THE EFFECT OF POLAR AND NON-POLAR SOLVENTS ON THE OPTICAL ROTATORY POWERS OF CERTAIN SATURATED AND UNSATURATED TERPENIC HYDROCARBONS.

by

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EXPERIMENTAL SECTION

INTRODUCTION.

The study of optically active organic compounds is one of the most fascinating branches of chemical research, a fact well demonstrated by the numerous investigations which have been carried out on this subject. Moreover, for the last thirty years it has been one of the main bridges across the gap separating pure organic chemistry from the theoretical work of the physicist and physical chemist, and hence its importance cannot be exaggerated. Many attempts have been made not only by hypothetical speculation but by deductive reasoning based on experimental fact, to derive quantitative relationships between optical rotatory power and the structure of the active molecule. Such attempts have involved detailed investigations of the effect on the rotatory power of certain factors such as molecular constitution, the wavelength of the light, the temperature and the nature of the solvent if any. One of these hypotheses, which was first put forward by Rule in 1924, has given interesting results in its practical applications. In the following introductory pages it is proposed to deal with the work which led to the development of this theory, particular attention being paid to its mode of explaining the influence of solvents on the optical rotatory power of a dissolved solute.

In 1890, Crum Brown advanced the hypothesis that if each of the radicals attached to an asymmetric carbon atom was represented by a function K , the magnitude of which was determined by the mass and constitution of the radical, then the rotatory power of the molecule would be given by a formula involving the continued difference of these functions. From experimental evidence he concluded that the function increased with the size of the radical, but he was able to give no indication of the manner in which it could be measured. Maxwell's electromagnetic theory of light and his identification of the square of the refractive index with the dielectric constant suggested that such a function might be electrical in nature. This idea was upheld to some extent by the work of several earlier investigators. Flürscheim (J.C.S., 1909, 718) studied the influence of substituents on the dissociation constants of acids and bases - a physical property which depended definitely on the distribution of electric forces within the molecule - and found that he could place them in a more or less well defined series thus:-

$NH_2 < NH.Me < OH < OCH_3 < \text{Halogens} < CH_3 < H < CN < NO_2$

A few years earlier Betti had initiated a series of researches which attempted to correlate the influence of substituents on optical activity with their other properties,/

TABLE I.

	$[M]_D^{20}$	Aldehyde Employed	k x 10^5 for derived acid.
p - Series	+ 2676°	p - Dimethyl-amino-benzoic	1 (?)
	+ 1154	Anisic	3.2
	+ 1049	p - Hydroxy - benzoic	2.9
	+ 691	p - Toluic	5.14
	+ 373	Benzoic	6.0
	+ 282	p - Chlorobenzoic	9.3
	+ 207	p - Nitrobenzoic	39.6
o - Series	+ 897°	o - Methoxybenzoic	8.0
	+ 373	Benzoic	6.0
	- 86	Salicylic	102.0
	- 128	o - Chlorobenzoic	132.0
	- 326	o - Toluic	12.0
	- 991	o - Nitrobenzoic	616.0

properties, a summary of the results being given in a later publication (Gazz. chim. Ital., 1923, 53, 424). Betti condensed the optically active base **d** - α - naphthol benzylamine with benzaldehyde and substituted benzaldehydes. The rotatory powers of the resulting compounds in benzene solution varied from + 2676° to - 991°, and when arranged in order of magnitude gave a series which agreed approximately with that representing the dissociation constants of the benzoic acids derived from the aldehydes employed. The following is a modified table of the results obtained.

(TABLE I opposite)

It will be seen from the table that the influence of substituents on rotatory power and dissociation constant in the case of the **p** - compounds gives two series which are practically identical in order:-

$[M]_D^{20} \quad NO_2 < Cl < H < CH_3 < (OH\ ,\ OCH_3) < N\ (CH_3)_2$

$k \quad NO_2 > Cl > H > CH_3 > (OCH_3\ ,\ OH) > N\ (CH_3)_2$

although the agreement in the case of the ortho compounds is not quite so good:-

$[M]_D^{20} \quad NO_2 < CH_3 < Cl < OH < H < OCH_3$

$k \quad NO_2 > Cl > OH > CH_3 > OCH_3 > H$

In 1914, Olivier (Rec. Trav. Chim., 1914, 244) investigated the influence of substituents on the chemical reactivity/

reactivity of atoms and groups. He examined the speed of formation of sulphones from p - bromo - benzenesulphonyl chloride and a p- substituted benzene and found that the substituents affected the velocity coefficients in the order:-

$Me > H > Halogens > NO_2$

Subsequently the same author examined the hydrolysis of p - substituted benzyl chlorides (ibid., 1923, 516, 775) and found the relative speeds to fall into a similar series:-

$Me > H > Halogens > COOH > NO_2$

From considerations such as these it seems evident that the similarity of substituent influence in all these cases was to be traced to a fundamental electrical change in the molecule due to the influence of the substituent group. Whilst these investigations were in progress, however, the theory of the structure of the atom and the mode of formation of valency bonds had been revolutionised by the work of Rutherford, Kossel, Lewis and Langmuir. Three main types of valency had been postulated:-

(a) Electrovalency in which a certain number of valency electrons passed completely from one atom in a molecule to the other atom, so that Lewis' octet rule was satisfied in each atom. This involved the formation of ions which had an independent existence and/

and were merely held together by electrostatic attraction. The existence of these ions in the solid state was brilliantly verified by Bragg's X-ray analysis of crystals and put the theory of salts on a more sound basis.

(b) Covalency in which two atoms combined by sharing electrons to complete their outside shells, each atom contributing an equal number of electrons. There should be therefore no redistribution of electricity and the atoms will be firmly bound into a compact molecule. This is the type of bond occurring most frequently in organic molecules.

(c) Coordinate link is a valency bond which, as in the case of the covalent link, involves the sharing of two electrons, but with the difference that both electrons are supplied by the same atom. A group which has such a link will act as a small electromagnet, i.e. it will be definitely "polar", the "donor" atom being positively charged and the "acceptor" atom being negatively charged. However, groups which only contain covalencies may also exhibit polarity to a greater or less extent. In such cases we may suppose that although there is no actual transfer of electrons from one atom to another, yet the sharing of electrons is not an equal one. The atom which has the greater share of the electrons, will have a small negative charge attached to it, whereas the other atom will have a/

a corresponding small positive charge. Hence we find the occurrence of so-called "partial polarities".

With this advance in theoretical speculations regarding valency and from a study of the above experimental work it soon became evident that some kind of polar effect was responsible for the above series and in 1922, Robinson (Ann. Rep. Chem. Soc., 1922, 98) referred to this type of substituent effect as the "general polar effect" to distinguish it from a type occurring in aromatic compounds termed the "alternating polar effect". A year later J.J. Thomson (Phil. Mag., 1923, 46, 497) put forward a method whereby the relative polarities of groups of simple structure could be obtained by comparing the specific inductive capacities of compounds of the type RX for long wavelengths.

In 1924, Rule (J.C.S., 1924, 1121) utilised this conception and calculated the specific inductive capacities for compounds of the type C_6H_5X. After making allowance for molecular weight and density, he found that the influence of the substituents, X, in affecting this factor was in the order

$$NO_2 > CN > COCH_3 > CHO > Cl > Br > Et > Me > H$$

which represented a progressively diminishing polar magnitude independent of sign. It is in this paper that Rule, from an examination of some experimental data/

data of other workers, dealing with various optically active organic compounds, first puts forward the hypothesis that the rotatory power of a molecule is a function of the moments of the four groups attached to the asymmetric atom, and that the influence of a substituent on the optical rotation will therefore depend in sign and magnitude on the polarity of the substituent. In order to test his hypothesis he initiated a series of investigations, but the evidence obtained in the earlier attempts were not conclusive owing to lack of clear distinction between electropositive and electronegative groups. The researches of later investigators however along lines suggested by Debye and Thomson cleared up this matter considerably, and subsequently Rule (Trans. Farad. Soc., 1930, 26, 321) restated and extended his earlier publications in the light of this more recent knowledge and showed that the hypothesis of a polar influence of substituent was upheld by experimental data.

The accurate measurement of the magnitude of these polar groups was made possible by a theory suggested by Debye (Physikal. Zeit., 1912, 13, 97) in order to explain the peculiar temperature variations in the dielectric constants of certain substances. In the molecules of such compounds Debye suggests that there exists a permanent "dipole", which arises when the mean electric centres of the electrons/

electrons and the positive atomic nuclei do not coincide. Such a molecule will therefore possess a definite electric moment. When a molecule of this type is placed in an electric field, it will tend to orient itself in the direction of the field. This field will exert a pull on the positive and negative charges and the dipole will be increased. This orientation tendency will be balanced by restoring forces due to the thermal agitation of the molecule. On this basis Debye deduced a method of evaluating the electric moment - denoted by μ -, the formula involving the dielectric constant and the refractive index of the substance concerned (Polare Molekeln, Leipzig, 1929). The most useful form of this expression is as follows:-

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} + P_A + \frac{4\pi N \mu^2}{9kT}$$

where ϵ is dielectric constant, n refractive index, k Boltzmann's constant and P_A is the atomic polarisation which is due to the influence of long infra red rays on the molecule and which is generally neglected in the calculation since its value is small. Since this calculation is made on the assumption that the dipole molecules are removed from each other's influence, measurements are made of the dielectric constant of the substance when it is either in the vapour/

vapour state or in dilute solution in a non-polar solvent. Numerous measurements of dipole moments were carried out under these conditions by various investigators among whom we may mention Smyth, Hojendahl, Errera and Williams, and it was not until the result of these investigations had been published that correlation between dipole moment and optical rotatory power could be established. Moreover, Ebert and Smyth from a variety of circumstances had arrived at the definite conclusion that the dipole moment was a property of the group within the molecule rather than of the molecule itself. For values of μ derived from Debye's equation, it should be noted that it is impossible to say in which direction the charges are distributed as between the group and the radical to which it is attached. In 1923, however, J.J. Thomson (loc. cit.) pointed out that the electric moment of a polysubstituted benzene should be the vector sum of the group moments, provided that these groups acted independently and that the hexagonal symmetry of the ring is not distorted by substitution. From the comparison of the observed moments of certain compounds with the values of the moments calculated from the above rule, it has been possible to differentiate between groups which have the negative end of their dipoles towards the phenyl nucleus and those which have the positive ends towards the nucleus.

We/

We may note that in the case of the group - NO_2 its dipole must be in the direction of its semipolar linkage, and we may assume therefore that when this group is attached to the benzene nucleus, there is a permanent electron shift away from the nucleus, i.e. - NO_2 is an electronegative group. On this basis the sign of any group may be found by applying the above vector rule to the appropriate substituted benzene derivatives. The vector rule does not apply quantitatively in practice and the reason for a number of discrepancies have been pointed out by Estermann (The Dipole Moment and Chemical Structure, edt. Debye, page 27).

Rule and his coworkers had meanwhile been examining the effect on the rotatory power produced by systematically inserting polar groups into an optically active molecule, and following up the above theory of dipole moments, Rule stated that in certain cases examined the "influence of substituents in general agrees closely with the sign and magnitude of their characteristic dipoles" (Rule, Thompson and Robertson, J.C.S., 1930, 1887). In this paper he examined a series of rotatory powers of mono-substituted l-menthyl acetates of the type $X.CH_2.CO.O\ C_{10}H_{19}$. The effect on the internal electrical field of the molecule due to the introduction of a group of an electronegative nature i.e. with its positive pole orientated/

orientated towards the parent molecule, may be regarded as the creation of a positive field in the portion of the molecule immediately adjoining the substituent, owing to the shift of electrons towards the substituent, e.g. $\underleftarrow{\overset{-}{\text{Cl}}.\overset{+}{\text{C}}\text{H}_2.\ \text{COO}\cdots\text{H}.}$ Such a shift in this case will for example assist ionisation of the corresponding acid. In the case of the menthyl esters of the above type, it is seen that a positive field is exerted on the asymmetric centre. From a study of the experimental results it was concluded that the greater the positive field exerted, the greater was the increase in negative rotatory power. When the substituent was electropositive, a negative field was set up e.g. $\underrightarrow{\overset{+}{\text{H}}_2\overset{-}{\text{N}}.\text{CH}_2.\text{CO.O}\cdots\cdots\text{H}}$ and the effect was to diminish the rotation.

The type of parallelism obtained between rotatory power and dipole moment of substituent group is exemplified in the following table (Trans. Farad. Soc., 1930, 325). The variation in the dissociation constant of the corresponding acetic acid is also included in the table.

TABLE II./

TABLE II.

$[M]^{20}_{D}$ for the Homogeneous Esters of Monosubstituted Acetic acids X $CH_2.CO.OH$.

Substituents.	$\mu \times 10^{18}$	k of acid	l-Menthyl ester	l-Octyl ester
$N(CH_3)_2$	1.4 e.s.u.	1.3 x 10	- 156.9°	-
H	-	1.8 "	157.3	- 11.9°
CH_3	0.4	1.4 "	160.2	- 13.0
COOH	0.9	160 "	160.2	-
OC_2H_5	-	23 "	160.6	-
OCH_3	1.2	33 "	165	- 16.3
OH	1.7	15 "	165	-
Br	1.5	138 "	169	- 28.8
Cl	1.5	155 "	171	- 17.9
CN	3.8	370 "	174	-

The order of the molecular rotation corresponds closely with that of the dipole moments of the groups and except for the carboxy derivative with the dissociation constant of the parent acids.

It should be noted that in certain cases examined, the agreement is either less complete or entirely irregular, possibly owing to changes in rotatory power following the varying degrees of association of the active compound in the homogeneous state or in solution. Whether or not the rotatory power is dependent on the difference between the polarities of the four radicals/

radicals attached, however, it appears to be established that in many cases the influence of substituents introduced into a given position in the molecule varies with their polar strength.

It was evident from the above investigations that the moments of attached groups was a fundamental property of the molecule, and the correlation of rotatory power with magnitude and disposition of dipoles within the molecule was a distinct advance. In discussing the disturbing influences exerted by electrical forces on the behaviour of a molecule, Debye had already referred to those due to the fields of neighbouring molecules, and to those of added solvent molecules. Little was known concerning the connexion between the physical nature of a solvent and its effect on an optically active solute; but, from the success attending the above investigations, it was concluded by Rule that similar methods might reveal the existence of a polar factor in solvent effect. The problem was therefore attacked from this point of view and more success has been obtained than in any previous attempt to solve it.

THE EFFECT OF SOLVENTS ON ROTATORY POWER.

As early as 1815, Biot had observed that the rotatory power of an optically active compound depended on the nature of the solvent in which it was dissolved/

dissolved; Patterson (J.C.S., 1901, 158) suggested that solvent influence was related to the "internal pressure" of the solvent which caused variation in the solution volume of the dissolved substance from solvent to solvent. This suggestion however received no support from Dawson (J.C.S., 1920, 1041) who put forward the idea that the change in rotatory power was due to compound formation between solvent and solute. However, in the work of later investigators no evidence could be found to support Dawson's hypothesis. In 1926, Rule and Mitchell while investigating the rotatory power of β-octyl esters of various monosubstituted acetic acids when dissolved in liquid media (J.C.S., 1926, 3202) noted that, although no general regularities could be detected for the solvents as a whole, in several closely related liquids such as the monosubstituted benzenes C_6H_5X, the rotatory power for the variations of X were given by the series $CH_3 > H > OEt > Cl > Br > I$. This is almost the exact reverse of the series representing the influence of the same substituents when present in the optically active molecule namely,

$$I > Br > Cl > OMe > CH_3 > H .$$

As a result of this it was suggested that "polar groups, whether present in the asymmetric compound or in the solvent, also exert an influence on neighbouring molecules, leading to corresponding changes in rotatory power/

power." (J.C.S., 1927, 58).

Further confirmation of this polar factor in solvent effect was demonstrated in the properties of 1-menthyl esters of peri-substituted naphthoic acids, among which the nitro-group greatly raises the rotation of 1-menthyl- 1 - naphthoate, whilst chlorine and the methoxy group lower the activity (Rule, Spence and Bretscher, J.C.S., 1929, 2516). It was observed that, whether the substituent decreased or increased the rotatory power, its characteristic influence tended to be exhibited to the maximum degree in hydrocarbon solvents. The effect of the peri-substituent appeared to be diminished, however, in highly polar solvents.

Two years later, the first systematic attempt to correlate solvent effect with polarity of solvent was made by Rule and McLean (J.C.S., 1931, 674), who employed as their active compound 1-menthyl methyl naphthalate, which was selected on account of its extreme sensitivity to change of solvent. They used four different series of solvents derived from the hydrocarbons methane, ethane, benzene and naphthalene. The type of agreement is shown by the following table extracted from the above paper.

TABLE III./

TABLE III.

Solvent	$[M]^{20}_{5461}$	$\mu \times 10^{18}$ e.s.u.
C_6H_5CN	- 372°	3.85
$C_6H_5NO_2$	- 423	3.98
C_6H_5CHO	- 432	2.75
O- $C_6H_4Cl_2$	- 433	2.24
C_6H_5Cl	- 463	1.52
C_6H_5I	- 465	1.50
C_6H_5Br	- 466	1.50
C_6H_5OMe	- 466	1.25
C_6H_6	- 543	0
$C_6H_5CH_3$	- 546	0
s - $C_6H_3(CH_3)_3$	- 583	0
C_6H_{12}	- 688	0

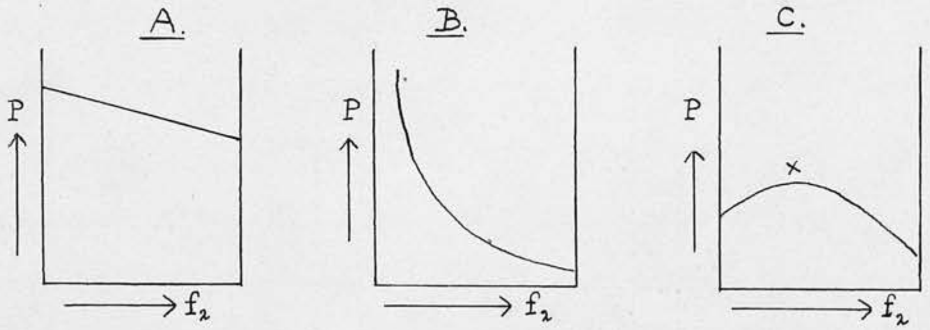
Similar types of series were obtained in the case of derivatives of the other hydrocarbons.

The most striking feature in the above series is the close relationship existing between the rotatory power of the dissolved ester and the polarity of the solvent, as expressed by the dipole moment. The rotation is lowest in solvents of high dipole moment, and highest in those of zero dipole moment. Solvents of intermediate polarity fall, on the whole, into the order of their dipole values, but minor divergences in this class frequently occur. It should be noted that/

that some optically active compounds, such as octyl bromide (Rule, Smith and Harrower J.C.S., 1933, 379) have their highest rotation in solvents of high dipole moment, their lowest values being given in solvents of zero dipole.

Rule and McLean (loc. cit.) advanced the opinion that the observed effects were due to the influence of the solvent dipole upon the internal field of the solute molecules acting either through deformation or dipole association.

In his monograph "Polare Molekeln" Debye divided polar compounds into three main categories according to the type of characteristic polarisation - dissociation diagram obtained by the progressive dilution of the compound with a non-polar solvent. When the contribution of the solvent was corrected for it was found that ether gave a straight line (A below), nitrobenzene a curve (B) and ethyl alcohol exhibited a polarisation curve (C) with a maximum X .



P = Polarisation f_2 = Mole fraction of polar substance in non-polar solvent.

Debye assumes that in compounds of type A and B we have dipole association of the type $(\overset{+}{-}\ \overset{-}{+})$, the molecules thus neutralising each other's fields. On dilution with a non-polar solvent these association complexes break up and hence the number of molecules existing in the free state is increased leading to a corresponding rise in the polarisation. In type C it is assumed that with increasing concentration, the alcohol moleculesfirst form a chain association thus (- +) (- +), which actually causes a rise in the polarisation. With further increase in concentration however these chains form association aggregates of the type $\begin{matrix}(-\ +)\ (-\ +)\\(+\ -)\ (+\ -)\end{matrix}$ This results in a partial neutralisation of the internal field and a corresponding decrease in the polarisation. In a similar manner the rotatory power of l-menthyl methyl naphthalate, as determined in mixtures of polar and non-polar liquids, were corrected approximately for the rotation due to the solution in the non-polar component. The partial rotation curves obtained thus for nitrobenzene and ether proved to be the inverse of the corresponding polarisation curves. This again demonstrated that the rotatory power of the solute increased with decreasing polarisation - or increasing polar association - of the solvent.

Many other types of optically active compounds. were examined and the majority of them gave remarkably good/

good agreement between rotatory power and dipole moment e.g. l-menthyl picryl ether (Rule and Tod, J.C.S., 1931, 1929), a number of derivatives of secondary β-octyl alcohol (Rule, Smith and Harrower, loc. cit.), l-menthone, d-bromocamphor etc. (Miss Barnett, Thesis, Edin., 1932).

Another method of attack in investigating solvent effect is to follow the variation in rotatory power for one solvent with change in concentration of the active compound. Dilution of an active compound by a non-polar liquid leads to changes in the rotatory power and this is readily explained on the assumption of the breaking up of solute-solute association complexes. The varying degree with which solvents can break up these complexes has also been suggested as the reason for the anomalous rotatory powers obtained in certain places e.g. nitro-octane (Rule, Smith and Harrower, loc. cit.) and d-ethyl tartrate (Rule, Barnett and Cunningham, J.C.S., 1933, 1217). In these cases it was found that the theory of association was supported by molecular weight data. It should be noted however that Smyth in "Dielectric Constant and Chemical Structure" p. 189, concludes that "a molecular orientation too slight to be apparent in its effect upon most physical properties of liquids may have a considerable effect upon the polarisation." It follows therefore that where no evidence of molecular/

molecular association from molecular weight data is found, this does not necessarily imply the absence of a small polar orientation sufficient to affect the polarisation and hence also the rotatory power.

As a result of the experimental data obtained by Rule and his coworkers, it was suggested that optically active solutes could be divided into four main classes, according to the nature of the substituent groups present and their reaction towards the solvent. (Rule, Smith and Harrower, loc. cit.). These were classified thus -

I. Non-polar solutes:- The chief representatives of this type are saturated hydrocarbons. No examples of this type had yet been investigated. It was suggested that, since the orientating forces between molecules of such a type would be small even when dissolved in a polar solvent, changes in the internal field of the asymmetric molecule would be small. As a result there should be little or no change in rotatory power with change in solvent medium. Representatives of this class are examined in the experimental part of this thesis.

II. Weakly-polar solutes:- Representatives of this group include the majority of unsaturated hydrocarbons, ethers, alcohols, esters and halogen derivatives. Although their molecules do not form definite association complexes, polarisation data show that some/

some degree of orientation exists between their molecules. This effect is almost completely eliminated by dilution with a non-polar solvent, but dilution with a polar solvent causes a more definite orientation to be set up between the molecules of solute and those of the solvent. The more polar the solvent, the more complete is the degree of orientation of solute and solvent molecules towards one another, and the more completely is the internal field of a polar substituent in the solute molecule neutralised. For dilute solutions, therefore, the rotatory power should be closely related to dipole moment of solvent.

III. Strongly polar solutes:- These include nitro-, cyano-, and ketonic compounds. These compounds are strongly associated in the homogeneous state and therefore, the change in rotatory power on dilution with a solvent will depend on the extent to which the latter is capable of breaking up these association complexes. Hence an irregular solvent effect may be found in this class, owing to solute-solute association in non-polar media and solute-solvent association in strongly polar media.

IV. Solutes which suffer electronic rearrangement when brought into contact with certain solvents are grouped in a separate class. This type of change is brought about by stable compound formation, co-ordination, ionisation etc. As representative of this/

this type we have carboxy-acids dissolved in basic solvents, bases in alkyl halides and alcohols in carboxy- and hydroxy- solvents. In such solvents, the change in rotatory power of these compounds will not be directly related to the dipole moment of the medium.

TEMPERATURE CHANGE AND SOLVENT EFFECT.

The above hypothesis of solvent effect and rotatory power allows a prediction to be made regarding the relative slopes of the temperature-rotation curves for solvents of the two extreme types.

Patterson, Dunn, Buchanan and Loudon (J.C.S., 1932, 1715) put forward the empirical generalisation that "in solvents which confer high rotation, the rotation should diminish or else increase slowly with rise in temperature, whereas in solvents of depressing influence it should increase fairly rapidly." This rule however had no theoretical basis.

From the polar theory of solvent effect, two chief mechanisms may be supposed to cause change in rotation with rise in temperature. First, the configuration or mean resting position of the molecule may be changed due to increased freedom of rotation. Secondly, when the active compound is dissolved in a polar solvent, a definite degree of orientation of solvent and solute molecules towards each other may be/

be established, and in general this degree of orientation diminishes with increased thermal agitation. Therefore, as the temperature rises, the characteristic optical displacement due to the polar solvent also diminishes; thus the temperature-rotation curve of a polar solvent should converge towards that of a non-polar medium.

This suggestion has been borne out by the work of Cunningham (Thesis, Edinburgh, 1933) on dimethylene tartrate and by Crawford (Thesis, Edinburgh, 1934) who utilised l-benzoin and its methyl ether.

It is worthy of note that the polar theory of optical rotatory power may be correlated with a physical theory deduced mathematically by Kuhn (Trans. Farad. Soc., 1930, 293). In its original form, the theory correlated optical rotatory power with position and circular dichroism of the absorption bands in the spectrum of the molecule. Later considerations (Kuhn, Stereochemie, Freudenberg, 1932, p. 417) indicate that change in rotation may in many cases, result from an alteration in the anisotropic properties of the band, without any appreciable change in its position. The connecting link between the polar hypothesis and the above theory is found in the researches of Scheibe (Ber., 1926, 59, 2619) on ketones in the presence of different solvents. Scheibe observed a progressive displacement of the typical/

typical ketonic band towards the far ultra-violet region, as the polarity of the solvent increased. If, therefore, the rotation of an active ketonic derivative is governed by the position of the band (as the original theory of Kuhn suggests), this change should lead to a progressive alteration in the rotatory power. While the experimental work in this thesis was in progress, a theory of optical activity was put forward by S.F. Boys (Proc. Roy. Soc., 1934, A. 144, 655, 675) and since this theory supported certain conclusions which had already been drawn from this experimental work, it is dealt with in some detail in the discussion. Certain other physical theories will also be examined in the same place, from the point of view of their applicability to the present investigation.

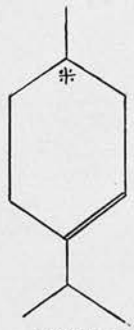
This investigation was carried out to obtain some information regarding the effect of solvents on the optical rotatory power of very weakly polar and non-polar solutes. Certain saturated and unsaturated hydrocarbons, the majority of the terpene class, have now been subjected to a detailed examination with regard to change in solvent, change in concentration and change in temperature when dissolved in polar and non-polar solvents respectively. Readings have been made for various wavelengths of light in the visible region, in order to obtain information regarding the nature of the dispersion.

DISCUSSION.

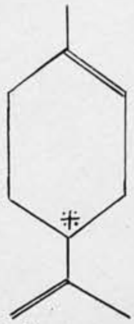
The change in rotatory power brought about by the addition of solvents to very weakly polar and non-polar solutes, as exemplified by optically active unsaturated and saturated hydrocarbons respectively, has not previously been subjected to a systematic examination. Nor has it been possible to make any definite prediction regarding the probable nature of the optical variations in these cases, although from the data already gained from the study of optically active compounds of polar type it has been suggested (Rule, Harrower and Smith, loc. cit.) that for non-polar saturated hydrocarbons any such variations would be small in magnitude and not related to the dipole moment of the solvent medium.

Of the various hydrocarbons examined in the present thesis, three are unsaturated compounds of the terpene series.

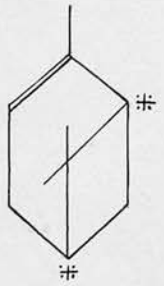
d - p -$\Delta^{(3)}$- Menthene and d-limonene possess one and two double bonds, respectively, in the molecule and are ideal compounds for the purpose in that they contain only one asymmetric carbon atom. d-Pinene,



d-p-$\Delta^{(3)}$-Menthene



d-Limonene



d-Pinene

the third unsaturated compound to be investigated, contains in its molecule one double bond and two asymmetric carbon atoms.

d-p-$\triangle^{(3)}$-Menthene.

