CCVII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part IV.**
The Rotations of the Normal Secondary Alcohols of the Formula $C_2H_5 \cdot CH(OH) \cdot R$.

By ROBERT HOWSON PICKARD and JOSEPH KENYON.

SEVERAL optically active carbinols of the general formula $R^1 \cdot CH(OH) \cdot R^2$ have already been synthesised and described (*loc. cit.*); of these, ten belong to the series of the formula

(hereafter called the "methyl" series), and eight belong to the series of the formula $CH(CH_3)_2 \cdot CH(OH) \cdot R$ (hereafter called the "isopropyl" series) (where R in each case represents a normal aliphatic radicle). Another series containing thirteen similar carbinols of the formula $C_2H_5 \cdot CH(OH) \cdot R$ having been now prepared, it is possible to contrast the rotatory powers of the members

* For Part I of this series see T., 1911, **99**, 45; Part II, T., 1912, **101**, 620, and Part III, *ibid.*, 1427.

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of this "ethyl" series with those of the members of the "methyl" and "isopropyl" series, since the corresponding members of each series only differ from one another as regards chemical constitution in containing the methyl, isopropyl, or ethyl groups.

In Fig. 4 (p. 1929) it will be seen that in the "methyl" series $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{R}$, where R =propyl to undecyl, the molecular rotatory powers of the carbinols in the homogeneous state (at least at the boiling points) increase regularly as the molecular weight

FIG. 1.

and size of the growing chain R increases, whilst the figures in table I, Part II, and Fig. 3 (p. 1927) show that in the "isopropyl" series the molecular rotatory powers of the carbinols in the homogeneous state increase rapidly until R =butyl, the higher members of the series having molecular rotatory powers only slightly higher than, or possibly equal to, that of the member with R =butyl.

It is now found that in the homogeneous state the molecular rotatory powers of the members of the ethyl series (see table I and Fig. 1) offer a decided contrast to those of each of the other series.

They increase slowly but definitely as the growing chain R increases in size from propyl to (at least) pentadecyl, but in addition to this normal increase (indicated by the dotted line in Fig. 1), there is a further increase in the molecular rotatory power exhibited by those members of the series in which the growing chain contains 5 (or 6), 10 (or 11), and 15 carbon atoms. This exaltation from the normal increase is greater when the growing chain contains five than when it contains ten carbon atoms, and is far less pronounced in the member containing fifteen carbon atoms in the growing chain.

TABLE I.

Rotatory Powers of the Normal Secondary Alcohols of the Formula $C_2H_5 \cdot CH(OH) \cdot R$.

R. (A normal alkyl group.)	In the homogeneous state.				Dispersion.* $\alpha_D/\alpha_{H\>green}$	In 5 per cent. solution in	
	$[\alpha]_D^{20^\circ}$	$[M]_D^{20^\circ}$	$[\alpha]_{gr}^{20^\circ}$	$[M]_{gr}^{20^\circ}$		ethyl alcohol $[M]_D^{20^\circ}$	benz- ene. $[M]_D^{20^\circ}$
Methyl	13.87°	10.30	16.09	11.91	0.845	10.77	10.44
Ethyl	Optically inactive.						
Propyl	1.97	2.01	2.24	2.29	(0.88)‡	1.17	1.87
Butyl	8.13	9.43	9.58	11.11	0.850	11.17	10.80
Amyl	8.22	10.69	9.64	12.53	0.856	14.47	13.26
Hexyl	7.38	10.63	8.63	12.43	0.858	13.86	13.82
Heptyl	6.68	10.58	7.76	12.26	0.864	9.81	12.11
Octyl	6.25†	10.74†	7.23	12.43	0.863	10.69	12.18
Nonyl	5.97†	11.09†	6.92	12.86	0.866	11.35	12.48
Decyl	6.23†	12.44†	7.21	14.42	0.865	13.46	14.62
Undecyl	5.87†	12.56†	6.80	14.55	0.865	13.38	15.30
Dodecyl	5.53†	12.61†	6.40	14.59	0.865	12.44	15.32
Tridecyl	5.11†	12.38†	5.92	14.32	0.863	12.75	15.44
Tetradecyl	(Has not been prepared)						
Pentadecyl	4.77†	12.88†	5.49	14.83	0.865	12.91	16.63

* These figures represent the average value of the rotatory dispersive powers calculated at intervals of 20° from 20° to 160° (or to the boiling points of the carbinols) as given in table II.

† Values at 20° extrapolated from curves based on observations recorded on p. 1954. These carbinols melt at about or above 20°.

‡ See footnote, p. 1931.

Frankland has already suggested (T., 1899, 75, 368) that a maximum (or constant) rotatory power in a homologous series of optically active compounds would probably be attained when the growing chain contained five or six carbon atoms, since it is at that part of the series where it is expected from stereochemical considerations that the growing chain would all but return on itself. Our results appear to show conclusively that in the "ethyl" series, $C_2H_5 \cdot CH(OH) \cdot R$, there is a continuous gradual increase in the molecular rotatory powers as the growing chain increases, with

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a further special exaltation each time that the growing chain of carbon atoms returns on itself.

When discussing some of our previous results, Frankland (T.,

FIG. 2.

1912, 101, 660) suggested that some solvents like alcohol might "permit of a more unrestricted development of the rotatory effect of the homologous group (growing chain) than is the case when the

same compounds are examined in the liquid condition." This is actually the case when these carbinols are examined in ethyl-alcoholic solution. Thus, as will be seen from Fig. 2, the values of the rotatory powers of the members of the "ethyl" series follow those obtained when they were examined in the homogeneous state, but the effect due to the special stereochemical configuration of the growing chain when this contains about five or ten carbon atoms is much more pronounced. Similar results are obtained when the carbinols are examined polarimetrically in benzene solution. This same effect is also to be observed when the carbinols of the *isopropyl* series are examined in ethyl-alcoholic solution.

FIG. 3.

Thus (see Fig. 3), in the homogeneous state, an approximately constant value of the molecular rotatory power is reached for the butyl member, but in ethyl alcohol it is at the amyl member that the approximately constant value of the molecular rotatory power is attained. When the members of the "methyl" series are examined in ethyl alcohol or in benzene, the values obtained for the molecular rotatory powers (Fig. 4) are at first sight very confusing. Maxima on the irregular curves will be observed corresponding with methylpropylcarbinol, methylamylcarbinol, methyloctylcarbinol, and methyldecylcarbinol, and the curves are in striking contrast to the regular curve show-

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ing the values of the molecular rotatory powers determined at the boiling point of the carbinols in the homogeneous state. The maxima on these curves, corresponding with methylamyl- and methyldecyl-carbinols are, of course, to be attributed to the special configuration of the growing chain. However, adopting a different nomenclature, methylpropylcarbinol, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{C}_3\text{H}_7$, and methyloctylcarbinol, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{C}_8\text{H}_{17}$, can be designated pentan- β -ol and decan- β -ol. It will now be seen that the maxima corresponding with these two carbinols containing five and ten carbon atoms respectively in the molecule can be attributed to the special configuration of the *normal chain of carbon atoms comprising the whole molecule*. So that the polarimetric examination of these solutions has afforded most conclusive evidence of the special effect that a normal chain of five (or ten) carbon atoms has on the rotatory power of a compound. In the "ethyl" series $\text{C}_2\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{R}$, a similar effect where the compounds (as distinct from the growing chain) contain five or ten carbon atoms, has not been observed—pentan- γ -ol (diethylcarbinol) is symmetrical, and therefore optically inactive, whilst the values obtained for the molecular rotatory power of decan- γ -ol (ethylheptylcarbinol) occupy a normal position on the three curves illustrating the observations in the homogeneous state, in ethyl-alcoholic solution and in benzene solution. The results recorded in this paper appear then to afford a very striking confirmation of Frankland's suggestion made fourteen years ago. Although this was based on the then conventional idea of the rigid tetrahedron model of the carbon atom, yet it, in common with theories such as Baeyer's Strain Theory, is not upset by more modern conceptions of the carbon atom. The carbon atom can be imagined to be a sphere with valency (or combining force) radiating from the centre like "lines of force" to the surface of the sphere (Werner). The further postulation of a greater concentration of the forces about the points of contact of the sphere with a regular tetrahedron circumscribed by it would explain perhaps better than the older idea of the rigid tetrahedron model the peculiar effect of a chain containing about five carbon atoms on the rotatory power of the compound.

The opinion of the authors, expressed in Part I (p. 47, *loc. cit.*), that in a reinvestigation of the problem of the relation between rotatory power and chemical constitution it was desirable to restrict the polarimetric examinations to those of liquids in the homogeneous state is now shown to be untenable. It is obvious that some effects due to the configuration of the molecule are only to be observed in solution, and are marked at all temperatures up

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FIG. 4.

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to the boiling point, when the compounds are examined in the homogeneous state.*

There does not appear to be any simple numerical relation between the various values obtained for the molecular rotatory powers of the members of these homologous series, and it does not seem probable from the results obtained (even after giving due weight to the obvious objection that they relate to only one class of compounds) that any such numerical relation exists between the rotatory powers of the members of any homologous series.

The following hypothesis based merely on a consideration of the space occupied by the four groups attached to the asymmetric carbon atom appears to explain the results obtained for the three series of carbinols as well as those obtained for eight series of simple esters derived from the "methyl" series of carbinols which will be described in Part V.

In a homologous series of optically active compounds represented by $Cabcd$, the usual effect of increasing the size of d (representing the growing chain) is to alter in a regular manner (usually to increase) the molecular rotatory power of the compounds. When the groups (or atoms) represented by a , b , and c occupy a relatively small space, as, for example, in the "methyl" series of carbinols, $CH_3 \cdot CH(OH) \cdot R$, the values of the molecular rotatory powers of the homogeneous compounds increase regularly with the increasing size of the chain, and only in solution are affected by the peculiar configuration of the chain, when this returns on itself.

When, however, the space occupied by the groups (or atoms) represented by a , b , and c is larger, the increase in molecular rotatory power as d increases in size may become less regular; either (i) it may be specially affected, when the chain returns on itself, as in the "ethyl" series, $C_2H_5 \cdot CH(OH) \cdot R$, or (ii) there may be a relatively large increase until d contains five carbon atoms with an increase of a much smaller order beyond, as, for example, in a series of esters, such as those of *sec.*-octyl alcohol with normal aliphatic acids,† in which there is a large increase in the value of the molecular rotatory power for each member of the series up to the *n*-valerate, and a still further, but relatively much smaller, increase for each member from the valerate to the palmitate; or (iii) when the space occupied by the groups a , b , and c is still greater, an "approximate maximum" is reached when the growing chain contains fewer than five carbon atoms, as, for

* This point has an obvious bearing on the assumed connexion between association and alteration of rotatory power in various solvents, and will be discussed in the next paper of this series.

† See Part V.

example, for the carbinols of the "isopropyl" series,

(when these are examined in the homogeneous state), and in a series* of *n*-dodecoates of the "methyl" carbinols,

in both of which the values of the molecular rotatory power increase rapidly up to that for the member with R containing four carbon atoms with a much smaller increment for the higher members.

Optical Dispersion.

