

THE OPTICAL ROTATORY POWER OF CERTAIN  
TARTRATES.

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Thesis submitted for the degree of Ph. D. of

Glasgow University

by

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# THE OPTICAL ROTATORY POWER OF CERTAIN TARTRATES.

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## GENERAL INTRODUCTION.

## GENERAL INTRODUCTION.

Although Biot discovered in 1815 that certain organic compounds possess the power of rotating the plane of polarised light, it was not until the close of the century that the problem of optical activity began to receive systematic study. It was known, however, that the rotatory power varies with the wave-length of the polarised light, with change of temperature, with change of solvent, and with alteration in solution concentration, but the importance of these factors in the study of polarimetric behaviour was not fully appreciated. Frankland (J.C.S., 1894, 65, 760) urged that more consideration should be paid to the effect of temperature on rotation. Winther (Zeits. phys. Chem., 1905, 52, 200) repeated Frankland's plea in a somewhat stronger manner. He stated that much useless work would be done if the old traditional methods of taking the rotation for a single wave-length (generally for  $\text{Na}_\text{D}$ ) and for a single temperature (generally room-temperature) were continued, and advocated that rotation should be measured for different wave-lengths and over a range of temperature. Such measurements, he maintained, would be better able to reveal relationship between the optical rotatory powers of related chemical compounds.

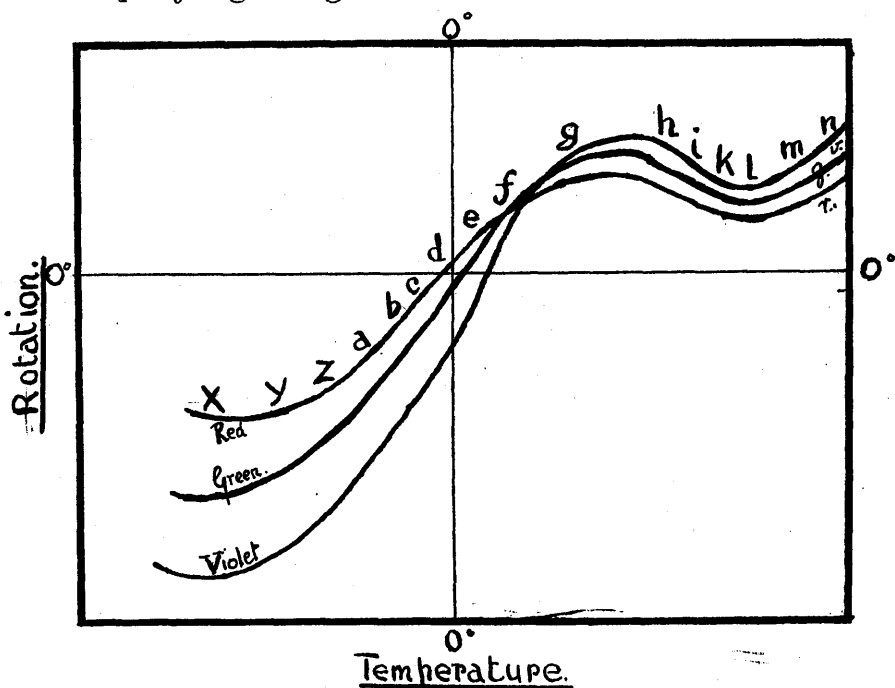
The data began to accumulate very rapidly, but it was some time before any generalisation was put forward. Some investigators confined their attention to the study of the variation in rotation with change in wave-length, external conditions being constant, and sought to express this dispersion data in a mathematical form. Biot's inverse square law (Mem. Acad. Sci., 2, 85),  $\alpha = \frac{k}{\lambda^2}$ , put forward in 1817, was re-expressed and given a theoretical significance by Drude (Lehrbuch der Optik, 1900, 380). The formula,  $\alpha = \sum \frac{k_n}{\lambda - \lambda_n}$ , which had been verified for quartz, was first applied to organic compounds by Lowry and Dickson (J.C.S., 1913, 103, 1067), and since then has been used in the analysis of the dispersion of many substances. Another modification of this dispersion equation was recently advanced by ~~Khuh~~ (Zeits. phys. Chem., 1929, 4B, 14; Trans. Far. Soc., 1930, 26, 293).

Other workers preferred to seek some method of interpreting the diverse phenomena by considering the various factors which influence optical activity.

After reviewing the knowledge of the optical rotatory power of the tartrates and pointing out characteristic features in their temperature-rotation curves, Professor Patterson (J.C.S., 1913, 103, 145) suggested a method of harmonising, qualitatively, the relation between temperature and rotation for light of all refrangibilities of the tartrates, both in the homogeneous state and in solution. This generalisation

was developed in subsequent papers (J.C.S., 1916, 109, 1140 ; Proc. Roy. Soc. Edin., 1918-19, 39, 18 ).

Professor Patterson suggests that, if the rotation of tartaric acid or its derivatives could be examined over a sufficient range, the temperature-rotation curves for different colours of light would be periodic in character, showing a number of maxima and minima as represented in the accompanying diagram.



Unfortunately, the observation of rotation over such a range is limited by temperature considerations and the stability of the compounds concerned, and thus the region to that can be examined experimentally is small.

It is postulated, however, that the effect of solvents or of change in constitution is to cause a displacement in the fundamental temperature-rotation curves as a whole to

a higher or a lower temperature with a change in the amplitude of the curves. The high- and the low-temperature regions of the fundamental temperature-rotation curves can thus be obtained and examined experimentally.

For example, the temperature-rotation curves for ethyl tartrate (Patterson, J.C.S., 1916, 109, 1145) are of the same form as the region e f g in the diagram, whilst the curves for a solution of the same compound in quinoline (ibid.) correspond to the portion i k l m. The effect of the quinoline is similar to that of considerable increase in the temperature values of the region of observation, with a certain amount of change in the amplitude of the curves, dependent on their displacement from the axis of zero rotation.

The recognition of a fundamental set of temperature-rotation curves for tartrates gives a method of correlating ~~the~~ their diverse optical behaviour in a qualitative manner. It is also suggested that such a scheme can be applied to describe the behaviour of other active compounds.

Immediately after this qualitative generalisation was put forward, Armstrong and Walker (Proc.Roy.Soc., 1913, A, 88, 392) introduced the "characteristic diagram" to show the relationship between the rotation phenomena exhibited by solutions of fructose and the proportions of the isodynamic forms present. They found that the dispersion data for optically active compounds could be represented on such a



diagram. Within the next year, Pickard and Kenyon (Proc.C.S., 1913, 296; J.C.S., 1914, 105, 843, 1115, 2262, 2677) succeeded in establishing the use of this diagram as a means of correlating the specific rotation data for a compound in the homogeneous state as well as in solution. They also found that the rotatory powers of many derivatives of similar constitution could be incorporated on the same diagram. Indeed, in summing up, Kenyon (J.C.S., 1914, 105, 2235) goes further, saying that "the characteristic diagram seems to afford a convenient method of finding out whether a given group of homologous compounds all have the same configuration."

Subsequent work by Pickard and Kenyon, Frankland, Patterson, and others has shown how useful this method is.

Although constructed at first from theoretical considerations, the characteristic diagram is now only regarded as an empirical but convenient method of summarising dispersion data. It shows that by plotting the rotation values for different wave-lengths relative to those for a particular wave-length (in general,  $Hg_g$ ) the smooth curves so obtained for each colour indicate a relationship in the dispersion curves which is not appreciably altered by change of temperature or by derivative formation. Patterson has shown (J.C.S., 1916, 109, 1202) that the diagram cannot be expected to represent accurately the rotation dispersion of a compound under all conditions, and many exceptions have been noted

in the literature. Despite this, the regularity with which the method may be applied seems to indicate that there is some fundamental significance to be attached, a significance probably not unconnected with the spatial relationships of those atoms directly associated with the asymmetric atom.

In 1916, Professor Patterson (J.C.S., 1916, 109, 1181) suggested a more convenient method of drawing the characteristic diagram, and this is the method now used. A horizontal line is taken as reference line, and along it are plotted the rotations for some particular colour, generally mercury-green. At any given rotation for mercury-green there are plotted above and below, not the actual rotations for the other colours involved, but the differences between these rotation values and the corresponding values for mercury-green. Positive values are always plotted upwards from the reference line and negative values downwards. This means that the actual rotation at any point on the line for a given colour is the horizontal distance from the zero point plus the vertical distance from the reference line. Reference to a characteristic diagram in the main part of this thesis will illustrate how these directions are carried out.

These two methods -- the conception of a fundamental temperature-rotation curve, and the characteristic diagram -- afford, in the one case, a qualitative,

and, in the other, a quantitative means of expressing the results of the temperature-rotation determinations, and consequently both are employed for the correlation of the results obtained in the investigations described in Parts I and II of this thesis.

The subject matter of this thesis has been set out in two parts : Part I concerns " The optical rotatory power of the Nitrobenzyl Tartrates and their derivatives ; and Part II gives an account of " The optical rotatory power of Methyl, Ethyl, n-Propyl, and n-Butyl Dibenzoyl-d-tartrates. "

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PART I.

THE OPTICAL ROTATORY POWER OF THE NITROBENZYL TARTRATES

AND THEIR DERIVATIVES.

THE OPTICAL ROTATORY POWER OF THE NITROBENZYL TARTRATES  
AND THEIR DERIVATIVES.

The three isomeric dinitrobenzyl tartrates and their diacetyl and dibenzoyl derivatives were prepared in order that their optical rotatory powers might be determined and correlated in such a way as to make a definite contribution to our knowledge of the phenomenon of optical activity.

Unfortunately, all these compounds, with the exception of di-o-nitrobenzyl diacetyl-d-tartrate of melting point 75°C., melt at temperatures over 100°C., and thus determinations of the effect of temperature on the rotation of these tartrates in the homogeneous state, although not altogether impossible to make, were considered to be inconvenient. For this reason the investigation had to be carried out using suitable solvents. The only two media found to act in this capacity for all of these compounds are pyridine and quinoline. Since the results obtained would probably afford a means of making definite comparisons, it was decided almost at the commencement to use throughout the research solutions of approximately the same concentration, and, owing to the fact that several of these tartrates are not very soluble, this concentration had, of necessity, to

be as low as 1.5--1.6%. For the more soluble ortho-compounds use was also made of nitromethane and ethylene dibromide as solvent media.

When either pyridine or quinoline was employed for temperature-rotation determination, care had to be taken not to raise the temperature too high; for, it was noticed that about 80°C. a brown colour develops in such solutions, indicating, therefore, that a reaction of some sort occurs under these conditions. This reaction, which occurs more readily for pyridine solutions and which quite probably is a decomposition, was not investigated. If the temperature of the solution is not raised high enough to give this effect, it is found that, on cooling, the rotation reverts to its original values, thus indicating that no change in the solute has taken place. Neither nitromethane nor ethylene dibromide when used ever showed a like effect.

Although, in the following pages, the results for all the para-compounds are treated collectively, as also are those for the meta-derivatives, it has been found much more convenient, on account of their complexity, to discuss in separate sections the data for each of the ortho-compounds.

The details of the preparations and of the temperature-rotation determinations for, in general, six wave-lengths are given in the experimental section, page 44.

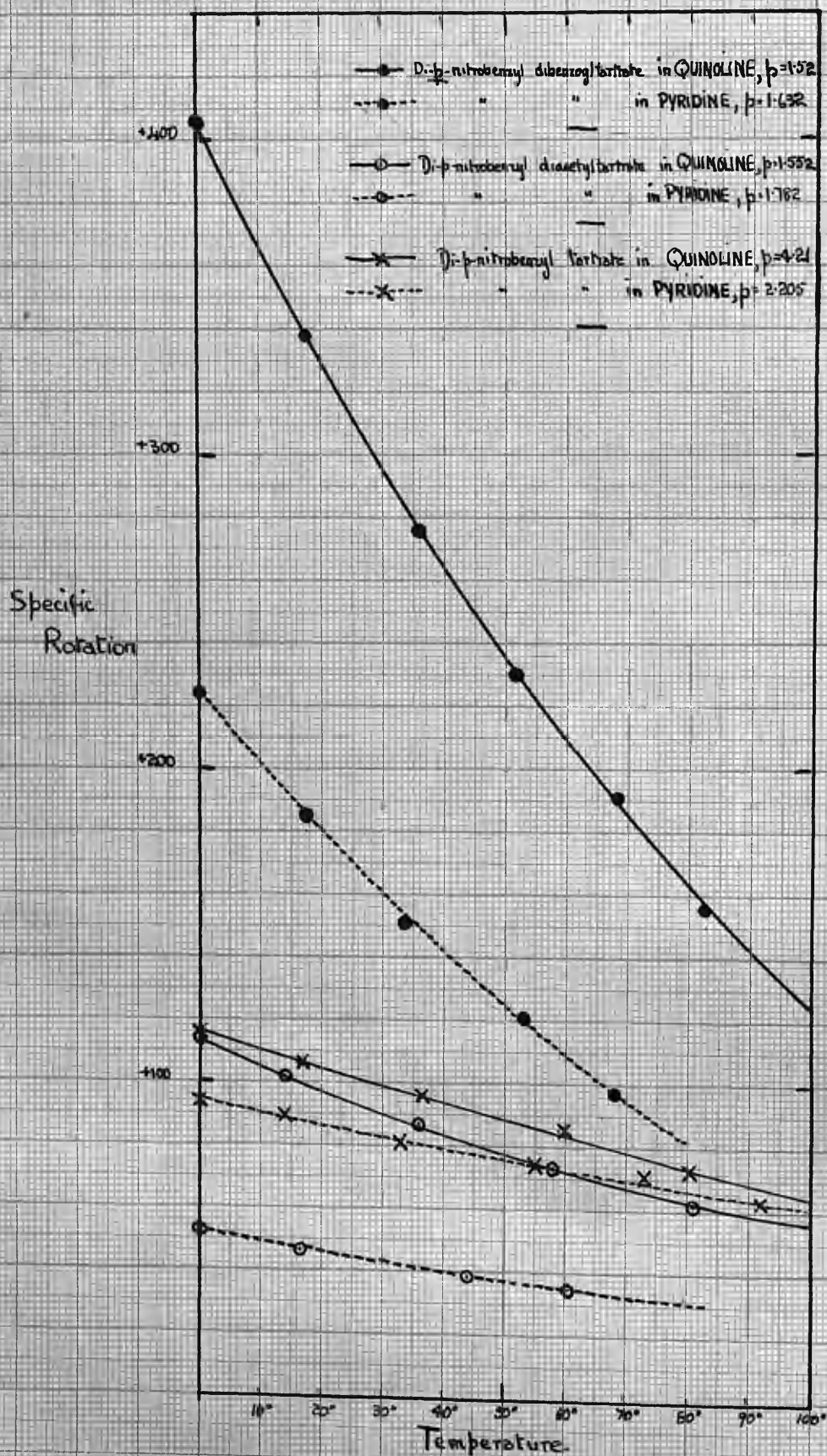


FIG. 1. Temperature-rotation curves for *p*-nitrobenzyl tartrates.

Di-p-nitrobenzyl d-Tartrate and Derivatives.

Di-p-nitrobenzyl tartrate and its diacetyl and dibenzoyl derivatives were examined in pyridine and quinoline solutions, and, in order that the relationship between all the results may be clearly demonstrated without any undue confusion, the T-R\* curves for mercury-green ( $\lambda = 5461 \text{ ÅU}$ ), alone of all the six wave-lengths employed, are given in Fig. I. Many points are evident.

The acetyl derivative is less active and the benzoyl derivative more active than the parent ester when examined in the same solvent.

Quinoline as a solvent has, in all cases, a more elevating effect on the rotation than pyridine, and for each compound the gradient of the T-R curve is greater for the quinoline solution.

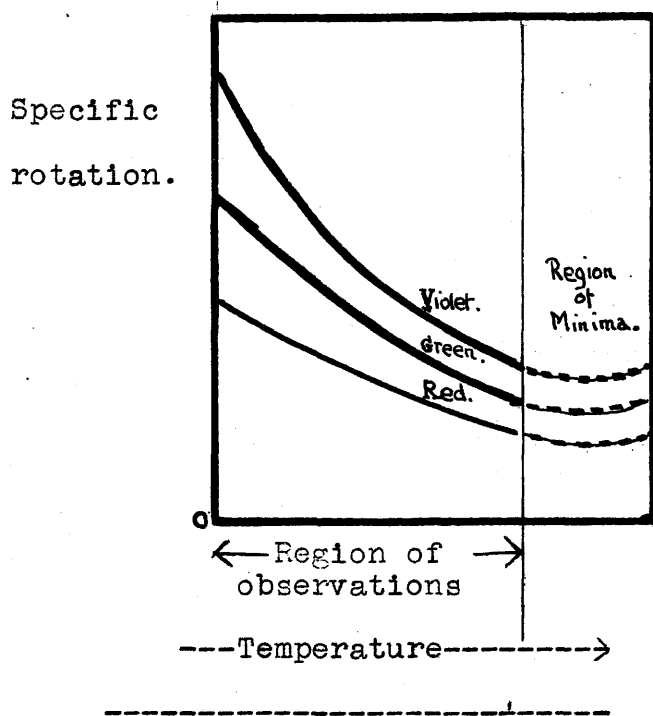
All the curves, which are confined to the positive region of rotation, are convex to the point of origin of the graph, and no curve shows any easily identifiable characteristic, such as a region of maximum, point of inflexion, region of minimum, or intersection of the axis of zero rotation. Even when, for each solution, the complete set of T-R curves for all six wave-lengths is examined, nothing definitely characteristic is revealed, except perhaps that specific rotation is greatest for the lowest wave-length.

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\*Temperature-rotation.



There are no signs of any tendency to intersect, and it would appear that all the curves seem to be approaching a region of minima, which quite probably occurs, in all cases, on the positive side of the line of zero rotation. This feature in the complete sets of T-R curves can be represented diagrammatically, as in the accompanying diagram.



From Fig I, it is apparent, that, if this is a correct interpretation of the results, the minimum for green light must occur at different rotation values for each solution of these compounds : a point which cannot be developed much further from the data at hand.

With regard to the abnormally high values of

specific rotation possessed by the quinoline solution (p = 1.522) of di-p-nitrobenzyl dibenzoyltartrate, it is to be pointed out that these are the highest ever recorded for any tartrate.

The values for the specific rotation for green and for violet at 0°C, are

$$[\alpha]_{5461}^0 + 405.8^\circ \quad \text{and} \quad [\alpha]_{4358}^0 + 792.7^\circ$$

Krecke (Arch. Néerland, 1872, 7, 119) found that, in aqueous solution, the specific rotatory power of tartar emetic is extraordinarily great. Lowry and Austin (Phil. Trans., 1922, A, 222, 249) re-examined the rotation of potassium antimonyl tartrate in aqueous solution, and from their results, it is found that the specific rotation values are ( for 5.516g. in 100cc.)

$$[\alpha]_{5461}^{20} + 171.8^\circ \quad \text{and} \quad [\alpha]_{4358}^{20} + 304.1^\circ$$

Thus the quinoline solution of the nitrobenzyl dibenzoyltartrate is much more active than the classical example of a very active tartrate.