The influence of aliphatic solvents on the rotatory power of menthene is given below in table I, which also lists the dipole moments of the solvents employed (these values are taken from a table of dipole moments compiled by Sidgwick, Trans. Farad, Soc., 1934, 30). The concentration <u>c</u> , of d-menthene used varied within narrow limits from 2.378 in nitromethane to 3.372 in methyl iodide solution. All readings are taken at 20°.

$l = ?$

TABLE I./

TABLE I.

Influence of Aliphatic Solvents on the Rotatory Power of d-Menthene.

Solvent	n_D (solvent)	α^{20}_{5893}	$[M]^{20}_{5893}$	$\mu \times 10^{18}$ e.s.u.
$CH_3.CHO$	1.3316	5.61°	145.8°	2.68
CH_3NO_2	1.3815	5.12	148.5	3.03
$(CH_3)_2CO$	1.3592	6.68	149.2	2.76
CH_3CN	1.3441	5.48	150.6	3.16
$CH_3.COOH$	1.3718	5.96	152.0	1.73 (.60)
CH_3OH	1.3284	5.74	152.0	1.66
CS_2	1.6276	7.09	152.3	0
C_6H_{14}	1.3754	6.26	152.5	0
$C\ Cl_4$	1.4607	5.70	153.2	0
(homogeneous)	1.4542	45.75	155.5	(small)
$CHCl_3$	1.4459	6.18	156.1	1.18
CH_2Cl_2	1.4245	6.18	158.4	1.55
CH_3I	1.5297	7.99	163.7	1.08

The first conclusion to be drawn from the above table is that solvents of high dipole moment lower the value of the rotatory power. The solvent influence in this respect resembles that found for the majority of optically solutes of polar type. There is a general agreement between the depression of rotatory power and the polarity of the solvent, broken however by the displacement of the three closely related halogen derivatives chloroform, methylene chloride and methyl iodide. Solutions of menthene in these solvents give values of the rotatory power higher than those found for the homogeneous hydrocarbon or for solutions in non-polar solvents. The displacement may possibly be a specific effect of the halogenated aliphatic compounds on the unsaturated d-menthene but, in the light of later work, it is of interest to note that each of these solvents had a refractive index n_D^{20}, greater than 1.4 and in the case of methyl iodide greater than 1.5. Moreover the homogeneous substance itself has $n_D^{20} = 1.4542$ and its rotatory power falls into position with the values found for solutions in the halogenated solvents. As will be described in more detail later, the majority of physical theories concerning optical rotatory power assume for an optically active substance an expression/

expression of the type

$$\underline{[M]_D^{20} = k. \; (f(n_D^{20}))}$$

where **k** is a constant for a given active substance. Such a relationship has not yet been demonstrated in practice but, on this hypothesis it is seen that $[M]$ should vary with some function of the refractive index of the medium. The effect should be more noticeable with optically active compounds of low polarity, since, in such cases optical changes due to association should be small. The displacement of the halogenated solvents in Table I therefore, might be explained on the assumption that an increase in rotatory power also occurs with increase in the refractive index of the medium. The strongly polar aliphatic solvents in use have all low refractive indices and yield solutions of lower rotatory powers. The hypothesis, however, does not explain the position of carbon disulphide which, being non-polar and very highly refractive would have been expected to increase the rotatory power of d-menthene when the latter substance is dissolved in it.

The effect of aromatic solvents on the rotatory power of d- menthene is given in Table II; the concentration of active substance employed varied from within the limits 2.388 in the case of mesitylene to 3.450 in the case of cyclohexane (C_6H_{12}).

TABLE II./

TABLE II.

Influence of Aromatic Solvents on the Rotatory Power of d-Menthene.

Solvent	n_D (solvent)	α^{20}_{5893}	$[M]^{20}_{5893}$	μx 10^{18} e.s.u.
$C_6H_5CO.Me$	1.5332	6.30°	142.4°	2.97
$C_6H_5NO_2$	1.5504	5.44	145.3	3.90
$C_6H_5O\ Me$	1.5164	5.54	147.1	1.25
C_6H_5I	1.6180	7.02	147.3	1.25
C_6H_5CN	1.5278	6.17	148.6	3.85
o-$C_6H_4Cl_2$	1.5490	5.85	148.9	2.24
$C_6H_5.CH_3$	1.4950	5.77	149.0	0.37
C_6H_5Br	1.5601	6.58	149.6	1.56
C_6H_5Cl	1.5250	6.80	151.4	1.52
(homogeneous)	1.4542	45.75	155.5	(small)
s-$C_6H_3Me_3$	1.4962	5.38	155.5	0
C_6H_{12}	1.4273	7.78	155.6	0
C_6H_6	1.5014	5.92	156.3	0

As in the case of the aliphatic solvents, it is seen that highly polar aromatic media give lower values of the rotatory power than weakly polar ones and that the highest rotations are recorded in non-polar solvents.

In this group there is no clear evidence of an influence related to the refractive index of the solvent. For example the highly refractive iodobenzene occupies a position between two liquids of considerably lower values. Further, although the aromatic solvents as a class possess higher refractive indices than the aliphatic solvents employed, they do not yield solutions of higher rotatory power. This absence of any marked relationship to the refractive properties is seen on comparing the rotatory powers of homogeneous menthene and of its solutions in the non-polar solvents mesitylene, cyclohexane and benzene. In the absence of any appreciable difference in the dipole moments of these liquids, it might have been expected that they would arrange themselves according to the order of their refractive indices. This however is not the case.

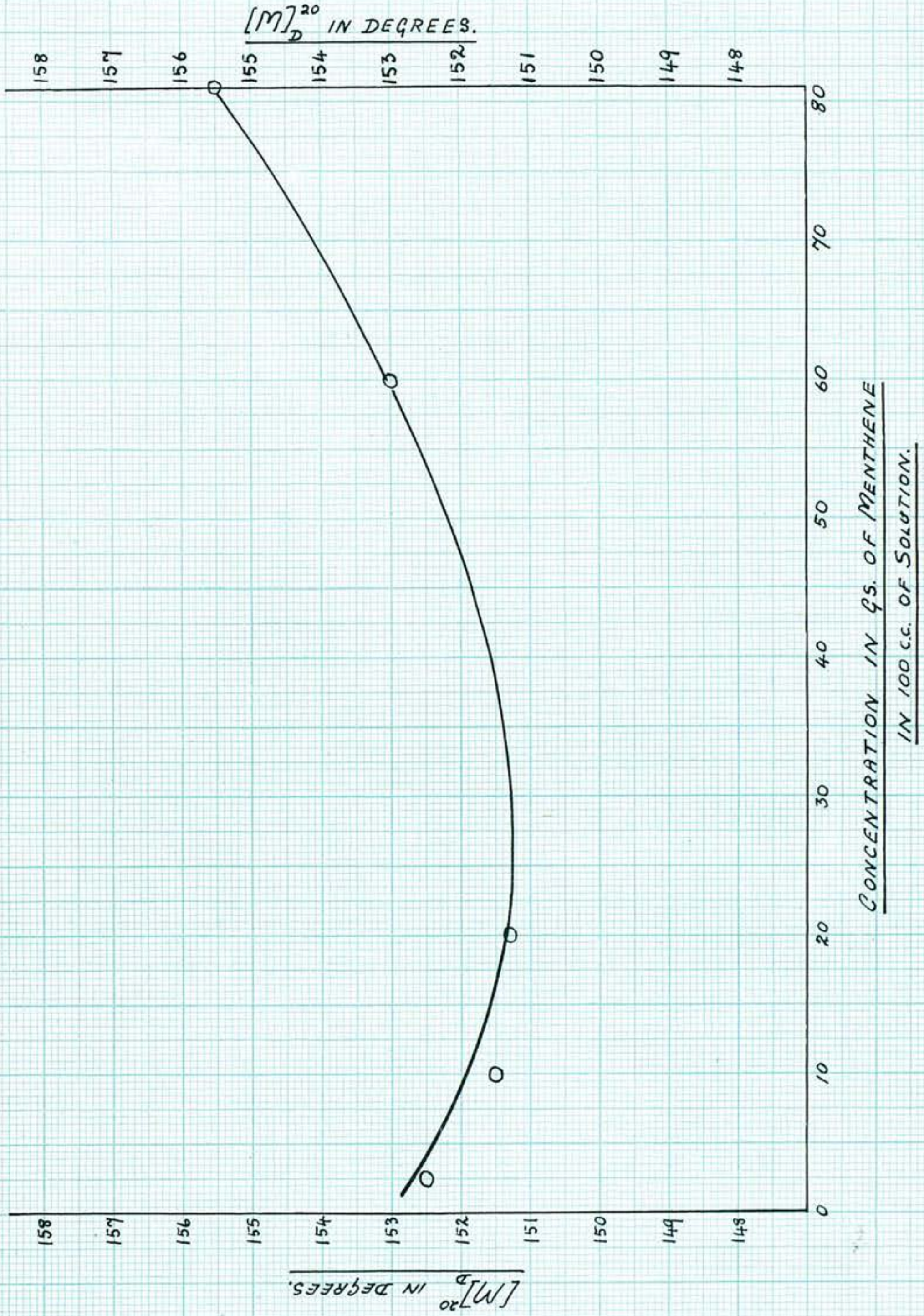
Since the dissolution of menthene in a polar solvent causes a lowering of its rotatory power, a solution of menthene in a non-polar solvent should show an increase in the rotation, since any menthene-menthene complexes should tend to be split up by

this/

GRAPH I.

GRAPH I.

ROTATORY POWER OF d-MENTHENE IN HEXANE SOLUTION.

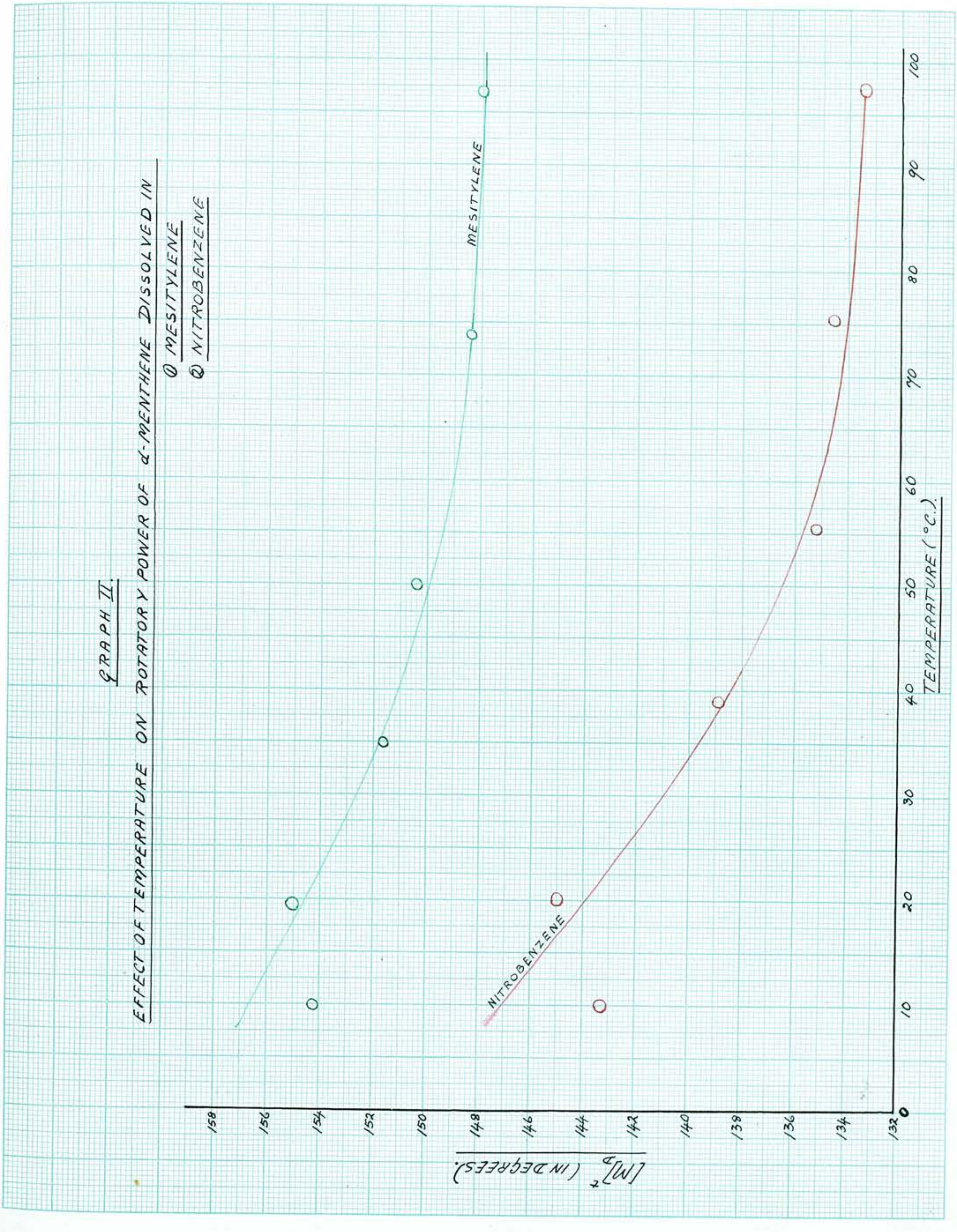


this means. As we see from table I, this does not occur. An interesting point was brought out, however, in the case of the solvent hexane. The rotatory powers of solutions of various concentrations of d-menthene in this non-polar solvent were determined and a curve obtained by plotting rotatory power against concentration. This curve (Graph I) was found to give a minimum value of the rotation when the concentration had fallen to 20%. This may possibly be explained by supposing that the initial fall in the rotation is due to the influence of decreased refractivity of the medium being greater than the influence of decreased association of the menthene. When, however, the concentration of menthene in hexane falls to 20%, the latter effect may predominate, leading thereafter to an increase in the rotation. The observed changes are however small.

It should be noted **that** no support for the polarity effect in solutions of menthene, can be obtained from observations concerning the effect of temperature on the rotatory power of menthene dissolved in mesitylene and nitrobenzene respectively. Rule has pointed out that the curves obtained by plotting the rotatory powers of an active compound dissolved in a polar and a non-polar solvent against temperature should tend to converge towards one another as the temperature rises, provided a definite polar influence due to solvent

influence/

GRAPH II.

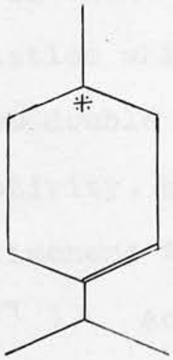

GRAPH II.
EFFECT OF TEMPERATURE ON ROTATORY POWER OF d-MENTHENE DISSOLVED IN
① MESITYLENE
② NITROBENZENE
MESITYLENE
NITROBENZENE
TEMPERATURE (°C.)
0
10
20
30
40
50
60
70
80
90
100
[M]ᵗ_D (IN DEGREES.)
132
134
136
138
140
142
144
146
148
150
152
154
156
158

influence is exhibited (see introduction, p. 22)

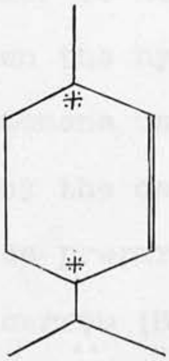
The curves obtained in the case of menthene are shown in Graph II. They show no tendency to converge at higher temperatures, the small observed changes being in the opposite direction.

On the whole, however, it may be concluded that the influence of solvents on the rotatory power of d - p - △ (3) - menthene is mainly dependent on the dipole moment of the solvent medium. A secondary effect may possibly be related to the refractive index of the solvent, but this is not clearly indicated and is subject to a number of exceptions.

A possible source of irregularity in the solvent effect may be found in the observation of Gachard (see preparative section, p. 84) who concluded from an examination of its Raman spectra that menthene, prepared by this method appeared to contain about 10-20% of p - △ (2) - menthene as well as the △ (3) - form. The former isomer, although containing only one double bond, has two asymmetric



p - △ (3) - Menthene.



p - △ (2) - Menthene.

centres. Moreover, a consideration of the position of the double bond shows that association occurring here acts directly through a single linkage on the electrical field of both asymmetric atoms, whereas in the case of the $\triangle(3)$ - form, association at the double bond has to act through a chain of carbon atoms on the electrical field of the asymmetric atom and hence the effect will be very much lessened. There should thus be a greater tendency for the former isomeride to have its rotatory power changed with the dipole moment of the solvent, whereas for the latter isomeride the tendency should be less evident and the effect of variation of the refractive index of the medium should be a more predominant influence. This may account to some extent for the anomalous position of certain solvents.

d- Limonene.

The effect of solvents on the rotatory power of d- limonene was next studied, in order to note the type of variation which occurred when the hydrocarbon contained two double bonds. The limonene used was of a high activity, being obtained by the debromination of d- limonene tetrabromide (see preparative section p. 87). According to Escourrou (Bull. Soc. Chim., 1928, (IV), 43, 1204.), who investigated the oxidation/

oxidation of the hydrocarbon with ozone, the natural product, which has not been submitted to chemical purification, is a mixture of terpinolene, α-terpinene and limonene, the latter forming about 80% of the whole. No further investigations have been made on this point, but it should be noted that if such is the case, the terpinolene and the terpinene should be removed by bromination, since they give liquid bromides. Hence the sample of limonene isolated from the purified crystalline bromo-derivative should be relatively pure.

The results obtained with the aliphatic solvents are given in table III, the concentration varying from 1.956 in chloroform to 2.161 in methyl alcohol.

TABLE III./

TABLE III.

Influence of Aliphatic Solvents on Rotatory Power of d-Limonene.

Solvent	n_D^{20} (solvent	α^{20}_{5893}	$[M]^{20}_{5893}$	$\mu \times 10^{18}$ e.s.u.
CH_3OH	1.3284	4.75°	149.5°	1.66
CH_3CN	1.3441	4.54	150.8	3.16
CCl_4	1.4607	4.85	154.4	0
$(CH_3)_2CO$	1.3592	4.68	154.5	2.76
$CH_3.CHO$	1.3316	4.62	156.6	2.68
$CHCl_3$	1.4459	4.51	156.8	1.18
C_6H_{14}	1.3754	4.86	157.3	0
CH_2Cl_2	1.4245	4.83	158.0	1.55
$CH_3.COOH$	1.3718	4.62	158.7	1.73(.60)
$CH_3.NO_2$	1.3815	4.72	158.3	3.03
CH_3I	1.5297	5.00	166.8	1.08
CS_2	1.6276	5.20	166.6	0
(homogeneous)	1.4713	52.18	168.9	$<0.5^*$

(* The value quoted above for the dipole moment of limonene is taken from a paper by Wolf and Volkmann, Zeit. phys. Chem., (B), 1929, 3, 139.)

The first point to be noted in the above table is that there is no definite polar effect traceable. All these aliphatic solvents give values of the rotatory power lower than that of the homogeneous limonene, although in methyl iodide and carbon disulphide the rotations are much greater than those given in the other solvents. These two solvents have refractive indices which are much greater than those of any of the other aliphatic solvents examined; hence it would appear that solvents of high refractive index tend to raise the rotatory power. On the other hand, solvents of low refractive index tend to yield solutions of low optical activity. This is well shown in the positions of methyl alcohol and acetonitrile.

An even more definite effect of this type is evident among the aromatic solvents given in table IV below. Here the concentration of d- limonene employed varies from 1.960 in iodobenzene to 2.170 in chlorobenzene.

TABLE IV./

TABLE IV.

Influence of Aromatic Solvents on the Rotatory Power of d- Limonene.

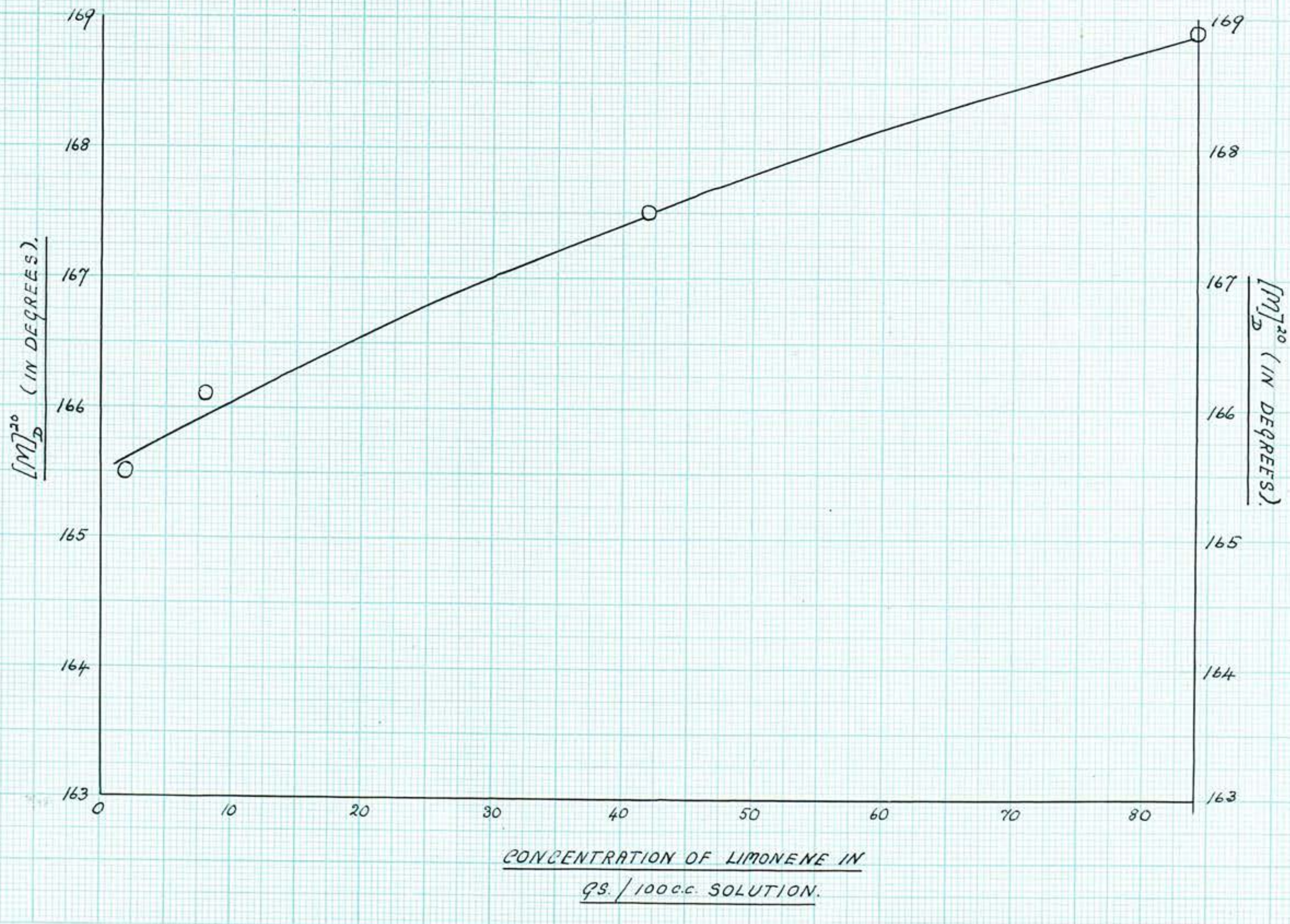
Solvents	n_D^{20} (solvent)	α_{5893}^{20}	$[M]_{5893}^{20}$	$\mu \times 10^{18}$ e.s.u.
C_6H_{12}	1.4273	4.88°	157.9°	0
$C_6H_5.CH_3$	1.4950	4.86	165.2	0.37
s-$C_6H_3(CH_3)_3$	1.4962	4.95	165.2	0
C_6H_6	1.5014	4.99	165.5	0
$C_6H_5OCH_3$	1.5164	5.00	167.3	1.23
C_6H_5CN	1.5278	4.93	167.3	3.94
(homogeneous)	1.4713	52.18	168.9	$<$0.5
C_6H_5Cl	1.5250	5.40	169.2	1.52
$C_6H_5COCH_3$	1.5332	5.04	169.5	2.97
o-$C_6H_4Cl_2$	1.5490	5.04	170.5	2.24
C_6H_5CHO	1.5453	5.29	170.8	2.75
$C_6H_5NH_2$	1.5863	5.17	172.5	1.52
C_6H_5I	1.6180	5.02	174.3	1.25
$C_6H_5NO_2$	1.5504	5.39	177.2	3.94

An examination of the above figures shows a very complete parallel between refractive index of solvent and rotatory power of the solution, the relationship being such that a rise in the one property corresponds to a rise in the other. This agreement is broken only by small displacements in the positions of the strongly polar compounds nitrobenzene and benzaldehyde, which would appear to indicate that superimposed upon the refractive index effect is a minor one due to the polarity of the medium. The latter is exerted in such a manner that increasing dipole moment tends to raise the rotatory power, thus displacing these solvents into a slightly lower position in the table than would correspond to their refractive properties.
The assumption of a major influence related to the refractive index of the solvent is further confirmed by a comparison of table IV with table III, showing that the aliphatic liquids, which have, on the whole, considerably lower refractive indices, also yield solutions of much lower activity.

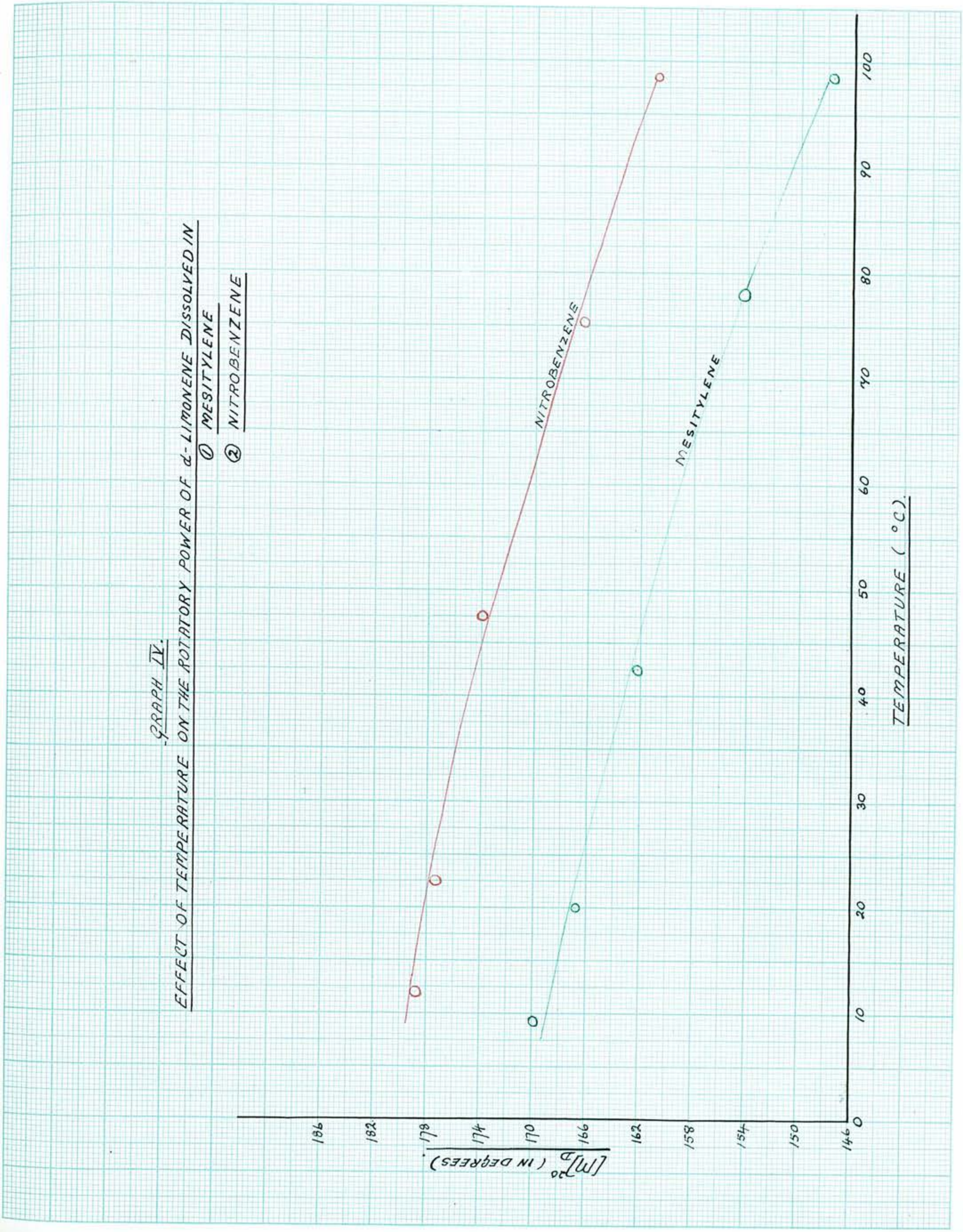
A curious point for which no explanation can be suggested is the abnormally high position in tables III and IV assumed by the homogeneous limonene, the rotation of which is greater than corresponds to its refractive index. One consequence of this displacement is that when limonene is diluted with the non-polar liquids benzene, toluene or carbon disulphide, the/

GRAPH III.

