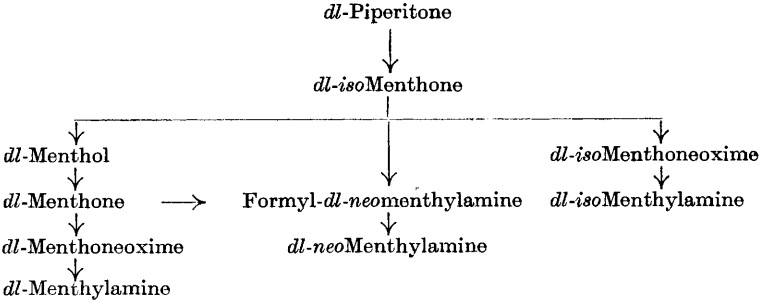
CCXCIV.—*Researches in the Menthone Series. Part III. Optically Inactive Menthylamines.*

By JOHN READ, ALISON MARY RITCHIE COOK, and (in part) MARY ISOBEL SHANNON.

THIS communication deals mainly with the preparation and characterisation of *dl*-menthylamine, *dl*-*neo*menthylamine, and *dl*-*iso*menthylamine. Up to the present, the only definite data available concerning externally compensated menthylamines would appear to be contained in Wallach's description of a so-called " i-Menthylamine," and certain of its derivatives, prepared by the reduction of *dl*-menthoneoxime (*Annalen*, 1913, **397**, 218). As shown below, these derivatives are to be regarded as characteristic of *dl*-*iso*menthylamine rather than of *dl*-menthylamine.

The utilisation of *dl*-piperitone as a starting point for the preparation of the three stereoisomeric optically inactive menthylamines in question follows from an application of the methods which have been laid down in the two preceding communications of this series (J., 1925, **127**, 2782; this vol., p. 2210). It may therefore be sufficient to indicate the scheme of operations briefly by means of a diagrammatic summary :



In all three instances homogeneous products were isolated without difficulty. The three optically inactive bases give rise to distinctive series of derivatives, the majority of which may be readily obtained crystalline. A broad resemblance may be traced between *dl*-menthylamine and *dl*-*iso*menthylamine, whilst *dl*-*neo*menthylamine presents certain unique features. Thus, the hydrochlorides of the first two bases are practically insoluble in ether and do not melt below 250°; *dl*-*neo*menthylamine hydrochloride, however, dissolves readily in ether, and even in light petroleum, and melts at 184—185°. This base is also characterised by the beauty of its crystalline derivatives : thus, it has been possible to submit both the externally compensated and the optically active hydrochloride and formyl derivative of the *neo*-base to goniometric examination, with results of considerable interest. Such similarities and differences between the bases accord satisfactorily with the relative molecular configurations recently advanced for them (this vol., p. 2213), in which menthylamine and *iso*menthylamine differ only in the asymmetry of carbon atom (1). A similar resemblance is to be anticipated between *neo*menthylamine and the still unknown *neoiso*menthylamine, which, in accordance with the scheme indicated, display a corresponding configurational relationship.

With certain exceptions, including most of the carbamide derivatives, the externally compensated derivatives of all three bases possess lower melting points than their optically active components. In view of the unusually interesting stereochemical relationships existing between the three optically inactive and six optically active menthylamines which are now readily available, starting from *dl*-, *d*-, and *l*-piperitone, we propose to undertake further studies of these bases and their derivatives, including a complete investigation of the optical resolution of the externally compensated forms. It is hoped also to prepare *neoiso*menthylamine, possibly by a suitable application of the Walden inversion. For the present, the appended summary of melting points and specific rotatory powers affords a comprehensive survey of some of the most important derivatives of the three bases now known. The values of $[\alpha]_D$, denoted by the prefixed + or − signs, were observed in water for the hydrochlorides and in chloroform for the remaining derivatives (this vol., pp. 2219, 2222) :

