CLXXVII.—*Researches in the Menthone Series. Part IV.* iso*Menthols and* iso*Menthones.*

By John Read, George James Robertson, and Alison Mary Ritchie Cook.

Of the four possible externally compensated menthols, the two derived from *dl*-menthone—namely, *dl*-menthol (m. p. 34°) and *dl*-*neo*menthol (m. p. 51°)—were characterised in 1912 by Pickard and Littlebury (J., **101**, 109). Much uncertainty has existed, however, respecting the two remaining compounds, *dl*-*iso*menthol and *dl*-*neoiso*menthol, derived from *dl*-*iso*menthone. Bedos (*Bull. Soc. chim.*, 1926, **39**, 674) claims to have demonstrated the existence of the four racemic menthols and the two corresponding racemic menthones through a study of the interaction between magnesium *iso*propyl bromide and the two isomeric 2-chloro-5-methyl*cyclo*hexanols. This claim is open to serious criticism. In the first place, neither of the supposed new menthols was crystalline, whereas we show below that *dl*-*iso*menthol, prepared by the action of nitrous acid upon *dl*-*iso*menthylamine (J., 1926, 2232), melts at 53·5°. Secondly, the menthol prepared by Bedos from either of the above sources, or by the action of magnesium *iso*propyl bromide on the oxide of methyl-Δ^3-*cyclo*hexene, gave an inactive menthone which, from its inability to furnish crystalline derivatives, was neither pure *dl*-menthone nor *dl*-*iso*menthone (compare Read and Cook, J., 1925, **127**, 2783). Thirdly, the base obtained by reducing the liquid oxime of this menthone corresponded in no particular with *dl*-*iso*menthylamine (J., 1926, 2230).

In the present communication, we show that the mixture of menthols obtained in the reduction of *dl*-piperitone by sodium and alcohol contains *dl*-menthol as well as *dl-iso*menthol; the mixture is being further examined with the object of isolating the other two stereoisomerides. By the action of nitrous acid on *d*- and *l-iso*menthylamine, derived through *d*- and *l-iso*menthone from *l*- and *d*-piperitone, we have also been able to prepare *d*- and *l-iso*menthol. The constants for the *d*-component, m. p. 81·5°, $[\alpha]_D^{15}$ $+ 27{\cdot}0°$ in alcohol, are in satisfactory agreement with the data recorded by Beckmann (*Ber.*, 1909, **42**, 846) for *d-iso*menthol derived ultimately from the oxime of " inverted " *l*-menthone, the values being m. p. 83°, $[\alpha]_D$ $+ 26{\cdot}3°$. Moreover, Zeitschel and Schmidt (*Ber.*, 1926, **59**, 2298) have recently recorded m. p. 85°, $[\alpha]_D$ $+ 23{\cdot}6°$, for a specimen of *d-iso*menthol of unspecified origin. The form of the melting-point curve of mixtures of the *d*- and *l*-modifications is that of a conglomerate. *dl-iso*Menthol has a melting point only slightly higher than that of *dl-neo*menthol, but whilst *d*- and *l-neo*menthol are oils the optically active *iso*menthols have a melting point 28° higher than that of the externally compensated form; *d*- and *l*-menthol also melt at a higher temperature than *dl*-menthol. These relationships, which are of particular interest in view of the apparent configurational resemblance between the menthols and the *iso*menthols (compare J., 1926, 2213), point to the possibility of *d*- and *l-neoiso*menthol displaying a lower melting point than *dl-neoiso*menthol.