INFLUENCE OF CONCENTRATION ON THE ROTATORY POWER OF d-LIMONENE IN BENZENE SOLUTION.



GRAPH IV.



GRAPH IV.

EFFECT OF TEMPERATURE ON THE ROTATORY POWER OF d-LIMONENE DISSOLVED IN
① MESITYLENE
② NITROBENZENE

the rotatory power falls in spite of the increasing refractive index of the medium. For cyclohexane, hexane and carbon tetrachloride, however the rotatory changes are in the direction to be expected from the fall in refractive index. Self-association of limonene might result in an increased rotatory power being observed for the homogeneous liquid, but it is highly improbable that the degree of association could be so great as to give rise to displacements of the order of magnitude under discussion. It must be assumed that in this case the refractive index of the solvent represents the main factor governing the rotation, but that other influences are also operative, possibly connected with the polarity or the as yet little understood van der Waal forces. As may be seen in graph III, when rotatory power in benzene solution is plotted against concentration, the result is a smooth curve without maximum or minimum.

As was to be expected in the absence of any appreciable polar influence of the solvent, the temperature-rotation curves for solutions of limonene in the non-polar mesitylene and the strongly polar nitrobenzene respectively show no tendency to converge with rise of temperature. The curves in question (see graph IV) are practically parallel, the rotation falling as the refractive index diminishes. As will be shown later the curves illustrating the change in the/

the refractive indices of mesitylene and nitrobenzene with rise in temperature are also represented by parallel lines.

Owing to the extremely low polarity of the optically active solutes, it appears evident that menthene and limonene possess little tendency to enter into dipole association with polar solvents, as is illustrated by the fact that the main solvent influence appears to be related to the refractive index rather than to the dipole moment. If this conclusion is correct, it is probable that for a saturated hydrocarbon, which would exhibit zero dipole moment, the polar properties of the solvent would be almost completely subordinated to their refractive indices, in so far as their influence upon the rotatory power of the hydrocarbon is concerned. Optically active saturated hydrocarbons of the simpler aliphatic type are not readily prepared, and it was therefore decided to study the behaviour of d- pinane, which may be prepared by the hydrogenation of d- pinene. In order to complete the comparison, however, an examination of the changes undergone by the unsaturated parent compound, d-pinene, was first made.

d- α - Pinene.

The rotatory powers found for solutions in aliphatic solvents are given in table V, the concentrations/

concentrations varying from 4.022 in the case of CCl_4 to 4.212 in the case of methyl alcohol.

TABLE V.

Influence of Aliphatic Solvents on the Rotatory Power of d-α-Pinene.

Solvent	n_D^{20} (solvent)	α_{5893}^{20}	$[M]_{5893}^{20}$	$\mu \times 10^{18}$ e.s.u.
CS_2	1.6276	3.39°	55.6°	0
CH_3I	1.5297	3.69	60.5	1.08
(homogeneous)	1.4651	20.48	64.3	(small)
C_6H_{14}	1.3754	4.08	68.9	0
CCl_4	1.4607	4.10	69.4	0
CH_3OH	1.3284	4.39	71.1	1.66
$(CH_3)_2CO$	1.3592	4.30	72.1	2.76
$CH_3.CHO$	1.3316	4.39	73.6	2.68
CH_2Cl_2	1.4245	4.46	75.3	1.55
$CHCl_3$	1.4459	4.57	75.9	1.18
CH_3NO_2	1.3815	4.65	76.0	3.03
CH_3CN	1.3441	4.65	76.2	3.16
CH_3COOH	1.3718	4.70	76.4	1.73(.60)

From an examination of the above table we see that a comparatively marked polar effect is indicated. The lowest rotations are given in solvents of zero or low polarity and the highest rotations in highly polar solvents/

solvents. The positions of carbon disulphide and methyl iodide would suggest that, as a minor influence, solvents of high refractivities tend to lower the rotatory power, since the refractive indices of these two liquids are much higher than those of the other aliphatic solvents used. It would appear, however, that the polar effect is sufficiently strong to mask any changes due to the refractive index in the case of the other solvents. A solvent which gives a somewhat higher rotation than would be anticipated from its dipole moment is acetic acid. This is possibly related to the tendency of acids to polymerise pinene to form dipinene. Although no such polymerisation takes place with weak acids, a strain on the pinene molecule may well be produced which, although it leads to no chemical change, may produce disturbances in the electrical field of the molecule and hence, a change in the rotatory power.

The aromatic solvents listed in table VI below, show a similar type of series. Here the concentration varies from 4.016 in toluene to 4.166 in acetophenone.

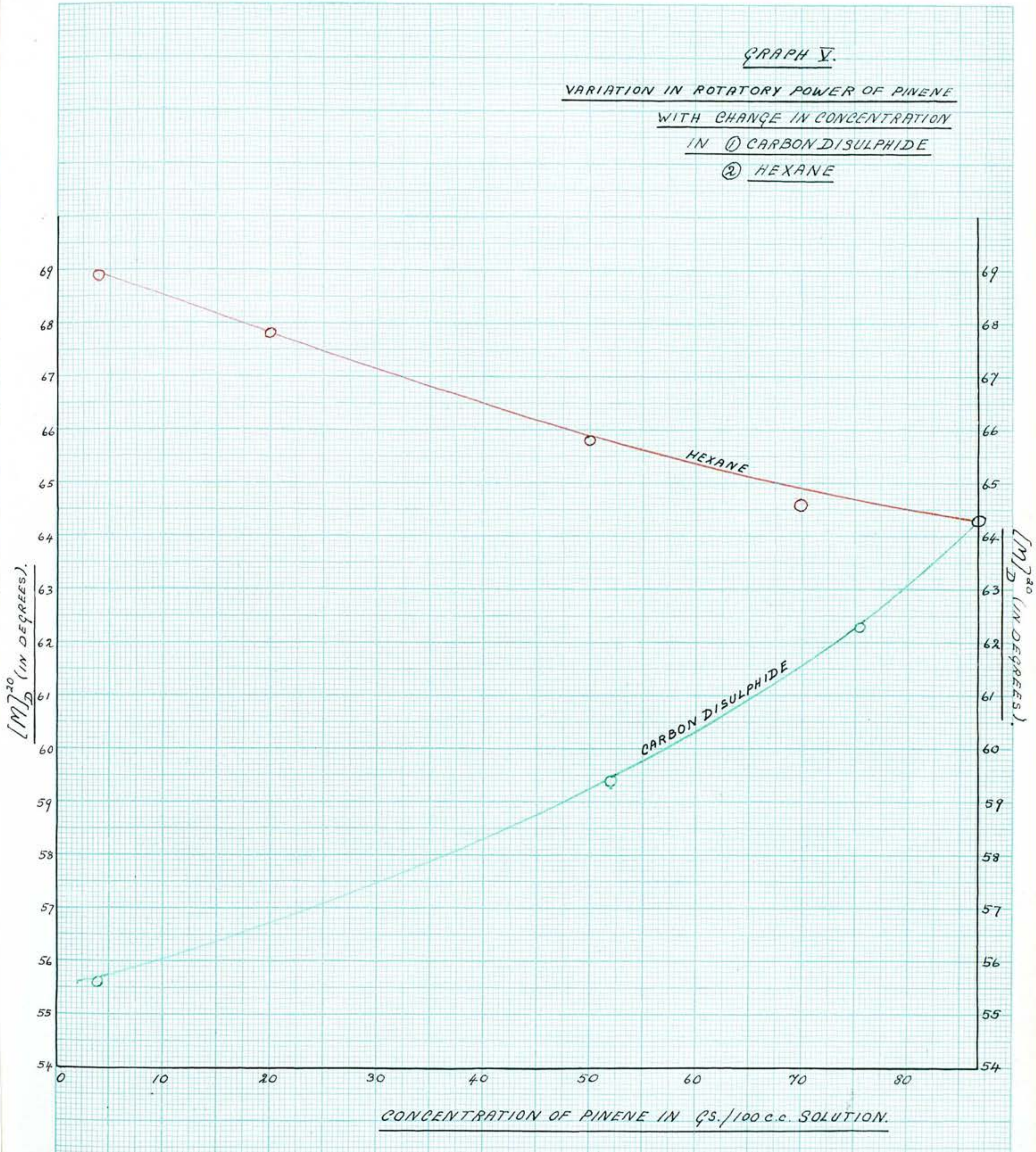
TABLE VI./

TABLE VI.

Influence of Aromatic Solvents on the Rotatory Power of d- α - Pinene.

Solvent	n_D^{20} (solvent)	α_{5893}^{20}	$[M]_{5892}^{20}$	$\mu \times 10^{18}$ e.s.u.
s-$C_6H_3(CH_3)_3$	1.4962	3.76°	62.3°	0
C_6H_6	1.5014	3.86	63.4	0
C_6H_{12}	1.4273	3.89	63.7	0
(homogeneous)	1.4651	20.48	64.3	(small)
$C_6H_5OCH_3$	1.5164	3.91	65.2	1.25
C_6H_5I	1.6180	3.93	65.6	1.25
$C_6H_5CH_3$	1.4950	3.88	65.7	0.37
C_6H_5Cl	1.5250	4.10	67.9	1.52
o-$C_6H_4Cl_2$	1.5490	4.20	70.7	2.24
$C_6H_5NH_2$	1.5863	4.17	70.7	1.52
$C_6H_5COCH_3$	1.5332	4.40	71.8	2.97
C_6H_5CN	1.5278	4.42	73.4	3.85
$C_6H_5NO_2$	1.5504	4.56	76.2	3.90

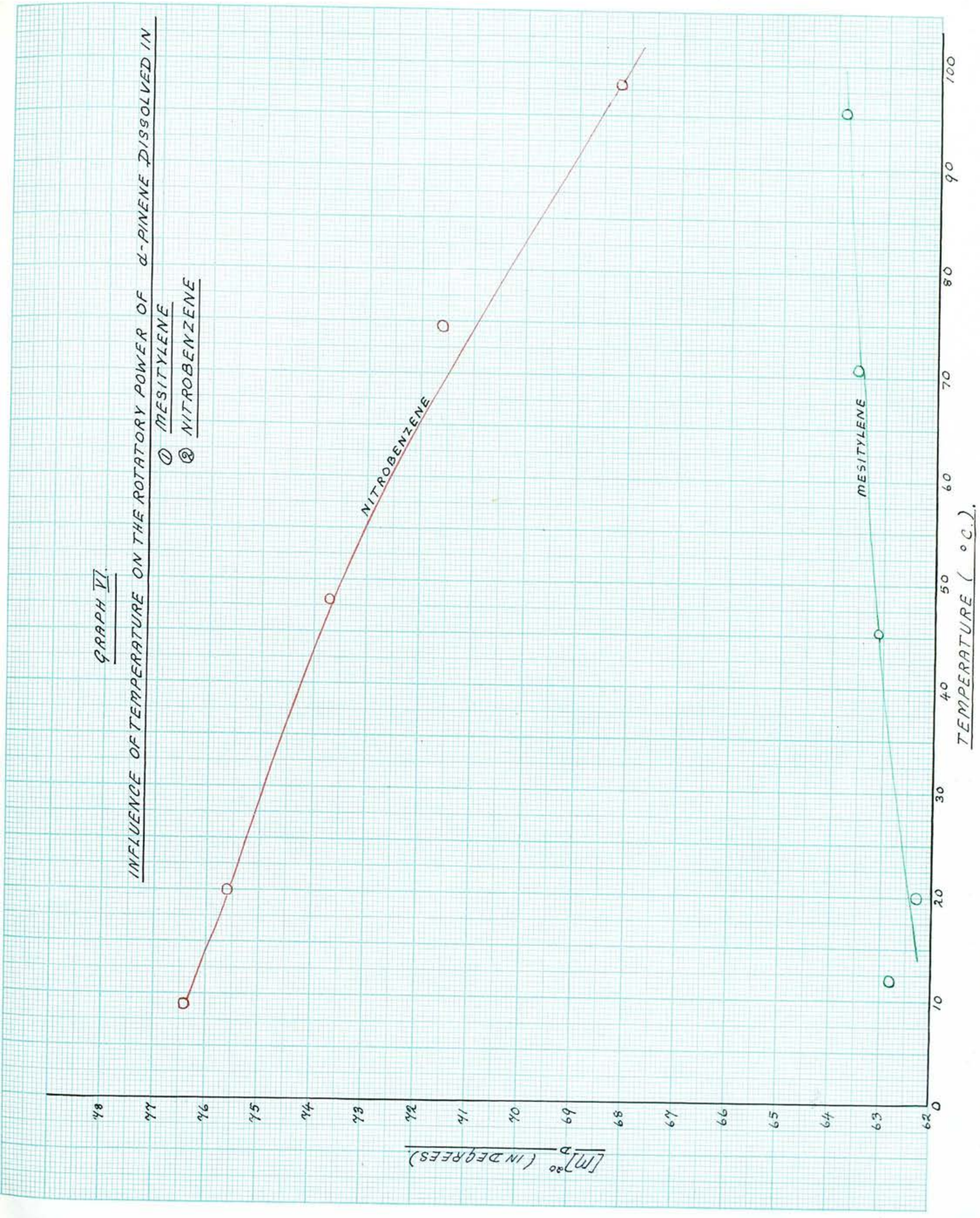
GRAPH V.


GRAPH V.
VARIATION IN ROTATORY POWER OF PINENE
WITH CHANGE IN CONCENTRATION
IN ① CARBON DISULPHIDE
② HEXANE
HEXANE
CARBON DISULPHIDE
$[M]_D^{20}$ (IN DEGREES).
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
0
10
20
30
40
50
60
70
80
CONCENTRATION OF PINENE IN GS./100 c.c. SOLUTION.

In this table as in table V, it is found that d- pinene yields solutions of highest optical activity in solvents of high dipole moment, whereas low rotations are given by solvents of zero polarity. On the other hand the minor influence of highly refractive aliphatic solvents in depressing the rotatory power does not appear to be sufficiently powerful to be traced in the positions in table VI of iodobenzene and aniline, which possess the highest refractive indices of the aromatic group.

An examination of the graphs for concentration against rotatory power was made for solutions of pinene in carbon disulphide and in hexane. Two uniform curves were obtained (graph V), the influence of increasing concentration being to lower the rotation in hexane and to increase the rotation in carbon disulphide. These changes are in agreement with the known alteration in the refractive index of the medium, on the assumption that an increase in this property corresponds to fall in dextro-rotation.
It is evident from tables V and VI that the changes in rotatory power brought about by diluting pinene with the non-polar solvents carbon tetrachloride, mesitylene and benzene are also explainable on this basis. For cyclohexane and toluene however, the variations in rotatory power are small and not in the/

GRAPH VI.



GRAPH VI.

INFLUENCE OF TEMPERATURE ON THE ROTATORY POWER OF d-PINENE DISSOLVED IN

① MESITYLENE

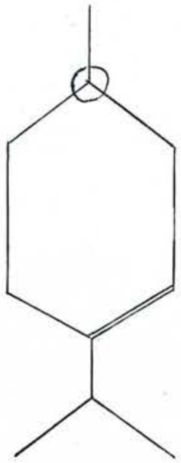
② NITROBENZENE

the direction anticipated from change in the refractive index.

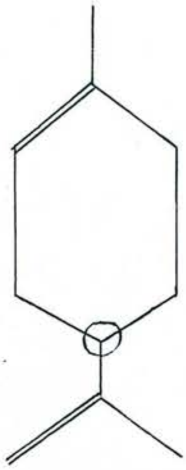
The occurrence of effects due to both polarity and refractive index of the solvent medium is brought out extremely well in the temperature-rotation curves for solutions of pinene in mesitylene and nitrobenzene. (Graph VI). The rotation of pinene in nitrobenzene decreases rapidly with rise in temperature, whereas its rotation in mesitylene rises slightly with rise in temperature. It is evident at once that these two curves tend to cut at higher temperatures and hence reverse the order of the rotatory powers. It is suggested that, at low temperatures, the chief factor governing the rotatory power is the polarity of the solvent nitrobenzene, association between solute and solvent resulting in an increase in the rotatory power. When the temperature rises, however, these solvent-solute complexes begin to break up and the refractivities of the two solvents then assume a greater importance with respect to their effect on the rotatory power. Since, as we have seen from table V, high refractivity of the solvent medium tends in the case of pinene to decrease the rotatory power, the nitrobenzene temperature-rotation curve crosses the corresponding mesitylene curve and at still higher temperatures these two solvents assume their correct relative/

relative positions with regard to the effect of their refractivities on the rotatory power of the solute.

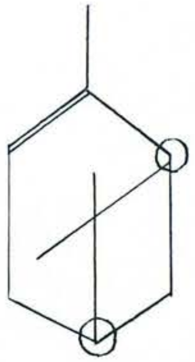
At this stage it is convenient to review the results obtained for the three optically active, unsaturated hydrocarbons under discussion, and in order



Δ(3)-Menthene



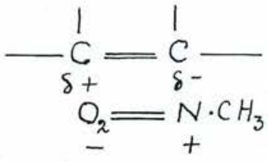
Limonene



α-Pinene

to emphasise the molecular difference involved, their formula are reproduced for the purpose of drawing attention to the position of the asymmetric atoms (encircled) and the double bonds. It is generally assumed that the small dipole moment of an unsaturated hydrocarbon is located at the double bond, and that in unsymmetrical compounds one end of the bond is feebly positive and the other feebly negative. Hence the influence of a strongly polar solvent upon the rotatory power of such a compound is probably propagated by dipole association of the usual type

e.g.



$$\begin{array}{c} | \qquad\quad | \\ -\underset{\delta+}{C} = \underset{\delta-}{C}- \\ \underset{-}{O_2} = \underset{+}{N}\cdot CH_3 \end{array}$$

This will result in a modification of the electrical field exerted by the double bond in the active molecule, and thus bring about a change in rotation which may be assumed to vary according to the degree of dipole association, and the distance of the double bond from the asymmetric atom.

Reference to tables **I - VI** shows that d- pinene in solution exhibits a very definite polar influence in both aromatic and aliphatic solvents. With menthene the effect is also clearly marked, if a little less regular, but in the case of limonene the polar influence could only be traced somewhat irregularly with aromatic solvents and not at all with aliphatic media. These results may be understood if we assume that in pinene the electrical influences propagated from the double bond pass in both directions round the cyclohexane ring and produce similar changes in the rotatory contributions of the two asymmetric atoms at positions 2 and 4. In this event the summation of the two effects would be expected to reveal itself in a marked polar influence of the solvent, which would tend to dominate any secondary changes due to variations in the refractive index.

In the case of menthene the electronic deformations undergone by the double bond have a longer distance to travel than in that of pinene, which may possibly account for the relatively smaller optical changes/

changes observed. With limonene, however, the problem is more complex; the molecule only possesses one asymmetric atom, but has two double bonds from which solvent effects may be transmitted. From the more erratic nature of the optical changes observed with limonene it would appear that these effects do not assist one another but are in opposition.

It is not possible to draw very definite conclusions regarding the relationship between refractive infex of solvent and the rotatory powers of solutions of menthene and pinene. Such an influence is, however, clearly indicated in the case of limonene, where it masks to some extent any influence due to the polar nature of the solvent medium.

d- Pinane.

By employing a fully saturated optically active hydrocarbon as solute, it was to be anticipated that the refractive index would become the main effect in all cases, and in order to test this conclusion the behaviour of d- pinane was next investigated.

In table VII the solvents are all grouped together, irrespective of whether they are aliphatic or aromatic in type, and the list has been extended by the inclusion of derivatives of naphthalene, pyridine and quinoline, and certain aliphatic solvents of high/

high refractive index. The concentration of pinane varies from 4.346 in bromobenzene to 1.972 in nitromethane (the solubility in the latter solvent being low.)

TABLE VII/

TABLE VII.

Influence of Solvents on Rotatory Power of d- Pinane.

Solvent	n_D^{20} (solvent)	α^{20}_{5893}	$[M]^{20}_D$	$\mu \times 10^{18}$ e.s.u.
CH_3CN	1.3441	0.97°	25.8°	3.21
CH_3OH	1.3284	1.26	26.4	1.68
CH_3COOH	1.3718	1.26	26.9	1.73 (.60)
CH_3NO_2	1.3815	0.78	27.3	3.05
C_5H_{12}	1.3560	1.32	27.4	0
CH_3CHO	1.3316	1.33	27.7	2.72
C_6H_{14}	1.3754	1.37	27.8	0
$(CH_3)_2CO$	1.3592	1.42	28.9	2.76
CH_2Cl_2	1.4245	1.44	29.0	1.51
$CHCl_3$	1.4459	1.40	30.2	1.05
C_6H_5CN	1.5278	1.49	30.8	3.85
CH_2Br_2	1.5413	1.58	31.4	1.89
(homogeneous)	1.4630	19.54	31.5	0 (?)
CCl_4	1.4607	1.44	31.6	0
pyridine	1.5088	1.60	32.3	2.11
s-$C_6H_3Me_3$	1.4962	1.66	32.5	0
$C_6H_5NO_2$	1.5504	1.62	32.5	3.90
CH_3I	1.5297	1.59	32.6	1.35
C_6H_6	1.5014	1.59	32.9	0
C_6H_5.COMe	1.5332	1.68	33.2	2.97

TABLE VII. (continued)

Solvent	n_D^{20} (solvent)	α^{20}_{5893}	$[M]^{20}_D$	$\mu \times 10^{18}$ e.s.u.
C_6H_5CHO	1.5453	1.57	33.2	2.75
$C_6H_5CH_3$	1.4950	1.65	33.7	0.37
C_6H_5OMe	1.5164	1.74	34.5	1.25
C_6H_5Cl	1.5250	1.58	34.7	1.56
o-$C_6H_4Cl_2$	1.5490	1.73	34.7	2.24
α-$C_{10}H_7Cl$	1.6332	1.73	34.9	1.59
C_6H_5Br	1.5601	2.21	35.1	1.56
α-$C_{10}H_7Br$	1.6558	1.70	35.1	1.58
$CHBr_2.CHBr_2$	1.6344	1.77	35.3	1.0 (?)
C_6H_5I	1.6180	1.77	35.6	1.25
α-$C_{10}H_7OMe$	1.6201	1.88	35.6	1.3 (?)
$C_6H_5NH_2$	1.5863	1.71	36.4	1.60
CH_2I_2	1.7427	0.95	36.6	1.10
quinoline	1.6246	1.88	38.6	2.11
CS_2	1.6276	1.96	38.7	0
α-$C_{10}H_7I$	1.7054	0.98	39.7	1.43

The above table summarises the rotatory powers of d- pinane dissolved in thirty-six solvents of widely varying types. It appears at once from the figures given that the main influence exerted by the solvent medium is not polar, since values of $\mu > 2$ and $\mu < 1$ are distributed evenly throughout the whole range of rotatory powers. The main factor influencing the optical rotation of d- pinane in the various solutions is undoubtedly the refractive index of solvent employed. For dilute solutions, this value is practically identical with the refractive index of the mixture, the latter quantity probably having a sounder theoretical basis. All solvents which lower the rotatory power of d- pinane, with the exception of benzonitrile and methylene bromide, have lower refractive indices than that of the homogeneous liquid. On the other hand, solvents which have refractive indices higher than that of d- pinane, raise the rotatory power.

For a solution in carbon tetrachloride, which has $n_D^{20} = 1.4607$, a value differing but little from the refractive index of d- pinane itself ($n_D^{20} = 1.4630$), the observed rotatory power coincides within the limit of experimental error with that of the homogeneous substance. It may thus be concluded that an increase in the refractive index of the medium leads/

leads to a rise in the rotatory power of the solution. At the same time a very small polar effect of the solvent may be traced, which appears to be in such a direction that a rise in polarity tends to lower the rotation. This would account for the minor displacements towards the lower rotatory powers at the top of the table observed in the cases of the strongly polar compounds benzonitrile, nitrobenzene, benzaldehyde, acetophenone, nitromethane etc. There is no doubt that although the degree of solute-solvent association in the case of a saturated hydrocarbon may only be slight, the influence of a polar solvent molecule on the electrical field of such an optically active compound has an appreciable effect on the rotatory power. The magnitudes of the rotatory power found with the heterocyclic solvents pyridine and quinoline fall into the position expected of them from a consideration of their refractive indices. The rotations given in the majority of the solvents derived from benzene fall into an intermediate position between those given in most of the aliphatic solvents and those in naphthalene derivatives. This is also to be expected from the refractive indices of these types. There is no need, however, to arrange these solvents into groups of similar molecular type, as must be done when tracing the influence of the polarity of the solvent on the rotatory power of a polar solute.

Relationships/

Relationships between rotatory power and the refractive index of the medium have been deduced previously on theoretical grounds by several investigators. They have never before been established from experimental results, probably owing to the limited number of solvents used and the fact that most of the optically active compounds employed have had a group or groups of definite polarity. In such cases, as has been shown in the earlier part of this thesis, the polar effect of the solvent almost entirely masks any regularities due to the refractive index of the medium, even with very weakly polar solutes such as unsaturated hydrocarbons.

In this connection it was thought pertinent to determine whether or not the experimental data obtained in this thesis lent quantitative support to any of the physical theories put forward. Three of the most widely accepted of such theories were chosen for testing.

The first of these is due to Born (Physik. Z., 1915, 16, 251; Ann. Physik, 1918, 55, 177) who, employing a conception of resonators coupled in pairs, deduced a somewhat complicated mathematical formula in which the rotatory power was obtained as a function of the refractive index and characteristic frequency, etc., of the active compound. For any given active compound/

compound the only part of this formula which could change with change in solvent medium was the refractive index function. Hence, for a given wavelength, Born's formula could be made to show how the rotatory power of active compound should vary with the refractive index of a solvent medium. The expression deduced by Born is

$$\underline{[M] = \text{constant} \times (n^2 + 2)^2} \;\ldots\ldots\ldots\ldots\; \text{I}$$

A modification of the above theory was made later by Gans (Z. Physik, 1923, 17, 353; Ann. Physik., 1926, 79, 548.), as a result of which the expression I was cast into the form

$$\underline{[M] = \text{constant} \times (n^2 + 2)} \;\ldots\ldots\ldots\ldots\; \text{II}$$

The third theory to be discussed was published by S.F. Boys while this experimental work on pinane was in progress (vide Rule and Chambers, Nature, 1934, 133, 910.) and certain ideas put forward in it were interesting in that they supported the previous work of Rule and his coworkers and also the results of the present investigation. The views of Boys (Proc. Roy. Soc., A, 144, 655, 675; 1934) are based on the idea that each atom in a molecule becomes an oscillating electric doublet under the influence of a light wave. In simple cases the total polarisation of the molecule can be calculated, allowance being made for the effect of such doublets on the field of the/

the wave itself, and from this are derived the velocities within the medium of the two constituents of plane polarised light, namely d- circularly and l- circularly polarised light. The difference between these two velocities leads to the rotation. On this basis Boys derives the following general formula,

$$[\alpha]_\lambda = \frac{72900(n^2+2)(n^2+5).\Sigma R_A R_B R_C R_D.I}{32\pi^2\lambda^2 M N^3} \text{......} \quad \mathrm{III}$$

where <u>n</u> is the refractive index of the medium in which the rotation is measured, <u>R_A etc.</u>, are the total refractivities of each group attached to the asymmetric atoms, <u>M</u> is the molecular weight of the compound, <u>N</u> is Avogadro's number and <u>I</u> is a factor involving interatomic distances. This formula is for the general case where several asymmetric centres exist in the molecule but, unfortunately, its complexity renders the calculation impossible to apply to common optically active substances. Also there is no way of finding accurately all the interatomic distances involved. Boys, therefore deduced a simplified formula **IV** for the case of a compound containing four different radicals attached to a central asymmetric atom, all the radicals being assumed to be small -

$$\overline{\underline{\mathrm{IV}}}$$

$$[\alpha]_\lambda = \frac{C(n^2+2)(n^2+5)R_A R_B R_C R_D(1+F)(a-b)(a-c)(a-d)(b-c)(b-d)(c-d)}{\lambda^2.M.(a+b+c+d)^4}$$

where n is the refractive index of the medium, R_A etc., the total refractivities of each attached group, C is a constant, a, b, c and d are the effective radii of the groups in Ångström units as calculated from their volumes, and $F = f(\triangle a) + f(\triangle b) + f(\triangle c) + f(\triangle d)$ a factor which has not much influence on the numerical result.

