INFLUENCE of SUBSTITUTION and SOLVENT ACTION on the OPTICAL ROTATION of ORGANIC COMPOUNDS: SOME β-OCTYL ESTERS of SUBSTITUTED ACETIC ACIDS.

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C O N T E N T S.

The first conception of any relationship existing between optical activity and chemical constitution was put forward independently in 1874 by van't Hoff and Le Bel. According to their theory, all optically active compounds, whether in the fused state or in solution, contain within the molecule at least one asymmetric atom. Assuming that such a relationship does exist, it has not yet been found possible to determine the magnitude of the rotation in terms of the physical or chemical properties of the radicals which make up the asymmetric molecule.

Crum Brown[1] suggested that, if each of the radicals had assigned to it a value K which determined its influence on the rotation, then the rotation of the molecule would be governed by the differences between these values. Although he was able to conclude from experimental evidence that this value increases with the size of the radical, no more definite meaning has yet been attached to this function K.

Guye[2] took another view of the subject by considering rotatory power to be dependent on the weight of the four groups attached to the asymmetric carbon /

1. Proc. Roy. Soc. Edinb., 1890, 17, 181.
2. Compt. rend., 1890, 110, 714; 1893, 116, 1378.

carbon atom and on the distances of their respective centres of gravity from this atom. Therefore, when two of the groups are equal in weight and their space arrangement about the asymmetric atom is similar, the substance should be inactive. But Guye, himself, discovered that two different groups of equal mass did not destroy optical activity, and Walden [1] has shown that the acyl derivatives of the malic esters have approximately the same rotation irrespective of the mass of the acid radical.

Since the theories of Crum Brown and Guye, a great many investigations have been made with a view to establishing a relationship between optical activity and molecular structure.

Rupe,[2] as a result of his earlier investigations, considered the presence of unsaturated groups as causing an increased rotation, which diminishes with the increased distance of the unsaturated residue from the active radical. But Hilditch [3] found that the introduction of phenyl groups produces unaccountable irregularities depending on the position of the phenyl group in relation to the double bond. Thus unsaturation seems to bring about an irregularity in the rotatory effect, /

1. Zeit. Phys. Chem., 1895, 17, 245.
2. Annalen, 1903, 327, 157.
3. Journal of the Chemical Society, 1908, 93, 700; 1911, 99, 218.

effect, although not necessarily an increased rotation.[1].

Another generalisation has resulted from the work of Pickard and Kenyon [2] on three series of active secondary alcohols. In the ethyl series, $C_2H_5CH(OH).R$, there are sudden increments, or decrements, of rotation as the number of carbon atoms in R reaches 5, 10, and 15, and also similar but smaller changes in the value of the rotation when the whole chain makes five or a multiple of five carbon atoms. In addition, this effect is often greater in alcoholic solution. These results have been explained by Frankland [3] on the basis of Baeyer's strain theory as being due to the influence of the end of the chain as it returns upon itself in space. A similar effect has been observed by Hilditch [4] among the dimenthyl esters of dicarboxylic acids, the ester of adipic acid having an abnormally high rotation.

Tschugaeff [5] examined the menthyl esters of the homologous series of aliphatic acids, and found that the greatest differences in the rotation occurred in the first two or three members of the series /

1. Frankland, J.C.S., 1912, 101, 661; Rupe, Trans. Faraday Soc., 1914, 10, 5.
2. J.C.S., 1911, 99. 45; 1912, 101, 620, 1427; 1913, 103, 1923; 1914, 105, 830, 2228,2262.
3. J.C.S., 1899, 75, 368.
4. J.C.S., 1909, 95, 1581.
5. Ber., 1898, 31, 364.

series and that the subsequent introduction of methylene groups produced less and less change in the rotation until, in many cases, a constant value was finally reached. In another series of esters of active amyl alcohol examined by Guye and Chavanne (compt. rend. 1895, 120, 152), the same thing has been observed. The rotation constants of the amyl and menthyl esters of benzoic acid and its side-chain homologues also show that the active group is influenced chiefly by the atoms in its vicinity, for, as the carboxyl group is removed further from the nucleus, the values gradually approximate to those of the aliphatic esters. Although the proximity of the phenyl group to the active radical usually raises the rotation, it produces the reverse effect in the esters of carvoxime.[1].

Similar conditions are revealed by Cohen's[2] work on the effect of the ortho, meta, and para substituents on the rotation of menthyl benzoate, i.e., the group nearest to the active radical generally produces the greatest effect. Cohen concludes that the ortho substituent may either raise or lower the rotatory power, but, whichever occurs, the effect of the same substituent in the meta and para positions is negligible. His conclusion, however, /

1. Rupe and Walden, Annalen, 1912, 395, 136.
2. J.C.S., 1914, 105, 1895.

however, is not borne out by the results for the corresponding octyl esters (Rule and Numbers, J.C.S., 1926, 2116). These authors have found that, in the case of octyl esters of substituted benzoic acids, the ortho substituent causes a decided increase in the rotatory power when in the meta and para positions.

A further conclusion resulting from their work on these octyl esters is that in the ortho position the m-directive nitro and carboxyl groups increase the rotation, whereas the o-,p-directive methoxy and chloro groups decrease the rotation. These same effects were pointed out by Rule [1] to exist in the case of menthyl benzoate, and he also showed that the relative influence of a number of different substituents on the rotation of the menthyl esters of substituted benzoic acids is in close agreement with their relative polarity and with their relative influence on the nitration of mono-substituted benzenes.

The rotations of halogen substituted menthyl esters of the aliphatic acids have been examined by Tschugaeff [2], Cohen [3], and Hilditch [4], from whose work it appears that the introduction of a halogen usually /

1. J.C.S., 1924, 125, 1122.
2. J. Russ. Phys. Chem. Soc., 1902, 34, 606.
3. J.C.S., 1911, 99, 1061.
4. J.C.S., 1912, 101, 202.

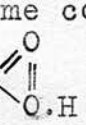
usually raises the rotation and that the effect is in the inverse order of the atomic weight of the halogen. These effects are also noticed in the active esters of substituted benzoic acids.

A large number of compounds have been prepared by Betti [1] by the condensation of an active base with substituted benzaldehydes, and an examination of their rotatory powers in benzene solution has shown that the influence of substituents on rotation corresponds with their influence on the acidity of the corresponding benzoic acids. A similar substituent effect has been found in the menthyl esters of monosubstituted acetic acids [2]. This effect differs from that mentioned above for active esters of o-substituted benzoic acids, however, in which substituents appear to fall into two separate groups, according as they are m-directive or o-,p-directive [3].

The effect of a solvent on the activity of the dissolved substance is often very marked. This effect depends also on both temperature and concentration, and up till now no satisfactory connection has been established between the chemical nature of the active substance and the variation of its activity with change of solvent.

Pickard /

1. Gazzetta, 1923, 53, 417.
2. Rule and Smith, J.C.S., 1925, 127, 2188.
3. Rule and Numbers, J.C.S., 1926, 2116.

Pickard and Kenyon[1], from their work on the carbinols of the methyl series $CH_3.CH(OH).R$, have suggested that variation of temperature and solvents each alters the degree of association of esters and consequently their rotatory power. However, this kind of association seems to be distinct from the union of two or more molecules, and probably does not involve any alteration in the mass of the molecules, but can be accounted for by changes in the valency of the oxygen atoms in the group - CO.OR. These authors also suggest that the association, which, in the cases of the esters, has so great an effect on their rotatory power, is of two kinds, and the phenomenon might be described as a change in the size of, or space occupied by, the molecules of the substance. One kind occurs only in the case of molecules of simplest chemical constitution as, for example, in the case of the carbinols of the methyl series $CH_3.CH(OH).R$, where the presence of a solvent facilitates the more unrestricted spatial development of the chain of carbon atoms, and hence its specific action on the rotatory power. This development is masked when the compounds are examined in the homogeneous state. The second kind of association they attribute to the exercise of supplementary valencies of the oxygen atom. For example, the carboxylic group, under some conditions, is better represented by the formula  than by the /

1. J.C.S., 1914, 105, 830.

the more general form $-C\overset{O}{\underset{O.H}{<}}$, and it is possible that increase of temperature would tend to convert a compound of the type $R.C\overset{O}{\underset{O.R}{<}}$ into $R.C\overset{O}{\underset{O.R}{<}}$ and so affect its rotatory power.[1] This same change might possibly be brought about by certain solvents.

Another factor governing rotatory power is the wave-length of the light used in the measurement. Biot found that, for certain substances, the rotation varied inversely as the square of the wave-length of the light employed, thus having what is called normal and simple dispersion, so that by plotting the reciprocal of the rotation against the squares of the wave-lengths the values should lie on a straight line. Other substances, however, under certain conditions, show an increased or decreased rotation with increase or decrease of the wave-length, i.e., they have anomalous dispersion. Such substances [1], he suggested, showed anomalous dispersion because of the presence in the substance of two optically active components of different dispersive power. Armstrong and Walker [2] have correlated the different specific rotatory powers exhibited under different conditions of temperature and solution by apparently homogeneous substances, /

1. J.C.S., 1914, 105, 830.

2. Proc. Roy. Soc., 1913, A, 88, 388.

substances, such as ethyl tartrate, by assuming that the rotatory power of each of the constituent isomerides is constant under all conditions and that the composition of the "mixture" is a linear function of the specific rotatory power for light of a given wave-length. From these they construct rotation-composition diagrams which they call "characteristic" diagrams. Pickard and Kenyon, however, have not found any direct evidence to show that any one of the esters prepared as described by them is a mixture of two isomerides.

The effect of different solvents can also, in certain cases, be accounted for on the dissociation hypothesis, since, for imperfect electrolytes such as the organic acids, the extent of electrolytic dissociation is influenced by dilution and change of temperature, with a corresponding change in the rotation.

Patterson [1] has come to the conclusion that the only effect which change of temperature, solvent, and concentration has on tartaric ester and its derivatives is to shift the position of the rotation curve, and from this he suggests that the "characteristic" diagram for a particular substance will depend on the region of the temperature-rotation /

1. J.C.S., 1916, 109, 1139, 1176.

temperature-rotation curves from which the data are taken, and consequently any given substance may have more than one "characteristic" diagram. He also summarises his results in the following words: "Since the dispersion curves for the same and for related active substances at widely different temperatures and under very different conditions are only slightly different, the parts played by so-called secondary causes such as polymerisation, solvation, dissociation, dynamic isomerism, or residual affinity are either non-existent or are very unimportant in regard to the phenomena of optical activity".

In the following thesis an account is given of the preparation and properties of some active secondary β-octyl esters of substituted acetic acids, and of the manner in which their rotatory powers are influenced by the presence of solvents.

E X P E R I M E N T A L.

The optically active Octyl Alcohol used in the preparation of the octyl esters of the substituted acetic acids described later was prepared according to Kenyon's modification [1] of the method of Pickard and Kenyon [2], and had a rotation of $\alpha_D^{16} = \pm 8.19^\circ$. $l = 1$

Optical measurements were made using a "Schmidt & Haensch" polarimeter capable of holding a two decimetre observation tube. This instrument was specially fitted by A. Hilger, Ltd., with a direct vision spectroscopic attachment for reading rotations with the three mercury lines (yellow, green, and violet).

A considerable amount of trouble was experienced in devising an arrangement whereby a continuous flow of water at constant temperature could be made to pass through the jacket of the observation tube. The most successful results were obtained by making use of the following device:- Water, from a constant head, was slowly passed down the inner tube of a copper condenser into a thermostat, then through the polarimeter tube and finally back through the outer condenser jacket to waste.

All outside tubes were lagged, and in this way the /

1. J.C.S. 1922, 121, 2540.
2. J.C.S. 1907, 91, 2058.

the temperature inside the tube could be maintained within 0·1° over a set of readings.

Mercury Lamp:- A Cooper Hewitt Silica Lamp for direct current circuits was used as the source of mercury light.

PREPARATION of *l*-β-OCTYL METHOXYACETATE.

This ester was prepared from monochloracetic acid in three stages as follows:-

(1) $Cl.CH_2.COOH \xrightarrow{CH_3ONa} CH_3O.CH_2.COOH$

(2) $CH_3O.CH_2.COOH \xrightarrow{SOCl_2} CH_3O.CH_2.COCl$

(3) $CH_3O.CH_2.COCl \xrightarrow{l\text{-}\beta\text{-Octyl Alcohol}} CH_3O.CH_2.COOC_8H_{17}$.