	Menthylamines.		*neo*Menthylamines.		*iso*Menthylamines.	
Derivative.	*dl*-.	*l*-.	*dl*-.	*d*-.	*dl*-.	*d*-.
Hydrochloride.	>250°	>280° * −36·6°†	184—185°	189° +21·5°	>250°	>250° +23·6°
Formyl.	77—78	102—103* −83·8*	86	117—118 +53·8	45—47	45—46 +31·3
Acetyl.	123—124	145* −81·7*	160—161	169—170 +53·0	Liquid	77—79 +30·7
Benzoyl.	145—146	157 −62·8	101—102	121·5 +22·7	127—128	97—98 +18·3
β-Naphthalene-sulphonyl.	145—146	135 −53·3	209—210	208 +43·7	141—142	80—81 −2·8
Benzylidene.	Liquid	69—70 −132·5	Liquid	45—46 +61·7	41—44	67—68 +90·7
Salicylidene.	Liquid	57—58 −119·2	69·5	99—100 +30·0	95	122 +77·6
Carbamide.	157	134—136*	162—163	155—156*	203—204	141·5—142·5 +29·0
Phenylcarbamide.	162	140—141*	183—184	177—178*	142—143	142 +21·8
Phenylthiocarbamide.	151	135*	169—170	178—179*	137	114·5—115·5 +46·7

* Wallach, *Annalen*, 1893, **276**, 306; 1898, **300**, 278.
† Tutin and Kipping, J., 1904, **85**, 65.

The tabulated constants show the importance of selecting suitable derivatives in diagnosing a particular menthylamine, as the values for the same derivative of two stereoisomerides are in some instances almost identical.

It may now be pointed out that Wallach's "i-Menthylamine" (*loc. cit.*), since it is stated to have been prepared by reducing *dl*-menthoneoxime, would be expected to yield derivatives possessing the properties recorded in the second column of the above table. Apart from the hydrochloride, which cannot easily be used in discriminating between *dl*-menthylamine and *dl*-*iso*menthylamine, the carbamide (m. p. 151—152°) is the sole derivative which fulfils this condition even approximately. The phenylcarbamide (m. p. 135—136°) and the phenylthiocarbamide (m. p. 136—137°) melt at practically the same temperatures as the corresponding *dl*-*iso*-menthylamine derivatives, whilst the melting point, 141—142°, quoted for the benzylidene derivative is perhaps a misrendering of 41—42°. It would thus appear, as suggested in another connexion (J., 1925, **127**, 2783), that Wallach's "inactive menthone" consisted of *dl*-*iso*menthone, which upon oximation in an alkaline medium would yield a mixture of *dl*-*iso*menthoneoxime and *dl*-menthoneoxime.

The need for a careful observance of the experimental conditions adopted in preparing the various stereoisomeric menthylamines and related substances is emphasised further by the results of attempts to utilise *dl*-piperitoneoxime as a source of optically inactive menthylamines. These experiments, which were conducted prior to the successful operations outlined above, although affording no useful method of preparing pure menthylamines, are of considerable interest as suggesting a possible line of approach from piperitone to piperitylamine and piperitol.

EXPERIMENTAL.

Preparation and Characterisation of dl-*Menthylamine.*—*dl*-Menthoneoxime (10 g.; m. p. 81—82°), prepared from *dl*-piperitone via *dl-iso*menthone, *dl*-menthol, and *dl*-menthone (J., 1925, **127**, 2782), was dissolved in absolute alcohol (75 c.c.) and reduced with metallic sodium (15 g.) on a boiling water-bath, further quantities of absolute alcohol (60 c.c.) being added as needed, in order to effect the complete solution of the sodium. Upon steam distilling the product and evaporating the distillate to dryness with dilute hydrochloric acid, crude, crystalline dl-*menthylamine hydrochloride* was obtained in almost theoretical yield. Upon recrystallisation from boiling acetone containing a little methyl alcohol, it separated in small, glistening needles, which did not melt below 250° (Found : Cl, 18·4. $C_{10}H_{21}N,HCl$ requires Cl, 18·5%). The substance dissolves sparingly in boiling acetone or ethyl acetate, and readily in alcohol or water; it is practically insoluble in ether or light petroleum. The crude product of the reduction appeared to be substantially homogeneous, but in preparing derivatives the hydrochloride was recrystallised twice before use.

