VII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution.   Part I.   The Rotations of the Simplest Secondary Alcohols of the Fatty Series.*

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THE authors hope to communicate to the Society a series of papers in which will be discussed the qualitative and quantitative dependence of rotatory power on chemical constitution, and feel it desirable to state at the outset their reasons for commencing yet a further investigation of this interesting problem.

It is obvious that in the present state of knowledge much of the previous work * in this field is very difficult to correlate even in a qualitative manner.   Now there are numerous investigations of the type, as, for example, (*a*) the very extended and careful researches of P. F. Frankland and his co-workers on the rotatory powers of derivatives of the optically active glyceric and tartaric acids ; (*b*) the independent work of Tschugaeff and of Rupe on the bornyl and menthyl esters of various acids, and (*c*) the paper of one of us and Littlebury on the esters of *l*-menthylcarbamic acid, in which in each case the effect of various substituents on the rotatory power of some one optically active substance has been studied ; that is to say, in the above instances the effect of substituting the alcoholic or carboxylic hydrogen atoms in glyceric and tartaric acids, in borneol, menthol, and menthylcarbamic acid.   In the compounds described in such investigations the substituent is not attached to an asymmetric carbon atom, and is in many cases far removed from it in the molecule, whilst in several of the parent substances of such investigations there are more than one such carbon atom.   It is thus often impossible to decide how far the effect of the substituent is due to its relative mass and how far to its structure, this particularly being the case in compounds containing the menthyl radicle (compare Pickard and Littlebury, Trans., 1907, **91**, 301).

In addition to this difficulty there is also the additional one that it is often doubtful whether conclusions drawn from one group of comparatively complex compounds can be applied safely to those drawn from another group of widely differing constitution.   Thus, for example, confusion may be introduced if the effect on the rotatory power of substituting the alcoholic hydrogen atoms be compared in such widely different compounds, as, for example, glyceric acid, menthol, or the

* Up to the end of 1904 this is admirably summarised by Walden (*Ber.*, 1905, **38**, 345).

optically active amyl alcohol of fusel oil. Again, many of the compounds compared in such investigations are solids at the ordinary temperature, and the rotations of these have been determined in solution, although the effect of solvents on rotatory power is as yet little understood. Further, the effect of temperature on the rotatory powers of the pure liquids, considerable as it is in many cases, has been often disregarded, although in this respect the investigations of Frankland leave little to be desired.

These and similar difficulties are well exemplified when a comparison is made of the rotatory powers of the various compounds of β-phenylpropionic, cinnamic, and phenylpropiolic acids which have been prepared by several investigators to show the relative effect of unsaturation on optical activity.

In table I will be found a list of the molecular rotatory powers of several of the compounds previously described, and also those of the esters of the three acids with d- and l-methyl-n-hexylcarbinol (Trans., 1907, **91**, 2058). These esters of a simple secondary alcohol give results differing from those obtained with more complicated secondary alcohols, such as menthol and borneol.

TABLE I.

Molecular Rotatory Powers of Esters and Salts of β-Phenylpropionic Cinnamic, and Phenylpropiolic Acids.

	Acid.		
Ester or Alkaloid.	β-Phenyl-propionic.	Cinnamic.	Phenyl-propiolic.
l-Amyl alcohol * .... (Methylethylcarbincarbinol)	$+5\cdot0°$	$+16\cdot4°$	$+12\cdot1°$
l-Menthol †	$-161\cdot9$	$-247\cdot8$	—
,, ‡	$178\cdot3$	$235\cdot5$	$-215\cdot9$
,, § { a.....................	$171\cdot5$	$171\cdot6$	$-166\cdot7$
,, § { b.....................	$162\cdot6$	$184\cdot3$	$157\cdot6$
d-Borneol § { a................	$+86\cdot5$	$+82\cdot5$	$+87\cdot6$
{ b.....................	$82\cdot9$	$82\cdot6$	$89\cdot4$
d-Methyl-n-hexylcarbinol ‖......	$+32\cdot1$	$+104\cdot4$	$+131\cdot1$
l-Methyl-n-hexylcarbinol ‖	$-32\cdot8$	$-103\cdot4$	$-130\cdot9$
Coniine ¶	$-5\cdot1$	$-20\cdot6$	$-19\cdot7$
Cinchonine ¶.......................	$+381\cdot9$	$+475\cdot2$	$+511\cdot6$

* Walden (*Zeitsch. physikal. Chem.*, 1896, **20**, 569). In the nomenclature of Marckwald (*Ber.*, 1902, **35**, 1599), this alcohol is d-amyl alcohol.

† Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 606).

‡ Rupe (*Annalen*, 1909, **369**, 311). Determinations in 10 per cent. benzene solution.

§ Hilditch (*Trans.*, 1908, **93**, 14). Determinations in 10 per cent. solution, (*a*) in chloroform, (*b*) in acetone.

‖ The unsaturated esters have been quantitatively reduced to the saturated ester (see page 67).

¶ Hilditch (*Trans.*, 1908, **93**, 713). Determinations in 4 per cent. chloroform solution.

These results (table I) show at once that no general conclusions can be drawn as to the quantitative effect on the rotatory powers of the alcohols and alkaloids named when the alcoholic hydrogen atom is displaced by acid radicles (or salts are formed with acids) of closely related constitution, but differing in the degree of unsaturation, for in some cases the ethylenic, and in the others the acetylenic, compound has the greater rotation.

It is, however, convenient at this juncture to recall that the vast amount of painstaking and laborious work in this field has led to certain well-founded, but very wide, generalisations.   These need not now be re-stated, but are well exemplified by the investigations quoted in the table, which (with others) show that (we believe in every known case) the effect of unsaturation is exhibited in the exaltation of rotatory power.

Considerations such as these make the following conditions desirable for a re-investigation of this subject : (1) the active compounds compared should contain only one asymmetric carbon atom; (2) the effect of various radicles on the rotatory power should only be compared when these are attached directly to the asymmetric carbon atom, and (3) the compounds should be liquids and their rotatory powers should be measured in the pure state and at different temperatures.

Thus, whilst previous investigators have as a rule studied the variation in the rotatory power of some one compound caused by inactive substituents, the object of the present authors is to compare the rotatory powers of different series of comparatively simple compounds.   Optically active compounds, however, of the type required are very little known, and it becomes therefore necessary to prepare them specially.

No class of compounds seems so likely as the alcohols to fulfil in general the third condition laid down, whilst the ease with which all types of alcohols can now be synthesised, thanks to the Grignard reaction and the catalytic reactions of the Toulouse school, makes this class of compounds particularly suitable for the purpose in view. Now one of us and Littlebury have described (Trans., 1907, **91**, 1973) a method for what is believed to be the complete resolution of racemic alcohols, namely, by the fractional crystallisation of the salts formed by the combination of various optically active bases with the acid esters of the alcohol and a polybasic acid, whilst the present authors in a similar way carried out the first successful resolution (*loc. cit.*) of an aliphatic alcohol, namely, that of methyl-*n*-hexylcarbinol with $[a]_D^{17} \pm 9\cdot9°$.   The method has since been found to be a general one, and can be applied to several types of alcohols (see preliminary note, Proc., 1909, **25**, 167) ; therefore, those types of alcohols which contain one asymmetric carbon atom, since they can be synthesised

and resolved into their optically active components, and since they have as a rule low melting points, appear to be very suitable for a re-investigation of the problem of the dependence of rotatory power on chemical constitution.

However, before describing the results obtained so far in this direction, attention should be called to the following evidence, which will furnish an answer to the very obvious question as to whether such results might not be vitiated by an incomplete resolution of the racemic alcohols.   Now, firstly, that the method has effected complete resolutions in some cases seem certain.   For example, one of us and Littlebury (*loc. cit.*) prepared by this method four borneols, which all severally gave, when oxidised, camphors identical in rotatory power with the maximum exhibited by the natural products ; thus the *d*-borneol and the *l-iso*borneol prepared each gave pure *d*-camphor, whilst the *l*-borneol and the *d-iso*borneol gave pure *l*-camphor.   Again, the *d*-methyl-*n*-heptylcarbinol described below has an equal but opposite rotatory power to that of the specimen of the same compound isolated from oil of rue by Power and Lees * (Trans., 1902, **81**, 1592). Secondly, in the case of the fourteen alcohols, the resolutions of which are described below (with two exceptions),† there have been obtained either both the dextro- and lævo-rotatory forms of the alcohols with equal and opposite rotations, or both forms of the same acid ester with equal and opposite rotation, or two preparations of the same acid ester having identical rotations by fractional crystallisation of the salts of two different alkaloids or two preparations of the alcohol with dentical positive rotation from two different acid esters.   Thirdly, the recorded rotatory powers (see table II, p. 49) of the alcohols belonging to the same series show a gradual alteration as the series is ascended, and thus agree well one with the others.   Fourthly, an exhaustive series of experiments failed to give any evidence against the optical purity of methyl-*n*-hexylcarbinol with $[a]_D^{17} \pm 9 \cdot 9°$.   In these, (*a*) the diethyl and dimethyl esters of *d*- and *l*-tartaric acid were allowed to remain in presence of hydrogen chloride with an excess or a deficiency of the *d*- or the *l*-alcohol, under which conditions the β-octyl group more or less completely displaces the methyl or ethyl group in the tartaric esters ; (*b*) *d*- and *l*-tartaric acid were each treated in the same way with the two alcohols; (*c*) the β-octyl esters of the tartaric acids thus obtained were each hydrolysed partly with an insufficiency, or completely with an excess, of potassium hydroxide. In view of the experiments of Marckwald and McKenzie (*Ber.*, 1901,

* *d*-Methyl-*n*-nonylcarbinol, as now obtained by synthesis, has a higher positive rotation than the lævorotatory alcohol isolated by these investigators from the same oil.

† Methyl-*n*-decyl- and phenylmethyl-carbinols.