Formula IV was applied by Boys to the calculation of the rotatory powers of certain simple optically active compounds such as amyl alcohol and amylamine, and the calculated rotation was found to be in good agreement with that experimentally observed.

From the point of view of the present work the most striking pronouncement made by Boys concerned the interpretation of solvent effect according to this theory. From the above formulae we see that changes in the refractive index of the medium, or in the refractivity or effective radii of the attached should all lead to corresponding changes in the rotatory power.

In the case of a completely non-polar active solute, where association is at a minimum, it is deduced that changes in rotatory power should go hand in hand with changes in the refractive index of the medium, the latter variation arising from alterations in solvent, concentration, temperature or wavelength of light employed. In the case of more polar solutes, solvent/

solvent-solute association and solute-solute association may take place, and hence may tend to influence the refractivities or effective radii of the attached groups. This will tend to mask completely any change brought about by variation of the refractive index of the medium. Boys suggests that the effect of solvents in this case may go hand in hand with the dielectric constants of the solvents. As has already been shown by Rule this is the decisive physical property in the majority of cases, although the relationship is more fundamentally referred to the dipole moment of the solvent (see introductory section of this thesis p. 16).

If we write Boys formula in the same form as Born and Gans we obtain

$$[M] = \text{constant} \times (n^2 + 2)(n^2 + 5) \quad \ldots\ldots\ldots \quad V$$

It is thus evident that if we measure the refractive indices of the solutions employed, we can compare observed values of [M] for d- pinane with the values of [M] calculated on the basis of each of these theories. The constant in each formula was first calculated from the observed values of the rotation and refractive index of the homogeneous substance, e.g. in the case of Boys' formula

$$\text{constant} = \frac{[M]_1}{(n_1^2 + 2)(n_1^2 + 5)} \qquad (\lambda = 5893,\ t = 20^{\circ})$$

where/

where $[M]_1$ = observed rotation for homogeneous d-pinane

n_1 = observed refractive index for homogeneous d-pinane.

The constants for Born's and Gans' formulae were calculated in a similar manner. The molecular rotations thus evaluated are given in the following table (VIII) together with values experimentally observed. The concentrations varied from 4.346 in bromobenzene to 1.972 in nitromethane. The values of the refractive indices (n_D^{20}) of the solutions were also determined experimentally and are listed in the second column of the table. Solvents are arranged in order of increasing magnitude of the rotatory power of the solutions.

TABLE VIII./

TABLE VIII.

Comparison of Observed Values of Rotatory Power for d- Pinane in various Solvents with Calculated Values based on Theoretical Grounds.

Solvent	n_D^{20}	$[M]_{5893}^{20}$	$[M]_{5893}^{20}$ (calculated)		
	(solution)	(observed)	(i) Born	(ii) Gans	(iii) Boys
CH_3OH	1.3266	26.4°	26.1°	28.6°	27.1°
CH_3NO_2	1.3864	27.3	28.2	29.7	28.9
C_5H_{12}	1.3640	27.4	27.4	29.3	28.2
C_6H_{14}	1.3835	27.8	28.1	29.6	28.8
$(CH_3)_2CO$	1.3653	28.9	27.5	29.3	28.3
$CHCl_3$	1.4489	30.2	30.9	31.1	31.0
C_6H_5CN	1.5255	30.8	34.6	32.9	33.7
CH_2Br_2	1.5385	31.4	35.1	33.1	34.1
(homogeneous)	1.4630	31.5	-	-	-
CCl_4	1.4616	31.6	31.6	31.5	31.5
s-$C_6H_3Me_3$	1.4944	32.5	33.2	32.1	32.7
$C_6H_5NO_2$	1.5468	32.5	35.8	33.5	34.6
CH_3I	1.5291	32.6	34.7	33.0	33.9

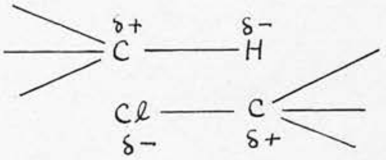
TABLE VIII. (continued)

Solvent	n_D^{20}	$[M]_{5893}^{20}$	$[M]_{5893}^{20}$ (calculated)		
	(solution)	(observed)	(i) Born	(ii) Gans	(iii) Boys
C_6H_6	1.4992	32.9°	33.4°	32.4°	32.9°
$C_6H_5CO.Me$	1.5310	33.2	34.8	33.1	34.0
C_6H_5CHO	1.5431	33.2	35.6	33.4	34.4
C_6H_5Me	1.4930	33.7	33.1	32.2	32.6
C_6H_5O Me	1.5141	34.5	34.0	32.7	33.3
C_6H_5Cl	1.5229	34.7	34.5	32.9	33.6
o-$C_6H_4Cl_2$	1.5466	34.7	35.7	33.5	34.6
C_6H_5Br	1.5580	35.1	36.5	33.8	35.0
$CH\ Br_2.CH\ Br_2$	1.6303	35.3	39.9	35.3	38.0
C_6H_5I	1.6162	35.6	39.4	35.1	37.4
$C_6H_5NH_2$	1.5842	36.4	37.8	34.4	36.1
CH_2I_2	1.7341	36.6	46.0	38.0	42.7
CS_2	1.6246	38.7	39.6	35.2	38.0

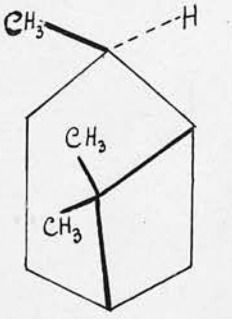
The first point to note is that each of the three formulae yields values for the rotatory powers of pinane in solution which are in comparatively close agreement with those experimentally determined. Further the values of [M] obtained by the use of Boys' formula are intermediate in magnitude between those obtained by using the formulae of Gans and Born respectively. For non-polar solvents whose refractive indices are less than that of homogeneous pinane, it appears that the values of the rotation calculated by using Born's formula agree most closely with the observed values. These solvents are hexane and pentane, in which it would be expected that association, due to slight polarity or van der Waal's forces, would be at a minimum. The polar solvents give rotations lower than the calculated values, and since this is found to occur in all polar solutions of high and low refractive indices it is convenient here to suggest a reason for this displacement.

A saturated hydrocarbon is certainly completely non-polar in so far as its behaviour in a uniform electric field is concerned, owing to the fact that the weak polarities of the carbon to hydrogen links cancel out. The dipole moment of each **CH** link has been estimated to be of the order 0.2×10^{-18} e.s.u. and is therefore in any case extremely small. Nevertheless it is not unreasonable to assume that a molecule/

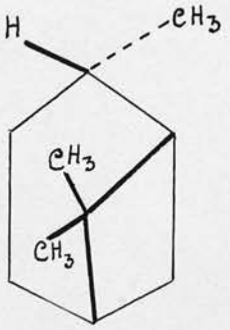
molecule of a saturated hydrocarbon may behave as a very weakly polar substance towards a point charge in its immediate neighbourhood and hence also to an adjacent strongly polar molecule e.g.



In many cases the comparatively symmetrical structure of the hydrocarbon would merely present a large number of alternative dipoles through which a feeble attraction towards a strongly polar solvent molecule might be exerted and the total effect of such changes on the internal field would sum up to zero. In special cases, however, extreme structural irregularity may favour certain points through which such effects may be propagated, with the result that in the summation these effects no longer nullify one another and thus produce a real change in the internal field. If this is possible, very weak polar influences of such a nature are to be expected with pinane, the spatial disposition of which is highly irregular. This may



cis- isomer



trans- isomer

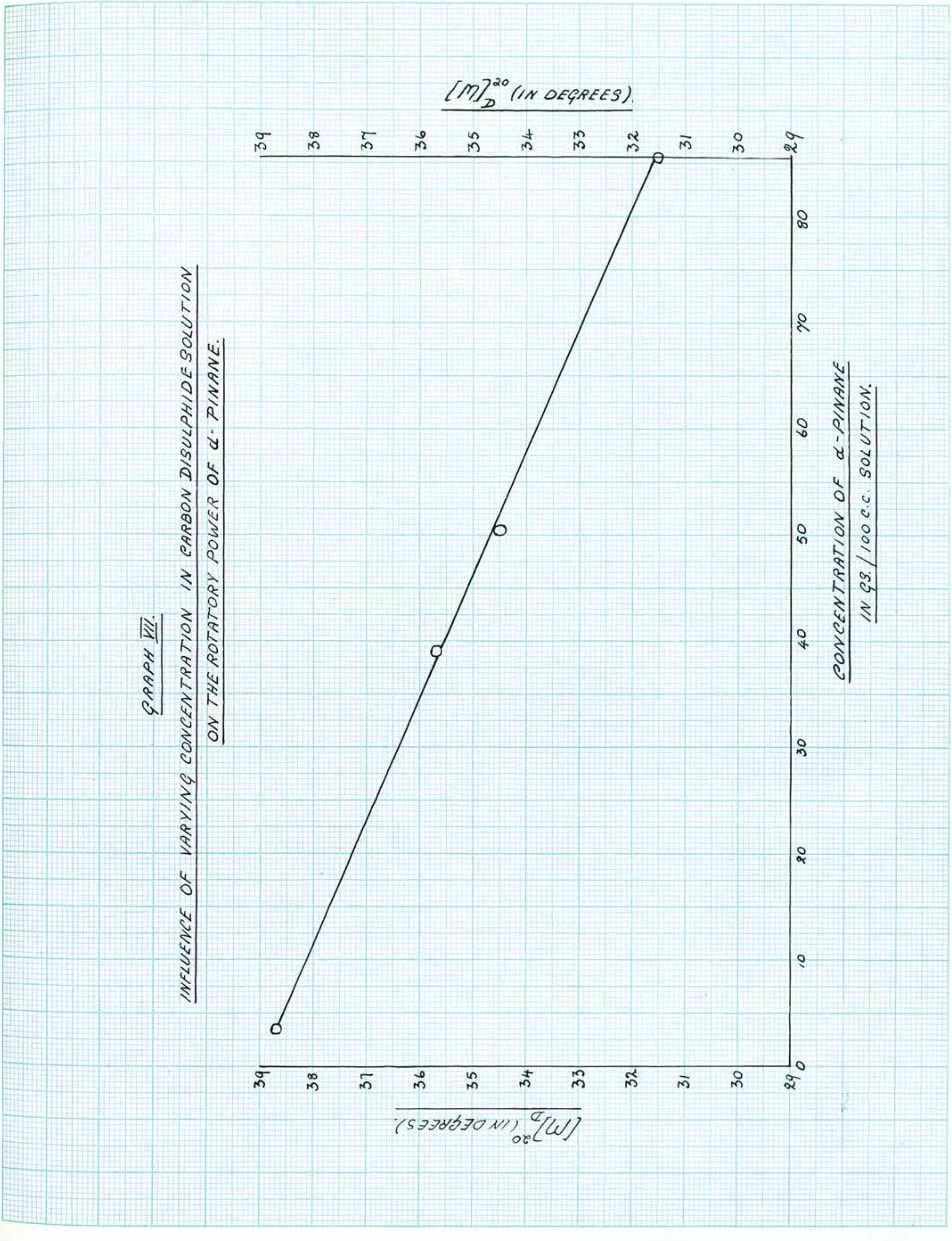
explain to some extent the minor displacements noted in the case of the polar solvents. It will be seen from the formulae that pinane can exist in cis- or trans- forms and there is no indisputable evidence as to which structural isomer we are dealing with in this case.

Non-polar solvents with refractivities greater than that of the homogeneous liquid, e.g. carbon tetrachloride, mesitylene, benzene, toluene and carbon disulphide, produce experimental values of the rotatory power less than those calculated from Born's formula and in better agreement with those calculated according to Boys' formula. The solution given by the highly refractive non-polar solvent carbon disulphide has an observed rotation in fairly good agreement with that calculated from Boys' formula.

On the whole the values obtained from the formulae of Boys and Born correspond better with the observed values than those calculated according to Gans. In the last case the rotation is a function of n^2 whereas in the first two cases it is a function of n^4. The presence of the minor polar effect, acting in the opposite direction to the refractive index, i.e. increased polarity of solvent decreasing the rotation, is readily seen from this table.

It should be noted that the constants occurring in/

GRAPH VII.



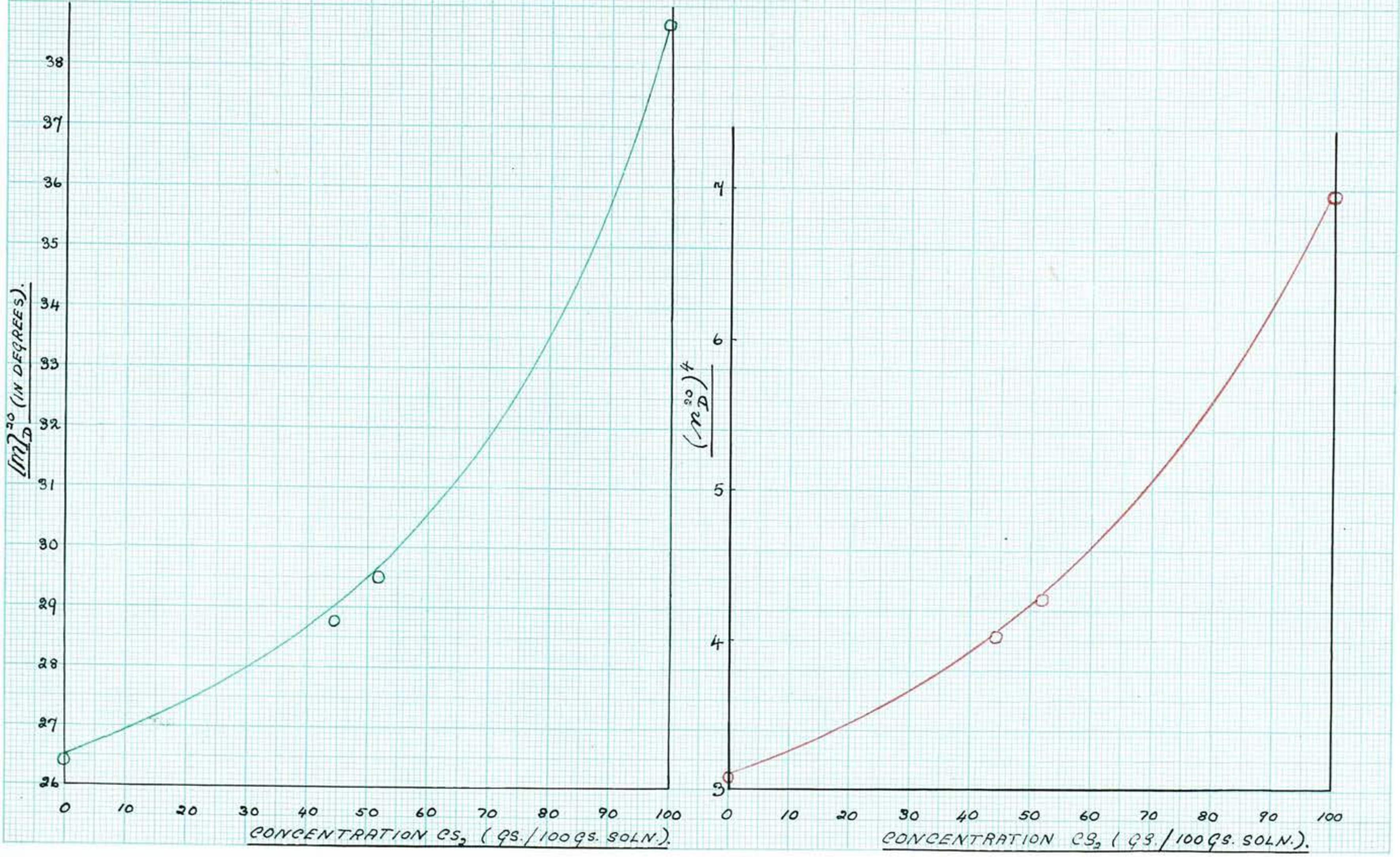
GRAPH VII.

INFLUENCE OF VARYING CONCENTRATION IN CARBON DISULPHIDE SOLUTION ON THE ROTATORY POWER OF α-PINANE.

in the above formulae are calculated on the assumption that in homogeneous pinane the molecules are completely non-associated. This may not be the case, for even although the polar forces are extremely small, non-polar association, due to van der Waal's forces, may be present. In all probability however, any error introduced into the calculation by not taking account of this association, will be very small. If such association were present one would expect some slight irregularity to be shown in the concentration-rotation curve for pinane in a non-polar solvent. This was found not to be the case when the rotatory powers of d- pinane in carbon disulphide solution were examined. The graph obtained is shown in figure VII. It is seen that a linear variation of rotatory power with concentration occurs and this relationship can be explained solely from the point of view of the refractive index effect, since for two non-polar liquids the refractive index of the mixture is an additive property.

The rotations of d-pinane were also determined in various mixtures of methyl alcohol and carbon disulphide, two solvents of low and high refractive indices respectively. The concentration of the optically active compound in each mixture was about 3.5. The curve obtained is shown in graph VIII (a) and/

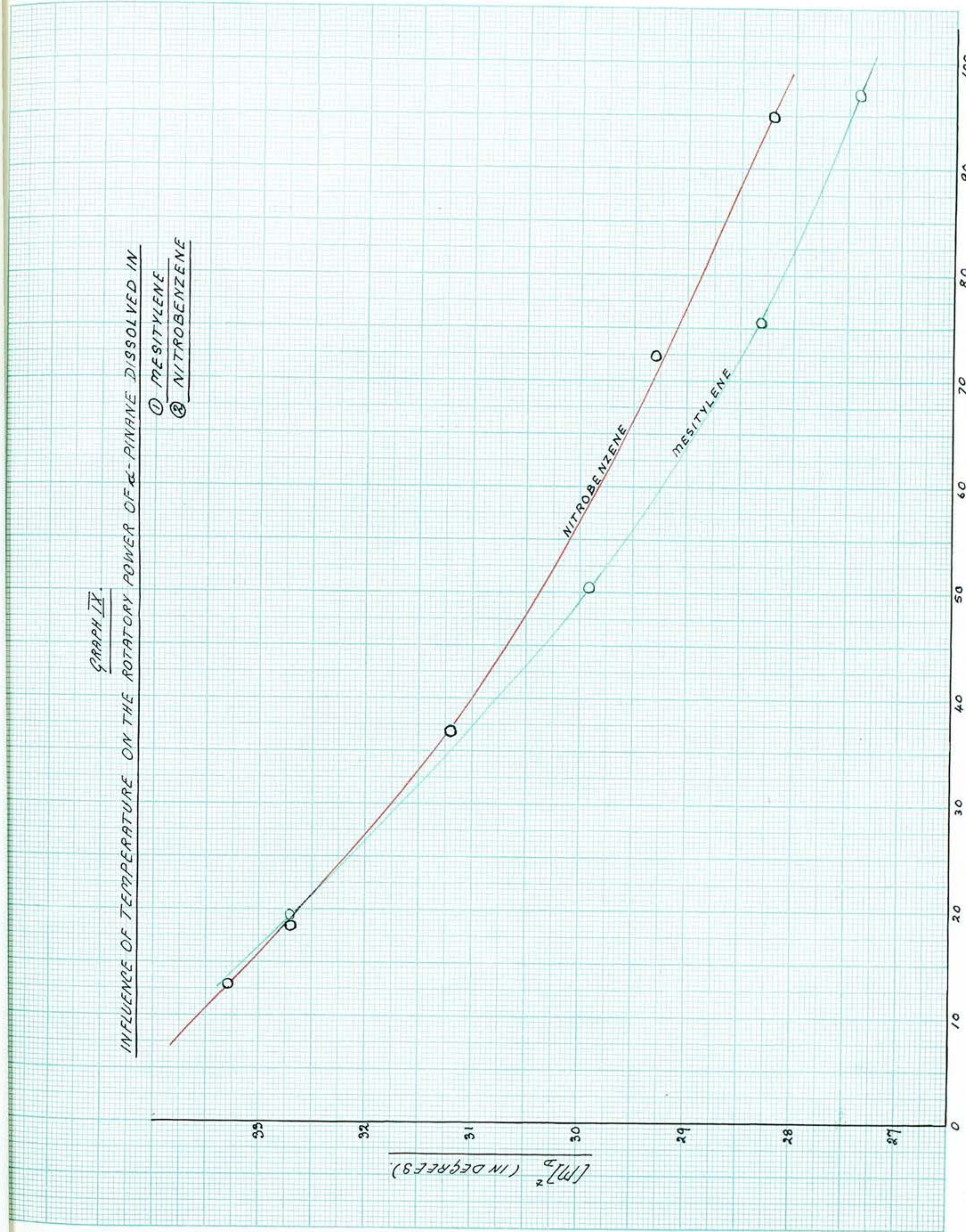
GRAPH VIII



(a)
ROTATORY POWERS OF d-PINANE DISSOLVED (C = 3·5) IN VARYING MIXTURES OF CS_2 AND MeOH

(b)
CURVE OBTAINED BY PLOTTING $(n_D^{20})^4$ OF MIXTURES OF d-PINANE, MeOH AND CS_2 AGAINST CONCENTRATION OF CS_2.

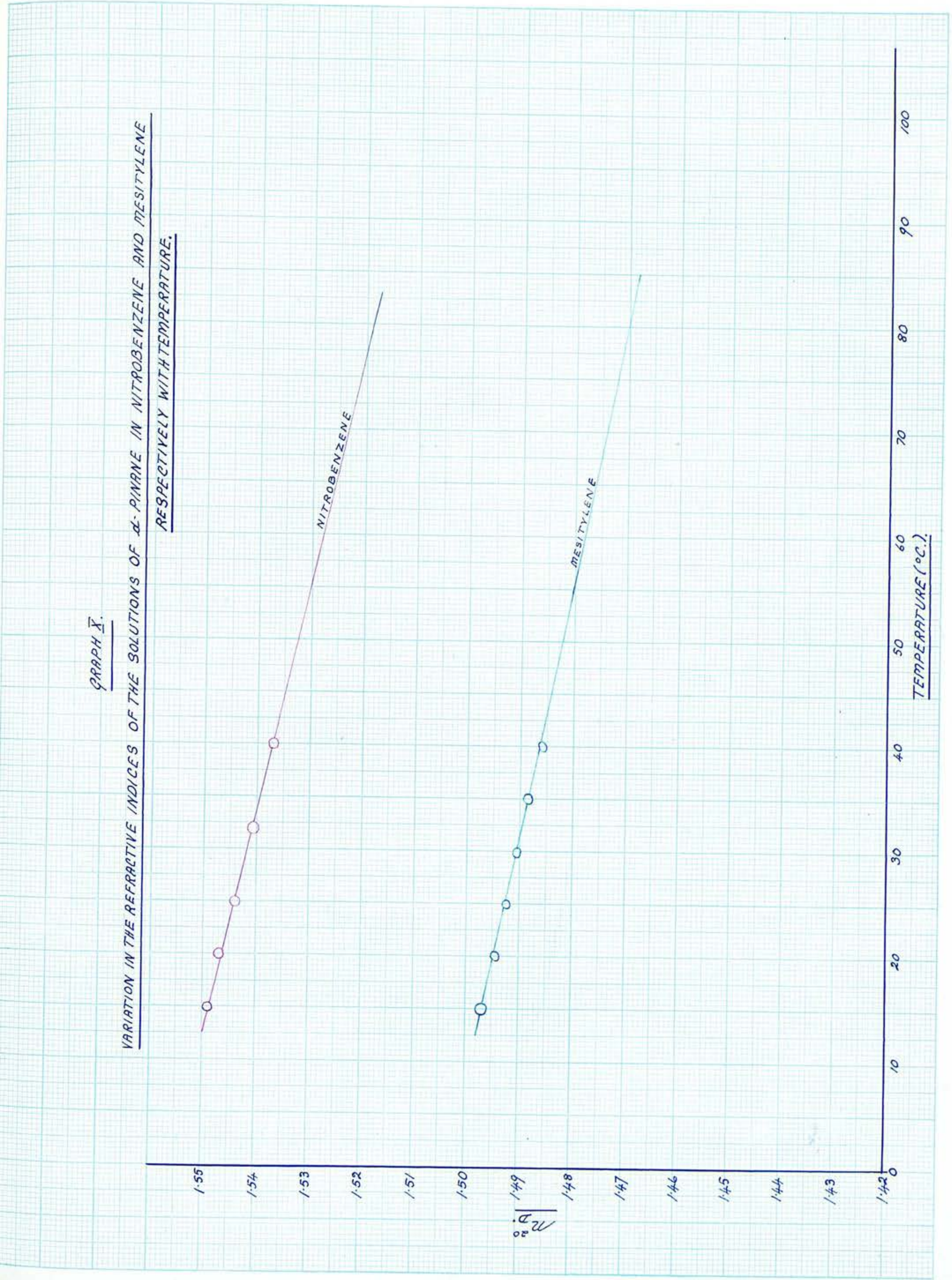
GRAPH IX.


GRAPH IX.
INFLUENCE OF TEMPERATURE ON THE ROTATORY POWER OF α-PINANE DISSOLVED IN
① MESITYLENE
② NITROBENZENE
NITROBENZENE
MESITYLENE
TEMPERATURE (°C.)
0
10
20
30
40
50
60
70
80
90
100
$[M]_D^t$ (IN DEGREES)
33
32
31
30
29
28
27

and it will be noted that the rotatory powers decrease uniformly as the concentration of carbon disulphide decreases, i.e. as the refractive index of the mixture decreases. For comparison, the curve obtained by plotting the fourth power of the refractive indices of the solutions against concentration of carbon disulphide in the solvent medium is given in Graph VIII (b). The curve obtained is of the same type as that shown in Graph VIII (a). In this case one of the solvent components, methyl alcohol, is a polar compound and the graphs are represented by smooth curves instead of the straight line found for carbon disulphide and pinane mixtures.

The variations of the rotatory powers of solutions of d-pinane in nitrobenzene and mesitylene respectively with temperature also support the ideas put forward. The curves obtained are shown in graph IX. They may be explained by supposing that at low temperatures, the polar effect exerts an appreciable if small influence in nitrobenzene solution, depressing the rotatory power so that it is slightly less than that found for a solution in mesitylene, a solvent of zero dipole and lower refractive index.
As the temperature is raised however, the association complexes in the nitrobenzene solution are broken up and the refractive index of the solution becomes the main influence governing the rotatory power. Hence at/

GRAPH X.



GRAPH X.

VARIATION IN THE REFRACTIVE INDICES OF THE SOLUTIONS OF α-PINANE IN NITROBENZENE AND MESITYLENE RESPECTIVELY WITH TEMPERATURE.

at higher temperatures the predominant influence in both solutions becomes the refractive index of the medium, the rotation in nitrobenzene solution thus being greater than that in mesitylene solution. An examination of the variations of the refractive indices of these two solutions with temperature shows that linear relationships are obtained in both cases, the straight lines obtained being practically parallel. This is shown in Graph X.

d- Carane

It was thought worth while to extend this investigation to another saturated hydrocarbon of the terpene series, d- carane. This was prepared (see preparative section of this thesis p.98) by distilling the hydrazone of pulegone over solid potassium hydroxide. The resulting hydrocarbon gave a high rotation ($[\alpha]_D > +50^\circ$) but as is pointed out in the experimental section of this table was not stable to alkaline permanganate. This may be explained as the normal behaviour of a compound containing a three membered carbon ring, but since the mechanism of the preparation is somewhat obscure the possibility of the presence of a considerable proportion of unsaturated hydrocarbon in the product could not be discounted. The magnitude of the molecular/

molecular refractivity of a hydrocarbon often indicates whether or not it contains an unsaturated linkage or a ring of carbon atoms. With this idea in mind, the molecular refractivities of d- pinane, d- carane and dihydroterpinolene (p - Δ (4:8) - menthene) were calculated, the first two from experimentally determined values of n_D^{20} and d_4^{20} and the latter from values in a paper by Semmler (Ber., 1914, <u>47</u>, 386). These values are tabulated below (Table IX).

TABLE IX.

Compound	n_D^{20}	d_4^{20}	Molecular Refractivity $= \frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$
d- Pinane	1.4630	.8560	44.39
d- Carane	1.4590	.8408	44.84
Dihydro-terpinolene	1.4582	.8189	46.60

These values of the molecular refractivity provide no evidence against the view that the substance under examination is the saturated compound carane. There is however no simple chemical method of differentiating between any unsaturated products which may be present and carane. The main product of the above reaction is certainly not dihydroterpinolene since this hydrocarbon is optically inactive.

The/

The rotatory power of the above product was examined therefore in the aliphatic and aromatic series of solvents. The results with the aliphatic series are given below in table X, in which the concentration varies from 3.506 in hexane to 3.668 in nitromethane. A value of benzene is also included in the table since the sample of carane (?) used for the aromatic solvents had a somewhat higher rotatory power.