The rotations of the carbinols of the three series have been determined for yellow (sodium) and green (mercury) light at temperatures from 20° to 160° (or to the boiling points of the carbinols). For each carbinol the dispersion value appears to be a constant (within the possible experimental error) over the range of temperature employed. Similar results have now been obtained by the authors in the case of ten series of compounds, so that optical dispersion may be considered generally to be independent of the temperature, as Walden has already assumed from his investigation of five esters of ricinoleic acid (*Ber.*, 1903, **36**, 781). The differences in the values of the dispersive power of the various members of a series of homologous compounds do not run parallel with the variations in the rotatory powers; thus, in the "methyl" series, all the members from the propyl to the undecyl have the same dispersive power (yellow/green 0·847), whilst that for the ethyl member is slightly less (0·840). Similar results have been obtained for the "isopropyl" series, each of the carbinols from the ethyl to the decyl member of this series having the same value for the dispersion (0·842), which varies from that of the methyl member; whereas in the "ethyl" series the methyl member (which is, of course, the ethyl member of the "methyl" series) with the value 0·840, and the propyl member with the value 0·88,† have dispersive powers varying widely from those of the butyl, amyl, and hexyl members, which have yellow/green values 0·850, 0·856, 0·858 respectively, thus approaching the constant value 0·865 given by the other (heptyl to pentadecyl) members of the series. These variations from the constant for the series are difficult to explain, but will be further discussed in a paper with Dr. T. M. Lowry, who has made some very accurate determinations of the dispersive

* See Part V.

† Owing to the low rotatory power of the carbinol this value is probably not as accurate as the others given. There is, however, no doubt that the value of dispersive power (yellow/green) is much higher than that for the other members of the series.

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powers of these carbinols at 20°, the results of which agree with those obtained by the present authors over the wide range of temperature employed.

Effect of Temperature on the Rotatory Powers.

The rotatory powers of the carbinols of the "ethyl" series are affected only very slightly by an increase of temperature, except in the case of methylethylcarbinol, which, although common to both the "methyl" and "ethyl" series, possesses physical constants abnormal to each. The effect of temperature on the rotatory powers is very much less in the "ethyl" than in the "methyl" and "isopropyl" series; so slight is this that it is difficult (considering the possibility of experimental error) to determine definitely any singular points in the temperature-rotation curves. Table II shows the values obtained from the smoothed curves at temperatures from 20° to 160°. There do not appear to be any obvious regularities in the temperature-rotation curves. Thus, for the propyl, butyl, and amyl members of the series, the molecular rotatory powers increase with the temperature up to the neighbourhood of their boiling points; for the hexyl, heptyl, and octyl members they increase to a maximum at about 120°, 80°, and 140° respectively; for the nonyl, decyl, and dodecyl members, the rotatory powers decrease as the temperature increases up to about 130°, and then fall as the temperature rises further, whilst for the undecyl, tridecyl, and pentadecyl members they decrease slowly as the temperature increases up to 160°. In nearly all these cases the variation in the molecular rotatory powers is not much larger than the possible experimental error in their determination. A comparison of the maximum values of the expression $[M]_D^{25}$ (as suggested by Patterson, this vol., p. 147) does not bring out any fresh regularities, at least between the limits $t^\circ = 20^\circ$ to 160° .

General Properties of the Optically Active Carbinols.

The members of the "ethyl" series of carbinols have not been described previously in the optically active form, except *d*-methyl-ethylcarbinol, *d*- and *l*-ethylhexylcarbinol (see Part I., *loc. cit.*), and *d*-ethyl-*n*-amylcarbinol. The latter has been recently isolated in the laboratory of Messrs. Schimmel (Semi-Annual Reports, April, 1912, 103, and April, 1913, 82) from the by-products of low boiling point obtained in the rectification of menthol, and from this source had a rotatory power slightly lower than that of the synthetical carbinol now described.

These carbinols resemble those of the "methyl" and "isopropyl"

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TABLE II.

Molecular Rotatory Powers for Sodium-yellow and Mercury-green Light and Dispersion Values of the Series C₂H₅·CH(OH)·R at Various Temperatures.

	At 20°.	40°.	60°.	80°.	100°.	120°.	140°.	160°.
-Methylethylcarbinol	yellow	+10·02°	9·34°	8·73°	8·31°	—	—	—
	green	11·91	11·05	10·31	9·82	—	—	—
	disp.	0·842	0·845	0·847	0·846	—	—	—
l-Ethyl-n-propylcarbinol	yellow	-2·01°	2·06°	2·12°	2·22°	2·44°	—	—
	green	2·29	2·34	2·42	2·54	2·75	—	—
	disp.	0·881	0·881	0·877	0·875	0·882	—	—
d-Ethyl-n-butylcarbinol	yellow	+9·43°	9·49°	9·58°	9·67°	9·78°	10·06°	—
	green	11·11	11·18	11·26	11·38	11·50	11·83	—
	disp.	0·849	0·850	0·850	0·850	0·850	0·850	—
d-Ethyl-n-amylcarbinol	yellow	+10·69°	10·82°	10·95°	11·06°	11·14°	11·24°	11·32°
	green	12·53	12·69	12·79	12·93	13·04	13·11	13·08
	disp.	0·853	0·854	0·856	0·855	0·855	0·856	0·858
l-Ethyl-n-hexylcarbinol	yellow	-10·63°	10·91°	11·10°	11·14°	11·15°	11·04°	10·91°
	green	12·43	12·72	12·86	12·93	12·96	12·90	12·77
	disp.	0·856	0·858	0·863	0·861	0·860	0·856	0·854
l-Ethyl-n-heptylcarbinol	yellow	-10·55°	10·64°	10·66°	10·70°	10·64°	10·49°	10·38°
	green	12·23	12·28	12·32	12·36	12·30	12·14	12·01
	disp.	0·863	0·864	0·867	0·866	0·865	0·864	0·863
l-Ethyl-n-octylcarbinol	yellow	-10·74°	10·86°	10·96°	10·99°	11·00°	11·10°	10·91°
	green	13·43	12·55	12·68	12·73	12·75	12·89	12·68
	disp.	0·864	0·866	0·864	0·864	0·862	0·861	0·863

TABLE II. (*continued*).

	At 20°.	40°.	60°.	80°.	100°.	120°.	140°.	160°.
<i>l</i> -Ethyl- <i>n</i> -nonylcarbinol								
yellow	* -11.09°	10.55°	10.33°	10.26°	10.21°	10.21°	10.33°	10.51°
green	*12.36	12.25	11.91	11.80	11.76	11.81	11.90	12.12
disp.	0.863	0.862	0.867	0.869	0.868	0.864	0.868	0.868
<i>d</i> -Ethyl- <i>n</i> -decylcarbinol								
yellow	* +12.44°	*12.35°	12.28°	12.20°	12.13°	12.11°	12.11°	12.17
green	14.42	14.33	14.22	14.14	14.03	13.97	13.96	14.00
disp.	0.862	0.862	0.863	0.863	0.865	0.867	0.868	0.869
<i>l</i> -Ethyl- <i>n</i> -undecylcarbinol								
yellow	* -12.56°	*12.37°	12.28°	12.24°	12.19°	12.19°	12.16°	12.16°
green	*14.55	*14.35	14.23	14.22	14.21	14.19	14.16	14.10
disp.	0.863	0.862	0.863	0.861	0.858	0.858	0.859	0.862
<i>l</i> -Ethyl- <i>n</i> -dodecylcarbinol								
yellow	* -12.61°	*12.41°	12.26°	12.15°	12.13°	12.10°	12.20°	12.36°
green	*14.59	*14.32	14.15	14.07	14.04	14.02	14.12	14.30
disp.	0.864	0.867	0.866	0.863	0.864	0.863	0.864	0.865
<i>l</i> -Ethyl- <i>n</i> -tridecylcarbinol								
yellow	* -12.38°	*12.34°	*12.34°	12.25°	12.11°	11.97°	11.76°	11.57°
green	*14.32	*14.35	*14.29	14.20	14.01	13.81	13.61	13.43
disp.	0.865	0.861	0.863	0.862	0.864	0.866	0.862	0.864
<i>l</i> -Ethyl- <i>n</i> -pentadecylcarbinol								
yellow	* -12.87°	*12.80°	*12.80°	12.79°	12.72°	12.71°	12.63°	12.31°
green	*14.83	*14.80	*14.80	14.79	14.72	14.72	14.62	14.28
disp.	0.868	0.865	0.865	0.865	0.864	0.863	0.864	0.863

* Values from extrapolated curves of densities and observed rotations. All values given in the table are read off or calculated from smoothed curves based on observations recorded on p. 1954.

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series as regards immunity from "racemisation" * under many conditions (see Part II, *loc. cit.*, p. 622), whilst in general their physical properties (see table III) vary in a regular manner, except for the small breaks which occur in the regularity of the densities at the hexyl and dodecyl members (compare similar breaks in the "isopropyl" series and in the series of esters of *ac*-tetrahydro-2-naphthol, Parts II and III, *loc. cit.*).

The odours of the lower members of the series resemble those of the "methyl" series containing the same number of carbon atoms in the growing chain, the group R in the formulæ $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{R}$

TABLE III.

Optically Active Alcohols of the Formula $\text{C}_2\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{R}$.

	Boiling point.	Melting point.	n_D^{20} .†	D_4^{20} .	$\frac{n-1}{d} \cdot M$.	Mol. Refr. for CH_2 .	Differ- ence D_4^{80} .
Methylethylcarbinol ...	69°/758 mm.	—	1.3954	0.8080	36.2	7.7	—
Diethylcarbinol*	114.5°/752 „	—	1.4094	0.8198	43.9	7.5	—
Ethyl- <i>n</i> -propylcarbinol	133°/733 „	—	1.4141	0.8213	51.4	7.9	0.7671
Ethyl- <i>n</i> -butylcarbinol .	66°/18 „	—	1.4206	0.8227	59.3	7.7	0.7679
Ethyl- <i>n</i> -amylcarbinol .	76°/16 „	—	1.4252	0.8247	67.0	8.0	0.7711
Ethyl- <i>n</i> -hexylcarbinol .	97°/17 „	—	1.4308	0.8265	75.0	7.9	0.7796
Ethyl- <i>n</i> -heptylcarbinol	108°/15 „	—	1.4336	0.8272	82.9	7.7	0.7798
Ethyl- <i>n</i> -octylcarbinol..	117°/16 „	17°	1.4367	0.8295	90.6	—	0.7827
Ethyl- <i>n</i> -nonylcarbinol	130°/15 „	25	—	—	—	—	0.7833
Ethyl- <i>n</i> -decylcarbinol.	139°/12 „	32	—	—	—	—	0.7865
Ethyl- <i>n</i> -undecyl- carbinol	146°/10 „	38	—	—	—	—	0.7885
Ethyl- <i>n</i> -dodecyl- carbinol	168°/14 „	45	—	—	—	—	0.7921
Ethyl- <i>n</i> -tridecyl- carbinol	152°/4 „	50	—	—	—	—	0.7907
Ethyl- <i>n</i> -pentadecyl- carbinol	172°/2 „	56	—	—	—	—	0.7858

* Optically inactive.

† Determined with a Féry refractometer and correct to about ± 0.0002 .

and $\text{C}_2\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{R}$ seemingly being the portion of the molecule to which the characteristic odour is due. Beyond the member with $\text{R}=\textit{n}$ -decyl the odours are increasingly faint, ethyl-*n*-pentadecylcarbinol being practically odourless. No marked difference in odour between the optically active and inactive forms was observed in any case. The carbinols, when oxidised with chromic acid, readily yield in a pure state the ketones of the general formula $\text{C}_2\text{H}_5\cdot\text{CO}\cdot\text{R}$, which form semicarbazones in the usual way. The constants of these compounds are given in table IV, and differ

* It is very doubtful if any of these optically inactive carbinols exist in the liquid state as racemates (see investigations on the viscosity of several of these carbinols by Thole, this vol., p. 19).

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in several instances from those previously recorded in the literature. The semicarbazones of the series $C_2H_5 \cdot CO \cdot R$ all crystallise readily from aqueous ethyl alcohol, but in the case of the higher members of the series melt at about the same temperature, and therefore, like the semicarbazones of the series $CH_3 \cdot CO \cdot R$, are of little use for the characterisation of the ketones.

TABLE IV.

Ketones of the General Formula $C_2H_5 \cdot CO \cdot R$.