34, 469) on the varying velocity of esterification of an optically active acid with the two optical isomerides of an alcohol and the varying rate of hydrolysis of the corresponding esters, it was to be expected that such experiments carried out under many varied conditions (including those detailed by them) would yield a product of rotatory power different from $[a]_D^{17} \pm 9 \cdot 9°$ if this were not the constant relating to optically pure methyl-n-hexylcarbinol.   In no case, however, was a sample of the alcohol obtained as a result of these experiments of either lower or higher rotatory power.

Resolution of Fourteen Alcohols.

The resolution of fourteen alcohols is described in this section ; twelve of these are of the general formula $CH_3 \cdot CH(OH) \cdot R$, where R represents the normal groups ethyl to undecyl, isobutyl and phenyl, whilst the other two have the formula $C_2H_5 \cdot CH(OH) \cdot R'$, where R′ represents n-hexyl and phenyl.   The preparation of these active alcohols has been repeated, and in all cases but two—methyl-n-decyl- and phenylmethyl-carbinol—the pure optically active alcohols have been obtained in at least two ways.   In Figs.* 1 and 2 is illustrated the variation of the specific rotations with the temperature, and table II shows how in the series methyl-n-propyl- to methyl-n-undecyl-carbinol the molecular rotatory powers tend to approach a common value.   These resolutions have been carried out by the method described (loc. cit.) for methyl-n-hexylcarbinol, that is, by the fractional crystallisation from acetone or aqueous acetone of the alkaloidal salts of either the hydrogen phthalic or succinic esters.   Where a

TABLE II.

Specific and Molecular Rotatory Powers of the Dextrorotatory Alcohols.

Alcohol.	$[a]_D^{20}$	$[M]_D^{20}$	$[a]_D^{50}$	$[M]_D^{50}$	$[a]_{20}^{90}$	$[M]_{Dj}^{90}$
Methylethylcarbinol	$+13 \cdot 87°$	$+10 \cdot 3°$	$+12 \cdot 48°$	$+9 \cdot 2°$	$+11 \cdot 84°$	$+8 \cdot 8°$
Methyl-n-propylcarbinol...	$13 \cdot 70$	$12 \cdot 1$	$12 \cdot 89$	$11 \cdot 3$	$12 \cdot 56$	$11 \cdot 2$
Methyl-n-butylcarbinol ...	$11 \cdot 57$	$11 \cdot 8$	$11 \cdot 02$	$11 \cdot 2$	$10 \cdot 90$	$11 \cdot 1$
Methyl-n-amylcarbinol ...	$10 \cdot 32$	$12 \cdot 0$	$9 \cdot 89$	$11 \cdot 5$	$9 \cdot 60$	$11 \cdot 1$
Methyl-n-hexylcarbinol ...	$9 \cdot 76$	$12 \cdot 7$	$9 \cdot 17$	$11 \cdot 9$	$8 \cdot 99$	$11 \cdot 7$
Methyl-n-heptylcarbinol ...	$8 \cdot 99$	$12 \cdot 9$	$8 \cdot 55$	$12 \cdot 3$	$8 \cdot 30$	$12 \cdot 0$
Methyl-n-octylcarbinol ...	$8 \cdot 68$	$13 \cdot 7$	$8 \cdot 14$	$12 \cdot 9$	$7 \cdot 80$	$12 \cdot 3$
Methyl-n-nonylcarbinol ...	$8 \cdot 13$	$14 \cdot 0$	$7 \cdot 66$	$13 \cdot 2$	$7 \cdot 28$	$12 \cdot 5$
Methyl-n-decylcarbinol ...	$7 \cdot 78$	$14 \cdot 5$	$7 \cdot 27$	$13 \cdot 5$	$6 \cdot 89$	$12 \cdot 8$
Methyl-n-undecylcarbinol .	$7 \cdot 22$	$14 \cdot 4$	$6 \cdot 67$	$13 \cdot 3$	$6 \cdot 39$	$12 \cdot 7$
Methylisobutylcarbinol ...	$20 \cdot 54$	$20 \cdot 9$	$19 \cdot 25$	$19 \cdot 6$	$18 \cdot 32$	$18 \cdot 7$
Ethyl-n-hexylcarbinol	$8 \cdot 05$	$11 \cdot 6$	$8 \cdot 17$	$11 \cdot 8$	$8 \cdot 30$	$12 \cdot 0$
Phenylmethylcarbinol	$42 \cdot 86$	$52 \cdot 3$	$42 \cdot 68$	$52 \cdot 1$	$41 \cdot 60$	$50 \cdot 8$
Phenylethylcarbinol.........	$27 \cdot 73$	$37 \cdot 7$	$32 \cdot 52$	$44 \cdot 2$	$35 \cdot 54$	$48 \cdot 3$

* It should be noted that in Fig. 2 the scale of the ordinates is one-third that of the scale of the ordinates in Fig. 1.

resolution was effected, in all cases brucine formed the least soluble salt (lBdA) with the dextrorotatory hydrogen phthalic esters and the dextrorotatory hydrogen succinic esters of the two alcohols containing the phenyl group, whilst with the purely aliphatic alcohols this alkaloid formed the least soluble salt (lBlA) with the lævorotatory

Fig. 1.

SPECIFIC ROTATORY POWER
AT DIFFERENT TEMPERATURES
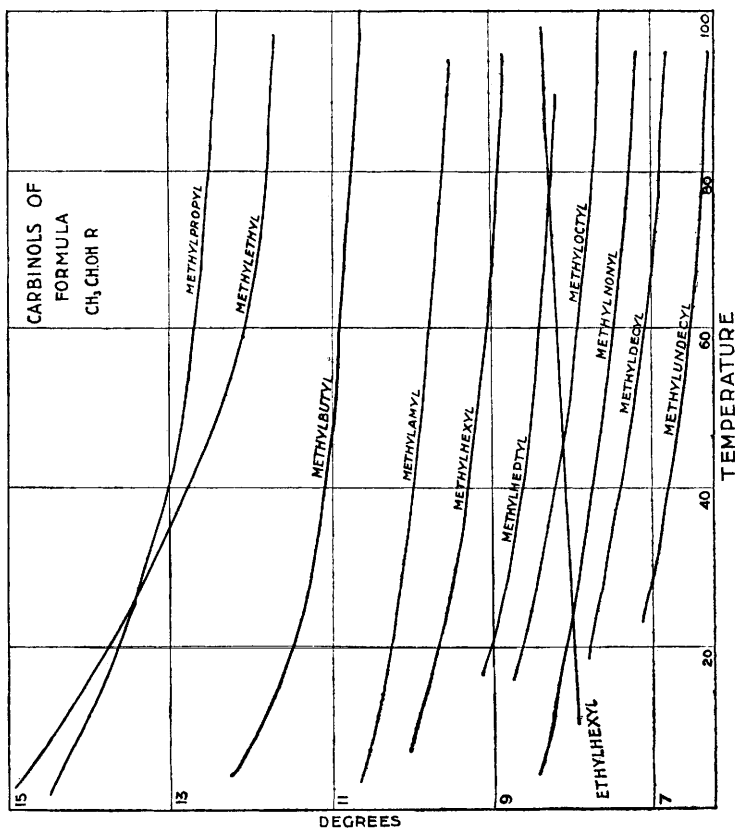
ester.   Similar results were obtained with strychnine, whilst cinchonidine gave results of an opposite character, as with this alkaloid the least soluble salts were lBlA and lBdA in the case of the hydrogen phthalates and succinates respectively.   Thus, for example, the following salts were found to be the least soluble component of the mixture of salts formed by neutralising the hydrogen ester with the

base : brucine and strychnine d-β-heptyl hydrogen phthalate, cinchoni-dine l-β-heptyl hydrogen phthalate, brucine d-δ-methyl-β-amyl hydrogen phthalate, brucine l-δ-methyl-β-amyl hydrogen succinate, and cinchoni-dine l-phenylethylcarbinyl hydrogen succinate.

Under the successful conditions employed in the other cases, no

Fig. 2.

SPECIFIC ROTATORY POWER
AT DIFFERENT TEMPERATURES
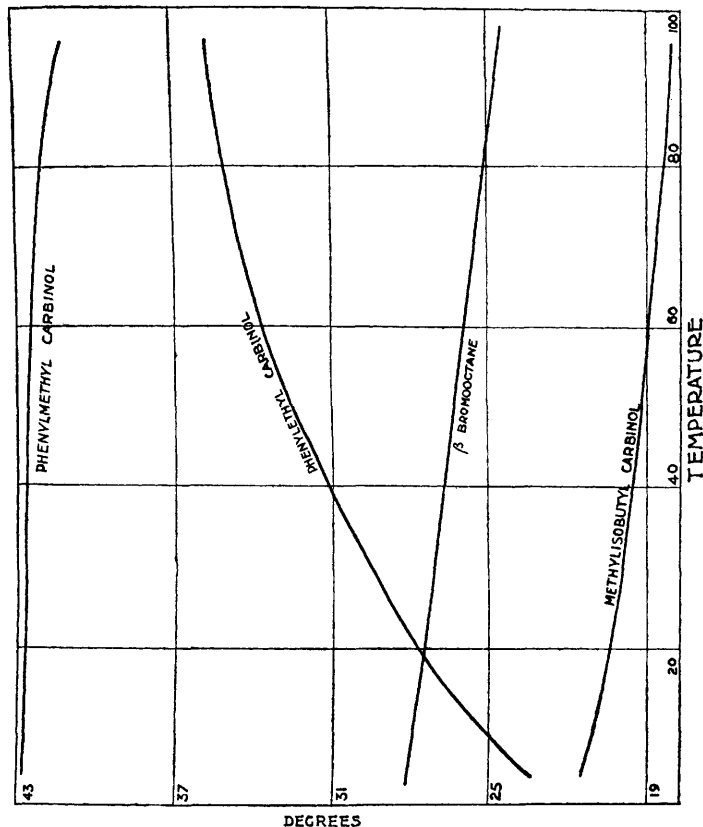
resolution was effected with the brucine, strychnine, or cinchonidine salts of the hydrogen phthalates of either phenylmethyl- or phenyl-ethyl-carbinols, or with any salts of the hydrogen esters of tetra-chlorophthalic acid.