(1). Methoxyacetic Acid.

This compound was prepared by the method described by Sommelet * for the preparation of ethoxyacetic acid, except that methyl alcohol was used instead of ethyl alcohol.

92 grammes of sodium were dissolved in 928 gms. of /

* Bulletin de la Societe chimique de France, 1907, (IV), 366.

of methyl alcohol contained in a round flask fitted with a reflux condenser; then, without allowing the liquid to cool, a solution of 189 gms. of monochloracetic acid in its own weight of methyl alcohol was gradually added. At each addition an energetic action took place with deposition of sodium chloride. As the acid was added fairly quickly the boiling of the liquid was not interrupted, and it only required about twenty minutes of external heating to complete the reaction. The flask now contained a brownish-yellow liquid from which alcohol was removed by distillation in a current of steam. There remained an aqueous solution of sodium chloride and of sodium methoxyacetate. When cold, the solution was acidified by adding concentrated hydrochloric acid which resulted in sodium chloride being deposited. The latter was next filtered off, and the acid extracted with ether and dried over anhydrous sodium sulphate. After several days the sodium sulphate was removed by filtration, the ether evaporated, and the acid submitted to distillation under diminished pressure. On repeated distillation a liquid b.p. 100·5°/16 mm. was obtained which solidified in the condenser.

Yield ?

(2). Preparation of Methoxyacetyl Chloride.

The following method of preparation is also according to Sommelet* :-

23 gms. of methoxyacetic acid were mixed with 30 gms. of purified thionyl chloride at the ordinary temperature, but as the reaction was feeble the mixture was heated on a water-bath at 40°C. and then at 60°C. until there was no longer any gas evolved. The mixture was distilled, and, after removal of excess thionyl chloride, there was obtained a yield of 22 gms. of crude acid chloride. This was used without further purification, as the chloride tends to decompose on distillation.

(3). Preparation of β-Octyl Ester.

The ester was prepared by making use of the following method, as described in U.S. Pat. 836914, R. Berendes, Elberfeld, F. Bayer & Co. (slightly modified).

Reaction Mixture:-

ℓ-β-Octyl Alcohol	...	17 gms.
Pyridine ...	...	15 "
Benzene ...	...	98 "
Methoxyacetyl Chloride	...	21 "

* Bull. Soc. Chim., 1907 (IV), 368.

This mixture was heated on a water-bath for 5 hours, shaken with dilute hydrochloric acid to extract the pyridine and afterwards with dilute sodium carbonate solution and with water. The benzene solution was then separated from the water and dried over calcium chloride. The benzene was removed and the residue distilled in vacuo.

After being twice fractionated under diminished pressure a third fractionation produced no change in the rotatory power.

Yield:- 16 gms. of ester b.p. 120-121°/15 mm.
(62% of the theoretical amount).

0.1639 gms. ester gave 0·3918 gms. CO_2 and 0·1623 gms. H_2O;

C = 65·19; H = 11·10.

$C_{11}H_{22}O_3$ requires C = 65·28; H = 10·99.

DENSITY DETERMINATIONS.

In the case of this ester density determinations were carried out using a calibrated pyknometer holding about 2 ccs. at room temperature. The densities were calculated with reference to that of water at 4°C.

t^o	20·5	40·7	57·6	80·9
$d_{4^o}^{t}$	0·9721	0·9568	0·9435	0·9253

Temperature	Length of Observation Tube in mm.	Rotation α	$\frac{\alpha_{vi}}{\alpha_D}$
20.9° 20.5 20.7 20.6	50	α_D = 3.90° α_{ye} = 4.08 α_{gr} = 4.60 α_{vi} = 7.33	1.88
38.5° 38.7 38.6 38.5	50	α_D = 3.51 α_{ye} = 3.65 α_{gr} = 4.12 α_{vi} = 6.52	1.86
60.5° 60.4 60.9 60.3	50	α_D = 3.20 α_{ye} = 3.33 α_{gr} = 3.73 α_{vi} = 5.88	1.84
93.7° 93.2 93.7 93.5	50	α_D = 2.70 α_{ye} = 2.81 α_{gr} = 3.20 α_{vi} = 4.84	1.79

l-β-Octyl Methoxyacetate.

MEASUREMENT of ROTATORY POWERS.

The rotatory powers of this ester were first measured in the homogeneous state in a jacketed tube, round which hot water from a thermostat was circulated.

In the following determinations all rotations are negative.

(TABLE opposite).

When the above rotations were plotted against the corresponding temperatures, smooth curves were obtained from which the values of the rotatory power at 20°, 40°, 60°, 80°, and 90° were found to be as follows:-

TABLE /

l-β-Octyl Methoxyacetate.

Rotatory Powers at Different Temperatures.

Temperature.	Density	α_D	α_{ye}	α_{gr}	α_{vi}	$[\alpha]_D$	$[\alpha]_{ye}$	$[\alpha]_{gr}$	$[\alpha]_{vi}$
20°	.9726	−3.93	− 4.10	− 4.63	− 7.35	− 8.08	− 8.43	− 9.52	− 15.11
40°	.9570	3.50	3.64	4.11	6.59	7.31	7.61	8.59	13.77
60°	.9418	3.14	3.26	3.70	5.90	6.67	6.92	7.86	12.53
80°	.9261	2.84	2.96	3.38	5.25	6.13	6.39	7.30	11.34
90°	.9185	2.73	2.84	3.26	4.95	5.95	6.18	7.10	10.77

ROTATORY POWERS in DIFFERENT SOLVENTS.

A number of measurements were made of the rotatory powers of the β-octyl esters of methoxy-, chloro-, bromo-, and iodo-acetic acids when contained in 5% solution in a number of different solvents at 20°. All solvents used were specially purified, acetone being from the bisulphite compound.

Owing to the yellow colour of the iodobenzene it was not possible to obtain a value for the violet line for the esters in this solvent. A similar difficulty occurred with the iodo-ester in bromobenzene and pyridine.

For convenience of reference, figures in this and following tables are calculated to the second decimal place, but, owing to the small observed rotations, the accuracy is in many cases limited to two significant figures, or even less. These tables are given on pages 19, 24, 29, 34.

TABLE. /

ROTATORY POWER of *l*-β-OCTYL METHOXYACETATE

Length of Observation Tube 20 cms., except in the case of

Solvent	Weight in 25 ccs. Solvent.	Rotation. α_D	α_{gr}	α_{vi}	$\frac{\alpha_{vi}}{\alpha_D}$
Ethylene Dibromide	1.2242	- 0.93	- 1.06	- 1.80	1.94
Ester ✱ (homog.)	--	- 7.86	- 9.26	-14.70	1.87
Carbon Tetrachloride	1.2267	- 0.63	- 0.72	- 1.15	1.83
Ethyl Acetate	1.1931	- 0.59	- 0.71	- 1.15	1.95
Nitromethane	1.2055	- 0.59	- 0.70	- 1.12	1.90
Acetone	1.2503	- 0.59	- 0.67	- 1.11	1.88
Acetic Acid	1.1961	- 0.55	- 0.63	- 0.97	1.76
Chloroform	1.2015	- 0.55	- 0.62	- 0.97	1.76
s-Tetrachlorethane	1.2872	- 0.58	- 0.64	- 1.04	1.79
Ethyl Alcohol	1.2285	- 0.55	- 0.64	- 1.04	1.89
Benzene	1.2710	+ 0.05	+ 0.07	+ 0.24	4.80
Phenetole	1.1883	+ 0.30	+ 0.34	+ 0.72	2.40
Chlorobenzene ✱	0.5141 in 10 ccs.	+ 0.18	+ 0.23	+ 0.44	2.44
Bromobenzene ✱	0.5198 in 10 ccs.	+ 0.18	+ 0.23	+ 0.44	2.44
Pyridine	1.2290	+ 0.56	+ 0.68	+ 1.16	2.07
Iodobenzene ✱	0.4945 in 10 ccs.	+ 0.31	+ 0.37	--	--
Carbon Disulphide	1.2058	+ 0.70	+ 0.79	+ 1.80	2.57

in VARIOUS 5% SOLUTIONS at 20°.

those Solvents marked ⁂, where a 10 cm. tube was used.

Specific Rotation.			Molecular Rotation.		
$[\alpha]_D$	$[\alpha]_{gr}$	$[\alpha]_{vi}$	$[M]_D$	$[M]_{gr}$	$[M]_{vi}$
− 9.50	− 10.82	− 18.38	− 19.21	− 21.88	− 37.00
− 8.08	− 9.52	− 15.11	− 16.34	− 19.25	− 30.56
− 6.42	− 7.34	− 11.72	− 12.98	− 14.85	− 23.70
− 6.18	− 7.44	− 12.05	− 12.49	− 15.04	− 24.36
− 6.12	− 7.26	− 11.61	− 12.38	− 14.68	− 23.48
− 5.90	− 6.70	− 11.10	− 11.93	− 13.55	− 22.45
− 5.75	− 6.58	− 10.14	− 11.62	− 13.30	− 20.50
− 5.72	− 6.45	− 10.09	− 11.57	− 13.04	− 20.40
− 5.63	− 6.22	− 10.10	− 11.39	− 12.58	− 20.42
− 5.60	− 6.51	− 10.58	− 11.32	− 13.16	− 21.39
+ 0.49	+ 0.69	+ 2.36	+ 0.99	+ 1.40	+ 4.77
+ 3.16	+ 3.58	+ 7.57	+ 6.39	+ 7.24	+ 15.31
+ 3.50	+ 4.47	+ 8.56	+ 7.08	+ 9.04	+ 17.31
+ 3.46	+ 4.42	+ 8.46	+ 7.00	+ 8.94	+ 17.11
+ 5.70	+ 6.92	+ 11.80	+ 11.53	+ 13.99	+ 23.86
+ 6.27	+ 7.48	--	+ 12.68	+ 15.12	--
+ 7.26	+ 8.19	+ 18.66	+ 14.68	+ 16.56	+ 37.73

PREPARATION of *l*-β-OCTYL CHLORACETATE.

This ester was prepared as follows:-

16 gms. of *l*-β-octyl alcohol dissolved in benzene was refluxed with 14 gms. of purified chloracetyl chloride (equimolecular quantities of chloride and alcohol) on a water-bath for nine hours. The benzene was then distilled off, and the residue subjected to fractional distillation under diminished pressure.

A constant value for the rotatory power was obtained after four fractionations.

Yield:- 22 gms. of ester b.p. 119 - 121°/15 mm (87% of the theoretical amount).

A determination of chlorine by Stepanow's method gave 17.6%.

$CH_2Cl.COOC_8H_{17}$ requires 17.2% Cl.

DENSITY /

DENSITY DETERMINATIONS.

Density determinations were carried out using a calibrated pyknometer holding about 2 cc.

The densities were calculated with reference to that of water at 4°C.

t°	20.3°	39.4°	58.4°	81.1°
$d_{4^{\circ}}^{t^{\circ}}$	0.9900	0.9747	0.9603	0.9413

MEASUREMENT of ROTATORY POWERS.

In the following determinations a one decimetre jacketed tube was used, and all rotations are negative.

TABLE. /

l-β-COTYL CHLORACETATE.

Temperature	Length of Observation Tube in mm.	Rotation. α	$\frac{\alpha_{vi}}{\alpha_D}$
18.7° 19.0 18.6 18.8	100	α_D = 8.64° α_{ye} = 9.04 α_{gr} = 10.14 α_{vi} = 16.09	1.86
38.2° 38.3 38.3 38.7	100	α_D = 7.82 α_{ye} = 8.24 α_{gr} = 9.19 α_{vi} = 14.78	1.89
59.5° 59.6 59.7 59.7	100	α_D = 7.06 α_{ye} = 7.21 α_{gr} = 8.10 α_{vi} = 12.94	1.83
89.9° 90.0 89.7 90.3	100	α_D = 6.13 α_{ye} = 6.47 α_{gr} = 7.24 α_{vi} = 11.51	1.88

The above rotations were plotted against the corresponding temperatures and the values of the rotations at 20°, 40°, 60°, 80°, and 90° were read off from the smooth curves.

l-β-OCTYL CHLORACETATE.

Rotatory Powers at Different Temperatures.