TABLE X.

Influence of Solvents on Rotatory Power of d- Carane.

Solvent	α^{20}_{5893}	$[M]^{20}_{5893}$	$\mu \times 10^{18}$ e.s.u.	n^{20}_{D} (solution)
CS_2	3.71°	71.8°	0	1.6240
$CHCl_3$	3.93	74.5	1.18	1.4490
$CH_3.CHO$	3.82	74.9	2.68	1.3905
CH_3NO_2	4.04	76.0	3.03	1.3855
CH_3CN	3.89	76.3	3.16	1.3502
CCl_4	3.89	76.4	0	1.4622
(homogeneous)	23.34	76.90	0 (?)	1.4590
$(CH_3)_2CO$	3.94	76.9	2.76	1.3651
CH_3OH	4.00	77.1	1.66	1.3603
C_6H_{14}	3.92	77.2	0	1.3835
CH_2Cl_2	4.03	79.0	1.55	1.4277
CH_3I	4.16	80.4	1.08	1.5286
C_6H_6	3.69	72.4	0	1.5003

The/

The order of these solvents shows little agreement either with dipole moment or refractive index. Carbon disulphide - a solvent of zero dipole and high refractive index - lowers the rotation, whereas methyl iodide raises the rotation. The maximum range of the rotatory power is small being only 8.6° for the molecular rotation.

The series obtained for the aromatic solvents is given below in table XI. Here the concentration varies from 3.407 in the case of nitrobenzene to 3.612 in the case of acetophenone. The sample of carane employed here had a slightly higher rotation than that used in the case of the aliphatic solvents.

TABLE XI./

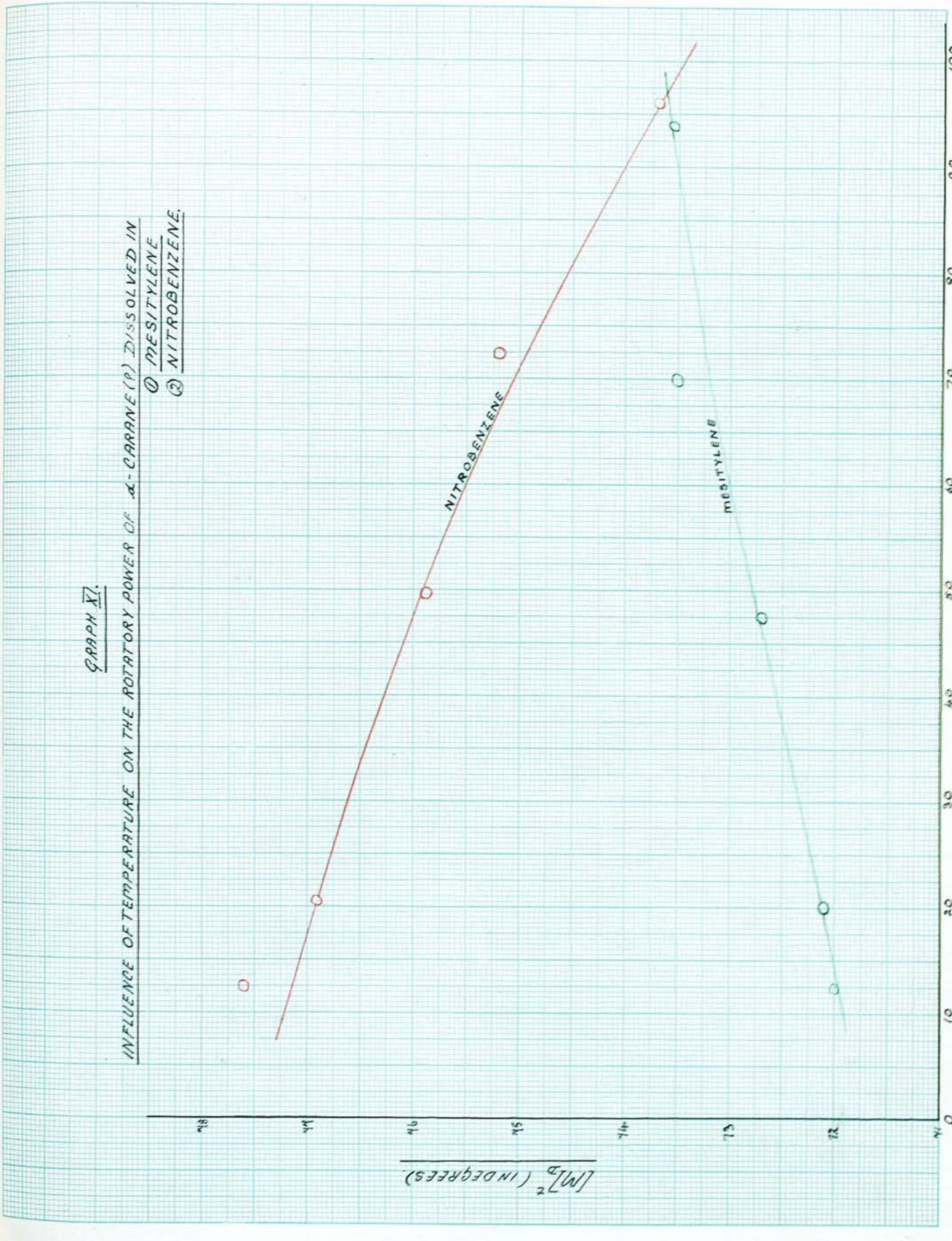
TABLE XI.

Influence of Solvents on Rotatory Power of d- Carane.

Solvent	α_{5893}^{20}	$[M]_{5893}^{20}$	$\mu \times 10^{18}$ e.s.u.	n_D^{20} (solution)
C_6H_5I	3.75°	72.4°	1.30	1.6190
s-$C_6H_3Me_3$	3.72	72.4	0	1.4971
C_6H_5O Me	3.83	73.4	1.23	1.5158
o-$C_6H_4Cl_2$	3.82	73.5	2.33	1.5458
$C_6H_5CO.Me$	3.85	73.6	2.89	1.5326
C_6H_5CN	3.78	74.2	3.94	1.5273
$C_6H_5NH_2$	3.80	74.8	1.60	1.5823
C_6H_5Br	3.78	74.8	1.56	1.5577
C_6H_5Cl	3.90	74.9	1.52	1.5244
C_6H_6	3.90	75.8	0	1.5023
$C_6H_5CH_3$	4.04	76.7	0.37	1.4990
$C_6H_5NO_2$	3.80	77.0	3.94	1.5599
(homogeneous)	24.40	80.10	0 (?)	1.4590
CS_2	3.68	75.9	0	1.6239
CH_3I	4.32	83.7	1.08	1.5286

As in the case of the aliphatic media the effect of aromatic solvents on the rotatory power of d-carane is irregular. The lowest rotation is given in the solvent of highest refractive index, iodobenzene (cf. carbon disulphide), which suggests that a high refractive index tends to lead to a lowered rotation. (similar to the case of pinene, Table VI p. 44). It would appear that the polar effect tends to act in the opposite direction, i.e. a solvent of high polarity increases the rotation. This conclusion is uncertain but is supported to some extent by the temperature-rotation curves for mesitylene and nitrobenzene solutions, respectively, which are shown in graph ~~IX~~ XI. The similarity to the corresponding curves obtained in the case of pinene is striking (see graph VI ~~facing~~ p. 45(a)). At low temperatures, it appears that the high rotation of d- carane in nitrobenzene solution is due to the fact that the polarity effect is the predominating influence. As the temperature rises, however, the increased thermal agitation decreases the orientation of the solvent and solute molecules towards each other and hence the polar influence is weakened. The refractive index of the medium then assumes the more important role and hence the rotation in nitrobenzene tends to be lower than that given in mesitylene at the same temperature, on the assumption that the higher the refractive index the/

GRAPH XI.

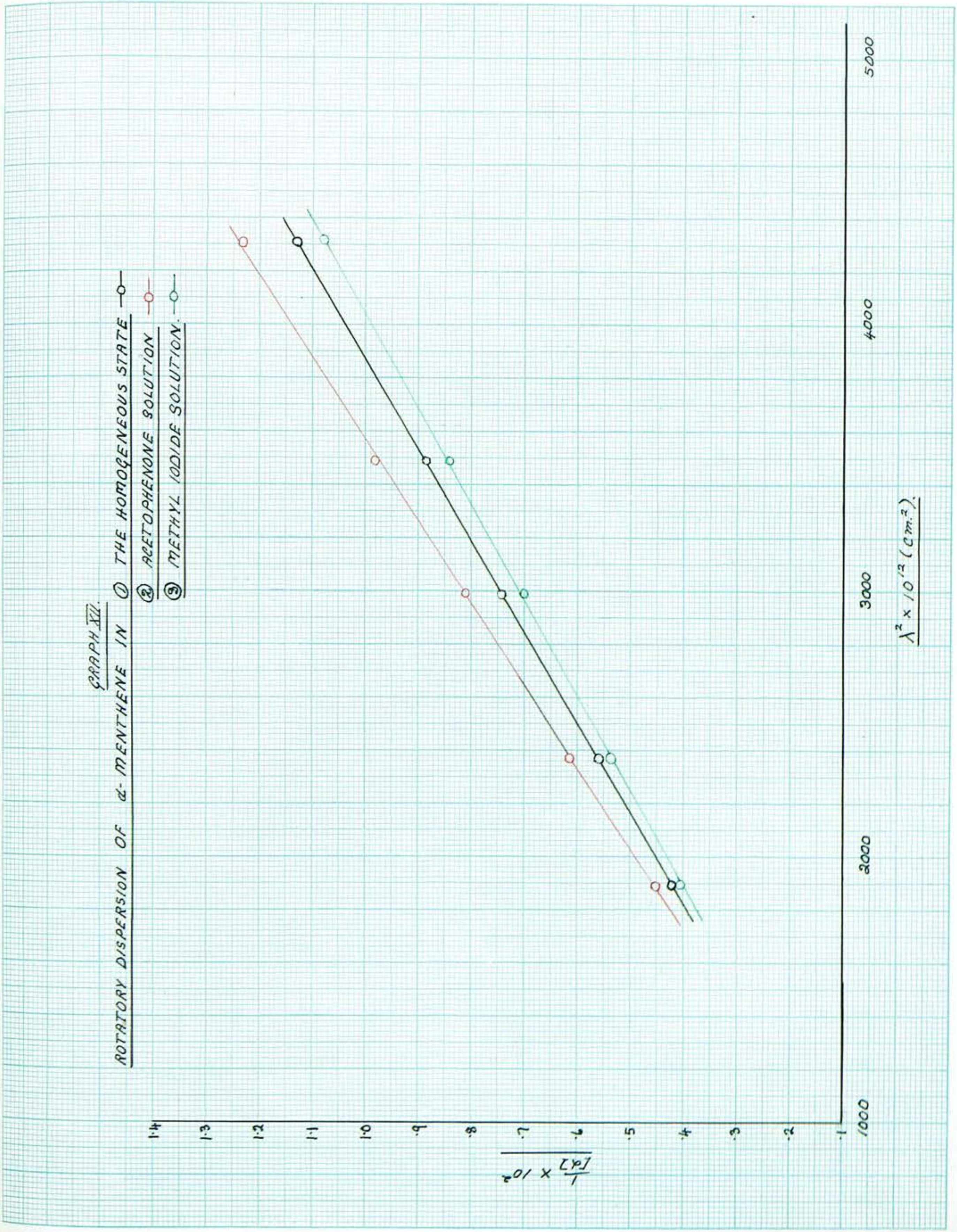

GRAPH XI.
INFLUENCE OF TEMPERATURE ON THE ROTATORY POWER OF α-CARANE(?) DISSOLVED IN
① MESITYLENE
② NITROBENZENE.
NITROBENZENE
MESITYLENE
TEMPERATURE (°C.)
0
10
20
30
40
50
60
70
80
90
100
$[M]_D^t$ (IN DEGREES).
71
72
73
74
75
76
77
78

the lower the rotation. Actual cutting of the two curves would appear to take place at 100°. The rise in rotation with rise in temperature of the mesitylene solution also suggests that the refractive index is the chief effect in this case throughout, decreasing refractive index raising the rotation.

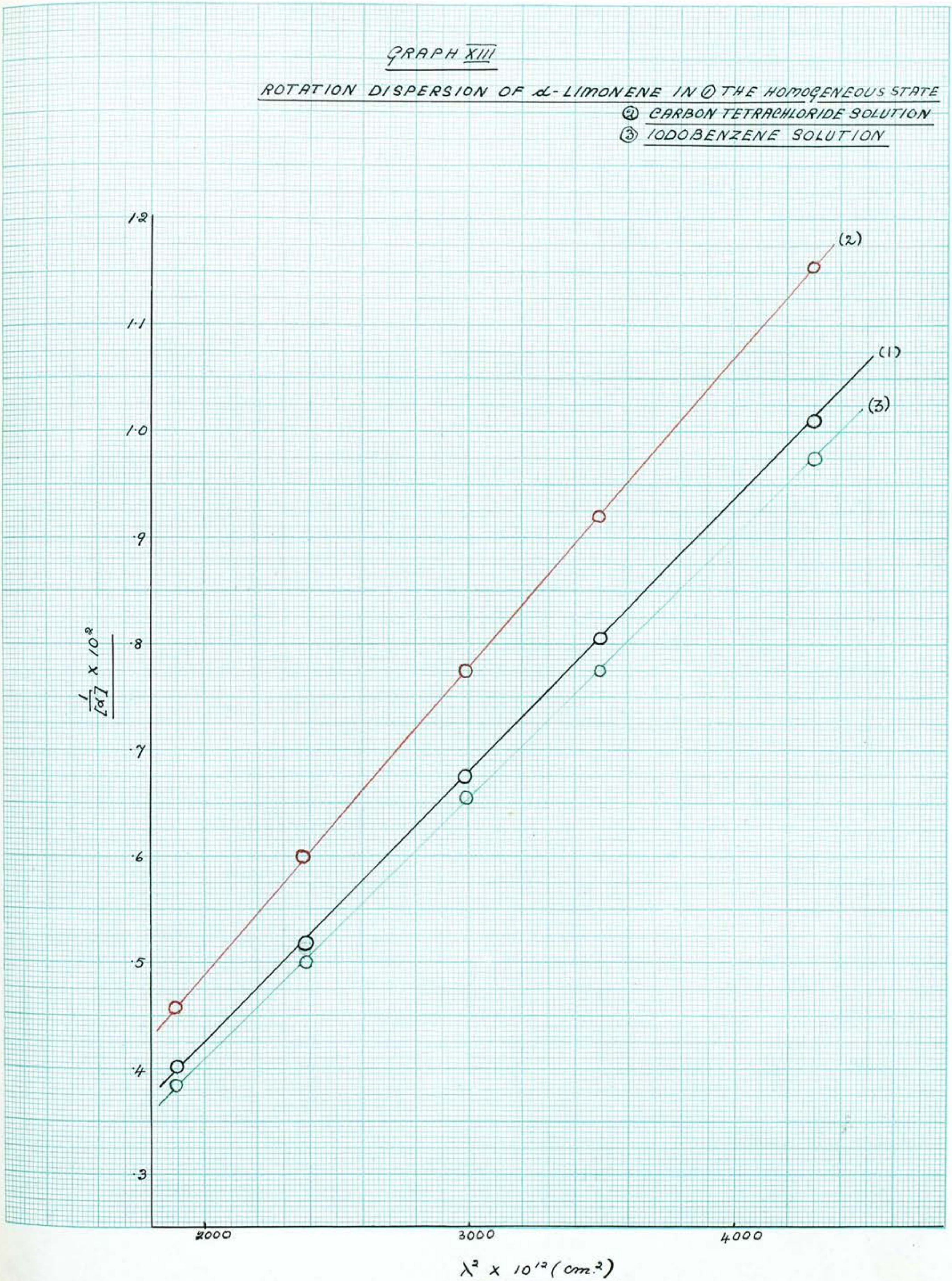
It should be noted that in the purification of pinane and carane, the use of alkaline permanganate to remove the last traces of unsaturated hydrocarbon was not altogether satisfactory. Kishner (Chem. Abstracts., 1913, 104, 153) points out that as the concentration of an unsaturated hydrocarbon in a mixture diminishes, its rate of oxidation decreases, until finally it may become less than that at which the saturated compound oxidises. In the case of pinane the optical rotation agreed with the value previously recorded for the spectroscopically pure saturated hydrocarbon, although Lowry, who has examined the absorption spectrum of a sample of the same product used in this thesis, noted that general absorption began somewhat earlier in the ultra-violet region than would be expected, suggesting that a trace of pinene may have been present. (Lowry, Private communication.). This impurity if actually present, however, appeared to have no effect on the rotatory power in the visible region, nor could any of the displaced rotations be explained on this basis. Judging/

Judging from the rotatory power of the product, the amount of pinene present could not have exceeded 0.05%. In the case of carane it is not improbable that the rate of oxidation of this substance may be of the same order as the rate of oxidation of any unsaturated hydrocarbons present, and it is certain that the removal of the latter is incomplete.

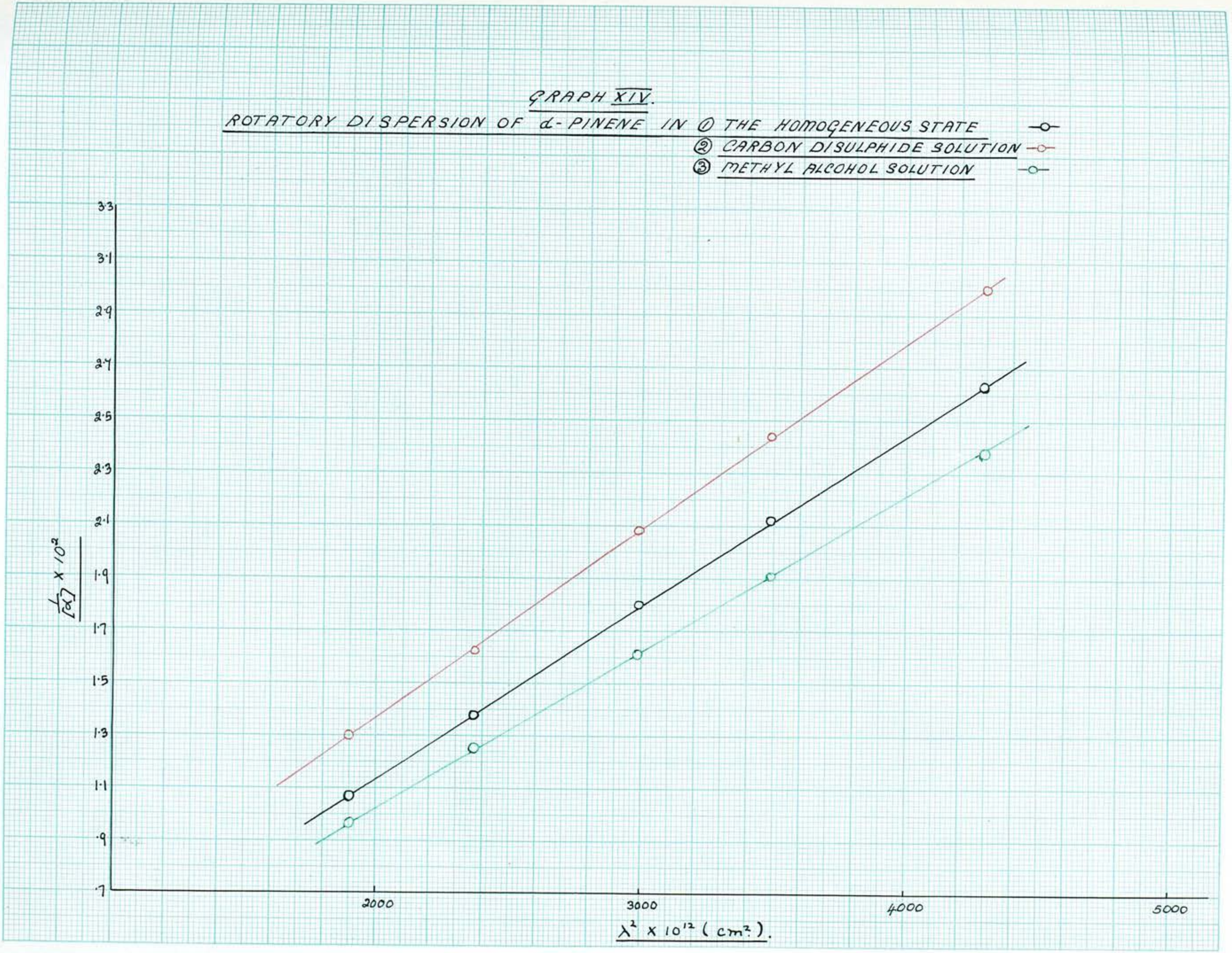
GRAPH XII.


GRAPH XII.
ROTATORY DISPERSION OF α- MENTHENE IN ① THE HOMOGENEOUS STATE
② ACETOPHENONE SOLUTION
③ METHYL IODIDE SOLUTION.
1·4
1·3
1·2
1·1
1·0
·9
·8
·7
·6
·5
·4
·3
·2
·1
$\frac{1}{[\alpha]} \times 10^2$
1000
2000
3000
4000
5000
$\lambda^2 \times 10^{12}$ (cm.^{2}).

GRAPH XIII.


GRAPH XIII
ROTATION DISPERSION OF d-LIMONENE IN ① THE HOMOGENEOUS STATE
② CARBON TETRACHLORIDE SOLUTION
③ IODOBENZENE SOLUTION
1·2
1·1
1·0
·9
·8
·7
·6
·5
·4
·3
1/[α] x 10²
(2)
(1)
(3)
2000
3000
4000
λ² x 10¹² (cm.²)

GRAPH XIV.



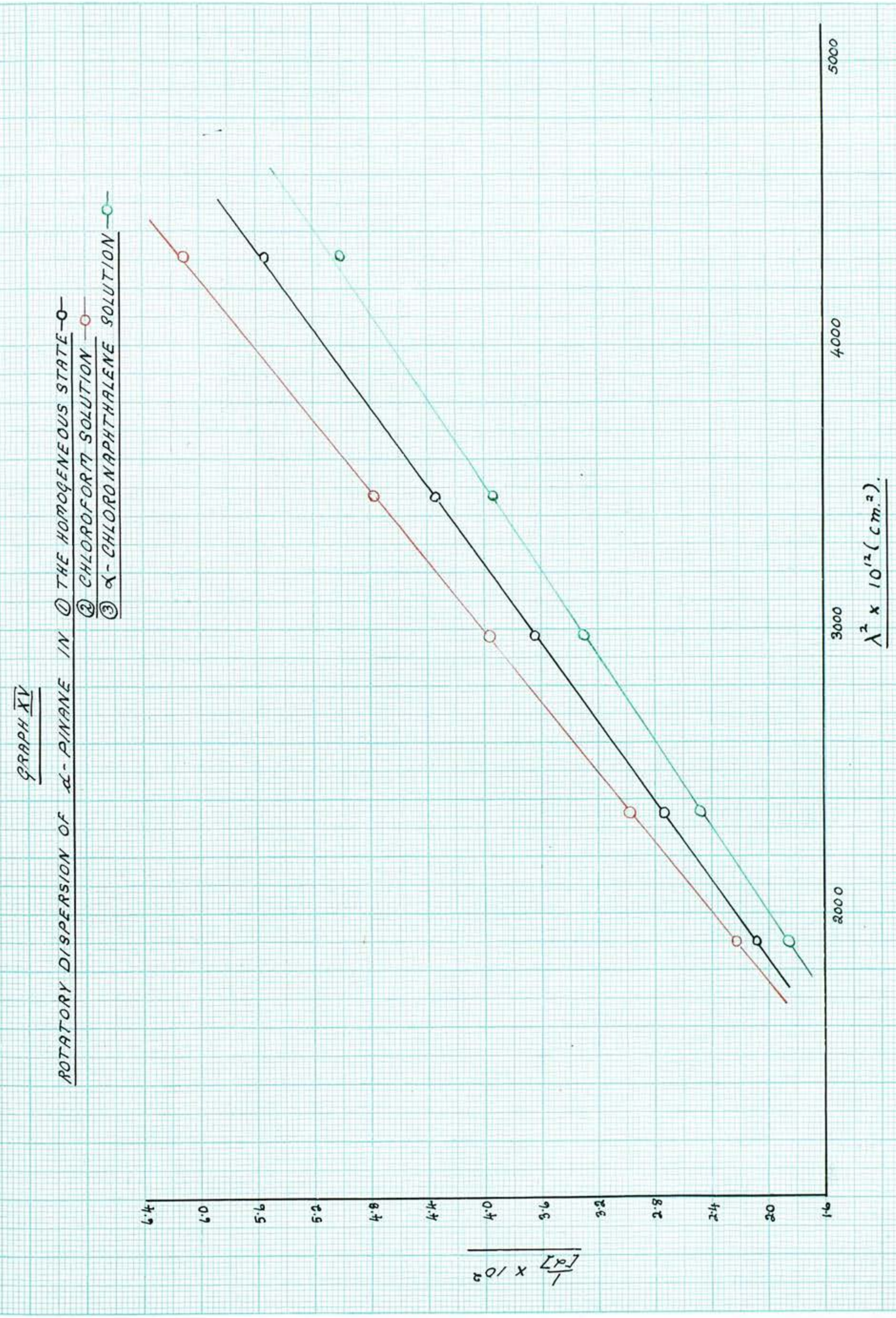
GRAPH XIV.

ROTATORY DISPERSION OF d-PINENE IN ① THE HOMOGENEOUS STATE

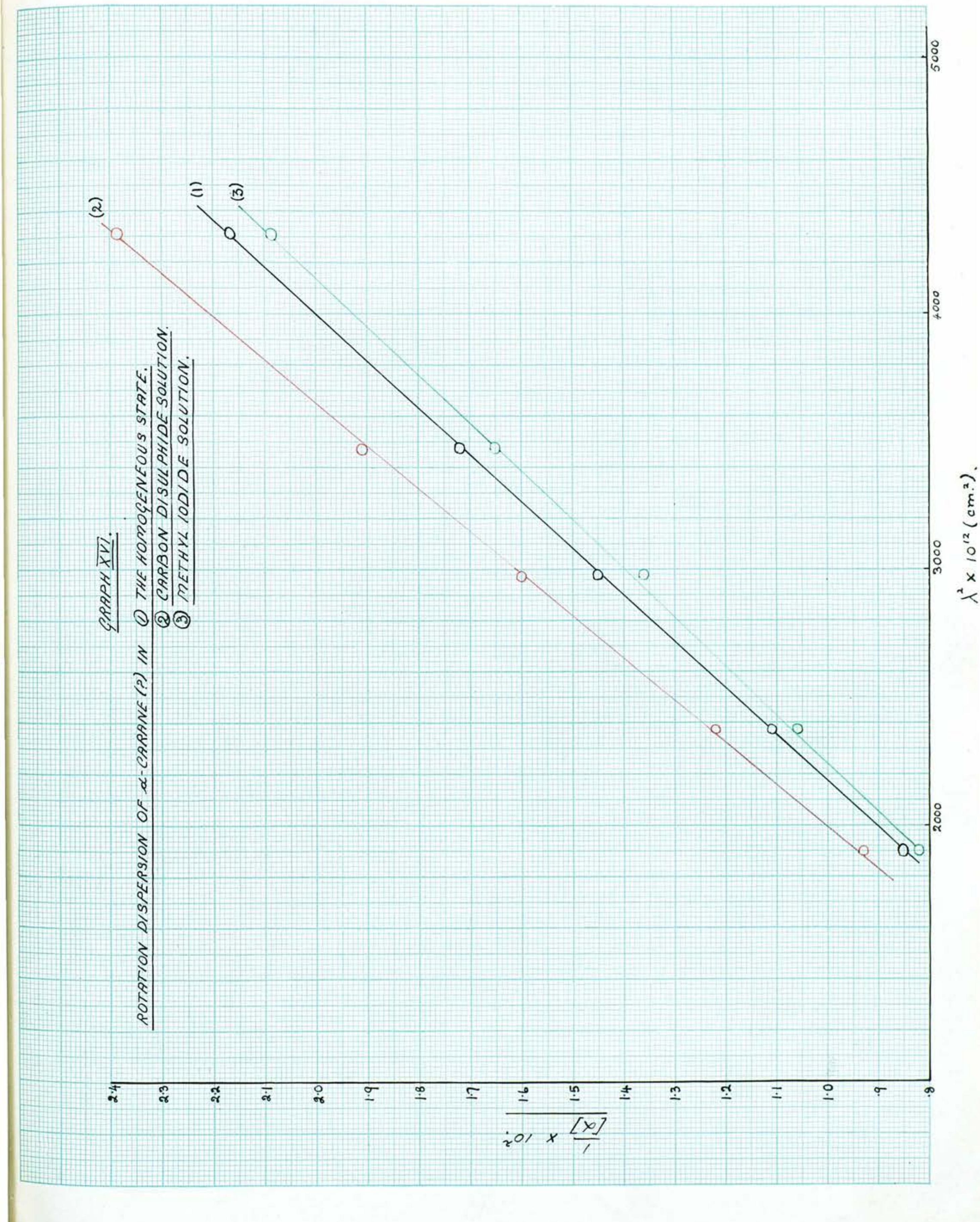
② CARBON DISULPHIDE SOLUTION

③ METHYL ALCOHOL SOLUTION

GRAPH XV.