In the optically pure state, none of the fourteen alcohols has previously been described, except methyl-n-heptylcarbinol, the lævo-

E 2

rotatory isomeride of which was isolated from oil of rue by Power and Lees (*loc. cit.*).

By fermentation methods, Combes and Le Bel (*Bull. Soc. chim.*, 1880, [ii], **33**, 106, 147 ; 1893, [iii], **9**, 676) obtained methylethyl- and methyl-*n*-butyl-carbinols with specific rotatory powers not exceeding $[a]_D - 0.5°$ and $[a]_D - 8°$ as against $[a]_D^{20} + 13.87°$ and $[a]_D^{20} + 13.70°$ respectively for the pure alcohols, whilst Meth (*Ber.*, 1907, **40**, 695) obtained methylethylcarbinol with $[a]_D$ less than $1°$ by a method discussed in a former paper by one of us and Littlebury (*loc. cit.*). Marckwald (*Ber.*, 1905, **38**, 809) has also obtained phenylmethyl- carbinol with $[a]_D^{21} + 2.7°$ (as against $[a]_D^{21} + 42.87°$) by the action of nitrous acid on *l*-phenylethylamine with $[a]_D^{22} - 39.51°$.   Haller (*Compt. rend.*, 1910, **151**, 697) has quite recently isolated from cocoa- nut oil, feebly dextrorotatory forms of methyl-*n*-heptylcarbinol with $[a]_D + 2.41°$, and methyl-*n*-nonylcarbinol with $[a]_D + 1.40°$, lævo- rotatory specimens of these having been previously isolated from oil of rue by Power and Lees (*loc. cit.*).

The number of optically active alcohols here described is obviously too small to admit of any discussion of the results in so far as they affect the main object of the investigation.   Attention, however, may be drawn to the following points.   The rotatory powers of the series of alcohols described do not differ much in general character from some of the series of normal esters described by other investigators, as, for example, the series of the normal esters of diacetylglyceric acid (Frankland, Trans., 1897, **71**, 270), where the rotatory powers gradually ascend to a maximum.   Determinations of the molecular rotatory powers of the hydrogen phthalic esters in chloroform solution gave results * which run practically parallel with those of the alcohols in the pure state, although in the case of the esters the first member occupies apparently a normal place in the series and has not, as in the case of the alcohols (as also in so many series described by other investigators), an abnormal rotatory power.

At the outset of the investigation it was thought possible that amongst the alcohols of the type $CH_3 \cdot CH(OH) \cdot R$, some simple numerical relation might be found to exist among the numbers expressing the rotatory powers.   It will be seen at once, however, that no comparison is feasible, if the influence of temperature be taken into account. Whilst the curves in Fig. 1 relating to the series (methylethyl- carbinol excepted) become parallel as the temperature increases, yet at no temperature up to $100°$ (the limit of the present experiments†)

* See table, p. 63.

† The question as to a possible relation or constant existing at or above the boiling points of the alcohols for the molecular rotatory powers is reserved for further discussion when more material is available.   The values of the rotatory

can the rotatory powers of the members of the series be compared with those of the alcohols of other types (see Fig. 2), or indeed with that of methylethylcarbinol.

The question of the (as yet unsolved) problem of the effect of association on the rotations of pure liquids (compare Walden, *loc. cit.*) naturally arises in this connexion. Does association account for the great differences in the temperature-coefficients as illustrated in Figs. 1 and 2 ? Now these alcohols as judged by Ramsay and Shields' capillarity ascension method or by Longinescu's empirical formula * (*Ann. Sci. Univ. Jassy*, 1903, **2**, 126) are only slightly associated. Thus empirically the association factor for

d-Methylethylcarbinol	is 1·33	*d*-Methyl-*n*-nonylcarbinol	is 1·01
d-Methyl-*n*-propylcarbinol	,, 1·24	*d*-Ethyl-*n*-hexylcarbinol	,, 1·03
d-Methyl-*n*-butylcarbinol	,, 1·15	*d*-Methyl*iso*butylcarbinol	,, 1·14
d-Methyl-*n*-amylcarbinol	,, 1·14	*d*-Phenylmethylcarbinol	,, 1·12
d-Methyl-*n*-hexylcarbinol	,, 1·08	*d*-Phenylethylcarbinol	,, 1·08
d-Methyl-*n*-heptylcarbinol	,, 1·05		

whilst, for example, by the capillarity ascension method *d*-methylethylcarbinol between 19·8° and 36·8° has a mean association factor 1·8, and *d*-methyl-*n*-hexylcarbinol between 15° and 34° has 1·5.† Now the similarity of the temperature-coefficients for the alcohols in the series, despite the decrease in association as the molecular weight increases and the striking differences in the temperature-coefficients of phenylmethyl- and phenylethyl-carbinols, of methyl- and ethyl-*n*-hexyl-carbinols, and of methylethylcarbinol and the rest of the series, seems to show that association has a very slight, if any, common influence on the rotation of these pure liquids. Since, however, it is a matter of some difficulty to measure small differences in association, the question of its influence on the rotatory powers of the individual alcohols could not be followed further.

The striking differences observed in the cases just mentioned in the variation of rotatory power with the temperature may be due partly to stereochemical causes, but possibly also to the more profound changes on the rotatory power of a complex, $R \cdot CH(OH) \cdot CH_2-$, caused by hydrogen than by a radicle (CH_3).

Methyl*iso*butylcarbinol was resolved at an early stage of the investigation to ascertain whether the differences in the rotatory powers of aliphatic alcohols corresponding with small differences in constitution were likely to be large. The exaltation in rotatory power powers of methyl-*n*-butyl- and methyl-*n*-octyl-carbinols commence to rise at about 125°, these being the only two alcohols investigated at the higher temperatures.

* $\dfrac{T}{100D} = \sqrt{n}$, where T = b. p. on the absolute scale, $D = d_4^0$, and n = the mean number of atoms in the molecule.

† It has often been observed that the capillarity ascension method gives higher values for the association factor than those obtained by empirical calculation.

caused by the *iso*butyl as compared with the *n*-butyl group is considerable, and affords additional evidence of powerful influence of constitution on rotatory power.

The halides corresponding with some of the alcohols have been prepared, the molecular rotatory powers being recorded in table III. In every case the conversion of the alcohol into a halide (Cl, Br or I) was accompanied by a change of sign in the rotation. Attempts to reconvert these halides into the optically pure alcohols have not as yet proved successful, and the preparation of them with any degree of certainty that racemisation has been avoided is tedious and very costly. This portion of the work has therefore not been extended for the present in case further physical measurements of the alcohols themselves appear desirable as the investigation proceeds. It will be noticed from Fig. 2 that the specific rotation of d-β-bromo-octane sinks regularly as the temperature increases, the curve being a straight line, and in this respect analogous among the alcohols only with ethyl-n-hexylcarbinol, for which, however, the specific rotation rises regularly with the temperature. The association factor for d-β-bromo-octane, calculated by Longinescu's formula, is $1\cdot07$.

The authors are greatly indebted to Dr. T. M. Lowry for the determinations of the refractive indices of the dextrorotatory alcohols as recorded in table IV. Dr. Lowry has also undertaken the determination of the magnetic and optical rotatory dispersion. * In respect to the optical rotatory dispersion a somewhat striking

TABLE III.

Rotatory Powers of the Halides.

	$[\alpha]_D^{17}$.	$[M]_D^{17}$.	$[\alpha]_D^{17}$.	$[M]_D^{17}$.
β-Iodobutane	$-31\cdot98°$	$-58\cdot8°$	—	—
β-Iodopentane	$-37\cdot15$	$-57\cdot0$	—	—
β-Iodohexane	$-38\cdot35$	$-80\cdot9$	—	—
β-Iodo-octane	$-40\cdot56$	$-90\cdot4$	$+39\cdot82°$	$+88\cdot8°$
γ-Iodononane	$-17\cdot50$	$-44\cdot4$	$+17\cdot65$	$+44\cdot8$
β-Bromo-octane	$-27\cdot47$	$-53\cdot0$	$+27\cdot53$	$+53\cdot1$
γ-Bromononane	$-13\cdot39$	$-27\cdot7$	$+12\cdot90$	$+26\cdot7$
β-Chloro-octane	$-20\cdot44$	$-30\cdot4$	$+20\cdot40$	$+30\cdot3$
γ-Chlorononane	$-\ 8\cdot03$	$-13\cdot0$	$+\ 7\cdot71$	$+12\cdot5$
α-Chloroethylbenzene ...	$-\ 5\cdot80$	$-\ 8\cdot2$	—	—
α-Chloropropylbenzene..	$-\ 3\cdot87$	$-6\cdot0$	$+\ 3\cdot79$	$6\cdot0$

connexion between this and the anomalous temperature-coefficients already mentioned has been observed. Thus, in a private communication, he states that those active alcohols of which the specific rotatory power varies normally with the temperature (see curves in Fig. 1 for methyl-n-propyl- to methyl-n-undecyl-carbinol) appear to give a constant value for the ratio $\alpha_{4379}/\alpha_{5461}$, which affords the most

* The results of these determinations will be published separately.

convenient measure of their rotatory dispersion; on the other hand, those alcohols which have a different temperature-coefficient of optical rotatory power (methylethyl-, ethyl-n-hexyl-, methylisobutyl-, phenyl-methyl-, and phenylethyl-carbinols) also differ in optical rotatory dispersion from the normal series, $CH_3 \cdot CH(OH) \cdot R$ (where $R = n\text{-}C_3H_7$ to $n\text{-}C_{11}H_{23}$), of active alcohols referred to above; there is, however, no simple relationship between the sign of the temperature-coefficient and the relative magnitude of the dispersion ratio.

TABLE IV.

Refractive Indices of the Dextrorotatory Alcohols.