dl-*Menthylamine chloroplatinate* crystallises from hot water in small, deep orange prisms, m. p. 201—202° (decomp.). The *picrate* is deposited from warm alcohol in well-defined, transparent, pale yellow prisms, m. p. 196—198°. Free dl-*menthylamine* is a liquid which resembles *l*-menthylamine closely in its odour and general properties.

The *formyl* derivative was prepared by heating the free base with an excess of anhydrous formic acid in a sealed tube at 200° for 5 hours. It crystallises from light petroleum in clusters of minute, glistening prisms, m. p. 77—78°. *Acetyl*-dl-*menthylamine*, prepared by the interaction of the free base and acetic anhydride in dry ether, separates from ether–light petroleum in long, silky needles, m. p. 123—124°. *Benzoyl*-dl-*menthylamine*, obtained by the Schotten–Baumann reaction, is deposited from methyl alcohol in elongated, transparent prisms, m. p. 145—146°. β-*Naphthalenesulphonyl*-dl-*menthylamine*, prepared similarly, crystallises from methyl alcohol in clusters of small, transparent prisms, m. p. 145—146°. *Benzylidene*-dl-*menthylamine* was readily produced by mixing the free base and benzaldehyde in ether; it forms a colourless oil at the ordinary temperature. *Salicylidene*-dl-*menthylamine*, prepared similarly, is a pale yellow oil.

dl-*Menthylcarbamide* separated as an oil upon mixing *dl*-menthylamine hydrochloride and potassium cyanate in aqueous solution; it crystallised slowly when kept, and was deposited from acetone in soft, opaque needles, m. p. 157°.

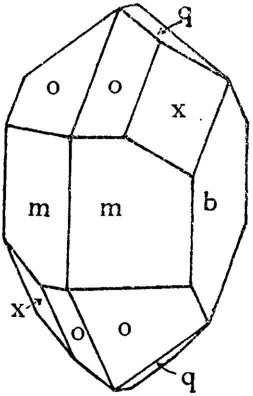
dl-*Menthylphenylcarbamide*, made by mixing the free base and phenylcarbimide in dry ether, was deposited from methyl alcohol in soft needles, m. p. 162°. dl-*Menthylphenylthiocarbamide*, prepared in an analogous manner, crystallised from methyl alcohol in small, lustrous, elongated prisms, m. p. 151°.

Action of nitrous acid on dl-*menthylamine.* Upon treating an aqueous solution of *dl*-menthylamine hydrochloride (5 g.) with the calculated amount of sodium nitrite solution, added drop by drop at 70°, effervescence occurred and an oil was produced. This was removed by steam distillation, extracted with ether, and dried over anhydrous sodium sulphate. Upon distillation, most of the product passed over at 104—107°/20 mm.; the distillate had $n_D^{16^\circ}$ 1·4600 and consisted of *dl*-menthol and *dl*-Δ^3-menthene.

Preparation and Characterisation of dl-neo*Menthylamine.*—The product obtained by heating *dl*-*iso*menthone with ammonium formate (compare *Annalen*, 1898, **300**, 283; this vol., p. 2217) was freed from unchanged ketone by steam distillation; the residual crude formyl derivative was then extracted with ether and distilled under diminished pressure. The fraction distilling at 160—170°/10 mm. crystallised partly when kept for several days. The crystalline material was separated from the accompanying viscid syrup by filtration with suction, followed by treatment on porous plate and recrystallisation from light petroleum–ether. The resulting pure *formyl*-dl-neo*menthylamine*, $C_{10}H_{19}$·NH·COH, formed large, transparent prisms, m. p. 86°, the average yield being about 20% of the crude product. *dl*-Menthone furnished the same substance when treated similarly. Formyl-*dl*-*neo*menthylamine dissolves readily in most of the common organic solvents, and is considerably more soluble than formyl-*d*-*neo*menthylamine (this vol., p. 2219); from light petroleum, in which it is only moderately easily soluble, it separates in fine needles attaining a length of 3 cm. Slow deposition from light petroleum–ether usually results in the formation of compact prisms, although the needles often appear towards the end of the crystallisation. No difference in melting point was observed between the two forms. The appended crystallographic description has been kindly supplied by Dr. T. V. Barker, of the Department of Mineralogy, University of Oxford:

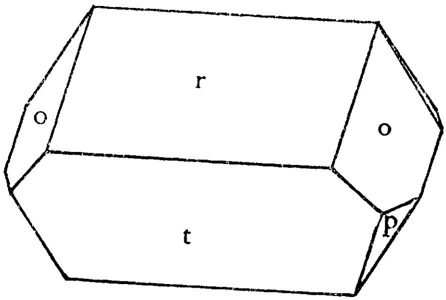
"The substance is dimorphous. One form is orthorhombic and exhibits a close similarity to the *d*-component previously described (this vol., p. 2219). It is therefore either a conglomerate or a pseudoracemic substance; and although the character of the melting-point curve favours the former possibility (this vol., p. 2220), the evidence in another direction is somewhat inconclusive. On the one hand, the crystals exhibit well-developed hemihedral facets, *x* of Fig. 1, permitting a mechanical segregation into right- and left-handed forms; but, on the other hand, individual crystals so selected do not melt sharply at a temperature of 117—118° like the *d*-component, but soften and finally melt at temperatures ranging between 90° and 105°. The crystal habit for the right-handed variety (geometrically) is given in Fig. 1, the list of forms being *b*(010), *m*(110), *q*(011), together with *o*(111) developed holohedrally and *x*(121) hemihedrally. The inverse form $x'(1\bar{2}1)$ is of course exhibited by the left-handed variety. The axial ratios, $a : b : c =$ 0·8506 : 1 : 0·7208, were derived from the following results of measurement of four crystals (two of each kind) :

Fig. 1.



Formyl-dl-neo*menthylamine.*

Fig. 2.



dl-neo*Menthylamine hydrochloride.*

	b.	*m.*	*o.*	*x.*	*q.*
φ	0° 0′	*49° 37′	49° 44′ (−7)	30° 29′ (−2)	0° 0′
ρ	90 0	90 0	*48 3	59 13 (−6)	35 58 (−11)

"Optically, the axial plane is *b*(010) and the positive acute bisectrix is normal to *a*(100). The axial angle for red is considerably greater than for violet.

"The second form is acicular and optically different from the first form, since, although the sign of the double refraction is again positive, the axial angle for red light is less than that for violet.

The needles have a positive elongation optically, and the axial plane is transverse."

A large single crystal of the substance, weighing about 0·2 g., showed a slight but distinct dextrorotation when dissolved in absolute alcohol. The melting point of the substance prepared as above was the same as that of an equimolecular mixture of formyl-*d*-*neo*menthylamine and formyl-*l*-*neo*menthylamine, prepared as described in an earlier communication (this vol., p. 2220).

When hydrolysed with boiling concentrated hydrochloric acid (*Annalen*, 1893, **276**, 308), formyl-*dl*-*neo*menthylamine yielded about its own weight of dl-neo*menthylamine hydrochloride*, $C_{10}H_{19}{\cdot}NH_2,HCl$. This substance dissolves readily in most of the common organic solvents, including light petroleum, but it is less soluble than the externally compensated compound. When dissolved in warm light petroleum, it is obtained on slow deposition at the ordinary temperature in large, transparent crystals, m. p. 184—185° (Found: Cl, 18·4. $C_{10}H_{21}N,HCl$ requires Cl, 18·5%). The preparation appeared to be homogeneous. Crystals of this substance were kindly examined by Dr. T. V. Barker, who reports as follows:

" The crystals of *dl*-*neo*menthylamine hydrochloride show no resemblance to those of the *d*-component previously described (this vol., p. 2219), and accordingly represent a truly racemic substance. The system is monoclinic, the forms exhibited being *r*(101), $t(\bar{3}01)$, *o*(111) and $p(\bar{1}11)$ as illustrated by Fig. 2. The two crops examined were not very suitable for measurement, so the elements, $a : b : c = 3{\cdot}367 : 1 : 1{\cdot}652$, $\beta = 92° 39'$, are not very accurate. Following are the mean results of measurement of four crystals, reduced in terms of a hypothetical vertical zone:

	o.	*r.*	*p.*	*s.*
ϕ	61° 45′	61° 45′	*113° 59′	*144° 59′
ρ	*34 30	90 0	34 0 (−32)	90 0

" Optically, negative; the axial plane is *b*(010), one optic axis making an angle of about + 20° with the vertical."

A large single crystal, weighing about 0·3 g., showed no optical activity when dissolved in water.

dl-neo*Menthylamine chloroplatinate* crystallises from water in minute, orange prisms, m. p. 206—207° (decomp.); it is more soluble in water than the corresponding derivatives of *dl*-menthylamine and *dl*-*iso*menthylamine. The *hydrobromide* crystallises from alcohol in lustrous, elongated prisms and does not melt below 220°. It dissolves only sparingly in ether and is practically insoluble in light petroleum. The *picrate* crystallises from alcohol in orange prisms or lustrous, yellow needles, m. p. 183—184°; the dimorphism is less pronounced than in the case of *dl*-*iso*menthylamine picrate. Free dl-neo*menthylamine* is a liquid with an odour closely resembling that of *l*-menthylamine; the physical constants have not yet been determined.

Acetyl-dl-neo*menthylamine* crystallises from light petroleum–ether in fine, silky needles, m. p. 160—161°. *Benzoyl*-dl-neo*menthylamine* crystallises from light petroleum in long, glistening needles, m. p. 101—102°. β-*Naphthalenesulphonyl*-dl-neo-*menthylamine* is sparingly soluble in boiling methyl alcohol, from which it separates in small, glistening plates, m. p. 209—210°. *Benzylidene*-dl-neo*menthylamine* is a colourless oil at the ordinary temperature, but it crystallises when immersed in a freezing mixture. *Salicylidene*-dl-neo*menthylamine* crystallises from methyl alcohol in stout, yellow needles, m. p. 69·5° (Found: C, 79·2; H, 9·3. $C_{17}H_{25}ON$ requires C, 78·8; H, 9·3%).

dl-neo*Menthylcarbamide* separated in the crystalline condition upon mixing aqueous solutions of *dl-neo*menthylamine hydrochloride and potassium cyanate; upon recrystallisation from acetone it formed transparent, elongated prisms, m. p. 162—163°, which became opaque when kept for a few days. dl-neo*Menthylphenylcarbamide* separated from methyl alcohol in elongated, transparent prisms, capable of goniometric measurement, m. p. 183—184°. dl-neo*Menthylphenylthiocarbamide* crystallised from methyl alcohol in small, transparent prisms, m. p. 169—170°.

All the above derivatives were made from recrystallised *dl-neo*menthylamine hydrochloride; they were obtained pure without difficulty, and appeared to be homogeneous.

Action of nitrous acid on dl-neo*menthylamine.* Upon treatment with nitrous acid in the way described above, *dl-neo*menthylamine hydrochloride (5 g.) yielded a colourless oil, the bulk of which distilled at 130° under atmospheric pressure; the distillate had $n_D^{18°}$ 1·4550, and appeared to consist essentially of *dl*-Δ^3-menthene.