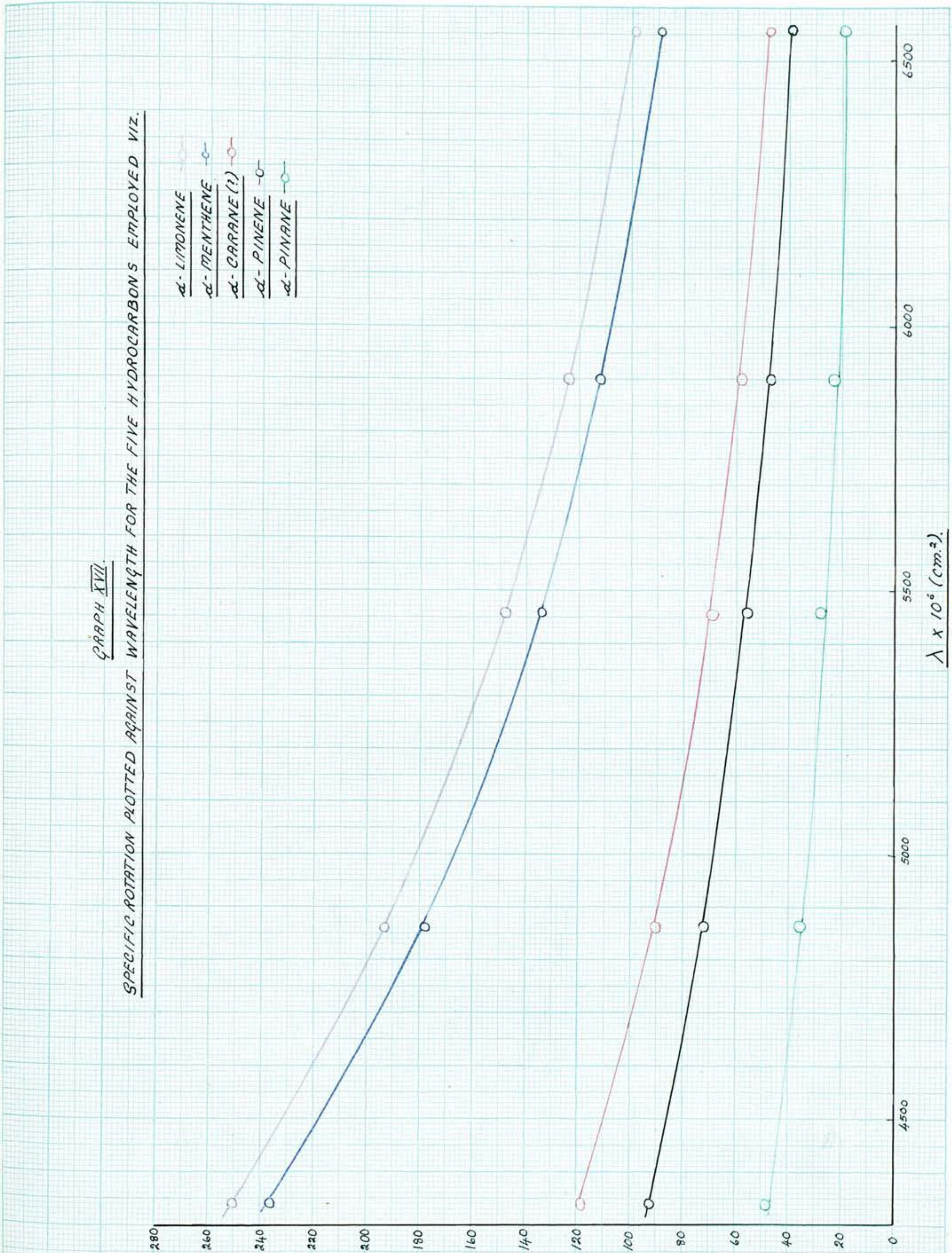

GRAPH XV
ROTATORY DISPERSION OF α-PINANE IN ① THE HOMOGENEOUS STATE
② CHLOROFORM SOLUTION
③ α-CHLORONAPHTHALENE SOLUTION
$\frac{1}{[\alpha]} \times 10^2$
6·4
6·0
5·6
5·2
4·8
4·4
4·0
3·6
3·2
2·8
2·4
2·0
1·6
2000
3000
4000
5000
$\lambda^2 \times 10^{12}$ (cm.²)

GRAPH XVI.



GRAPH XVI.

ROTATION DISPERSION OF α-CARANE (?) IN ① THE HOMOGENEOUS STATE.
② CARBON DISULPHIDE SOLUTION.
③ METHYL IODIDE SOLUTION.


GRAPH XVII.
SPECIFIC ROTATION PLOTTED AGAINST WAVELENGTH FOR THE FIVE HYDROCARBONS EMPLOYED VIZ.
d- LIMONENE
d- MENTHENE
d- CARANE (?)
d- PINENE
d- PINANE
λ x 10⁶ (cm.²).
4500
5000
5500
6000
6500
[α]²⁰ Dλ (IN DEGREES.)
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0

Rotation Dispersion of the Above Hydrocarbons in the Visible Region.

All the hydrocarbons examined above showed simple and normal dispersion, i.e., the plot of $\frac{1}{[\alpha]^{20}_{\lambda}}$ against λ^2 gave straight line relationships in all cases. Very small variations occurred in the linearity of the rotation-dispersion curves of the solutions but, in all instances, they were within the limits of the experimental error. The curves obtained for the one substance in different solvents were not parallel but tended to converge at the violet end.

The types of relationship obtained for the above hydrocarbons are exemplified in graphs XII to XVI which show the curves for the homogeneous liquids and for solutions in two solvents which respectively, raise and lower the rotatory power of the given hydrocarbon. The curves obtained by plotting $[\alpha]^{20}_{\lambda}$ against λ for these five hydrocarbons are given in graph XVII in order to compare their rotatory dispersions.

The most interesting of the above cases is the rotatory dispersion of pinane (graph XV). Lowry has examined a sample of this hydrocarbon with respect to its rotation-dispersion in the visible and ultraviolet portions of the spectrum and he has found that the rotation rises somewhat steeply in the latter region (Lowry, Private communication). Darmois had previously/

previously obtained a similar type of rotation - dispersion curve for this hydrocarbon prepared by the same method (Darmois, Ann. chim. phys., 1911, 22, 281).

No examination of the physical theories of rotatory power given above was attempted as regards their application to the rotation-dispersion of d- pinane. In the case of Boys' theory a knowledge of the refractivity factor (see p. 57) would be necessary for a thorough investigation as to its validity from this point of view. This factor can not be readily calculated in this case owing to the complex structure of the hydrocarbon involved.

EXPERIMENTAL SECTION.

PURIFICATION OF SOLVENTS.

All solvents used were specially purified, the methods adopted for purification being briefly described below:-

(1) Acetic acid. Kahlbaum's 100% acetic acid was cooled until about two-thirds frozen; the liquid portion was decanted off and the crystalline mass fractionated. M.p. 16°. B.p. 118-118.2°.

(2) Acetone. B.D.H. "bisulphite purified" acetone was dried over anhydrous calcium chloride and fractionated. B.p. 55-56°.

(3) Acetonitrile. B.D.H. acetonitrile was dried over calcium chloride and fractionated, giving a colourless product. B.p. 81°.

(4) Acetophenone. B.D.H. acetophenone was partially crystallised and the crystalline portion filtered off, dried and fractionated. M.p. 20°. B.p. 201.8 - 201.9°.

(5) Aniline. B.D.H. "from sulphate" (A.R.) was dried and fractionated giving a colourless liquid boiling at 182.9-183°.

(6) Anisole. B.D.H. anisole was boiled under reflux for three hours with sodium. It was then separated, washed with water, dried and fractionated. It was colourless and free from phenol. B.p. 153.8°.

(7) Acetaldehyde. B.D.H. acetaldehyde was dried over calcium chloride, boiled over succinic acid to remove basic impurities and fractionated. B.p. 20.8°.

(8) Benzaldehyde. B.D.H. benzaldehyde was washed with Na_2CO_3 solution, dried and fractionated care being taken to expose to the air as little as possible. B.p. 179-179.2°. It was preferable to distil the aldehyde immediately before use.

(9) Benzene. B.D.H. "extra pure" benzene was partially frozen out and the solid mass dried and fractionated. M.p.5.5°. B.p. 80-80.1°.

(10) Benzonitrile. B.D.H. product was dried and partially frozen out; the crystalline portion was fractionated under reduced pressure. It was obtained as a colourless liquid of M.p. -12.9° and B.p. 82.5°/ 15 mm.

(11) Bromobenzene. B.D.H. product was well washed with sodium carbonate solution and water, dried over anhyd. calcium chloride and fractionated. B.p. 154.8 - 155.2°

(12) α- Bromonaphthalene. B.D.H. product was washed, dried and fractionated under reduced pressure. B.p. 171.5 - 172°/15 mm.

(13) Carbon Disulphide. B.D.H. carbon disulphide (A.R.) was shaken with mercury to remove sulphur, dried over calcium chloride and repeatedly fractionated. B.p. 46 - 46.2°.

(14)/

(14) Carbon Tetrachloride. The sample used had already been carefully purified. It was dried and fractionated. B.p. 77.6 - 77.8°.

(15) Chlorobenzene. B.D.H. chlorobenzene was washed with sodium carbonate and water, dried over anhydrous calcium chloride and fractionated. B.p. 131.6 - 132°.

(16) Chloroform. Macfarlane and Co.'s chloroform (B.P.) was shaken with concentrated sulphuric acid for ¼ hour to remove alcohol. It was then washed with sodium hydroxide solution and water, dried over anhydrous potassium carbonate and fractionated. B.p. 60.7 - 60.9°.

(17) α- Chloronaphthalene. B.D.H. α - chloronaphthalene was treated same way as the corresponding bromide. B.p. 124 - 125°/11 mm.

(18) Cyclohexane. The B.D.H. product ("spectroscopically pure") was dried and fractionated. B.p. 80.1 - 80.3°.

(19) o - Dichlorobenzene. The B.D.H. product was cooled to - 20° to freeze out traces of p- dichlorobenzene. It was then washed with water, dried over anhydrous calcium chloride and fractionated. B.p. 60 - 61°/11 mm.

(20) Hexane. B.D.H. hexane "for spectroscopy" dried and fractionated. B.p. 67 - 68.5°

(21) Iodobenzene. The B.D.H. product was washed with sodium carbonate solution and water, dried over calcium chloride and fractionated under reduced pressure. B.p. 72.5 - 73°/ 14 mm.

(22) α- Iodonaphthalene. This was prepared from α- aminonaphthalene by diazotisation and acting on the diazo solution with potassium iodide in the presence of copper bronze. The oil formed was separated, steam distilled, extracted with ether and fractionated thrice in vacuo. Final fraction collected, boiled at 130°/ 1.5 mm.

(23) Mesitylene. The B.D.H. product was dried over calcium chloride and fractionated. B.p. 164-165°.

(24) Methyl Alcohol. Hopkins and Williams' methyl alcohol (puriss.) was refluxed for eight hours over magnesium ribbon and then fractionated. B.p. 63.7-63.8°.

(25) Methylene bromide. The B.D.H. product was washed, dried over calcium chloride and fractionated. B.p. 96.0 - 96.2°.

(26) Methylene Chloride. The B.D.H. product treated as in case of the corresponding bromide. Colourless middle fraction boiling at 41.8 - 42.2°.

(27) Methylene Iodide. The B.D.H. product was washed with dilute sodium carbonate solution and water. It was dried over calcium chloride and fractionated in vacuo. B.p. 66°/11 mm.

(28) Methyl Iodide. The Hopkins and Williams' product was washed with sodium carbonate solution and water. It was dried and fractionated. B.p. 42.7 - 43°.

(29)/

(29) α-Naphthyl Methyl Ether. This was prepared by the action of dimethyl sulphate on α-naphthol. The product was shaken with caustic soda soln. till neither the copper powder and carbon tetrachloride test nor suspension in alkali with diazotised anilin, gave a positive result for α- naphthol. It was dried and fractionated. B.p. 163°/25 mm.

(30) Nitrobenzene. The B.D.H. product (A.R.) was partially frozen out, and fractionated under reduced pressure. M.p. 5.6 - 5.7°. B.p. 90 - 91°/15 mm.

(31) Nitromethane. The B.D.H. product was washed with water, dried over calcium chloride and fractionated. B.p. 100.8 - 101.1°.

(32) Pentane. B.D.H. "standard" pentane was shaken with concentrated sulphuric acid, then with alkali solution and finally washed with water. It was dried and fractionated. B.p. 35 - 37°.

(33) Pyridin. The B.D.H. product (A.R.) was dried over solid caustic potash and distilled in vacuo. B.p. 19°/12 mm.

(34) Quinoline. Hopkins and Williams' quinoline was treated as in the case of pyridin. B.p. 142°/12 mm.

(35) Tetrabromoethane. The B.D.H. product was washed with sodium carbonate solution and water, dried and fractionated in vacuo. B.p. 125°/15 mm.

(36) Toluene. The B.D.H. product, "free from sulphur", was refluxed over sodium for three hours,washed, dried over calcium chloride and fractionated. B.p. 109.7 - 109.8°.

PREPARATIVE.

Preparation of d - p - Menthene

Tschugaeff, Ber., 1899, 33, 3332

(A) Methyl Menthylxanthogenic Ester.

To a boiling solution of l-menthol (100 gs.) in dry toluene (70 gs.) were introduced in small pieces 16 gs. of sodium. After the first vigorous reaction was over, the solution was boiled gently for twenty hours on an oil bath whereby the theoretical quantity of sodium was dissolved. The supernatant liquid was decanted from the excess sodium, 200 c.c. of sodium dried ether were added followed by the theoretical amount of carbon disulphide (56 gs.), the mixture being well cooled under running water. The resulting dark brown solution was then treated with methyl iodide (94 gs.) and when the fairly lively reaction had ceased, the liquid was boiled under reflux for one hour on the water bath. Water was added, the upper layer removed and, after the ether and the toluene had been distilled off - the latter under reduced pressure - , the residue was poured into absolute alcohol (100 c.c.). After a short time the whole crystallised to a solid mass which was filtered and washed with rectified spirit. The ester crystallised in fine colorless needles melting at 39°. The yield was 110 gs.

(B)/

(B) d-Menthene.

The menthylxanthogenic ester when dry-distilled, decomposed to give chiefly menthene and methyl mercaptan. The distillate, after being heated on the water-bath to drive off the more volatile portion, was redistilled in vacuo, boiled under reflux for two hours over sodium and eventually twice distilled in vacuo. The final distillate was collected at 62°/ 15 mm. The yield was 30 gs.

The sample of d-menthene obtained had $[\alpha]_D^{20}$ = 112.70° (α_D^{20} = 45.75° in a 0.5 dm. tube) and d_4^{20} = 0.8120.

Tschugaeff (loc. cit.) quotes $[\alpha]_D^{20}$ = 115.64° and d_4^{20} = 0.8122 and Zelikov (Ber., 1904, 37, 1377), who prepared it by a different method, quotes $[\alpha]_D^{20}$ = 112.75°.

According to Tschugaeff, the menthene obtained by this method is the p- Δ(3) - form. Recently, however, R. Gachard (Bull. Inst. Pin., 1933, 42-48, 67-72, 79-87, 97-102,; Brit. Chem. Abstracts, 1933 A, 717), mainly from an examination of the Raman spectra, has arrived at the conclusion that the product obtained by the dehydration of menthol by the above method consists of a mixture of Δ(2) - and Δ(3)-p- menthenes, the latter form being usually predominant.

Purification of Optically impure d-Limonene.

A sample of limonene (B.D.H.) was distilled once over sodium at atmospheric pressure and twice in vacuo. In the second vacuum distillation the fraction coming over at $60-61^\circ$/13 mm. was collected (cf. Hantzsch, Ber., 1912, 45, 553, who quotes the boiling point of limonene as 58.1°/10.8 mm. and Richter and Wolff, Ber., 1930, 63, 1724, who quote 64.6°/15 mm. This fraction was found to have $\alpha_D^{20} = 66.78^\circ$ (l = 1 dm.). It was distilled again in vacuo, a portion being collected at 60.5°/13 mm. This was found to have $\alpha_D^{20} = 66^\circ.84^\circ$ (l = 1 dm.). It was evident that the limonene sample contained a large amount of dipentene which could not be separated by fractional distillation. From an examination of the literature however, a chemical method of obtaining limonene with a high rotatory power from a partially racemic sample appeared to be practicable. This involves conversion of the terpene to the mixed tetrabromide. Recrystallisation of the latter yields pure d- limonene tetrabromide which may be decomposed under suitable conditions to give pure d- limonene.

(I) d-Limonene Tetrabromide.

The first attempted preparation of the tetrabromide was by the method of Wallach (Ann., 1885, 225, 304, 318.). Bromine was dropped into an ice-cooled/

cooled solution of limonene in acetic acid until a faint yellow colour persisted. Water was added till a turbidity appeared in the solution and the mixture was set aside overnight. A very poor yield of crystalline tetrabromide was obtained together with large amounts of an oily liquid which showed no signs of crystallising in a freezing mixture of calcium chloride and ice. Simonsen ("The Terpenes." Vol. I, p. 131) suggests that these oily bromides may be a mixture of geometrically isomeric forms, but points out that no direct proof of this has been furnished.

A better yield was obtained by following the procedure of Godlewsky (Chem-Ztg., 1898, 22, 827) which appears to be a modification of a method due to Baeyer and Villiger (Ber., 1894, 27, 448). A solution of limonene in equal parts by weight of ether and amyl alcohol was added drop by drop to an ethereal solution of bromine cooled by ice-water and mechanically stirred. Thus, limonene (13.6 gs.) dissolved in a mixture of amyl alcohol (40 c.c.) and ether (40 c.c.) was added to a solution of bromine (32 gs.) in 40 c.c. of ether. The resulting solution was of a pale yellow colour and was left overnight to allow the ether to evaporate slowly. The amount of crystalline bromide obtained was 15 gs.

From 120 gs. of partially racemic limonene, 130 gs./

gs. of mixed tetrabromides were obtained. This impure bromide, after three recrystallisations from ethyl acetate gave 70 gs. of pure d- limonene tetrabromide melting at 104° and with $[\alpha]^{20}_{5893}$ = + 77.7° (in $CHCl_3$ with l = 1 dm. and c. = 6.766, α^{20}_{5893} = 5.26°).

This rotation compares well with that quoted by von Braun and Lemke (Ber., 1923, 56, 1652) namely $[\alpha]^{20}_{D}$ = 74.5 (in $CHCl_3$ with l = 1 dm. and c = 22.24, α^{20}_{D} = 16° 41). They also state that their sample of tetrabromide melted at 104° (in agreement with values found by previous investigators).

(II) d-Limonene.

Godlewsky (C., 1899, I, 1241) obtained d-limonene from the tetrabromide by the action of zinc dust on its alcoholic solution. The resulting limonene, after purification showed d^{20} = 0.8584 and $[\alpha]^{20}_{D}$ = + 125.5°. Von Braun and Lemke (loc. cit.) employed as the debrominating agent, magnesium and worked in ethereal solution. Their final product, on purification, had d^{20}_{4} = 0.8411 and $[\alpha]^{20}_{D}$ = 126.84° (α^{20}_{D} = 55°3' in 0.5 dm. tube) The latter authors claim that their higher specific rotation indicates that slight racemisation occurs in Godlewsky's method; this claim however could only be justified if actual values of α were compared, since there is some disparity/

disparity in the values of the two densities given. The procedure of von Braun and Lemke is certainly carried out under milder conditions. A modification of this method was therefore adopted.

The pure tetrabromide (70 gs.) was dissolved in sodium-dried ether (500 c.c.). To this solution dry magnesium ribbon (36 gs.) was added with a trace of iodine. The ethereal solution, after a preliminary warming to start the reaction, was found to boil quite briskly at room temperature. Cooling in ice as recommended by von Braun and Lemke was not employed. When the reaction slackened, the solution was boiled gently on the water bath for two hours. It was filtered from the magnesium bromide and excess magnesium and the ether was distilled off, the residue being impure limonene. It was distilled once, boiled under reflux for an hour over a small piece of sodium and then redistilled in vacuo, the portion distilling at 60.5 - 61.0°/13 m.m. being collected. The sample had $d_4^{20} = 0.8403$ and $[\alpha]_D^{20} = 124.21^\circ$ ($\alpha_D^{20} = 52.18^\circ$ with $l = 0.5$ dm.), values which compare well with the figures quoted by Godlewsky and von Braun.

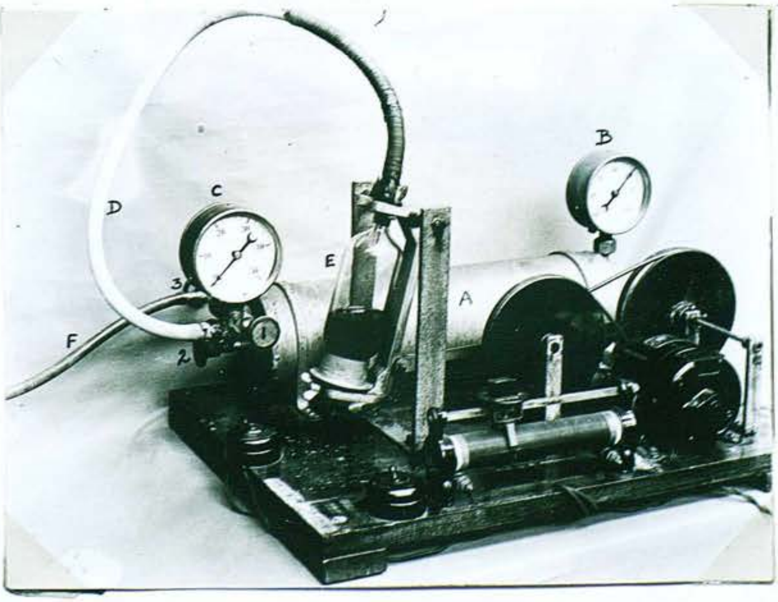
Preparation of d- Pinane.

This was the first saturated hydrocarbon to be prepared during the present work and was obtained by the hydrogenation of d- α -pinene in the presence of/

of platinum black as a catalyst.

The d-α-pinene (Kahlbaum) was purified by distilling in steam (a trace of sodium carbonate was previously added to the distilling flask), drying over anhydrous sodium sulphate and distilling twice under atmospheric pressure, the fraction boiling at 154.5°/757 m.m. being collected. The pinene had $d^{20}_{4} =$ 0.8667 (cf. Ross and Somerville, J.C.S., 1926, 220 who quote $d^{20}_{4} = 0.8665$) and $[\alpha]^{20}_{D} = 47.3^\circ$ ($\alpha^{20}_{D} = 20.48^\circ$ with $l = 0.5$ dm.)

The hydrogenation was carried out in an apparatus of the type due to Adams and Voorhees (see Organic Synthesis (published by Wiley and Co.), Vol. VIII (1928), p.10) This apparatus was designed by Dr L.A. Bigelow and is shown in the following photograph.



The hydrogen is contained in a cylinder of special steel **A** the pressure inside the cylinder being read on the Bourdon gauge **B**. There is an inlet valve at this end whereby the cylinder can be filled. The initial pressure in the cylinder is about 55 lbs./sq. in. The hydrogenation vessel **E** is made of stout Pyrex glass and is screwed on to the shaker by means of wing bolts. It is connected to the Bourdon gauge C by special pressure tubing D and hence through the set of valves to the tank **A**. All joins are covered over with vacuum wax.

The liquid to be hydrogenated (a solution or in certain cases the homogeneous substance) is placed with the catalyst in vessel **E** which is then stoppered to the tube D and screwed down to the shaker as shown. With valves 1 and 3 open, the air is pumped out of the reaction vessel through **F**. Valve 3 is then closed and valve 2 is opened. The hydrogen is allowed to enter the reaction vessel until a reading of 34 lbs is recorded on the gauge C. The two valves are then closed. The shaker is started, the speed of shaking being regulated by a slide resistance. The rate of hydrogenation can be obtained by the rate of fall of the pointer on C.

The scale of this gauge was calibrated by noting the fall in the pointer when 0.01 mole of benzoin dissolved/

dissolved in 50 c.c. benzene was hydrogenated using 0.1 g. of Adam's catalyst. The fall from 34 lbs to 18 lbs i.e. 16 lbs,was found to correspond to the absorption of .01 mole of hydrogen.

Several variations in the method of hydrogenation were employed to obtain the best yield in a reasonable time. These are given below in the order in which they were utilised. In each case samples of pinene from the same stock were used.

(A). The pinene was hydrogenated in the homogeneous state using platinum black as a catalyst prepared by Vavon's modification (Bull. Soc. Chim., 1911, 9, 256) of Loew's method. (Ber., 1890, 23, 289).

Chloroplatinic acid (1 g.) was dissolved in 1 c.c of water and 1.5 c.c. commercial formalin was added to the resulting solution. The mixture was cooled in ice water and to it, a solution of 1 g. of caustic soda in 1 c.c. of water was added, drop by drop, stirring with a glass rod being resorted to during the addition. The solution was left overnight at room temperature. It was filtered through a hardened paper, washed several times with a small quantity of water and then with larger quantities. The filtrate was tested till it no longer gave a cloudiness with silver nitrate. Washing was continued two or three times more, and paper plus platinum was placed in a vacuum/

vacuum desiccator to dry. Yield of dry platinum black was 0.3 - 0.4 g. This process was repeated with identical quantities. Total yield = 0.6 g.

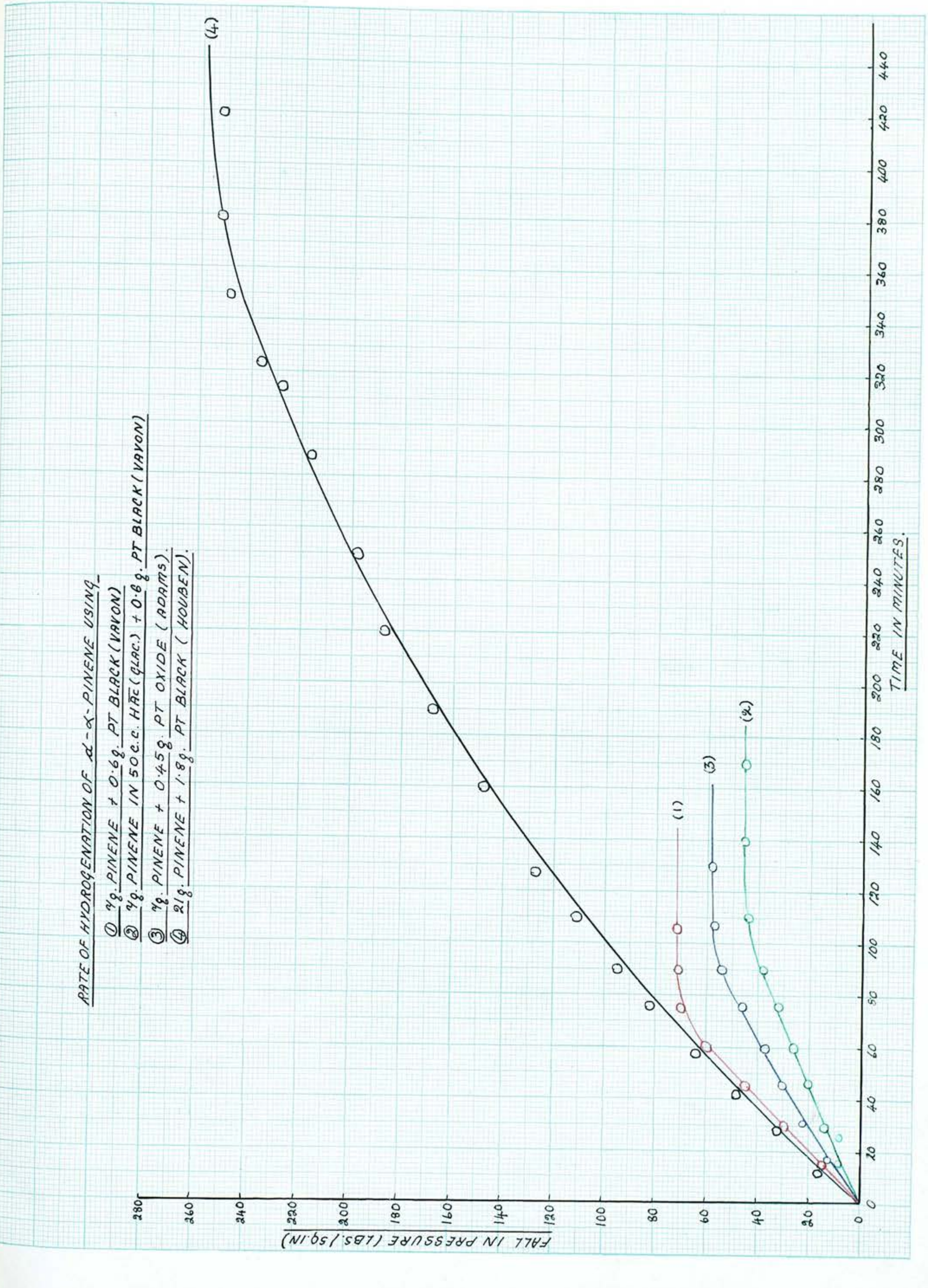
Pinene (7 gs.) in the homogeneous state was shaken with 0.6 g. of this catalyst. Hydrogen was quickly absorbed, a drop in pressure of 72 lbs. being recorded in 86 minutes, the rate of absorption thereafter being zero. The theoretical amount of hydrogen required for 7 gs. of pinene corresponds to a pressure fall of 80 lbs. Total conversion = 90%.