Temperature.	Density	α_D	α_{ye}	α_{gr}	α_{vi}	$[\alpha]_D$	$[\alpha]_{ye}$	$[\alpha]_{gr}$	$[\alpha]_{vi}$
20°	0.9903	- 8.58	- 8.99	- 10.06	- 16.03	- 8.67	- 9.08	- 10.16	- 16.19
40°	0.9742	7.74	8.17	9.17	14.67	7.94	8.39	9.41	15.05
60°	0.9582	7.02	7.42	8.32	13.33	7.32	7.74	8.68	13.91
80°	0.9422	6.39	6.76	7.57	12.09	6.78	7.17	8.03	12.83
90°	0.9342	6.12	6.47	7.23	11.54	6.55	6.93	7.74	12.35

ROTATORY POWER of *l*-β-OCTYL CHLORACETATE

Length of Observation Tube 20 cms., except in the case of

Solvent	Weight in 25 ccs. Solvent.	Rotation. α_D	Rotation. α_{gr}	α_{vi}	$\frac{\alpha_{vi}}{\alpha_D}$
Ethylene Dibromide	1.2710	− 1.05	− 1.20	− 2.06	1.96
Ester * (homog.)	--	− 8.58	−10.06	−16.03	1.87
Carbon Tetrachloride	1.2133	− 0.77	− 0.91	− 1.48	1.91
Ethyl Acetate	1.2322	− 0.71	− 0.90	− 1.43	2.01
Nitromethane	1.2635	− 0.69	− 0.80	− 1.25	1.81
s-Tetrachlorethane	1.2284	− 0.64	− 0.74	− 1.27	1.98
Acetone	1.2688	− 0.65	− 0.80	− 1.23	1.89
Ethyl Alcohol	1.2806	− 0.64	− 0.78	− 1.21	1.89
Chloroform	1.2252	− 0.60	− 0.72	− 1.10	1.83
Acetic Acid	1.2078	− 0.54	− 0.66	− 1.06	1.96
Benzene	1.2592	− 0.04	− 0.05	− 0.09	2.25
Phenetole	1.1941	+ 0.24	+ 0.32	+ 0.60	2.50
Chlorobenzene *	0.4950 in 10 ccs.	+ 0.16	+ 0.23	+ 0.41	2.56
Bromobenzene *	0.4924 in 10 ccs.	+ 0.21	+ 0.22	+ 0.42	2.00
Iodobenzene *	0.4988 in 10 ccs.	+ 0.24	+ 0.29	--	--
Carbon Disulphide	1.2275	+ 0.51	+ 0.66	+ 1.52	2.98
Pyridine	1.2677	(+ 0.57)	(+ 0.63)	(+ 1.11)	1.95

in VARIOUS 5% SOLUTIONS at 20°.

those Solvents marked x, where a 10 cm. tube was used.

Specific Rotation.			Molecular Rotation.		
$[\alpha]_D$	$[\alpha]_{gr}$	$[\alpha]_{vi}$	$[M]_D$	$[M]_{gr}$	$[M]_{vi}$
− 10.33	− 11.80	− 20.26	− 21.34	− 24.39	− 41.88
− 8.67	− 10.16	− 16.19	− 17.92	− 20.99	− 33.45
− 7.93	− 9.38	− 15.25	− 16.39	− 19.38	− 31.51
− 7.20	− 9.13	− 14.51	− 14.88	− 18.87	− 29.98
− 6.83	− 7.91	− 12.37	− 14.11	− 16.35	− 25.57
− 6.51	− 7.53	− 12.92	− 13.45	− 15.56	− 26.70
− 6.40	− 7.88	− 12.12	− 13.22	− 16.29	− 25.04
− 6.25	− 7.61	− 11.81	− 12.91	− 15.72	− 24.41
− 6.12	− 7.35	− 11.22	− 12.65	− 15.19	− 23.18
− 5.59	− 6.83	− 10.97	− 11.55	− 14.11	− 22.67
− 0.40	− 0.50	− 0.89	− 0.83	− 1.03	− 1.85
+ 2.51	+ 3.35	+ 6.28	+ 5.19	+ 6.92	+ 12.98
+ 3.23	+ 4.65	+ 8.28	+ 6.67	+ 9.61	+ 17.11
+ 4.26	+ 4.47	+ 8.53	+ 8.80	+ 9.24	+ 17.62
+ 4.81	+ 5.81	--	+ 9.94	+ 12.00	--
+ 5.19	+ 6.72	+ 15.48	+ 10.73	+ 13.89	+ 31.99
(+ 5.62)	(+ 6.21)	(+ 10.95)	(+ 11.61)	(+ 12.83)	(+ 22.62)

PREPARATION of *l*-β-OCTYL BROMACETATE.

This ester was prepared as follows:-

31 gms. of bromacetyl bromide was dissolved in chloroform and refluxed with 20 gms. of *l*-β-octyl alcohol (equimolecular quantities of bromide and alcohol) on a water-bath for six hours. The chloroform was distilled off, and the residue subjected to fractional distillation under reduced pressure. Several fractionations were required before a product of constant rotatory power was obtained.

Yield:- 24 gms. of ester b.p. 121°/15 mm.
(63% of theoretical amount).

A determination of Bromine by Stepanow's method gave 31.7%.

$CH_2Br.COOC_8H_{17}$ requires 31.8% Br.

DENSITY /

DENSITY DETERMINATIONS.

Density determinations were again carried out using a calibrated pyknometer holding about 2 ccs.

The densities were calculated with reference to that of water at 4°C.

t^o	22.6	40.8	59.6	83.8
$d_{4^o}^{t^o}$	1.1731	1.1549	1.1360	1.1127

MEASUREMENT of ROTATORY POWERS.

Except where otherwise stated a 50 mm. jacketed metallic tube was used in the following determinations.

In the following determinations all rotations are negative.

TABLE. /

l-β-OCTYL BROMACETATE.

Temperature	Length of Observation Tube in mm.	Rotation α	$\frac{\alpha_{vi}}{\alpha_D}$
22° 22.5 22.5 22	100	α_D = 13.34 α_{ye} = 13.89 α_{gr} = 15.71 α_{vi} = 26.58	1.99
37.8° 37.5 37.7 37.7	100	α_D = 12.40 α_{ye} = 13.02 α_{gr} = 14.67 α_{vi} = 24.72	1.99
53.4° 53.4 53.4 53.5	50	α_D = 5.67 α_{ye} = 6.03 α_{gr} = 6.75 α_{vi} = 11.29	1.99
75.6° 75.4 75.7 75.4	50	α_D = 5.20 α_{ye} = 5.49 α_{gr} = 6.24 α_{vi} = 10.24	1.97

The above rotations were plotted against the corresponding temperatures and the values of the rotations at 20°, 40°, 60°, 80°, and 90°. were read off from the smooth curves.

l-β-OCTYL BROMACETATE.

Rotatory Powers at Different Temperatures.

Temperature.	Density	α_D	α_{ye}	α_{gr}	α_{vi}	$[\alpha]_D$	$[\alpha]_{ye}$	$[\alpha]_{gr}$	$[\alpha]_{vi}$
20°	1.1756	- 13.46	- 14.13	- 15.97	- 26.85	- 11.45	- 12.02	- 13.58	- 22.84
40°	1.1557	12.20	12.82	14.44	24.41	10.56	11.09	12.50	21.12
60°	1.1358	11.10	11.68	13.19	22.04	9.77	10.26	11.62	19.41
80°	1.1161	10.21	10.72	12.30	20.00	9.15	9.61	11.02	17.92
90°	1.1062	9.86	10.36	12.00	19.11	8.91	9.36	10.85	17.27

ROTATORY POWER of *l*-β-OCTYL BROMACETATE

Length of Observation Tube 20 cms., except in the case of

Solvent	Weight in 25 ccs. Solvent.	Rotation. α_D	Rotation. $\alpha_{gr.}$	Rotation. $\alpha_{vi.}$	$\frac{\alpha_{vi}}{\alpha_D}$
Ethylene Dibromide	1.2109	− 1.17	− 1.32	− 2.32	1.98
Ester ✠ (homog.)	--	− 13.46	− 15.97	− 26.85	1.99
Carbon Tetrachloride	1.2654	− 1.13	− 1.37	− 2.33	2.06
Ethyl Acetate	1.2657	− 1.07	− 1.29	− 2.20	2.05
Ethyl Alcohol	1.2584	− 1.06	− 1.28	− 2.17	2.05
Acetic Acid	1.2618	− 1.04	− 1.22	− 2.10	2.02
Acetone	1.1302	− 0.91	− 1.12	− 1.82	2.00
Nitromethane	1.2537	− 0.95	− 1.16	− 1.99	2.09
Chloroform	1.2159	− 0.88	− 1.02	− 1.69	1.92
s-Tetrachlorethane	1.3139	− 0.90	− 1.07	− 1.76	1.96
Benzene	1.2478	− 0.40	− 0.46	− 0.78	1.95
Phenetole	1.3415	− 0.21	− 0.28	− 0.39	1.86
Chlorobenzene ✠	0.4970 in 10 ccs.	− 0.05	− 0.06	− 0.09	1.80
Bromobenzene ✠	0.4607 in 10 ccs.	− 0.03	− 0.04	− 0.06	2.00
Iodobenzene ✠	0.5130 in 10 ccs.	+ 0.02	+ 0.05	--	--
Carbon Disulphide	1.2924	+ 0.05	+ 0.07	+ 0.39	7.80
Pyridine	1.2641	(+ 2.28)	(+ 2.72)	(+ 4.83)	2.12

in VARIOUS 5% SOLUTIONS at 20°.

those Solvents marked ×, where a 10 cm. tube was used.

Specific Rotation.			Molecular Rotation.		
$[\alpha]_D$	$[\alpha]_{gr}$	$[\alpha]_{vi}$	$[M]_D$	$[M]_{gr}$	$[M]_{vi}$
− 12.08	− 13.63	− 23.95	− 30.33	− 34.23	− 60.15
− 11.45	− 13.58	− 22.84	− 28.76	− 34.10	− 57.37
− 11.16	− 13.53	− 23.02	− 28.02	− 33.98	− 57.81
− 10.57	− 12.74	− 21.73	− 26.55	− 32.00	− 54.58
− 10.53	− 12.71	− 21.56	− 26.44	− 31.92	− 54.14
− 10.30	− 12.09	− 20.80	− 25.86	− 30.35	− 52.24
− 10.06	− 12.39	− 20.13	− 25.25	− 31.11	− 50.55
− 9.47	− 11.57	− 19.84	− 23.78	− 29.05	− 49.82
− 9.05	− 10.49	− 17.37	− 22.73	− 26.34	− 43.62
− 8.56	− 10.18	− 16.74	− 21.50	− 25.57	− 42.04
− 4.01	− 4.61	− 7.81	− 10.07	− 11.58	− 19.62
− 1.96	− 2.61	− 3.63	− 4.92	− 6.55	− 9.12
− 1.01	− 1.21	− 1.81	− 2.54	− 3.04	− 4.55
− 0.65	− 0.87	− 1.30	− 1.63	− 2.19	− 3.26
+ 0.39	+ 0.97	--	+ 0.98	+ 2.44	--
+ 0.48	+ 0.68	+ 3.77	+ 1.21	+ 1.71	+ 9.47
(+ 22.55)	(+ 26.90)	(+ 47.76)	(+ 56.63)	(+ 67.56)	(+ 119.9)

PREPARATION of α-β-OCTYL IODOACETATE.

This ester was prepared according to the method of Bodroux and Taboury [*].

(1) Preparation of Magnesium Iodide:-

27 gms. of pulverised iodine were introduced, in small portions at a time, into a round bottomed flask containing 3 gms. of magnesium turnings and 50 gms. of ether (dried over sodium). The reaction, energetic at first, became less so, and, finally, in order to obtain a colourless solution, it was necessary to boil for two hours.

(2) Preparation of α-β-Octyl Iodoacetate:-

$$2\ CH_2Cl.COOC_8H_{17} + MgI_2 \longrightarrow 2\ CH_2I.COOC_8H_{17} + MgCl_2.$$

22 gms. of α-β-octyl chloracetate (prepared as described previously) was added at once to the ethereal solution of magnesium iodide (twice the theoretical amount). There was no vigorous reaction, and, after standing for one hour, the mixture was decomposed with water, and extracted with ether. The ethereal extract was shaken with mercury to remove free iodine, and then dried over anhydrous sodium sulphate. After removal of the ether, the residue was subjected to distillation under reduced pressure. About 3 ccs. of liquid, coloured /

[*] Bull. Soc. Chim., 1907, IV (1), 909.

coloured with iodine, distilled below 145° under 20 mm. pressure. The next portion, almost colourless, distilled at 146-147° under 17 mm. pressure. About 3 ccs. of a dark red non-volatile liquid were left in the distillation flask.

