CCLXXVI.—*The Alcohols of the Hydroaromatic and Terpene Series. Part V. The Geometrical and Optical Isomerism of the Methyl*cyclo*hexanols.*

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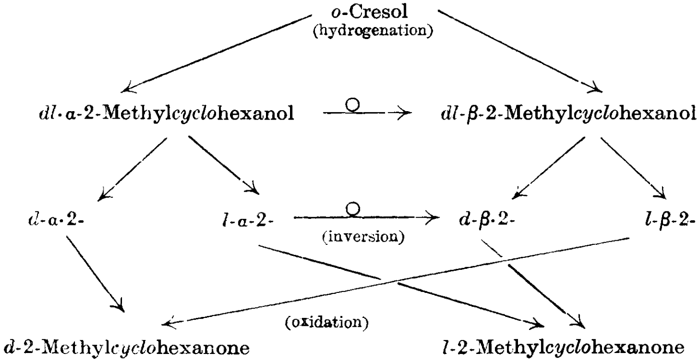
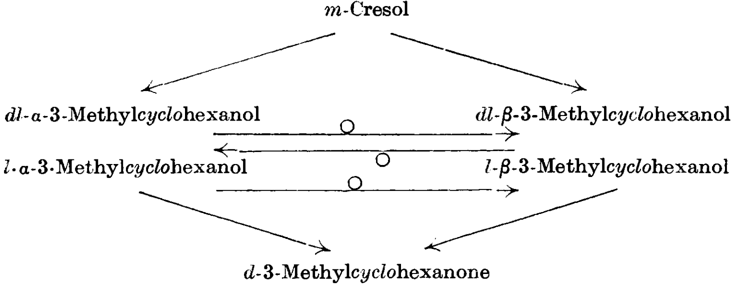
MODERN chemical theory predicts that both hexahydro-*o*-cresol and hexahydro-*m*-cresol should exist in two geometrically isomeric forms, each capable of resolution into optical antipodes, and, further, that hexahydro-*p*-cresol should exist in two geometrically isomeric forms incapable of such resolution. Although many indications occur in chemical literature of the partial separation of these substances, no conclusive evidence of their isolation in a pure state exists. These substances have now been prepared and evidence of their chemical purity will be given.

The two isomeric methyl*cyclo*hexanols derived from each cresol are characterised by widely differing viscosities and the convention has been adopted of naming the more viscous isomeride the α- and the less viscous the β-. It will be pointed out, nevertheless, that in all probability the α-isomerides are the *trans*-, and the β- the *cis*-methyl*cyclo*hexanols. By means of a viscosity–composition diagram, constructed for mixtures of α- and β-2-methyl*cyclo*hexanols, it has been found possible to study the effect of experimental conditions on the relative proportions of the two isomerides formed by various methods of preparation.

It is possible to effect the complete geometrical interconversion of the α- and β- forms of the methyl*cyclo*hexanols through the medium of the *p*-toluene-sulphonic esters. Partly in this way and partly by the oxidation of the optically active methyl*cyclo*hexanols to the corresponding ketones, the relative configurations of the isomerides have been deduced. The following diagram represents some of the results obtained :



In the case of the isomerides derived from *m*-cresol somewhat different results were obtained, since the *l*-α- and the *l*-β-3-methyl*cyclo*hexanols yielded the same ketone on oxidation, whereas the *l*-α-2- and the *l*-β-2-methyl*cyclo*hexanols yielded ketones of opposite sign of rotation.



(*a*) *Preparation of the Geometrical Isomerides of Methyl*cyclo*hexanol.*

Numerous investigators have prepared derivatives of the methyl*cyclo*hexanols and have generally assumed that the reduction product of the corresponding cresol or ketone is homogeneous. Three instances, however, are recorded in which samples of methyl*cyclo*hexanol, derived from the same parent compound, have been found to possess different properties : Knoevenagel (*Annalen*, 1897, **297**, 150) synthesised 3-methyl*cyclo*hexanol from acetoacetic ester and formaldehyde ; two variations of the synthesis yielded products with slightly different physical properties. Skita (*Annalen*, 1923,

431, 1) hydrogenated the three cresols under various conditions and obtained from each two different products. Godchot and Bedos (*Compt. rend.*, 1922, **174**, 461; *Bull. Soc. chim.*, 1925, **37**, 1451) showed that the 2-methyl*cyclo*hexanol prepared by the hydrogenation of *o*-cresol (Sabatier and Mailhe, *Compt. rend.*, 1905, **140**, 350) differed from that obtained by the action of magnesium methyl iodide on *cyclo*hexene oxide.

In the work now described, the mixture of isomerides resulting from the hydrogenation of each cresol has been separated by the fractional crystallisation of a solid ester. In the cases of the 2- and the 4-methyl*cyclo*hexanols, two pure products were obtained in each instance by crystallisation of the hydrogen phthalic esters. This method could not be used to separate the isomerides in hydrogenated *m*-cresol, since the mixture of hydrogen phthalic esters crystallised only with extreme slowness. Systematic fractional crystallisation of the *p*-nitrobenzoic esters, however, yielded two pure substances.

The homogeneity of these compounds was tested in all cases by crystallisation from various solvents. The pure esters were separately hydrolysed and the free methyl*cyclo*hexanols, thus obtained, converted into other solid derivatives; these, also, were found to suffer no change on repeated crystallisation.

(*b*) *The Optically Active Forms of the Geometrical Isomerides of 2- and of 3-Methyl*cyclo*hexanols.*

*α- and β-2-Methyl*cyclo*hexanols.*—The optically active forms of both these alcohols were obtained by the systematic fractional crystallisation of alkaloidal salts of their hydrogen phthalic esters. These optical resolutions presented difficulties similar to those encountered in the resolution of *dl*-menthol and of *dl-neo*menthol (Pickard and Littlebury, J., 1912, **101**, 109) and in both cases special methods had to be employed in order to attain optical purity.

*α- and β-3-Methyl*cyclo*hexanols.*—*d*-3-Methyl*cyclo*hexanone, obtained by the action of hydrolytic agents on pulegone (Wallach, *Annalen*, 1896, **289**, 337), was reduced and the resulting mixture of 3-methyl*cyclo*hexanols converted into their *p*-nitrobenzoic esters. Crystallisation of this mixture yielded an ester unaltered by further crystallisation, which, on hydrolysis, gave *l*-α-3-methyl*cyclo*hexanol with the same viscosity and density as that obtained from *m*-cresol.

It was not found possible to separate the optically active β-ester from the complex mixture of esters in the mother-liquors, owing possibly to the fact that, since the natural ketone is not optically pure, the mixture of esters contains small amounts of the *dl*-α-, *dl*-β-, and *l*-β- as well as the *l*-β-ester which was isolated. *l*-β-3-Methyl*cyclo*hexanol was obtained by the geometrical inversion of the *l*-α-alcohol by the methods described in section (*e*) of this paper.