However great the rotatory power of this solution is at 0°C, it is very sensitive to temperature change. On passing from this temperature to 100°C. the rotation diminishes by about 290°, a very remarkable decrease.

All sets of T-R curves for every solution are similar in feature to that region of the fundamental T-R curve for tartrates which is specified as 1 k. (Page 3).

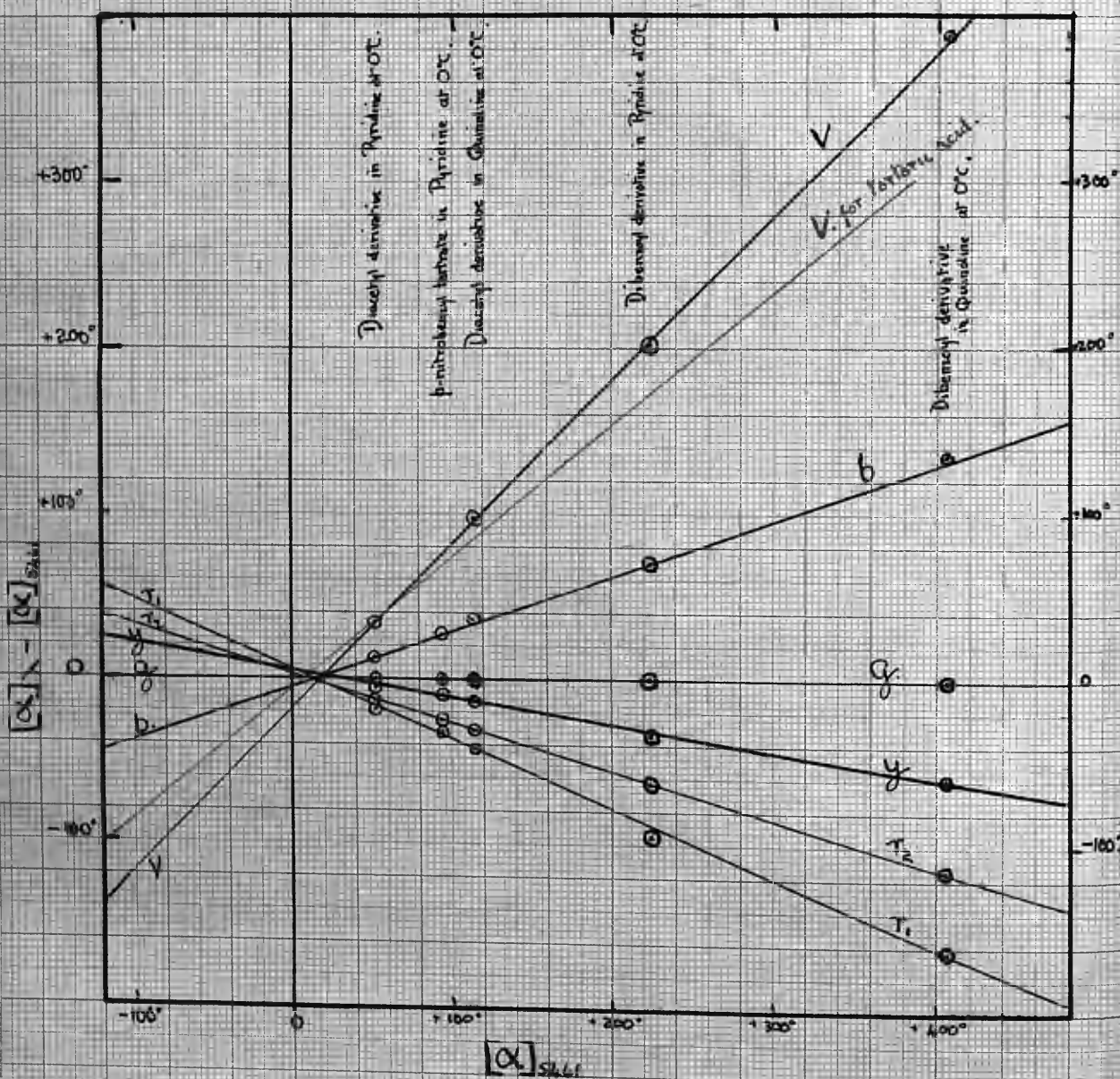


FIG. II. Characteristic diagram for p-nitrobenzyl tartrate and its derivatives.

Although, as has already been pointed out, all the T-R curves seem to be tending towards minima of positive rotation, no solvent was found which depresses the rotation of any of the compounds to show such a region as k l m.

Fig. II gives the characteristic diagram constructed from the rotation values of the solutions at 0°C. only. The other values fit quite closely on to the lines, and there are no apparent irregularities. The rational zero (Patterson, J.C.S., 1916, 109, 1183) for violet and green is approximately +14°, whilst the dispersion ratio  $v/g$  calculated with reference to this value is 1.985. For purposes of comparison, it has been found most convenient to refer to the values for violet and green, since variations in the dispersion ratios are then quite apparent. Adopting the characteristic diagram for tartaric acid --based on the results of Lowry and Austin (Phil. Trans., 1922, A, 222, 249)-- as a standard to which all tartrate diagrams should be compared, the violet line for this is given in Fig. II. It is clearly shown that the tartrate dispersion is modified not a little in the p-nitrobenzyl compounds.

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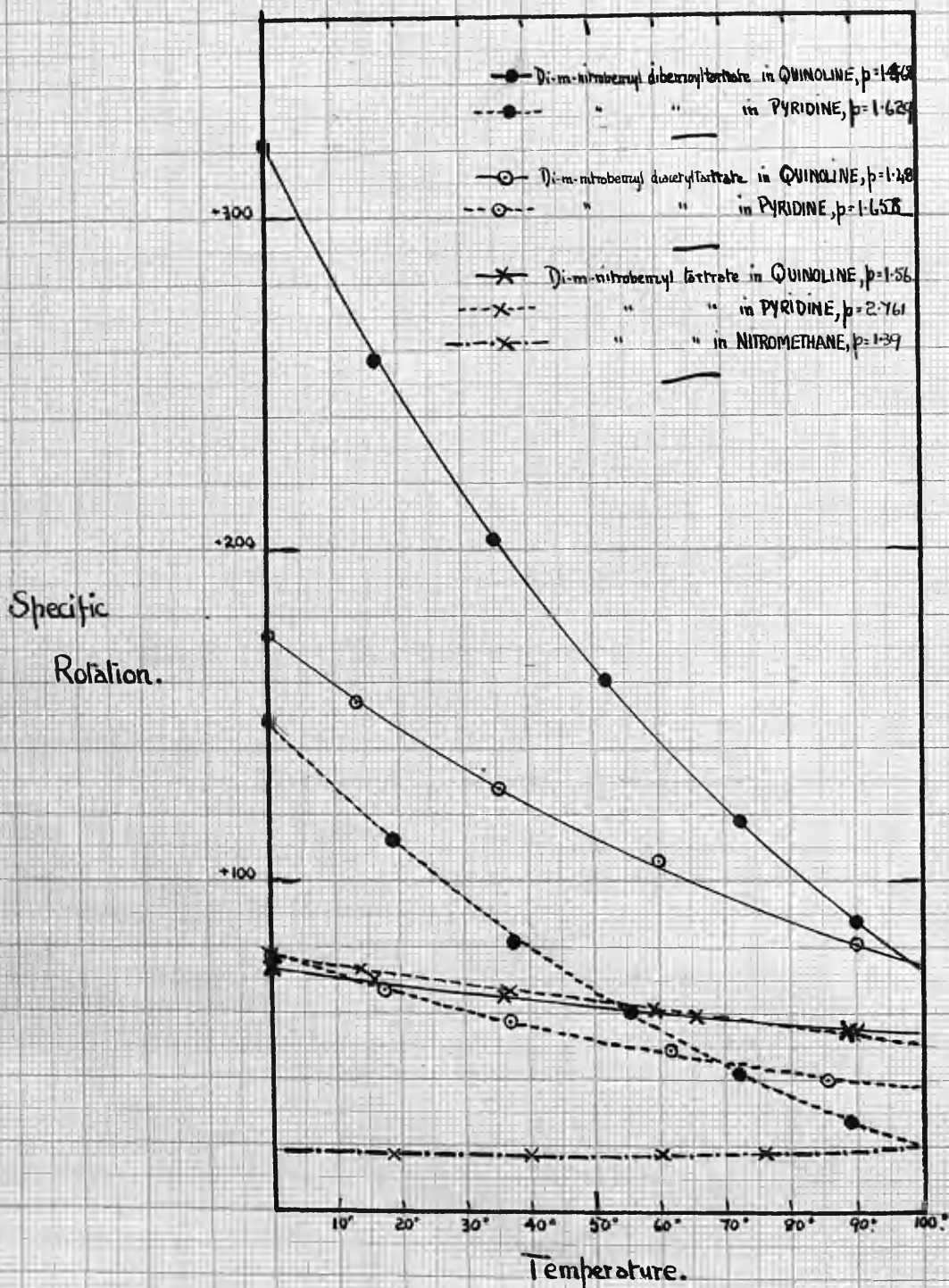


FIG. III. Temperature-rotation curves for di-m-nitrobenzyl tartarate and its derivatives.

### Di-m-nitrobenzyl d-Tartrate and Derivatives.

This nitrobenzyl tartrate and its diacetyl and dibenzoyl derivatives were examined polarimetrically in pyridine and in quinoline. The m-nitrobenzyl tartrate itself, being, unlike its para-isomer, soluble in nitromethane, was also examined in that solvent. The T-R curves for mercury-green, given in Fig. III, are similar to those for the p-compounds (c.f., Fig. I), with slight variations.

All curves are for positive values of rotation.

The di-m-nitrobenzyl diacetyltartrate is more active than the parent nitrobenzyl tartrate, and the dibenzoyl derivative is most active of all.

Where the m-nitrobenzyl tartrate is concerned, there is but little difference between the pyridine and the quinoline curves, the former being initially the higher, but cutting the other at about 50°C.. The nitromethane solution is not very active. For the other two compounds, the quinoline solutions in each case are more active than the pyridine.

All the T-R curves are convex to the origin of the graph and to the axis of zero rotation. With the exception of the nitromethane solution of m-nitrobenzyl tartrate which shows a minimum of positive rotation, all other rotation curves descend towards the zero line with increase of temperature, and no T-R curve possesses any identifiable

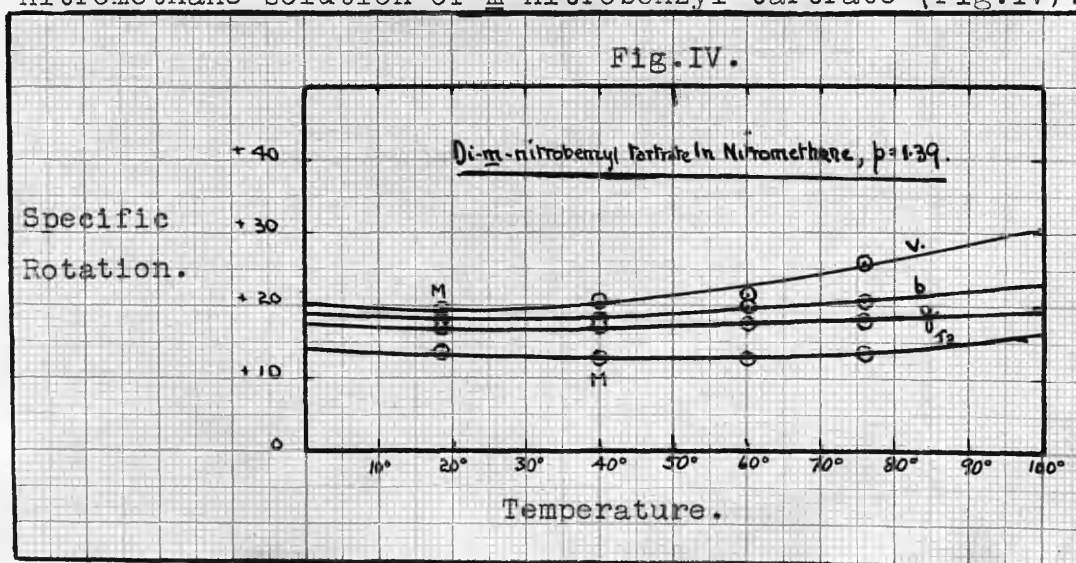


characteristic. It is to be noted, however, that, when the value of rotation at  $0^{\circ}\text{C}$ . for each compound varies with change of solvent, the gradient of the T-R curve,  $\frac{d[\alpha]}{dT}$ , is greater the higher the initial rotation. This point is well illustrated by the results for the three solutions of di-m-nitrobenzyl tartrate.

The quinoline solution of the dibenzoyl derivative is highly active, but not to the same extent as its para-isomer.

The values of the specific rotations at  $0^{\circ}\text{C}$ . are  $[\alpha]_{5461}^0 +322.3^{\circ}$  and  $[\alpha]_{4358}^0 +606.6^{\circ}$ .

When for each solution the T-R curves for all six wave-lengths are examined, it is seen that, when the rotations decrease with increase in temperature, the curves for the shortest wave-lengths being uppermost, there is no intersection. The indication is rather that, in all cases, the curves are falling towards a region of minima, which is beyond the range of experimental observation except in the case of the nitromethane solution of m-nitrobenzyl tartrate (Fig.IV).



From this graph it will be seen that the rotation is highest in value for light of the lowest wave-length, the rotation at any temperature decreasing in magnitude in the order violet, blue, green, red. The minimum for violet occurs at a lower temperature and at a higher value in rotation than for the other colours. Indeed, it seems to be characteristic of such a region of minima of positive rotation in the T-R curves that the minimum moves to a higher temperature and a lower rotation with increase in wave-length ; for ,this conclusion is in accordance with the features observed in the few other recorded instances of such a region. Iso-Butyl diacetyl-d-tartrate in the homogeneous state shows this relation of minima of positive rotation quite clearly, whilst for the same compound in s-tetrachlorethane ( $p = 20.034$ ) and for ethyl tartrate in quinoline ( $p = 13.601$ ) the region is not so well defined (Patterson, J.C.S., 1916, 109, 1139). The results given by Pickard and Kenyon (J.C.S., 1913, 103, 1934) for d-ethyl-n-decylcarbinol are only for two colours, and are insufficient to show anything definite.

By consideration of the foregoing data, it seems reasonable to conclude that, in general, the T-R curves obtained for the solutions of m-nitrobenzyl tartrate and its derivatives correspond to the portion i k of the fundamental T-R curves for tartrates (page 3), and that the T-R minima for the nitromethane solution of the parent ester



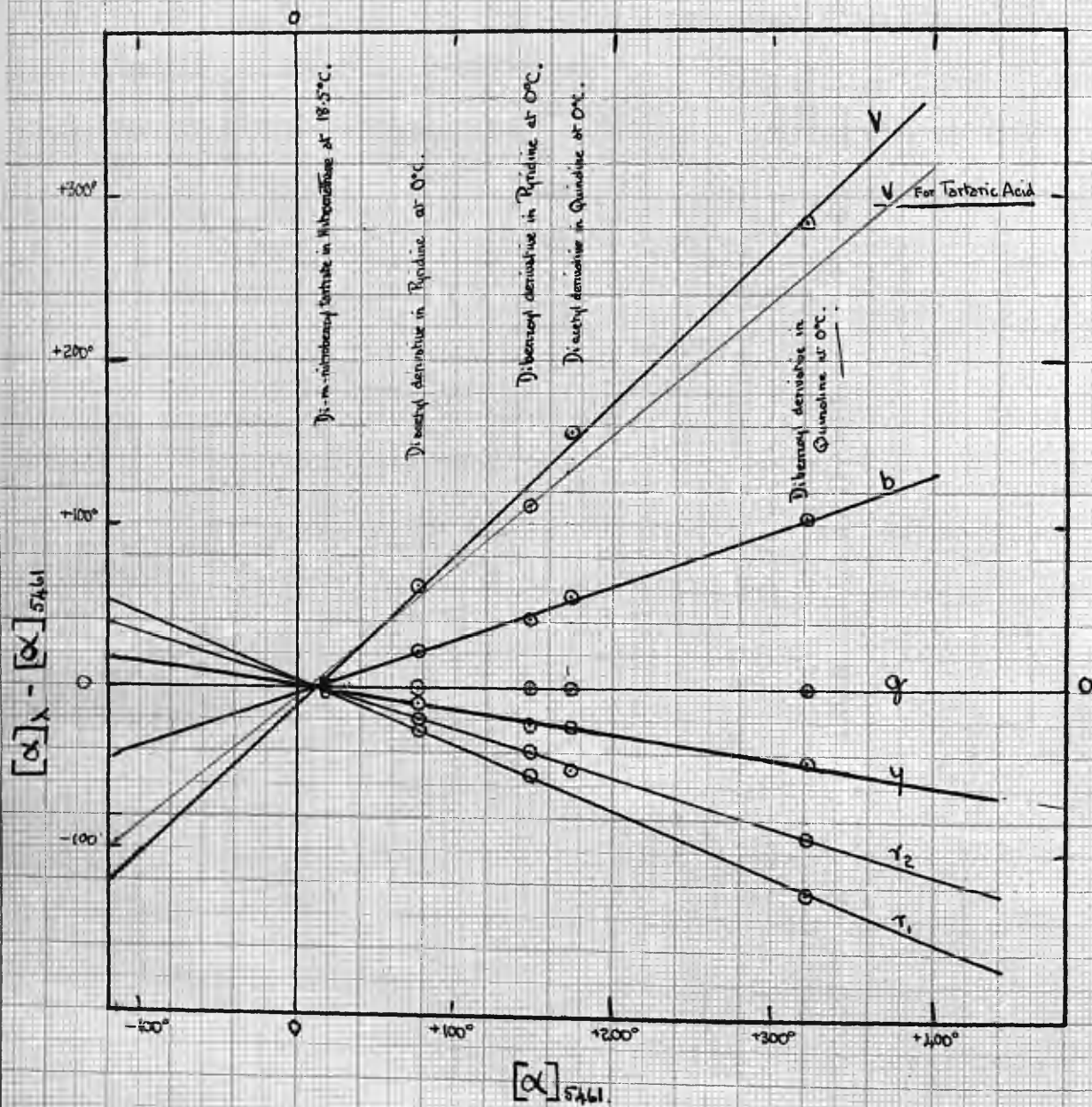


FIG. V. Characteristic diagram for di-m-nitrobenzyl tartrate and its derivatives.

is indicative of the region k l m. This correlation is the same as that for the p-nitrobenzyl compounds, and means that, in general, with the nitro group in either the para- or the meta-position there is very little alteration in the rotatory power of the isomers.