(B) In this case 7g. pinene were dissolved in 50 c.c. glacial acetic acid (purified for solvent work) and shaken up with 0.6 g. platinum black (the above catalyst washed with ether and revived by drawing air through it). The rate of absorption was slower and fell to zero when 46 lbs. fall in pressure had been recorded. This shows a conversion of 58%. In order to check whether there was much change in activity of the catalyst it was washed again with ether and air was drawn through it. A run was carried out as in (A) and it was found that a fall of 70 lbs. pressure was recorded in 140 minutes. The effect of the acetic acid was therefore to inhibit the hydrogenation. No advantage was therefore to be gained in using it as a solvent.

(C) In this case platinum oxide prepared after the method of Adams (Organic Synthesis, VIII (1928) pp. 10, 82.) was used as a catalyst. 1 g. platinum chloride was dissolved in 3 c.c of water, and to the solution was added 10 gs. sodium nitrate (A.R.). The mixture was heated in a porcelain casserole with a small bunsen flame. Fusion occurred and oxides of nitrogen were given off. Brown platinum oxide gradually separated. After evolution of gas had greatly ceased, the mixture was heated with full force of bunsen flame for half-an-hour. It was allowed to cool and 50 c.c. of water were added. The oxide was washed twice by decantation, was transferred to a filter, washed until free from chloride, and dried in a vacuum desiccator. Yield = 0.45 g.

As before, 7 g. of pinene were shaken with 0.45 g. of this catalyst. In about two hours a fall of 60 lbs. pressure was recorded, the velocity of absorption then approaching zero. This represents about 75% conversion and hence is not so good as method (A).

(D) The preparation of the catalyst was similar to method (A). The solution however was mechanically stirred during the addition of the alkali. The reduction was then completed by warming to 55 - 60° for half-an-hour. The catalyst was washed by decantation until/



RATE OF HYDROGENATION OF d-α-PINENE USING_

① 7g. PINENE + 0·6g. PT BLACK (VAVON)
② 7g. PINENE IN 50c.c. $H\overline{Ac}$ (GLAC.) + 0·6g. PT BLACK (VAVON)
③ 7g. PINENE + 0·45g. PT OXIDE (ADAMS).
④ 21g. PINENE + 1·8g. PT BLACK (HOUBEN).

Attempted Preparation of d-Methyl-menthane.

This preparation involved four stages.

(A) 1-Menthone.

This compound was prepared by a modification of a method due to Beckmann (Annal., 1889, 250, 329). To a mixture of sodium bichromate (108 gs) and concentrated sulphuric acid (900 c.c) were added 135 gs. of 1-menthol. A strong colour appeared probably due to the formation of a chromium compound. The mixture was stirred vigorously, a large amount of heat was evolved and a compound was thrown out in the form of small black crystals, which eventually liquefied with formation of 1-menthone.

When the reaction mixture had cooled, the upper brown oily layer was extracted with ether. The ethereal extract was washed with water and dilute sodium hydroxide solution until all coloured impurities had disappeared. The clear colourless liquid was purified by steam-distilling, extracting with ether, drying over anhydrous sodium sulphate and distilling twice in vacuo. The final distillate was collected at 103 - 104°/20 mm. and had $\alpha_D^{20} = -6.20^\circ$ (1 = 0.25). Yield equalled 76% theoretical.

(B)/

(B) 1-3-Methyl-menthol.

This was prepared according to the method of Read and Watters (J.C.S., 1929, 2165), by acting on menthone with methyl magnesium iodide. To an ice cooled solution of the Grignard reagent prepared from magnesium (8.5 g.), methyl iodide (50 g.) and dry ether (300 c.c.) was added gradually, 36 g. 1-menthone dissolved in an equal volume of dry ether. The reaction proceeded somewhat vigorously. When all the menthone had been added, the mixture was kept overnight. The magnesium compound was decomposed with dilute hydrochloric acid, the ethereal layer was separated, washed with water and dried over sodium sulphate. The ether was evaporated and the residual liquid distilled under diminished pressure when a clear oil boiling at 103° - $104^{\circ}/20$ mm. was obtained. It gave $\alpha_{D}^{20} = -2.47^{\circ}$ in a 0.5 dm. tube. Yield 26 gs.

Read and Watters (loc. cit.) obtained an oil boiling at 101 - $102^{\circ}/17$ mm. and having $[\alpha]_{D}^{16} = -6.47^{\circ}$.

(C) d- 3 - Methyl-menthene.

1- Methyl-menthol (26 gs) was heated with twice its weight of anhydrous oxalic acid for five/

five hours at 140° whereby it was dehydrated to form methyl-menthene. The oily layer was separated washed several times with water, dried over sodium sulphate and distilled in vacuo. A liquid was collected boiling at 69° - 72°/10 mm. It showed $\alpha_D^{20} = 34.35°$ (1 = 0.5 dm.) Yield 18 gs.

(D) Attempted Hydrogenation of d-Methyl-menthene.

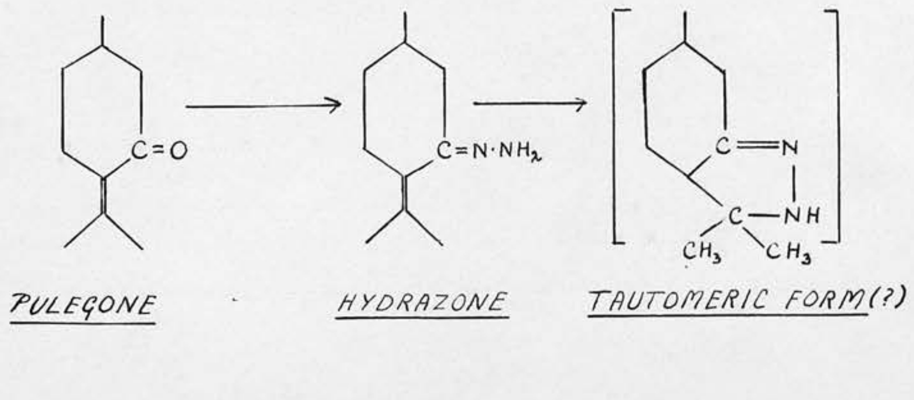
In the first attempt, 1.4 g. d-methyl-menthene were shaken up with 0.1 g. of Vavon's platinum catalyst (q.v.). The menthene was dissolved in 25 c.c. dry benzene (B.D.H., "extra pure".). The gauge showed a fall of 2 lbs. and then stopped. The solution was shaken for two hours but no further fall was recorded. The catalyst showed a tendency to coagulate suggesting the presence of an impurity in the menthene. The latter substance was therefore again distilled in vacuo over a piece of sodium. The distillate boiled at 68°- 70°/10 mm. and had $\alpha_D^{20} = 34.28°$ (1 = 0.5 dm.). An identical quantity of menthene was again shaken up under the same conditions with however the same result as before. Similar attempts were made using Adam's catalyst and platinum black made by method (D) in the preparation of pinane, but without success. In the latter case an attempt was made using 10 gs. of the menthene in the homogeneous state and 1 g./

1 g. of catalyst. A fall of 20 lbs. was recorded in one hour and the pointer then remained steady even after five hours shaking. This suggests about a 10% conversion which was useless for present purposes. Owing to pressure of time therefore the above attempts were discontinued. It is suggested that their failure is due to the presence of some impurity in the methylmenthene prepared by this method which is not readily removed by physical means.

Preparation of d- Carane.

According to Kishner and Sawadowski (C., 1912, I, 1456) carane may be prepared by distilling pulegone hydrazone over solid caustic potash. Since pulegone is readily obtainable it was thought worth while to endeavour to obtain some of this hydrocarbon and compare the variation of its rotatory power with that of pinane. The preparation involved two stages.

(A) Pulegone hydrazone.



Pulegone (Judex Chem. Co.) was dried over sodium sulphate and distilled once in vacuo, the fraction boiling at 94 - 95°/10 mm. being collected. It had $\alpha_D^{20} = + 10.78^\circ$ (l = 0.5) and $n_D^{20} = 1.4892$.

To a solution of 40 gs. of hydrazine hydrate (50% aq.) in 100 c.c. absolute alcohol were added 40 gs. of pulegone. The mixture was well shaken and a large amount of heat was evolved. It was boiled under reflux for eight hours on the water bath, and the excess alcohol and hydrazine hydrate were then distilled off in vacuo. The hydrazone was not distilled but was utilised immediately in the next stage. It had $\alpha_D^{20} = - 3.78^\circ$ (l = 0.5) and $n_D^{21} = 1.4946$ cf. $[\alpha]_D = - 5.55^\circ$ and $n_D = 1.4943$ (Kishner, loc. cit.) On shaking the hydrazone with slight excess of phenyl isothiocyanate a white solid was obtained which, after recrystallisation from methyl alcohol, melted at 176° (in agreement with melting point obtained by Kishner).

Yield of hydrazone = 40 gs.

A second lot of hydrazone was prepared as above and had $\alpha_D^{20} = - 3.35^\circ$ (l = 0.5) and $n_D^{20} = 1.4949$.

(B) d- Carane.

The hydrazone was distilled very slowly over solid potassium hydroxide, the temperature of the vapour/

vapour coming over fluctuating between 160° and 170°. The distillate was washed with water and then several times with a very dilute solution of potassium permanganate in aqueous sodium carbonate. It was finally steam-distilled, extracted with ether and dried over sodium sulphate and distilled over sodium. Fraction boiling at 166 - 166.5°/752 mm. was collected. It gave $d_4^{20} = 0.8408$, $[\alpha]_D^{20} = 55.66^\circ$ ($\alpha = 23.34^\circ$ in $l = 0.5$ dm.) and $n_D^{20} = 1.4590$.

A second sample was prepared which boiled at the same temperature and had the same density and refractive index, but had $[\alpha]_D^{20} = 58.04^\circ$ ($\alpha = 24.40^\circ$ with $l = 0.5$ dm.).

It is evident that the identification of the hydrocarbon thus isolated is a matter of some doubt. The product obtained was certainly not stable to alkaline permanganate solution, but this might be expected in a hydrocarbon containing a three carbon ring. This point will be further referred to in the discussion.

EXPERIMENTAL RESULTS.

The polarimetric readings were taken on a Haensch and Schmidt instrument with an accuracy of ± 0.01°. The source of illumination employed was a Neron 6 volt lamp set up with a Haensch and Schmidt Doppel-Monochromator whereby the complete range of wavelengths in the visible spectrum could be obtained. The following five wavelengths were employed when measuring Rotation - Dispersions viz.,

6563 Å, 5893 Å, 5463 Å, 4861 Å, 4358 Å.

The monochromator was calibrated at regular intervals by comparison with readings taken on an Adam Hilger polarimeter using the mercury arc lamp as a source of illumination and the wavelengths 5463 Å, and 4358 Å. In comparing solvent effects all readings were taken at a temperature of 20°.

The effect of temperature on the rotation was determined by using a jacketted tube through which water, from a thermostat regulated at various temperatures, was pumped. Temperatures about 100°C. were obtained by passing steam from a generator through the jacket.

Measurements of refractive index were made on a Pulfrich refractometer at a temperature of 20° (unless otherwise stated), the source of light used being the sodium flame.

It should be noted that in the following tables the solvents are represented by formulae and, among others, cyclohexane is represented by C_6H_{12}, pyridin by C_5H_5N and quinoline by C_9H_7N.

I. Effect of Solvents on the Optical Rotatory Power of d- p - Menthene.

$t = 20^\circ$, $d_4^{20} = 0.8120$

l = 2 dm. (except for homogeneous liquid, where l = 0.5 dm.)

A. Aliphatic Solvents.

Solvent	C.	α_{6563}	α_{5893}	α_{5463}	α_{4861}	α_{4356}
CH_3CHO	2.662	4.36°	5.61°	6.79°	9.02°	11.82°
CH_3NO_2	2.378	4.04	5.12	6.16	8.13	11.02
$(CH_3)_2CO$	3.084	5.27	6.68	8.05	10.61	14.34
CH_3CN	2.514	4.32	5.48	6.56	8.69	11.75
$CH_3.COOH$	2.706	4.66	5.96	7.13	9.46	12.71
CH_3OH	2.608	4.49	5.74	6.90	9.12	12.22
C_6H_{14}	2.834	4.90	6.26	7.52	9.97	13.37
$C S_2$	3.214	5.56	7.09	8.54	11.28	15.11
$C Cl_4$	2.574	4.45	5.70	6.83	9.06	12.14
(homog.)	-	35.91	45.75	54.64	72.49	96.17
$CH Cl_3$	2.732	4.86	6.18	7.42	9.81	13.12
CH_2Cl_2	2.690	4.85	6.18	7.40	9.83	13.13
CH_3I	3.372	6.24	7.99	9.61	12.64	16.83

d- p - Menthene (contd.)

Solvent.	$[\alpha]_{6563}$	$[\alpha]_{5893}$	$[\alpha]_{5463}$	$[\alpha]_{4861}$	$[\alpha]_{4356}$
CH_3CHO	81.9°	105.4°	127°4	169°9	222° 1
$CH_3\ NO_2$	84.9	107.6	129.5	171.0	231.7
$(CH_3)_2CO$	85.4	108.1	130.5	172.0	232.5
CH_3CN	85.9	109.0	130.8	172.9	233.7
CH_3COOH	86.1	110.1	131.7	174.8	234.9
CH_3OH	86.2	110.1	132.3	174.8	234.3
C_6H_{14}	86.5	110.5	133.2	175.9	235.9
$C\ S_2$	86.5	110.4	132.9	175.5	235.1
$C\ Cl_4$	86.6	111.0	133.0	176.0	235.3
(homog.)	88.41	112.70	134.60	178.50	236.80
$CH\ Cl_3$	89.0	113.1	135.8	179.6	240.1
CH_2Cl_2	90.2	114.8	137.5	182.7	244.1
CH_3I	92.5	118.6	142.5	187.4	249.5

d- p - Menthene (contd.)

B. Aromatic Solvents.

Solvent	C.	α^{20}_{6563}	α^{20}_{5893}	α^{20}_{5463}	α^{20}_{4861}	α^{20}_{4356}
$C_6H_5CO.Me$	3.046	4.95°	6.30°	7.55°	9.94°	13.72°
$C_6H_5NO_2$	2.584	4.29	5.44	6.57	8.67	(11.98)
C_6H_5OMe	2.600	4.37	5.54	6.83	8.81	11.81
C_6H_5I	3.288	5.52	7.02	8.44	11.14	14.95
C_6H_5CN	2.860	4.82	6.17	7.41	9.80	13.12
o - $C_6H_4Cl_2$	2.716	4.59	5.85	7.07	9.34	12.50
$C_6H_5CH_3$	2.676	4.56	5.77	6.98	9.26	12.32
C_6H_5Br	3.035	5.17	6.58	7.93	10.49	13.98
C_6H_5Cl	3.100	5.33	6.80	8.16	10.90	14.45
(homogen.)	-	35.91	45.75	54.64	72.49	96.17
s-$C_6H_3Me_3$	2.388	4.25	5.38	6.45	8.55	11.33
C_6H_{12}	3.450	6.15	7.78	9.40	12.41	16.54
C_6H_6	2.614	4.73	5.92	7.18	9.45	12.59

d-p-Menthene (contd.)

Solvent	$[\alpha]_{6563}$	$[\alpha]_{5893}$	$[\alpha]_{5463}$	$[\alpha]_{4861}$	$[\alpha]_{4356}$
$C_6H_5.CO.Me$	81.4	103.4	123.8	163.2	225.2
$C_6H_5.NO_2$	83.0	105.3	127.2	167.8	(226.5)
$C_6H_5.O\ Me$	84.0	106.6	128.4	169.3	227.1
C_6H_5I	84.0	106.7	128.4	169.4	227.9
C_6H_5CN	84.3	107.7	129.4	171.3	229.4
o - $C_6H_4Cl_2$	84.5	107.9	130.0	172.0	230.1
$C_6H_5.CH_3$	85.2	108.0	130.5	173.1	230.3
C_6H_5Br	85.0	108.4	130.8	173.0	230.1
C_6H_5Cl	86.1	109.7	131.6	175.8	233.9
(homogen.)	88.41	112.70	134.60	178.50	236.80
s-$C_6H_3Me_3$	89.0	112.7	135.0	179.0	237.2
C_6H_{12}	89.3	112.8	136.2	179.7	239.7
C_6H_6	90.3	113.2	137.3	180.6	241.0

I. Change in Rotatory Power of d-p-Menthene with Concentration in Hexane.

$t = 20^\circ$

C. Concentration	2.834	10.08	20.03	60.21	homogeneous.
α_{6563}	4.90°	8.74°	17.28°	52.32°	35.91°
α_{5893}	6.26	11.07	21.95	66.76°	45.75
α_{5463}	7.52	13.22	26.24	80.88	54.64
α_{4861}	9.97	17.48	34.68	106.35	72.49
α_{4356}	13.37	23.06	45.64	142.40	96.17
$[\alpha]_{6563}$	86.5°	86.1°	86.0°	86.9°	88.41°
$[\alpha]_{5893}$	110.5	109.8	109.6	110.9	112.70
$[\alpha]_{5463}$	133.2	131.2	131.0	134.0	134.60
$[\alpha]_{4861}$	175.9	173.5	173.2	176.6	178.50
$[\alpha]_{4356}$	235.9	228.5	228.1	236.5	236.80
$[M]_{5893}$	152.5°	151.5°	151.3°	153.0°	155.5°

II. Effect of Solvents on the Optical Rotatory Power of d- Limonene.

$t = 20^{\circ}$ $l = 2$ dm. (except for homogeneous liquid where $l = .5$)

$$d_4^{20} = 0.8403.$$

A. Aliphatic Solvents.

Solvents	c	α_{6563}	α_{5893}	α_{5463}	α_{4861}	α_{4356}
CH_3OH	2.161	3.81°	4.75°	5.65°	7.34°	9.55°
CH_3CN	2.048	3.66	4.54	5.38	6.99	9.12
CCl_4	2.136	3.90	4.85	5.76	7.44	9.72
$(CH_3)_2CO$	2.060	3.75	4.68	5.55	7.22	9.41
$CH_3.CHO$	2.006	3.71	4.62	5.50	7.16	9.34
$CHCl_3$	1.956	3.62	4.51	5.37	6.99	9.14
C_6H_{14}	2.100	3.89	4.86	5.76	7.54	9.86
CH_2Cl_2	2.078	3.86	4.83	5.72	7.46	9.73
$H\ \overline{Ac}$	1.980	3.70	4.62	5.48	7.12	9.27
CH_3NO_2	2.028	3.79	4.72	5.62	7.37	9.55
CH_3I	2.038	4.00	5.00	5.92	7.73	10.13
$C\ S_2$	2.122	4.16	5.20	6.21	8.09	10.56
(homogeneous)	-	41.60	52.18	62.00	81.06	105.58

d- Limonene. (contd.)

Solvent	$[\alpha]_{6563}$	$[\alpha]_{5893}$	$[\alpha]_{5463}$	$[\alpha]_{4861}$	$[\alpha]_{4356}$
CH_3OH	88.2°	109.9°	130.7°	169.8°	220.8°
CH_3CN	89.4	110.8	131.4	170.7	222.7
$C\ Cl_4$	91.3	113.5	134.8	174.2	227.5
$(CH_3)_2CO$	91.1	113.6	134.9	175.0	228.3
CH_3CHO	92.5	115.1	137.1	178.5	232.8
$CHCl_3$	92.6	115.3	137.3	178.7	233.7
C_6H_{14}	92.6	115.6	137.1	179.4	234.5
CH_2Cl_2	92.9	116.2	137.6	179.5	234.7
H Ac	93.4	116.6	138.4	179.8	234.2
CH_3NO_2	93.1	116.3	138.0	180.6	234.4
CH_3I	98.1	122.7	145.4	189.8	248.7
$C\ S_2$	98.0	122.5	146.3	190.6	248.8
(homogeneous)	99.02	124.21	147.83	192.92	251.30

d-Limonene (contd.)

B. Aromatic Solvents.

Solvent	c.	α_{6563}	α_{5893}	α_{5463}	α_{4861}	α_{4356}
C_6H_{12}	2.102	3.89°	4.88°	5.79°	7.55°	9.89°
$C_6H_5.CH_3$	2.000	3.88	4.86	5.77	7.55	9.89
$s\text{-}C_6H_3(CH_3)_3$	2.038	3.96	4.95	5.89	7.68	10.05
C_6H_6	2.050	4.00	4.99	5.92	7.74	10.13
$C_6H_5.OCH_3$	2.032	3.99	5.00	5.93	7.74	10.12
$C_6H_5.CN$	2.008	3.94	4.93	5.87	7.63	10.02
(homogeneous)	—	41.60	52.18	62.00	81.06	105.58
$C_6H_5.Cl$	2.170	4.30	5.40	6.41	8.36	10.97
$C_6H_5.CO.CH_3$	2.022	4.02	5.04	5.99	7.86	10.29
$o\text{-}C_6H_4Cl_2$	2.010	4.03	5.04	5.98	7.85	10.31
$C_6H_5.CHO$	2.110	4.23	5.29	6.29	8.22	10.80
$C_6H_5.NH_2$	2.044	4.15	5.17	6.14	8.00	10.45
C_6H_5I	1.960	4.02	5.02	5.95	7.81	10.22
$C_6H_5NO_2$	2.072	4.31	5.39	6.41	8.41	-

d-Limonene (contd.)

Solvent	$[\alpha]_{6563}$	$[\alpha]_{5893}$	$[\alpha]_{5463}$	$[\alpha]_{4861}$	$[\alpha]_{4356}$
C_6H_{12}	92.5°	116.1°	137.7°	179.6°	235.3°
$C_6H_5.CH_3$	97.0	121.5	144.3	188.8	247.3
s-$C_6H_3(CH_3)_3$	97.2	121.4	144.5	188.4	246.7
C_6H_6	97.6	121.7	144.4	188.7	247.3
$C_6H_5.OCH_3$	98.4	123.0	146.2	190.4	249.1
$C_6H_5.CN$	98.1	123.0	146.4	190.3	249.5
(homogeneous)	99.02	124.21	147.83	192.92	251.30
C_6H_5Cl	99.1	124.4	147.9	192.6	253.0
$C_6H_5.CO.CH_3$	99.4	124.6	148.3	194.3	254.7
o-$C_6H_4Cl_2$	100.5	125.4	148.7	195.6	256.7
$C_6H_5.CHO$	100.5	125.6	149.3	194.7	256.6
$C_6H_5.NH_2$	101.5	126.7	150.2	195.7	256.0
C_6H_5I	102.5	128.1	152.0	199.5	260.8
$C_6H_5NO_2$	104.5	130.3	154.9	203.6	-

II. Change in Rotatory Power of d-Limonene with Concentration in Benzene.

$t = 20^\circ$

C. Concentration	2.050	8.128	42.18	homogeneous
α_{6563}	4.00°	8.00°	41.40°	41.60°
α_{5893}	4.99	9.94	51.95	52.18
α_{5463}	5.92	11.74	61.58	62.00
α_{4861}	7.74	15.40	80.49	81.06
α_{4356}	10.13	20.07	-	105.58
$[\alpha]_{6563}$	97.6°	97.7°	98.2°	99.02°
$[\alpha]_{5893}$	121.7	122.3	123.2	124.21
$[\alpha]_{5463}$	144.4	144.5	146.0	147.8
$[\alpha]_{4861}$	188.7	189.5	190.8	192.9
$[\alpha]_{4356}$	247.3	247.5	-	251.3
$[M]_{5893}$	165.5°	166.1°	167.5°	168.9°

III. Effect of Solvents on the Optical Rotatory Power of d-α- Pinene.

$$t = 20^{\circ}, \qquad d^{20}_{4} = 0.8667,$$

l = 2 dm. throughout (except for homogeneous liquid where l = 0.5 dm.)

(A) Aliphatic Solvents.

Solvent	c.	α_{6563}	α_{5893}	α_{5463}	α_{4861}	α_{4356}
CS_2	4.142	2.76°	3.39°	3.99°	5.08°	6.34°
CH_3I	4.150	2.98	3.69	4.31	5.54	7.02
(homogeneous)	-	16.45	20.48	24.12	31.29	40.38
C_6H_{14}	4.038	3.28	4.08	4.84	6.48	8.34
CCl_4	4.022	3.29	4.10	4.89	6.51	8.37
CH_3OH	4.212	3.51	4.39	5.20	6.81	8.83
$(CH_3)_2CO$	4.062	3.46	4.30	5.10	6.62	8.60
CH_3CHO	4.060	3.52	4.39	5.19	6.77	8.75
CH_2Cl_2	4.028	3.53	4.46	5.25	6.91	8.93
$CHCl_3$	4.104	3.65	4.57	5.41	7.08	9.16
CH_3NO_2	4.172	3.72	4.65	5.52	7.22	9.35
CH_3CN	4.166	3.74	4.65	5.54	7.23	9.38
$CH_3CO.OH$	4.184	3.76	4.70	5.59	7.33	9.60

d-α- Pinene. (contd.)

Solvent	$[\alpha]_{6563}$	$[\alpha]_{5893}$	$[\alpha]_{5463}$	$[\alpha]_{4861}$	$[\alpha]_{4356}$
CS_2	33.3°	40.9°	48.2°	61.4°	76.6°
CH_3I	35.9	44.5	52.5	66.8	86.5
(homogeneous)	38.0	47.3	55.6	72.2	93.2
C_6H_{14}	40.6	50.5	60.4	80.2	103.2
CCl_4	40.9	51.0	60.8	80.5	104.1
CH_3OH	41.8	52.3	61.7	80.8	104.8
$(CH_3)_2CO$	42.6	53.0	62.8	81.5	105.9
$CH_3.CHO$	43.4	54.1	63.9	83.4	108.6
CH_2Cl_2	43.8	55.4	65.2	85.8	110.8
$CHCl_3$	44.5	55.8	65.9	86.3	111.6
CH_3NO_2	44.6	55.9	66.2	86.6	112.1
CH_3CN	44.9	56.0	66.5	86.8	112.8
$CH_3.CO.OH$	45.0	56.2	66.8	87.5	114.8

d- Pinene (contd.)

B. Aromatic Solvents.

Solvent	c.	α_{6563}	α_{5893}	α_{5463}	α_{4861}	α_{4356}
s-$C_6H_3(CH_3)_3$	4.106	3.00°	3.76°	4.48°	5.80°	7.44°
C_6H_6	4.138	3.11	3.86	4.58	5.92	7.65
C_6H_{12}	4.156	3.13	3.89	4.61	5.97	7.68
(homogeneous)	-	16.45	20.48	24.12	31.29	40.38
$C_6H_5.OCH_3$	4.082	3.16	3.91	4.61	5.97	7.72
C_6H_5I	4.080	3.18	3.93	4.63	5.99	7.78
$C_6H_5CH_3$	4.016	3.10	3.88	4.59	5.94	7.70
C_6H_5Cl	4.114	3.28	4.10	4.84	6.28	8.14
o - $C_6H_4Cl_2$	4.040	3.37	4.20	4.97	6.46	8.41
$C_6H_5.NH_2$	4.026	3.38	4.17	4.98	6.44	-
$C_6H_5.CO.CH_3$	4.166	3.52	4.40	5.21	6.75	8.80
$C_6H_5.CN$	4.092	3.53	4.42	5.24	6.99	9.06
$C_6H_5NO_2$	4.068	3.66	4.56	5.40	7.04	-

d- Pinene (contd.)