Alcohol.	n_D^{20}.	$d_4^{20°}$.	$\dfrac{n-1}{d} \cdot M$.	Difference for CH_2.
Methylethylcarbinol	1·3954	0·8080	36·2	7·8
Methyl-n-propylcarbinol	1·4053	0·8103	44·0	7·8
Methyl-n-butylcarbinol	1·4135	0·8150	51·8	7·8
Methyl-n-amylcarbinol	1·4209	0·8185	59·6	7·8
Methyl-n-hexylcarbinol	1·4256	0·8214	67·4	7·8
Methyl-n-heptylcarbinol	1·4299	0·8230	75·2	7·9
Methyl-n-octylcarbinol	1·4344	0·8250	83·1	7·9
Methyl-n-nonylcarbinol	1·4369	0·8270	91·0	8·0
Methyl-n-decylcarbinol	1·4423	0·8315	99·0	
Ethyl-n-hexylcarbinol	1·4308	0·8260	75·1	
Phenylmethylcarbinol	1·5211	1·0135	63·7	7·4
Phenylethylcarbinol	1·5200	0·9940	71·1	
Methylisobutylcarbinol	1·4103	0·8077	51·8	

It is believed that the present paper shows that synthetical methods may be used to obtain accurate comparative values of the rotatory powers of optically active alcohols. It is hoped that the further investigation of several other series of alcohols and also of acids of similar constitution may give values which will be capable of easier interpretation in a quantitative manner than the results of those investigators who have preceeded the present authors in this field.

EXPERIMENTAL.

The Racemic Alcohols.

Of the fourteen racemic secondary alcohols which have been investigated, thirteen * have been prepared either by the interaction of an aldehyde and a Grignard reagent, or by the reduction of the corresponding ketone in aqueous alcoholic solution with sodium.

The reactions between acetaldehyde and magnesium ethyl bromide, magnesium propyl bromide (or chloride), and magnesium isobutyl bromide respectively; between n-heptaldehyde and magnesium ethyl bromide; between n-octaldehyde and magnesium methyl iodide, and

* Methyl-n-hexylcarbinol is obtained commercially by the distillation of a castor oil soap with sodium hydroxide.

between benzaldehyde and magnesium methyl and ethyl iodides all proceed smoothly, and were carried out in the usual manner, the cheaper reagent being used in slight excess.   In this way 50 to 70 per cent. yields were obtained of crude methylethylcarbinol (b. p. 92—99°),* methyl-*n*-propylcarbinol (b. p. 118—122°), † methyl*iso*-butylcarbinol (b. p. 125—132°), † ethyl-*n*-hexylcarbinol (b. p. 118—121°/65 mm.), methyl-*n*-heptylcarbinol (b. p. 91°/12 mm.), phenylmethylcarbinol (b. p. 100°/18 mm.),‡ and phenylethylcarbinol (b. p. 105—108°/10 mm.).‡

The reaction between magnesium *n*-butyl iodide and acetaldehyde gave only about 10 per cent. of the calculated yield of methyl-*n*-butyl-carbinol (b. p. 136°), whilst methyl-*n*-heptylcarbinol and methyl-*n*-octylcarbinol form a very small proportion of the products formed by the reactions between acetaldehyde and magnesium *n*-heptyl and *n*-octyl iodides.

The *n*-octaldehyde used was prepared from *n*-octyl alcohol by Sabatier's excellent method for the conversion of primary alcohols into the corresponding aldehydes.   The alcohol was heated in a flask, which was surrounded by a metal-bath kept at 200°.   A rapid current of pure hydrogen passing through this flask carried the alcohol to a glass tube of which 50 cm. were packed with pumice stone covered with finely divided copper, and which was heated to 300—315°.   The aldehyde was washed out of the condensed products by a solution of sodium hydrogen sulphite, and the process repeated four times with the unconverted alcohol.   The *sodium hydrogen sulphite* compound of *n*-octaldehyde was crystallised from aqueous alcohol, and obtained in nacreous leaflets, which did not melt below 270°.   Decomposition of this compound with a strong solution of sodium carbonate, distillation of the product in a current of steam, and subsequent rectification gave a 50 per cent. yield (calculated from the alcohol used) of *n*-octaldehyde (b. p. 77°/23 mm.).   No by-products were observed in this preparation, the loss being due very largely to inefficient condensation of the products carried over by the hydrogen.

The ketones required, $CH_3 \cdot CO \cdot R$, were prepared by passing the various acids, $R \cdot CO_2H$, mixed with five to seven times their weight of glacial acetic acid, over thorium oxide heated to 400° (Senderens, *Compt. rend.*, 1909, **149**, 995 *et seq.*).   The thoria was mixed with glass wool and loosely packed into a tube of Jena glass heated for 50 cm. of its length.   The normal acids used were hexoic, nonoic,

* Methylethylcarbinol requires careful and repeated fractionation to separate it from ether.

† Both of these crude alcohols contained paracetaldehyde.

‡ Each of these alcohols had a peculiar characteristic and pungent odour, which was not removed by repeated distillation, but was not present in the optically active isomerides.

undecoic, and lauric acid. The solutions of these in acetic acid were passed through the slightly inclined tube from a dropping funnel at an hourly rate of about 50 c.c. In each case the products were practically neutral, and no charring took place in the heated tube. Fractional distillation of the products gave from 70 to 90 per cent. yields (calculated from the weight taken of the acids named) of the ketones of the general formula $CH_3 \cdot CO \cdot R$, and from 30 to 10 per cent. yields of the ketones with the formula $R \cdot CO \cdot R$. The methyl n-amyl ketone prepared in this manner was identical with a sample of the same compound purchased from Schuchardt, which had been prepared by the distillation of a mixture of barium hexoate and acetate. Some properties of the ketones prepared are set out in table V.

TABLE V.

Ketone.			Melting point.	Boiling point.	Melting point of semicarbazone.*
Methyl n-amyl	ketone	....	—	150°	123·0°
Methyl n-octyl	,,	....	—	210	121·5
Methyl n-decyl	,,	....	20°	144°/11 mm.	122—123
Methyl n-undecyl	,,	....	29	160°/16 mm.	126·0
Diamyl	,,	....	—	223°	—
Dioctyl	,,	....	53	—	—
†Didecyl	,,	....	64	—	—
Diundecyl	,,	.........70—71		—	—

* All obtained from aqueous alcohol in the form of prismatic needles.

† The oxime of this ketone crystallises from aqueous needles in hair-like needles, which melt at 27·5°, and readily regenerates the ketone when boiled with dilute hydrochloric acid.

It will be seen that the semicarbazones are of little value for the characterisation of the ketones, $CH_3 \cdot CO \cdot R$, for these all melt at about 123°, whilst the ketones, $R \cdot CO \cdot R$ (where R contains more than five carbon atoms), do not form semicarbazones by the ordinary methods for the preparation of these compounds.

The nonoic and undecoic acids used in the preparation of the above-mentioned ketones were obtained in almost quantitative yields * by Darzens' method (*Compt. rend.*, 1907, **144**, 329), in which the ethyl esters of Δ^1-nonylenic acid † and commercial undecenoic acid were reduced by hydrogen in the presence of finely divided nickel heated to 180°.

* Thus, for example, in one set of experiments 300 grams of undecenoic acid were esterified and reduced. After hydrolysis of the resulting saturated ester and distillation of the acid, 260 grams of undecoic acid (m. p. 28°) were obtained. From this was prepared 174 grams of methyl n-decyl ketone along with a quantity of didecyl ketone, 43 grams of the acid being recovered ; 133 grams of methyl-n-decyl-carbinol were obtained by the reduction of this ketone.

† Δ^1-Nonylenic acid was prepared by the excellent method of Harding and Weizmann (*Trans.*, 1910, **97**, 299).

The ketones of the general formula $CH_3 \cdot CO \cdot R$, as described above, and also methyl n-butyl ketone and methyl n-nonyl ketone (purchased from Kahlbaum) were reduced in alcoholic solution by means of sodium, the procedure of Thoms and Mannich (*Ber.*, 1903, **36**, 2544) adopted for their reduction of methyl n-nonyl ketone being followed. The alcohols * thus obtained were (the yields varying from 70—80 per cent.) : methyl-n-butylcarbinol (b. p. 136°), methyl-n-amylcarbinol (b. p. 158—160°), methyl-n-octylcarbinol (b. p. 210—211°), methyl-n-nonylcarbinol (b. p. 119°/12 mm.), methyl-n-decylcarbinol (m. p. about 5°, b. p. 140°/15 mm.), and methyl-n-undecylcarbinol (b. p. 151°/11 mm.).

The Racemic Hydrogen Phthalic Esters.

The hydrogen phthalic esters were prepared by heating the alcohols with phthalic anhydride (equal mols.) for about ten hours at 115° in an oil-bath, except in the case of methylethyl- and methyl-n-propyl-carbinols, which were heated on a water-bath. The products, which generally contained some phthalic acid and unaltered an-hydride, were poured when cold into a solution of sodium carbonate. After keeping for some hours to allow of the hydrolysis of any anhydride, the alkaline solutions were extracted three times with ether to remove unesterified alcohols and neutral phthalic esters, both of which dissolve to a considerable extent in aqueous solutions of the sodium alkyl phthalates.* The acid esters were then precipitated by hydrochloric acid, either as oils or solids of low melting point, and were extracted with chloroform. Phthalic acid, being insoluble in dry chloroform, is thus readily removed, whilst the dried extracts after complete removal of the chloroform, at first on a water-bath, and finally under diminished pressure, consisted of the hydrogen phthalates in the form of opaque, crystalline masses. These acid esters are very soluble in all the common organic media, but some of them crystallise readily from light petroleum. The melting points of the racemic hydrogen phthalates are recorded in table IX, p. 63, along with those of the corresponding active compounds, whilst the composition and purity of each were checked by titration in alcoholic solution with sodium hydroxide.

The following compounds were also obtained :

Phenylmethylcarbinyl hydrogen phthalate,

$$CO_2H \cdot C_6H_4 \cdot CO_2 \cdot CHMe \cdot C_6H_5,$$
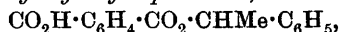
which crystallises in opaque leaflets from either glacial acetic acid or benzene, and melts at 108°.

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* All these alcohols were comparatively much purer than those obtained by the Grignard reactions.