The *iso*menthols now described provide the only sources at present available for the preparation of practically pure specimens of *dl-iso*menthone and its optically active components. Although *l*- and *d*-piperitone upon catalytic hydrogenation yield preparations of *d*- and *l-iso*menthone with values of $[\alpha]_D^{15°}$ as high as ± 70°, it has been pointed out in an earlier communication (J., 1926, 2211) that the optical purity of such preparations is unsatisfactory. Since Beckmann's chromic acid mixture has little inverting action on *d-iso*menthone (*loc. cit.*, p. 2215), it was anticipated that careful oxidation of the *iso*menthols with this reagent would furnish the corresponding *iso*menthones in a state of approximate purity. A specimen of *d-iso*menthone prepared in this way had $[\alpha]_D^{15°}$ $+ 91{\cdot}7°$, a value which agrees satisfactorily with $[\alpha]_D$ $+ 93{\cdot}2°$, observed by Beckmann (*loc. cit.*; compare also Barrowcliff, J., 1907, **91**, 875, and Zeitschel and Schmidt, *loc. cit.*). This ketone gives a viscid oxime, whilst the melting points recorded for the semicarbazone range from 154° (Beckmann) to 164° (Zeitschel and Schmidt). The semicarbazone prepared by us, when recrystallised once from light petroleum containing a little methyl alcohol, formed minute needles melting indefinitely at 125—138° and having $[\alpha]_D^{15^\circ} + 23{\cdot}8^\circ$ in absolute alcohol ($c = 1{\cdot}5$); the isolation of a homogeneous derivative from this product proved so tedious that we recommend the characterisation of *d*-*iso*menthone by means of the hydrochloride of the oxime, which is readily obtained in well-defined prisms, m. p. 132°, $[\alpha]_D^{15^\circ} + 38{\cdot}6^\circ$ in chloroform ($c = 4{\cdot}0$).

It is probable that preparations of *d*- (or *l*-)*iso*menthone made as indicated still contain a small proportion of *l*- (or *d*-)menthone, but accepting the values $[\alpha]_D^{15^\circ} + 91{\cdot}7^\circ$ and $[\alpha]_D^{20^\circ} - 29{\cdot}6^\circ$ for *d*-*iso*menthone and *l*-menthone, respectively, it now becomes possible to calculate with a close approximation to accuracy the composition of various equilibrium mixtures of these two readily interconvertible ketones (J., 1926, 2210). Thus, when equilibrated with alcoholic sodium ethoxide, *l*-menthone gave a mixture containing only 30% of *d*-*iso*menthone; this proportion rose to 37% when the ketone was maintained at 200°, and to 46% when it was treated with melting 90% sulphuric acid. Furthermore, *d*-pulegone and *l*-Δ^4-*p*-menthen-3-one, when hydrogenated in presence of colloidal palladium (*loc. cit.*), yielded mixtures containing, respectively, 52% and 60% of *d*-*iso*menthone; whilst the product furnished by *l*- (or *d*-)piperitone contained as much as 82% of *d*- (or *l*-)*iso*menthone, the absence of *dl*-piperitone from the preparations used being assumed.

Although the isolation of pure derivatives of *dl*-*iso*menthone has been described in these researches (J., 1926, 2783), it has hitherto been impossible to obtain the pure ketone, owing to the inversion which accompanies its regeneration from such derivatives. *dl*-*iso*Menthone may now be made, however, through the oxidation of *dl*-*iso*menthol; the preparation of the ketone by this method, for the purpose of determining its physical constants, is at present engaging our attention.

Owing to their method of formation, we regard the *iso*menthols as corresponding in molecular configuration to the *iso*menthylamines. In the configurational scheme recently advanced for the menthylamines (J., 1926, 2213), the *cis*- and *trans*-configurations were adopted for menthones and *iso*menthones, respectively. Measurements of the parachors (compare Sugden and Whittaker, J., 1925, **127**, 1868) recently made by Dr. P. G. Carter in this College indicate, however, that the menthones and *iso*menthones possess the *trans*- and *cis*-configurations, respectively, the mean values of [*P*] being determined as follows: *dl*-menthone, 400·9; *l*-menthone, 403·2; *dl*-*iso*menthone, 405·3; *d*-*iso*menthone, 404·6. The calculated value for $C_{10}H_{18}O$, 1 non-polar double bond, 1 six-membered ring, is [*P*] 405·1. The specimens of *iso*menthone used for these measurements were prepared by the catalytic hydrogenation of *dl*- and *l*-piperitone, and were thus contaminated with the corresponding menthones, as indicated above. The results agree broadly with the observations of Zeitschel and Schmidt (*loc. cit.*), who found that *d*-*iso*menthone gave slightly higher values for refractive index and density than *l*-menthone; the Auwers–Skita rule thus favours the *trans*-configuration for menthone, although the question cannot yet be considered as decisively settled.