Yield:- 20 gms. of ester b.p. 146-147°/17 mm.
(63% of theoretical amount).

There was no change in the rotatory power on fractionation.

A determination of iodine by Stepanow's method gave 42.6%.

$CH_2I.COOC_8H_{17}$ requires 42.6% I.

DENSITY DETERMINATIONS.

Density determinations were carried out using a calibrated pyknometer holding about 2 ccs.

The densities were calculated with reference to that of water at 4°C.

t°	21.2°	41.9°	64.3°
$d_{4^\circ}^{t}$	1.3013	1.2812	1.2587

d-β-OCTYL IODOACETATE.

MEASUREMENT of ROTATORY POWERS.

In the following determinations a one decimetre jacketed tube was used, and all rotations are positive.

Temperature.	Length of Observation Tube in mm.	Rotation. α	$\frac{\alpha_{vi}}{\alpha_D}$
20°	100	α_D = 19.08°	2.07
20		α_{ye} = 19.89	
19.8		α_{gr} = 22.72	
19.7		α_{vi} = 39.49	
37.9°	100	α_D = 17.63	2.05
37.9		α_{ye} = 18.32	
37.8		α_{gr} = 20.89	
38.2		α_{vi} = 36.10	
62°	100	α_D = 15.79	2.01
63		α_{ye} = 16.36	
63		α_{gr} = 18.58	
63		α_{vi} = 31.80	

d-β-OCTYL IODOACETATE.

Rotatory Powers at Different Temperatures.

Temperature.	Density	α_D	α_{ye}	α_{gr}	α_{vi}	$[\alpha]_D$	$[\alpha]_{ye}$	$[\alpha]_{gr}$	$[\alpha]_{vi}$
19.7°	1.3029	--	--	--	+ 39.49	--	--	--	+ 30.31
19.8°	1.3028	--	--	+ 22.72	--	--	--	+ 17.44	--
20°	1.3026	+ 19.08	+ 19.89	--	--	+ 14.65	+ 15.27	--	--
37.8°	1.2848	--	--	+ 20.89	--	--	--	+ 16.26	--
37.9°	1.2847	+ 17.63	+ 18.32	--	--	+ 13.72	+ 14.26	--	--
38.2°	1.2844	--	--	--	+ 36.10	--	--	--	+ 28.11
62°	1.2606	+ 15.79	--	--	--	+ 12.53	--	--	--
63°	1.2597	--	+ 16.36	+ 18.58	+ 31.80	--	+ 12.99	+ 14.75	+ 25.24

Owing to the ester becoming coloured yellow with rise of temperature, it was not possible to determine the value of the rotatory power at temperatures above 63°.

ROTATORY POWER of α-β-OCTYL IODOACETATE

Length of Observation Tube 20 cms., except in the case of

Solvent	Weight in 20 ccs. Solvent.	Rotation. α_D	$\alpha_{gr.}$	$\alpha_{vi.}$	$\frac{\alpha_{vi}}{\alpha_D}$
Ethyl Alcohol	0.5155 in 10 ccs.	+ 1.62	+ 1.97	+ 3.36	2.07
Acetone	1.0066	+ 1.53	+ 1.82	+ 3.17	2.07
Ethyl Acetate	1.0184	+ 1.54	+ 1.84	+ 3.21	2.08
Ester ✻ (homog.)	--	+ 19.08	+ 22.72	+ 39.49	2.07
Acetic Acid ✻	0.4846 in 10 ccs.	+ 0.70	+ 0.84	+ 1.48	2.11
Nitromethane ✻	0.5050 in 10 ccs.	+ 0.71	+ 0.87	+ 1.53	2.15
Carbon Tetrachloride	1.0232	+ 1.42	+ 1.70	+ 3.00	2.11
Ethylene Dibromide	0.9941	+ 1.37	+ 1.64	+ 2.79	2.04
Chloroform	1.0279	+ 1.32	+ 1.55	+ 2.64	2.00
s-Tetrachlorethane✻	0.5425 in 10 ccs.	+ 0.65	+ 0.76	+ 1.35	2.08
Benzene	1.2837 in 25 ccs.	+ 0.65	+ 0.78	+ 1.35	2.08
Phenetole	0.9964	+ 0.55	+ 0.65	+ 1.10	2.00
Chlorobenzene ✻	0.4917 in 10 ccs.	+ 0.20	+ 0.23	+ 0.44	2.20
Bromobenzene ✻	0.4896 in 10 ccs.	+ 0.15	+ 0.17	--	--
Carbon Disulphide	0.9690	+ 0.23	+ 0.26	+ 0.26	1.13
Iodobenzene ✻	0.5168 in 10 ccs.	+ 0.05	+ 0.07	--	--
Pyridine	1.1197	(- 1.97)	(- 2.37)	--	--

in VARIOUS 5% SOLUTIONS at 20°.

those Solvents marked *, where a 10 cm. tube was used.

Specific Rotation.			Molecular Rotation.		
$[\alpha]_D$	$[\alpha]_{gr}$	$[\alpha]_{vi}$	$[M]_D$	$[M]_{gr}$	$[M]_{vi}$
+ 15.71	+ 19.11	+ 32.59	+ 46.82	+ 56.96	+ 97.14
+ 15.20	+ 18.08	+ 31.49	+ 45.30	+ 53.89	+ 93.85
+ 15.12	+ 18.07	+ 31.52	+ 45.07	+ 53.86	+ 93.96
+ 14.65	+ 17.44	+ 30.31	+ 43.67	+ 51.98	+ 90.33
+ 14.44	+ 17.33	+ 30.54	+ 43.04	+ 51.65 *	+ 91.03
+ 14.06	+ 17.23	+ 30.30	+ 41.90	+ 51.36	+ 90.31
+ 13.88	+ 16.61	+ 29.32	+ 41.37	+ 49.51	+ 87.40
+ 13.78	+ 16.50	+ 28.07	+ 41.07	+ 49.18	+ 83.68
+ 12.84	+ 15.08	+ 25.68	+ 38.27	+ 44.94	+ 76.54
+ 11.98	+ 14.01	+ 24.88	+ 35.72	+ 41.76	+ 74.16
+ 6.33	+ 7.60	+ 13.15	+ 18.87	+ 22.66	+ 39.19
+ 5.52	+ 6.52	+ 11.04	+ 16.45	+ 19.43	+ 32.91
+ 4.07	+ 4.68	+ 8.95	+ 12.14	+ 13.95	+ 26.68
+ 3.06	+ 3.47	--	+ 9.12	+ 10.34	--
+ 2.37	+ 2.68	+ 2.68	+ 7.06	+ 7.99	+ 7.99
+ 0.97	+ 1.35	--	+ 2.89	+ 4.02	--
(- 17.59)	(- 21.17)	--	(- 52.43)	(- 63.10)	--

Note on the Observed Rotations of the Halogen Esters in Pyridine.

It was suspected that the values for the rotations of the halogen esters in pyridine solution (see pages 24, 29, 34) represented compound formation. This was tested in the case of the bromo-ester, using a one-decimetre tube and a 5% solution at 20°. The following figures were obtained:-

Time. (after mixing ester with solvent).	Observed Rotation α_D.	Specific Rotation $[\alpha]_D$.
2 mins.	+ 0.75	+ 14.82
3 "	+ 0.84	+ 16.60
8 "	+ 0.98	+ 19.36
2½ hours.	+ 1.08	+ 21.34
24 "	+ 1.16	+ 22.92

Attempted PREPARATION of α-β-OCTYL CYANOACETATE.

α-β-octyl alcohol (10 gms.) and ethyl cyanoacetate (8.7 gms.), 1 mol. equiv., mixed in a distilling flask connected with a condenser were gently heated over an Argand burner so that about one drop of ethyl alcohol per minute was collected, and the heating was continued for five hours. The product was then submitted to fractional distillation under diminished pressure, but it was not possible to obtain a fraction of constant boiling-point. Cooling one of the fractions in a freezing-mixture was also tried, but no solidification took place.

The following method of preparation was then tried:-

6 gms. of α-β-octyl chloracetate were mixed with 3 gms. potassium cyanide (about double the theoretical amount of cyanide) in a flask and 5 ccs. methyl alcohol added. The mixture was refluxed on an air-bath for three hours. The product was then filtered off from the solid present and extracted with ether. The latter caused the further precipitation of solid which was filtered off. The solid in the reaction flask was washed with ether and this extract added to the other and dried over anhydrous sodium sulphate. After removal of the ether /

ether the residue was distilled under reduced pressure, but again no constant boiling fraction was obtained. The fraction which distilled at 120°-156° at 18 mm. was placed in a 50 mm. tube, but, owing to the small volume of liquid, only a rough determination of the rotation could be made. $\alpha_D = +3.5^\circ$ and $[M]_D = +14^\circ$, assuming density to be approximately 1.

DISCUSSION of RESULTS.

The experimental results described in the foregoing pages are discussed below under the separate headings of

(1) Dispersion

(2) Influence of substitution

(3) Influence of solvent.

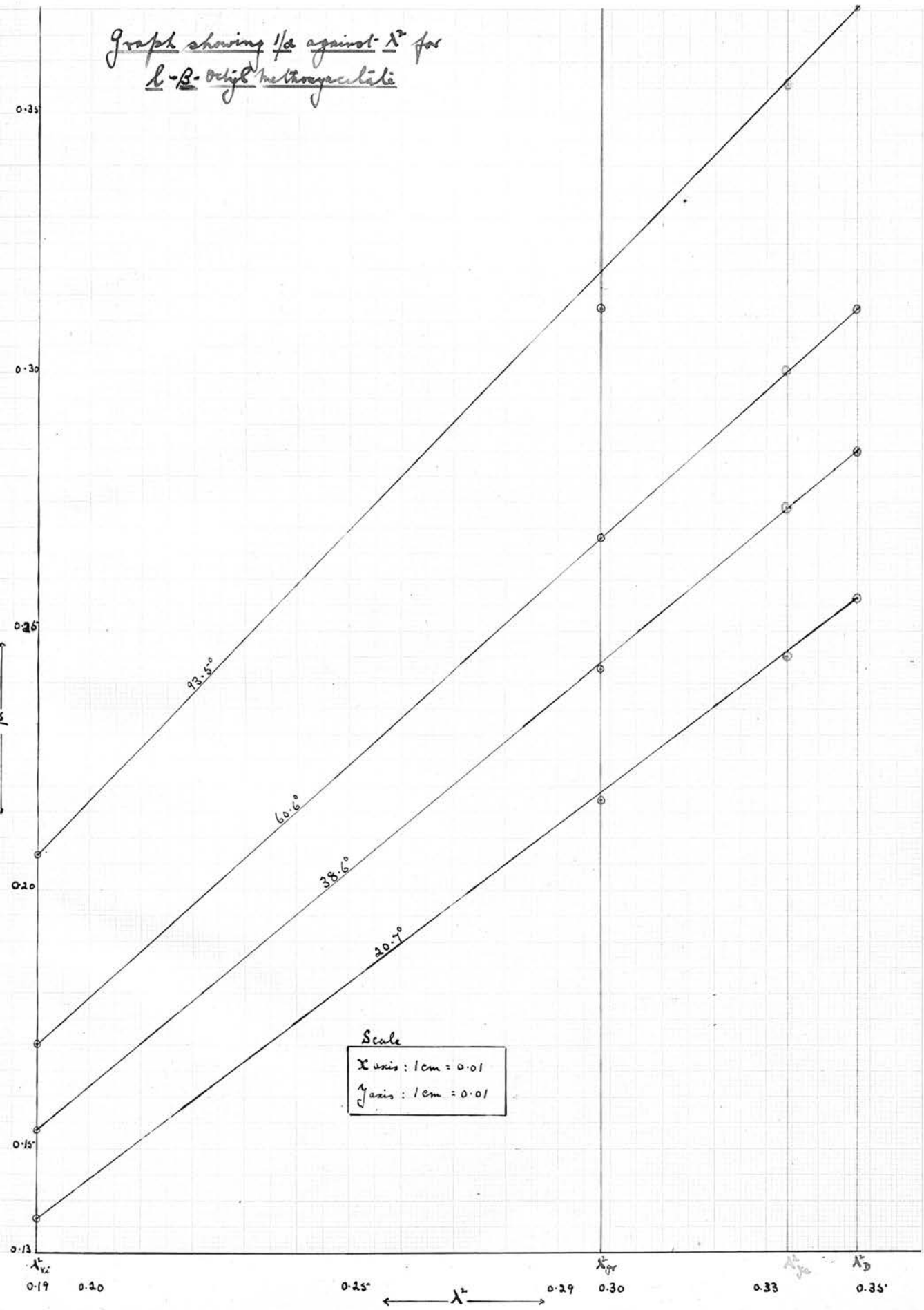
(1) DISPERSION.

