and 44% of benzoyl-*l*-menthylamine.

The mixed benzylidene derivatives had $\alpha_D$ — 0·83°, $[\alpha]_D$ — 19·7° (*c* 2·1040), corresponding to about 58% of the *d*-*neo*-derivative. The mixed salicylidene derivatives had $\alpha_D$ — 1·03°, $[\alpha]_D$ — 20·9° (*c* 2·4640), corresponding to 66% of the *d*-*neo*-derivative. In all three cases the recovered hydrochloride contained an excess of *l*-menthylamine hydrochloride.

(2) *Mixture of* l-*menthylamine and* d-iso*menthylamine.* In a series of experiments conducted in a precisely similar way, the mixture of acetyl derivatives had $[\alpha]_D$ — 11·1°, corresponding to 63% of the *d*-*iso*-derivative; the analogous data for the propionyl and salicylidene derivatives were $[\alpha]_D$ — 13·4° (61% *d*-*iso*-), and $[\alpha]_D$ — 15·1° (53% *d*-*iso*-). In all three instances the hydrochloride of the residual bases contained an excess of *l*-menthylamine hydrochloride. In the experiment with benzaldehyde, no appreciable difference in reaction velocity could be established between *l*-menthylamine and *d*-*iso*-menthylamine.

(3) *Mixture of* l-*menthylamine and* d-neoiso*menthylamine.* In each of the four cases investigated, *d*-*neoiso*menthylamine reacted more rapidly than *l*-menthylamine. The observed rotatory powers of the mixed derivatives and the derived percentage of the *d*-*neoiso*-derivative were as follows: acetyl, $[\alpha]_D$ — 37·9°, 55%; propionyl, $[\alpha]_D$ — 33·3°, 57%; benzoyl, $[\alpha]_D$ — 31·1°, 61%; benzylidene, $[\alpha]_D$ — 77·2°, 56%. The residual base contained an excess of *l*-menthylamine in each instance.

(4) *Mixture of* d-neo*menthylamine and* d-iso*menthylamine.* The mixture of acetyl derivatives had $[\alpha]_D$ + 42·0° and thus consisted of practically equal amounts of each. The product yielded by interaction with benzoyl chloride had $[\alpha]_D$ + 21·7° and contained a preponderance of benzoyl-*d*-*neo*menthylamine; in this case, however, the values of $[\alpha]_D$ for the two derivatives (+ 22·7° and + 18·3°) do not admit of a satisfactory calculation being made. The mixture of benzylidene derivatives had $[\alpha]_D$ + 74·0°, corresponding to 58% of benzylidene-*d*-*neo*menthylamine, and the hydrochloride of the recovered bases contained an excess of *d*-*iso*menthylamine hydrochloride.

(5) *Mixture of* d-iso*menthylamine and* d-neoiso*menthylamine.* The

mixture of propionyl derivatives had $[\alpha]_D + 10{\cdot}6°$, and hence contained 61% of propionyl-*d*-*neoiso*menthylamine; the corresponding values for the benzylidene derivatives were $[\alpha]_D + 16{\cdot}8°$, 59%. In both cases the unchanged base contained an excess of *d*-*iso*menthylamine. The mixture of benzoyl derivatives had $[\alpha]_D + 4{\cdot}3°$, and hence contained approximately equal amounts of the two constituents.

*Condensation of Menthylamines with* d-, l-, *and* dl-*Camphor*-10-*sulphonyl Chloride.*—The acid chlorides were prepared by heating the corresponding acids with thionyl chloride. The *d*-compound had m. p. 70°, $[\alpha]_D + 32{\cdot}3°$ (*c* 3·3, chloroform); the *l*-compound had m. p. 70°, $[\alpha]_D - 32{\cdot}0°$; the *dl*-compound melted at 85° (compare J., 1907, **91**, 522; 1912, **101**, 754).

(1) *Menthylamines.* In all cases the condensation was brought about by mixing the acid chloride with the pure base (slightly more than 1 mol.) in dry benzene. After remaining over-night, the mixture was made slightly alkaline with dilute aqueous sodium hydroxide and shaken until no further reaction occurred. The benzene solution was washed with water and shaken with a slight excess of dilute hydrochloric acid in order to recover the unchanged base. The derivative, when isolated from the dried benzene, was usually purified by recrystallisation from absolute alcohol, although light petroleum was employed for the derivatives of *neo*menthylamine. All the stereoisomerides under notice crystallised in colourless needles or small prisms. The recorded values of $[\alpha]_D$ were observed in benzene solution (*c* about 1·5 g. in 100 c.c.; $l = 2$; $t =$ about 16°).

