CCXLIV.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXX. The Resolution of Methyl*cyclo*hexylcarbinol.*

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IN the earlier part of this series of investigations a description was given of the resolution of methyl-*n*-hexylcarbinol and of methylphenylcarbinol into their optically active modifications, together with an account of their optical properties (J., 1907, **91**, 2058; 1911, **99**, 45). It became of interest, therefore, to prepare and examine the optically active forms of methyl*cyclo*hexylcarbinol, a compound which occupies a position intermediate between the above-mentioned alcohols.

When *dl*-methyl*cyclo*hexylcarbinol is heated with phthalic anhydride at 105—115° it is completely converted into the corresponding unsaturated hydrocarbon, whilst at lower temperatures no combination between the alcohol and the anhydride takes place. The hydrogen phthalic ester was therefore prepared by the interaction of phthalic anhydride and the potassium derivative of the alcohol in dry benzene solution; it crystallises from acetic acid in small needles, m. p. 140°. By the crystallisation of the *brucine* salt of this acid ester four times from acetone, the optically pure *d*A*l*B salt was obtained as felted masses of fine, hairy needles, m. p. 179°. On decomposition this salt yields pure *d*-methyl*cyclo*hexylcarbinol hydrogen phthalate, which crystallises from light petroleum in agglomerates of fine needles, m. p. 75°.

The more soluble fractions of the brucine salt on decomposition gave a hydrogen phthalic ester which had $[\alpha]_D^{20^\circ}$ $-27°$ in 5% solution in ethyl alcohol. This was converted into the *cinchonine* salt, which, after several crystallisations from a mixture of chloroform and acetone, gave the optically pure *l*A*d*B salt in large, hard crystals, m. p. 160—165°. On decomposition this salt gives the pure *l*-methyl*cyclo*hexylcarbinyl hydrogen phthalate of m. p. 75°. This difference in the melting points of the *dl*- and the *d*- and *l*-forms of the hydrogen phthalic ester is not only unusually large, but it is in the opposite sense to that shown by the corresponding esters of β-octanol. A mixture of approximately equal amounts of the *d*- and *l*-hydrogen phthalic esters melts at 70—75°, then resolidifies, and melts again at 137—140°. Moreover, whilst the solubilities of the active forms of methyl*cyclo*hexylcarbinyl hydrogen phthalate are much greater than that of the inactive form, the converse is the case with the corresponding β-octyl hydrogen phthalates.

Optically pure *d* (and *l*)-methyl*cyclo*hexylcarbinols are readily obtained by passing a current of steam into solutions of the corresponding hydrogen phthalic esters dissolved in a slight excess of sodium hydroxide solution. They are colourless, somewhat viscous liquids of menthol-like odour.

d-Methyl*cyclo*hexylcarbinyl acetate, prepared by the action of acetic anhydride on the *d*-alcohol, is a colourless, mobile liquid with an odour resembling that of amyl acetate. The rotatory powers for light of four different wave-lengths of the *d*-alcohol and of the *d*-acetate in the homogeneous state have been determined at various temperatures between 20° and 140°. Determinations of density and of refractive index have also been made and the data are recorded in the experimental part.

When the specific rotatory powers for light of various wavelengths of the *d*-alcohol are plotted against temperature, a set of almost parallel curves is obtained showing that the rotatory power gradually falls with rise of temperature; the type of curve is very similar to that given by *d*-β-octanol. The temperature–rotation curves of these two alcohols differ from that of *d*-phenylmethylcarbinol in that, whilst the former show that the influence of temperature in diminishing the rotatory power becomes less pronounced as the temperature is increased, the latter shows that the influence of temperature becomes more pronounced at the higher temperatures.

Whereas the acetate of *d*-β-octanol possesses the same sign of rotation as its parent alcohol, the acetate of *d*-methyl*cyclo*hexylcarbinol is lævorotatory. With rise of temperature the dextrorotation of the former ester increases in magnitude, whilst the lævorotation of the latter ester becomes greater in magnitude. Moreover, the value of the rotatory dispersion $\alpha_{4358}/\alpha_{5461}$ for the former ester changes from 1·507 at 20°, becoming anomalous at temperatures above 145°, whilst the value of this ratio for the latter ester varies from 2·05 at 20° to 1·87 at 128°.