The characteristic diagram (Fig.V) for the meta-compounds has been constructed in the same manner as in the previous case. The dispersion data do not, however, fit so well. The rational zero is  $+10^\circ$ , and the rational dispersion coefficient for  $v/g$  is 1.923, showing a little difference in the dispersion relationship from that of the para-isomers. The 'v' line for tartaric acid, given for purposes of comparison, indicates that the tartrate dispersion is modified in the m-nitrobenzyl tartrates.

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#### Di-o-nitrobenzyl d-tartrate.

By reason of their appearance, the T-R curves for di-o-nitrobenzyl tartrate in solution in nitromethane, quinoline, and pyridine are given in full( See Figs.VI and VII). In all of these, the curves for the longest wave-length are nearest the axis of zero rotation and the rest of the curves are displaced in the normal order. All the rotations are positive.

FIG. VI. T-R curves for di-*o*-nitrobenzyl tartrate.

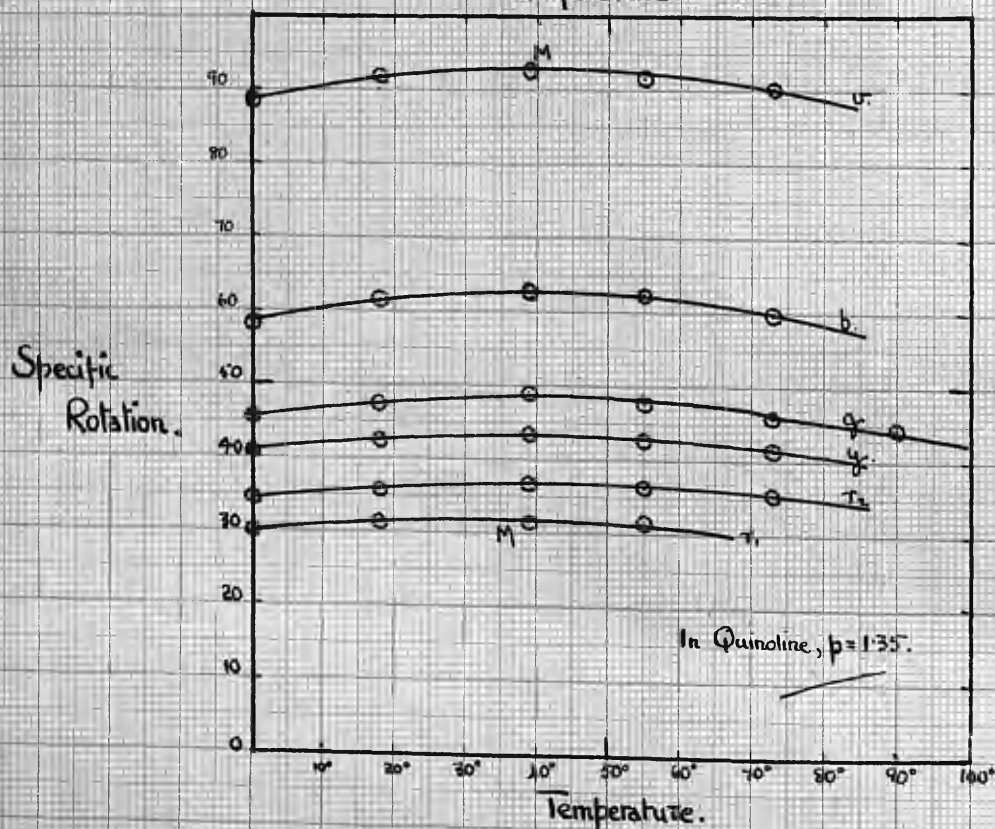
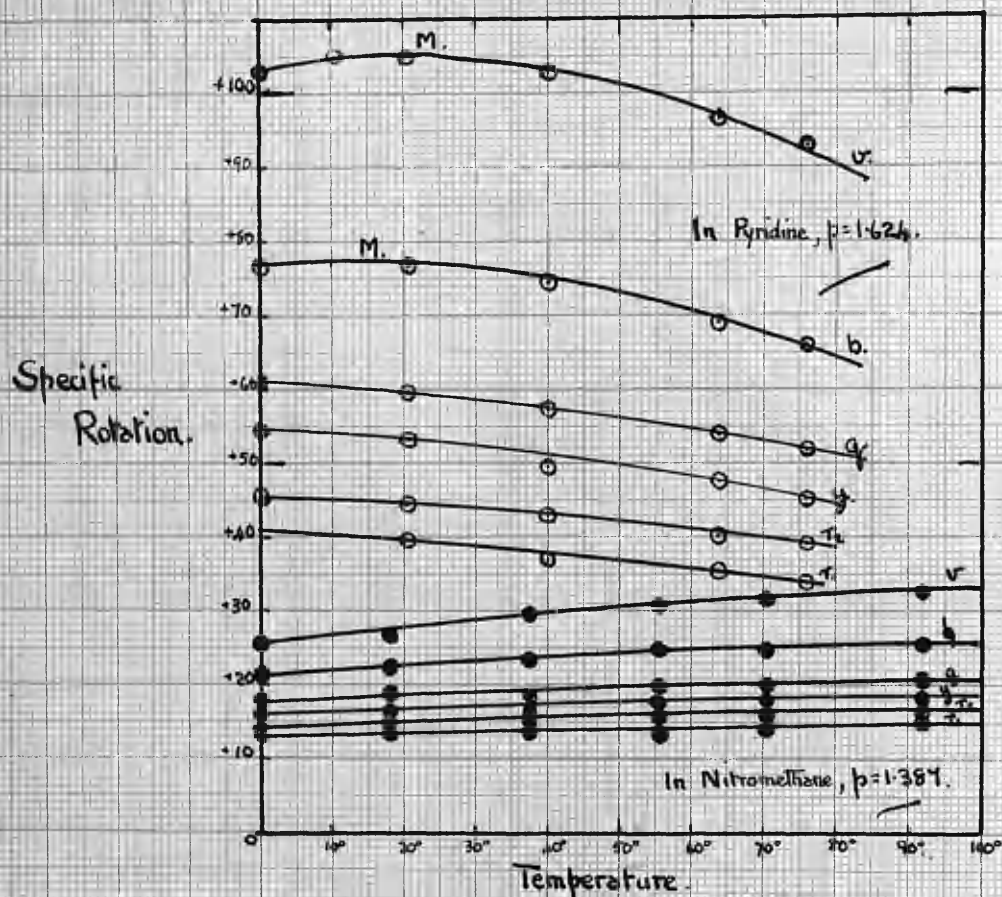


FIG. VII. T-R curves for di-*o*-nitrobenzyl tartrate.

For nitromethane solution ( $p = 1.387$ , Fig. VI), with rise of temperature, the specific rotations for the various wave-lengths increase but little, and show a tendency to approach a region of maxima of positive rotation, which would probably be reached, if examination could be effected to such a temperature, at about  $150^{\circ}\text{C.}$ , when the specific rotation for green would have a value of approximately  $+22^{\circ}$ . Although on the fundamental T-R curves for tartrates this series of maxima corresponds to the portion g h, to the right of the region of visible anomaly, e f g, there is no indication from the results for the nitromethane solution that any of the T-R curves intersect with one another at some temperature less than  $0^{\circ}\text{C.}$  The dispersion curve for this solution at  $0^{\circ}\text{C.}$  is of the normal type, and, when the reciprocal of the rotation is plotted against the square of the wave-length, there is very little deviation from the straight line relationship expected for "simple" dispersion. Which means that the evidence for intersection of the T-R curves at a lower temperature is negative.

The T-R curves for the quinoline solution ( $p = 1.35$ , Fig. VII) are altogether further displaced from the zero axis than those for nitromethane. Maxima of rotation are evident for all six wave-lengths, and, although not well defined, it may be that the maximum for the longest wave-length occurs at the lowest temperature -- a feature of such

regions. The region of maxima lies between the temperatures of 30\* and 40°C. The trend of the curves from 0° to 30°C does not suggest that any intersection takes place at a lower temperature than zero.

For the pyridine solution ( $p = 1.624$ , Fig.VI) the rotation curves are slightly higher, but of the same type. Maxima are only apparent for violet and blue, and the maximum for violet light is at a higher temperature (20°C.) than that for blue (11°C.). The fact that no maxima appear in the curves for the other wave-lengths, is a definite piece of evidence in favour of the generalisation on the movement of the maximum of positive rotation : the maximum moves to a higher temperature and higher rotational value with decrease in wave-length.

Although in no case can it be shown that there is a region of visible anomaly on the low-temperature--sides of the curves for any of these solutions, the T-R curves are all of the same type and may be referred to the same region of the fundamental T-R curves for tartrates, the region g h.

Comparing the effects of the solvents, pyridine, of the three, gives the highest rotations, the quinoline solution is slightly less active, whilst the nitromethane gives a solution with small rotatory power.

Referring once more to Figs.VI and VII, it will





be seen that the movement of the region of maxima in passing from one solvent to the other, from nitromethane to quinoline, and thence to pyridine, is to a lower temperature and a higher rotational value --a movement in accordance with previous observations for similar regions (Patterson, J.C.S., 1908, 93, 1844 et seqq.). This point is clear when the values for one wave-length only are considered. Thus, the values for green being considered, for nitromethane the maximum may occur at 150°C. and +22° specific rotation, for quinoline it occurs at 40°C. and +49°, and for pyridine the maximum for green probably would be found at -5°C. with a value of +61.5°.

From a consideration of this movement of the region of maxima, it can therefore be said that pyridine as a solvent tends to move the fundamental T-R curves as a whole further towards a lower temperature than does quinoline, which has a greater effect than nitromethane.

From the characteristic diagram (Fig.VIII), it is seen that the rotation values do not fit on smooth lines, and that this irregularity of the points gives little indication as to the position of the normal violet line for di-o-nitrobenzyl d-tartrate. This is to be expected for such regions where the curves for different colours reach maximum values at different temperatures (c.f., Patterson, J.C.S., 1916, 109, 1195 et seqq.). As before, the violet

FIG. IX. T-R curves for di-*o*-nitrobenzyl diacetyl-*d*-tartrate.

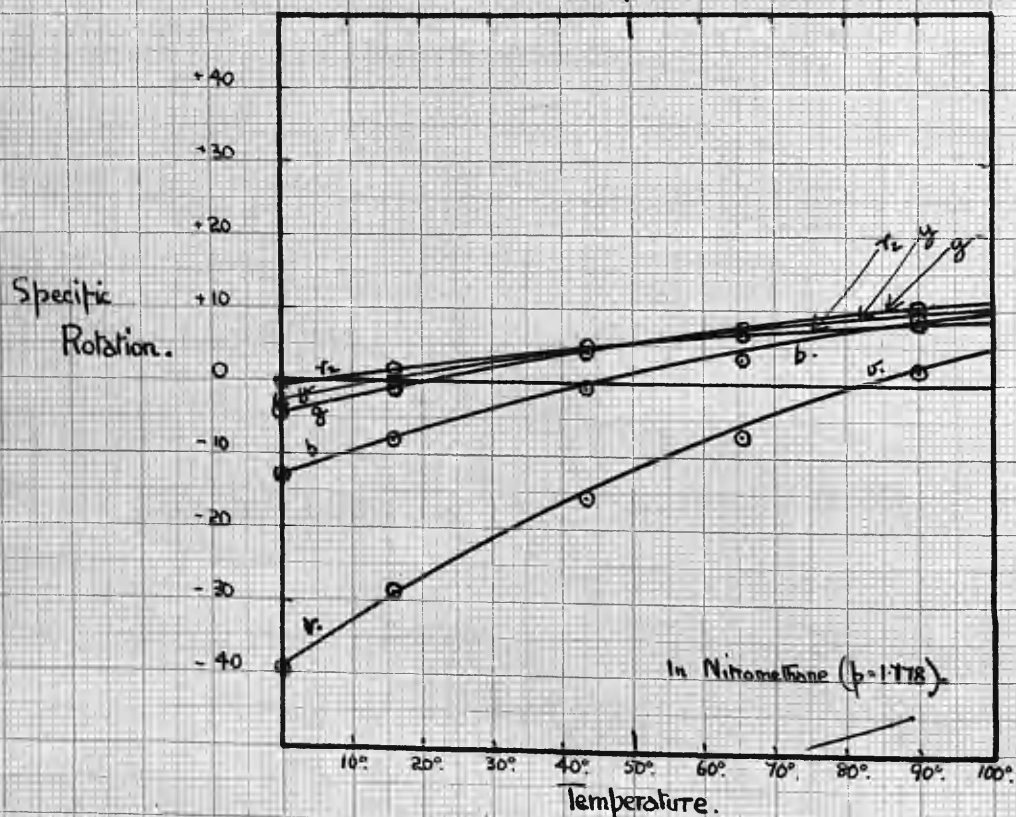
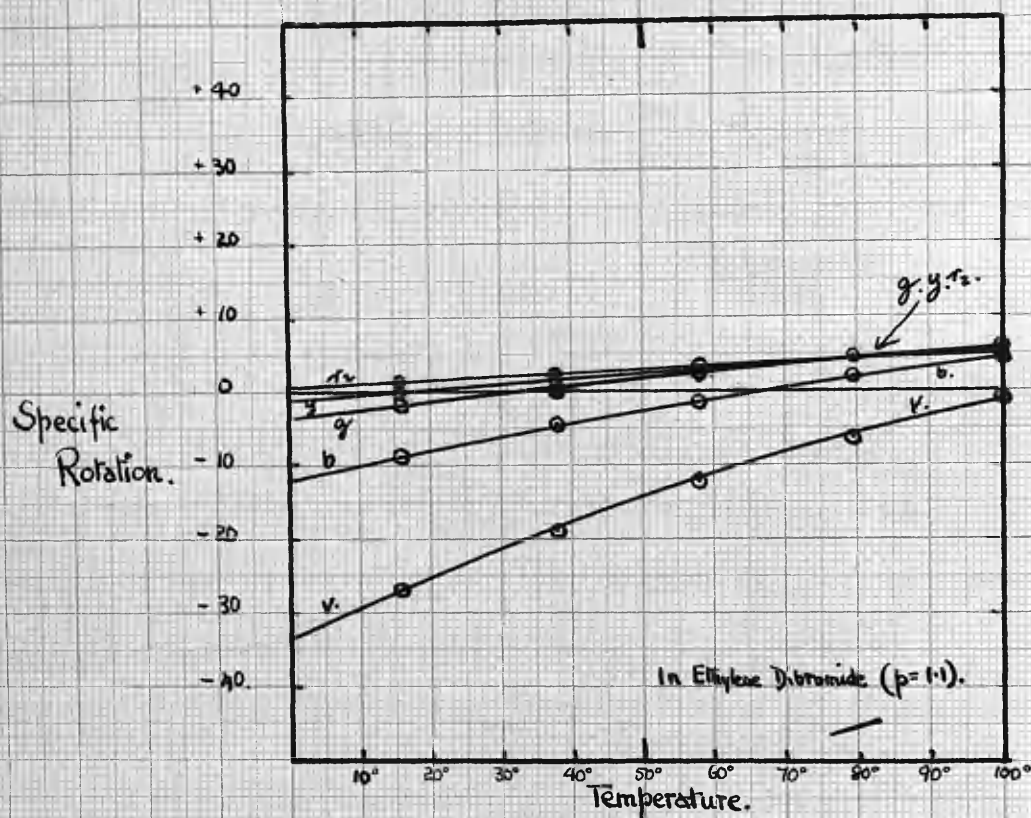


FIG. X. T-R curves for di-*o*-nitrobenzyl diacetyl-*d*-tartrate.



line for tartaric acid shows that there is an appreciable modification of the tartaryl dispersion ratios.

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Di-o-nitrobenzyl Diacetyl-d-tartrate.

The polarimetric behaviour of this ester was first of all determined for the solvents quinoline, pyridine, nitromethane and ethylene dibromide, and the complete results, for the five wavelengths used, are given in IX, X, and XI. The curves for pyridine, nitromethane, and for ethylene bromide, are all similar to one another. Those for quinoline are singular in that they are quite unlike the others in general appearance.

The solutions in pyridine, in nitromethane, and in ethylene dibromide give rotation curves rising from negative, or low positive, values and intersecting with one another with increase of temperature. The solutions give regions of visible anomaly entirely in the positive region of rotation. In no case, however, is the intersection complete.