Name of ketone.	Melting point.*	Boiling point.	Semicarbazone. Melting point.†
Ethyl methyl	—	78.6°	135—136°
Diethyl	—	101°	139
Ethyl <i>n</i> -propyl	—	123°	112°
Ethyl <i>n</i> -butyl	—	149—150°	99—100°
Ethyl <i>n</i> -amyl	—	165—166°	112°
Ethyl <i>n</i> -hexyl	—	185—186°	111°
Ethyl <i>n</i> -heptyl	—	211°	100—101°
Ethyl <i>n</i> -octyl	—	227°	89°
Ethyl <i>n</i> -nonyl	19°	134°/18 mm.	87°
Ethyl <i>n</i> -deyl	25°	140°/17 "	90°
Ethyl <i>n</i> -undecyl	33°	148°/10 "	89°
Ethyl <i>n</i> -dodecyl	38°	174°/20 "	90.5°
Ethyl <i>n</i> -tridecyl	40—41°	184°/17 "	86°
Ethyl <i>n</i> -pentadecyl	50°	198°/14 "	76°

* Determined by "cooling curve" method.

† These melting points, which were determined in a capillary tube, in several cases vary slightly according to the rate of heating. The figures given were obtained when the rate of heating was slow.

EXPERIMENTAL.

The experimental work has been carried out on similar lines to those described in Parts I to III. The externally compensated carbinols have been synthesised either by Grignard reactions or by the reduction of the corresponding ketones. The formation of a secondary alcohol by the interaction of a magnesium alkyl haloid and a normal aldehyde, $R \cdot CHO$, proceeds quite smoothly for aldehydes with R containing at least up to sixteen carbon atoms, but takes place only to a slight extent if the normal alkyl group is larger than *n*-propyl. The ketones were prepared (like those described in Parts I and II) by the catalytic decomposition (according to Senderens' method, *Compt. rend.*, 1909, 149, 995) by contact with heated thorium oxide of mixtures of the required acids, these being, except where otherwise stated, the pure acids supplied by Kahlbaum. The thorium oxide was placed in a transparent silica "combustion" tube, the average yield from the process being apparently slightly better than when a Jena-glass tube is used, whilst the convenience in working is much greater.

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It is noteworthy that, whilst the hydrogen phthalic esters of the "methyl" series are easily resolved by the fractional crystallisation of the brucine salts, the corresponding compounds of the "ethyl" series (like those of the *isopropyl* series) are in most cases more readily resolved by the aid of strychnine, as in several cases brucine appears to form a "partly racemic" salt, which is less soluble than either the *l*B*l*A or *l*B*d*A salt. The experimental results agree well with one another, so that it has not been thought necessary to publish the large mass of analytical details. Each stage of the processes described below has been checked by analysis, but all details, for example, of the titration of the acid esters with alkali, of the combustions of the semicarbazones, and of the alkaloidal salts, etc., and of the determination of the rotatory powers of the successive crops in the resolutions, have been omitted from the description. Both the dextro- and lævoro-rotatory forms of the carbinol have been obtained only in a few cases. The completeness of the resolutions has been to some extent assured by the following method. A quantity of the alkaloidal (generally strychnine) salt has been obtained with a rotation and melting point which remained unaltered by further recrystallisation. The mother liquors were then carefully worked up, and the salt thus obtained was subjected to another series of crystallisations. The resolution was deemed complete when the second lot of salt obtained in this manner had the same constants as the first lot. In each case as the strychnine salts are not always very definite compounds, the esters from each lot were prepared and examined separately in the polarimeter.

Preparation of the Hydrogen Phthalic Esters.

The hydrogen phthalic esters of the carbinols (see table V) were prepared by the following method. Equimolecular proportions of carbinol and phthalic anhydride are heated at 110—120° for about ten hours. The product is dissolved in very dilute sodium carbonate solution, and very carefully purified from non-acid substances by repeated extraction with ether. The solution, which when working up 100 grams of carbinol would amount to about 6 litres, is completely freed from dissolved ether by blowing a current of air through it for some hours. Then after the addition of an excess of hydrochloric acid the hydrogen phthalate is either drained off and dissolved in chloroform or at once extracted with that solvent. The chloroform solution is washed repeatedly with water, and carefully dried with recently fused calcium chloride, a process which removes all but mere traces of phthalic acid. The chloroform is then completely removed by distillation on a water-

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bath, the last traces under diminished pressure, and the hydrogen phthalate (if solid) crystallised from petroleum of low boiling point. In most cases scrupulous adherence to these conditions is necessary to ensure the success of the subsequent resolution, which largely depends on the purity of the hydrogen phthalate.*

TABLE V.

The Hydrogen Phthalic Esters of the Carbinols, $C_2H_5 \cdot CH(OH) \cdot R$.

Hydrogen phthalate of carbinol with R=	Melting point of optically		Rotations in			
	Inactive.	Active.	Chloroform.		Ethyl alcohol.	
			$[\alpha]_D$.	$[M]_D$.	$[\alpha]_D$.	$[M]_D$.
<i>n</i> -Propyl	76—77°	73—74°	4·18°	10·45°	3·77°	9·42
<i>n</i> -Butyl	53—54	47—48	16·65	43·95	19·82	52·3
<i>n</i> -Amyl	62—63	66—68	17·06	59·7	21·67	60·2
<i>n</i> -Hexyl	47—49	54—55	14·12	41·2	19·45	56·8
<i>n</i> -Heptyl	Oil	32—33	12·67	38·8	17·30	52·9
<i>n</i> -Octyl	Oil	Oil	11·90	38·1	16·19	51·5
<i>n</i> -Nonyl	31—32	25	11·82	39·5	15·60	52·1
<i>n</i> -Decyl	46—47	34—35	12·84	44·7	17·71	61·6
<i>n</i> -Undecyl ...	58—60	36—37	13·79	49·9	17·43	63·1
<i>n</i> -Dodecyl ...	54—55	46—47	13·16	49·5	16·98	63·8
<i>n</i> -Tridecyl ...	51—52	51	12·55	49·0	16·47	63·2
<i>n</i> -Pentadecyl.	39—41*	34—35	12·16	50·8	15·62	65·3

* Not quite pure.

In all the determinations of the rotatory power of solutions recorded in this paper the material stated, usually about 1 gram, was made up to 20 c.c. at 20° with the solvent and the solution examined at 20° in a 2-dm. tube.

Methylethylcarbinol (sec.-Butyl Alcohol), $C_4H_{10}O$.

The preparation of *d*-sec.-butyl alcohol has been described briefly in Part I. Large quantities being required for this and other work, the methods have been modified as follows: Bright magnesium turnings (72 grams) are placed in a flask (capacity, 2 litres), and covered with ether† (250 c.c.). The flask is fitted with an inverted condenser, and a solution of dry ethyl bromide (340 grams), dissolved in an equal volume of ether, is added gradually, the mixture being shaken vigorously during the whole operation, which occupies about two hours. The flask is then placed in a large pneumatic trough standing on wooden rockers, and packed round with a mixture of ice and salt. A solution of acetaldehyde (150 grams) in twice its volume of ether is then slowly run in to

* It is thought desirable to emphasise this point as want of purity of the hydrogen phthalate appears to be the cause of failure on the part of some investigators to repeat resolutions previously described.

† Commercial ether which has been washed successively with concentrated sulphuric acid, water, a solution of sodium hydroxide and water, dried over calcium chloride, and distilled over phosphoric oxide.

the mixture from a tap funnel during the course of two hours, whilst the contents of the flask are agitated by moving the trough. The mixture is allowed to remain overnight, and then the uncombined acetaldehyde and about two-thirds of the ether are removed by distillation, the flask being placed in a bucket of water warmed to 45° . One operator can conveniently control simultaneously three series of such operations. The products from nine lots of material are poured with constant stirring into a large tank containing about 12 litres of a mixture of a saturated solution of ammonium chloride and crushed ice. The ethereal solution is then syphoned off, and the remaining liquid placed in flasks (capacity 5 litres), through which a current of steam is blown so long as the distillate smells of the alcohol. The distillates are collected together, and the alcohol concentrated by a repetition of the last operation. The ether in the syphoned liquid is removed by distillation, and the alcohol purified by distillation in a current of steam. The combined distillates are then saturated with sodium chloride, and extracted five times with ether. The ethereal extracts are now dried with several successive lots of recently ignited potassium carbonate, and then distilled very slowly through a long and efficient fractionating column. This last operation needs to be repeated four times, owing to the difficulty of separating ether and *sec.*-butyl alcohol. The average yield of the crude *sec.*-butyl alcohol (the fraction boiling between 85° and 101°) is well represented by that obtained from a batch of nine lots of material which amounted to 1265 grams.

The hydrogen phthalic ester is prepared by the method described on p. 1937, except that the mixture of the crude alcohol and phthalic anhydride is heated on a water-bath for about twelve hours. The amount of pure hydrogen phthalic ester obtained from the 1265 grams of crude alcohol mentioned above amounted to 3204 grams.

The resolution of methylethylcarbinol in large quantities is most easily carried out by a method which is illustrated by the details of one such resolution: The pure *sec.*-butyl hydrogen phthalate (965 grams) was dissolved in warm acetone (4 litres), and after the addition of anhydrous brucine (1738 grams), kept at about 40° for an hour. The solution was then filtered from undissolved brucine and concentrated, the flask being placed in a water-bath, and about 950 c.c. of acetone distilled off. After remaining for some hours in the ice-chest, the crop of crystals (*A*) was collected, whilst the filtrate (3000 c.c.) was concentrated further, and yielded another crop (*A*₁), the filtrate from which, when acidified in the manner described in Part I (p. 62), gave 260 grams of the hydrogen

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phthalic ester with $[\alpha]_D -20.0^\circ$ in ethyl alcohol. Crop *A* was recrystallised from 3 litres of acetone, giving crop *B* and the crop *A*₁ from the mother liquor of crop *B* giving crop *B*₁. Crop *B* was then recrystallised five times (crops *C*, *D*, *E*, *F*, *G*) from methyl alcohol, 1200 c.c. of solvent being used for each operation, since the solubility of salt decreases at about the same rate as the size of the crops; thus crop *D* weighed 1 kilo. and crop *G* 680 grams. Crop *B*₁ was then recrystallised successively from the mother liquors of crops *C* to *G*, and then a further six times from fresh methyl alcohol, the yield of salt being 180 grams. The total yield of salt (860 grams) was hydrolysed in the usual manner, and gave 276 grams of the pure *d*-sec.-butyl hydrogen phthalate,* with $[\alpha]_D +38.44^\circ$ in ethyl alcohol. To obtain the alcohol from the ester the best procedure (giving a yield of 85 per cent.) is as follows: The ester (1 mol.) is dissolved in water containing sodium hydroxide ($2\frac{1}{2}$ mols.), the solution warmed for a few minutes, and the alcohol removed by a current of steam. The alcohol is separated after the addition of potassium carbonate to the distillate, and dried by treatment with successive lots of freshly-ignited potassium carbonate, and finally with barium oxide. It then boils constantly at $99^\circ/760$ mm., and has the rotation previously recorded (see Part I, 64).

Owing to the special interest attaching to this *d*-methylethyl-carbinol as the optically active alcohol of simplest constitution, further experiments were carried out to obtain the pure *l*-alcohol, so that other evidence as to the completeness of the resolution might be obtained.