A comparison of the various data of the three alcohols and of their derivatives is given in Table I.

EXPERIMENTAL.

dl-Methyl*cyclo*hexylcarbinol, prepared according to the method of Sabatier (*Compt. rend.*, 1904, **139**, 344) by the addition of an ethereal solution of magnesium *cyclo*hexyl iodide to a well-cooled ethereal solution of acetaldehyde, was obtained as a somewhat viscous liquid, b. p. 85—95°/10—12 mm. A considerable quantity of an unsaturated hydrocarbon was produced and the yield of carbinol under the most favourable conditions was only 35%. *dl*-Methyl*cyclo*hexylcarbinyl hydrogen phthalate was prepared by

TABLE I.

	Methyl-*n*-hexyl-carbinol.	Methyl-*cyclo*hexyl-carbinol.	Methyl-phenyl-carbinol.
d-Alcohol $[\alpha]_D^{20°}$ (homogeneous)	+ 9·76°	+ 5·68°	+42·86°
$[\alpha]_{5461}^{20°}$ (homogeneous)	10·39	7·23	51·92
$\alpha_{4358}/\alpha_{5461}$	1·653	1·74	1·738
$n_D^{20°}$	1·4256	1·4635 (at 25°)	1·5211
$d_{4°}^{20°}$	0·8221	0·9254	1·0135
d-Acetate $[\alpha]_D^{17°}$	+ 7·65°	− 3·12°	—
$\alpha_{4358}/\alpha_{5461}$	1·507	2·05	—
$d_{4°}^{17°}$	0·8569	0·9500	—
d-Hydrogen phthalic ester $[\alpha]_D^{20°}$ in 5% alcoholic solution	+48·1°	+55·4°	—
M. p. *dl*-	55°	140°	108°
d- or *l*-	75°	75°	—

TABLE II.

Determinations of Rotatory Power in Ethyl-alcoholic Solution.

$T = 20°$. $l = 200$ mm. A = Cinchonine salt of *l*-methyl*cyclo*hexylcarbinyl hydrogen phthalate. B = *d*-Methyl*cyclo*hexylcarbinyl hydrogen phthalate. C = *l*-Methyl*cyclo*hexylcarbinyl hydrogen phthalate.

	G. in 100 c.c. of soln.	α_{5893}.	α_{5461}.	α_{4358}.	$[\alpha]_{5893}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
A.	5·01	+7·75°	—	—	+77·3°	—	—
B.	5·00	+5·54	+6·68°	+12·80°	+55·4	+66·8°	+128·1°
C.	−5·00	−5·50	—	—	−55·0	—	—

adding the alcohol (26 g.) to powdered potassium (7·8 g.) suspended in dry benzene (200 c.c.) and, when all the potassium had dissolved, mixing the resulting solution with phthalic anhydride (29·6 g.) dissolved in warm benzene (200 c.c.). The resulting mixture, after being maintained at 80° for 50 hours, was poured into a dilute solution of sodium carbonate mixed with crushed ice. After being worked up in the usual way and crystallised from 85% acetic acid, the hydrogen phthalic ester was obtained in 85% yield.

d-*Methyl*cyclo*hexylcarbinyl Hydrogen Phthalate.*—To a solution of the *dl*-hydrogen phthalic ester (28 g.) in hot acetone (200 c.c.) brucine (39·4 g.) was added, and the mixture kept hot until solution was complete. After cooling, the liquid became filled with bulky crystals of the brucine salt. These were filtered off and recrystallised three times from acetone. The solubility of the salt decreased rapidly as optical purity was approached, and for the last recrystallisation about 1 litre of acetone was required. The various crops of pure brucine salt obtained by systematically working up the mother-liquors were dissolved in alcohol and the solution was

TABLE III.