Considering the results for these three solutions, with change of solvent there is an alteration in the amplitude of the curves; not very much, it is true, but there

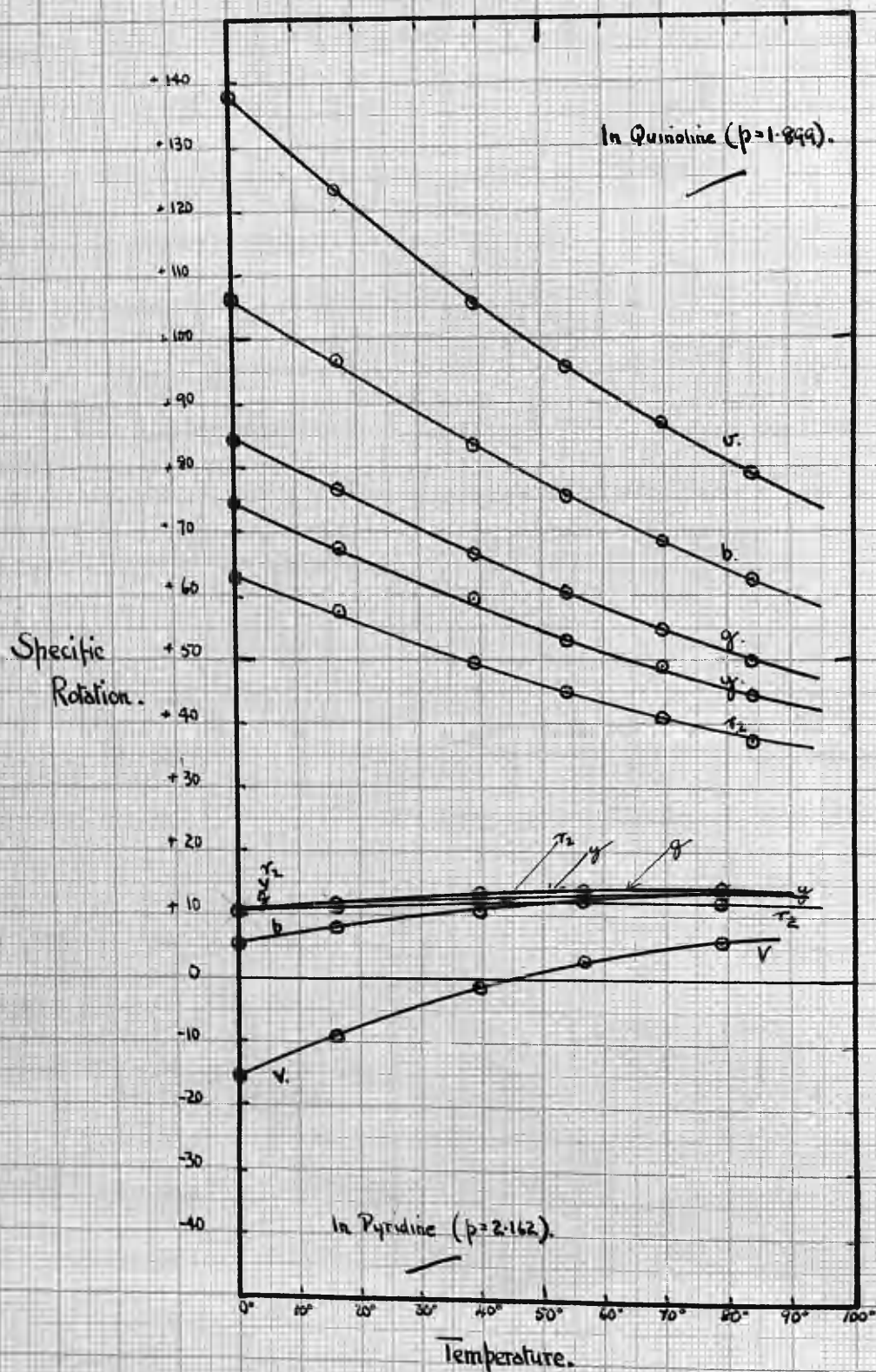


FIG. XI. T-R curves for di-o-nitrobenzyl diacetyl-d-tartrate.

is an indication that, in changing from ethylene bromide to nitromethane, and thence to pyridine, the specific rotation values of the points of intersection for two wavelengths increase, and the temperature at which the intersection takes place decreases. For example, the T-R curves for blue and green light cut at the following values of specific rotation and temperature :-

	Specific Rotation.	Temperature.
Ethylene bromide.....	+8°.....	115°C.
Nitromethane .....	+14°.....	110°C..
Pyridine .....	+15°.....	75°C.

It is most likely that the curves for violet and green intersect in a similar order.

The curves for the three solutions -- ethylene bromide, nitromethane, and pyridine --- seem to be tending, after intersection, towards a region of positive maxima. Indeed, in the curves for the pyridine solution (Fig.XI), a maximum is evident in the curve for red ( $r_2$ ), at 50°C. and at a value of +13° specific rotation.

Although these curves are not exactly the same as those observed for ethyl tartrate in the homogeneous state (Patterson, J.C.S., 1916, 109, 1145), they are similar, and may thus be considered as examples of the region e f on the fundamental T-R curves for tartrates (page 3).

The T-R curves for the quinoline solution (p = 1:899,

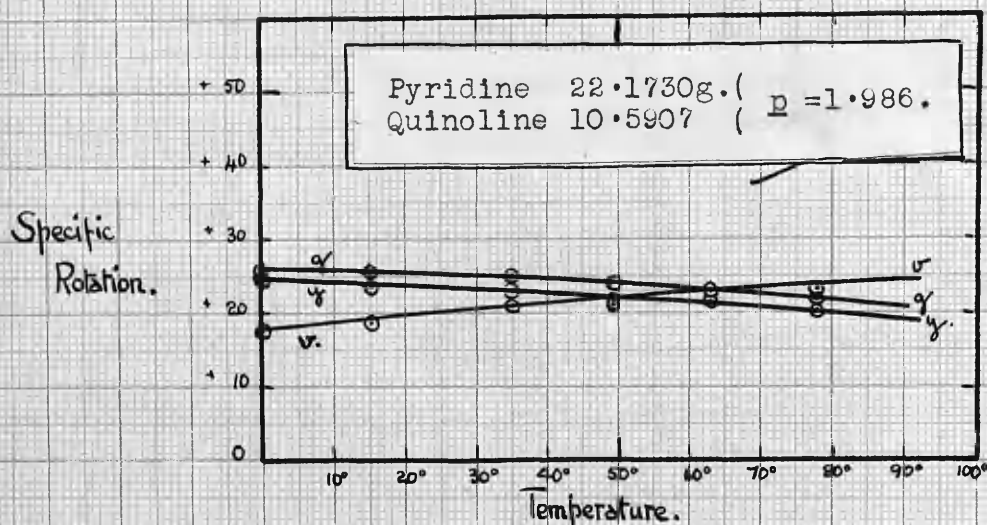


FIG. XII. T-R curves for di-o-nitrobenzyl diacetyl-d-tartrate in a mixture of pyridine and quinoline.

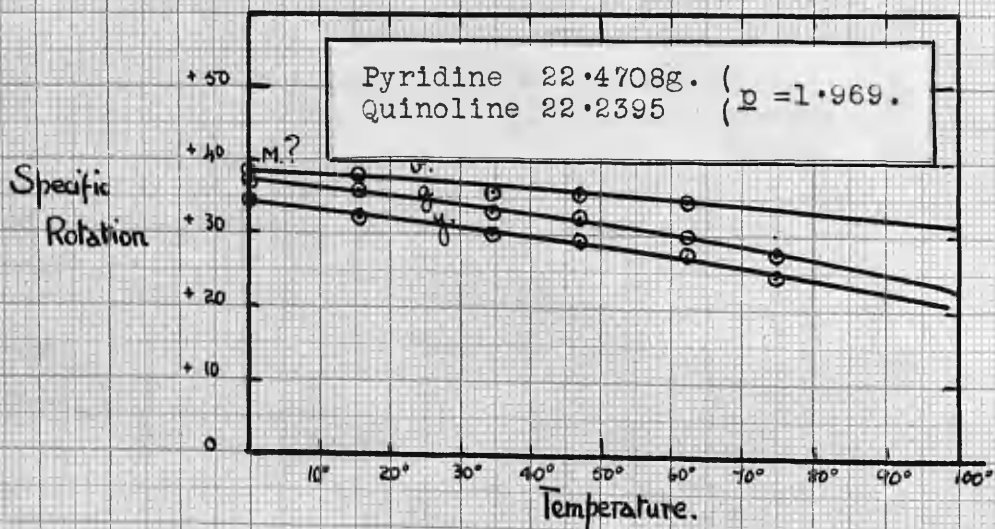


FIG. XIII. T-R curves for di-o-nitrobenzyl diacetyl-d-tartrate in a mixture of pyridine and quinoline.

Fig. XI) are all on the positive side of the axis of zero rotation, and all descend from moderately high values with increase of temperature, the curve for the longest wave-length being lowest in the series. There are no identifiable characteristic features, such as maxima or minima; the curves seem to be tending towards minima of positive rotation like those for the para- and meta-compounds. The T-R curves for this solution are of the type represented in the part i k of the fundamental T-R curves.

If the reference of the curves for the pyridine and quinoline solutions to the regions e f and i k, is a correct interpretation, there is very little discontinuity between the two sets of curves (c.f., Fig XI), and between the effects of the two solvents on the rotation.

In an attempt to show this relationship experimentally, the rotation of the ester was examined in mixtures of the two solvents pyridine and quinoline (Figs., XII and XIII). For the solvent containing twice as much pyridine as quinoline (Fig. XII), a region of visible anomaly is shown in the T-R curves, and, since the curves for violet, yellow, and green intersect, it can be said that, compared with pyridine itself, this mixed solvent displaces the region of intersection towards a lower temperature with an increase in rotation values. Using equal proportions by weight of

the two solvents (pyridine and quinoline), the series of curves (Fig. XIII), with that for violet uppermost, shows a gradual fall off in rotation with increase in temperature, and from their shape there is an indication that very probably all curves pass through maxima of positive rotation at some temperature just under  $0^{\circ}\text{C}$ . The rotations are for higher values -- a fact which is in accordance with the generalisation already referred to in the case of di-o-nitrobenzyl tartrate (page 20), that, if a solvent displaces a maximum in a T-R curve to a lower temperature, the rotational values are increased.

If we assume in the case of the quinoline solution (Fig. XI) that the region of maxima has been displaced to a much lower temperature, it is to be expected that the rotational values will be, as they actually are, much higher than those for pyridine and the mixed solvents. This analysis of the results obtained by the use of mixed solvents demonstrates quite clearly the connexion between the different types of T-R curves obtained for this ester in pyridine and quinoline, and is additional evidence in favour of the supposition that the curves belong to the portions i k and e f, on each side of the positive maxima on the fundamental T-R curves for tartrates (page 3).

It was found that no single characteristic diagram



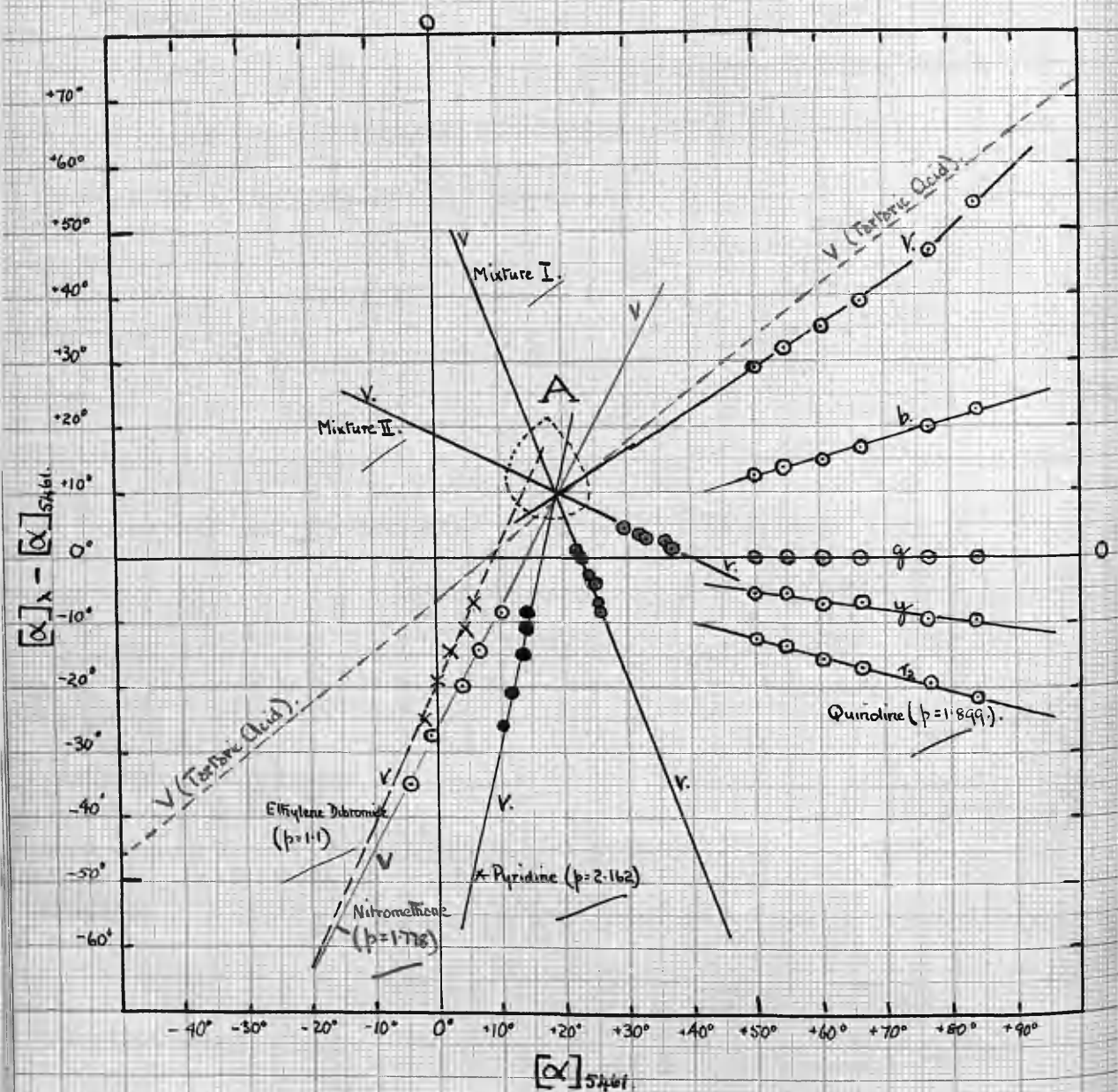


FIG. XIV. Characteristic diagrams for di-o-nitrobenzyl diacetyl-d-tartrate.

can summarise all the dispersion values for this diacetyl compound in the solvents used . For clarity, the results for the quinoline solution are plotted in full, and in all other cases the violet line only is given (Fig. XIV). Each solution gives a separate and distinct diagram.

The diagram for the quinoline solution is of the normal type, being somewhat similar in appearance to those for the para- and meta-compounds. It has a much lower rational zero (violet-green) of  $+4^{\circ}$ , and a smaller dispersion coefficient  $v/g$  of 1.629.

The displacement of the violet lines for the other solutions is not quite unexpected; for it has already been pointed out (page 22) that the curves for blue and green light cut each other at different values in different solutions, and that this probably is the case for the curves for violet and green. This variation in the value for the rational zero (violet-green) for the same compound in different solutions showing anomalous dispersion is not in agreement with the regularities that have been hitherto assumed as the property of such a region.

Winther's results for the T-R curves for aqueous and alcoholic solutions of tartaric acid (Zeit. phys. Chem., 1902, 41, 183) show a similar behaviour, and can thus be taken as confirmatory. A very probable explanation of the variation in the value of the rational zero is suggested by an examination of the T-R curves (Figs. IX, X, and XI). These show that



for the longest wave-lengths, there is very little increase in rotation with rise in temperature, and indicate that the curves are approaching maxima of positive rotation. Indeed, it has already been noted (page 22) that there is a maximum in the curve for red light(  $r_2$ ) for the pyridine solution (Fig. XI). Such proximity to regions of maximum rotation very probably plays a major part in modifying the dispersion to the extent indicated by the characteristic diagram. As will be seen from the diagram, there is a certain regularity in the disposition of the violet lines; they all seem to concur at one point, A, from which they subtend varying angles with the reference line for green light. There seems to be little significance in this.

The characteristic diagram thus fails to give a satisfactory summary of the dispersions of di-o-nitrobenzyl diacetyl-d-tartrate in solvents.

Summing up on solvent effect, in order of magnitude, quinoline gives the most optically active solution, then comes pyridine, and almost equal depressant effect is given by nitromethane and ethylene bromide. With reference to the fundamental curves, the solvents are in the same order, quinoline bringing into view a higher temperature portion than that given by nitromethane. The T-R curves for this last solvent seem to be rising with increase of temperature from a region of negative minima, x y z (page 3).

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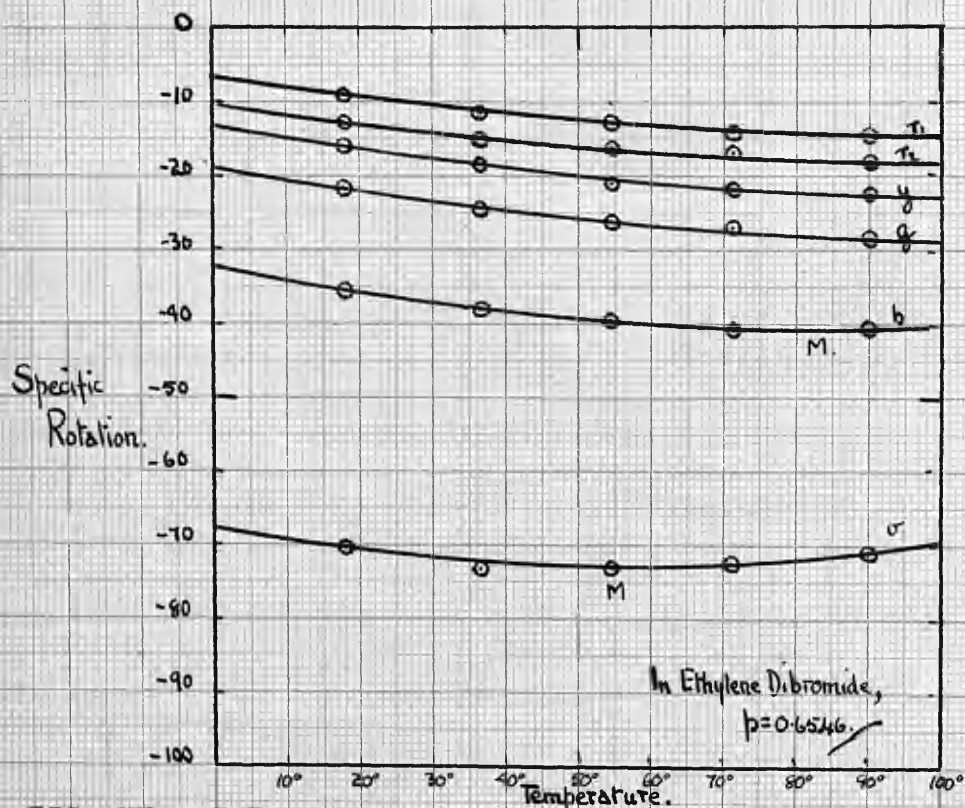


FIG. XV. T-R curves for di-o-nitrobenzyl dibenzoyl-d-tartrate.

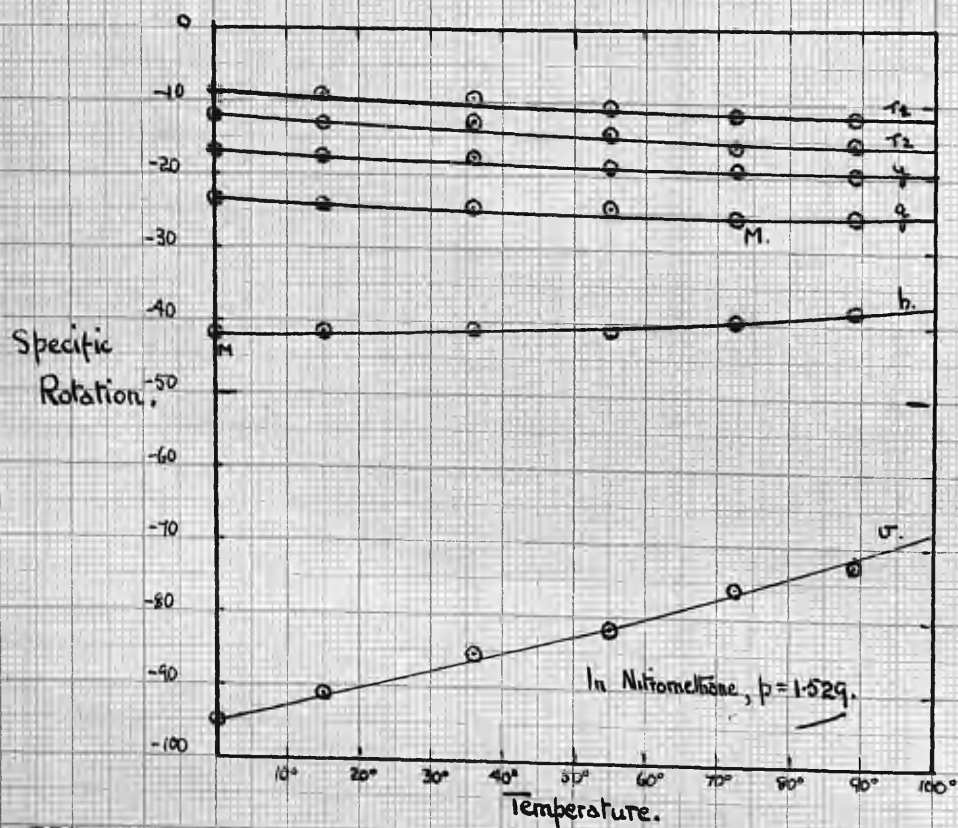


FIG. XVI. T-R curves for di-o-nitrobenzyl dibenzoyl-d-tartrate.