The portions of ester of highest lævorotatory power (approximately $[\alpha]_D -20^\circ$ in ethyl alcohol) were collected from several preparations of the *d*-alcohol, and converted into the acid potassium salt (see Part I, p. 59), which was then crystallised four times from acetone. This process did not alter the lævorotation of the ester, but the partly lævorotatory alcohol obtained from it was otherwise in a high state of purity. This was then converted into the hydrogen succinic ester, which gave a crystalline *cinchonidine* salt very soluble in organic solvents. This salt after five recrystallisations from a small quantity of acetone was obtained as small, transparent prisms melting at $54-55^\circ$, had $[\alpha]_D -85.03^\circ$ in ethyl alcohol, and was unaltered in rotatory power after further recrystallisation. The *hydrogen succinic ester* obtained from this

* The rotation of this ester in chloroform, which is pure and recently distilled, is much higher ($[\alpha]_D +40.54^\circ$) than the value ($[\alpha]_D +33.54^\circ$) given in Part I. The rotations of this and other phthalic esters, when determined in chloroform solution, vary greatly with the purity of the solvent.

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salt was a clear mobile oil, which had $[\alpha]_D -12.50^\circ$ in chloroform. When hydrolysed in the manner described for the corresponding *d*-hydrogen phthalic ester it gave the pure *l*-sec.-butyl alcohol, which in a 25 mm. tube had $\alpha_D^{22} -2.70^\circ$, the corresponding value obtained for the *d*-sec.-butyl alcohol in a 100 mm. tube being $\alpha_D^{22} -10.83^\circ$.

Methylethylcarbinol appears to have abnormal values for certain physical constants; thus, working with a sample of the *d*-alcohol prepared by us, Dunstan and Thole (compare this vol., p. 127) obtained abnormal values for log viscosity, whilst as recorded in Part II (p. 626) Dr. T. M. Lowry obtained a value for the optical dispersive power ($Hg_{\text{green}}^{\text{violet}} 1.662$) differing from the constant value (1.651) which he obtained for the other members of the "methyl" series. Suspicion having arisen that these anomalies might be due to the hygroscopic character of the alcohol and the presence of traces of water, the following experiments were carried out to test the point.

A series of polarimetric readings with the purest *d*-alcohol were made in a jacketed tube, through which warm water circulated. The successive readings in a 100 mm. tube were for $\alpha_{Hg \text{ green}}$ at 20° , $+13.02^\circ$; at 30° , 12.33° ; at 49° , $+11.29^\circ$; at 44° , $+11.55^\circ$; at 49° , $+11.28^\circ$; at 44° , $+11.60^\circ$; at 65° , $+10.51^\circ$; at 74° , $+10.27^\circ$; at 83° , $+9.90^\circ$; at 90° , $+9.70^\circ$; and at 96° , $+9.48^\circ$; whilst for α_D the readings taken at the same time were at 20° , $+10.94^\circ$; at 29° , $+10.46^\circ$; at 55° , $+9.31^\circ$; at 41.5° , $+9.88^\circ$; at 38° , $+10.01^\circ$; at 61° , $+9.04^\circ$; at 80° , $+8.46^\circ$; at 73.5° , $+8.68^\circ$; at 68° , $+8.93^\circ$; at 95° , $+8.12^\circ$; at 88° , $+8.26^\circ$. The values were plotted, and from the smoothed curves the following values of the dispersive power $\alpha_D/\alpha_{Hg \text{ green}}$ were obtained: at 20° , 0.842; at 40° , 0.845; at 60° , 0.847; at 80° , 0.846; at 90° , 0.846, the mean being 0.845. This sample was then allowed to remain for three days over barium oxide, and then re-examined in the polarimeter, with the result that all the new readings were found to lie on the curves previously obtained. One per cent. of water was next added to the sample, and the following readings obtained: for $\alpha_{Hg \text{ green}}$ at 19.5° , $+12.18^\circ$; at 30.5° , $+11.73^\circ$; at 35° , $+11.38^\circ$; at 47° , $+10.81^\circ$; at 59° , $+10.37^\circ$; at 66° , $+10.03^\circ$; at 78° , $+9.72^\circ$; at 82° , $+9.62^\circ$; at 86° , $+9.50^\circ$; for α_D at 19.5° , $+10.17^\circ$; at 44° , $+9.26^\circ$; at 38° , $+9.46^\circ$; at 91.5° , $+7.86^\circ$; at 81° , $+8.13^\circ$; at 72° , $+8.37^\circ$; at 63° , $+8.62^\circ$, whence the following values for the dispersive power were calculated; at 20° , 0.835; at 40° , 0.840; at 60° , 0.842; at 80° , 0.841; at 90° , 0.840, the mean value being 0.840. *sec*-Butyl alcohol appears to form with water a binary mixture, which boils at about 94° . The apparent

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molecular weight of the alcohol in a 3 per cent. aqueous solution as measured by the depression of the freezing point was 75.8 (calculated 74). Equimolecular proportions of the alcohol and water are quite miscible; such a mixture when examined in the polarimeter in a 100 mm. tube gave $\alpha_D^{21} + 7.29^\circ$, $\alpha_{\text{Hg green}}^{21} + 8.66^\circ$, whence the dispersion value is 0.842. After three hours the polarimetric reading was $\alpha_{\text{Hg green}}^{19} + 8.75^\circ$, after five days $\alpha_D^{19} + 7.36^\circ$, after one month $\alpha_{\text{Hg green}}^{19.5} + 8.76^\circ$, $\alpha_{\text{Hg violet}}^{19.5} + 14.52^\circ$, whence the optical rotatory dispersion mercury violet/green is 1.657° . Further polarimetric readings of a pure sample of *d*-sec.-butyl alcohol gave, in a 2-dcm. tube, $\alpha_{\text{violet}}^{20} + 42.26^\circ$ and $\alpha_D^{21} + 25.52^\circ$, whence the rotatory dispersion is 1.656. It therefore seems certain that the value of the rotatory optical dispersion of *sec*-butyl alcohol, although different from the normal values shown by other members of both the "methyl" and "ethyl" series, is not appreciably affected by traces of water.

Ethyl-n-propylcarbinol, $\text{C}_6\text{H}_{14}\text{O}$.

The crude carbinol was prepared in the usual manner by the interaction of magnesium *n*-propyl chloride and propaldehyde. The yield from twice the gram-molecular quantities was 62 grams of the crude alcohol boiling at $130\text{--}140^\circ$.

Resolution.—The optically inactive hydrogen phthalic ester (97 grams) in the form of the hard rhombs (m. p. $76\text{--}77^\circ$), in which it crystallises from light petroleum, was dissolved in acetone (about 2 litres), and the solution heated to about 40° for half-an-hour with brucine (153 grams), filtered, concentrated to about 500 c.c., and allowed to remain overnight in the ice-chest. The crystalline salt was then collected, and the process of crystallisation repeated several times, increasingly smaller amounts of solvent being employed. After four more such crystallisations, 52 grams of the *brucine* salt were obtained in hard and transparent, prismatic rods, melting at $132\text{--}133^\circ$, and with $[\alpha]_D - 8.92^\circ$ in ethyl alcohol. To this salt were added a further 23 grams (with $[\alpha]_D - 8.70^\circ$), obtained by working up all, but the first, mother liquors in the manner described for the strychnine salts of the dextrorotatory hydrogen phthalates of ethyl- and *n*-amyl-isopropylcarbinols (Part II, p. 632), six crystallisations being carried out and fresh solvent employed for the last three. These 75 grams were once more recrystallised from acetone, and the salt with $[\alpha]_D - 8.91^\circ$ decomposed in the usual manner (see Part I, p. 61). The levorotatory *hydrogen phthalic ester* (26 grams) crystallised from light petroleum in small, prismatic needles, melted at $73\text{--}74^\circ$, and had $[\alpha]_D - 4.12^\circ$ in chloroform and $[\alpha]_D - 3.75^\circ$ in ethyl alcohol. The pure ester (22 grams) was dissolved in a hot aqueous solution of

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potassium hydroxide (14 grams), and the *l*-ethyl-*n*-propylcarbinol removed by a current of steam. After extraction with ether in the usual manner, there were obtained 7.7 grams, boiling at 133–134°/733 mm. The first mother liquor from the crystallisation of the brucine salt was decomposed, and the ester (18 grams) with $[\alpha]_D + 2.3^\circ$ in ethyl alcohol converted into the strychnine salt in the usual manner (Part II, p. 632), chloroform and ethyl alcohol being the solvents employed. After five crystallisations the pure *strychnine* salt (11 grams) was obtained. The salt melted at 191–192°, had $[\alpha]_D - 21.26^\circ$ in chloroform, and, when decomposed in the usual manner, yielded the pure dextrorotatory ester, which, when crystallised from light petroleum, melted at 73–74° and had $[\alpha]_D + 4.18^\circ$ in chloroform and $[\alpha]_D + 3.77^\circ$ in ethyl alcohol. Equal amounts of the *d*- and *l*-esters were dissolved in light petroleum, and the solution seeded with the optically inactive ester, when the resulting crop of crystals melted at 75–76°. The *d*-carbinol boiled at 133–134°/733 mm., and in a 25 mm. tube gave $\alpha_D^{19} + 0.45^\circ$. The carbinol, recovered from the esters with lower rotations, was oxidised by warming gently with a solution of chromic acid, and yielded ethyl *n*-propyl ketone. This boiled at 122–124°, and formed a semicarbazone, which separates from ethyl alcohol in long, prismatic needles, and melts at 112°.

Ethyl-n-butylcarbinol, $C_7H_{16}O$.

The material required for the preparation of the optically active carbinol was obtained by the reduction of the corresponding ketone. The latter was prepared by passing a mixture of *n*-valeric (150 grams) and propionic (450 grams) acids through a silica tube heated to 400° and containing thorium oxide. The unchanged acids were collected and passed through the tube again, the total yield of crude ketone boiling at 147–148° being 105 grams. This ethyl *n*-butyl ketone was reduced in moist ethereal solution by finely-divided sodium, and gave 95 grams of the crude ethyl-*n*-butylcarbinol boiling at 150–152°. This carbinol, when treated with phthalic anhydride, gave 173 grams of the hydrogen phthalic ester, which crystallises from light petroleum in slender needles melting at 53–54°. This ester (151 grams) was converted into the *strychnine* salt by heating its solution in methyl alcohol with the alkaloid (190 grams). The pure salt crystallises in hard, lustrous prisms, melts at 176°, and has $[\alpha]_D - 24.31^\circ$ in chloroform. The first five crystallisations from fresh lots of methyl alcohol gave 9.5 grams of the pure salt, whilst the second crop from the second mother liquor was recrystallised from the succeeding three filtrates and four more times from fresh lots of solvent,

yielding a further 10 grams of the salt. The *esters* obtained from the crops of pure salt weighed 4.5 and 3.5 grams respectively, and had $[\alpha]_D +16.53^\circ$ and $+16.65^\circ$ in chloroform. The resolution was repeated with 82 grams of the inactive ester, and 9 grams of the active ester (with $[\alpha]_D +16.24^\circ$ in chloroform) obtained. The *hydrogen phthalic* ester of *d*-ethyl-*n*-butylcarbinol crystallises readily from light petroleum in lustrous, prismatic needles, melts at $47-48^\circ$, has $[\alpha]_D +19.82^\circ$ in ethyl alcohol, and is easily hydrolysed by potassium hydroxide. The dextrorotatory carbinol was isolated in the usual manner, and boiled at $66^\circ/18$ mm. The strychnine salts of the *d*- and *l*-esters do not vary very widely in solubility in methyl alcohol, the first mother liquor in the first resolution described above giving an ester only having $[\alpha]_D -2.0^\circ$ in chloroform. Two series of experiments were carried out, in which strongly dextrorotatory and levorotatory hydrogen phthalic esters were converted into the corresponding brucine salts. When either lot of brucine salt was recrystallised several times from acetone it was found that the least soluble portion in each case gave an ester, which was optically inactive. It thus appears that brucine forms a partly racemic salt with the hydrogen phthalic ester of ethyl-*n*-butylcarbinol.

Ethyl-n-amylcarbinol, $C_8H_{18}O$.