† Such solutions cannot be warmed to 70° or above without undergoing some decomposition.

An *acid potassium* salt of β-butyl hydrogen phthalate,

$$CO_2K \cdot C_6H_4 \cdot CO_2 \cdot C_4H_9, CO_2H \cdot C_6H_4 \cdot CO_2 \cdot C_4H_9,$$

which crystallises from acetone in very slender needles, melts at 166—168°, and is decomposed by warm water.

Found, $K = 8 \cdot 07$. $C_{24}H_{27}O_8K$ requires $K = 8 \cdot 09$ per cent.

The Racemic Hydrogen Succinates.

Several acid esters of succinic acid were prepared by a method similar to that employed for the corresponding phthalates. They are, however, best extracted by ether instead of chloroform, traces of succinic acid being readily removed from the ethereal solutions by washing with water. The following carbinols gave hydrogen succinates in the form of viscous oils which did not solidify when kept at $-10°$: methylethyl-, methyl-*n*-propyl-, methyl-*n*-butyl-, methyl-*n*-nonyl-, methyl*iso*butyl-, and phenylethyl-carbinols, whilst that of phenyl-methylcarbinol crystallises from light petroleum in beautiful nacreous leaflets, and melts at 60—61°.

Brucine Salts of the Acid Esters.

The method adopted in each case for the preparation of the pure brucine salt of the dextrorotatory acid ester was : A solution of pure* racemic acid ester in acetone is boiled with the calculated amount (equal mols.) of brucine,† which is added in small portions at a time until the alkaloid is completely dissolved. The solution, having been filtered (if necesary) while warm, is then concentrated, and set aside in the ice-chest for some hours. The crop of crystals is collected and recrystallised several times under the same conditions. The first mother liquor when acidified yields a lævorotatory acid ester, and is used for the preparation of the pure lævorotatory alcohol, whilst that from the first recrystallisation yields an acid ester, which is usually slightly dextrorotatory, and can be conveniently used for the preparation of the strychnine salt of the pure dextrorotatory acid ester. The melting points and rotation of the brucine salts become constant after three to ten crystallisations, whilst in most cases the solubility in warm acetone decreases to a considerable extent as the salt becomes pure. The actual solubility of the pure salts of the phthalates varies considerably and most irregularly even in the homologous series described (see table VI) ; thus, for example, in the case of the member of the series corresponding with octane, 100 grams of the pure brucine salt would require about 10 litres of hot acetone to dissolve it,

* The success of the resolution largely depends on the purity of the acid ester.

† All the alkaloids mentioned in this paper were the purest commercial specimens supplied by Merck, and were recovered unchanged in rotation.

whilst the same quantity of the salt of that corresponding with nonane would require less than half a litre. The composition of the brucine salts, as well as of the other alkaloidal salts described in this paper, was determined by an estimation of the nitrogen content. In every case, as was to be expected, the salt contained one molecule of each component. The brucine salts of the acid esters of succinic acid are, as a rule, much more soluble in acetone than the salts of the corresponding phthalates. The following salts were also prepared : *Dibrucine phthalate*, $C_{54}H_{58}O_{12}N_4$, which crystallises from warm alcohol in glistening lamellæ, which melt and decompose at 113°, and are very slightly soluble in cold alcohol or chloroform. *Brucine hydrogen phthalate*, $C_{31}H_{32}O_8N_2$, which crystallises from alcohol in clusters of prismatic needles, melts at 216°, and when dissolved in chloroform has $[a]_D + 13 \cdot 52°$. *Brucine hydrogen succinate*, $C_{27}H_{32}O_8N_2$, crystallises from aqueous alcohol in needles, melts at 217—219°, and in absolute ethyl alcohol has $[a]_D - 17 \cdot 70°$.

TABLE VI.

Brucine Salts.

Brucine salt of the hydrogen phthalate of	Melting point.	Rotatory power * in ethyl alcohol.	
		Specific.	Molecular.
d-Methylethylcarbinol	154—155°	− 2·93°	− 18·1°
d-Methyl-*n*-propylcarbinol	154—155	− 3·91	− 24·6
d-Methyl-*n*-butylcarbinol	144—145	4·04	26·0
d-Methyl-*n*-amylcarbinol.........	137—138	4·42	29·1
d-Methyl-*n*-hexylcarbinol	151	5·44	36·6
d-Methyl-*n*-heptylcarbinol	140—142	4·97	34·1
d-Methyl-*n*-octylcarbinol.........	136—138	6·01	42·1
d-Methyl-*n*-nonylcarbinol	113—116	5·22	37·2
d-Methyl-*n*-decylcarbinol	123—124	6·06	44·1
d-Methyl-*n*-undecylcarbinol ...	120—122	5·69	42·2
d-Methyl*iso*butylcarbinol.........	167—168	4·19	26·9
d-Ethyl-*n*-hexylcarbinol	108—110	11·41	78·5
hydrogen succinate of			
d Phenylmethylcarbinol	110·5	+ 15·33	+ 94·4
d-Phenylethylcarbinol	103—105	16·28	100·2
l-Methyl*iso*butylcarbinol	95	− 22·41	− 133·6

* In all cases mentioned in this paper where the rotatory power of a compound has been observed in solution, the solution was prepared by making up 1 gram of the compound to 20 c.c. with the solvent.

Cinchonidine and Strychnine Salts of the Acid Esters.

The cinchonidine salts of the acid esters were prepared, as a rule, in the same way as the brucine salts, but when dissolved in hot acetone they often decompose and deposit the alkaloid. It was found preferable in some cases to adopt the following method, which was employed for the preparation of the strychnine salts : Equimolecular proportions

of the alkaloid and the acid ester are dissolved in chloroform ; the chloroform is then distilled off, and whilst the salt is still in the pasty condition, it is dissolved by the addition of the requisite amount of boiling acetone.   For each recrystallisation the salt is dissolved in chloroform, and a like procedure followed.

Most of the cinchonidine salts are very soluble in acetone, and do not crystallise at all readily from aqueous acetone. The strychnine salts of the optically pure acid esters are only very slightly soluble in cold acetone, and are always partly decomposed when boiled with acetone.   The strychnine salts described in table VIII were all prepared from samples of acid esters possessing a slight positive rotation.   Strychnine salts of the *dl*-hydrogen phthalates were unaltered in rotation by recrystallisation in the manner described, whilst the rotation of the strychnine salt of a partially active hydrogen phthalate of phenylmethylcarbinol was not affected by crystallisation.

TABLE VII.

Cinchonidine Salts.

Cinchonidine salt of the *hydrogen phthalate* of	Melting point.	Rotation in ethyl alcohol.	
		Specific.	Molecular.
l-Methyl-*n*-amylcarbinol	108—109°	− 70·36°	− 392·6°
l-Methyl-*n*-hexylcarbinol	112—116	68·02	389·0
l-Ethyl-*n*-hexylcarbinol................	115—118	60·47	354·3
hydrogen succinate of			
d-Methyl-*n*-butylcarbinol	89— 90	76·73	380·6
d-Methyl*iso*butylcarbinol	100—102	76·54	379·6
l-Phenylethylcarbinol	161—162	118·46	628·2

TABLE VIII.

Strychnine Salts.

Strychnine salt of the *hydrogen phthalate* of	Melting point.	Rotation in chloroform.	
		Specific.	Molecular.
d-Methylethylcarbinol............... ..	149—152°	− 20·04°	− 27·8°
d-Methyl-*n*-propylcarbinol	179—-181	− 18·56	30·7
d-Methyl-*n*-amylcarbinol	203—204	− 18·89	31·7
d-Methyl-*n*-hexylcarbinol	180	− 18·74	32·7
d-Methyl-*n*-heptylcarbinol	142—143	− 19·47	32·2
d-Methyl-*n*-octylcarbinol...............	136—137	− 18·37	34·8
d-Methyl-*n*-nonylcarbinol	144—145	− 17·11	38·2
d-Methyl-*n*-undecylcarbinol	142—143	− 18·69	36·6

*Optically Active Acid Esters of the Alcohols.**

The optically active acid esters were readily obtained from the brucine and cinchonidine salts when alcoholic solutions of these were

* Attempts were made to resolve the hydrogen tetrachlorophthalic esters of methylethyl-, methyl*iso*butyl-, methyl-*n*-propyl-, and methyl-*n*-butyl-carbinols by fractional crystallisation of the brucine and cinchonidine salts, but in no case was any resolution effected under the conditions tried.

poured into dilute hydrochloric acid.   Although the oily esters, which were at once precipitated, in many cases solidified to crystalline masses, it was generally found necessary to dissolve them in ether, so that by repeated washing with very dilute hydrochloric acid the hydrochloride of the alkaloid could be completely removed.   The strychnine salts were decomposed in a somewhat different manner. Alcoholic solutions of these were poured into dilute ammonia, and, after the strychnine had been removed by filtration, the acid esters were obtained on the addition of hydrochloric acid.

The acid phthalic esters (see table IX) were all obtained as crystalline masses after removal of the solvent, and in some cases are readily recrystallised from light petroleum, but, like the acid succinic acids and all the corresponding racemic compounds, they are very soluble in the common organic media.   The optically active acid succinic esters were only isolated in three cases, being usually hydrolysed at once. They are all oils, which decompose when distilled, so that the observed rotatory powers may be mis-leading, as the solvent (ether) may not have been completely removed. The hydrogen ·succinate of d-methyl*iso*butylcarbinol had $[a]_D + 14\cdot52°$ in chloroform, and the corresponding lævo-compound, $[a]_D - 14\cdot37°$; d-β-hexyl hydrogen succinate had $[a]_D + 6\cdot19°$ in chloroform, whilst the hydrogen succinate of phenylethylcarbinol had $a - 20\cdot06°$ in a 25-mm. tube.

The Optically Active Alcohols.

The alcohols, except in the case of methylethyl- and methyl-n-undecyl-carbinols, were obtained by the following method : The acid ester is dissolved in a hot concentrated aqueous solution of potassium hydroxides ($2\frac{1}{2}$ mols.), and the alcohol formed by the hydrolysis is distilled over in a current of steam.   It is then extracted from the distillate by ether, and the ethereal solution is dried by long keeping over freshly ignited potassium carbonate.