EXPERIMENTAL.

dl-iso*Menthol and its Optically Active Components*.—dl-iso*Menthol*. *dl*-*iso*Menthylamine hydrochloride (26·6 g.), obtained by reducing *dl*-*iso*menthoneoxime (J., 1926, 2230), when recrystallised twice from hot acetone containing a little methyl alcohol and then treated with sodium nitrite (10 g.) in aqueous solution at 70°, yielded a partly crystalline product (14·0 g.), which was forthwith distilled in steam. A fraction (8·7 g.) of the dry material distilling at 95—100°/10 mm. and having $n_{\mathrm{D}}^{16^\circ}$ 1·4660 deposited crystalline dl-iso*menthol* (2·6 g.) at the ordinary temperature; after being kept for a few days on porous plate in a desiccator, this substance was obtained in small, glistening needles, m. p. 53·5°, with an odour similar to but considerably milder than that of *l*-menthol. The hydrochloride (33 g.) of the base formed on reducing the viscid mother-liquor from crystalline *dl*-menthoneoxime (*loc. cit.*, p. 2231) yielded a liquid mixture of menthols when treated similarly with nitrous acid; the bulk (14·5 g.) of the product distilled at 95—110°/20 mm. and had $n_{\mathrm{D}}^{16^\circ}$ 1·4660, but it proved impracticable to isolate crystalline material either from this fraction or from a refractionated portion (1·8 g.) having b. p. 97—100°/10 mm. and $n_{\mathrm{D}}^{14^\circ}$ 1·4665. dl-iso*Menthyl hydrogen phthalate*, prepared by the method of Pickard and Littlebury (J., 1912, **101**, 113), crystallised from light petroleum containing a little ether in small clusters of minute prisms, m. p. 107—108° (Found: *M*, by titration, 301. $C_{18}H_{24}O_4$ requires *M*, 304). *dl*-*iso*Menthol regenerated from this derivative by hydrolysis with hot alcoholic sodium hydroxide melted unchanged at 53·5°. The *hydrogen succinate* was obtained in the form of an oil which yielded a crystalline mass on cooling and seeding with the supposed *dl*-*iso*menthyl hydrogen succinate (m. p. 72—73°) described below; as the material was very soluble in organic solvents and available only in small amount, a satisfactory purification of this specimen could not be effected (*vide infra*). The *phenylurethane* was liquid at the ordinary temperature.

d-iso*Menthol*. Crude *d*-*iso*menthylamine hydrochloride (120 g.), prepared from the viscid oxime of *d*-*iso*menthone (J., 1926, 2221) and having $[\alpha]_D^{15^\circ}$ + 20·6° in aqueous solution, was dissolved in a hot mixture of acetone (1200 c.c.) and methyl alcohol (175 c.c.). The first two fractions to separate (40·4 g.) consisted of pure *d-iso*menthylamine hydrochloride, having $[\alpha]_D^{15^\circ}$ + 23·6° in aqueous solution (c = 2·3), whilst the residue, upon fractional crystallisation from acetone, followed by ethyl acetate, yielded a further quantity (11·8 g.) of this substance. The more soluble fractions of the material gave values of $[\alpha]_D$ ranging from + 17·2° to + 18·9° in aqueous solution.

Upon treating *d-iso*menthylamine hydrochloride (20 g.) in cold aqueous solution with the calculated amount of sodium nitrite, a crystalline separation of the nitrite of the base was obtained. The mixture was warmed to 70° and finally heated on the water-bath until the evolution of nitrogen ceased. When distilled with steam, the oily product (11·4 g.) crystallised partly in the receiver. About 15% of the original *d-iso*menthylamine was recovered unchanged. After two successive fractional distillations of material (28·8 g.) obtained in this way, the first fraction (4·9 g.) had b. p. 54—58°/12 mm., $n_D^{15^\circ}$ 1·4583, and $\alpha_D^{15^\circ}$ + 27·2° (l = 1); whilst the fourth fraction (12·4 g.), which became almost wholly crystalline, had b. p. 96—98·5°/11 mm. These fractions consisted, respectively, of approximately pure *d*-Δ^3-menthene (partly racemised) and *d-iso*menthol, and the intermediate fractions were composed of mixtures of these two substances. After purification on porous plate, d-iso*menthol* was obtained in small needles, m. p. 81·5°, $[\alpha]_D^{15^\circ}$ + 24·0° in benzene (c = 2·5), $[\alpha]_D^{15^\circ}$ + 27·0° in absolute alcohol (c = 1·8). The odour was indistinguishable from that of *dl-iso*menthol. d-iso*Menthyl hydrogen phthalate* crystallises from methyl alcohol in aggregates of small prisms, m. p. 107·5—108·5°, $[\alpha]_D^{15^\circ}$ + 27·5° in chloroform (c = 3·4). The *hydrogen succinate* was obtained as a yellowish, viscid liquid, $[\alpha]_D^{15^\circ}$ + 22·5° in chloroform (c= 3·8).