Di-o-nitrobenzyl Dibenzoyl-d-tartrate.

This ester was examined in the solvents nitromethane, ethylene bromide, pyridine, and quinoline. The results are given in Figs. XV, XVI, and XVII, and as for the diacetyl derivative, the curves for quinoline are different in appearance from those for the other solvents, which are similar to one another.

The curves for pyridine, nitromethane, and ethylene bromide, all lie on the negative side of the axis of zero rotation, and the curves for the longest wave-lengths are nearest the axis with the others displaced in a normal order. All these curves are characterised by the presence of minima.

For the nitromethane solution (FigXVI), the rotation for violet light decreases continuously with increase in temperature, but for blue and green, minima of rotation -- regarding rotation in the absolute sense -- occur at very widely separated temperatures,  $0^{\circ}\text{C.}$  and  $72^{\circ}\text{C.}$ , respectively. The rotations for the other wave-lengths increase slightly with increase of temperature.

Ethylene bromide as a solvent gives a similar set of T-R curves (Fig.XV), with minima apparent only for violet and blue . The curves for all other colours draw away from the zero axis with temperature increase. The minima occur

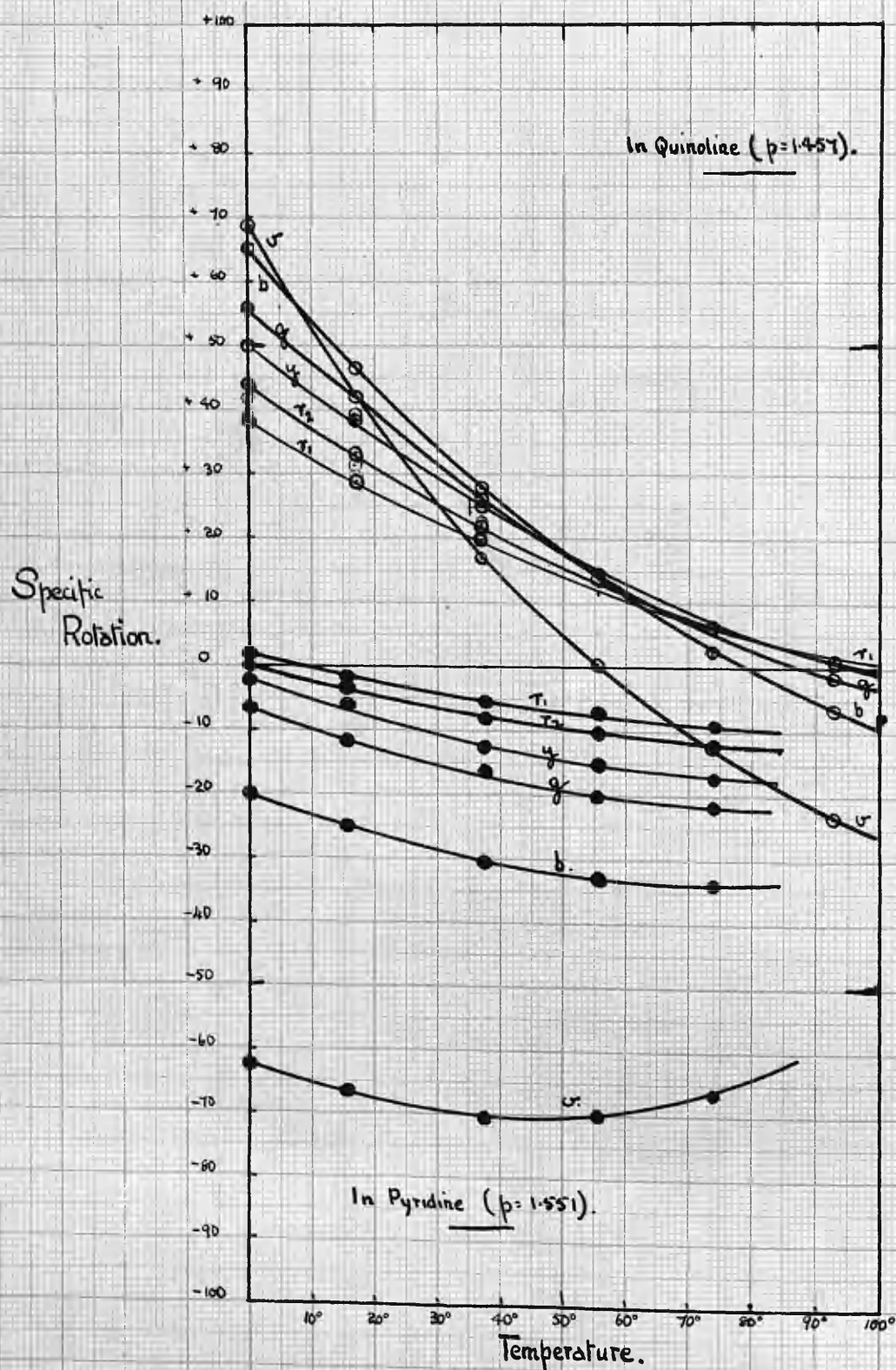


FIG. XVII. T-R curves for di-o-nitrobenzyl dibenzoyl-d-tartrate.

at the widely separated temperatures of  $55^{\circ}$  for violet and  $80^{\circ}\text{C.}$  for blue. The rotational values of these maxima are  $-41^{\circ}$  and  $-73^{\circ}$ , respectively.

For the pyridine solution (Fig.XVII) there is only a decided minimum in the curve for violet, and this occurs at  $42^{\circ}\text{C.}$  for the value of  $-71^{\circ}$  specific rotation. All the other curves seem to be tending to minima at much higher temperatures.

For each of these solutions, there is an exaggerated displacement of the minima in each set of T-R curves, and this displacement is for decrease in wave-length towards a lower temperature and greater negative rotational values. Passing from one solution to the next, from nitromethane to ethylene bromide and then to pyridine, the rotation values at  $0^{\circ}\text{C.}$  decrease in negative value, and the minimum for any wave-length, say for violet, moves towards a higher temperature with decrease in rotational value.

These conclusions with regard to the movement of negative minima are in agreement with those of Patterson in the investigation on the rotatory power of iso-butyl dibenzoyl-d-tartrate ( Proc. Roy. Soc. Edin.,1918-19, 39,18), and with those of Wood and Nicholas for a similar region displayed in the T-R curves for ethyl dibenzoyltartrate (J.C.S.,1928, 1671et seqq.).

This type of T-R curve, being very similar to that

for iso-butyl dibenzoyl-d-tartrate, is therefore referred to the negative minima region, x y z , of the fundamental tartrate curves (page 3).

The curves for the quinoline solution ( $p = 1.457$ , Fig. XVII) are of a type entirely different from any hitherto observed for any other tartrate. At  $0^{\circ}\text{C}$ ., the rotations are all positive in value, with that for violet greatest. Increase in temperature causes all the rotations to decrease and, the curves intersecting at positive values, at  $100^{\circ}\text{C}$ . all are negative in value and in the reverse sequence. This region of visible anomaly is not quite a complete mirror-image of that for ethyl tartrate where the rotations increase through a region of intersection. It is to be noticed that there are points of inflexion in the curves for violet and green. These are not very decided, but may indicate the presence of maxima further to the left. From the displacement of the curves at  $100^{\circ}\text{C}$ . and from their direction, it is obvious that there is a distinct continuity with the curves for the pyridine solution. The inference therefore is that the T-R curves for the solutions in pyridine, ethylene bromide, and in nitromethane (in that order), indicate how the T-R curves for the quinoline solution would continue on increase of temperature --that is, to a region of negative minima.

The compound, di-o-nitrobenzyl dibenzoyl tartrate, was obtained from d-tartaric acid by simple chemical reactions

not prone to give rise to a Walden inversion. Analysis of the dispersion data, from the standpoint of the characteristic diagram (Fig. XVIII) shows that the region of anomaly is entirely positive and that the diagram is similar to, but not quite the same as, that for di-o-nitrobenzyl tartrate. From these considerations, it is to be concluded that the dibenzoyl compound is of the d configuration. This conclusion is in accordance with the generalisation of Wood and Nicholas ( J.C.S., 1928, 1671 et seqq.; Chem. News, 1929, 139, 401 - 5 ; 1930, 140, 3 -6, 36 -41, 53 -55.) that for compounds of d configuration, the inflexions and maxima (criteria of anomalousness) in dispersion curves occur entirely in the positive region of rotation, while these dispersion curves cross the axis in such a way that  $\frac{d\alpha}{d\lambda}$  is always positive.

If it is the case that the dibenzoyl derivative is of the same configuration as its parent nitrobenzyl ester, the T-R curves should show some similarity to a region of the same fundamental T-R curves for tartrates. Such a region of visible anomaly as shown by the quinoline solution has no counterpart in the general curves (page 3), but if the other solutions are to be referred to the region x y z, the curves analogous to those for quinoline must be sought at lower temperatures. For these reasons, therefore, the fundamental T-R curves for tartrates has to be amended as



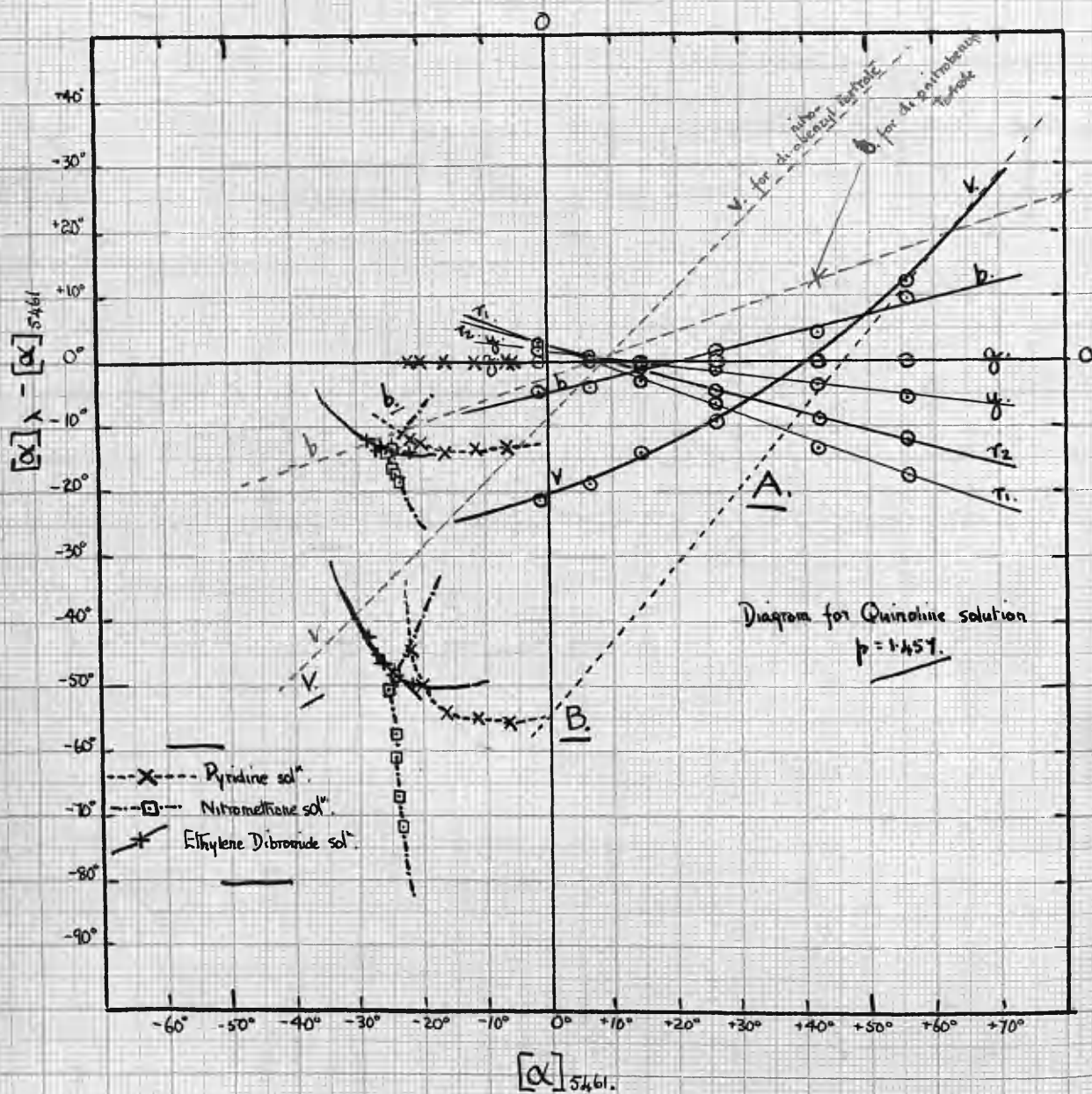
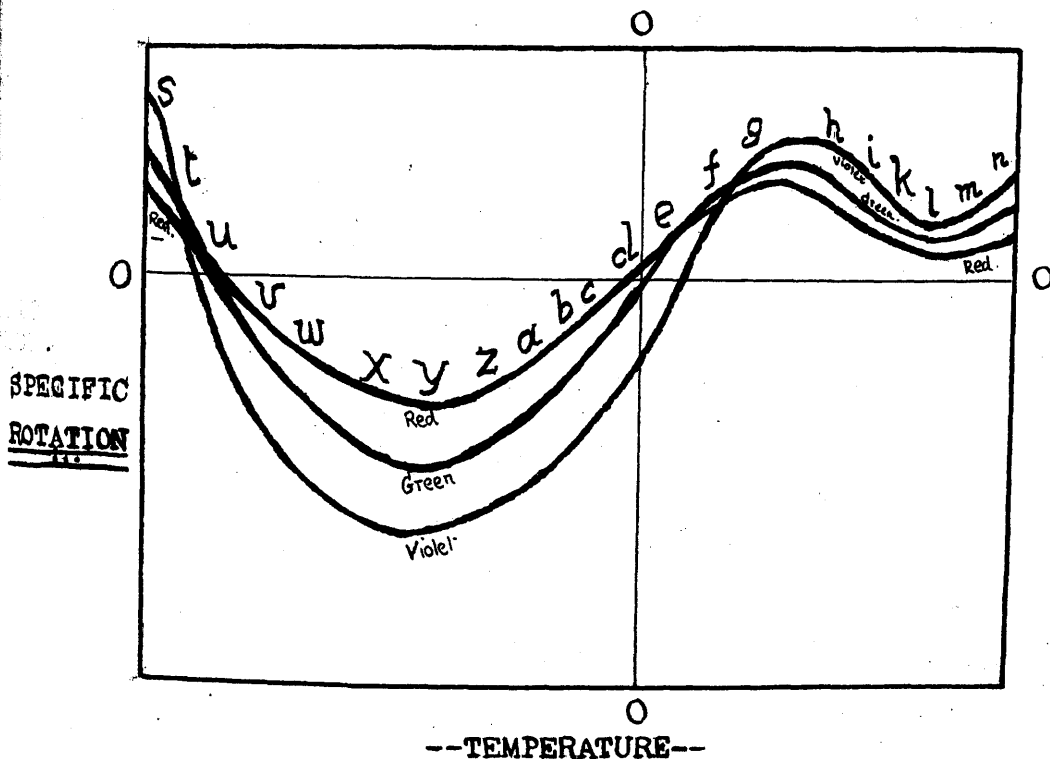


FIG. XVIII. Characteristic diagrams for di-p-nitrobenzyl dibenzoyl-d-tartrate.



in the accompanying diagram.



In this new diagram, the region s t u v corresponds to the behaviour of di-o-nitrobenzyl dibenzoyl-d-tartrate in quinoline.

This being the case, then, it is not surprising that the characteristic diagram for the dibenzoate (Fig.XVIII) differs markedly in degree, but not in kind, from that of the parent ester. The rational zero (violet-green) is about  $+40^\circ$ , and the dispersion coefficient ( $v/g$ ) is not constant owing to the proximity of the negative minimum, which causes the violet line on the characteristic diagram

to be deflected towards the zero of the diagram. This deflection is not apparent for the other lines.

A suggestion was made by Patterson (J.C.S., 1916, 109, 1202) that in consequence of the apparent periodic character of the temperature-rotation curves for active compounds, "Any given substance may very probably have several characteristic diagrams and several rational zeros," depending on the region of the T-R curves from which the data are taken. "If these rational zeros are very different in value it might be possible readily to detect the trend of the two separate diagrams."

In accordance with this suggestion, the data for the pyridine, ethylene bromide and nitromethane solutions, corresponding to T-R curves in the X y z region of the fundamental curves (page 31), should plot out on lines intermediate to those for the quinoline solution and, perhaps, to those for o-nitrobenzyl tartrate itself. To facilitate comparison, the violet and blue lines only for these three intermediate solutions are given (Fig. XVIII). Each set of these lines, the violet and blue, representing values at minima of rotation, minima which are displaced to different values with change of solvent, do not, and cannot be expected to, coincide. On the diagram, they each by a change in direction indicate that a change in the dispersion ratios is occurring.

It has already been pointed out that the violet line on the characteristic diagram for the dibenzoyl compound is, for lower rotational values, deflected towards the origin of the diagram, showing how proximity to minima brings about modification. If it is assumed that the line A B, in Fig. XVIII, represents what is perhaps the violet line for the fundamental characteristic diagram of the region s t u v (page 31), then the violet lines for the nitromethane, ethylene bromide, and pyridine solutions can be regarded as showing a change from the one diagram to the other. Since the minimum for violet light is at the greatest negative value for nitromethane, it is probable that, if the T-R measurements could be carried out over a wider range than is actually the case, the characteristic values for violet would plot out along such a line A B for a considerable distance before modification set in to give the line actually obtained by experiment. This to a varying degree is possibly what would happen for all solutions and all wave-lengths, and seems to afford an explanation of the complexity of the dispersion data as evidenced by the characteristic diagram.