The optically inactive carbinol was prepared in a similar manner to that described for the corresponding *n*-butyl compound. A mixture of 145 grams of *n*-hexoic and 180 grams of propionic acids gave 124 grams of crude ethyl *n*-amyl ketone boiling between 160° and 170° . From this, 106 grams of the crude carbinol boiling at $168-172^\circ/753$ mm. were obtained and 197 grams of the corresponding hydrogen phthalic ester.

The resolution of the hydrogen phthalic ester of ethyl-*n*-amylcarbinol by the fractional crystallisation of the strychnine salt from methyl alcohol proceeds fairly readily. The ester (137 grams), which had been obtained from light petroleum in large, transparent plates melting at $62-63^\circ$, was dissolved in $1\frac{1}{2}$ litres of methyl alcohol, in which the strychnine (164 grams) was suspended. The resolution was carried out as in the case of ethyl-*n*-butylcarbinol. The pure *strychnine* salt of the *d*-ester, obtained after seven crystallisations, melted (when heated slowly) at $164-166^\circ$, and had $[\alpha]_D -24.41^\circ$ in chloroform. Systematic working up of the filtrate (fourteen further crystallisations) gave more of the salt, which with the former lot yielded 16.5 grams of the pure *d*-ester. This crystallised from light petroleum in hard, vitreous plates, melted at $66-68^\circ$, and had $[\alpha]_D +16.96^\circ$ in

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chloroform and $[\alpha] + 21.67^\circ$ in ethyl alcohol. The *d*-carbinol obtained in the usual manner boiled at $76^\circ/16$ mm. The *l*-ester recovered from the first mother liquor had $[\alpha]_D - 7.0^\circ$ in chloroform, but neither from this nor from the optically inactive ester could the pure *l*-ester be obtained by ten crystallisations of the brucine salt from acetone. This alkaloid forms a stable partly racemic salt, which softens at $102\text{--}107^\circ$, melts at $121\text{--}123^\circ$, has $[\alpha]_D - 9.01^\circ$ in ethyl alcohol, and when decomposed yields the inactive ester melting at $61\text{--}63^\circ$.

Ethyl-n-hexylcarbinol, $C_9H_{20}O$.

The resolution of this carbinol has been already described in Part I (*loc. cit.*). It has been repeated, using a hydrogen phthalic ester, which was prepared from a sample of the carbinol obtained by the reduction of the corresponding ketone. Analogous results were obtained, various lots of ester from the pure brucine, *strychnine* and *cinchonidine* salts having respectively $[\alpha]_D + 14.03^\circ$, $+ 14.12^\circ$, and $- 13.73^\circ$ in chloroform.* The strychnine salt crystallises from methyl alcohol in prisms, melts at $146\text{--}147^\circ$, and has $[\alpha] - 23.41^\circ$. The carbinols obtained from these different lots of esters had rotatory powers identical with those previously described (*loc. cit.*).

Ethyl-n-heptylcarbinol, $C_{10}H_{22}O$.

Ethyl n-heptyl ketone, $C_{10}H_{20}O$, is readily prepared by the Senderens catalytic process. A mixture of *n*-octoic (200 grams) and propionic (400 grams) acids passed twice over thoria heated to 400° gave 146 grams of the ketone, which boiled at 211° . It is much more readily reduced by sodium in moist ethereal solution than in moist ethyl-alcoholic solution. From the above quantity of ketone 130 grams of the corresponding *ethyl-n-heptylcarbinol*, boiling at 213° , were obtained. The oily *hydrogen phthalic* ester of this could not be made to crystallise even when cooled to a low temperature, and seeded with a speck of the *lævorotatory* form described below. It is readily resolved by means of strychnine, the details of one experiment being as follows: The ester (157 grams) and strychnine (171 grams) were dissolved in chloroform, which was then removed as completely as possible on a water-bath, the resulting paste being rapidly dissolved in acetone (1 litre) previously heated to its boiling point. The crop (*A*) of crystals (m. p. $119\text{--}122^\circ$) deposited when this solution cooled was recrystal-

* The esters described in Part I (*loc. cit.*) had $[\alpha]_D + 13.78^\circ$ and $- 13.62^\circ$ in chloroform. An obvious miscalculation of the molecular rotatory powers recorded in Part I, table IX, is corrected in table V of this paper (see p. 1938).

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lised by a similar process, giving crop *B*, which was then recrystallised eight times from fresh lots of methyl alcohol, 72 grams of the pure *strychnine* salt of the *l*-ester being obtained. The salt melts at 140–141°, and has $[\alpha]_D -18.18^\circ$ in pure chloroform. The mother liquors from crops *A* and *B* were decomposed, and gave respectively 52 grams and 19 grams of ester with $[\alpha]_D +6.4^\circ$ and $+4.2^\circ$ in pure chloroform. The 72 grams of the above-mentioned salt and a further small amount obtained by systematically working up the alcoholic mother liquors gave 25 grams of the *l*-ester, which solidified on cooling to a fairly hard, crystalline mass. This was pressed out on a porous tile, when it melted at 32–33°, and had $[\alpha]_D -17.30^\circ$ in ethyl alcohol and -12.67° in chloroform. Samples of the ester with $[\alpha]_D$ in chloroform about $+5^\circ$ and -3° respectively formed brucine salts, which crystallised readily from acetone. Each lot when crystallised repeatedly from acetone gave the same (partly racemic) *brucine* salt, which melted at 112–114°, had $[\alpha]_D -7.46^\circ$ in ethyl alcohol, and from which an optically inactive and oily ester was obtained. *l*-Ethyl-*n*-heptylcarbinol is readily obtained by the hydrolysis of the *l*-ester in the usual manner, is volatile in a current of steam, and boils at 108°/15 mm.

Ethyl-n-octylcarbinol, $C_{11}H_{24}O$.

Two separate mixtures of *n*-nonoic (150 grams) and propionic (460 grams) acids when treated by the Senderens process, gave yields of *ethyl n-octyl ketone*, $C_{11}H_{22}O$, amounting to 108 and 105 grams respectively. This crude ketone boiled at 223–228°, and was not readily reduced by sodium in boiling ethyl alcohol. Thus, 105 grams of the ketone, when reduced by these means in the usual manner, only gave 50 grams of crude ethyl-*n*-octylcarbinol, which boiled at 225–230°, and was readily converted into the oily *hydrogen phthalic* ester. This was easily resolved by the aid of strychnine. A mixture of the ester (116 grams) and strychnine (122 grams) was dissolved in boiling methyl alcohol, and the crude salt obtained from this solution crystallised six times from fresh amounts of the solvent. The melting point (142–143°) and the rotatory power ($[\alpha]_D -16.75^\circ$ in chloroform) of the strychnine salt thus obtained were unaltered by three further recrystallisations. The oily *l*-ester from the salt thus purified amounted to 16.5 grams, and had $[\alpha]_D +16.10^\circ$ in ethyl alcohol, and $[\alpha]_D -11.90^\circ$ in chloroform. *l*-Ethyl-*n*-octylcarbinol is volatile with steam, boils at 117°/16 mm., and when cooled sets to a mass of crystalline needles, which melt at 17°. Samples of the ester having low dextro- and lævo-rotatory powers formed brucine salts, which were very soluble in acetone. These salts, after several recrystallisations, became less

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soluble, and yielded specimens of ester which were almost optically inactive. An ester of very low rotatory power yielded a carbinol, which boiled at 229°.

Ethyl-n-nonylcarbinol, $C_{12}H_{26}O$.

Ethyl-*n*-nonylcarbinol was prepared by the action of magnesium ethyl bromide on *n*-decaldehyde. The required aldehyde was obtained by the general method discovered independently by Le Sueur (T., 1904, **85**, 827) and Blaise (*Compt. rend.*, 1904, **138**, 697). Three hundred grams of *n*-undecic acid* were brominated with 516 grams of bromine and red phosphorus in the usual manner, 342 grams of α -bromo-*n*-undecic acid, $C_{11}H_{21}O_2Br$, boiling at 178–183°/14 mm., and melting at 10°, being obtained.† The bromo-acid (776 grams) was dissolved in $6\frac{3}{4}$ litres of water, $1\frac{1}{2}$ kilos. of commercial sodium hydroxide were added, and a rapid current of superheated steam was blown for twenty hours through the mixture, which was placed in a large and deep earthenware vessel (an ordinary domestic "bread mug"). After acidification, the solid obtained was crystallised from light petroleum, and gave 570 grams of the pure α -hydroxy-*n*-undecic acid, $C_{11}H_{22}O_3$, which melts at 74°. The hydroxy-acid was rapidly distilled in portions of 15 grams from small flasks under ordinary pressure, and the products redistilled under diminished pressure, the whole series of operations being repeated with the portions boiling above 110°/14 mm. In this manner 88 grams of *n*-decaldehyde (b. p. 98°/13 mm.) were obtained from 240 grams of the hydroxy-acid. The freshly distilled aldehyde (88 grams) was then added in the

* *Preparation of undecic acid.*—A large quantity of *n*-undecic acid was prepared for the synthesis of ethyl-*n*-nonyl- and ethyl-*n*-decyl-carbinols. The details of the preparation are as follows: The slow distillation under 40 mm. pressure of 18 kilos. of crude castor oil in half-kilo. lots gave, after careful fractionation of the products, 1180 grams of *n*-undecenoic acid and 1605 grams of *n*-heptaldehyde. The acid was esterified by the Fischer—Speier method (*Ber.*, 1895, **28**, 3252), using 4540 grams of 96 per cent. ethyl alcohol and 394 grams of concentrated sulphuric acid. After careful fractionation 1162 grams of ethyl *n*-undecenoate were obtained and reduced catalytically in an atmosphere of hydrogen in the presence of finely divided nickel heated to 170° (Darzens, *Compt. rend.*, 1907, **144**, 329). The ester was passed four times over the nickel (the refraction being practically unaltered by the fourth operation), was then well shaken with one per cent. solution of potassium permanganate, dried in the usual way and again carefully fractionated, 975 grams of ethyl undecenoate (b. p. 140°/20 mm.) being obtained. When hydrolysed, the yield of undecic acid, which melted sharply at 28° and boiled at 179°/28 mm., amounted to 774 grams. Further quantities of this acid were prepared in a similar manner from undecenoic acid obtained from Kahlbaum.

† In a second preparation, 434 grams of the bromo-acid were obtained from 346 grams of *n*-undecic acid.

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usual manner to a slight excess of magnesium ethyl bromide, and gave 85 grams of *ethyl-n-nonylcarbinol*, which boils at $133^{\circ}/14$ mm., and when cooled sets to a gelatinous, microcrystalline mass, melting at 12° . From this amount of carbinol were obtained 126 grams of the *hydrogen phthalic* ester, which after some days in the ice-chest set to a hard, crystalline mass, melting at 31 – 32° . It is readily resolved by the fractional crystallisation of the strychnine salt from methyl alcohol. The yield from equal quantities (123 grams) of the racemic ester and strychnine, after eight crystallisations of the salt of the pure *l*-ester, amounted to 18 grams. Further quantities of the salt were obtained from the mother liquors, twenty-one crystallisations being carried out. The *strychnine* salt of the *l*-ester melts at 129 – 130° , and has $[\alpha]_D -16.12^{\circ}$ in chloroform. The *l*-ester, of which in all 16 grams were obtained, solidifies in rosettes of needles, which melt at 25° , and has $[\alpha]_D -15.60^{\circ}$ in ethyl alcohol and $[\alpha]_D -11.82^{\circ}$ in chloroform. *l-Ethyl-n-nonylcarbinol* is volatile in a current of steam, boils at $130^{\circ}/15$ mm., and sets to a hard, crystalline mass, which melts at 25° . The odour of the carbinol is very similar to that of methyl-nonylcarbinol (and ketone).