The above and other experiments indicated that *d-iso*menthylamine reacts with nitrous acid to form *d*-Δ^3-menthene and *d-iso*menthol in the approximate ratio of 1 to 2, the combined yield being about 80% of the calculated amount. Only about one-third of the *d-iso*menthol formed was actually isolated in the pure crystalline condition.

l-iso*Menthol*. *l-iso*Menthylamine hydrochloride (6 g.), prepared in the way already described (J., 1926, 2222), and having $[\alpha]_D^{15^\circ}$ — 22·6° in dilute aqueous solution, was treated with nitrous acid as described above. The fraction (0·8 g.) of the product boiling at 103—107°/19 mm. rapidly became crystalline, and when purified on porous plate yielded l-iso*menthol*, m. p. 80·5°, $[\alpha]_D^{15^\circ}$ — 24·1° in absolute alcohol (c = 1·8).

Melting-point Curve of Mixtures of d- *and* l-iso*Menthol.*—Mixtures of *d-iso*menthol (m. p. 81°) and *l-iso*menthol (m. p. 79·5—80·5°) of known compositions were prepared by direct weighing. In each case the mixture was gently fused, with stirring, the melting point being then observed in the usual way for the resolidified material. Several observations were made in each instance, and the melting points were found to be well defined and consistent. Mixtures containing 100, 89·6, 73·6, 60·1, 50·0, and 26·3% of *d-iso*menthol melted at 81·5°, 77°, 67—68°, 58—59°, 51·5°, and 65°, respectively. The corresponding melting-point curve appears to conform, within the limits of experimental error, to Roozeboom's Fig. 6 (*Z. physikal. Chem.*, 1899, **28**, 507). The observed melting point for the equimolecular mixture of *d-* and *l-iso*menthol (51·5°), which must thus be regarded as a conglomerate, agrees satisfactorily with the value recorded above for *dl-iso*menthol prepared directly from *dl-iso*menthylamine. No depression was observed in the melting point of a mixture of specimens of *dl-iso*menthol prepared in these two ways.

Preparation and Characterisation of Optically Pure d-iso*Menthone.*—*d-iso*Menthol (4 g.), m. p. 81·5°, $[\alpha]_D^{15^\circ}$ + 24·0° in benzene, was added to Beckmann's chromic acid mixture at 30° (compare *Annalen*, 1889, **250**, 325). Upon shaking the mixture vigorously, the temperature rose to 50°, at which point the black chromium derivative decomposed. The resulting *d-iso*menthone was at once extracted from the cooled mixture with ether, the extract being then washed four times with water and dried over sodium sulphate. The treatment with dilute sodium hydroxide solution, adopted by Beckmann, was omitted. The crude product (3·3 g.) had $n_D^{16^\circ}$ 1·4555, and represented 82·5% of the calculated yield. The first fraction (2·75 g.), distilling at 86—87°/12 mm., was regarded as pure d-iso*menthone.* It had $n_D^{16^\circ}$ 1·4545, $\alpha_D^{15^\circ}$ + 82·16°, $[\alpha]_D^{15^\circ}$ + 91·7° (assuming $d = 0{\cdot}896$; compare J., 1923, **123**, 2922). The odour was less penetrating than that of *l*-menthone.