The graphs obtained by plotting the reciprocal of the observed rotations of the homogeneous octyl esters against the squares of the wave-lengths of the light employed are given on pages 39,40, 41, 42.

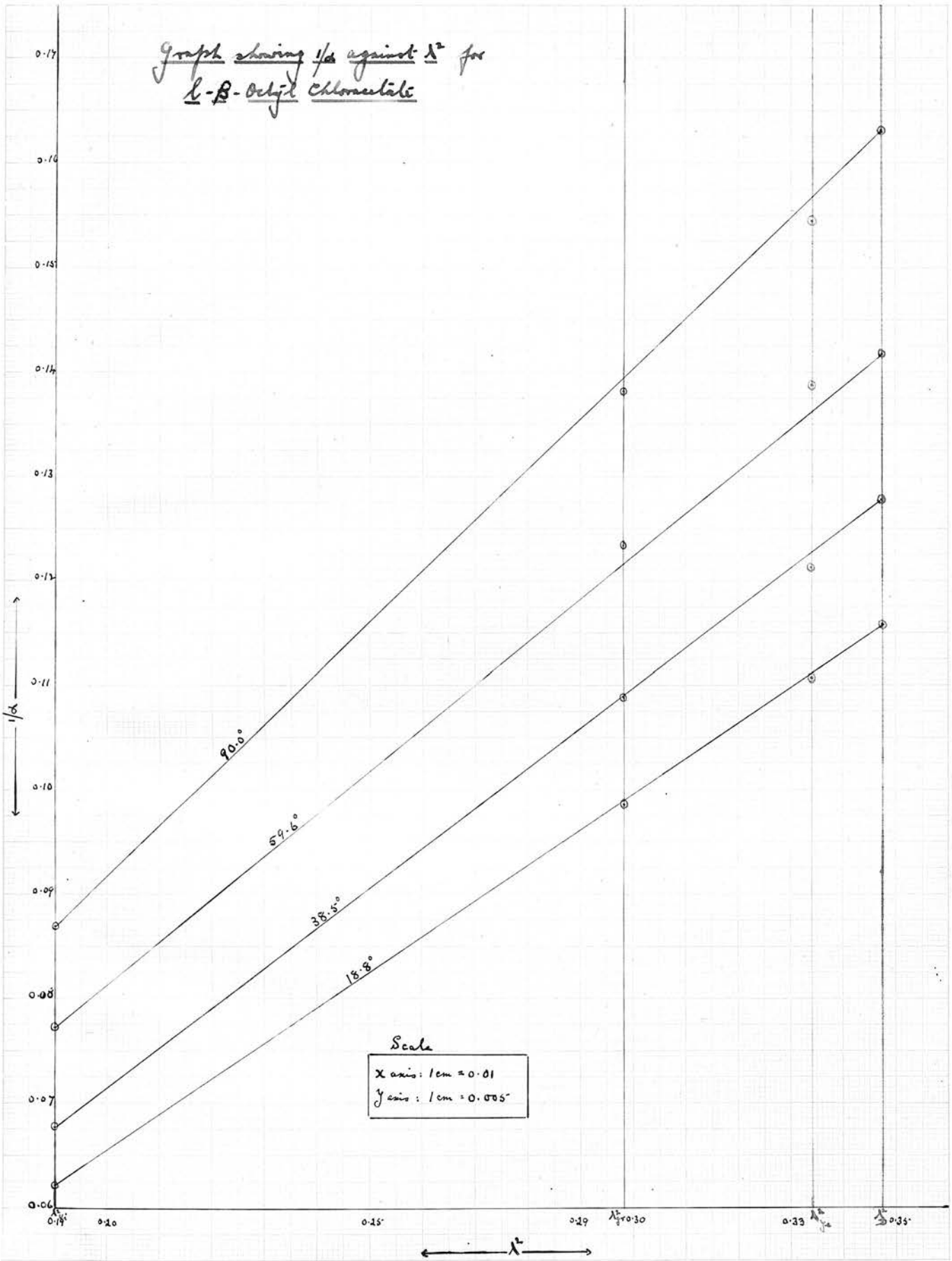
Pickard and Kenyon (loc. cit.) have concluded that the octyl esters of aliphatic carboxylic acids exhibit complex dispersion,* which may become anomalous under certain conditions of temperature and in the presence of certain solvents. From the above graphs it appears that the dispersion of the substituted acetic esters under examination is also complex.

The complexity of the dispersion is most pronounced in the chloro-, bromo-, and iodo-acetic esters at the higher temperatures of experiment. At lower temperatures, and in the case of the methoxy ester, the graphs approximate more closely to /

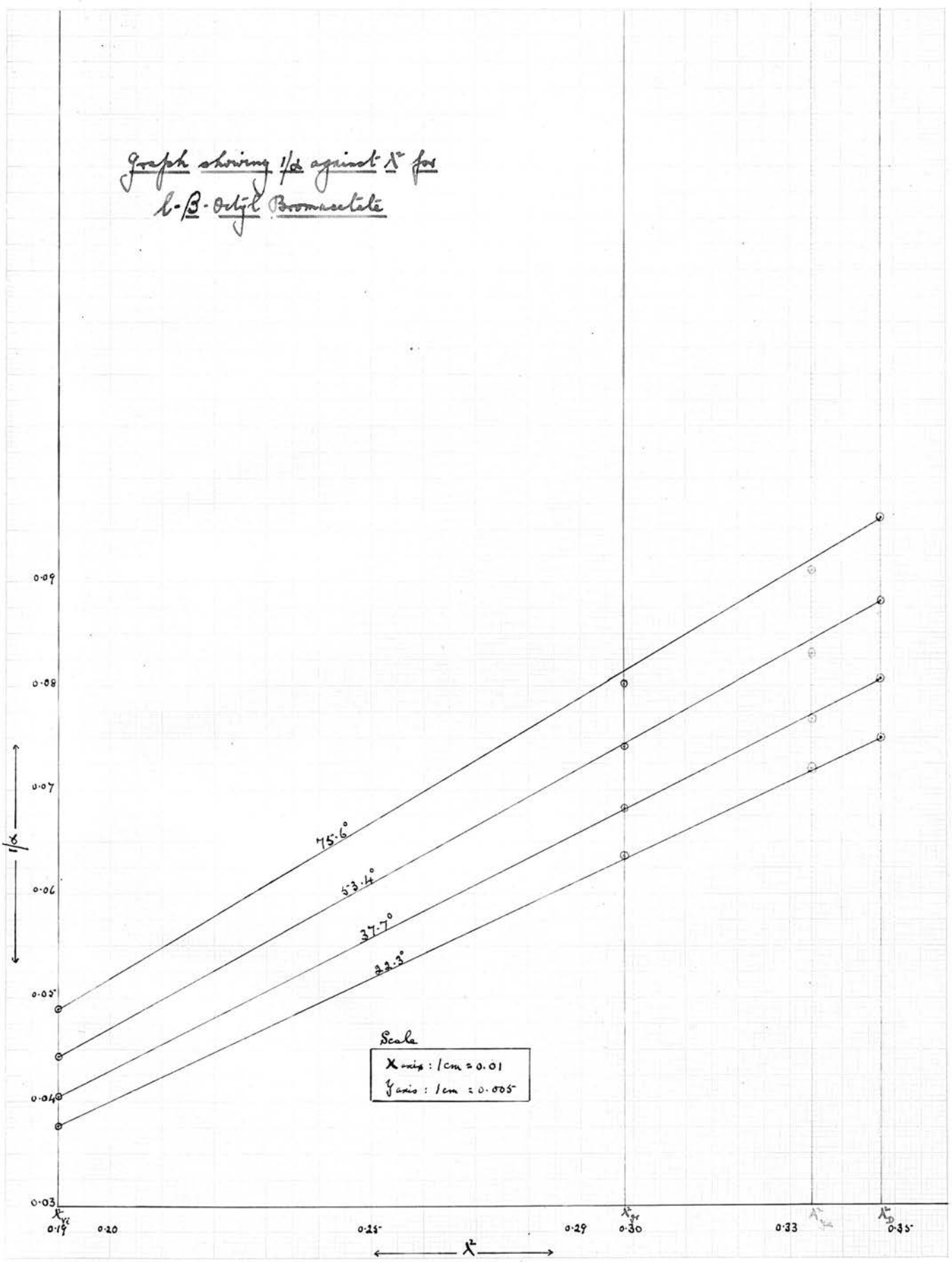
* See also Hunter, J.C.S., 1924, 125, 1389.


Graph showing 1/a against λ² for
l-β-octyl methoxycellulose
0·35
0·30
0·26
0·20
0·15
0·13
93·5°
60·6°
38·6°
20·7°
Scale
x axis : 1 cm = 0·01
y axis : 1 cm = 0·01
λ²V.I.
λ²Hg
λ²D
0·19
0·20
0·25
0·29
0·30
0·33
0·35
λ²

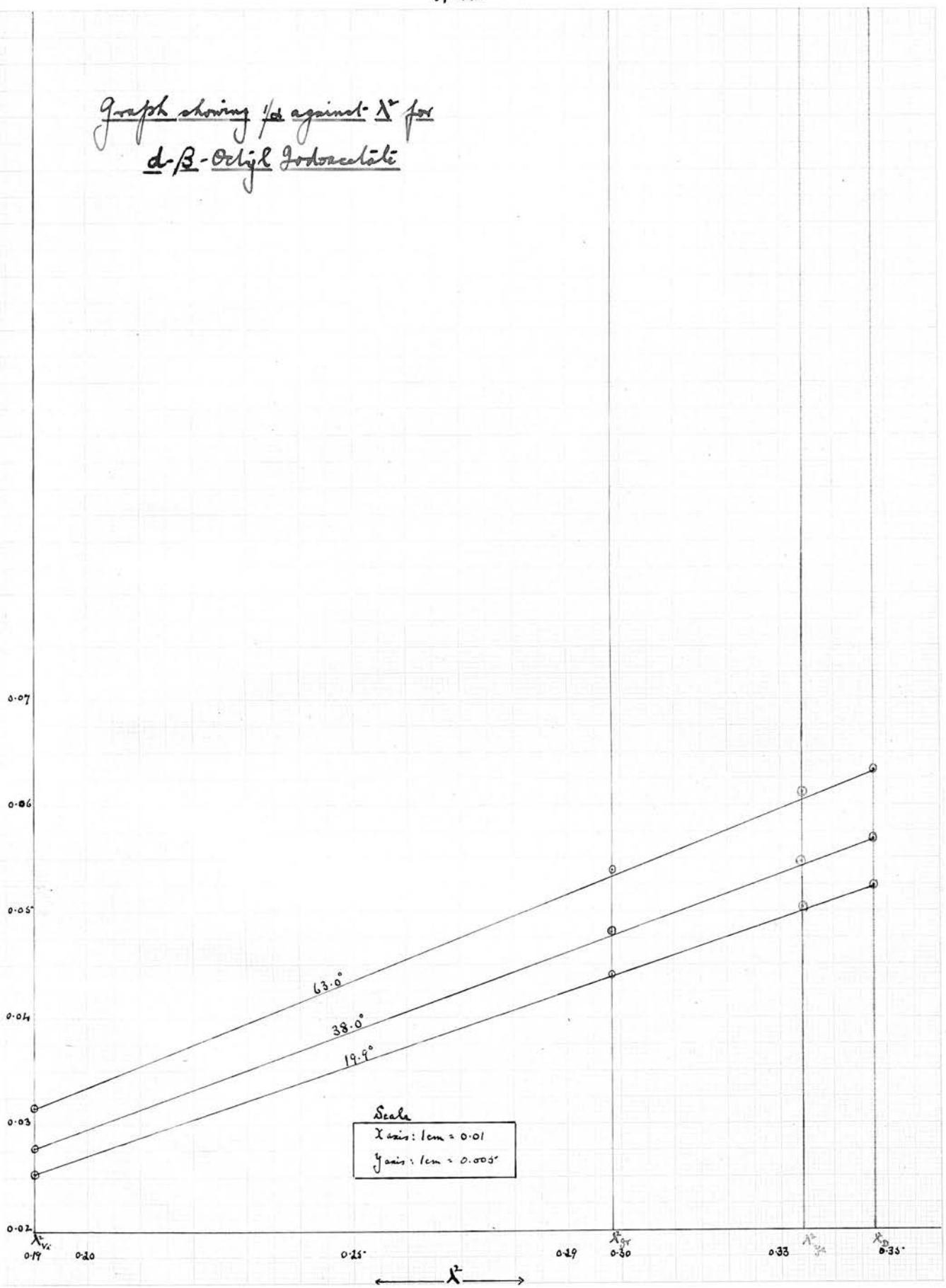
Graph showing $1/\alpha$ against λ^2 for l-β-Octyl Chloroiodide



Graph showing 1/α against λ² for
l-β-Octyl Bromoacetate



Graph showing $\frac{1}{d}$ against λ^2 for d-β-Octyl Iodoacetate



to a straight line. In the diagram for the methoxy ester (page 39) the value for λ^{2}_{gr} at 93° lies some distance off the line passing through the extreme points. Owing to the large scale employed in this particular case, however, the deviation, large as it appears, represents only a difference of 0.08° from the linear value.