The optical purity of *l*-α-3- and of *l*-β-3-methyl*cyclo*hexanols, both of which yield the 3-methyl*cyclo*hexanone of the same sign and magnitude of optical rotatory power on oxidation, was confirmed by converting *l*-α-3-methyl*cyclo*hexanol into the hydrogen phthalic ester and fractionally crystallising the strychnine salt of this ester. No alteration of the rotatory power of the ester could be obtained.

α-4-*Methyl*cyclo*hexanol.*—Although this substance possesses a symmetrical structure according to the classical theories, an attempt was made, nevertheless, to obtain it in optically active forms by the crystallisation of the strychnine salt of the hydrogen phthalic ester, but without success.

(*c*) *The Physical Properties of the Geometrical Isomerides.*

It was found that the members of the complete series of six geometrical isomerides possessed widely differing viscosities and since the importance of viscosity as a means of studying geometrical isomerism has been emphasised by Thole (J., 1912, **101**, 552), it is of interest to develop the matter theoretically.

Discussing the relation between viscosity and geometrical isomerism in the light of the work of Beck on the viscosity of fused oximes (*Z. physikal. Chem.*, 1904, **48**, 674) and of his own on the viscosity of geometrically isomeric acids and their esters, Thole suggests that two sets of factors are operative :

(*A*) When the groups responsible for geometrical isomerism possess small residual affinity, the *cis*-compound will have the greater viscosity, since the proximity of these groups tends spatially to potential ring formation—a condition which is well known to enhance viscosity (Thole, J., 1914, **105**, 2004).

(*B*) When the groups have considerable residual affinity, the *cis*-isomeride will have the smaller viscosity, because the proximity of the groups is favourable to the *intra*molecular neutralisation of the residual affinities, thus lowering the net residual affinity of the molecule. The *inter*molecular association is consequently decreased and the viscosity of the compound lowered.

Since the hydroxyl group has large residual affinity, it is probable that the *trans*-methyl*cyclo*hexanols will possess the greater viscosities and, also, that the greatest difference will be observed between the viscosities of the isomerides of 2-methyl*cyclo*hexanol, since it is clear that effect *B* will be the more strongly operative the nearer the dominant groups are to each other. These predictions are borne out by the measurements of the viscosities of the six geometrical isomerides, which are as follows :

Methyl*cyclo*hexanol.	η^{25°.	Difference (α- minus β-).
dl-α-2-	0·336	0·181
dl-β-2-	0·155	
dl-α-3-	0·251	0·054
dl-β-3-	0·197	
α-4-	0·385	0·138
β-4-	0·247	

It will also be seen that, in accordance with the " boat " formula for the *cyclo*hexane ring (*vide infra*), the para-substitutents are apparently closer together than the meta-, although not as close as the ortho-.

These measurements were then extended to the methyl*cyclo*hexanyl acetates. The result of converting an alcohol into an acetate—from the point of view of the postulates of Thole—is to reduce the residual affinity of one of the dominant groups, because an acetic ester is almost invariably less viscous than its parent alcohol. Thus, in the series of the six methyl*cyclo*hexanyl acetates, the effect *B* will have less influence than it had in the alcohol series and, indeed, the effect *A* may become dominant in some cases—most likely in the case of the 3-methyl*cyclo*hexanyl acetates where the effect *B* was already weak in the alcohol series.

Measurement of the viscosities of the methyl*cyclo*hexanyl acetates showed that, in the case of the 3-isomerides, the expected reversal of the order of the viscosities takes place.

Methyl*cyclo*hexanyl acetate.	η^{25°.	Difference (α- minus β-).
dl-α-2-	0·0233	+0·0022
dl-β-2-	0·0211	
dl-α-3-	0·0174	−0·0021
dl-β-3-	0·0195	
α-4-	0·0217	+0·0021
β-4-	0·0196	

A similar behaviour is shown by the melting points of the derivatives of the 3-methyl*cyclo*hexanols—the α-derivatives having the higher melting point when they contain a free carboxyl group and the lower when they contain no group of high residual affinity.

	Hydrogen phthalic ester.	*p*-Nitrobenzoate.	*p*-Toluenesulphonate.
dl-α-3-Methyl*cyclo*hexanyl ...	M. p. 93—94°	58°	39—40°
dl-β-3-Methyl*cyclo*hexanyl ...	,, 82—83	65	46—47

All the derivatives of α-2-methyl*cyclo*hexanol, and most of the derivatives of α-4-methyl*cyclo*hexanol, have higher melting points than the corresponding β-derivatives.

Each of the above co-relations has been based on the assumption that the α-compounds possess the *trans*-configuration and since these relations agree amongst themselves, the truth of this assumption becomes probable.

The anomalous results given by cyclic geometrical isomerides which contain the dominant groups in the meta-position has already been noted by Stewart (" Stereochemistry," p. 150, 1907 edn.).

Similar relations appear to exist between the magnitudes of the optical rotatory powers of *l*-α- and *l*-β-3-methyl*cyclo*hexanols and their derivatives, since the β-alcohol and its hydrogen phthalic ester possess higher rotatory powers than those of the corresponding α-compounds, whilst the β-acetic ester has a lower value than the α-acetic ester :

	α_{5893}.	$[\alpha]_{5893}$ hydrogen phthalic ester.	α_{5893} ($l = 0{\cdot}5$) acetic ester.
l-α-3-Methyl*cyclo*hexanol	−1·74°	−13·51°	−10·83°
l-β-3-Methyl*cyclo*hexanol	−3·37	−26·93	− 4·51

l-α-2-Methyl*cyclo*hexanol and its derivatives all possess higher rotatory powers than the corresponding β-compounds.

Four optically inactive isomerides would be expected from each cresol if the configurations of the *cyclo*hexane ring, postulated by Sachse (*Ber.*, 1890, **23**, 1363; *Z. physikal. Chem.*, 1892, **10**, 203; 1893, **11**, 185) exist in a stable state. No evidence, however, of more than two isomerides was obtained by the crystallisation of the solid esters of any of the hydrogenated cresols. Some indication as to which configuration of the ring is present in the compounds examined was obtained in the following way. If the influence of effect *A* on the viscosities of the methyl*cyclo*hexanols is neglected, the difference between the viscosities of the members of any pair of geometrical isomerides should be approximately proportional to the difference of the distances between the methyl and the hydroxyl groups in the *cis*- and in the *trans*-forms. These distances were measured on the " chair " and " boat " models of the different isomerides, the latter giving maximum and minimum values owing to the fact that it possesses transverse rotational movement (compare Wightman, J., 1925, **127**, 1421). The values obtained from the " boat " model are in agreement with the viscosity measurements, but those obtained from the stiff " chair " model are widely at variance. This would tend to show that the " boat " model corresponds to the structure of the majority of the molecules in the substances examined.

(*d*) *The Relative Amounts of the Geometrical Isomerides produced by Different Methods of Preparation.*

The hydrogenation of the cresols by the method of Sabatier and Senderens yielded mixtures containing but small amounts of the β-isomerides and, since large amounts of these isomerides were required, other methods of preparation were employed. In all cases the percentage proportions of the two isomerides in each of these mixtures (for they all proved to be mixtures) was found by observing the viscosity of a specially purified sample and comparing this value with those on a viscosity–composition diagram which had been previously constructed by determining the viscosities of samples of the pure isomerides mixed in known proportions.