Part of the ketone so prepared was oximated in aqueous-alcoholic solution with hydroxylamine acetate, sodium bicarbonate having been added beforehand until the solution was only faintly acid to litmus. After 3 days, d-iso*menthoneoxime* was precipitated by the addition of water and extracted with ether. When freed from the last traces of the solvent, it was obtained as a colourless, viscid oil, having $n_D^{17^\circ}$ 1·4830 and $[\alpha]_D^{15^\circ}$ + 45·1° in absolute alcohol ($c = 2{\cdot}2$). The oil could not be induced to crystallise by applying any of the usual methods. When cooled in liquid air, either alone or in contact with light petroleum, it gave a brittle, vitreous mass, which reverted to a viscid liquid at the ordinary temperature. The p-*nitrobenzoyl* derivative is an oil. d-iso*Menthoneoxime hydrochloride*, obtained by passing dry hydrogen chloride into a cooled ethereal solution of the oxime, is the most characteristic derivative of *d-iso*menthone yet prepared. It crystallises from acetone containing a little absolute alcohol in large, transparent prisms of tabular habit, m. p. 132°, $[\alpha]_D^{15°} + 38{\cdot}6°$ in chloroform ($c = 4{\cdot}0$). With care, crystals of this substance might be characterised goniometrically. The hydrochloride reverts completely to its components in presence of water. A further purification of the oxime was therefore attempted by shaking an ethereal solution of this derivative with water containing an equivalent amount of sodium bicarbonate. After drying in a vacuum at 60°, the resulting viscid liquid had $n_D^{14°}$ 1·4865, and $[\alpha]_D^{15°} + 46{\cdot}0°$ in absolute alcohol ($c = 3{\cdot}8$).

In the course of the above characterisation of *d-iso*menthone, the following related derivatives were prepared for purposes of comparison. dl-iso*Menthoneoxime hydrochloride* crystallises from acetone in clusters of transparent prisms, m. p. 127—128° (decomp.). dl-*Menthoneoxime hydrochloride* cannot be recrystallised in the ordinary way, owing to the ease with which it is hydrolysed in presence of moisture. After being washed with anhydrous ether and dried on porous plate in a vacuum, it was obtained in minute needles, m. p. 94°. l-*Menthoneoxime hydrochloride*, purified similarly, formed long, slender prisms, m. p. 118—119°, $[\alpha]_D^{15°} - 89{\cdot}1°$ in chloroform ($c = 2{\cdot}1$). The p-*nitrobenzoyl* derivative of *l*-menthoneoxime was prepared by heating equivalent amounts of the oxime and *p*-nitrobenzoyl chloride in pyridine solution on the water-bath; it separated from alcohol in pale yellow needles, m. p. 102·5°.

Attempts to prepare neoiso*Menthols and* neoiso*Menthylamines.*—1. The liquid mixture of menthols obtained by the reduction of *dl*-piperitone with sodium and absolute alcohol (J., 1925, **127**, 2784), when freed from *dl*-α-phellandrene, distilled at 90—97°/8·5 mm. and had $n_D^{15°}$ 1·4675. Treatment with phthalic anhydride (J., 1912, **101**, 113) yielded a partly crystalline mass (140 g.), which was fractionally crystallised from light petroleum, with the addition of a little absolute alcohol when necessary. The first two fractions melted at 107—112° (40 g.) and 82—87° (49 g.), respectively, whilst the residue was a viscid liquid. After three recrystallisations, the first fraction yielded large, transparent plates, which showed no alteration of melting point (131—132°) when mixed with *dl*-menthyl hydrogen phthalate. The original mixture thus contained some *dl*-menthol. The second fraction of the phthalate upon similar treatment yielded rosettes of soft needles, m. p. 93—94°, which upon hydrolysis with alcoholic sodium hydroxide yielded a menthol, m. p. 46—47°. A mixture of this preparation with pure *dl-iso*-

menthol (m. p. 53—53·5°) melted at 47—52°. The viscid fraction of the phthalate has not yet been examined further.

A specimen of crystalline menthol (m. p. 32—40°), obtained by cooling a portion of the above crude liquid menthol (b. p. 90—97°/8·5 mm.), gave a vitreous mass when heated with phthalic anhydride. Prolonged partial crystallisation from light petroleum furnished two kinds of crystals, the less soluble of which formed opaque clusters of soft needles, m. p. 103—104° (Found : C, 70·7; H, 8·3. $C_{18}H_{24}O_4$ requires C, 71·1; H, 7·9%). A more soluble series of fractions, obtained in larger amount, consisted of hard clusters of glistening prisms, m. p. 91—94° (Found : C, 70·4; H, 7·8%). Both kinds of crystals gave analytical results agreeing with those required for menthyl hydrogen phthalates, and upon hydrolysis yielded specimens of menthol melting at 46—49° and 39—42°, respectively. The corresponding mixed melting points with pure *dl-iso*menthol were 49—53° and 40—52°. The phthalate melting at 103—104° was therefore practically pure *dl-iso*menthyl hydrogen phthalate.