Once more the characteristic diagram fails to summarise quantitatively the dispersion relationships for solutions of an ortho-compound in several solvents.

The comparative effect of solvents on the rotation

of di-o-nitrobenzyl dibenzoyl-d-tartrate is in the same order of magnitude as for the diacetyl compound, but with reference to the fundamental T-R curves (page 31) the sequence is reversed. Quinoline gives a solution with rotation curves corresponding to those for the low temperature region of the general curves, s t u v, and pyridine, ethylene bromide, and nitromethane (in that order) give curves which are more displaced towards the higher temperature region, although these curves are of the same type as the region x y z .

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#### THE EFFECT OF SOLVENTS ON ROTATION.

In an investigation such as this , where the T-R curves for the active compounds in the homogeneous condition have not been determined, the effect of solvents on rotation cannot be definitely guaged since there are no standards to which reference can be made. All that can be done is to give an indication of the relationship between the rotatory powers of the various solutions of each compound. Magnitude of rotation is not so decisive

in this respect as the presence, or proximity, of an easily identifiable region, such as a maximum, in the T-R curves -- that is, if the assumption of a fundamental T-R curve for active compounds is at all valid. It is sometimes the case when solvents are arranged in accordance with magnitude of solution rotation that this is not the same sequence as is obtained by reference to the fundamental T-R curves, and this fact is due to the periodicity of the curves. A point in favour of this latter method is that it gives a directional interpretation of solvent effect; that is to say, it indicates how solvent effect alters the shape of the T-R curves to show a movement along the fundamental curves.

For almost all of the nitrobenzyl tartrates and their derivatives the sequence of solvents in order of rotation magnitude is the same; the quinoline solution gives the greatest positive rotation values, pyridine comes next, and the lowest rotation values are always given by nitromethane and ethylene bromide. There are two exceptions to this generalisation. It has been shown for di-m-nitrobenzyl tartrate and for its o-isomer that the quinoline solutions are less active than the pyridine (pages 14 and 19).

When the form of the T-R curves is considered, matters are much more complicated.

For the meta- and para-compounds all the T-R curves are of the same form and have been referred to the same portion, i k l, of the fundamental diagram (c.f. page 31). It has thus been assumed that the quinoline solution, being in all cases but one more active than pyridine, gives curves typical of a region of the fundamental curves to the left of that for pyridine. The nitromethane solution of m-nitrobenzyl tartrate gives curves showing positive minima and have therefore been regarded as for the region k l m, to the right of that for pyridine. The effect of the solvents can be regarded diagrammatically so :-

$\begin{array}{ccccc} ik & & ik & & klm \\ \text{Quinoline} & \dots\dots & \text{Pyridine} & \dots\dots & (\text{Nitromethane}). \\ - & - & - & - & - \end{array}$

In the case of m-nitrobenzyl tartrate there is an exception to this generalisation ; for the T-R curves for pyridine are higher than those for quinoline and have therefore to be regarded as for a region to the left of that for the latter solvent.

For the ortho-compounds, the relationship between T-R curves given by the various solutions have already been discussed in the sections for each of the compounds. Since the sequence of the solvents is not always the same, the relationships are indicated below in the diagrammatic form used for the meta- and para-compounds.

For the parent ester, di-o-nitrobenzyl tartrate,

(see pages 19 and 20) we have:-

g h	g h	g h
<u>Nitromethane.....</u>	<u>Quinoline.....</u>	<u>Pyridine.</u>
Lowest rotation		Highest rotation

-----

For the diacetyl derivative the order is :-

(See pages 22, 23, and 26).

d e f	e f	i k
<u>Ethylene bromide.</u>	<u>Nitromethane).</u>	<u>Pyridine.....</u>
Lowest rotation		Highest rotation.

-----

For o-nitrobenzyl dibenzoyltartrate (pages 29, 31, and 33)

the effect is in the order:-

s t u v	x y z	x y z	y z
<u>Quinoline....</u>	<u>Pyridine...</u>	<u>Ethylene bromide..</u>	<u>Nitromethane..</u>
Highest rotation			Lowest rotation(-ve).

-----

The above diagrammatic representation shows that the direction of T-R displacement is altered but that the order according to rotation magnitude for each compound remains the same. This means that quinoline as a solvent for these compounds tends to give rotational effects which are removed as far as possible from minimum rotation, whilst ethylene bromide and nitromethane, of the solvents used, depress the rotation towards minimum regions, not

always so much as to give such a region, but in that direction.

It cannot therefore be said that the effect of these solvents on the rotation of the various compounds is very regular. Such being the case, then, from the rotations of the compounds in one solvent, no finality can be reached regarding the effects of constitution on the rotatory power. The general behaviour of the compounds in the various solvents would seem to give more definiteness to the decision, but this method must be applied with caution.

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#### CONSTITUTION AND ROTATORY POWER.

The relating of constitution and rotatory power cannot be, in this instance, taken as final for the compounds themselves, since it is deduced from the rotatory power of solutions. But there is every reason to believe that it cannot be far from the truth, in that it is based more on general behaviour rather than on the results for one particular solvent.

There are two parts in this correlation; the first is concerned with the effect of derivative formation, and the second with the relationship between the optical activities



of position isomers.

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When the T-R curves of the dibenzoyl and the diacetyl derivatives are compared with those of the parent nitrobenzyl esters, it is shown that a certain regularity exists in the rotatory powers of each family of compounds.

In the case of the para-compounds (page 10), the diacetyl derivative is less active and the dibenzoyl compound more active than the nitrobenzyl tartrate in the same solvent. That is, all the curves having been referred to the same region, i k, of the fundamental T-R curves, the introduction of two acetyl groups depresses the rotation to the right, towards the region of minimum rotation, k l m, and benzoylation causes the curves to be modified towards the left of the region occupied by the parent nitrobenzyl tartrate in the same solvents. Expressing this diagrammatically, we have:-

i k

- Dibenzoyltartrate....Tartrate....Diacetyltartrate,  
 this being the order of the disposal of the curves for these compounds along the fundamental T-R curves.

The effect of benzoylation is the same for the meta-compound (page 14), but the diacetyl compound, more active than the nitrobenzyl tartrate in quinoline, is less active in pyridine. No definite conclusion can therefore

be formed as to the effect of acetylation on the optical activity of m-nitrobenzyl tartrate.

For the ortho-compounds, it has been shown that the nitrobenzyl tartrate itself gives for the three solvents, nitromethane, pyridine, and quinoline, curves exhibiting positive maxima, and therefore belonging to the region g h (pages 19 and 20). The diacetyl compound shows in the same solvents curves which are spread over a much wider range, from e f in ethylene bromide, nitromethane and pyridine, to i k in quinoline (pages 22, 23, and 26). Despite this extreme sensitivity of rotation, it seems quite likely that in general rotatory power the diacetyl compound has to be referred to a lower portion of the fundamental T-R curves than the nitrobenzyl tartrate. The results for the dibenzoyl compound for the four solvents, quinoline, pyridine, ethylene bromide, and nitromethane, all lie in the low-temperature region of the fundamental curves, the region s t ...y z (page 31; see pages 29, 31, and 33). Thus the effect of derivative formation on rotation is, but for the slight irregularities of the diacetyl compounds, the same for the three isomeric nitrobenzyl tartrates. The dibenzoyl compound always gives curves which are referrable to a region on the low-temperature side of that on the fundamental T-R curves to which the results for the nitrobenzyl tartrate have been compared. The diacetyl compounds seem to occupy an intermediate position.

The results recorded for the three isomeric nitrobenzyl tartrates and their diacetyl and dibenzoyl derivatives afford striking examples of the effect of position isomerism on optical rotatory power. The T-R curves for the solutions of the meta- and para-isomers all belong to the same region, i k l (m), of the general curves, and are very similar, those of one isomer to the other. The results for the ortho-compounds, however, are entirely dissimilar and spread over a wide range of the fundamental T-R curves, from s t u v...to...i k, showing that the curves for the ortho-isomers correspond to a lower temperature region of the general curves than for the meta- and para-compounds.

The dispersion data for the meta- and para-compounds fit on to their respective characteristic diagrams, which are most similar, whilst the behaviour of any one of the ortho-derivatives in its different solutions cannot be summarised on one diagram.

Enough has been said to stress the similarity in rotational behaviour of the meta- and para-compounds, and to show how different is the behaviour of the ortho-isomers. This finding is in accordance with that for many examples already recorded in the literature. In general, it is found that the rotational behaviour of the ortho-isomer is at variance with that of the others. Many

explanations have been advanced to account for this optical peculiarity. Indeed, the effect of position isomerism on optical rotation is a subject that has received much attention during the last forty years.

Founded on the ideas of Guye (Compt. rend., 1893, 116, 1378; and other papers), Frankland (with Wharton, J.C.S., 1896, 69, 1583) suggested that the rotatory power of a position isomer not only depends on the mass of the radicle containing the varying substituent but also on the moment about the asymmetric centre. It was claimed, therefore that the variation in activity is due to the relative positions of the centre of gravity of each aromatic nucleus with respect to the active atom. The work of Cohen, in a series of nine papers to the Chemical Society from 1903 to 1911, does not support this theory. Cohen concludes that the nature of the substituent group - not the mass-, as well as its distance from the active centre, has considerable modifying influence on the rotation (J.C.S., 1914, 105, 1892). This hypothesis has been adversely criticised by Singh (J.C.S., 1919, 566; 1920, 980), who claims that no simple connexion can be observed between the nature of the substituent group or element in an organic compound and its rotatory power. Singh's conclusions, however, are based on his observations of the rotatory powers of active compounds in solvents for only one wave-length and for only a single temperature.

On the grounds that the T-R curve and the dispersion relationships are fundamental properties of optically active compounds which must be considered in such investigations as this, the evidential significance of Singh's results can scarcely be regarded as prejudicial to Cohen's theory. In 1930, Rule gave a re-expression of the conception in his suggestion that the probable reason for the optical peculiarity of the ortho-compounds, in general, is connected with the spatial proximity and changed vectorial orientation of the dipole in that direction (Trans. Faraday Soc., 1930, 26, 355).

The spatial relationship has been stressed, and seems to afford sufficient explanation in the case of the nitrobenzyl tartrates and their derivatives, the similarity in behaviour of the meta- and para-isomers being due to the substituent nitro-group in each pair of isomers occupying similar spatial positions with regard to the asymmetric centres. In the ortho-compounds, it is quite probable that the nitro-groups are differently disposed towards the active centres than in the other isomers, and consequently the rotational behaviour is modified to a different extent.

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EXPERIMENTAL.

The temperature-rotations of these compounds were, in general, observed for the following six wave-lengths (expressed in Å.U.) :-

$r_1$ .	$r_2$ .	y.	g.	b.	v.
6716	6234	5790	5461	4916	4358.

The technical details with regard to the method of obtaining these wave-lengths are fully described in a paper by Professor Patterson, J.C.S., 1916, 109, 1142 - 44.

Di-p-nitrobenzyl d-tartrate.

This ester was prepared by the action of p-nitrobenzyl bromide (23 g.) on sodium d-tartrate ( 12 g.) in aqueous alcohol (Reid, J.Amer.Chem.Soc., 1917, 39, 124). The product was recrystallised from absolute alcohol until of constant rotation in pyridine. Yield 20%. The tartrate is in the form of very fine white crystals, m.p. 164.5° (c.f., m.ps. of 163° and 162.7° given by Reid, l.c. pages 124 and 701).

The T-R of this compound was observed for solutions in pyridine and quinoline.

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Contractions:

t. --- temperature (°C). d. -- density.  
p -weight of solute in 100 g. of solution.

In quinoline.  $p = 4.213$ .

(Fig. I)

t.	d.	$[\alpha]_{r_1}$	$[\alpha]_{r_2}$	$[\alpha]_{y_1}$	$[\alpha]_{y_2}$	$[\alpha]_b$	$[\alpha]_v$
0°	*1.125	+70.57	+83.22	+100.2	+116.1	+150.3	+213.5
17	1.108	64.36	76.15	91.22	106.4	137.7	194.6
36.5	1.092	59.0	69.45	83.49	95.79	124.5	177.3
59.25	1.074	52.62	61.42	74.04	85.61	111.3	156.1
90.5	1.049	45.71	53.25	63.43	73.16	93.93	135.2

\*Densities marked thus are derived by extrapolation from the others which are experimental.

-----

In pyridine.  $p = 2.205$ .

(Fig. I)

0°	*1.0097	+61.15	+68.89	+83.14	+93.80	+121.5	.....
14	0.9956	54.50	64.30	78.54	89.54	114.1	+158.2
33	0.9770	51.31	60.29	71.17	80.97	107.1	146.9
55	0.9543	47.19	54.87	63.63	74.57	97.74	131.2
73	*0.9362	44.25	50.58	60.87	70.57	88.06	122.6
92	0.9168	41.57	46.62	56.69	62.77	83.75	110.6

-----

Di-p-nitrobenzyl diacetyl-d-tartrate.

This compound was prepared from the nitrobenzyl tartrate by the action of acetyl chloride, a little pyridine having been added to assist the reaction. Purified by several recrystallisations from absolute alcohol, this derivative was obtained in the form of fine white crystals of m.p. 141.5°.

Yield, 60%. (Found: N, 5.644. Calc: N, 5.556%)

In quinoline,  $p = 1.552$ .

( Fig. I)

t.	d.	$[\alpha]_{r_1}$	$[\alpha]_{r_2}$	$[\alpha]_v$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
0°	*1.1117	+71.15	+82.54	+99.02	+113.8	+149.6	+210.6
14	1.101	62.09	74.37	88.39	102.1	132.3	184.6
36	1.084	54.83	63.13	75.16	86.98	113.1	155.6
58	1.067	46.72	54.41	63.08	73.65	97.07	132.0
81	1.048	--	45.74	53.43	62.0	81.41	113.1

-----

In pyridine,  $p = 1.782$ .

( Fig.I)

0°	*1.0067	+34.35	+39.08	+46.5	+52.84	+66.19	+86.28
16.5	0.9913	30.91	35.19	42.03	46.82	58.92	76.90
44	0.9642	26.69	29.52	--	38.43	48.98	63.65
60.5	0.9471	23.10	26.36	--	34.76	43.17	56.58

-----

Di-p-nitrobenzyl dibenzoyl-d-tartrate.

To p-nitrobenzyl tartrate (3 g.) dissolved in pyridine excess benzoyl chloride ( 18 g.) was slowly added in the warm. After standing overnight, the reaction mixture was poured into water and gently warmed to decompose the excess benzoyl chloride. The benzene extract of this was



washed with dilute hydrochloric acid, water, and then with sodium carbonate solution. After drying over anhydrous potassium carbonate, the benzene was distilled off, and the residue recrystallised from aqueous alcohol. The benzoate is in the form of white flaky crystals, m.p. 114°. Yield, 55.7%. (Found: N, 4.61. Calc: N, 4.46%)

This compound is more soluble than the others previously described, being soluble in benzene, nitromethane, and chloroform, as well as pyridine and quinoline.

In quinoline,  $p = 1.522$ .

( Fig. I)

t.	d.	$[\alpha]_r$	$[\alpha]_{r_2}$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
0°	*1.1125	+243.8	+289.4	+346.9	+405.8	+541.9	+792.7
17.5	1.099	200.6	240.5	289.9	338.3	450.9	658.0
35.75	1.085	168.1	192.4	235.5	275.9	367.7	537.1
51.5	1.073	--	164.9	199.1	230.5	307.7	447.8
68.25	1.059	--	136.7	162.9	190.7	253.9	368.4
82.5	1.047	--	113.2	134.7	155.8	209.1	303.7

---

In pyridine,  $p = 1.631$ .

( Fig. I)

0°	*1.008	+129.4	+161.0	+190.4	+224.0	+295.2	+425.8
17.5	0.9906	113.4	132.3	160.1	185.6	243.8	353.8
33.5	0.9745	93.71	110.0	132.6	151.0	201.1	292.6
53	0.9550	74.63	87.44	103.0	120.7	157.9	228.3
68	0.9396	61.37	70.96	81.77	97.25	126.6	183.1

---

Di-m-nitrobenzyl d-tartrate.

This compound was prepared by the method of Miss I. Caldwell (Hons. B.Sc. Thesis, June, 1927). A mixture of tartaric acid ( 11g.) and m-nitrobenzyl alcohol ( 32g.) was heated in a current of dry air for fifteen hours at 140°C. The syrup thus obtained was dissolved in methyl alcohol and, on standing for several days, the nitrobenzyl tartrate separated out as a solid. It was purified by repeated recrystallisation from methyl alcohol, and was obtained as white and hard crystals, m.p.119°. Yield, 50%.  
(Found: N, 6.72. Calc: N, 6.67%)

In quinoline. p = 1.56.

( Fig. III)

t.	d.	$[\alpha]_r$	$[\alpha]_F$	$[\alpha]_V$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
0°	*1.1135	+47.31	+54.81	+64.33	+73.50	+92.04	+122.2
16	1.101	45.39	51.77	60.95	70.17	88.65	118.2
36	1.085	42.30	48.46	57.03	64.71	83.85	109.4
65.5	1.062	38.69	43.49	51.99	58.99	75.09	103.3
90	1.042	34.98	40.44	48.72	54.94	70.46	92.28

In nitromethane. p = 1.39.

( Figs. III and IV)

18.5°	1.144	--	+13.69	--	+17.03	+18.09	+19.54
40	1.114	--	12.72	--	17.07	18.11	20.50
60.25	1.087	--	12.86	--	17.42	19.73	21.30
76	1.065	--	13.60	--	17.95	20.73	25.89

In pyridine,  $p = 2.761$ .

( Fig. III)

t.	d.	$[\alpha]_D$	$[\alpha]_{D_2}$	$[\alpha]_Y$	$[\alpha]_G$	$[\alpha]_B$	$[\alpha]_V$
0°	*1.01	+48.54	+57.06	+66.68	+76.95	+97.97	+130.7
14	0.9968	45.97	54.23	63.72	72.73	91.83	121.9
37	0.9745	42.90	49.72	57.62	66.37	84.10	113.0
59	0.9523	39.54	45.42	53.57	60.85	77.14	103.6
88.25	0.9217	35.00	40.40	47.73	53.87	68.74	92.10

---

Di-m-nitrobenzyl diacetyl-d-tartrate.

This compound was prepared by the same method as the para-isomer. White crystalline solid, m.p. 107°.(c.f. Miss Caldwell - l.c. - gives a m.p. 100°). Yield, 33%.  
( Found: N, 5.64. Calc: N, 5.55%)

In quinoline,  $p = 1.479$ .