The samples of the reduction products were subjected to a rigid purification before the determination of their viscosities, since the method of estimating the proportions of the two isomerides demands that the samples should be of high purity.

By applying this procedure to the mixtures obtained by the various methods, the following results were obtained :

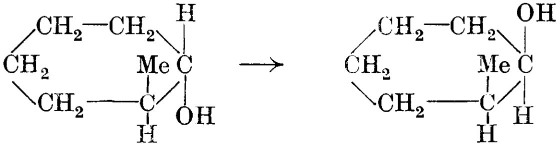
	Method of preparation.	% α-Isomeride.
(i)	Hydrogenation of *o*-cresol by Sabatier and Senderens's method at 175° (nickel catalyst)	67
(ii)	Reduction of 2-methyl*cyclo*hexanone by sodium and boiling ethyl alcohol	77
(iii)	Reduction of 2-methyl*cyclo*hexanone by sodium and moist ether	81
(iv)	Reduction of 2-methyl*cyclo*hexanone by Skita's method (platinum catalyst)	38
(v)	Hydrogenation of *m*-cresol by Sabatier and Senderens's method at 100°	80
(vi)	Hydrogenation of *m*-cresol by Sabatier and Senderens's method at 180°	82
(vii)	Reduction of 3-methyl*cyclo*hexanone by sodium and boiling ethyl alcohol	86

The mixture of methyl*cyclo*hexanols obtained in experiment (iv) was prepared by shaking an aqueous–acetic acid solution of 2-methyl*cyclo*hexanone containing colloidal platinum in an atmosphere of hydrogen, the instructions given by Skita being closely followed (*loc. cit.*). Since the product was apparently the same as that prepared by Skita (yielding a phenylcarbamate, m. p. 94—96°; Skita gives 95°), it is clear, in view of the result given above, that the substance described by this author as *cis*-2-methyl*cyclo*hexanol is actually a mixture of the *cis*- and *trans*- forms.

(*e*) *The Geometrical Inversion and the Relative Configurations of the Methyl*cyclo*hexanols.*

In a series of preliminary experiments, the methyl*cyclo*hexanols were found to be singularly inert towards reagents which often effect the geometrical inversion of cyclic geometrical isomerides. Thus heating with water at 120° produced no change in the proportion of the geometrical isomerides present in a mixture of α- and β-2-methyl*cyclo*hexanols, and protracted boiling with alcoholic sodium hydroxide caused but a slight increase in the proportion of α-4-methyl*cyclo*hexanol in a mixture of the α- and β-forms.

It is clear, however, that if the configuration of the carbon atom to which the hydroxyl group is attached could be reversed, a *trans*-methyl*cyclo*hexanol would be converted into the corresponding *cis*-isomeride, thus :—



Hence the valuable method, apparently one of general application, discovered by Phillips (J., 1923, **123**, 43) for reversing the configuration of optically active secondary alcohols seemed adaptable to the present problem. Following this method, the *p*-toluenesulphonic ester of *dl*-α-2-methyl*cyclo*hexanol was prepared and allowed to react with potassium acetate in alcoholic solution. From the products of the reaction a methyl*cyclo*hexanyl acetate was isolated which, on hydrolysis, yielded *dl*-β-2-methyl*cyclo*hexanol apparently uncontaminated with the α-isomeride.

Similar experiments, carried out with *dl*-α-3- and *dl*-α-4-methyl*cyclo*hexanyl *p*-toluenesulphonates, yielded *dl*-β-3- and *dl*-β-4-methyl*cyclo*hexanols. A lævorotatory *l*- + *dl*-α-2-, and *l*-α-3-methyl*cyclo*hexanyl *p*-toluenesulphonates yielded *d*- + *dl*-β-2-, and *l*-β-3-methyl*cyclo*hexanols by a similar treatment.

It has also been found that the reverse transformation can be effected. This has been demonstrated by the formation of *dl*-α-3-methyl*cyclo*hexanol from *dl*-β-3-methyl*cyclo*hexanyl *p*-toluenesulphonate.

The importance of these interconversion experiments in the study of the stereochemistry of the methyl*cyclo*hexanols is considerable, since not only do they provide a ready means of preparing the β-isomerides and a method of determining the relative configurations of the different isomerides, but they also provide a check on the purity of the β-isomerides, which, in some cases, are very difficult to purify.

It will be seen from the diagrams on p. 2053 that the configurational relations between (i) the 2-methyl*cyclo*hexanols and 2-methyl*cyclo*hexanone on the one hand and between (ii) the 3-methyl*cyclo*hexanols and 3-methyl*cyclo*hexanone on the other, represent two different types.

Examples of both these types of relations have been already recorded in this series of communications (Part I, J., 1907, **91**, 1979; Part II, J., 1912, **101**, 109; Part IV, J., 1925, **127**, 1472), although only the type (i) apparently has been recorded elsewhere. In type (i), the same ketone is obtained by oxidation of alcohols of opposite signs of rotatory power—a state of affairs which also exists between *l*-menthol and *d*-*neo*menthol, which yield *l*-menthone (Part II); between *l*-borneol and *d*-*iso*borneol, which give *l*-camphor (Part I); and between the tanacetyl alcohols, which yield tanacetone (Tschugaev, *Ber.*, 1912, **45**, 1293).

In (ii), however, the same ketone is obtained by oxidation of alcohols of the same sign of rotatory power, the only other example recorded being *l*-α- and *l*-β-fenchyl alcohols, which give *d*-fenchone on oxidation (Part IV).

EXPERIMENTAL.

(*a*) *The Separation of the Geometrical Isomerides.*

The cresols were hydrogenated at 175° by the method of Sabatier and Senderens at the laboratories of Messrs. Crossfield & Co. *o*-Cresol was found the most difficult to hydrogenate. Some *m*-cresol was also hydrogenated at 100° and at 180° by the Technical Research Works, Ltd., using the special electrolytically prepared nickel catalyst described by Lush (*J. Soc. Chem. Ind.*, 1923, **42**, 219T). To both these firms the authors tender their sincere thanks.

The crude products were fractionally distilled several times through a rod-and-disk column under reduced pressure. Three groups of fractions were collected in each case: methyl*cyclo*hexanones, b. p. 62—64°/20 mm., methyl*cyclo*hexanols, b. p. 77—80°/20 mm., and cresols, b. p. 85—100°/20 mm. The second sets of fractions were separately heated with phthalic anhydride (10% excess) at 110° for 12 hours. The product was then poured, while still liquid, into a slight excess of sodium carbonate solution, the resulting solution filtered, diluted to a large volume with water, and extracted ten times with benzene. The aqueous portion was freed from benzene by the passage of air and the acid ester precipitated by the addition of acid. The ester thus obtained was freed from phthalic acid by dissolving it in chloroform, drying and filtering the solution, and removing the chloroform, first by distillation and finally in a vacuum.

dl-α-2-*Methyl*cyclo*hexanyl Hydrogen Phthalate.*—The mixture of crude esters obtained by the action of phthalic anhydride on hydrogenated *o*-cresol was submitted to fractional crystallisation from glacial acetic acid. Some four to five crystallisations of the principal crop yielded an ester unchanged by further crystallisation from either acetic acid or benzene. dl-α-2-*Methyl*cyclo*hexanyl hydrogen phthalate* thus obtained formed a white, crystalline powder, m. p.