Preparation and Characterisation of dl-iso*Menthylamine.*—*dl*-Piperitone was converted to *dl-iso*menthone by successive treatment with (*a*) sodium and alcohol and (*b*) chromic acid, crystalline *dl-iso*menthoneoxime being then prepared in the manner indicated in a former communication (J., 1925, **127**, 2782). The pure oxime (m. p. 99—100°), upon reduction with sodium and absolute alcohol in the manner described above for *dl*-menthoneoxime, furnished an almost theoretical yield of the crude crystalline hydrochloride of *dl-iso*menthylamine. Repeated recrystallisation from acetone indicated the substantial homogeneity of the product.

dl-iso*Menthylamine hydrochloride* dissolves readily in water or alcohol, but is practically insoluble in ether or light petroleum. It is moderately easily soluble in boiling acetone containing a little methyl alcohol, from which it crystallises in small, glistening needles which do not melt below 250° (Found : Cl, 18·6. $C_{10}H_{21}N,HCl$ requires Cl, 18·5%). The viscid mother-liquor from crystalline *dl-iso*menthoneoxime (*loc. cit.*) also furnished a crystalline hydrochloride when treated as outlined above; when recrystallised twice from boiling acetone containing a little methyl alcohol, this product yielded a fraction which appeared to consist of pure *dl-iso*menthylamine hydrochloride, since it readily gave rise to identical derivatives (Found : Cl, 18·4%).

dl-iso*Menthylamine chloroplatinate* crystallises from water in pale orange needles, m. p. 212—213° (decomp.). The *picrate* exhibits dimorphism when crystallised from boiling water containing a little methyl alcohol, forming either feathery, orange needles or elongated, pale yellow prisms, m. p. 171—173°. Free dl-iso*menthylamine* resembles *l*-menthylamine in odour; its physical constants will be reported later.

Formyl-dl-iso*menthylamine* is distinguished by its great solubility in organic solvents, including light petroleum, from which it crystallises in soft needles, m. p. 45—47°. *Acetyl*-dl-iso*menthylamine* is a colourless oil, which dissolves readily in the ordinary organic solvents; it crystallises only when cooled in a freezing mixture. *Benzoyl*-dl-iso*menthylamine* crystallises from acetone in soft, glistening needles m. p. 127—128°. A recrystallised specimen of menthylamine hydrochloride obtained by reducing the syrupy mother-liquor from *dl-iso*menthoneoxime yielded a mixed product (4·7 g.) upon benzoylation. A small fraction (0·5 g.) which remained undissolved after treatment with ether was deposited from methyl alcohol in colourless needles, m. p. 184°, and was found to be identical with a benzoylmenthylamine obtained from *dl*-piperitoneoxime (*vide infra*). The ether extract furnished fractions melting indefinitely at temperatures between 115° and 145°. β-*Naphthalenesulphonyl*-dl-iso*menthylamine* crystallises from methyl alcohol in small needles, m. p. 141—142°. *Benzylidene*-dl-iso*menthylamine* is very soluble in organic solvents; it separates from methyl alcohol in radial aggregates of small, glistening prisms, m. p. 41—44°. *Salicylidene*-dl-iso*menthylamine* crystallised from methyl alcohol in yellow, elongated prisms, m. p. 95°; it was identical with the derivative made by mixing equal quantities of salicylidene-*d-iso*menthylamine and salicylidene-*l-iso*menthylamine, as described in a previous communication (this vol., p. 2223).

dl-iso*Menthylcarbamide* separated as a crystalline product when prepared in the usual way; it was deposited from acetone containing a little methyl alcohol in small, glistening needles, m. p. 203—204°. dl-iso*Menthylphenylcarbamide* crystallises from methyl alcohol in transparent plates, m. p. 142—143° (Found: C, 74·2; H, 9·4. $C_{17}H_{26}ON_2$ requires C, 74·5; H, 9·4%). dl-iso*Menthylphenylthiocarbamide* crystallises from methyl alcohol in small, hard prisms, m. p. 137°.