Ethyl-n-decylcarbinol, $C_{13}H_{28}O$.

A mixture of 156 grams of *n*-undecic acid,* with 220 grams of propionic acid, passed over thoria, heated to 420° , gave 109 grams of *ethyl n-decyl ketone*, $C_{13}H_{26}O$,† which boils at $140^{\circ}/17$ mm., sets to a mass of pearly plates melting at 25° , and has only a very faint odour. In boiling *isoamyl* alcohol, it is reduced by sodium to the corresponding *carbinol* (yield, 72 per cent.), which boils at $148^{\circ}/20$ mm., solidifies in the ice-chest to a waxy mass of platelets, and melts at 14.5° . The racemic *hydrogen phthalic* ester is very soluble in light petroleum, melts at 46 – 47° , and can be resolved by the fractional crystallisation of the strychnine salt from methyl alcohol. The resolution was carried out twice, most perplexing results being obtained, as the least soluble strychnine salts separating out at different stages appeared to correspond in an erratic manner with both that of the *l*-ester and that of the *d*-ester. The resolution was then repeated a third time, care being taken to carry out each crystallisation under similar conditions as to temperature, the details of the crops being as follows: 117 grams of the racemic ester and 114 grams of strychnine were dissolved in half a litre of methyl alcohol, the crystals (crop *A*) which separated out being recrystallised six times (crops *B* to *G*), each

* Completely free from undecenoic acid.

† A second preparation gave 96 grams of the ketone from a mixture of 128 and 300 grams of respective acids.

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time from about 100 to 150 c.c. of the solvent. Crop *E* weighed 16 grams, and melted at 131–132°; crop *F*, weighing 13 grams, was identical with crop *G* as regards melting point (132°) and rotatory power ($[\alpha]_D - 24.80^\circ$ in chloroform), and was the pure *strychnine* salt of the *d*-ester.* The mother liquor from crop *A* was concentrated, and crop *B*₁, amounting to 55 grams, obtained. Crop *B*₁ was recrystallised from the mother liquor of crop *C*, the crystals, crop *C*₁, amounting to 35 grams. In a similar manner crops *D*₁, *E*₁, *F*₁ were obtained, *F*₁ † being then recrystallised five times from fresh lots of solvent, giving crops *G*₁, *H*₁, *K*₁, *L*₁, and *M*₁. The crystals of crop *M*₁, which amounted to 9 grams, when heated very slowly, melted at 119–120°, had $[\alpha]_D - 14.58^\circ$ in chloroform, and consisted of the *strychnine* salt of the *l*-ester.‡ The remaining liquors were decomposed, details relating to the respective esters obtained from them being given in table VI.

TABLE VI.

Resolution of the Hydrogen Phthalic Ester of Ethyl-n-decylcarbinol.

Weight of ester (in grams).	derived from the mother liquor of crop	Rotation $[\alpha]_D$. in chloroform.*
23.0	<i>A</i>	- 2.6°
36.0	<i>B</i> ₁	+ 0.8
13.0	<i>C</i> ₁	+ 3.4
5.0	<i>D</i> ₁	+ 2.6
11.0	<i>E</i> ₁	+ 1.4
2.0	<i>F</i> ₁	+ 3.1
3.0	<i>G</i> ₁	- 3.6
2.5	<i>H</i> ₁	- 8.1
1.0	<i>K</i> ₁	- 9.9
0.5	<i>L</i> ₁	- 11.9
0.5	<i>M</i> ₁	- 13.1

* Not specially purified. The same sample of chloroform was used for each of the determinations recorded.

The *d*- and *l*-esters obtained from the corresponding pure *strychnine* salts (crop *G* to the *d*-ester and crop *M*₁ to the *l*-ester) solidified after evaporation of their solutions in ether to hard, crystalline masses, each of which melted at 35–35.5°. Determinations of the rotatory power gave the following results: For the *d*-ester, $[\alpha]_D + 12.84^\circ$ and $+ 17.58^\circ$; for the *l*-ester, $[\alpha]_D - 12.83^\circ$ and $- 17.71^\circ$; the determinations in each case being in chloroform and ethyl alcohol respectively.

0.1 Gram of both esters was separately and accurately weighed out, mixed, and dissolved in pure chloroform. After evaporation of the solvent, the resulting hard, crystalline mass melted sharply

* *Sic*.

† The mother liquor from the crop *G* was decomposed along with crop *G* to obtain the *d*-ester.

‡ *Sic*.

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at 46°, that being the melting point of the racemic ester previously obtained.* The optically active forms of *ethyl-n-decylcarbinol* are volatile in a current of steam, and each melts at 32°. Approximately equal amounts of each were mixed together on a porous tile, when the mixture rapidly fused, and was absorbed by the tile, the temperature of the room being 17°, and the melting point of the racemic carbinol 14.5°. The *d*-carbinol (from the *d*-ester) boiled at 139°/12 mm., and the *l*-carbinol at 140°/15 mm., each crystallising from ethyl alcohol in long and slender, silky needles.

Ethyl-n-undecylcarbinol, $C_{14}H_{30}O$.

Ethyl n-undecyl ketone, $C_{14}H_{28}O$, is readily prepared by passing a mixture of equal amounts of lauric and propionic acids over thorium oxide oxide heated to 425°, the yield being just over 60 per cent. of the lauric acid employed. It boils at 148°/10 mm., solidifies in nacreous plates, melts at 33° (compare Blaise and Guérin (*Bull. Soc. chim.*, 1903, [iii], **29**, 1208), and when dissolved in boiling amyl alcohol, is reduced by sodium to the corresponding

* Another remarkable case which in some respects is possibly analogous to the uncommon phenomena just described has been investigated in these laboratories. Pope and Read (T., 1912, **101**, 758) have described the externally compensated and optically active hydroxyhydrindamines, recommending the latter as serviceable bases for the resolution of externally compensated acids. With the kind concurrence of Prof. W. J. Pope we have prepared and resolved a large quantity of the externally compensated hydroxyhydrindamine, following the directions given in the above-mentioned paper. However, as we had available the ammonium salt of only *d*- α -bromocamphor- π -sulphonate we expected to be able to prepare only the *l*-hydroxyhydrindamine as Pope and Read obtained the *lBdA*-salt as the least soluble component of the mixture formed by addition of an aqueous solution of ammonium *d*- α -bromocamphor- π -sulphonate (1 mol.) to an aqueous solution of *dl*-hydroxyhydrindamine hydrochloride (2 mols.). To our surprise, however, we obtained instead the *dBdA*-salt, from which was obtained the pure *d*-hydroxyhydrindamine with $[\alpha]_D +22.8^\circ$ in water as described by Pope and Read. Our colleague, Mr. Yates, then carefully repeated the resolution, not only as described by Pope and Read, but also under varied conditions of temperature and concentration, and used throughout the ammonium salt of the dextrorotatory acid only. In each case the salt separating out was the *dBdA*-isomeride (m. p. 152°). Prof. Pope then very kindly forwarded a small specimen of the *lBdA*-salt (m. p. 221°). Following then the directions of Pope and Read, the accumulation of partially levorotatory hydroxyhydrindamine hydrochloride was (by use of the seed) converted into the *lBdA*-salt by the double decomposition of the hydrochloride and the ammonium *d*- α -bromocamphor- π -sulphonate in the required proportions calculated from the rotatory power of the hydrochloride. In this way a good yield of both the dextrorotatory and levorotatory forms of hydroxyhydrindamine was obtained from the resolution, the ammonium salt of the dextrorotatory acid only being employed. These bases appear to have no advantage over the commoner alkaloids for use in the resolution of externally compensated hydrogen phthalic or succinic esters.

ethyl-n-undecylcarbinol (yield, 80 per cent.), which boils at $173^{\circ}/25$ mm., solidifies in stellate masses of long needles with a pearly lustre, and melts at 25° . The *hydrogen phthalic* ester of the carbinol crystallises from light petroleum, and melts at $58-60^{\circ}$. The resolution of this ester by the fractional crystallisation of the strychnine salts from methyl alcohol was carried out in a manner as described for similar compounds. Thus, 158 grams of the ester and 145 grams of strychnine were dissolved in methyl alcohol, and the crop of crystals (160 grams) deposited when the solution was cooled was recrystallised six times, there being obtained 37 grams of the *strychnine* salt of pure *l*-ester, which crystallises from methyl alcohol in clear, transparent prisms, melts at $100-101^{\circ}$, and has $[\alpha]_D -13.96^{\circ}$ in chloroform. The mother liquors were systematically worked up as usual, the product obtained after three recrystallisations from fresh solvent having identical properties with those of the main lot (37 grams) of the pure salt. The *l-hydrogen phthalic* ester is very soluble in light petroleum, from which it crystallises in feathery needles, melts at 33° , and has $[\alpha]_D -13.79^{\circ}$ and -17.43° in chloroform and ethyl alcohol respectively. *l-Ethyl-n-undecylcarbinol* is only very slowly volatile in a current of steam, boils at $146^{\circ}/10$ mm. or $160^{\circ}/15$ mm., sets on cooling to a hard, crystalline mass, can be recrystallised from ethyl alcohol, from which it separates in stout prisms, and melts at 38° .

Ethyl-n-dodecylcarbinol, $C_{15}H_{32}O$.

This carbinol was prepared by interaction of magnesium ethyl bromide and *n*-tridecaldehyde. The required aldehyde was prepared by Le Sueur's method (*loc. cit.*), but the yields were poor, as from 240 grams of pure α -hydroxymyristic acid only 62 grams of the pure aldehyde were obtained. The Grignard reaction proceeds quite smoothly, in two separate experiments the yields obtained of the carefully fractionated carbinol being 36 and 14 grams from 48 and 14 grams respectively of the aldehyde. *Ethyl-n-dodecylcarbinol* boils at $163^{\circ}/12$ mm., and sets on cooling to an opaque, crystalline mass, which melts at 32° . Seventy-three grams of the pure racemic *hydrogen phthalic* ester were obtained from 50 grams of the racemic carbinol. The ester crystallises from light petroleum, and melts at $54-55^{\circ}$. The resolution of the ester by the fractional crystallisation of the strychnine salt from methyl alcohol proceeded with unusual rapidity. Seventy-three grams of the ester and 65 grams of strychnine were dissolved in methyl alcohol (100 c.c.). After cooling, 82 grams of crystals were deposited, whilst the ester obtained from the mother liquor had $[\alpha]_D +9.3^{\circ}$ in chloroform. After three recrystallisations of

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these crystals, the *strychnine* salt of the pure *l*-ester was obtained. This salt, which was unaltered by three further recrystallisations, melted at 103—104°, and had $[\alpha]_D -12.45^\circ$ in chloroform. The *l*-ester (20 grams) obtained from the salt crystallised from light petroleum, melted at 46—47°, and had $[\alpha]_D -13.16^\circ$ and -16.98° in chloroform and ethyl alcohol respectively. 1-*Ethyl-n-dodecylcarbinol* is not volatile in a current of steam, boils at 168°/14 mm., sets on cooling to a hard, crystalline mass, separates from ethyl alcohol in long, silky needles, melts at 45°, and has no odour.

Ethyl n-dodecyl ketone, $C_{15}H_{30}O$, was prepared by the oxidation of the carbinol with chromic acid, and is slowly volatile in a current of steam. Thus purified, it is obtained in large, glistening plates, which melt at 38°.

Ethyl-n-tridecylcarbinol, $C_{16}H_{34}O$.

A mixture of equal amounts of myristic and propionic acids passed over thoria heated to 420° gave a 60 per cent. yield of *ethyl n-tridecyl ketone*, $C_{16}H_{32}O$, which boils at 184°/17 mm., and crystallises from light petroleum in lustrous leaflets, melting at 42°. When reduced by sodium in boiling *isoamyl* alcohol, it gave the corresponding *carbinol*, which boils at 176°/16 mm., and on cooling sets to a hard, crystalline mass, melting at 37—38°. The *hydrogen phthalic* ester separates from light petroleum in clusters of silky needles, and melts at 51—52°.