The influence exerted by solvents on the character of the dispersion is mentioned on page 53.

(2) INFLUENCE of SUBSTITUTION.

The figures obtained for the rotatory powers of the different esters in the homogeneous state at temperatures ranging from 20° to 90° are summarised in the following table:- ⁂

TABLE. /

⁂ To avoid confusion the figures in this and in subsequent tables are all quoted as for the derivatives of *d*-β-octyl alcohol, although in some cases the experimental work was actually carried out with the *l*-isomeride.

Influence of Temperature on the Molecular Rotation of *d*-β-Octyl Esters of monosubstituted Acetic Acids in the homogeneous state.

Substituent Group.	Temperature.	$[M]_D$.
$-OCH_3$	20°	+ 16.34
	40	+ 14.78
	60	+ 13.49
	80	+ 12.40
	90	+ 12.03
-Cl	20°	+ 17.92
	40	+ 16.41
	60	+ 15.12
	80	+ 14.01
	90	+ 13.53
-Br	20°	+ 28.76
	40	+ 26.52
	60	+ 24.53
	80	+ 22.98
	90	+ 22.38
-I	20°	+ 43.67
	37.9	+ 40.90
	62	+ 37.36

It will be seen that the molecular rotations are comparatively small in magnitude, although greater than that for the unsubstituted ester.

In /

In each case the values fall rapidly with rise of temperature, thus resembling octyl alcohol and octyl acetate in behaviour (Pickard and Kenyon, J.C.S., 1911, 99, 45; J.C.S., 1914, 105, 835).

The relative influence of different substituents is brought out in the following table, which contains the molecular rotatory powers of the esters at 20°, together with the corresponding values obtained by Pickard and Kenyon (loc. cit.) for β-octyl acetate, β-octyl propionate, and β-octyl butyrate:-

Substituent.	$[M]_D$	Temperature.
H	+ 11.77	20°
CH_3	+ 12.99	"
OCH_3	+ 16.34	"
C_2H_5	+ 17.90	"
Cl	+ 17.92	"
Br	+ 28.76	"
I	+ 43.67	"

From the above figures it is seen that the relative influence of different substituents is given by $H < CH_3 < OCH_3 < C_2H_5 < Cl < Br < I$.

A point of interest is that the effect of the three halogen atoms increases with increase in atomic weight and not in the reverse order, as has been found to hold for the menthyl esters of these acids /

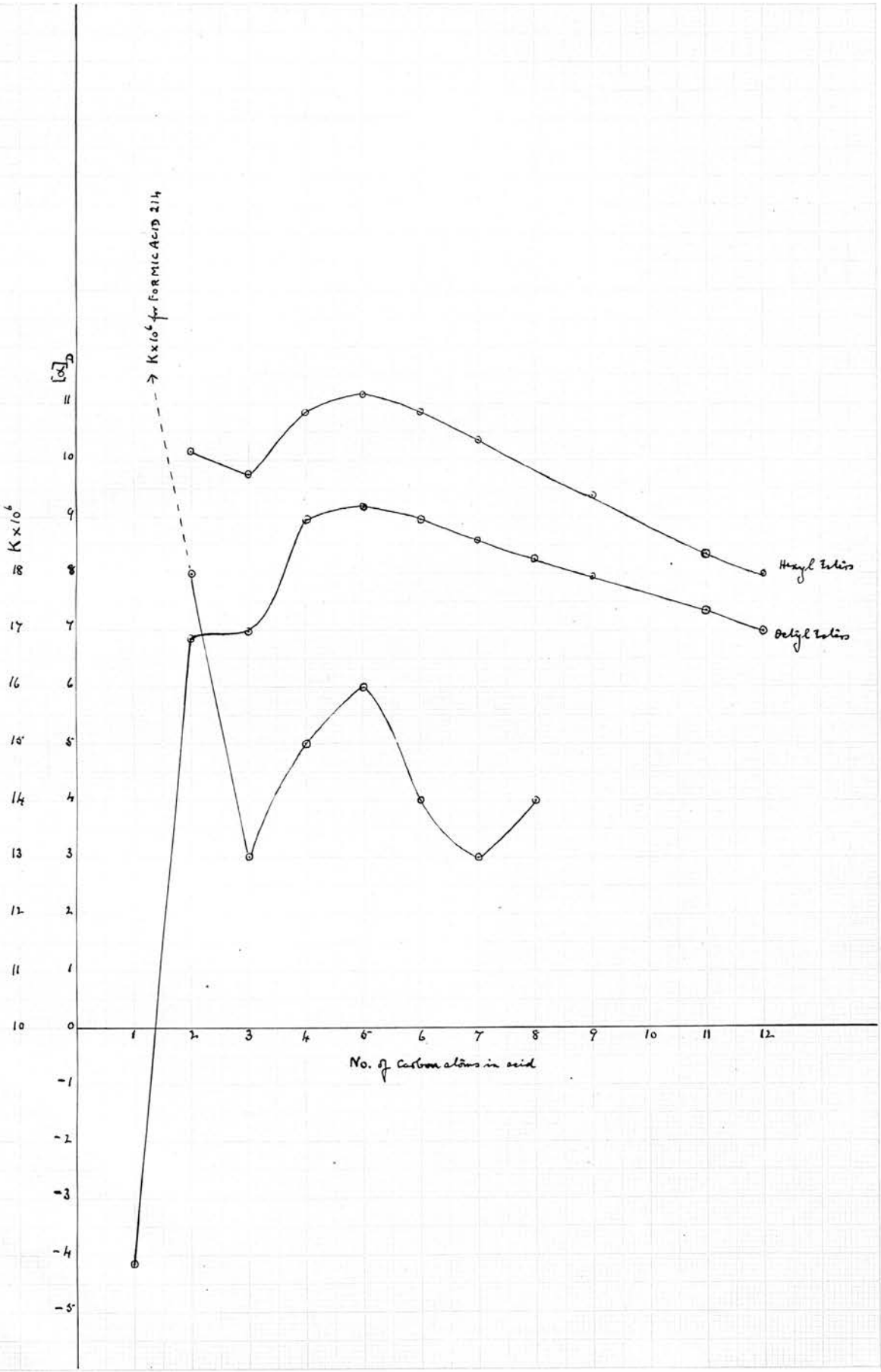
acids (Hilditch, J.C.S., 1912, 101, 202) and for the menthyl esters of o-substituted benzoic acids (Cohen, J.C.S., 1914, 105, 1892). In the menthyl dibenzoyl tartrates, however, it had been shown that nuclear substitution affects the rotatory power in a similar sense to the above, viz., H, CH_3, Cl, Br, I (Frankland, Carter, and Adams, J.C.S., 1912, 101, 2470).

Except for this inversion, the influence of the substituents on the molecular rotation of β-octyl acetate is in close agreement with what has been termed their general polar character (cf. Robinson, J.C.S., Ann. Rep., 1922, p. 98).

A similar group arrangement has been observed in connection with the rotatory powers of the corresponding menthyl esters of substituted acetic acids, where $H < C_2H_5 < CH_3 < OCH_3 < I < Br < Cl$ (see Rule and Smith, J.C.S., 1925, 127, 2189): In the influence of substituents on the acidity of acetic acid, $(C_2H_5, CH_3) < H < OCH_3 < I < Br < Cl$: in the molecular inductive capacity of monosubstituted benzenes or aliphatic hydrocarbons, $H < CH_3 < C_2H_5 < OCH_3 < I < Br < Cl$: and in a number of cases of chemical reactivity (Rule, J.C.S., 1924, 125, 1121; Rule and Paterson, ibid. 2155).

It does not appear to have been pointed out before that the initial disturbances observed by Pickard and Kenyon in the rotatory powers of certain homologous /

homologous series of aliphatic esters, and which may take the form of a depression at the acid containing 3 carbon atoms coupled with an exaltation at the 5-acid, are paralleled by a similar disturbance in the acidic strengths of the acids. This is illustrated in the diagram on page 48, in which the dissociation constants of the acids R.COOH are plotted together with the specific rotatory powers of the corresponding sec-hexyl and sec-octyl esters.


→ K x 10⁶ for FORMIC ACID 214
[α]D
K x 10⁶
Hexyl Esters
Octyl Esters
No. of Carbon atoms in acid
1
2
3
4
5
6
7
8
9
10
11
12

(3) INFLUENCE of SOLVENT.

The rotatory power of β-octyl acetate has been determined in 5% solution in a number of solvents by Pickard and Kenyon (loc. cit.). The authors show that of the fourteen solvents employed by them, ethylene dibromide raises the value as compared with that of the homogeneous ester, and the remaining thirteen diminish the rotation. Some of the latter solvents exert so marked an effect that the sign of the rotation is reversed. The same solvents have now been examined in regard to their influence on the octyl esters of methoxy-, chloro-, bromo-, and iodo-acetic acids, in order to see whether any marked variations in rotatory power could be brought into relationship with the specific properties of solvent or substituent.

A large number of determinations have been made with this object, measurements being recorded for the Hg_{vi}, Hg_{gr}, and D lines. The results for the D line, together with the corresponding figures obtained by Pickard and Kenyon for β-octyl acetate, are summarised in the following table:-

TABLE. /

MOLECULAR ROTATIONS $[M]_D$ of ESTERS in VARIOUS 5% SOLUTIONS at 20°.