124—125° (0·5121 g. required 0·0783 g. of sodium hydroxide for complete neutralisation. Calc., 0·0783 g.).

dl-α-2-*Methyl*cyclo*hexanol*.—The pure acid ester (1 mol.) was dissolved in a solution of sodium hydroxide (2·2 mols.) in water (five times the weight of ester), and the mixture distilled in a current of steam. The distillate was extracted three times with ether and the united ethereal extracts were dried with potassium carbonate. After the removal of the ether, the residual alcohol was distilled. dl-α-2-*Methyl*cyclo*hexanol*, b. p. 78—79°/20 mm., thus obtained formed a colourless, viscous liquid with an odour reminiscent of that of cocoanut oil.

dl-β-2-*Methyl*cyclo*hexanyl Hydrogen Phthalate*.—The mother-liquors from the preparation of the α-ester were poured into ice-water, and the precipitated ester collected, dried, and crystallised from light petroleum. Pure dl-β-2-*methyl*cyclo*hexanyl hydrogen hthalate* was finally obtained as large, stellate masses, m. p. 89—90° (0·3307 g. required 0·0506 g. of sodium hydroxide for complete hydrolysis. Calc., 0·0505 g.).

The following method was found to possess considerable advantages over that just described for the preparation of a pure *dl*-β-2-methyl*cyclo*hexanyl ester. The hydrogen phthalic esters, recovered from the mother-liquors from the preparation of the α-ester, were hydrolysed, and the resulting alcohols converted into the *p*-nitrobenzoates. By systematic fractional crystallisation of this mixture from methyl alcohol, pure dl-β-2-*methyl*cyclo*hexanyl* p-*nitrobenzoate* m. p. 35—36°, was obtained as light yellow plates.

dl-β-2-*Methyl*cyclo*hexanol* was obtained by the hydrolysis of either the hydrogen phthalic ester or of the *p*-nitrobenzoate. It formed a colourless, viscous liquid, b. p. 77—78°/20 mm., and possessed an odour indistinguishable from that of its geometrical isomeride.

α-4-*Methyl*cyclo*hexanyl hydrogen phthalate* was obtained by the crystallisation, from glacial acetic acid, of the mixture of hydrogen phthalic esters formed by the action of phthalic anhydride on hydrogenated *p*-cresol. Five crystallisations of the principal crop yielded pure α-4-*methyl*cyclo*hexanyl hydrogen phthalate*, m. p. 119—120° (0·3007 g. required 0·0461 g. of sodium hydroxide for complete neutralisation. Calc., 0·0458 g.).

α-4-*Methyl*cyclo*hexanol*, b. p. 78—79°/20 mm., was obtained from the corresponding hydrogen phthalic ester in the usual way and possessed an odour similar to, although distinct from, that of the 2-methyl*cyclo*hexanols.

β-4-*Methyl*cyclo*hexanyl Hydrogen Phthalate*.—The hydrogen phthalic esters recovered from the mother-liquors from the preparation of the α-ester were crystallised from light petroleum. After many crystallisations, β-4-*methyl*cyclo*hexanyl hydrogen phthalate*, m. p. 72—73°, was obtained as a white, crystalline powder, unaltered in melting point by further crystallisation. This substance was found very difficult to isolate in a pure condition (0·3150 g. required 0·0481 g. of sodium hydroxide for complete neutralisation. Calc., 0·0482 g.).

β-4-*Methyl*cyclo*hexanol*, b. p. 78—79°/20 mm., was obtained from the hydrogen phthalic ester in the usual manner and possessed an odour similar to that of the α-isomeride.

dl-α-3-*Methyl*cyclo*hexanyl* p-*Nitrobenzoate*.—It was found impossible to purify the mixture of hydrogen phthalic esters resulting from the action of phthalic anhydride on hydrogenated *m*-cresol; the corresponding mixture of *p*-nitrobenzoic esters, however, can be readily separated into its components by crystallisation from methyl alcohol. This mixture was prepared by treating hydrogenated *m*-cresol (1 mol.; purified from 3-methyl*cyclo*hexanone and unchanged cresol) with a solution of *p*-nitrobenzoyl chloride (1 mol.) in benzene (8 volumes). Much heat was evolved, but the temperature was kept below 40°. After standing over-night, the mixture was repeatedly washed with water, with dilute hydrochloric acid, and with sodium carbonate solution. The benzene layer was distilled in a current of steam, and the residue of 3-methyl*cyclo*hexanyl *p*-nitrobenzoates, which solidified on cooling, was separated and dried. Crystallisation of these esters from methyl alcohol yielded two sets of crops, each of which was unchanged in melting point by further crystallisation from methyl alcohol, light petroleum, or acetone.

dl-α-3-*Methyl*cyclo*hexanyl* p-*nitrobenzoate* crystallised in well-formed, light yellow granules, m. p. 58°. dl-β-3-*Methyl*cyclo*hexanyl* p-*nitrobenzoate* separated in flat, feathery crystals, m. p. 65°. The corresponding alcohols were obtained by hydrolysis of these esters by means of a slight excess of alcoholic sodium hydroxide (considerable darkening, owing to the partial reduction of the nitrobenzoic acid, takes place if a large excess is employed). dl-α-3-*Methyl*cyclo*hexanol*, b. p. 77—78°/20 mm., and dl-β-3-*methyl*cyclo*hexanol*, b. p. 77—78°/20 mm., obtained in this way, formed colourless, viscous liquids both possessing odours stronger and sweeter than those of the 2- or the 4-methyl*cyclo*hexanols.

dl-α-3-*Methyl*cyclo*hexanyl hydrogen phthalate* was obtaind in the usual manner and formed a white, crystalline power, m. p. 93—94° (0·2111 g. required 0·0323 g. of sodium hydroxide for complete neutralisation. Calc., 0·0322 g.).

dl-β-3-*Methyl*cyclo*hexanyl hydrogen phthalate* formed white crystals, m. p. 82—83° (0·321 g. required 0·0488 g. of sodium hydroxide for complete neutralisation. Calc., 0·0490 g.).

The β-*eucaine* salts of the complete series of six optically inactive methyl*cyclo*hexanyl hydrogen phthalates were prepared by mixing an aqueous solution of the sodium salt of the hydrogen phthalic ester with an equimolecular amount of β-eucaine hydrochloride dissolved in water. The supernatant liquid was decanted and the residual gum crystallised from aqueous alcohol. In no case was the melting point of the salt found to change on repeated crystallisation.