The resolution of the ester was carried out in the usual manner by the fractional crystallisation of the *strychnine* salt from acetone containing a small amount of chloroform. A mixture of the ester (126 grams) and *strychnine* (108 grams) was dissolved in chloroform, which was then removed as completely as possible by distillation on a water-bath, the resulting paste being quickly dissolved in warm acetone. The crystals deposited from this solution weighed 67 grams, and were recrystallised six times in a similar manner, 27 grams of the *strychnine* salt of the pure *l*-ester being obtained. After recrystallisation of the products given by systematically working up the mother liquors, a further quantity of the pure salt was obtained, the *l*-ester from both lots of salt amounting to 26 grams. The *strychnine* salt of the *l*-ester crystallises from acetone in stout, glassy rods, melts at 103—104° and has $[\alpha]_D -14.66^\circ$ in pure chloroform. The *l*-ester crystallises from light petroleum in prismatic needles, melts at 51°, and has $[\alpha]_D -12.55^\circ$ and -16.47° in pure chloroform and ethyl alcohol respectively. 1-*Ethyl-n-tridecylcarbinol* is not readily volatile in a current of steam, it boils at 152°/4 mm., melts at 50°, separates

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from ethyl alcohol in rosettes of very slender needles, and is almost odourless.

Ethyl-n-pentadecylcarbinol, $C_{15}H_{38}O$.

A warm solution of palmitic acid (300 grams) in propionic acid (400 grams) was passed over thoria heated to 430° , and 114 grams of *ethyl n-pentadecyl ketone*, $C_{18}H_{36}O$, were obtained, 102 grams of pure palmitic acid being recovered. The ketone boils at $198^{\circ}/14$ mm., and sets on cooling to a crystalline mass, melting at 50° . When reduced in boiling *isoamyl* alcohol by means of sodium, the corresponding *carbinol* is formed, the yield being 70 per cent. This boils at $202^{\circ}/13$ mm., and melts at 43° . The *hydrogen phthalic ester*, as prepared in the usual manner, melted at $39-41^{\circ}$, but was probably not quite pure, as the solutions of the sodium salt are of a soapy character and difficult to extract with ether. The resolution of the ester was carried out by an analogous method to those described above. The ester (118 grams) and strychnine (80 grams) were dissolved in methyl alcohol, the solution concentrated, and allowed to remain in the ice-chest. The crop of crystals obtained melted at $84-87^{\circ}$, and was recrystallised six times from methyl alcohol, the final crop weighing 30 grams, and melting at $108-109^{\circ}$. The *strychnine* salt of the *l-ester* had $[\alpha]_D -12.57^{\circ}$ in chloroform, a further quantity being obtained from a systematic working up of the mother liquors (five operations), and recrystallising the product three times from fresh solvent. From both lots of the salt 19.5 grams of the *l-ester* were obtained; it melts at $32-33^{\circ}$, and has $[\alpha]_D -15.62^{\circ}$ and -12.16° in ethyl alcohol and chloroform respectively. *l-Ethyl-n-pentadecylcarbinol* boils at $172^{\circ}/2$ mm., melts at 56° , separates from ethyl alcohol in small, prismatic rods, and is odourless.

Density Determinations.

The following density determinations were carried out in a pycnometer holding 4 c.c., and are compared with water at 4° :

l-Ethyl-n-propylcarbinol: at 13.5° , 0.8246; at 53.5° , 0.7946; at 84° , 0.7627; at 104° , 0.7428.

d-Ethyl-n-butylcarbinol: at 13° , 0.8248; at 50° , 0.7985; at 88° , 0.7603; at 127° , 0.7245.

d-Ethyl-n-amylcarbinol: at 19° , 0.8234; at 48° , 0.8016; at 89° , 0.7648; at 125° , 0.7302.

d-Ethyl-n-hexylcarbinol (as given in Part I), and at 124° , 0.7480.

l-Ethyl-n-heptylcarbinol: at 12.5° , 0.8310; at 48° , 0.8071; at 90° , 0.7715; at 134° , 0.7330.

l-Ethyl-n-octylcarbinol: at 17° , 0.8308; at 50° , 0.8076; at 81° , 0.7823; at 128° , 0.7426.

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1-Ethyl-n-nonylcarbinol: at 32°, 0.8223; at 61°, 0.7999; at 91°, 0.7748; at 124°, 0.7467.

d-Ethyl-n-decylcarbinol: at 46°, 0.8139; at 69°, 0.7965; at 93°, 0.7755; at 128°, 0.7466.

1-Ethyl-n-decylcarbinol: at 43°, 0.8180; at 80°, 0.7889.

1-Ethyl-n-undecylcarbinol: at 53°, 0.8098; at 78°, 0.7896; at 98°, 0.7748; at 146.5°, 0.7354.

1-Ethyl-n-dodecylcarbinol: at 55°, 0.8115; at 82°, 0.7908; at 94°, 0.7816; at 132°, 0.7518.

1-Ethyl-n-tridecylcarbinol: at 67°, 0.8000; at 90°, 0.7843; at 119°, 0.7611; at 153°, 0.7335.

1-Ethyl-n-pentadecylcarbinol: at 73°, 0.8011; at 90°, 0.7876; at 121°, 0.7618.

Determination of the Rotatory Powers of the Carbinols in the Homogeneous State.

The determinations of the rotatory powers of the carbinols in the homogeneous state have been made in jacketed tubes, 50 mm. and 100 mm. in length, round which a heated mineral oil was circulated by a pump. The temperature was carefully observed by a standardised thermometer placed in the liquid under observation, and the general practice was to make a series of readings with (say) the yellow sodium light whilst the temperature was rising, and another series with the green mercury light whilst it was falling. In each case similar curves were obtained for both wave-lengths, and no evidence was obtained that any racemisation had ensued during the heating. The figures given below are either those obtained from observations in a 100 mm. tube or have been calculated for that length:

*1-Ethylpropylcarbinol: α_D at 22.5°, -1.62°; at 58°, -1.64°; at 87°, -1.68°; and at 108°, -1.72°.

α_{gr} at 22.5°, -1.84°; at 73°, -1.90°; at 102°, -1.94°; and at 117°, -1.96°.

d-Ethyl-n-butylcarbinol: α_D at 20.5°, +6.68°; at 54°, +6.54°; at 57°, +6.52°; at 70°, +6.46°; at 104°, +6.34°; and at 130°, +6.21°.

α_{gr} at 20.5°, +7.88°; at 77°, +7.54°; at 97°, +7.46°; at 105°, 7.40°; at 120°, +7.34°; and at 134°, +7.26°.

d-Ethyl-n-amylcarbinol: α_D at 18°, +6.79°; at 23°, +6.76°; at 55°, +6.69°; at 63°, +6.60°; at 94°, +6.46°; at 114°, +6.38°; at 130°, +6.28°; and at 160°, +6.05°.

α_{gr} at 23°, +7.94°; at 42°, +7.86°; at 52°, +7.80°; at 63°, +7.74°.

* Methyl-ethylcarbinol (see p. 1941).

+7.76°; at 82°, +7.66°; at 93°, +7.62°; at 108°, +7.48°; at 120°, +7.36°; at 133°, +7.30°; and at 145°, +7.20°.

l-Ethyl-*n*-hexylcarbinol: α_D at 19°, -6.10°; at 48°, -6.12°; at 56°, -6.14°; at 62°, -6.12°; at 70°, -6.10°; at 87°, -6.00°; at 111°, -5.86°; at 128°, -5.74°; and at 152°, -5.52°.

α_{gr} at 19°, -7.12°; at 45°, -7.16°; at 52°, -7.14°; at 64°, -7.06°; at 80°, -7.00°; at 101°, -6.90°; at 112°, -6.84°; at 131°, -6.66°; and at 149°, -6.50°.

l-Ethyl-*n*-heptylcarbinol: α_D at 21°, -5.54°; at 47°, -5.42°; at 72°, -5.33°; at 92°, -5.19°; at 100°, -5.14°; at 132°, -4.90°; and at 148°, -4.78°.

α_{gr} at 19.5°, -6.42°; at 63°, -6.20°; at 68°, -6.16°; at 73°, -6.12°; at 91°, -6.100°; at 96°, -5.96°; at 112°, -5.86°; at 135°, -5.64°; and at 142.5°, -5.60°.

l-Ethyl-*n*-octylcarbinol: α_D at 22°, -5.21°; at 38°, -5.17°; at 58°, -5.12°; at 86°, -4.98°; at 100°, -4.90°; at 132°, -4.72°; and at 145°, -4.64°.

α_{gr} at 20.5°, -6.02°; at 43°, -5.96°; at 76°, -5.80°; at 95°, -5.70°; at 116°, -5.56°; at 128°, -5.54°; and at 157°, -5.28°.

l-Ethyl-*n*-nonylcarbinol: α_D at 29.5°, -4.80°; at 31°, -4.76°; at 36°, -4.68°; at 62°, -4.44°; at 70°, -4.38°; at 85°, -4.32°; at 100°, -4.24°; at 122°, -4.12°; at 135°, -4.10°; and at 157°, -4.06°.

α_{gr} at 30°, -5.54°; at 51.5°, -5.20°; at 76°, -5.00°; at 90°, -4.90°; at 112°, -4.80°; at 137°, -4.68°; and at 152°, -4.64°.

d-Ethyl-*n*-decylcarbinol: α_D at 42°, +5.04°; at 63°, +4.90°; at 92°, +4.72°; at 107°, +4.64°; at 120°, +4.56°; at 131°, +4.50°; and at 158°, +4.38°.

α_{gr} at 38°, +5.90°; at 68°, +5.66°; at 83°, +5.54°; at 102°, +5.40°; at 127°, +5.20°; at 150°, +5.08°; and at 168°, +5.02°.

l-Ethyl-*n*-decylcarbinol: α_D at 76°, -4.82°.

l-Ethyl-*n*-undecylcarbinol: α_D at 42°, -4.74°; at 53°, -4.64°; at 79°, -4.52°; at 85°, -4.46°; at 105°, -4.40°; at 117°, -4.34°; at 138°, -4.18°; and at 166°, -4.02°.

α_{gr} at 41°, -5.49°; at 47.5°, -5.46°; at 53°, -5.40°; at 70°, -5.29°; at 90°, -5.19°; at 113°, -5.08°; at 119°, -5.04°; at 133°, -4.94°; and at 144°, -4.87°.

l-Ethyl-*n*-dodecylcarbinol: α_D at 53°, -4.40°; at 64°, -4.32°; at 84°, -4.20°; at 104°, -4.12°; at 134°, -4.02°; and at 158°, -3.92°.

α_{gr} at 46°, -5.14°; at 68°, -4.96°; at 75°, -4.92°; at 86°, -4.86°; at 99°, -4.78°; at 116°, -4.72°; at 130°, -4.64°; at 140°, -4.62°; and at 155°, -4.60°.

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1-*Ethyl-n-tridecylcarbinol*: α_D at 50° , -4.14° ; at 57° , -4.12° ; at 90° , -3.94° ; at 114° , -3.78° ; and at 148° , -3.58° .

α_{gr} at 58° , -4.78° ; at 78° , -4.66° ; at 98° , -4.50° ; at 125° , -4.30° ; and at 149° , -4.14° .

1-*Ethyl-n-pentadecylcarbinol*: α_D at 64° , -3.84° ; at 77° , -3.78° ; at 102° , -3.64° ; at 120° , -3.58° ; at 141° , -3.50° ; and at 154° , -3.40° .