Action of nitrous acid on dl-iso*menthylamine.* When treated with nitrous acid in the usual way, *dl-iso*menthylamine hydrochloride yielded a dl-iso*menthol*, crystallising in fine needles, m. p. 51—53°. Further quantities of this substance are being accumulated for the purpose of detailed characterisation.

The Reduction of Piperitoneoxime.—As an outcome of a series of somewhat tedious experiments carried out by Miss M. I. Shannon, B.Sc., Ph.D., it was found possible to isolate small amounts of some of the above derivatives of *dl-iso*menthylamine from the mixture of bases obtained by reducing *dl*-piperitoneoxime. The crystalline mixture of α- and β-oximes (J., 1922, **121**, 582) obtained from racemised piperitone (J., 1923, **123**, 2270) was reduced in small quantities (20 g.) in absolute alcohol (200 c.c.) by means of metallic sodium (40 g.) in the manner adopted for the menthoneoximes, further quantities of absolute alcohol (160 to 200 c.c.) being added at intervals in order to prevent the separation of solid sodium ethoxide. The resulting base was removed by steam distillation and evaporated to dryness on the water-bath with dilute hydrochloric acid : on an average, 20 g. of oxime yielded about 19 g. of crystalline hydrochloride. The product dissolved sparingly in light petroleum, moderately in warm ether, readily in boiling ethyl acetate, and freely in chloroform, benzene, acetone, alcohol, or water. For further work, it was recrystallised from hot ethyl acetate, from which it separated in small, glistening needles, m. p. 258—260° (decomp.) (Found : Cl, 18·6. $C_{10}H_{21}N,HCl$ requires Cl, 18·5%. $C_{10}H_{19}N,HCl$ requires Cl, 18·7%). Unsuccessful attempts were made to effect a more complete separation of the bases by fractionally crystallising the derived sulphate mixture, which was less soluble in organic solvents than the hydrochloride.

The free base isolated from the above recrystallised hydrochloride resembled the menthylamines closely in its ordinary characteristics. It distilled under atmospheric pressure in a current of hydrogen at 190—193°, and absorbed carbon dioxide from the air, forming a solid carbonate. The chloroplatinate gave a sparingly soluble fraction, crystallising from hot water in pale orange needles, m. p. 209—210° (Found : Pt, 27·1. $C_{20}H_{44}N_2Cl_6Pt$ requires Pt, 27·1%). The first fraction of the picrate (60 g.) separated from hot water in lustrous, yellow plates, m. p. 152—153°; the melting point remained unaltered after several recrystallisations, but the mother-liquor yielded a small quantity of acicular crystals melting rather indefinitely at about 130°. The crude benzoate (1·1 g.) melted indefinitely at about 134°, but after five recrystallisations from hot water a homogeneous fraction (0·2 g.), m. p. 182—183°, was obtained in fine, soft needles.

The crude benzoyl derivative (6 g.) when recrystallised four times from methyl alcohol yielded a small quantity (0·3 g.) of colourless needles, m. p. 184°; the melting point was unaffected by further recrystallisation, and the analysis corresponded to a benzoylmenthylamine (Found: C, 79·3; H, 9·7. $C_{17}H_{25}ON$ requires C, 78·8; H, 9·7%). Unlike the benzoate, this derivative was insoluble in hot water. The mother-liquors furnished fractions with lower and indefinite melting points. After repeated recrystallisation from light petroleum, followed by methyl alcohol, the crude *p*-toluenesulphonyl derivative gave a small fraction consisting of fine needles, m. p. 142—143°, the melting point being unaffected by further recrystallisation.

The crude salicylidene derivative (6·7 g.) after four recrystallisations from methyl alcohol gave a small fraction (0·25 g.) consisting of pale yellow, glistening needles, m. p. 93—94°. The crude piperonylidene derivative after repeated recrystallisation from methyl alcohol–ether gave a small fraction of fine needles melting very definitely at 235—236°.