β-Eucaine salt of	M. p.
dl-α-2-methyl*cyclo*hexanyl hydrogen phthalate	173—174°
dl-β-2- ,, ,, ,, ,,	154
dl-α-3- ,, ,, ,, ,,	149—150
dl-β-3- ,, ,, ,, ,,	171—172
α-4- ,, ,, ,, ,,	170—171
β-4- ,, ,, ,, ,,	170—171

The *methyl*cyclo*hexanyl phenylcarbamates* were prepared by allowing equimolecular amounts of the methyl*cyclo*hexanol and phenylcarbimide to stand in a closed vessel for a day. Since these compounds were used in conjunction with viscosity, to characterise a mixture of methyl*cyclo*hexanols, the resulting solid mass was crystallised once only from light petroleum. The melting points of these derivatives are in Table I.

(*b*) *The Optically Active Forms of the Geometrical Isomerides of* 2- *and of* 3-*Methyl*cyclo*hexanol.*

The d- *and* l-2-*Methyl*cyclo*hexanols.*—*dl*-α-2-Methyl*cyclo*hexanyl hydrogen phthalate gave with strychnine a crystalline salt, m. p. 190°, which after systematic fractional crystallisation yielded, on decomposition, a small amount of acid ester showing $[\alpha]_{5893}$ $-52{\cdot}2^\circ$ in benzene ($c = 5{\cdot}00$; $l = 2$). Since the salt decomposed easily into the alkaloid and the acid ester in acetone solution, optical purity could not be obtained in this manner. Ethyl alcohol was then substituted for acetone as a solvent; but whilst this prevented decomposition, the rapidity of the resolution decreased enormously. After the trial of some other alternatives, the following process was adopted: the strychnine salt of the inactive ester was crystallised once from ethyl alcohol and the crop and the mother-liquor were decomposed, yielding esters with approximately $[\alpha]_{5893} \pm 17^\circ$. These esters were then separately crystallised from acetic acid; the ester which crystallised was almost inactive, whilst the mother-liquors yielded esters having approximately $[\alpha]_{5893} \pm 48^\circ$. The united inactive esters were then recombined with strychnine and the above process was repeated until about 100 g. of the esters with $[\alpha]_{5893}$ + 48° and − 48° had been collected. Recombination of each of these sets of esters with strychnine gave, after many crystallisations from acetone, esters unaltered in rotatory power by further crystallisation of their strychnine salts from acetone or from ethyl alcohol.

d-α-2-*Methyl*cyclo*hexanyl hydrogen phthalate,* m. p. 122—123°, obtained in this way had $[\alpha]_{5893}$ + 63·2° in benzene ($c = 2{\cdot}84$; $l = 2$).

l-α-2-*Methyl*cyclo*hexanyl hydrogen phthalate,* m. p. 122°, had $[\alpha]_{5893}$ −63·5° under the same conditions.

d-α-2-*Methyl*cyclo*hexanol,* b. p. 78°/20 mm., and l-α-2-*methyl*cyclo*hexanol,* b. p. 78°/20 mm., were obtained from the corresponding hydrogen phthalic esters in the usual manner.

d- *and* l-β-2-*Methyl*cyclo*hexanols.*—The resolution of *dl*-β-2-methyl *cyclo*hexanyl hydrogen phthalate into its optically active components was found to be very difficult; after many preliminary experiments, the following process was adopted : the inactive ester was combined with *l*-α-phenylethylamine, and the resulting salt crystallised many times from acetone; 35% of the total ester was thus obtained with $[\alpha]_{5461}$ −19°, and this, on combination with strychnine, yielded a salt which rapidly attained optical purity when crystallised from acetone. l-β-2-*Methyl*cyclo*hexanyl hydrogen phthalate,* m. p. 97—98°, obtained from this salt, had $[\alpha]_{5461}$ −46·8° and $[\alpha]_{5893}$ −38·7° in benzene ($c = 5{\cdot}00$; $l = 2$).

The acid ester obtained from the mother-liquors of the above crystallisations, after being crystallised from light petroleum, yielded a fraction with $[\alpha]_{5461}$ + 22·1°. Recrystallisation of the strychnine salt of this ester from acetone gave the strychnine salt of d-β-2-*methyl*cyclo*hexanyl hydrogen phthalate.* The ester obtained from this salt had $[\alpha]_{5461}$ + 46·1° in benzene ($c = 5$; $l = 2$).

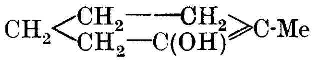
l-β-2-*Methyl*cyclo*hexanol,* b. p. 78—79°/29 mm., was obtained from the corresponding ester in the usual manner. The determined physical properties of this compound together with those of d-β-2-*methyl*cyclo*hexanol* which was obtained from the ester, are in Table II.

It is noteworthy that in the resolution of the α-isomeride by the use of strychnine, the *d*-form separates from acetone solution first, whereas, in the resolution of the β-isomeride, the *l*-form separates first. This, indeed, is to be expected, since it is shown in this communication that the *d*-α-isomeride is similar in configuration to the *l*-β-isomeride.

On oxidation by the method of Beckmann (*Annalen*, 1889, **250**, 325), *l*-α-2-methyl*cyclo*hexanol was converted into l-2-*methyl*cyclo-

hexanone, b. p. 59—60°/20 mm., showing $[\alpha]^{25°}_{4359}$ −43·0°, $[\alpha]^{25°}_{5461}$ −18·91°, and $[\alpha]^{25°}_{5893}$ −15·22° ($l = 0·5$); $d^{25°}_{4°}$ 0·9230.

This ketone rapidly racemised when treated with cold alcoholic sodium hydroxide, probably owing to passage through the symmetrical *enol*-tautomeride :



$$CH_2<\begin{matrix}CH_2\text{——}CH_2\\CH_2\text{—}C(OH)\end{matrix}>C\text{-}Me$$

Stable esters of the *enolic* form of 2-methyl*cyclo*hexanone have been prepared by Murat (*Ann. Chim.*, 1909, **16**, 108).

l-β-2-Methyl*cyclo*hexanol yielded, in a similar manner, a ketone with $[\alpha]^{18°}_{5893}$ + 14·21° ($l = 0·5$), $d^{18°}_{4°}$ 0·9262.

1-α- *and* 1-β-3-*Methyl*cyclo*hexanols.*—*d*-3-Methyl*cyclo*hexanone, b. p. 72°/25 mm., $\alpha^{25°}_{5893}$ + 10·6°, was obtained from pulegone by the method described by Rupe (*Annalen*, 1924, **436**, 184).

This ketone (1 mol.) mixed with ether (10 vols.) was poured on to sodium (3 atoms), and small quantities of water were added from time to time. After dissolution of the sodium, the separated ethereal layer was repeatedly washed with sodium bisulphite solution and with water, dried with potassium carbonate, the ether removed, and the residue distilled. A mixture of 3-methyl*cyclo*hexanols, b. p. 78—79°/20 mm., was thus obtained with $\alpha^{24°}_{5461}$ −3·58° (yield 80%). A residue of viscid, fluorescent oil remained in the flask.