α_{gr} at 61° , -4.44° ; at 67° , -4.42° ; at 71° , -4.40° ; at 96° , -4.30° ; at 113° , -4.20° ; at 118° , -4.16° ; at 136° , -4.10° ; and at 161° , -3.80° .

For the purpose of testing whether the optical rotatory dispersion $\text{Na}_{\text{yellow}}/\text{Hg}_{\text{green}}$ is constant over the available range of temperature, new preparations of methyl-*n*-butyl-, -*n*-hexyl-, and -*n*-nonyl-carbinols, as well as of *n*-propylisopropylcarbinol and *iso*-propyl-*n*-hexylcarbinol have been examined. The following polarimetric observations agree well with those recorded in Parts I and II.

d-*Methyl-n-butylcarbinol*: α_D at 20° , $+9.08^\circ$; at 42° , $+8.60^\circ$; at 64° , $+8.19^\circ$; at 80° , $+8.00^\circ$; at 96° , $+7.83^\circ$; at 110° , -7.73° ; and at 119° , -7.62° .

α_{gr} at 21° , $+10.82^\circ$; at 43° , $+10.06^\circ$; at 56° , $+9.79^\circ$; at 70° , $+9.49^\circ$; at 80° , $+9.33^\circ$; at 95° , $+9.13^\circ$; at 105° , $+9.07^\circ$; and at 123° , $+8.95^\circ$.

The values of the optical dispersive power calculated from the smoothed curves from these figures are: at 20° , 0.844; at 40° , 0.848; at 60° , 0.848; at 80° , 0.851; at 100° , 0.851; and at 120° , 0.848, the mean value being 0.848. This alcohol has been prepared recently in larger quantities, but the authors have not been able to prepare material with $[\text{M}]_D$ at the boiling point so high as that (11.3°) given in Part I, the value $[\text{M}]_D^{b.p.} 10.9^\circ$ being the highest obtained lately.

d-*Methyl-n-hexylcarbinol*: α_D at 20° , $+8.05^\circ$; at 48° , $+7.54^\circ$; at 54° , $+7.38^\circ$; at 70° , $+7.13^\circ$; at 104° , $+6.76^\circ$; at 110° , $+6.68^\circ$; and at 142° , $+6.35^\circ$.

α_{gr} at 19° , $+9.61^\circ$; at 48° , $+8.90^\circ$; at 62° , $+8.55^\circ$; at 74° , $+8.36^\circ$; at 95° , $+8.07^\circ$; at 120° , $+7.80^\circ$; and at 139.5° , $+7.63^\circ$. The values of the dispersive power calculated from these observations are: at 20° , 0.845; at 40° , 0.845; at 60° , 0.847; at 80° , 0.845; at 100° , 0.845; at 120° , 0.844; and at 140° , 0.842, the average value being 0.845.

d-*Methyl-n-nonylcarbinol*: α_D at 142° , $+5.24^\circ$.

α_{gr} at 23° , $+7.85^\circ$; at 45° , $+7.28^\circ$; at 57° , $+7.01^\circ$; at 70° , $+6.78^\circ$; at 95° , $+6.56^\circ$; at 113° , $+6.45^\circ$; at 135° , $+6.23^\circ$; and at 151° , $+6.12^\circ$.

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From these and previously recorded (Part I) observations, the calculated values of the optical dispersive power are: at 20°, 0·849; at 40°, 0·849; at 60°, 0·854; at 80°, 0·854; at 100°, 0·847; at 120°, 0·844; and at 140°, 0·845, the average value being 0·849.

d-Propyl-isopropylcarbinol: α_D at 19°, +17·66°; at 31°, +17·48°; at 45°, +17·18°; and at 98°, +15·54°.

α_{gr} at 19°, +20·94°; at 30°, +20·64°; at 40°, +20·40°; at 55°, +20·08°; at 65°, +19·74°; at 98°, +18·38°; at 111°, +17·88°; at 116·5°, +17·46°; and at 121°, +17·22°. These observations, with others previously recorded, give the following values of the optical rotatory dispersive power: at 20°, 0·844; at 40°, 0·844; at 60°, 0·842; at 80°, 0·840; at 100°, 0·843; at 120°, 0·843; and at 140°, 0·842, the average value being 0·843.

isoPropyl-d-hexylcarbinol: α_D at 18·5°, +17·86°.

α_{gr} at 18·5°, +21·24°; at 40°, +20·60°; at 62°, +19·94°; at 98°, +18·46°; at 112°, +17·96°; at 127°, +17·42°; and at 147°, +16·50°. The values of the optical rotatory dispersive power calculated from these and previously recorded observations are: at 20°, 0·841; at 40°, 0·842; at 60°, 0·840; at 80°, 0·839; at 100°, 0·840; at 120°, 0·840; at 140°, 0·840; and at 160°, 0·841, the average value being 0·840.

*Determinations of the Rotatory Power in Absolute Ethyl.
Alcohol.*

Carbinols, CH₃·CH(OH)·R.

	Weight taken in grams.	Observed rotation. α_D .	$[\alpha]_D$.	$[\eta]_D$.
Methyl-ethylcarbinol	1·0167	+1·48°	+14·55°	+10·77°
Methyl- <i>n</i> -propylcarbinol	1·0641	1·65	15·51	13·60
Methyl- <i>n</i> -butylcarbinol	1·0471	1·33	12·70	12·95
Methyl- <i>n</i> -amylcarbinol	1·0392	1·19	11·45	13·28
Methyl- <i>n</i> -hexylcarbinol	1·0923	1·07	9·79	12·73
Methyl- <i>n</i> -heptylcarbinol	1·1427	1·04	9·10	13·10
Methyl- <i>n</i> -octylcarbinol	1·0126	0·90	8·89	14·04
Methyl- <i>n</i> -nonylcarbinol	1·0229	0·83	8·11	13·95
Methyl- <i>n</i> -decylcarbinol	0·8694	0·69	7·94	14·76
Methyl- <i>n</i> -undecylcarbinol	1·0174	0·75	7·37	14·74

Carbinols, CH(CH₃)₂·CH(OH)·R.

<i>iso</i> Propylmethylcarbinol	0·9555	+0·51°	+5·34°	+4·70°
<i>iso</i> Propylethylcarbinol	1·0670	1·75	16·40	16·73
<i>iso</i> Propyl- <i>n</i> -propylcarbinol	0·9942	2·32	23·34	27·07
<i>iso</i> Propyl- <i>n</i> -butylcarbinol	1·0589	2·93	27·67	35·97
<i>iso</i> Propyl- <i>n</i> -amylcarbinol	0·9713	2·58	26·56	38·24
<i>iso</i> Propyl- <i>n</i> -hexylcarbinol	1·1242	2·73	24·28	38·36
<i>iso</i> Propyl- <i>n</i> -octylcarbinol	1·0002	2·15	21·50	39·99
<i>iso</i> Propyl- <i>n</i> -decylcarbinol	1·1852	2·18	18·34	39·38

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*Determinations of the Rotatory Power in Absolute Ethyl Alcohol (continued).**Carbinols, C₂H₅·CH(OH)·R.*

	Weight taken in grams.	Observed rotation. α_D	$[\alpha]_D$	$[M]_D$
Ethyl- <i>n</i> -propylcarbinol	1·0426	-0·12°	1·15°	1·17°
Ethyl- <i>n</i> -butylcarbinol	1·0070	+0·97	9·63	11·17
Ethyl- <i>n</i> -amylcarbinol	0·9791	+1·09	11·13	14·47
Ethyl- <i>n</i> -hexylcarbinol	1·0182	+0·98	9·63	13·86
Ethyl- <i>n</i> -heptylcarbinol	0·9990	-0·62	6·21	9·81
Ethyl- <i>n</i> -octylcarbinol	1·0449	-0·65	6·22	10·69
Ethyl- <i>n</i> -nonylcarbinol	1·1144	-0·68	6·10	11·35
Ethyl- <i>n</i> -decylcarbinol	0·9510	-0·64	6·73	13·46
Ethyl- <i>n</i> -undecylcarbinol	1·0728	-0·67	6·25	13·38
Ethyl- <i>n</i> -dodecylcarbinol	1·0988	-0·60	5·46	12·44
Ethyl- <i>n</i> -tridecylcarbinol	1·0461	-0·55	5·27	12·75
Ethyl- <i>n</i> -pentadecylcarbinol ...	1·0047	-0·48	4·78	12·91

*Determination of Rotatory Power of Carbinols, C₂H₅·CH(OH)·R, in Benzene.**Dextrorotatory Carbinols, CH₃·CH(OH)·R.*

Methyl- <i>n</i> -propylcarbinol ...	0·8059	+1·44°	+17·87°	+15·73°
Methyl- <i>n</i> -butylcarbinol	1·0111	1·41	13·95	14·23
Methyl- <i>n</i> -amylcarbinol	0·9918	1·36	13·71	15·90
Methyl- <i>n</i> -hexylcarbinol	1·1011	1·37	12·44	16·77
Methyl- <i>n</i> -heptylcarbinol ...	1·0090	1·19	11·90	16·98
Methyl- <i>n</i> -octylcarbinol	0·9953	1·14	11·46	18·10
Methyl- <i>n</i> -nonylcarbinol ...	1·0303	1·06	10·29	17·69
Methyl- <i>n</i> -decylcarbinol	0·6808	0·68	9·99	18·57
Methyl- <i>n</i> -undecylcarbinol ...	1·0180	0·89	8·74	17·48

	Weight taken in grams.	Observed rotation α_D	$[\alpha]_D$	$[M]_D$	Observed rotation α_{gr}	$[\alpha]_{gr}$	$[M]_{gr}$
<i>d</i> -Ethyl-methyl- carbinol	1·0632	+1·50	+14·11°	+10·44°	+1·71°	+16·09°	+11·91
<i>l</i> -Ethyl- <i>n</i> -pro- pylcarbinol ...	1·0356	-0·19	-1·83	-1·87	-0·28	-2·70	-2·75
<i>d</i> -Ethyl- <i>n</i> -bu- tylcarbinol ...	1·0092	+0·94	+9·31	+10·80	+1·08	+10·70	+12·41
<i>d</i> -Ethyl- <i>n</i> -amyl- carbinol	1·0196	+1·04	+10·20	+13·26	+1·16	+11·38	+14·79
<i>d</i> -Ethyl- <i>n</i> -hexyl carbinol	1·0417	+1·00	+9·60	+13·82	+1·13	+10·85	+15·62
<i>l</i> -Ethyl- <i>n</i> -hep- tylcarbinol ...	1·0434	-0·80	-7·67	-12·11	-0·94	-9·01	-14·24
<i>l</i> -Ethyl- <i>n</i> -octyl- carbinol	0·9886	-0·70	-7·08	-12·18	-0·86	-8·70	-14·96
<i>l</i> -Ethyl- <i>n</i> -no- nylcarbinol ...	1·0737	-0·72	-6·71	-12·48	-0·89	-8·29	-15·41
<i>l</i> -Ethyl- <i>n</i> -decyl- carbinol	0·9581	-0·70	-7·31	-14·62	-0·80	-8·35	-16·70
<i>l</i> -Ethyl- <i>n</i> -un- decylcarbinol.	1·0282	-0·75	-7·29	-15·60	-0·88	-8·56	-18·32
<i>l</i> -Ethyl- <i>n</i> -do- decylcarbinol.	0·9522	-0·64	-6·72	-15·32	-0·76	-7·98	-18·20
<i>l</i> -Ethyl- <i>n</i> -tri- decylcarbinol.	1·0650	-0·68	-6·38	-15·44	-0·83	-7·79	-18·85
<i>l</i> -Ethyl- <i>n</i> -penta- decylcarbinol.	1·0067	-0·62	-6·16	-16·63	-0·75	-7·45	-20·12

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