( Fig. III)

t.	d.	$[\alpha]_{D_2}$	$[\alpha]_Y$	$[\alpha]_G$	$[\alpha]_B$	$[\alpha]_V$
0°	*1.1122	-- +124	+150.4	+174.3	+230.8	+330.4
13.5	1.102	-- 110.4	131.7	153.8	202.4	291.8
35.5	1.084	-- 92.74	109.9	128.3	170.0	245.4
60	1.065	-- 76.45	89.74	106.0	139.8	200.0
90	1.041	-- 63.30	70.68	81.28	107.5	152.8

---

In pyridine,  $p = 1.658$ .

( Fig, III)

t.	d.	$[\alpha]_{r_1}$	$[\alpha]_{r_2}$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
0°	*1.0055	+50.07	+56.33	+66.83	+77.09	+98.83	+139.2
17.5	0.9888	42.82	49.00	58.87	67.04	85.33	120.0
37	0.9694	38.78	43.12	51.81	57.65	74.59	104.7
61.5	0.9448	32.65	36.24	41.51	48.89	62.66	87.22
85.5	0.9194	--	30.88	35.02	40.19	--	--

-----

Di-m-nitrobenzyl dibenzoyl-d-tartrate.

This ester was prepared by the action of benzoyl chloride on a pyridine solution of the m-nitrobenzyl tartrate, and purified by several recrystallisations from alcohol. Fine felted white needles are obtained, m.p. 109°. Yield, 16.72%.

(Found: N, 4.41. Calc: N, 4.46%)

-----

In quinoline,  $p = 1.468$ .

( Fig. III)

t.	d.	$[\alpha]_{r_1}$	$[\alpha]_{r_2}$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
0°	*1.1135	+197.0	+233.4	+277.5	+322.3	+426.1	+606.6
16.75	1.100	159.8	188.2	224.7	257.2	342.4	486.5
35	1.085	123.9	147.0	174.6	202.8	265.7	376.5
52	1.072	99.13	116.6	138.7	160.6	210.8	297.5
72.5	1.055	74.47	86.62	103.7	118.0	154.6	216.9
90	1.041	56.87	65.10	75.60	87.42	114.4	158.9.

In pyridine.  $n_D = 1.629$ .

( Fig. III)

t.	d.	$[\alpha]_{r_1}$	$[\alpha]_{r_2}$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
0°	*1.0075	+94.28	+109.1	+124.8	+147.9	+190.5	+259.4
19	0.9888	71.53	83.26	99.08	112.4	142.0	192.1
37.5	0.9701	53.18	61.87	72.13	81.62	103.4	138.1
55.5	0.9521	39.42	45.80	50.75	60.66	76.00	99.93
72	0.9353	28.85	32.75	34.55	42.27	52.32	67.84
89	0.9179	14.42	20.94	---	27.64	32.66	---

Di-o-nitrobenzyl tartrate.

This nitrobenzyl tartrate was prepared by heating a mixture of tartaric acid ( 10 g.) with excess of o-nitrobenzyl alcohol ( 30 g.) in a current of dry HCl gas for over five hours and dry air for one hour at a temperature of 110°. The product was boiled up in alcoholic solution with animal charcoal, filtered and allowed to crystallise. Repeated recrystallisation from alcohol yielded white nacreous crystals, m.p. 131°. Yield, 50%.  
( Found: N, 6.67. Calc: N, 6.67%)

This compound being more soluble than its position isomers was examined polarimetrically in nitromethane as well as in pyridine and quinoline.

In quinoline,  $p = 1.35$ .

( Fig. VII)

t.	d.	$[\alpha]_r$	$[\alpha]_2$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
0°	*1.1145	+30.12	+34.69	+40.93	+45.55	+58.29	+88.76
18	1.100	31.50	35.83	42.65	47.42	61.66	92.19
39	1.083	31.63	36.98	43.38	48.99	62.84	92.76
55	1.070	31.66	36.34	42.83	47.71	62.24	91.70
73	1.056	---	35.46	41.43	46.04	59.80	90.28
90	1.042	---	---	---	44.54	---	---

---

In pyridine,  $p = 1.624$ .

(Fig. VII)

0°	*1.0085	---	+45.40	+54.25	+60.81	+76.54	+103.0
20.5	0.9881	+39.68	44.51	53.20	59.39	76.74	105.0
40	0.9685	37.08	42.99	49.63	57.35	74.50	102.8
63.75	0.9443	35.67	40.27	47.68	53.93	69.05	96.58
76	0.9315	33.91	39.16	45.25	51.89	66.15	92.90

---

In nitromethane,  $p = 1.387$ .

( Fig. VII)

0°	*1.171	+13.05	+14.05	+15.97	+17.78	+21.67	+25.60
18	1.145	13.51	15.01	16.39	18.71	22.33	26.81
37.5	1.118	13.58	14.91	16.93	18.66	23.46	29.43
55.5	1.094	13.30	15.70	17.51	19.77	24.84	30.70
70.5	1.073	14.16	16.14	17.99	19.96	24.88	31.73
92	1.042	15.01	16.35	18.39	20.76	25.61	32.58.

---

Di-o-nitrobenzyl diacetyl-d-tartrate.

By the action of acetyl chloride on *o*-nitrobenzyl tartrate in pyridine solution a crystalline solid, m.p. 118-120°, was obtained. On analysis an indication is given that by this method of acetylation mainly the mono-acetyl derivative is formed.

( Found: N, 6.16. Calc: N, 6.047%)

The diacetyl compound was obtained by acetylation with acetic anhydride and sulphuric acid, and purified by recrystallisation from methyl alcohol. M.p. 75°.

( Found: N, 5.6. Calc: N, 5.556).

From 5g. of the nitrobenzyl tartrate 3.2g. of the acetate were obtained -- Yield, 53.25%.

This ester is much more soluble in pyridine and quinoline than *o*-nitrobenzyl tartrate.

In quinoline,  $p = 1.899$ .

(Fig. XI)

t.	d.	$[\alpha]_x$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
0°	*1.114	+62.88	+74.59	+84.26	+106.5	+138.2
16.75	1.101	57.51	67.33	76.78	96.70	123.6
39	1.083	49.63	59.40	66.53	83.39	105.7
54	1.071	45.06	53.13	60.46	75.46	95.74
69.5	1.059	41.19	49.12	54.80	68.50	86.84
84	1.047	37.42	44.39	50.05	62.50	78.93

In pyridine,  $p = 2.162.$ 

( Fig. XI)

t.	d.	$[\alpha]_{r_2}$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
0°	*1.0085	+10.61	+10.96	+10.64	+5.393	-15.46
16	0.9926	10.98	11.39	11.7	7.894	-9.059
39.5	0.9690	12.27	13.34	13.49	10.71	-1.253
56.75	0.9517	12.27	13.58	14.04	13.03	+3.098
69	0.9396	12.03	13.91	14.31	13.94	+6.063

---

In ethylene bromide,  $p = 1.1.$ 

( Fig. IX)

16°	2.175	+0.94	-0.16	-1.96	-8.778	-26.96
38	2.13	2.188	+1.361	+0.08	-4.455	-18.91
58	2.089	3.255	3.038	2.251	-1.601	-12.28
79.5	2.044	4.366	5.284	4.449	+1.974	- 6.507
100	1.999	5.685	5.772	6.198	4.691	- 0.99

---

In nitromethane,  $p = 1.778.$ 

(Fig. X)

0°	*1.1675	-0.7224	-2.38	-4.40	-13.06	-39.50
16	1.147	+1.38	+1.04	-1.165	-8.06	-28.85
43.5	1.11	4.81	4.59	+3.988	-0.89	-15.86
65.5	1.08	6.87	8.04	6.704	+3.29	-7.22
90	*1.0465	8.90	9.44	10.21	8.36	+1.78

---



In a mixture of pyridine (22.1730 g.) and quinoline (10.5907g.)

p = 1.986.

( Fig. XII)

t.	d.	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_v$
0°	*1.04	+24.47	+26.08	+17.76
15.25	1.026	23.59	25.77	18.78
35	1.007	23.02	24.99	20.95
49.25	0.9940	21.81	24.05	21.20
63	0.9809	21.56	22.94	22.94
78	0.9665	20.25	22.07	23.21

In a mixture of pyridine (22.4708g.) and quinoline (22.2395g.)

p = 1.969.

( Fig. XIII)

0°	*1.059	+34.68	+37.17	+38.56
15.5	1.045	32.23	35.91	38.19
34.5	*1.0275	29.94	33.13	35.88
47	1.016	29.26	32.32	35.48
62.25	1.003	27.57	29.82	34.35
74.75	0.9915	24.52	27.31	---

Di-o-nitrobenzyl dibenzoyl-d-tartrate.

This substance was prepared by the same method as its di-p- and di-m-isomers, and was obtained, after repeated

recrystallisations from absolute alcohol, in fine crystals of very slightly yellow colour, almost white. M.p. 126.5 -127°. With 5g. of nitrobenzyl tartrate as the starting material, 4g. of the tartrate were obtained, being a yield of 53.5%. ( Found: N, 4.62. Calculated: 4.46% )

In quinoline,  $p = 1.457$ .

( Fig. XVII )

t.	d.	$[\alpha]_{r_1}$	$[\alpha]_{r_2}$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
0°	*1.114	+ 38.23	+43.81	+50.08	+55.84	+65.24	+67.87
17	1.100	28.97	33.34	38.60	42.19	46.51	42.15
37	1.084	19.82	21.80	24.92	26.22	28.04	17.09
55.5	1.069	11.62	13.71	13.55	14.63	13.71	0.68
73.5	1.054	6.545	6.829	6.992	6.504	2.521	-12.36
92.75	1.038	6.909	1.322	-0.083	-1.529	-6.404	-23.18

In pyridine,  $p = 1.551$ .

( Fig. XVII )

0°	*1.0085	+2.08	+0.08	-2.16	-6.60	-19.84	-62.48
15.5	0.9922	-1.71	-3.25	6.09	11.5	25.19	66.67
37.5	0.9696	5.53	7.98	12.6	16.34	30.56	70.44
55.5	0.9519	7.11	10.21	14.95	20.03	32.82	69.95
74	0.9328	8.99	12.23	17.24	21.74	33.79	66.42

In ethylene bromide,  $p = 0.6546$ .

(Fig. XV)

t.	d.	$[\alpha]_{r_1}$	$[\alpha]_{r_2}$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
18°	2.175	-9.04	-12.86	-16.07	-21.73	-35.60	-70.63
36.5	2.137	11.57	15.01	18.63	24.35	38.02	73.23
54.5	*2.100	12.74	16.28	20.91	26.28	39.42	72.93
55	2.099	.	.	.	.	.	.
71.25	2.065	14.06	16.74	21.88	27.06	40.84	72.43
90	2.024	14.47	18.06	22.54	28.54	40.61	71.08

---

In nitromethane,  $p = 1.529$ .

( Fig. XVI)

0°	*1.1685	-8.82	-11.82	-16.87	-23.34	-41.82	-95.19
15	1.148	9.09	12.93	17.64	24.05	41.42	91.16
36	1.119	9.68	12.86	17.65	24.30	41.11	85.33
55	1.094	10.73	14.20	18.76	24.36	41.15	81.83
72.5	1.069	11.51	15.94	19.01	25.43	39.61	76.00
89	1.046	11.89	15.33	19.59	24.24	38.04	72.76

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THE OPTICAL ROTATORY POWER OF METHYL, ETHYL, n-PROPYL,  
AND n-BUTYL DIBENZOYL-d-TARTRATES.

In consequence of the new feature, a new type of anomalous region, in the general T-R curves for tartrates revealed by the examination of di-o-nitrobenzyl dibenzoyl-d-tartrate in quinoline solution (Part I, pages 29 - 31), it was resolved to seek for other examples of such behaviour among the tartrates in order to verify to some extent the amendment of the fundamental T-R curves for tartrates ( page 31).

Frankland and Wharton (J.C.S., 1896, 69, 1587) by their examination of the effect of temperature on the rotation for Na<sub>D</sub> of homogeneous ethyl dibenzoyltartrate were the first to demonstrate the existence of a maximum of negative rotation, or, if we regard rotation as absolute for each configuration, a negative minimum. It was also shown in the same paper that with increase in temperature the rotation for methyl dibenzoyltartrate is somewhat similar, in that it is negative and decreases. The melting point of methyl dibenzoyltartrate, 135°, being too high, observations could not be made for low temperatures, and the minimum of the T-R curve was not revealed.

Patterson and Moudgill (Proc. Roy. Soc. Edin., 1918, 39, 18) showed that the T-R curves for di-isobutyl dibenzoyl-

d-tartrate, in the homogeneous state and in solution in cinnamic aldehyde and ethylene bromide, are characterised by the presence of negative minima.

Wood and Nicholas (J.C.S., 1928, 1671) repeated Frankland and Wharton's observations for ethyl dibenzoyl-tartrate for eleven wave-lengths and confirmed that the T-R curves show negative minima.

Now, it had been found by Pictet (Jsb. Chem., 1882, 857 ; Arch. des Sciences phys. et nat., [III] VII, 82 - 97) that dibenzoyltartaric acid in alcoholic solutions possesses a high negative rotation for  $\text{NaD}$  and that the dimethyl, and diethyl, and di-isobutyl esters behave similarly.

All these facts seem to indicate that the simple dibenzoyltartrates, as a class, give T-R curves in the negative region.

An examination of Frankland and Wharton's curves for methyl and ethyl dibenzoyltartrates (see page 60) reveals several points.

It is seen that the rotation for the ethyl compound is considerably less than that for the methyl derivative at  $100^\circ$ , and that, although the curve for the former possesses a definite minimum, the curve for the methyl homologue rises continuously with rise of temperature.

Assuming that change in constitution and of solvent

Specific  
Rotation.

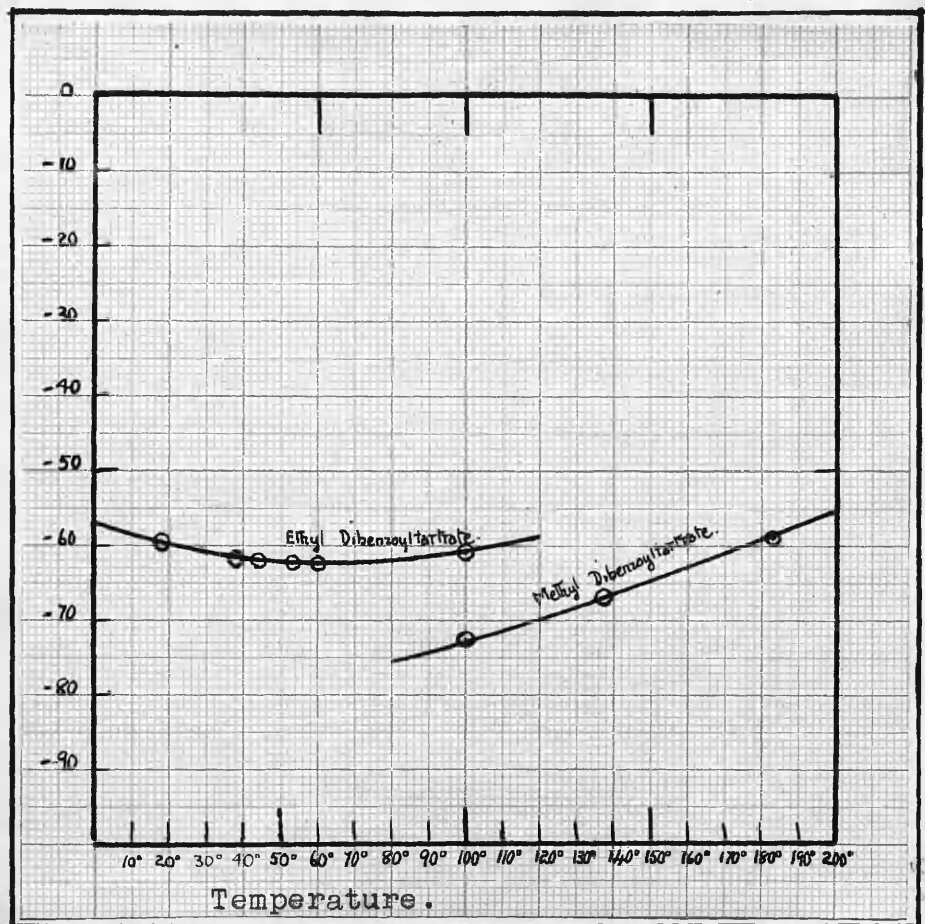
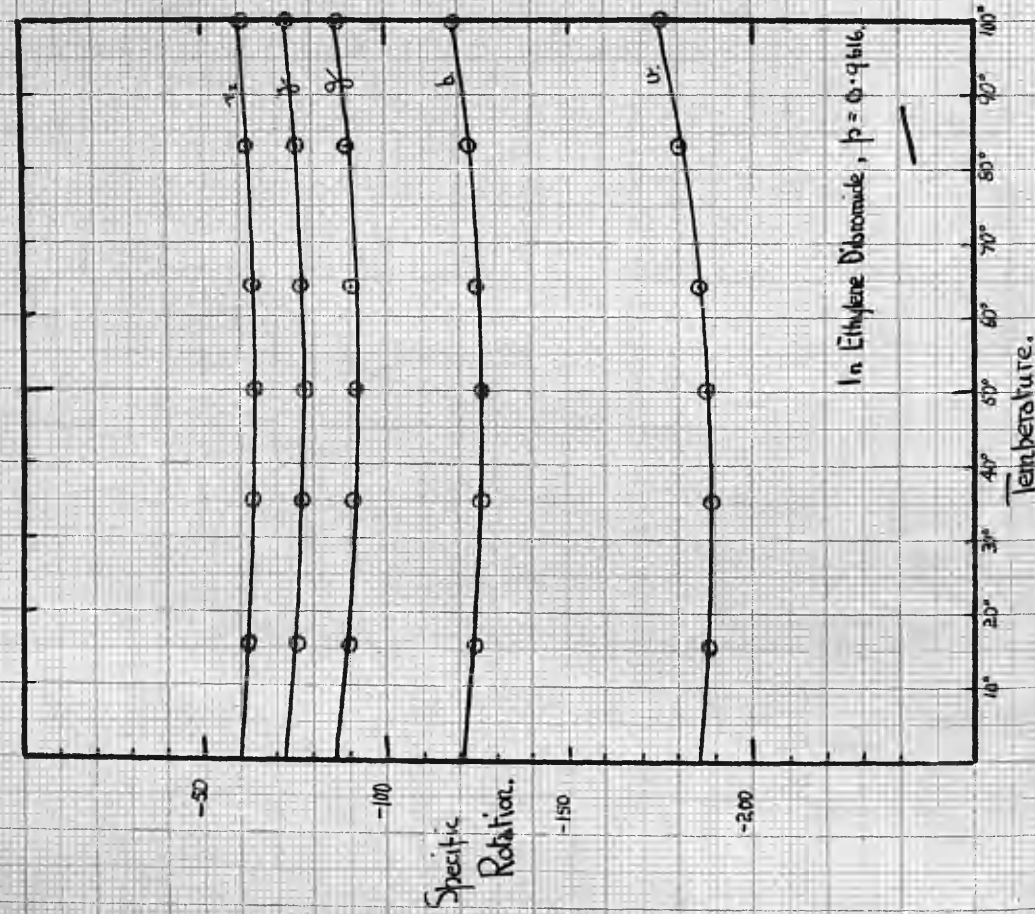