Six crystallisations of the *p*-nitrobenzoic ester of this alcohol yielded 1-α-3-*methyl*cyclo*hexanyl* p-*nitrobenzoate*, unchanged by further crystallisation either in melting point or in optical rotatory power ($[\alpha]_{5461}$ −3·8° in methyl alcohol, $c = 5·00$; $l = 2$; m. p. 45·5—46·5°) (Found : N, 5·4. $C_{14}H_{17}O_4N$ requires N, 5·3%).

1-α-3-*Methyl*cyclo*hexanol*, b. p. 78—79°/20 mm., obtained by the hydrolysis of this ester had $[\alpha]^{26·5°}_{5461}$ −4·22°, $d^{26·5°}_{4°}$ 0·9131, and $\eta^{25°}$ 0·251. When oxidised with chromic acid, it gave *d*-3-methyl*cyclo*hexanone, b. p. 66—67°/25 mm., with $\alpha^{23°}_{5893}$ + 11·54° ($l = 1$). *l*-β-3-Methyl*cyclo*hexanol, the preparation of which is described in the next section, yielded in a similar manner a ketone, b. p. 56—57°/14 mm., with $\alpha^{17°}_{5893}$ + 11·64°.

1-α-3-*Methyl*cyclo*hexanyl hydrogen phthalate*, m. p. 94—95°, obtained from the corresponding alcohol in the usual manner, had $[\alpha]^{19°}_{5461}$ −17·39° and $[\alpha]^{19°}_{5893}$ −13·51° in benzene ($c = 5·01$; $l = 2$).

The *methyl*cyclo*hexanyl acetates*, prepared by warming the alcohols with an excess of acetic anhydride on the water-bath for 2 hours, are colourless, mobile liquids possessing sharp, pleasant odours. The particular character of the odour varies rather markedly throughout the series.

TABLE I.

Methyl*cyclo*-hexanyl acetate.	B. p. /20 mm.	$d_{4^\circ}^{25^\circ}$.	$n_{5893}^{25^\circ}$.	$[R_L]_{5893}^{25^\circ}$.	η^{25°.
dl-α-2-	79—80°	0·9430	1·4389	43·48	0·0233
dl-β-2-	79—80	0·9434	1·4376	43·34	0·0211
dl-α-3-	81—82	0·9454	1·4313	43·94	0·0174
dl-β-3-	78—79	0·9430	1·4369	43·38	0·0195
α-4-	78—80	0·9380	1·4373	43·46	0·0217
β-4-	78—79	0·9337	1·4365	43·75	0·0196
Methyl*cyclo*hexanol.					
dl-α-2-	77—79	0·9228	1·4596	33·81	0·336
dl-β-2-	77—78	0·9228	1·4616	33·93	0·155
dl-α-3-	78—79	0·9104	1·4530	33·87	0·251
dl-β-3-	77—78	0·9091	1·4554	34·01	0·197
α-4-	78—79	0·9080	1·4544	34·02	0·385
β-4-	78—79	0·9180	1·4584	33·91	0·247

$[R_L]_{5893}$ calc., 33·85 (Eisenlohr's figures).

	M. p. of				
Methyl*cyclo*-hexanol.	hydrogen phthalate.	phenyl-carbamate.	*p*-nitro-benzoate.	hydrogen succinate.	*p*-toluene-sulphonate.
dl-α-2-	124—125°	105—106°	65°	44—46°	27—28°
dl-β-2-	89— 90	78— 80	35—36	30—31	—
dl-α-3-	93— 94	92— 93	58	Oil.	39—40
dl-β-3-	82— 83	101—103	65	—	46—47
α-4-	119—120	124—125	67	—	71—72
β-4-	72— 73	124	94	—	—

(*c*) *The Methyl*cyclo*hexanyl* p-*Toluenesulphonates.*

The solid mass produced by the interaction of finely powdered *p*-toluenesulphonyl chloride (1·02 mols.) and a solution of the methyl*cyclo*hexanol in pyridine (1·05 mols.) was ground under water, washed many times with dilute hydrochloric acid and water, dried, and crystallised from light petroleum.

All the members of this series of esters formed white, wax-like crystals which decomposed at about 160° with the evolution of a volatile substance (methyl*cyclo*hexenes). Unlike menthyl *p*-toluenesulphonate, which reacts almost immediately with aromatic amines to give menthene and the amine toluenesulphonate (Ferns and Lapworth, J., 1912, **101**, 273), the methyl*cyclo*hexanyl toluenesulphonates react only very slowly with aniline. The melting points of these derivatives are in Table I (the quantities of sodium hydroxide required for the complete hydrolysis of 1·0081 g. of the *dl*-α-2-ester, 1·0092 g. of the *dl*-α-3-ester, 1·0042 g. of the α-4-ester, and 1·0857 g. of the *l*-α-3-ester were 0·151, 0·150, 0·146, and 0·162 g. respectively. Calc. : 0·148, 0·149, 0·148, and 0·162 g.).

l-α-3-*Methyl*cyclo*hexanyl* p-*toluenesulphonate*, m. p. 36—37°, had $[\alpha]_{5461}^{19^\circ}$ − 26·3° and $[\alpha]_{5893}^{19^\circ}$ −21·0° in benzene ($c = 5·018$; $l = 2$).

In the following experiments a part only of the sulphonic ester was converted into carboxylic ester, and only this part was considered in calculating the percentage inversion referred to, which is the percentage conversion of an α-methyl*cyclo*hexanol into a β-methyl*cyclo*hexanol (or *vice versa*).

(i) *dl*-α-2-Methyl*cyclo*hexanyl *p*-toluenesulphonate (1 mol.), ethyl alcohol (1·5 times the volume of the molten sulphonic ester), and potassium acetate (4 mols.) were heated on the water-bath for 24 hours. The mixture was then poured into water, neutralised with sodium carbonate, and extracted five times with ether. The ether was removed from the dried ethereal extracts and the residue was distilled, first under ordinary pressure and finally under reduced pressure. In this manner were obtained a mixture of ethyl acetate and methyl*cyclo*hexene, b. p. 75—80/760 mm.; methyl*cyclo*hexene, b. p. 104—115°/760 mm.; methyl*cyclo*hexanyl ethyl ether b. p. 65—70°/20 mm., and 2-methyl*cyclo*hexanyl acetate, b. p. 76—81°/20 mm. The first fractions, freed from ethyl acetate by washing with water, yielded methyl*cyclo*hexene, b. p. 104—105°, $d_{4^\circ}^{18^\circ}$ 0·8077, $d_{4^\circ}^{22^\circ}$ 0·8052, $d_{4^\circ}^{26^\circ}$ 0·8023, and $n_{5893}^{18^\circ}$ 1·4409, whence $[R_L]_{5893}$ 31·41; calc., 31·76 (compare Wallach, *Ber.*, 1902, **35**, 2822; Markovnikov and Stadnikov, *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 389; Markovnikov and Tscherdintzev, *ibid.*, 1900, **32**, 302).