The carbamide (2·5 g.) separated as an oil which became partly crystalline after keeping for several weeks. Repeated treatment with dry ether, followed by recrystallisation from warm acetone, furnished a small quantity (0·25 g.) of lustrous, silky needles, m. p. 179—180°; the melting point was unaffected by further recrystallisation. The crude phenylthiocarbamide (4·5 g.) after four recrystallisations from methyl alcohol yielded a small quantity (1 g.) of colourless prisms, m. p. 135—136°. Efforts to prepare a crystalline phenylcarbamide, benzylidene derivative or anisylidene derivative were unsuccessful.

The least soluble components of the chloroplatinate, salicylidene derivative, and phenylthiocarbamide thus melt at practically the same temperatures as the corresponding derivatives of *dl-iso*-menthylamine, and their identity was confirmed by means of melting-point mixtures. The benzoyl derivative, m. p. 184°, appeared to be identical with a benzoyl derivative furnished in small amount by the reduction product from the viscid mother-liquor of *dl-iso*menthoneoxime (*vide supra*). The derived picrate, in spite of its unchanged melting point after recrystallisation, cannot be regarded as homogeneous. It may be concluded from the whole series of observations that the reduction of *dl*-piperitoneoxime leads to the formation of a mixture of bases, including *dl-iso*menthylamine.

A study of the action of nitrous acid on the crude hydrochloride (75 g.) indicated the possibility of incomplete reduction, so that some of the substances described above may be derivatives of *dl*-piperitylamine. The product of the reaction was a faintly yellow oil, which after two distillations under diminished pressure yielded the following fractions: (1) b. p. 60—65°/11 mm., $n_D^{15^\circ}$ 1·4622, 6·1 g.; (2) 65—70°/8 mm., 1·4650, 2·5 g.; (3) 70—92°/8 mm., 1·4699, 4·0 g.; (4) 92—94°/10 mm., 1·4708, 8·2 g.; (5) 95—98°/10 mm., 1·4715, 6·0 g.; (6) 98—107°/9 mm., 1·4729, 4·7 g. The first three fractions contained menthene ($n_D^{15^\circ}$ 1·4555) and possibly terpinene, whilst the last three possessed an odour of menthol ($n_D^{20^\circ}$ 1·4642) mingled apparently with that of piperitol ($n_D^{22^\circ}$ 1·4760).

A specimen of *l*-piperitoneoxime having $[\alpha]_D + 145{\cdot}0^\circ$ in benzene, prepared from *l*-piperitone having $[\alpha]_D - 34{\cdot}0^\circ$ (J., 1923, **123**, 2271), when reduced in a similar manner yielded a crude hydrochloride having $[\alpha]_D + 13{\cdot}4^\circ$ in a 1% aqueous solution.

Derivatives of l-*Menthylamine*.—We are indebted to Dr. G. J. Robertson for the following information concerning certain derivatives of *l*-menthylamine which are of interest in connexion with the work now described.

Benzoyl-l-*menthylamine* (compare J., 1904, **85**, 70) crystallises from methyl alcohol in coarse needles, m. p. 157°, $[\alpha]_D - 62{\cdot}8^\circ$ in chloroform ($c = 2{\cdot}33$). β-*Naphthalenesulphonyl*-l-*menthylamine* crystallises from methyl alcohol in long, stout prisms, m. p. 135°, $[\alpha]_D - 53{\cdot}3^\circ$ in chloroform ($c = 2{\cdot}03$). *Benzylidene*-l-*menthylamine* (compare *Annalen*, 1893, **276**, 305) forms coarse needles, m. p. 69—70°, $[\alpha]_D - 132{\cdot}5^\circ$ in chloroform ($c = 1{\cdot}71$). *Salicylidene*-l-*menthylamine* separates from methyl alcohol in coarse needles, m. p. 57—58°, $[\alpha]_D - 119{\cdot}2^\circ$ in chloroform ($c = 1{\cdot}75$).

We express our indebtedness to the Department of Scientific and Industrial Research for a maintenance grant to one of the authors (A.M.R.C.). The investigation is being continued.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS. [*Received, June* 16*th*, 1926.]