d-β-Octyl Acetate.	d-β-Octyl Methoxyacetate	d-β-Octyl Chloracetate	d-β-Octyl Bromacetate	d-β-Octyl Iodoacetate.
$C_2H_4Br_2$ + 16.84	$C_2H_4Br_2$ + 19.21	$C_2H_4Br_2$ + 21.34	$C_2H_4Br_2$ + 30.33	C_2H_5OH + 46.82
Ester + 11.77	Ester + 16.34	Ester + 17.92	Ester + 28.76	$CH_3.CO.CH_3$ + 45.30
$C_2H_2Cl_4$ + 10.17	CCl_4 + 12.98	CCl_4 + 16.39	CCl_4 + 28.02	$C_2H_5\overline{Ac}$ + 45.07
$CH_3.CO.CH_3$ + 9.56	$C_2H_5\overline{Ac}$ + 12.49	$C_2H_5\overline{Ac}$ + 14.88	$C_2H_5\overline{Ac}$ + 26.55	Ester + 43.67
CH_3NO_2 + 9.02	CH_3NO_2 + 12.38	CH_3NO_2 + 14.11	C_2H_5OH + 26.44	$\overline{HAc}$ + 43.04
$C_2H_5\overline{Ac}$ + 8.91	$CH_3.CO.CH_3$ + 11.93	$C_2H_2Cl_4$ + 13.45	$\overline{HAc}$ + 25.86	CH_3NO_2 + 41.90
$CHCl_3$ + 6.50	H $\overline{Ac}$ + 11.62	$CH_3.CO.CH_3$ + 13.22	$CH_3.CO.CH_3$ + 25.25	CCl_4 + 41.37
H $\overline{Ac}$ + 6.28	$CHCl_3$ + 11.57	C_2H_5OH + 12.91	CH_3NO_2 + 23.78	$C_2H_4Br_2$ + 41.07
C_2H_5OH + 6.06	$C_2H_2Cl_4$ + 11.39	$CHCl_3$ + 12.65	$CHCl_3$ + 22.73	$CHCl_3$ + 38.27
CCl_4 + 6.02	C_2H_5OH + 11.32	H $\overline{Ac}$ + 11.55	$C_2H_2Cl_4$ + 21.50	$C_2H_2Cl_4$ + 35.72
C_6H_6 − 1.38	C_6H_6 − 0.99	C_6H_6 + 0.83	C_6H_6 + 10.07	C_6H_6 + 18.87
$C_6H_5O.Et$ − 2.39	$C_6H_5O.Et$ − 6.39	$C_6H_5O.Et$ − 5.19	$C_6H_5O.Et$ + 4.92	$C_6H_5O.Et$ + 16.45
C_6H_5Cl − 5.33	C_6H_5Cl − 7.08	C_6H_5Cl − 6.67	C_6H_5Cl + 2.54	C_6H_5Cl + 12.14
C_5H_5N − 6.54	C_6H_5Br − 7.00	C_6H_5Br − 8.80	C_6H_5Br + 1.63	C_6H_5Br + 9.12
CS_2 − 15.42	C_5H_5N − 11.53	C_6H_5I − 9.94	C_6H_5I − 0.98	CS_2 + 7.06
	C_6H_5I − 12.68	CS_2 − 10.73	CS_2 − 1.21	C_6H_5I + 2.89
	CS_2 − 14.68	(C_5H_5N − 11.61)	(C_5H_5N − 56.63)	(C_5H_5N − 52.43)

For convenience of comparison the above table has been compressed into one page by making use of contractions or formulae for the solvents employed.

(Note:- $C_2H_4Br_2$ = ethylene dibromide $C_2H_2Cl_4$ = s-tetrachlorethane
C_5H_5N = pyridine).

Apart from the influence of certain solvents on the iodo-ester, it will be seen that the relative effects are very similar with all the esters examined. With the first four esters quoted ethylene dibromide produces an increase in rotatory power, and the remaining solvents a diminution. In every instance phenetole, carbon disulphide, and pyridine are to be found at or near the bottom of the list, thus producing a maximum depression in the value of the rotation, which in the majority of cases amounts to a change of sign.

The iodine atom in the iodo-ester, however, which is sufficiently active to produce a large increase in rotatory power when introduced into the parent compound, also exerts a strong specific influence on the manner in which the iodo-ester behaves towards solvents. The head of the list in this case is occupied by the oxygen-containing solvents, alcohol, acetone, ethyl acetate, and acetic acid, of which the latter brings about a very slight depression and the others an exaltation in the value of the rotation. Ethylene dibromide, on the other hand, diminishes the rotation of the iodo-ester considerably and occupies a position in the middle of the list. Carbon disulphide, as with the other esters, produces a marked depression in the rotatory power.

Pyridine, as might be expected, behaves somewhat /

somewhat exceptionally towards the halogenated esters, more especially towards the bromo- and iodo-compounds, and leads to a reversal of sign coupled with an abnormally large alteration in the magnitude of the rotation. This is undoubtedly related to the ease with which pyridine unites with alkyl halide groupings, a reaction which probably occurs most readily with iodo- and least readily with chloro-derivatives. In the case of the iodo-ester, evidence of chemical combination was given by the development of a certain amount of heat on mixing the two liquids. Very little change of temperature occurred when the bromo-compound was employed, nevertheless the alteration in rotatory power was equally marked. As may be seen on page 35, further experiment with the bromo-ester showed that the observed rotation in pyridine steadily rose to a limiting value from the time of mixing, thus confirming the formation of an addition compound. If the changes in rotation are due to the exercise of supplementary valencies between an atom or group of the active compound with the solvent molecule, it was anticipated that the three similar solvents chlorobenzene, bromobenzene, and iodobenzene would exert a graded influence in the sense Cl < Br < I. This was borne out by experiment, as may be seen from the values given on page 50.

On pages 54-57 will be found a number of "characteristic" diagrams of the esters in the homogeneous state and in solution. Owing to the very low magnitude of many of the observed rotations, it is difficult to determine with certainty whether the deviations from the straight lines of the diagram are due to experimental errors or to the complex dispersion of the esters. Some of the divergencies, however, are repeated for a given solvent with different esters and can be definitely traced to complex dispersion. A solvent of this type is carbon disulphide. The values for the iodo- and bromo-esters in pyridine solution are too large to be conveniently plotted on the diagrams, and a number of others have been omitted to avoid the overlapping of points.

The diagrams show the existence of a small region of anomalous dispersion in each case, with the possible exception of the iodo-ester.

On page 58 a number of rotations for the different esters in the homogeneous state or in solvents are correlated on the same "characteristic" diagram, and it will be seen that the points approximate fairly closely to the straight lines, but that the values for esters in carbon disulphide in every case lie outside the diagram.

"Characteristic" Diagram for two sp. ethyl methoxysuccinate

1. Solut. in 5% $C_2H_4Br_2$ at 20°
2. Homogeneous Solut. "
3. Solut. in 5% $CH_3COOC_2H_5$ "
4. " " " $CH_3.CO.CH_3$ "
5. " " " C_6H_6 "
6. " " " $C_6H_5.O.C_2H_5$ "
7. " " " $C_6H_5.Br$ "
8. " " " C_5H_5N "
9. " " " C_6H_5I "
10. " " " CS_2 "

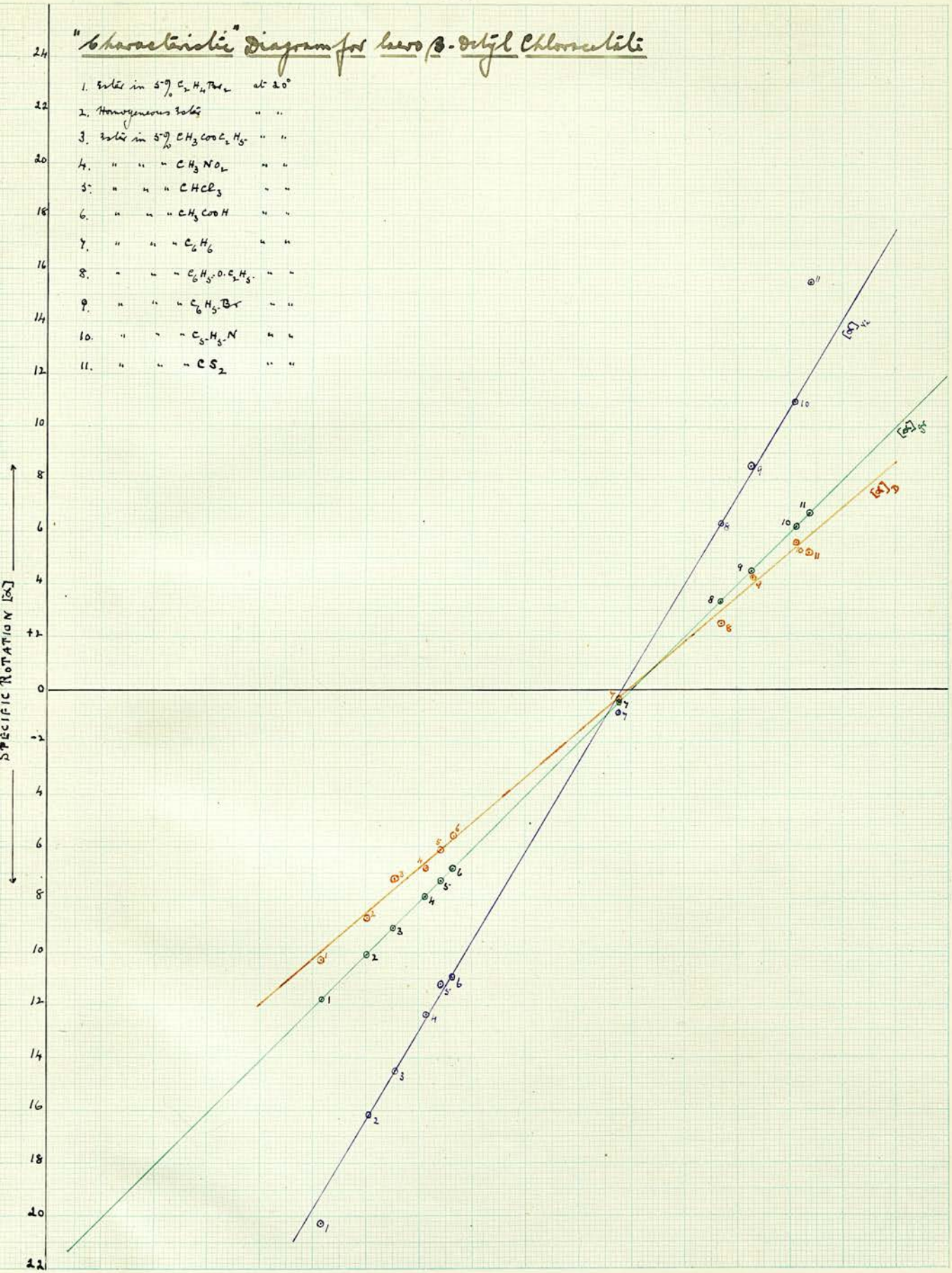
SPECIFIC ROTATION [α]

$[\alpha]_{\frac{1}{2}}$ $[\alpha]_{5^{\circ}}$ $[\alpha]_D$

"Characteristic" Diagram for Levo β-Octyl Chloroselli

1. Solvi in 5-% $C_2H_4Br_2$ at 20°
2. Homogeneous Solvi " "
3. Solvi in 5-% $CH_3COOC_2H_5$ " "
4. " " " CH_3NO_2 " "
5. " " " $CHCl_3$ " "
6. " " " CH_3COOH " "
7. " " " C_6H_6 " "
8. " " " $C_6H_5.O.C_2H_5$ " "
9. " " " $C_6H_5.Br$ " "
10. " " " C_5H_5N " "
11. " " " CS_2 " "

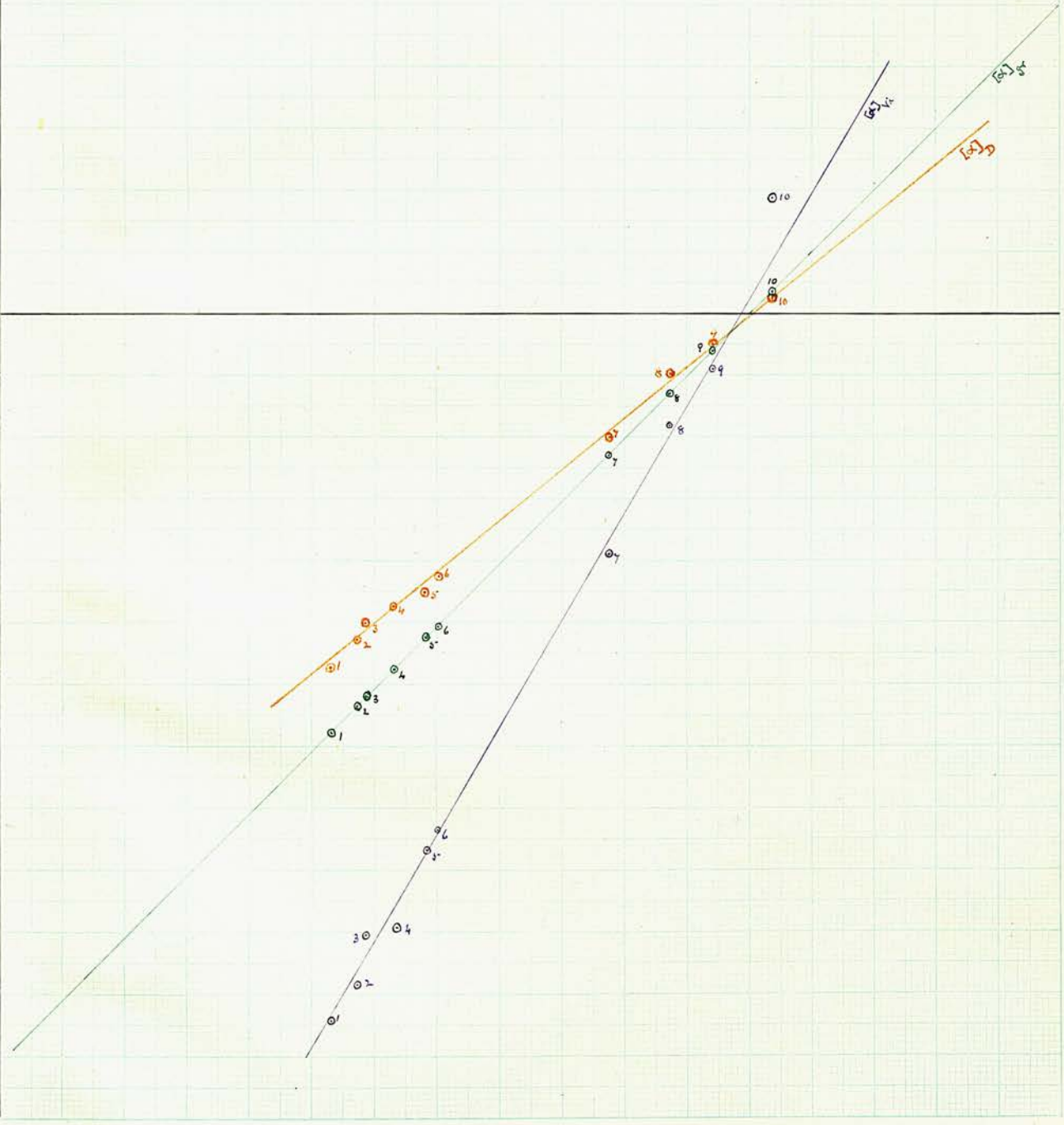
SPECIFIC ROTATION [α]