After repeated fractionation the third fraction yielded 2-methyl*cyclo*hexanyl ethyl ether, b. p. 69—70°/21 mm., $n_{5893}^{20^\circ}$ 1·4701, $d_{4^\circ}^{20^\circ}$ 0·922, whence $[R_L]_{5893}$ 43·5; calc., 43·4 (compare Murat, *loc. cit.*).

The ester fraction gave a methyl*cyclo*hexanyl acetate, b. p. 78—80°/20 mm., $d_{4^\circ}^{25^\circ}$ 0·9432, $n_{5893}^{25^\circ}$ 1·4382, which, after hydrolysis with alcoholic sodium hydroxide, yielded a methyl*cyclo*hexanol. After purification by conversion into the hydrogen phthalic ester, this substance was shown to be *dl*-β-2-methyl*cyclo*hexanol with $d_{4^\circ}^{25^\circ}$ 0·9226 and η^{25° 0·155.

The hydrogen phthalic ester, obtained from this alcohol in the usual manner, had m. p. 89—90°, which was not depressed by admixture of the *dl*-β-2-methyl*cyclo*hexanyl hydrogen phthalate previously prepared from *o*-cresol.

The yield of ester was 25%, of ether 20%, and of methyl*cyclo*hexene 40%.

(ii) *dl*-α-2-Methyl*cyclo*hexanyl *p*-toluenesulphonate was mixed with ammonium acetate (3 parts), and ethyl alcohol added until the whole formed a solution at 80°. After being heated for 18 hours on the water-bath, the mixture was worked up in a similar manner to that described above. The yields of methyl*cyclo*hexanyl acetate, methyl*cyclo*hexene, and methyl*cyclo*hexanyl ethyl ether were 70%, 15%, and 5% respectively. 2-Methyl*cyclo*hexanol obtained from the ester had $\eta^{25°}$ 0·180, whence the estimated inversion is 85%.

(iii) *dl*-α-2-Methyl*cyclo*hexanyl *p*-toluenesulphonate, mixed with benzene (7·5 vols.) and formic acid (anhydrous; 1·5 vols.), was heated for 18 hours on the water-bath. 2-Methyl*cyclo*hexanyl formate and methyl*cyclo*hexene were obtained each in 40% yield. On hydrolysis the former yielded 2-methyl*cyclo*hexanol with $\eta^{25°}$ 0·246, whence the estimated inversion is 40%.

(iv) *dl*-α-2-Methyl*cyclo*hexanyl *p*-toluenesulphonate, mixed with formamide (2·5 vols.) and formic acid (3·5 vols.), was heated for 18 hours on the water-bath. 2-Methyl*cyclo*hexanyl formate was obtained in 45% yield, and methyl*cyclo*hexene in 40% yield. The formic ester yielded 2-methyl*cyclo*hexanol with $\eta^{25°}$ 0·232 whence the inversion is 50%.

A similar experiment in which the formamide was replaced by water yielded ultimately 2-methyl*cyclo*hexanol with $\eta^{25°}$ 0·232, whence the inversion is 50%.

(v) *dl*-α-2-Methyl*cyclo*hexanyl *p*-toluene sulphonate, mixed with glacial acetic acid (5 vols.) and potassium acetate (equal in weight to the ester), was heated for 1 day on the water-bath. 2-Methyl*cyclo*hexanyl acetate was obtained in 50% yield, and methyl*cyclo*hexene in 30% yield. The acetic ester gave 2-methyl*cyclo*hexanol with $\eta^{25°}$ 0·180, whence the inversion is 82%.

(vi) *dl*-α-3-Methyl*cyclo*hexanyl *p*-toluenesulphonate was allowed to react with potassium acetate under the conditions described in experiment (i). 3-Methyl*cyclo*hexanyl acetate was obtained in 20% yield, 3-methyl*cyclo*hexanyl ethyl ether in 5% yield, and methyl*cyclo*hexene in 60% yield. The *dl*-β-3-methyl*cyclo*hexanol ultimately obtained with $\eta^{25°}$ 0·196 gave a phenylcarbamate, the m. p. of which, 101—102°, was not depressed by admixture of the previously prepared *dl*-β-3-methyl*cyclo*hexanyl phenylcarbamate. Thus the inversion is complete as far as the experimental methods used are capable of indicating it.

(vii) α-4-Methyl*cyclo*hexanyl *p*-toluenesulphonate was allowed to react with potassium acetate under the conditions described in (i). 4-Methyl*cyclo*hexanyl acetate was obtained in 30% yield, 4-methyl*cyclo*hexanyl ethyl ether in 10% yield, and methyl*cyclo*hexene in 40% yield. The ester yielded, on hydrolysis, β-4-methyl*cyclo*hexanol with $\eta^{25°}$ 0·247. The hydrogen phthalic ester derived from this alcohol had m. p. 72°, which was not depressed by the admixture of the β-4-methyl*cyclo*hexanyl hydrogen phthalate prepared directly from *p*-cresol. Thus the inversion is probably complete.

(viii) *l*-α-3-Methyl*cyclo*hexanyl *p*-toluenesulphonate was allowed to react with potassium acetate under the conditions described in (i). 3-Methyl*cyclo*hexanyl acetate was obtained in 20% yield, 3-methyl*cyclo*hexanyl ethyl ether in 5% yield, and methyl*cyclo*hexene in 60% yield. *l*-β-3-Methyl*cyclo*hexanol, η^{25° 0·196, was obtained by the hydrolysis of the ester.

l-β-3-*Methyl*cyclo*hexanyl hydrogen phthalate*, m.p. 70—71°, obtained from the above alcohol in the usual manner, had $[\alpha]^{19^\circ}_{5461}$ −32·7° and $[\alpha]^{19^\circ}_{5893}$ −26·81° in benzene ($c = 5{\cdot}01$; $l = 2$).

The methyl*cyclo*hexene obtained in this experiment, after purification by means of sodium, had b. p. 104—105°, $d^{26^\circ}_{4^\circ}$ 0·7950, and $n^{26^\circ}_{5893}$ 1·4408; whence $[R_L]_{5893}$ 31·88; calc., 31·76. The following determinations of rotatory power were made ($t = 26°$; $l = \frac{1}{2}$): α_{4359} + 88·75°; α_{5461} + 50·86°; α_{5790} + 44·62°; α_{5893} + 42·67°; α_{6708} + 31·99°.

(ix) *dl*-β-3-Methyl*cyclo*hexanyl *p*-toluenesulphonate was allowed to react with potassium acetate under the conditions employed in (i). *dl*-α-3-Methyl*cyclo*hexanol with η^{25° 0·249 was finally obtained.

(x) *d*-+*dl*-α-2-Methyl*cyclo*hexanyl *p*-toluenesulphonate (prepared from *d*-+*dl*-α-2-methyl*cyclo*hexanol, $\alpha^{17^\circ}_{5893}$ + 17·77°, $l = 1$) showed $\alpha^{17^\circ}_{5893}$ + 17·51° ($l = 1$) in the supercooled state. The reaction between this ester and potassium acetate under the conditions employed in (i) yielded ultimately *l*-+*dl*-β-2-methyl*cyclo*hexanol with $\alpha^{20^\circ}_{5893}$ −2·08°, methyl*cyclo*hexanyl ethyl ether with $\alpha^{20^\circ}_{5893}$ + 9·16°, and methyl*cyclo*hexene with $\alpha^{27^\circ}_{5893}$ −22·8°.