The optically active alcohols obtained were comparatively stable in the presence of alkali hydroxides.   Although as a matter of pre-caution they were removed from the prolonged action of potassium hydroxide as rapidly as possible by a current of steam during the hydrolysis, yet in two or three cases (notably those of methyl-n-hexyl-and methyl-n-undecyl-carbinols) by actual experiment it was found that the rotation was unaltered by continued boiling under a reflux condenser with aqueous alkalis.   The alcohols were obtained as colour-less, strongly refracting liquids or low melting solids.   They have faint characteristic odours, in all cases these being far less than those of the optically inactive isomerides.   There seems to be in some cases, for

TABLE IX.

The Hydrogen Phthalic Esters.

Hydrogen phthalate of	Melting point of		Rotations in				Origin of ester.†
			chloroform.		ethyl alcohol.		
	Racemic.	Active.	$[\alpha]_D$	$[M]_D$	$[\alpha]_D$	$[M]_D$	
Methylethylcarbinol	56—57°	*46—47°	+33·54°	+74·5°	+38·97°	+86·5°	B
	—		+33·51	+74·4	—	—	S
Methyl-n-propylcarbinol	*60—61	*34	+36·94	+87·2	—	—	S
Methyl-n-butylcarbinol	—	*29	+43·39	+108·5	+47·02	+117·5	B
	57—58	76·5	+43·89	+115·9	+48·64	+128·4	B
Methyl-n-amylcarbinol	—	—	+43·94	+116·0	—	—	S
	—	—	-43·81	-115·7	-48·52	-128·0	C
	55	—	+42·94	+119·3	+48·08	+133·7	B
Methyl-n-hexylcarbinol	—	75	-43·27	-120·3	-48·25	-134·2	C
	*42—44	58—59	+41·17	+120·1	+46·06	+134·5	B
Methyl-n-heptylcarbinol	—	—	+41·04	+119·9	—	—	S
	*48—49	*38—39	+39·01	+119·3	+45·19	+138·3	B
Methyl-n-octylcarbinol	—	—	+39·11	+119·7	—	—	S
	*49—50	*31—32	+37·34	+119·5	—	—	B
Methyl-n-nonylcarbinol	—	—	+37·19	+118·8	+44·29	+141·4	S
Methyl-n-decylcarbinol	50—51	*28	+35·59	+121·0	+43·41	+143·9	B
	58—59	*26	+35·54	+124·0	+41·13	+143·1	B
Methyl-n-undecylcarbinol	—	—	+35·13	+122·3	—	—	S
Ethyl-n-hexylcarbinol	47—49	54—55	+13·78	+19·9	+19·40	+27·9	B
	—	—	-13·62	-19·6	-19·45	-28·0	C

* Denotes a melting point determined of the crystalline mass drained on a porous tile without recrystallisation.

† B denotes from brucine salt; S from strychnine salt, and C from cinchonidine salt.

example, phenylethylcarbinol, a slight difference in the aroma of the dextrorotatory and lævorotatory forms.

Specimens of some of the alcohols of each type described were found to be unaltered in rotatory power after exposure to light for many months whilst stored in common glass bottles.   Several of them were reconverted into the hydrogen phthalic esters, these being readily obtained without recrystallisation with the maximum rotation observed, showing that at least these alcohols will not undergo racemisation when removed from natural products by the "phthalic anhydride" method (compare Haller, *Compt. rend.*, 1910, **151**, 697).   At least 30 c.c. of each of the active alcohols mentioned below have been obtained and the preparations repeated.   The densities have been determined in a pyknometer holding 3·5 c.c., and the rotations in jacketed tubes of 50 and 100 mm. long.

Methylethylcarbinol.—Since this alcohol is very difficult to separate from ether, it was "salted out" of the distillate obtained from the hydrolysis of the hydrogen phthalic ester by means of potassium carbonate.   Specimens of the dextrorotatory alcohol obtained from the brucine and strychnine salts of this acid ester agreed in rotatory power, this being unaltered by keeping over freshly-ignited barium oxide.

The dextrorotatory alcohol boiled at 99°/760 mm., had $d_4^{15·6}$ 0·8106, $_4^{27}$ 0·8025, $_4^{61·6}$ 0·7717, and $_4^{77·5}$ 0·7566 ; and $[a]_D$ +14·83° at 4·5°, +14·03° at 17·8°, +13·52° at 27°, +13·08° at 36·5°, +12·57° at 48·7°, +12·15° at 58°, +11·77° at 72°, and +11·83° at 91·7°.

The alkaloidal salts of the *l*-β-butyl hydrogen phthalate and of the corresponding succinates crystallise badly, and are decomposed when warmed with acetone.

Several attempts have been made by one of us and W. O. Littlebury to resolve this alcohol by the "menthylcarbimide" method (see Trans., 1906, **89**, 465, 1254).   dl-β-*Butyl* l-*menthylcarbamate*,

$$C_{10}H_{19}\cdot NH\cdot CO_2\cdot C_4H_9,$$
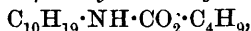
was readily obtained by warming equimolecular quantities of the carbinol and *l*-menthylcarbamide.   It crystallises in large prismatic tablets, which melt at 54°, and have M_D −162·4 in chloroform.

When recrystallised several times from aqueous ethyl alcohol, the melting point rose to 71°, and the molecular rotatory power fell to −152·4°.   The resolution, however, was not complete, as d-β-*butyl* l-*menthylcarbamate*, prepared from the dextrorotatory alcohol described above, melted at 72°, and had $[a]_D$ − 55·78° and M_D −142·2° in chloroform.   Experiments in this direction were not completed, as it was found impossible to hydrolyse the carbamate except by means of alcoholic potassium hydroxide, and then the separation of the carbinol from the ethyl (or methyl) alcohol used required too much material.

l-β-*Iodobutane.*—Several comparative experiments were carried out to determine the conditions for displacing the hydroxyl group of the carbinol by iodine without racemisation of the compounds. The product of highest lævorotatory power was obtained when the dextro-rotatory alcohol was saturated at 0° with hydrogen iodide (free from iodine) and warmed in a sealed tube for thirty minutes at a temperature not exceeding 60°. The lævorotatory iodo-compound thus prepared boiled at 118°, had d_4^{17} 1·5970, and $[\alpha]_D^{17}$ −31·98°. Attempts to convert this iodide into optically active methylethylcarbin-carbinol (*sec.*-butylcarbinol) by successive treatment with magnesium (in ethereal solution) and formaldehyde (trioxymethylene) gave negative results; under the conditions tried, the products were always optically inactive, racemisation probably taking place during the formation of the Grignard reagent.

d-*Methyl*-n-*propylcarbinol.*—This alcohol, prepared either from the brucine or the strychnine salt of the dextrorotatory hydrogen phthalic ester, boiled at 118·5—119·5°. Determinations of the density gave $d_4^{12\cdot3}$ 0·8169, $_4^{26\cdot8}$ 0·8058, $_4^{36\cdot8}$ 0·7967, $_4^{47\cdot3}$ 0·7871, $_4^{60\cdot5}$ 0·7751; and of the specific rotatory power: $[\alpha]_D^4$, +14·38°, +13·86° at 19°, +13·44° at 27·5°, +13·14° at 38°, +12 91° at 49°, +12·79° at 58·5°, +12·55° at 73°, and +12·56° at 90·5°.

l-β-*Iodopentane.*—This compound was prepared as follows: The dextrorotatory alcohol was saturated with pure hydrogen iodide at 0°, and heated at 100° in a sealed tube for thirty minutes. After purification in the usual manner, the iodide boiled at 143°, had d_4^{17} 1·5067, and $[\alpha]_D^{17}$ −37·15°.

d-*Methyl*-n-*butylcarbinol*, of identical rotatory power, was obtained from the brucine salt of the dextrorotatory hydrogen phthalic ester and from the cinchonidine salt of the dextrorotatory hydrogen succinic ester. It boiled at 137—138°, had $d_4^{16\cdot8}$ 0·8179, $_4^{37\cdot5}$ 0·8021, $_4^{50\cdot3}$ 0·7903, $_4^{71\cdot0}$ 0·7726, and $_4^{133}$ 0·7134, and $[\alpha]_D^7$ +12·08°, +11·60° at 19°, +11·45° at 26·8°, +11·27° at 35·7°, +11·05° at 48°, +10·87° at 59°, +10·77° at 72°, +10·77° at 93°, and +11·28° at 133°.

l-β-*Iodohexane* was prepared in a similar manner to the corresponding pentane derivative. It had d_4^{17} 1·4354, and $[\alpha]_D^{17}$ −38·35°.

d-*Methyl*-n-*amylcarbinol.*—This alcohol boiled at 73·5°/20 mm., had d_4^{20} 0·8190, $_4^{35}$ 0·8050, $_4^{51}$ 0·7920, $_4^{64}$ 0·7815, and $[\alpha]_D^{25}$ +10·21°, +10·14° at 31°, +9·95° at 46°, and +9·75° at 69·3°.

l-*Methyl*-n-*amylcarbinol* had very similar constants to the dextro-rotatory alcohol. It boiled at 74·5°/23 mm., had d_4^{20} 0·8184, and $[\alpha]_D^{3\cdot4}$ −10·52°, −10·48° at 17°, and −9·58° at 91°.

d- and l-*Methyl*-n-*hexylcarbinols.*—These alcohols (Pickard and Kenyon; *loc. cit.*) have been prepared in larger quantities than any of the other alcohols here described. The following additional

constants have been determined for the dextrorotatory compound: d_4^{25} 0·8170, d_4^{35} 0·8095, d_4^{46} 0·8019, and $[a]_D$ + 10·00° at 9°, + 9·51° at 25·5°, + 9·40° at 35·5°, + 9·19° at 48°, and + 8·98° at 91·5°.

dl-*Methyl*-n-*hexylcarbinol.*—Several investigators have observed that ordinary commercial methylhexylcarbinol (*sec.*-octyl alcohol) possesses a slight rotatory power. Samples supplied by Kahlbaum had a^{17} − 0·15° in a 2-dcm. tube. This alcohol was converted into the hydrogen phthalic ester, and recrystallised twice from glacial acetic acid and once from light petroleum. The alcohol recovered from this purified ester possessed approximately the same rotatory power. It was therefore assumed that the commercial alcohol contained a small amount of the *l*-alcohol. To it was then added the calculated amount of the *d*-alcohol, so that an inactive product was obtained. This was treated with phthalic anhydride, and the ester purified as before. The alcohol prepared by the hydrolysis of this thrice-recrystallised ester was found to be completely inactive. The experiments described below, in which an inactive methylhexylcarbinol was used, were carried out with a product prepared in this way.