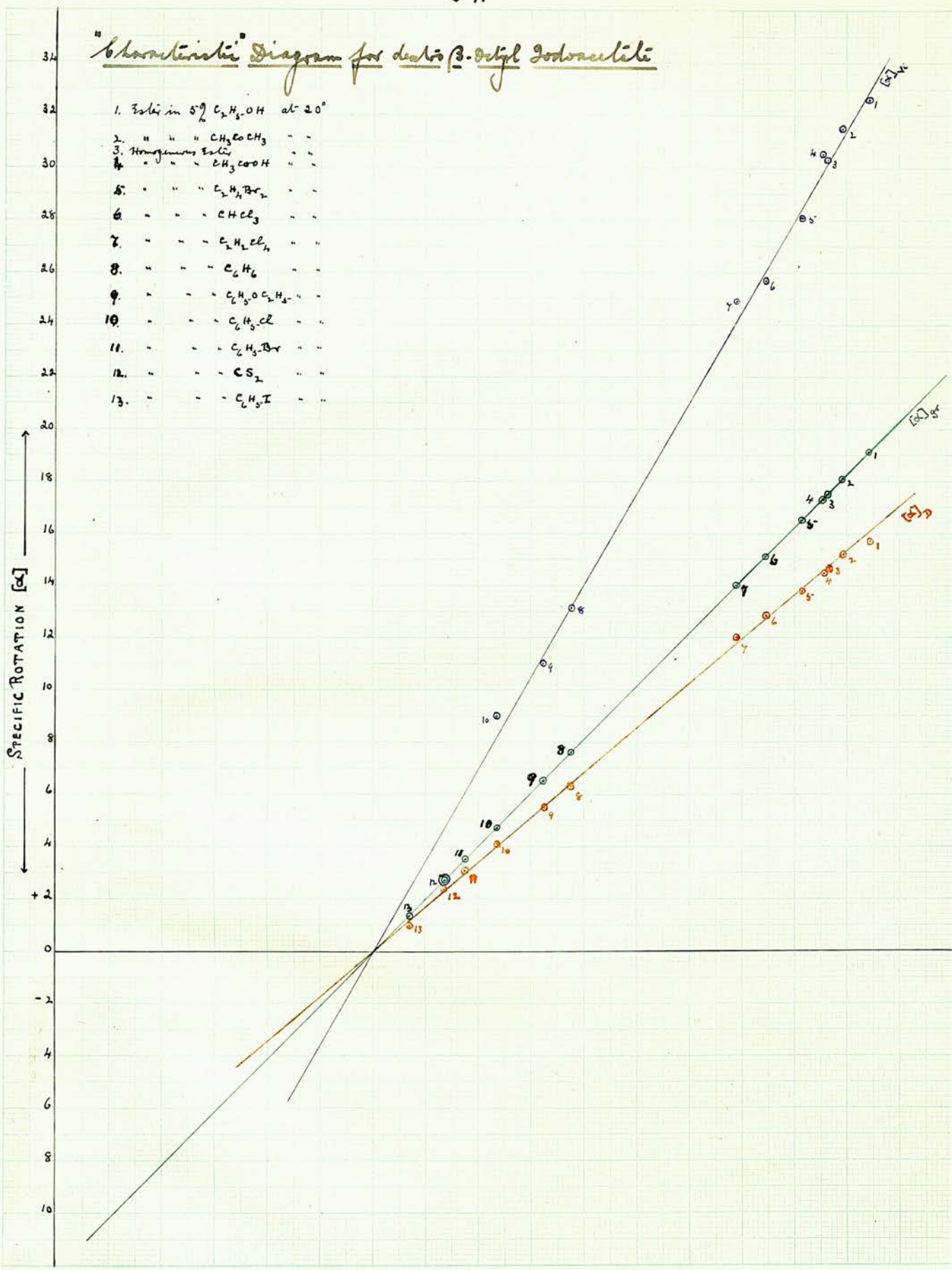
"Characteristic" Diagram for Laevo β-Octyl Bromoacetate

1. Homogeneous Solut at 20°
2. Solut in 5% $CH_3COOC_2H_5$ " "
3. " " " CH_3COCH_3 " "
4. " " " CH_3NO_2 " "
5. " " " $CHCl_3$ " "
6. " " " $C_2H_4Cl_4$ " "
7. " " " C_6H_6 " "
8. " " " $C_6H_5.O.C_2H_5$ " "
9. " " " $C_6H_5.Cl$ " "
10. " " " CS_2 " "

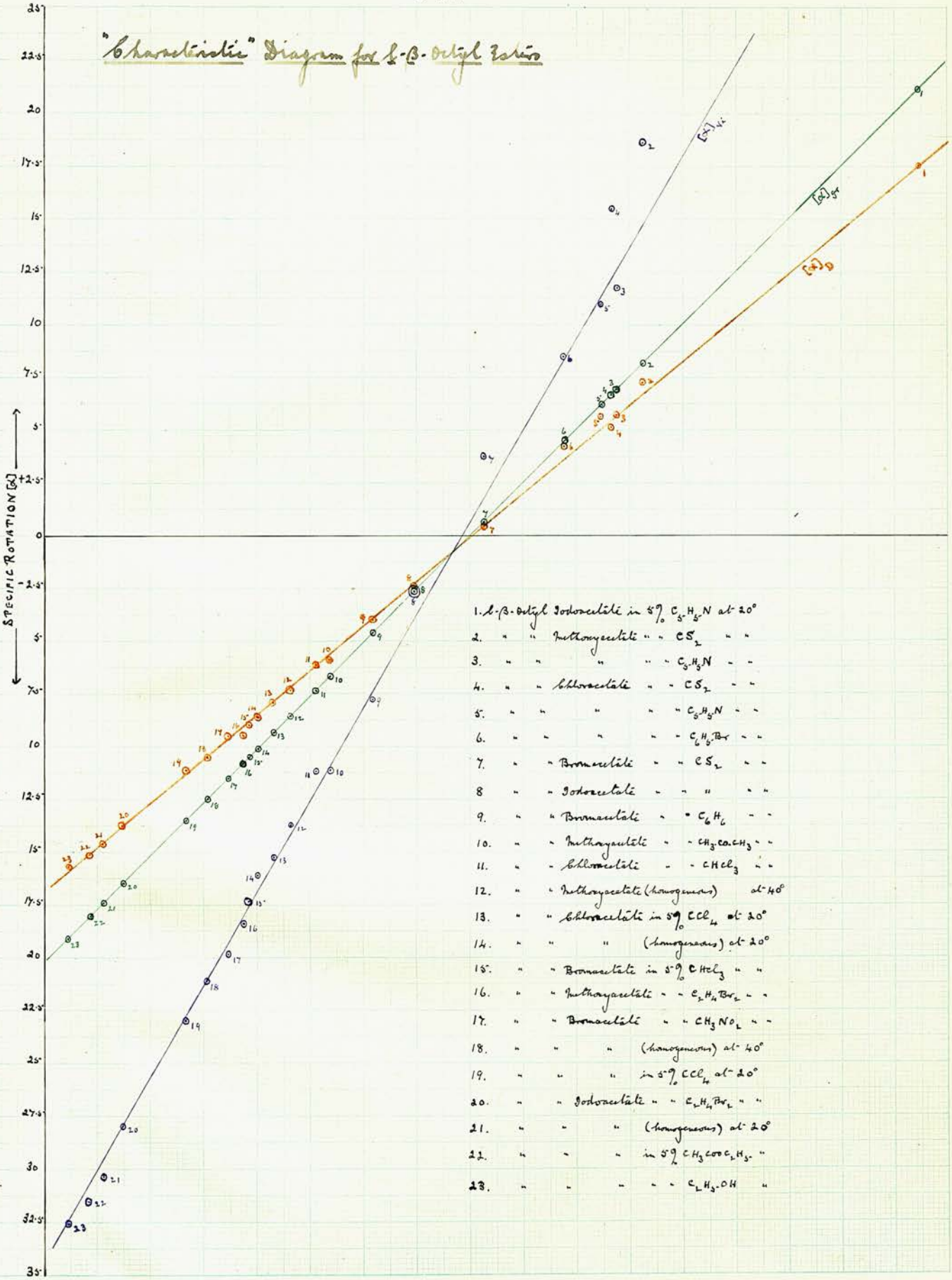
SPECIFIC ROTATION [α]



"Characteristik" Diagram for d-α-β-Octyl Jodonellite



"Characteristic" Diagram for l-β-Octyl Esters



1. l-β-Octyl Iodoacetate in 5% C_5H_5N at 20°
2. " " Methoxyacetate " " CS_2 " "
3. " " " " " " C_5H_5N " "
4. " " Chloroacetate " " CS_2 " "
5. " " " " " " C_5H_5N " "
6. " " " " " " C_6H_5Br " "
7. " " Bromacetate " " CS_2 " "
8. " " Iodoacetate " " " " "
9. " " Bromacetate " " C_6H_6 " "
10. " " Methoxyacetate " " $CH_3.CO.CH_3$ " "
11. " " Chloroacetate " " $CHCl_3$ " "
12. " " Methoxyacetate (homogeneous) at 40°
13. " " Chloroacetate in 5% CCl_4 at 20°
14. " " " (homogeneous) at 20°
15. " " Bromacetate in 5% $CHCl_3$ " "
16. " " Methoxyacetate " " $C_2H_4Br_2$ " "
17. " " Bromacetate " " CH_3NO_2 " "
18. " " " (homogeneous) at 40°
19. " " " in 5% CCl_4 at 20°
20. " " Iodoacetate " " $C_2H_4Br_2$ " "
21. " " " (homogeneous) at 20°
22. " " " in 5% $CH_3COOC_2H_5$ "
23. " " " " " $C_2H_5.OH$ "

SUMMARY.

(1) The active β-octyl esters of methoxy-acetic acid and of chloro-, bromo-, and iodo-acetic acids have been prepared in the pure state, and an examination made of the influence of temperature and solvents on their rotatory powers. The values so obtained are compared with those found in the literature for octyl esters of other substituted acetic acids.

(2) The homogeneous esters exhibit complex dispersion, which becomes more marked as the temperature is raised.

(3) The relative influence of a number of different substituents on the rotatory powers of β-octyl acetate is given by $H < CH_3 < OCH_3 < C_2H_5 < Cl < Br < I$, and is found to be in approximate agreement with their general polar character.

The influence of the halogens in this case, however, increases with increase in atomic weight, and not in the reverse order.

(4) The influence of sixteen solvents on the rotatory power of the esters is very similar to their influence on β-octyl acetate, as determined by Pickard and Kenyon, although the iodo-compound differs in some respects from the remaining compounds.

The writer desires to express his thanks to Dr. H.G. Rule for his valuable help and advice during the course of this work.