d-*Camphor*-10-*sulphonyl*-l-*menthylamine* had m. p. 139°, $[\alpha]_D - 28{\cdot}0°$ (Found: C, 65·0; H, 9·3. $C_{20}H_{35}O_3NS$ requires C, 65·0; H, 9·6%). *l*-Camphor-10-sulphonyl-*l*-menthylamine had m. p. 143°, $[\alpha]_D - 60{\cdot}9°$. The product obtained by the interaction of *l*-menthylamine and *dl*-camphor-10-sulphonyl chloride had m. p. 136—137°, $[\alpha]_D - 26{\cdot}6°$, after one recrystallisation. The interaction of *dl*-menthylamine and *d*-camphor-10-sulphonyl chloride yielded a crude product having $[\alpha]_D + 8{\cdot}3°$, and one recrystallisation gave material with m. p. 138°, $[\alpha]_D + 16{\cdot}0°$. The hydrochloride of the residual base had $\alpha_D + 0{\cdot}51°$, $[\alpha]_D + 10{\cdot}7°$ (*c* 2·3910, water), and thus contained about 35% of *l*- and 65% of *d*-menthylamine. Closely corresponding results attended the condensation of *dl*-menthylamine and *l*-camphor-10-sulphonyl chloride, the hydrochloride of the recovered base having $[\alpha]_D - 10{\cdot}0°$, corresponding to about 36% of *d*- and 64% of *l*-menthylamine.

(2) neo*Menthylamines.* d-*Camphor*-10-*sulphonyl*-d-neo*menthylamine* had m. p. 113°, $[\alpha]_D + 33{\cdot}1°$ (Found: C, 64·6; H, 9·7%).

l-*Camphor*-10-*sulphonyl*-d-neo*menthylamine* had m. p. 115°, $[\alpha]_D$ + 7·3° (Found : C, 65·0 ; H, 9·5%). *dl*-Camphor-10-sulphonyl chloride reacted similarly with *d*-*neo*menthylamine to yield a crude product which had m. p. 115°, $\alpha_D$ + 0·71°, $[\alpha]_D$ + 21·3° (*c* 1·6625). These values remained practically unaltered after two recrystallisations, the substance thus appearing to consist of dl-*camphor*-10-*sulphonyl*-d-neo*menthylamine* (Found : C, 64·8 ; H, 9·7%). A substance with identical properties was obtained by evaporating to dryness an alcoholic solution of equal weights of *d*-camphor-10-sulphonyl-*d*-*neo*menthylamine and *l*-camphor-10-sulphonyl-*d*-*neo*-menthylamine. The reaction between *l*-camphor-10-sulphonyl chloride and *dl*-*neo*menthylamine gave a crude product having m. p. 151°, $\alpha_D$ − 0·18°, $[\alpha]_D$ − 5·5° (*c* 1·6555); these values remained practically unaltered after the product had been twice crystallised from absolute alcohol (Found : C, 64·7 ; H, 9·7%). The unaltered *neo*menthylamine, recovered as hydrochloride, weighed 1·5 g. and had $\alpha_D$ − 0·07°, $[\alpha]_D$ − 3·1° (*c* 1·1060, water); it thus contained about 57% of the *l*-base and 43% of the *d*-base. A similar result attended reaction between *d*-camphor-10-sulphonyl chloride and *dl*-*neo*menthylamine, the residual base having $\alpha_D$ + 0·09°, $[\alpha]_D$ + 3·6° (*c* 1·2460, water).

(3) iso*Menthylamines*. *d*-Camphor-10-sulphonyl-*d*-*iso*menthylamine had m. p. 169°, $[\alpha]_D$ + 29·7°; and *l*-camphor-10-sulphonyl-*d*-*iso*menthylamine had m. p. 140°, $[\alpha]_D$ − 15·8°. *d*-Camphor-10-sulphonyl chloride reacted with *dl*-*iso*menthylamine to yield a crude product with $[\alpha]_D$ + 25·2°; after recrystallisation it had m. p. 170°, $[\alpha]_D$ + 25·0° (Found : C, 64·9 ; H, 9·6%). The hydrochloride of the recovered base had $\alpha_D$ + 0·17°, $[\alpha]_D$ + 5·1° (*c* 1·6520, water), and hence contained about 61% of *d*-*iso*menthylamine and 39% of *l*-*iso*menthylamine. The product obtained in a similar experiment with *l*-camphor-10-sulphonyl chloride gave $[\alpha]_D$ − 20·8° originally and $[\alpha]_D$ − 22·5°, m. p. 170°, after recrystallisation; the recovered hydrochloride had $[\alpha]_D$ − 6·0°.

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