Esters of Methyl-n-hexylcarbinol.

d-*β-Octylacetate*, $CH_3 \cdot CO_2 \cdot CHMe \cdot C_6H_3$.—This was obtained as a pleasant-smelling, mobile liquid, boiling at 86—88°/22 mm. It had d_4^{17} 0·8569, and $[a]_D^{17}$ + 7·65°, whilst when hydrolysed with potassium hydroxide it gave the optically pure *d*-alcohol.

d-*β-Octyl β-phenylpropionate*, $CH_2Ph \cdot CH_2 \cdot CO_2 \cdot CHMe \cdot C_6H_{13}$.—The acid was converted into the chloride by heating on the water-bath with the calculated amount of thionyl chloride. The product was then warmed with the *d*-alcohol until hydrogen chloride ceased to be evolved. The oily ester was then purified in the usual manner, and it was found that redistillation did not alter its rotatory power:

0·1176 gave 0·3354 CO_2 and 0·1036 H_2O. C = 77·78; H = 9·80.

$C_{17}H_{26}O_2$ requires C = 77·86; H = 9·92 per cent.

The ester is a transparent and odourless liquid of somewhat viscous character, which boils at 192—196°/27 mm., and has d_4^{17} 0·9483. The rotation observed in a 1-dcm. tube gave a_D + 11·56°, whence $[a]_D^{17}$ + 12·19°. A second preparation, made by the method of saturating a solution of the acid in the *d*-alcohol with hydrogen chloride, had $[a]_D^{17}$ + 12·26°.

The corresponding *laevo*-compound was prepared in a similar manner by the first of the methods indicated above. It boils at 200—202°/ 32 mm., and has d_4^{17} 0·9476. In a 1-dcm. tube it gave a_D − 11·85°, whence $[a]_D^{17}$ − 12·51°. From each of these two esters there were

recovered, by hydrolysis, alcohols with $[a]_D^{17} \pm 9.9°$. The corresponding inactive ester boils at 190—192°/27 mm., and has $d_4^{17}\,0.9815$.

Esters of Cinnamic Acid.—These were prepared by passing hydrogen chloride for forty-five minutes through a mixture of equivalent proportions of the alcohols and cinnamic acid, which was kept at 110°. The esters were purified in the usual manner, and were obtained as clear, colourless liquids without odour.

The d-*β-octyl cinnamate* thus prepared boiled at 218°/28 mm., had $d_4^{17}\,0.9694$, and in a 50-mm. tube $a^{17} + 19.48°$, whence $[a]_D^{17} + 40.19°$. The alcohol recovered from this ester had $[a]_D + 9.66°$. The ester, which was quite free from chlorine, when repeatedly treated with aluminium amalgam in moist ethereal solution was quantitatively converted into the corresponding ester of β-phenylpropionic acid, which had $[a]_D^{17} + 12.36°$.

The corresponding *laevo*-ester boiled at 211°/23 mm., had $d_4^{17} + 0.9692$, and $[a]_D^{17} - 39.78°$, whilst the *dl*-ester boiled at 213°/28 mm., and had $d_4^{17}\,0.9715$:

0.1261 gave 0.3620 CO_2 and 0.1065 H_2O.   C = 78.51 ; H = 9.38.
$C_{17}H_{24}O_2$ requires C = 78.46 ; H = 9.23 per cent.

Esters of Phenylpropiolic Acid.—The esters of phenylpropiolic acid were prepared in the same manner as those of cinnamic acid. They were obtained free from chlorine, and when hydrolysed gave the optically pure alcohols. They are colourless, highly refractive liquids, which possess faint odours. The d-ester boiled at 206—208°/ 20 mm., had $d_4^{17}\,0.9823$, and in a 50-mm. tube gave $a^{17°} + 24.95°$, whence $[a]_D^{17} + 50.80°$. Repeated treatment with aluminium amalgam in moist ethereal solution converted the unsaturated ester into the corresponding derivative of β-phenylpropionic acid, which had $[a]_D^{17} + 12.06°$. The *l*-ester boiled at 209°/27 mm., had $d_4^{17}\,0.9719$, and gave $a^{17} - 12.33°$ in a 25-mm. tube, whence $[a]_D^{17} - 50.75°$. The *dl*-ester boiled at 228—231°/48 mm., and had $d_4^{17}\,0.9757$.

Esters of the Tartaric Acids.—The rotatory powers of the esters of the tartaric acids with the methyl-*n*-hexylcarbinols have been determined in the hope that the results might be useful in supporting the conclusions of Patterson (Trans., 1907, **91**, 705) as to the non-validity of van't Hoff's theory of optical superposition. The rotatory powers observed were not in accordance with this theory, but owing to the failure of all attempts to prepare the corresponding esters of *i*-tartaric acid these results do not give a strict proof of its von-validity, such as Patterson has furnished in his work on the menthyl tartrates. McCrae has described ethyl β-octyl d-tartrate (Trans., 1901, **79**, 1103) and di-β-octyl d-tartrate (Trans., 1902, **81**, 1221) as viscous oils with a rancid odour, and the latter as having a yellow colour. The esters mentioned

in table X have all been obtained as highly-refracting, colourless liquids, somewhat viscous and practically odourless. The preparation of the di-β-octyl tartrates is readily carried out as follows: 40 grams of the required methyl-n-hexylcarbinol and 10 grams of the diethyl ester of the tartaric acid are mixed and saturated at a temperature below 0° with hydrogen chloride. After some days, the hydrogen chloride and about 5 c.c. of the mixture are distilled off under diminished pressure on a water-bath. The main bulk of the mixture is then again saturated with hydrogen chloride as before, and kept for a week. The excess of alcohol, along with the hydrogen chloride, is now removed by distillation under a pressure of about 20 mm., and the ester carefully fractionated under a pressure of about 6 mm. One distillation is generally sufficient to give a product of constant rotation, the neutral esters boiling between 202° and 210°/6 mm.

In view of the discrepancy between McCrae's results and those here recorded, specimens of di-β-octyl d-tartrate were prepared from Kahlbaum's alcohol (with a slight lævorotation) and both diethyl and dimethyl d-tartrate, each preparation being found to have $[a]_D^{17} + 10 \cdot 99°$, whereas McCrae's value is $[a]_D^{18} + 7 \cdot 06°$. Similar preparations from the pure dl-alcohol and diethyl and dimethyl d-tartrates had $[a]_D^{17} + 11 \cdot 18°$ and $+ 11 \cdot 02°$ respectively. In the preparation of these esters from Kahlbaum's alcohol it was found that the rotation of the unesterified alcohol varied slightly from that of the original sample. As purchased, it had, in a 2-dcm. tube, $a - 0 \cdot 14°$ to $- 0 \cdot 17°$, whilst the unesterified alcohol had $a - 0 \cdot 05°$ to $- 0 \cdot 07°$. In the course of the lengthy series of experiments summarised on p. 48, ethyl dl-β-octyl d-tartrate was isolated. It boils at 187—190°/7 mm., has $d_4^{17} 1 \cdot 0568$, and $[a]_D^{17} + 8 \cdot 55°$, a value higher than that recorded by McCrae (*loc. cit.*), who gives $[a]_D^{16} + 7 \cdot 63°$.

Attempts to prepare the pure β-octyl esters of i-tartaric acid were failures, these compounds apparently decomposing before distillation.*

TABLE X.

The Di-β-Octyl Esters of the Tartaric Acids.

Specific Rotatory Powers and Densities.

		d-Tartaric acid.	l-Tartaric acid.	r-Tartaric acid.
d-Methyl-n-hexylcarbinol,	$[a]_D^{17}$ ...	$+ 24 \cdot 06$	$+ 2 \cdot 06$	$+ 14 \cdot 12$
	d_4^{17}	$1 \cdot 0165$	$1 \cdot 0081$	$1 \cdot 0047$
l-Methyl-n-hexylcarbinol,	$[a]_D^{17}$ ...	$- 1 \cdot 93$	$- 24 \cdot 20$	$- 14 \cdot 03$
	d_4^{17}	$1 \cdot 0171$	$1 \cdot 0059$	$1 \cdot 0058$
dl-Methyl-n-hexylcarbinol,	$[a]^{17}$ ...	$+ 11 \ 02$	$- 11 \cdot 00$	—
	d_4^{17}	$1 \cdot 0148$	$1 \cdot 0069$	—

* The authors are greatly indebted to Dr. M. O. Forster, F.R.S., who attempted to distil a sample of one of these esters. He found that violent decomposition set in at about 160° when the pressure was only 0·5 mm.

*Halides Corresponding with the Methyl-*n-*hexylcarbinols.*

d- and *l-*Methyl-*n*-hexylcarbinols react fairly readily with hydrogen iodide, bromide or chloride, the formation of the halide being accompanied by a change in the sign of the rotation. The β-iodo-octanes are obtained when the alcohols are saturated at 0° with hydrogen iodide and kept for about five hours. In the case of the bromides and chlorides, the mixtures similarly prepared are heated at 100° in sealed tubes for one hour.

These halides are partly racemised if the reactions are not carried out under the above conditions, higher temperatures or prolonged heating always resulting in the products formed being of lower rotatory power. All the preparations obtained were unaltered in rotatory power after prolonged shaking with cold concentrated sulphuric acid. These active halides do not appear to undergo autoracemisation, as a specimen of *l-β*-bromo-octane was found to be unaltered in rotatory power two and a-half years after its preparation.