(*d*) *Physical Measurements.*

Viscosity.—The type of viscometer used in these determinations was the modification of the Ostwald pattern designed by Thole (J., 1910, **97**, 2596; 1913, **103**, 22) for the measurement of the viscosity of liquids of which only small quantities are available. Two instruments were used, one with a time of flow suitable for the measurement of the viscosities of the methyl*cyclo*hexanols, which was generously provided by Dr. Thole, and the other, with a narrower capillary, for the less viscous methyl*cyclo*hexanyl acetates.

The first instrument was calibrated with *cyclo*hexanol (Thole, J., 1914, **105**, 2011) and *l*-*iso*propyl-*n*-octylcarbinol (Dunstan and Thole, J., 1913, **103**, 130), and the second with nitrobenzene (Thole, *Z. physikal. Chem.*, 1910, **74**, 684) and with ethyl alcohol (Thole, J., 1914, **105**, 2004).

In addition to the usual precautions taken in determining viscosity, it was found necessary to distil the alcohols and their acetic esters under reduced pressure before each determination and to repeat this process, rejecting the first few drops, until approximately constant values were obtained; otherwise, owing to traces of absorbed water, no reliance could be placed in the results. The viscosity of a sample of methyl*cyclo*hexanol which had been kept for 8 months in a stoppered bottle, fell 30% but regained the normal value upon distillation. In no case was the observed time of flow less than 150 seconds.

The following viscosities of mixtures of *dl*-β-2- and *dl*-α-2-methyl*cyclo*hexanol were determined; *a* is the percentage of the latter alcohol :

a ...	100	81·2	74·6	66	60·8	60·5	47	25	0
$\eta^{25°}$	0·336	0·313	0·287	0·268	0·255	0·247	0·225	0·185	0·155

The rotatory powers of the methyl*cyclo*hexanols and of their acetic esters were determined in a jacketed tube ($l = 0·5$), round which hot oil was circulated for the readings at the higher temperatures. The light sources used were the sodium and lithium flame and the enclosed mercury arc. Densities were determined in a pyknometer of about 1·5 c.c. capacity.

TABLE II.

Determinations of the Density ($d_4^{t°}$) *and the Rotatory Power* (α 50 mm.) *of Compounds in the Homogeneous State.*

d-*a*-2-*Methyl*cyclo*hexanol.*

		α for λ =				
t.	$d_4^{t°}$.	6708.	5893.	5790.	5461.	4359.
20·5°	0·9271	+13·01°	+17·19°	+17·96°	+20·28°	+34·00°
48	0·9010	12·51	16·66	17·43	19·79	33·30
69	0·8810	12·30	16·31	17·00	19·28	32·60
95	0·8560	12·11	15·91	16·53	18·71	31·70

$\alpha^{20·5°}$ + 36° for λ 4220; + 39° for λ 4146; + 41° for λ 4046; + 43° for λ 3978; + 47° for λ 3820.

l-*a*-2-*Methyl*cyclo*hexanol.*

$\alpha^{20°}$ — 13·05° for λ 6708; — 17·81° for λ 5893; — 17·95° for λ 5790; — 20·32° for λ 5461; — 34·13° for λ 4359.

l-*β*-2-*Methyl*cyclo*hexanol.*

		α for λ =				
t.	$d_4^{t°}$.	6708.	5893.	5790.	5461.	4359.
20°	0·9272	−4·62°	−6·23°	−6·41°	−7·26°	−11·96°
49	0·9009	3·97	5·32	5·48	6·35	10·24
95	0·8560	3·08	4·09	4·24	4·81	7·98
112	0·8519	2·77	3·68	3·82	4·32	7·21
130	0·8220	2·49	3·31	3·43	3·87	6·46

l-*a*-3-*Methyl*cyclo*hexanol.*

$d_4^{t°}$ 0·9143 at 20°; 0·8919 at 51°; 0·8672 at 85°; 0·8303 at 121°.

(Owing to the small rotatory power of this compound, the determinations made in a 0·5 dcm. tube were untrustworthy and hence determinations were made in a 2 dcm. tube at 20°.)

α_{6780} — 5·41°; α_{5893} — 7·17°; α_{5790} — 7·59°; α_{5461} — 8·48°; α_{4359} — 14·03°.

TABLE II (*continued*).

		α for λ =				
t.	$d^{t°}_{4°}$.	6708.	5893.	5790.	5461.	4359.
1-β-3-*Methyl*cyclo*hexanol.*						
16·5°	0·9245	−2·53°	−3·37°	−3·63°	−4·06°	−6·58°
50	0·8991	2·23	2·91	3·10	3·45	5·64
75	0·8774	2·02	2·64	2·78	3·08	5·01
96	0·8551	1·72	2·23	2·35	2·76	4·37
119	0·8389	1·47	1·95	1·97	2·23	3·55
1-α-2-*Methyl*cyclo*hexanyl Acetate.*						
20	0·9458	−19·27	−25·42	−26·47	−29·96	−49·87
49	0·9221	18·42	24·31	25·36	28·82	47·98
66	0·9072	18·18	24·08	24·81	28·11	46·65
90	0·8851	17·35	22·88	24·05	27·28	45·50
112	0·8624	16·92	22·32	23·27	26·32	43·95
129	0·8478	16·32	21·52	22·62	25·61	42·80
1-β-2-*Methyl*cyclo*hexanyl Acetate.*						
20	0·9454	−9·11	−12·38	−12·81	−14·50	−25·88
52	0·9202	8·61	11·63	12·20	13·90	24·41
90	0·8848	7·85	10·65	11·13	12·66	22·33
108	0·8681	7·40	10·04	10·42	11·93	21·04
126	0·8509	7·24	9·62	10·10	11·35	19·72
1-α-3-*Methyl*cyclo*hexanyl Acetate.*						
16	0·9511	−8·13	−10·83	−11·34	−12·82	−21·69
49	0·9262	7·67	10·50	10·87	12·29	20·90
71	0·9071	7·60	10·05	10·54	11·94	20·22
90	0·8903	7·27	9·64	10·19	11·60	19·57
109	0·8724	7·17	9·63	9·87	11·35	19·22
125	0·8549	6·98	9·29	9·79	10·94	18·87
1-β-3-*Methyl*cyclo*hexanyl Acetate.*						
20	0·9448	−3·40	−4·51	−4·67	−5·30	−8·78
52	0·9197	3·31	4·30	4·45	5·10	8·30
77	0·8974	3·25	4·10	4·26	4·86	7·85
90	0·8849	3·15	3·91	4·07	4·72	7·54
109	0·8671	2·94	3·69	3·88	4·41	7·14
125	0·8502	2·70	3·48	3·66	4·10	6·70

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