Solvent	$[\alpha]_{6563}$	$[\alpha]_{5893}$	$[\alpha]_{5463}$	$[\alpha]_{4861}$	$[\alpha]_{4356}$
s - $C_6H_3(CH_3)_3$	36.5°	45.8°	54.5°	70.6°	90.6°
C_6H_6	37.6	46.6	55.4	71.5	92.5
C_6H_{12}	37.7	46.8	55.5	71.9	92.5
(homogeneous)	38.0	47.3	55.6	72.2	93.2
$C_6H_5.OCH_3$	38.7	47.9	56.5	73.1	94.6
C_6H_5I	39.0	48.2	56.8	73.5	95.4
$C_6H_5\ .CH_3$	38.9	48.3	57.2	74.0	95.9
C_6H_5Cl	39.9	49.9	58.9	76.4	99.0
o - $C_6H_4Cl_2$	41.7	52.0	61.5	80.1	104.1
$C_6H_5.NH_2$	42.0	52.0	61.9	80.2	-
$C_6H_5.CO.CH_3$	42.3	52.8	62.4	81.0	104.4
$C_6H_5.CN$	43.4	54.0	64.0	84.9	109.5
$C_6H_5NO_2$	46.0	56.0	66.4	86.5	-

III. Change in Rotatory Power of d- - Pinene with Concentration in

(1) Carbon Disulphide

$t = 20^{\circ}$

C. Concentration	4.142*	52.09**	75.36	(homogeneous)
α_{6563}	2.76°	9.33°	13.84°	16.45°
α_{5893}	3.39	11.57	17.24	20.48
α_{5463}	3.99	13.61	20.33	24.12
α_{4861}	5.08	17.56	26.28	31.29
α_{4356}	6.34	22.16	33.88	40.38
$[\alpha]_{6563}$	33.3°	35.3°	36.7°	38.0°
$[\alpha]_{5893}$	40.9	43.7	45.8	47.3
$[\alpha]_{5463}$	48.2	51.5	54.0	55.6
$[\alpha]_{4861}$	61.4	66.4	69.7	72.2
$[\alpha]_{4356}$	76.6	83.8	89.9	93.2
$[M]_{5893}$	55.6°	59.4°	62.3°	64.3°

* l = 2 dm. ** l = 0.5 dm.

(2) <u>Hexane</u>. $t = 20^{\circ}$

C. Concentration	4.038^{*}	20.03^{**}	50.06	$^{x}70.10$	(homogeneous)
α_{6563}	3.28°	8.01°	19.36°	13.38°	16.45°
α_{5893}	4.08	10.00	24.22	16.66	20.48
α_{5463}	4.84	11.87	28.58	19.58	24.12
α_{4861}	6.48	15.42	37.09	25.35	31.29
α_{4356}	8.34	20.05	47.67	32.85	40.38
$[\alpha]_{6563}$	40.6°	40.0°	38.7°	38.2°	38.0°
$[\alpha]_{5893}$	50.5	49.8	48.4	47.5	47.3
$[\alpha]_{5463}$	60.4	59.3	57.1	55.9	55.6
$[\alpha]_{4861}$	80.2	77.1	74.1	72.3	72.2
$[\alpha]_{4356}$	103.2	100.2	95.2	93.7	93.2
$[M]_{5893}$	68.9°	67.8°	65.8°	64.6°	64.3°

* $l = 2$ dm. ** $l = 1$ dm. ^{x} $l = 0.5$ dm.

IV. Effect of Solvents on the Optical Rotatory Power of d-Pinane.

$t = 20^{\circ}$ $d_4^{20} = 0.8560$

Solvent	l.	c.	α_{6563}	α_{5893}	α_{5463}	α_{4861}	α_{4356}
CH_3CN	2	2.548	.75°	.97°	1.14°	1.49°	1.94°
CH_3OH		3.294	.98	1.26	1.51	1.99	2.67
$CH_3.COOH$		3.230	.96	1.26	1.49	1.97	2.59
CH_3NO_2		1.972	.59	.78	.92	1.22	1.62
C_5H_{12}	"	3.320	1.02	1.33	1.60	2.11	2.75
$CH_3.CHO$		3.314	1.02	1.33	1.59	2.10	2.75
C_6H_{14}		3.402	1.06	1.37	1.65	2.19	2.90
$(CH_3)_2CO$		3.392	1.08	1.42	1.68	2.21	2.94
CH_2Cl_2		3.422	1.12	1.44	1.73	2.29	3.01
$CHCl_3$	"	3.204	1.09	1.40	1.66	2.19	2.90
C_6H_5CN		3.344	1.17	1.49	1.77	2.38	3.16
CH_2Br_2		3.472	1.25	1.58	1.91	2.50	3.32
(homog.)	1	-	15.49	19.54	23.42	31.08	41.27
CCl_4	2	3.146	1.13	1.44	1.72	2.28	3.01
C_5H_5N		3.412	1.22	1.60	1.89	2.49	-
$C_6H_5NO_2$		3.438	1.26	1.62	1.94	2.52	-
s-$C_6H_3Me_3$		3.522	1.28	1.66	1.97	2.60	3.49
CH_3I		3.366	1.24	1.59	1.90	2.50	3.32
C_6H_6	"	3.338	1.26	1.59	1.91	2.50	3.36

d- Pinane (contd.)

$t = 20^{\circ}$ $d_4^{20} = 0.8560$

Solvent	l.	c.	α_{6563}	α_{5893}	α_{5463}	α_{4861}	α_{4356}
$C_6H_5.CHO$		3.268	1.22°	1.57°	1.86°	2.42°	3.33°
$C_6H_5.COCH_3$		3.492	1.31	1.68	2.01	2.64	3.51
$C_6H_5CH_3$		3.378	1.30	1.65	1.97	2.59	3.44
$C_6H_5OCH_3$		3.478	1.36	1.74	2.06	2.75	3.59
C_6H_5Cl		3.146	1.24	1.58	1.87	2.48	3.25
o-$C_6H_4Cl_2$	"	3.442	1.35	1.73	2.05	2.71	3.56
α-$C_{10}H_7Cl$		3.412	1.36	1.73	2.07	2.73	3.62
C_6H_5Br		4.346	1.72	2.21	2.63	3.47	4.62
α-$C_{10}H_7Br$		3.340	1.32	1.70	2.01	2.69	-
$CHBr_2.CHBr_2$		3.458	1.39	1.77	2.10	2.73	3.65
C_6H_5I	"	3.428	1.37	1.77	2.11	2.78	-
α- $C_{10}H_7OMe$		3.642	1.50	1.88	2.25	2.94	-
$C_6H_5NH_2$		3.244	1.34	1.71	2.08	2.79	-
CH_2I_2	1	3.578	.73	.95	1.16	-	-
C_9H_7N	2	3.361	1.48	1.88	2.28	3.03	-
$C\ S_2$	2	3.492	1.55	1.96	2.38	3.19	4.25
α- $C_{10}H_7I$	1	3.410	-	.98	-	-	-

d-Pinane (contd.)

Solvent	$[\alpha]_{6563}$	$[\alpha]_{5893}$	$[\alpha]_{5463}$	$[\alpha]_{4861}$	$[\alpha]_{4356}$
CH_3CN	14.7°	18.7°	22.4°	29.2°	38.2°
CH_3OH	14.8	19.1	22.9	30.2	40.5
$CH_3.COOH$	14.9	19.5	23.1	30.5	40.1
CH_3NO_2	15.0	19.8	23.3	30.9	41.0
C_5H_{12}	15.4	20.0	24.1	31.7	41.3
CH_3CHO	15.4	20.1	24.1	31.7	41.5
C_6H_{14}	15.6	20.2	24.3	32.2	42.6
$(CH_3)_2CO$	16.0	20.9	24.7	32.6	43.2
CH_2Cl_2	16.4	21.0	25.3	33.5	44.0
$CH\ Cl_3$	17.0	21.8	25.9	34.2	45.3
C_6H_5CN	17.5	22.3	26.5	35.6	47.3
CH_2Br_2	18.0	22.8	27.5	36.0	47.9
(homogeneous)	18.10	22.83	27.36	36.31	48.21
$C\ Cl_4$	18.0	22.9	27.5	36.2	47.9
C_5H_5N	18.0	23.4	27.7	36.5	-
$C_6H_5NO_2$	18.3	23.6	28.2	36.7	-
s- $C_6H_3Me_3$	18.1	23.6	28.0	36.9	49.5
CH_3I	18.4	23.6	28.2	37.1	49.3

d-Pinane (contd.)

Solvent	$[\alpha]_{6563}$	$[\alpha]_{5893}$	$[\alpha]_{5463}$	$[\alpha]_{4861}$	$[\alpha]_{4356}$
C_6H_6	18.9°	23.8°	28.6°	37.5°	50.3°
$C_6H_5.CHO$	18.7	24.0	28.5	37.3	50.0
$C_6H_5.CO.CH_3$	18.8	24.1	28.8	37.8	50.1
$C_6H_5CH_3$	19.2	24.4	29.2	38.4	50.9
$C_6H_5OCH_3$	19.6	25.0	29.6	39.4	51.6
C_6H_5Cl	19.7	25.1	29.7	39.4	51.6
o- $C_6H_4Cl_2$	19.6	25.1	29.7	39.4	51.7
α- $C_{10}H_7Cl$	19.9	25.3	30.3	40.0	53.0
C_6H_5Br	19.8	25.4	30.3	39.9	53.1
α- $C_{10}H_7Br$	19.8	25.4	30.5	40.1	-
$CH Br_2.CHBr_2$	20.0	25.6	30.5	40.0	52.8
C_6H_5I	20.0	25.8	30.8	40.6	-
α-$C_{10}H_7OMe$	20.6	25.8	30.9	40.5	-
$C_6H_5NH_2$	20.7	26.4	32.0	42.9	-
CH_2I_2	20.9	26.6	32.4	-	-
C_9H_7N	22.0	28.0	33.9	44.9	-
$C S_2$	22.2	28.1	34.1	45.4	60.8
α-$C_{10}H_7I$	-	28.7	-	-	-

IV. Change in Rotatory Power of d-Pinane in Carbon Disulphide with change in Concentration.

t = 20°

Concentration	3.492*	38.6**	50.57	homogeneous
α_{6563}	1.55°	7.84°	9.96°	15.49°
α_{5893}	1.96	9.99	12.62	19.54
α_{5463}	2.38	11.96	15.13	23.42
α_{4861}	3.19	16.03	20.14	31.08
α_{4356}	4.25	21.53	26.84	41.27
$[\alpha]_{6563}$	22.2°	20.31°	19.70°	18.10°
$[\alpha]_{5893}$	28.1	25.88	24.96	22.83
$[\alpha]_{5463}$	34.1	30.98	29.92	27.36
$[\alpha]_{4861}$	45.4	41.53	39.82	36.31
$[\alpha]_{4356}$	60.8	55.76	53.07	48.21
$[M]_{5893}$	38.7°	35.7°	34.5°	31.5°

* l = 2 dms.   ** l = 1 dm.

Rotatory Power of d- Pinane in Mixtures of Solvents of High and Low Refractive Indices.

These readings were determined only for $\lambda = 5893$

Solvent	α^{20}_{5893}	$[M]^{D}_{20}$	n^{20}_{D}	C.
CS_2	1.96°	38.7°	1.6246	3.492
12.70 gs CS_2 + 12.1 gs MeOH	1.46	29.5	1.4377	3.426
6.36g CS_2 + 8 gs. MeOH	1.39	28.8	1.4162	3.328
Me OH	1.26	26.4	1.3266	3.294

V. Effect of Solvents on Optical Rotatory Power of d- Carane

$t = 20^\circ$ $d_4^{20} = 0.8408$

l = 2 dms. (except for homogeneous liquid where l = 0.5 dm.)

A. Aliphatic Solvents.

Solvent	c.	α_{6563}	α_{5893}	α_{5463}	α_{4861}	α_{4356}
CS_2	3.562	2.94°	3.71°	4.42°	5.82°	7.60°
$CHCl_3$	3.638	3.14	3.93	4.69	6.19	8.12
$CH_3.CHO$	3.518	3.05	3.82	4.51	5.97	7.83
CH_3NO_2	3.668	3.22	4.04	4.80	6.28	8.28
CH_3CN	3.516	3.11	3.89	4.63	6.02	7.90
CCl_4	3.510	3.09	3.89	4.66	6.03	7.95
(homogeneous)	-	18.57	23.34	27.66	36.33	47.59
$(CH_3)_2CO$	3.526	3.15	3.94	4.68	6.18	8.09
CH_3OH	3.580	3.21	4.00	4.76	6.23	8.16
C_6H_{14}	3.506	3.12	3.92	4.67	6.11	8.01
CH_2Cl_2	3.520	3.24	4.03	4.81	6.31	8.13
CH_3I	3.572	3.34	4.16	4.99	6.49	8.27
C_6H_6	3.518	2.95	3.69	4.39	5.79	7.58

d- Carane (contd.)

Solvent	$[\alpha]_{6563}$	$[\alpha]_{5893}$	$[\alpha]_{5463}$	$[\alpha]_{4861}$	$[\alpha]_{4356}$
CS_2	41.3°	52.1°	62.0°	81.7°	106.7°
$CHCl_3$	43.2	54.0	64.5	85.0	111.4
$CH_3.CHO$	43.4	54.3	64.1	84.8	111.3
CH_3NO_2	43.9	55.1	65.4	85.5	112.7
CH_3CN	44.2	55.3	65.9	85.6	112.5
CCl_4	44.0	55.4	66.4	85.9	113.2
(homogeneous)	44.16	55.66	65.78	86.40	113.20
$(CH_3)_2CO$	44.7	55.7	66.6	87.6	114.7
CH_3OH	44.8	55.9	66.5	87.1	114.1
C_6H_{14}	44.5	55.9	66.6	87.0	114.2
CH_2Cl_2	46.0	57.2	68.3	89.6	115.5
CH_3I	46.8	58.2	69.8	90.8	115.8
C_6H_6	41.9	52.4	62.4	82.3	107.7

d- Carane (contd.)

B. Aromatic Solvents

Solvent	c.	α_{6563}	α_{5893}	α_{5463}	α_{4861}	α_{4356}
C_6H_5I	3.594	2.99°	3.75°	4.47°	5.86°	7.70°
s-$C_6H_3Me_3$	3.544	2.96	3.72	4.42	5.80	7.68
C_6H_5O Me	3.588	3.04	3.83	4.54	5.95	7.80
o-$C_6H_4Cl_2$	3.588	3.03	3.82	4.53	5.94	7.80
$C_6H_5CO.Me$	3.612	3.06	3.85	4.58	5.96	7.84
$C_6H_5.CN$	3.516	3.01	3.78	4.47	5.82	-
$C_6H_5.NH_2$	3.504	3.02	3.80	4.50	5.86	-
C_6H_5Br	3.488	3.00	3.78	4.49	5.88	7.74
C_6H_5Cl	3.594	3.10	3.90	4.62	6.07	7.94
C_6H_6	3.554	3.07	3.90	4.63	6.09	7.93
$C_6H_5.CH_2$	3.634	3.25	4.04	4.77	6.28	8.22
$C_6H_5NO_2$	3.407	3.02	3.80	4.50	5.91	-
homogeneous	-	19.41	24.40	28.91	37.98	49.74
CS_2	3.346	2.93	3.68	4.40	5.76	7.57
CH_3I	3.564	3.42	4.32	5.24	6.73	8.75

d- Carane (contd.)

Solvent	$[\alpha]_{6563}$	$[\alpha]_{5893}$	$[\alpha]_{5463}$	$[\alpha]_{4861}$	$[\alpha]_{4356}$
C_6H_5I	41.8°	52.4°	62.5°	82.0°	107.7°
s-$C_6H_3Me_3$	41.8	52.5	62.4	81.8	108.3
C_6H_5O Me	42.3	53.3	63.2	82.9	108.7
o-$C_6H_4Cl_2$	42.2	53.4	63.1	82.8	108.7
$C_6H_5CO.Me$	42.4	53.4	63.4	82.5	108.6
C_6H_5CN	42.8	53.8	63.6	82.8	-
$C_6H_5NH_2$	43.0	54.3	64.2	83.7	-
C_6H_5Br	43.0	54.3	64.2	84.3	111.0
C_6H_5Cl	43.1	54.3	64.3	84.5	110.6
C_6H_6	44.3	54.9	65.2	85.7	111.6
$C_6H_5.CH_3$	44.7	55.6	65.6	86.4	113.1
$C_6H_5NO_2$	44.5	55.8	65.9	86.8	-
homogeneous	46.16	58.04	68.78	90.32	118.3
CS_2	43.8	55.0	65.8	86.1	113.1
CH_3I	48.0	60.6	73.5	94.4	122.8

I. Effect of Temperature on Rotatory Power of d - p - Menthene dissolved in

(A) Nitrobenzene

Temperature	21.3°	40.8°	59.9°	79.4°
d_4^t	1.195	1.181	1.166	1.151

c = 2.584 at 20°　　l = 1 dm.

Temperature	α_{6563}^t	α_{5893}^t	α_{5463}^t	α_{4861}^t
10.2°	2.16°	2.71°	3.24°	4.31°
19.8	2.15	2.72	3.27	4.32
39.3	2.06	2.56	3.05	4.04
55.5	1.97	2.48	2.96	3.98
75.5	1.88	2.44	2.88	3.78
97.2	1.82	2.38	2.80	3.68

Temperature	d_4^t	α_{5893}^t	$[M]_{5893}^t$
10.2°	1.206	2.71°	143.3°
19.8	1.199	2.72	144.9
39.3	1.184	2.56	138.1
55.5	1.172	2.48	135.2
75.5	1.158	2.44	134.6
97.2	1.138	2.38	133.4

(B) Mesitylene

Temperature	23.5°	41.0°	59.3°	79.0°
d_4^t	.8684	.8523	.8361	.8186

$c = 2.388$ at 20° $l = 1$ dm.

Temperature	α_{6563}^t	α_{5893}^t	α_{5463}^t	α_{4861}^t	α_{4356}^t
10.2°	2.14°	2.70°	3.22°	4.31°	5.71°
19.6	2.12	2.68	3.20	4.28	5.67
35.0	2.08	2.57	3.09	4.14	5.54
49.9	2.02	2.52	2.97	4.02	5.39
73.8	1.87	2.42	2.88	3.90	5.24
97.0	1.80	2.35	2.80	3.79	5.22

Temperature	d_4^t	α_{5893}^t	$[M]_{5893}^t$
10.2°	.8831	2.70°	154.3°
19.6	.8735	2.68	155.0
35.0	.8564	2.57	151.4
49.9	.8449	2.52	150.4
73.8	.8226	2.42	148.5
97.0	.8009	2.35	148.0

II. Effect of Temperature on Rotatory Power of d- Limonene dissolved in

(A) Nitrobenzene

Wgt. of solution = 11.983 gs.

Temperature	30.2°	45.1°	59.6°	79.4°
d_4^t	1.190	1.177	1.164	1.150

$c = 2.072$ at 20°

$l = 0.5$

Temperature	α_{6563}	α_{5893}	α_{5463}	α_{4861}
12.0°	1.08°	1.37°	1.63°	2.20°
22.6	1.07	1.35	1.60	2.16
47.6	1.04	1.30	1.53	2.04
75.2	.96	1.22	1.43	1.93
98.6	.92	1.16	1.38	1.87

Temperature	d_4^t	α^t_{5893}	$[M]^t_{5893}$
12.0°	1.205	1.37°	178.8°
22.6	1.197	1.35	177.4
47.6	1.175	1.30	173.9
75.2	1.153	1.22	166.4
98.6	1.134	1.16	160.9

(B) Mesitylene Weight of solution = 8.678 gs.

Temperature	35.2°	48.3°	62.3°	78.3°
d_4^t	.8565	.8460	.8361	.8183

C = 2.038 at 20°C. 1 = 0.5

Temperature	α_{6563}	α_{5893}	α_{5463}	α_{4861}	α_{4356}
12.2°	.99°	1.28°	1.51°	2.01°	2.70°
20.3	.97	1.25	1.48	1.95	2.60
43.3	.94	1.20	1.44	1.90	2.54
78.4	.84	1.10	1.30	1.75	2.35
98.0	.79	1.04	1.20	1.59	2.16

Temperature	d_4^t	α_{5893}^t	$[M]_{5893}^t$
12.2°	.875	1.28°	169.3°
20.3	.868	1.25	166.8
43.3	.851	1.20	162.3
78.4	.825	1.10	154.4
98.0	.811	1.04	147.6

III. Effect of Temperature on Rotatory Power of d- Pinene dissolved in

(A) Nitrobenzene

Temperature	35.0°	47.5°	62.1°	77.5°
d_4^t	1.181	1.168	1.156	1.140

c = 4.068 at 20° l = .5 dm.

Temperature	α_{6563}	α_{5893}	α_{5463}	α_{4861}
9.1°	.92°	1.15°	1.36°	1.77°
19.6	.915	1.14	1.35	1.76
48.1	.86	1.08	1.27	1.67
74.6	.82	1.03	1.22	1.60
98.1	.78	.98	1.17	1.53

Temperature	d_4^t	α^t_{5893}	$[M]^t_{5893}$
9.1°	1.199	1.15°	76.4°
19.6	1.191	1.14	75.6
48.1	1.166	1.08	73.7
74.6	1.145	1.03	71.6
98.1	1.127	.98	68.2

(B) Mesitylene

Temperature	27.5°	43.2°	61.5°	79.8
d_4^t	.8641	.8515	.8368	.8219

c = 4.106 at 20° l = 1 dm.

Temperature	α_{6563}	α_{5893}	α_{5463}	α_{4861}	α_{4356}
11.9°	1.51°	1.91°	2.25°	2.91°	3.95°
20.4	1.50	1.88	2.24	2.89	3.88
46.8	1.47	1.85	2.17	2.84	3.87
70.5	1.46	1.83	2.15	2.80	3.82
95.5	1.43	1.79	2.11	2.74	3.75

Temperature	d_4^t	α^t_{5893}	$[M]^t_{5893}$
11.9°	.8768	1.91°	62.8°
20.4	.8699	1.88	62.3
46.8	.8444	1.85	63.1
70.5	.8295	1.83	63.6
95.5	.8085	1.79	63.8

IV. Effect of Temperature on Rotatory Power of d- Pinane dissolved in

(A) Nitrobenzene

Temperature	27.7°	41.9°	59.2°	79.1°
d_4^t	1.190	1.174	1.156	1.117

Temperature	15.0°	20.0°	25.0°	32.0°	40.0°
n_D^t	1.5490	1.5468	1.5440	1.5403	1.5372

$c = 3.417$ at 20°C. $l = 1$ dm.

Temperature	α_{6563}^t	α_{5893}^t	α_{5463}^t	α_{4861}^t
13.1°	.61°	.83°	.99°	1.32°
18.5	.60	.81	.97	1.26
36.7	.57	.76	.93	1.22
72.6	.52	.69	.84	1.12
95.2	.48	.65	.79	1.05

Temperature	d_4^t	α_{5893}^t	$[M]_{5893}^t$
13.1°	1.207	.83°	33.3°
18.5	1.200	.81	32.7
36.7	1.180	.76	31.2
72.6	1.141	.69	29.3
95.2	1.116	.65	28.2

(B) Mesitylene

Temperature	28.9°	54.6°	67.5°	79.1°
d_4^t	.8585	.8350	.8238	.8170

Temperature	15.0°	20.0°	25.0°	30.0°	35.0°	40.0°
n_D^t	1.4969	1.4944	1.4923	1.4901	1.4877	1.4855

$c = 1.814$ at 20° $l = 1$ dm.

Temperature	α_{6563}^t	α_{5893}^t	α_{5463}^t	α_{4861}^t	α_{4356}^t
19.6°	.30°	.44°	.52°	.70°	.97°
50.5	.25	.38	.46	.63	.87
75.8	.22	.35	.43	.59	.82
96.4	.21	.33	.39	.56	.78

Temperature	α_{5893}^t	d_4^t	$[M]_{5893}^t$
19.6°	.44°	.8665	32.7°
50.5	.38	.8390	29.9
75.8	.35	.8168	28.3
96.4	.33	.7986	27.4

V. Effect of Temperature on Rotatory Power of d- Carane dissolved in

(A) Nitrobenzene

Temperature	30.3°	44.3°	59.2°	77.5°
d_4^t	1.178	1.165	1.150	1.133

Temperature	20.3°	25.2°	29.5°	35.2°	40.8°	49.0°
n_o^t	1.5599	1.5478	1.5457	1.5431	1.5406	1.5364

c = 3.407 at 20°   l = 1 dm.

Temperature	α_{6563}^t	α_{5893}^t	α_{5463}^t	α_{4861}^t
12.6°	1.53°	1.93°	2.28°	3.00°
20.5	1.51	1.90	2.25	2.95
49.8	1.47	1.84	2.16	2.87
72.6	1.42	1.78	2.10	2.76
96.0	1.36	1.71	2.01	2.65

Temperature	d_4^t	α_{5893}^t	$[M]_{5893}^t$
12.6	1.195	1.93°	77.6°
20.5	1.188	1.90	76.9
49.8	1.160	1.84	75.9
72.6	1.138	1.78	75.2
96.0	1.116	1.71	73.7

(B) Mesitylene

Temperature	26.2°	40.1°	53.6°	75.2°
d_4^t	.8551	.8449	.8339	.8171

Temperature	20.5°	26.5°	31.0°	35.2°	39.4°
n_D^t	1.4971	1.4945	1.4923	1.4900	1.4877

c = 3.544 at 20°   l = 1 dm.

Temperature	α_{6563}^t	α_{5893}^t	α_{5463}^t	α_{4861}^t	α_{4356}^t
12.5°	1.47°	1.86°	2.20°	2.90°	3.80°
20.2	1.47	1.85	2.19	2.88	3.79
47.6	1.43	1.82	2.15	2.82	3.69
70.5	1.42	1.80	2.12	2.76	3.61
94.3	1.38	1.76	2.06	2.67	3.52

Temperature	d_4^t	α_{5893}^t	$[M]_{5893}^t$
12.5°	.8655	1.86°	72.0°
20.2	.8596	1.85	72.1
47.6	.8385	1.82	72.7
70.5	.8206	1.80	73.5
94.3	.8022	1.76	73.5

SUMMARY.

(1) The optical rotatory powers and rotatory dispersions of five terpenic hydrocarbons, viz. d- menthene, d- limonene, d- pinene, d- pinane and d- carane (?), have been examined in dilute solution in various polar and non-polar organic solvents.

(2) The rotatory powers of the weakly polar, unsaturated hydrocarbons, d- menthene and d- pinene are shown to be mainly related to the polarity of the solvent medium. The rotatory power of d- limonene, on the other hand is chiefly comtrolled by the refractive index of the solvent medium. In the former cases a few displacements occur and are explained on the basis of a minor refractivity effect being present. Similarly in the latter case, a minor polar effect appears to be present. In order to bring out the above relationships clearly, it is necessary to compare solvents of a similar type, by grouping them into an aromatic and an aliphatic series.

(3) The rotatory power of the non-polar saturated hydrocarbon, d- pinane has been examined in solution in thirty-six solvents of widely varying/

varying types. It is shown that the rotation is governed by the refractive index of the solvent medium, very slight displacements occurring due to the presence of a minor polar effect. In this case there is no need to divide the solvents into various groups according to their chemical types.

(4) Several physical theories of optical activity are examined from the point of view of their application to the experimental results obtained for d- pinane.

(5) Owing to the known difficulty of effecting a satisfactory separation of unsaturated hydrocarbons from saturated cyclopropane derivatives, some doubt is cast upon the identification as d- carane of the hydrocarbon obtained by distilling pulegone hydrazone over caustic potash. An examination of the rotatory power of this product in various solutions reveals irregular variations.

(6) The effect of temperature variations upon solutions of the above compounds in a strongly polar and a non-polar solvent respectively has been determined. The observed results in the majority/

majority of cases, may be explained on the basis of the changes in the degree of solute-solvent association and in the refractive index of the mixture. Similar explanations hold for the variation in rotatory powers of the above compounds with changes in concentration in certain solutions.

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