Determinations of density (capacity of the pyknometer, about 2 c.c.).

d-Methyl*cyclo*hexylcarbinol, b. p. 82—83°/12 mm.
0·9262 at 19°; 0·9132 at 35°; 0·9042 at 49·5°; 0·8872 at 70°; 0·8740 at 89°; 0·8521 at 110°; 0·8335 at 127°.

d-Methyl*cyclo*hexylcarbinyl acetate, b. p. 98°/30 mm.
0·9473 at 20°; 0·9296 at 41·5°; 0·9133 at 60·5°; 0·8964 at 80°; 0·8686 at 110°; 0·8550 at 128°.

Refractive indices at 25° for light of various frequencies.

	λ.			
	6708.	5896.	5461.	4358.
d-Methyl*cyclo*hexylcarbinol	1·4608	1·4635	1·4654	1·4739
d-Methyl*cyclo*hexylcarbinyl acetate	1·4404	1·4433	1·4448	1·4524

Determinations of rotatory power at various temperatures (l = 50 mm.).

d-Carbinol.

α_{6708} = +1·99° at 22°; 1·85° at 40°; 1·76° at 56°; 1·70° at 72°; 1·64° at 90°; 1·60° at 105°; 1·56° at 119°.
α_{5893} = 2·60° at 22°; 2·42° at 40°; 2·30° at 56°; 2·17° at 72°; 2·04° at 90°; 1·95° at 105°; 2·31° at 119°.
α_{5461} = 3·30° at 22°; 2·95° at 40°; 2·82° at 56°; 2·70° at 72°; 2·46° at 90°; 2·35° at 105°; 2·31° at 119°.
α_{4358} = 5·75° at 22°; 5·28° at 40°; 5·03° at 56°; 4·81° at 72°; 4·55° at 90°; 4·39° at 105°; 4·25° at 119°.

d-Acetate.

α_{6708} = −1·05° at 18°; −1·49° at 42·5°; −1·82° at 60°; −2·00° at 75°; −2·39° at 104°; −2·59° at 128°.
α_{5893} = −1·50° at 18°; −2·02° at 42·5°; −2·30° at 60°; −2·58° at 75°; −2·99° at 104°; −3·14° at 128°.
α_{5461} = −1·87° at 18°; −2·56° at 41°; −2·90° at 60°; −3·25° at 80°; −3·58° at 104°; −3·14° at 128°.
α_{4358} = −3·84° at 18°; −4·97° at 41°; −5·57° at 60°; −6·00° at 75°; −6·63° at 104°; −6·98° at 128°.

l-Carbinol.

α_{5893} = −2·57° at 21°. α_{5461} = −3·26° at 21°. α_{4358} = −5·62° at 21°.

poured into dilute hydrochloric acid; the *d*-acid ester was then precipitated as an oil which rapidly set to a crystalline mass, which was moderately soluble in light petroleum. It was not possible to determine the rotatory power of the pure brucine salt owing to its sparing solubility in cold solvents.

l-*Methyl*cyclo*hexylcarbinyl Hydrogen Phthalate.*—The partially active lævorotatory hydrogen phthalic ester recovered from the more soluble fractions of the brucine salt may be directly converted into the cinchonine salt as described above or, more conveniently, may be recrystallised from light petroleum; owing to its smaller solubility, the *dl*-hydrogen phthalic ester then crystallises first.

After this crop has been rapidly removed, the filtrate is concentrated; there is then obtained a crystalline hydrogen phthalic ester of m. p. 71° and $[\alpha]_D - 53°$ in 5% solution in ethyl alcohol. This almost optically pure acid ester is obtained completely pure after two crystallisations of its cinchonine salt.

This cinchonine salt is somewhat unstable and with hot acetone alone undergoes considerable decomposition into its components. The following procedure was therefore adopted. The salt was dissolved in warm dry chloroform, the main bulk of the latter removed by distillation, and the residue mixed with warm acetone. This solution, on cooling, gave crystals of the cinchonine salt which could be recrystallised by a repetition of the same procedure.

Some of the materials used in the investigation were purchased with a grant from the Government Grant Committee of the Royal Society, for which the authors desire to express their indebtedness

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