No definite proof of the occurrence of a third crystalline menthol in the reduction product of *dl*-piperitone is provided by the above observations. It may be added that the crude crystalline mixture of menthols, m. p. 32—40°, readily yielded a crystalline product when heated with succinic anhydride; after two recrystallisations from light petroleum, an apparently homogeneous product was isolated in small, colourless plates, m. p. 72—73°. In view of the general behaviour of the menthol from which it was derived, this substance is regarded as dl-iso*menthyl hydrogen succinate* (Found : C, 66·0; H, 9·3. $C_{14}H_{24}O_4$ requires C, 65·6; H, 9·4%).

2. The mother-liquors from the recrystallisation of crude *d-iso*menthylamine hydrochloride (*vide supra*) were examined in various ways. A fraction of the hydrochloride having $[\alpha]_D$ + 18·5° (water) yielded a mixture of menthene and menthol when treated with nitrous acid. A liquid menthol fraction distilling at 93—98°/12 mm. had $n_D^{15°}$ 1·4654 and $[\alpha]_D^{15°}$ + 12·1° in benzene ($c = 3·0$). The corresponding partly crystalline menthol fraction furnished by pure *d-iso*menthylamine hydrochloride had $[\alpha]_D^{15°}$ + 18·5°. The acetyl derivative prepared from the same fraction of the hydrochloride was a viscid liquid having $[\alpha]_D^{15°}$ + 16·2° in chloroform. The crude salicylidene derivative had $[\alpha]_D^{15°}$ + 32·1° in chloroform ($c = 5·5$), m. p. 65—85°. After five recrystallisations from alcohol, the first fraction softened at 85° and melted at 107—112°, whilst the value of $[\alpha]_D^{15°}$ was + 61·1°. From these observations, it appears that the mother-liquors contained *d-iso*menthylamine, together with a lævorotatory base, and possibly also some *dl-iso*menthylamine.

3. The residual uncrystallisable syrup from the preparation of formyl-*d*-*neo*menthylamine (J., 1926, 2218) was hydrolysed with hydrochloric acid. The resulting solid mixture of hydrochlorides (69 g.) was extracted with ether in a Soxhlet apparatus in order to remove *d*-*neo*menthylamine hydrochloride. The residue (48 g.), when recrystallised from acetone containing a little methyl alcohol, gave a first fraction (10·6 g.) having $[\alpha]_D^{15^\circ}$ — 10·7° (water), whilst a final (fourth) fraction (15·2 g.) had $[\alpha]_D^{15^\circ}$ — 5·1°. The rotatory power of the first fraction corresponds to a mixture of 55·4% of *l*-menthylamine hydrochloride and 44·6% of *d*-*neo*menthylamine hydrochloride, it being assumed that no other base was present. This fraction, however, yielded a crude salicylidene derivative, m. p. 48°, having $[\alpha]_D^{15^\circ}$ — 72° (chloroform). The mixture indicated above would yield a product having $[\alpha]_D^{15^\circ}$ — 52·7°, and this would become — 34·6° if the assumed *d*-*neo*menthylamine were replaced by *d*-*iso*menthylamine. It thus appeared that a new lævorotatory salicylidene derivative must be present in the product derived from the first fraction of the hydrochloride. Similar results were obtained with the succeeding fractions, and eventually, after recrystallising the crude salicylidene derivative three times from light petroleum, a homogeneous product was obtained, having m. p. 99—100°, $[\alpha]_D^{15^\circ}$ — 17·9° (chloroform). This substance appears to be the salicylidene derivative of an active form of the hitherto unknown *neoiso*menthylamine (compare J., 1926, 2213, 2225), which base we hope to isolate and characterise in continuing our researches on menthylamines.

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United College of St. Salvator and St. Leonard,
University of St. Andrews.
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