Various constants for these halides are given in table XI; the following additional ones were determined for *l-β*-bromo-octane : $d_4^{13\cdot8}$ 1·0927, d_4^{26} 1·0805, d_4^{37} 1·0688, and d_4^{53} 1·0532 ; $[a]_D$ $-31\cdot07°$ at 4°, $-30\cdot33°$ at 13·1°, $-29\cdot05°$ at 30°, $-28\cdot62°$ at 37·4°, $-27\cdot81°$ at 50°, $-26\cdot56°$ at 69°, and $-25\cdot18°$ at 92°.

TABLE XI.

*Halides from Methyl-*n-*hexylcarbinol.*

	Boiling point.	d_4^{17}.	a^{17} in 50-mm. tube.	$_D^{17}$.
d-β-Iodo-octane	101°/22 mm.	1·3314	$+26\cdot51°$	$+39\cdot83°$
l-β-Iodo-octane	92°/12 ,,	1·3299	$-26\cdot97$	$-40\cdot56$
d-β-Bromo-octane ...	74°/18 ,,	1·0895	$+14\cdot98$	$+27\cdot53$
l-β-Bromo-octane ...	71°/14 ,,	1·0914	$-14\cdot99$	$-27\cdot47$
d-β-Chloro-octane ...	75°/28 ,,	0·8658	$+8\cdot83$	$+20\cdot40$
l-β-Chloro-octane ...	70°/25 ,,	0·8628	$-8\cdot82$	$-20\cdot44$

Several experiments were carried out in which the halides were treated under varying conditions with potassium acetate. Although in every case the resulting β-octyl acetate had a rotation opposite in sign to the halide used, yet it was never obtained optically pure, some racemisation invariably taking place during the formation of the acetate, whilst possibly the halides themselves were not optically pure.

d-*Methyl*-n-*heptyl*-, d-*Methyl*-n-*octyl*-, and d-*Methyl*-n-*nonyl-carbinols.*

These were each prepared in two ways, namely, from the brucine and from the strychnine salts of the dextrorotatory hydrogen phthalic esters.   The following constants were determined :

d-*Methyl*-n-*heptylcarbinol* boiled at 105°/19 mm., had $d_4^{13\cdot1}$ 0·8281, $_4^{25}$ 0·8202, $_4^{34\cdot2}$ 0·8129, $_4^{45\cdot5}$ 0·8043, $_4^{76}$ 0·7799, and $[\alpha]_D$ +8·98° at 19°, +8·88° at 26·5°, +8·71° at 34°, +8·55° at 49·5°, +8·44° at 66°, and +8·39° at 72°.

d-*Methyl*-n-*octylcarbinol* boiled at 110—111°/11 mm., had $d_4^{14\cdot3}$ 0·8293, $_4^{24\cdot5}$ 0·8220, $_4^{42\cdot3}$ 0·8096, $_4^{61}$ 0·7935, and $_4^{146}$ 0·7222, and $[\alpha]_D$ +8·74° at 17°, +8·55° at 26·4°, +8·37° at 35·4°, +8·02° at 58·9°, +7·75° at 93°, and +7·81° at 146°.

d-*Methyl*-n-*nonylcarbinol* boiled at 128°/20 mm. and solidified when cooled to a mass of stellate needles, which melted at 12°.   It had d_4^{14} 0·8318, $_4^{27\cdot1}$ 0·8226, $_4^{37\cdot5}$ 0·8145, $_4^{54\cdot9}$ 0·8017, $_4^{72\cdot5}$ 0·7896, and $[\alpha]_D$ +8·40° at 6°, +8·18° at 18°, +8·03° at 25·7°, +7·88° at 35°, +7·67° at 48·7°, +7·55° at 59°, +7·34° at 73°, and +7·27° at 92°.

d-*Methyl*-n-*decylcarbinol*, obtained from the brucine salt of the dextrorotatory hydrogen phthalic ester, boiled at 146°/24 mm., and, when cooled, set to a mass of stout, prismatic rods in a crystalline matrix.   This melted at 18·7°, had $d_4^{12\cdot}$ 0·8369 (in a supercooled condition), $_4^{27\cdot4}$ 0·8265, $_4^{38\cdot9}$ 0·8182, $_4^{51\cdot2}$ 0·8090, $_4^{60\cdot6}$ 0·8016, and $[\alpha]_D$ +7·80° at 19°, +7·66° at 27°, +7·51° at 36·5°, +73·2° at 46·5°, +7·15° at 57·5°, +7·00° at 71°, and +6·88° at 93°.

d-*Methyl*-n-*undecylcarbinol*, obtained either from the brucine or strychnine salt of the dextrorotatory phthalic ester, boiled at 156—157°/17 mm., and set to a glistening, crystalline mass of prismatic needles, which melted at 30°.   It had $d_4^{34\cdot1}$ 0·8215, $_4^{47\cdot3}$ 0·8109, $_4^{60\cdot6}$ 0·8012, and $[\alpha]_D$ +7·10° at 25·5° (when supercooled), +6·98° at 33·5°, +6·74° at 48°, +6·55° at 56·5°, +6·42° at 71·9°, and +6·37° at 93°.

d-*Methyl*isobutylcarbinol* was obtained from the brucine salt of the dextrorotatory hydrogen phthalic ester and from the cinchonidine salt of dextrorotatory hydrogen succinic ester.   It boiled at 65·5°/45 mm., had d_4^{19} 0·8083, $_4^{28}$ 0·8014, $_4^{50}$ 0·7824, $_4^{75\cdot5}$ 0·7596, and $[\alpha]_D$ +21·35° at 6·3°, +20·86° at 14°, +20·4° at 21·3°, +20·04° at 29·5°, +19·69° at 38·7°, +19·48° at 43°, +19·11° at 57°, +18·65° at 72°, and +18·25° at 94·3°.

l-*Methyl*isobutylcarbinol*, obtained from the brucine salt of the lævorotatory hydrogen succinic ester, had $[\alpha]_D^{14}$ −20·80°.

d-*Ethyl*-n-*hexylcarbinol*, obtained from the brucine salt of the dextro-rotatory hydrogen phthalic ester, boiled at 97°/17 mm., had $d_4^{16\cdot3}$ 0·8281, $_4^{26\cdot3}$ 0·8202, $_4^{37\cdot9}$ 0·8129, $_4^{54\cdot4}$ 0·8043, $_4^{78\cdot5}$ 0·7799, and $[\alpha]_D$ +8·09° at 6·1°

+8·05° at 20·6°, +8·13° at 37·8°, +8·14° at 48·2°, and +8·27° at 70·5°.

l-*Ethyl*-n-*hexylcarbinol*, obtained from the cinchonidine salt of the lævorotatory hydrogen phthalic ester, boiled at 94°/13 mm., had d_4^{17} 0·8277, and $[a]_D^{17}$ − 7·96°.

Table XII shows some of the properties of the γ-chloro-, bromo-, and iodo-nonanes, which were prepared by the methods used in the case of the corresponding β-octane derivatives. In each case the alcohol yielded a halogen derivative with a rotatory power of opposite sign.

TABLE XII.

γ-*Halogen Derivatives of* n-*Nonane.*

	Boiling point.		d_4^{17}.	$[a]_D^{17}$.
d-γ-Chlorononane	87—89°/24 mm.		0·8588	+7·71°
l-γ-Chlorononane	101°/40	,,	0·8540	−8·03
d-γ-Bromonouane	112°/32	,,	1·0900	+12·90
l-γ-Bromononane	96—97°/22	,,	1·0897	−13 39
d-γ-Iodononane	120°/27	,,	1·2940	+17·65
l-γ-Iodononane	122°/37	,,	1·2873	−17·50

d-*Phenylmethylcarbinol*, $C_6H_5 \cdot CH(OH) \cdot CH_3$, obtained from the brucine salt of the dextrorotatory hydrogen succinic ester, boiled at 100°/18 mm., had $d_4^{13\cdot3}$ 1·0191, $_4^{26\cdot2}$ 1·0079, $_4^{35\cdot2}$ 1·0019, $_4^{48}$ 0·9911, $_4^{55\cdot4}$ 0·9846, $_4^{80\cdot2}$ 0·9646, and $[a]_D$ +42·90° at 6°, +42·85° at 27°, +42·74° at 36·8°, +42·69° at 47°, +42·53° at 58°, +42·27° at 71°, and +41·33° at 94°.

d-*Phenylethylcarbinol*, obtained from the brucine salt of the dextro-rotatory hydrogen succinic ester, boiled at 115—116°/25 mm., had d_4^{17} 0·9962, and $[a]_D^{17}$ + 27·35°.

l-*Phenylethylcarbinol*, obtained from the cinchonidine salt of the corresponding lævorotatory ester, boiled at 115—116°/25 mm., had $d_4^{13\cdot8}$ 0·9982, $_4^{28\cdot8}$ 0·9872, $_4^{42\cdot7}$ 0·9755, $_4^{69\cdot5}$ 0·9538, and $[a]_D$ − 24·76° at 5·3°, − 26·83° at 15·2°, − 29·07° at 27·2°, − 30·34° at 35°, − 33·90° at 64·5°, and − 35·58° at 94°.

The corresponding chloro-compounds were obtained when these three alcohols were saturated at 0° with hydrogen chloride and kept for some hours.

l-α-*Chloroethylbenzene*, $C_6H_5 \cdot CHCl \cdot CH_3$, from the dextrorotatory carbinol, boiled at 86°/22 mm., had d_4^{17} 1·0642, and $[a]_D^{17}$ − 5·80°.

The lævorotatory phenylethylcarbinol yielded d-α-*chloropropylbenzene*, which boiled at 86—87°/15 mm., had d_4^{17} 1·0429, and $[a]_D^{17}$ + 3·79°. The corresponding dextrorotatory chloro-compound boiled at 95°/25 mm., and had d_4^{17} 1·0430 and $[a]_D^{17}$ − 3·87°.

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