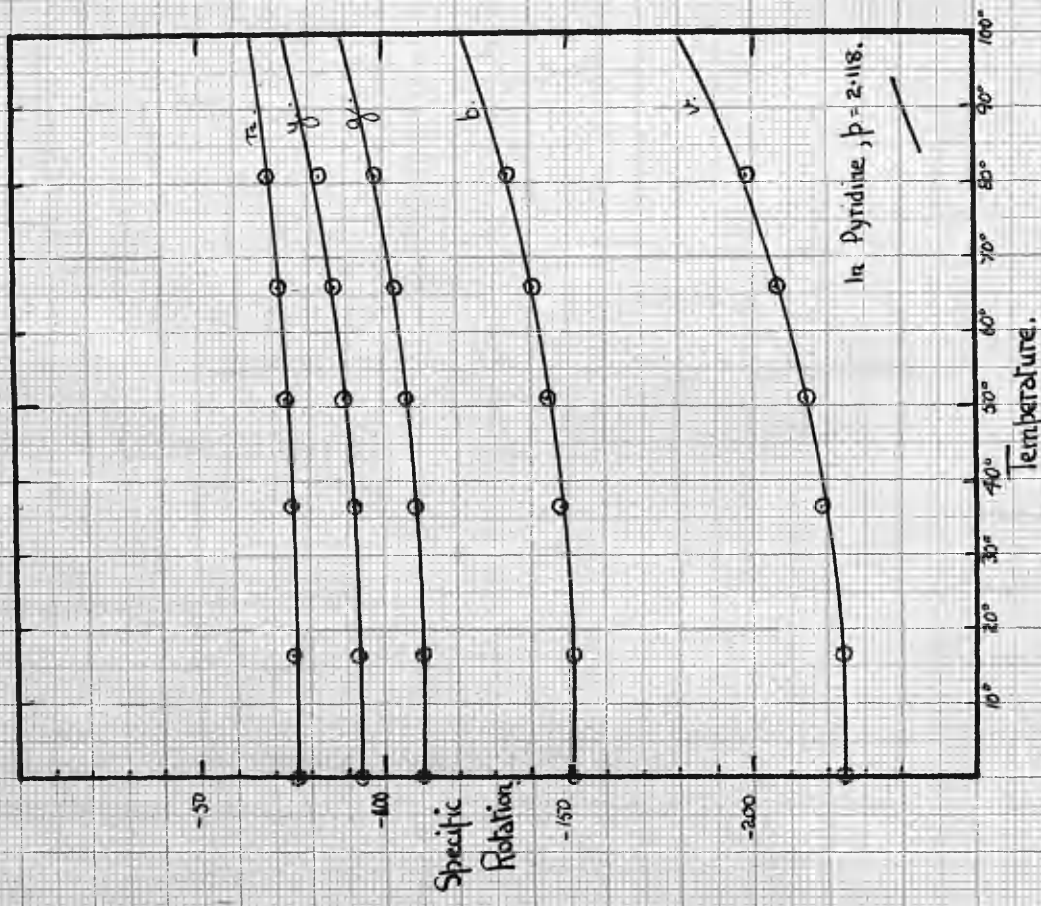
FIG. I. T-R curves for methyl and ethyl dibenzoyltartrates.

(Frankland and Wharton, J.C.S., 1896, 69, 1587)

have similar effects on the displacement of characteristic regions in T-R curves, then just as movement of a minimum in negative rotation to a lower temperature by a solvent means an increase in negative rotation ( Part I, page 28), the converse might be expected to apply in this case -- that is, the minimum for methyl dibenzoyltartrate occurs , quite obviously from Fig. I above, at a lower temperature and at a greater negative value than for the ethyl compound. If this is the case, then from the regular changes in rotation



**FIG. II.** T-R curves for dimethyl dibenzoyl-d-tartrate in ethylene bromide.



**FIG. III.** T-R curves for dimethyl dibenzoyl-d-tartrate in pyridine.

existing for a homologous series ( For summary see Kenyon, Trans. Far. Soc., 1930, 26, 439), it is to be expected that the minimum in T-R curves for the dibenzoyltartrates moves to a higher temperature and lower rotational value with increase in molecular weight. It may thus be possible that one of the di-alkyl benzoyltartrates gives T-R curves similar to those for di-o-nitrobenzyl dibenzoyl-d-tartrate in quinoline solution ( Fig. XVII, Part I).

To test this idea, the di-methyl, di-ethyl, di-n-propyl, and di-n-butyl esters of dibenzoyl-d-tartaric acid were prepared and examined, not in the homogeneous condition, but in the solvents pyridine, quinoline, and ethylene bromide. It was thought that by the use of solvents variation in rotation for the esters might be obtained to allow extension of the results.

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#### Dimethyl Dibenzoyl-d-tartrate.

Using concentrations of about 2% , the T-R curves for this compound in the three solvents, ethylene bromide, pyridine, and quinoline, were determined, and are given in full in Figs. II, III, and IV. From these it will be seen that all are in a region of negative rotation with the curve for the longest wave-length nearest the zero axis.



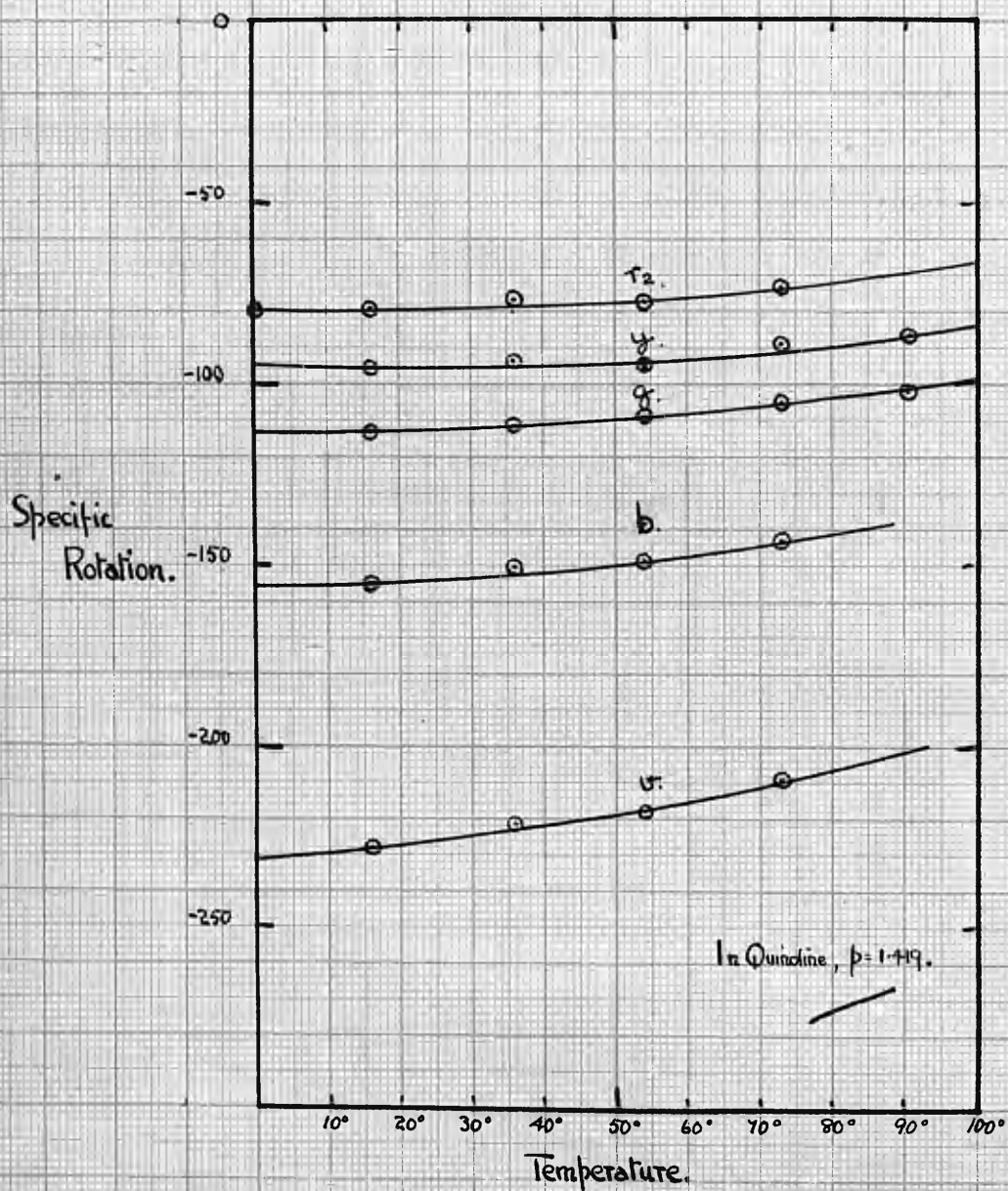


FIG. IV. T-R curves for dimethyl dibenzoyl-D-tartrate in quinoline.

and all the other curves arranged in a normal order.

The ethylene bromide solution (  $p = 0.9616$ , Fig. II) shows a region of negative minima, with the minimum displaced to a lower temperature and higher rotational value for decrease in wave-length -- the characteristic feature of such a region. The minimum for mercury-green light occurs at a temperature of  $50^{\circ}$  for a rotational value of  $-92^{\circ}$ .

For the pyridine solution (  $p = 2.118$ , Fig. III) the region of minima occurs at a lower range of temperature than for the ethylene bromide solution. The minima in the curves appear between the temperatures of  $0^{\circ}$  and  $15^{\circ}\text{C.}$ , the rotations thereafter decrease with heating. The specific rotation for green at the minimum is  $-111^{\circ}$ , the temperature being approximately  $5^{\circ}$ .

No minimum is apparent in any of the curves for the quinoline solution (  $p = 1.419$ , Fig. IV), and all rotations decrease with increase of temperature.

Comparing the effects of the three solvents on the rotation, it is seen that on changing from ethylene bromide to pyridine the region of minima is displaced towards a lower temperature and higher values. The same can be said of the change from pyridine to quinoline, for the minima disappear from the curves, which only indicate that they may have passed through minima of higher negative values at a lower temperature than  $0^{\circ}\text{C.}$  Referring this conclusion to the fundamental T-R curves for tartrates

( page 31), it is obvious, if the curves for the ethylene bromide solution are regarded as being in the very centre of the region of negative minima, x v z, that the effect of pyridine is to give a region a little to the right, x v z a, and that quinoline gives a displacement still further to the right, y z a, so that no minimum is present.

This interpretation of the relative effects of the solvents on rotation is not in agreement with the magnitude of the rotations. For example, the following are the values of the specific rotation for all three solutions at 0°C :-

	$[\alpha]_{5461}^{\circ}$
Ethylene bromide .....	-86° (by extrapolation)
Pyridine .....	-110.4°
Quinoline .....	-114°(by extrapolation)

From which it would seem that quinoline has the strongest depressant effect on the rotation, a conclusion which is not in accordance with that derived from a study of the form of the T-R curves as above. The solvents are in opposite sequences for these two methods of correlating their effect on the rotation.

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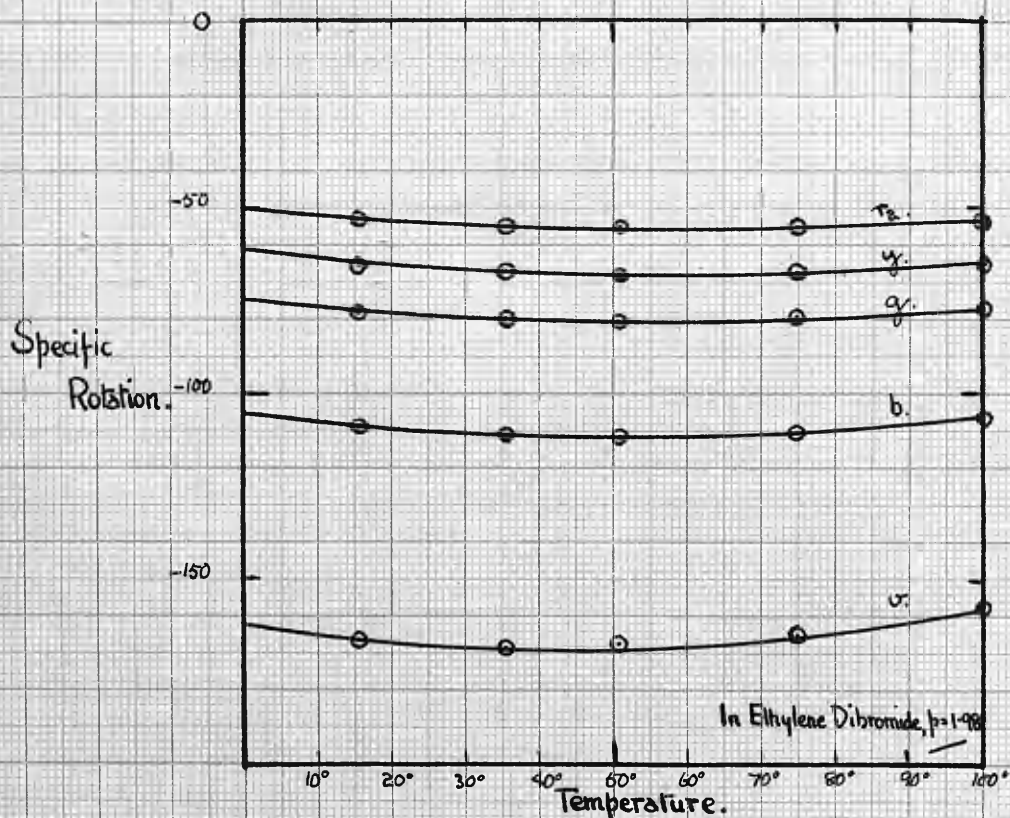


FIG. V. T-R curves for diethyl dibenzoyl-*d*-tartrate in ethylene bromide.

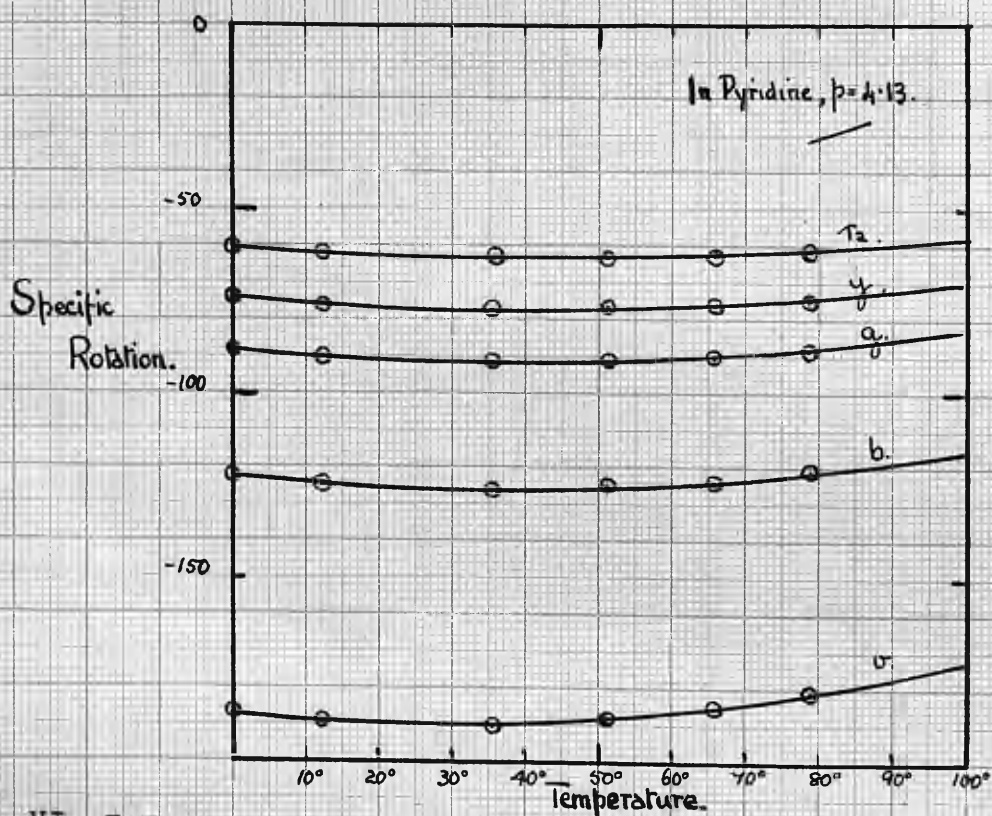


FIG. VI. T-R curves for diethyl dibenzoyl-*d*-tartrate in pyridine.

Diethyl Dibenzoyl-d-tartrate.

The T-R curves for this compound in the three solvents ( Figs. V, VI, and VII) are somewhat similar to those for the methyl homologue.

The curves for the ethylene bromide solution (  $p = 1.984$ , Fig. V) still show between  $0^{\circ}$  and  $100^{\circ}\text{C}$ . a complete region of negative minima. The minimum for green light occurs at  $-81^{\circ}$  specific rotation and about  $55^{\circ}\text{C}$ .

The T-R curves for pyridine (  $p = 4.13$ , Fig. VI) possess minima at lower temperatures and of greater rotational values than those for ethylene bromide. The minimum for green occurs at  $40^{\circ}\text{C}$ . and has the value of  $-92^{\circ}$ .

When the ethyl dibenzoyltartrate is dissolved in quinoline (  $p = 2.874$ , Fig. VII), the curves are still concave to the zero axis but the negative minima are indicated only at the high-temperature end of the graph. The minimum in the green curve has the values  $-80^{\circ}$  specific rotation and  $76^{\circ}\text{C}$ .

On the same graph (Fig. VII) is drawn the green ( $\lambda = 5461 \text{ \AA.U.}$ ) line for the homogeneous compound. This is based on Wood and Nicholas's results (loc.cit.), the values for this wave-length being obtained by intrapolation.

The effect of the solvents on the magnitude of the rotation can be judged from the values of the rotations for green light at  $0^{\circ}\text{C}$ ., as given in the following table:-

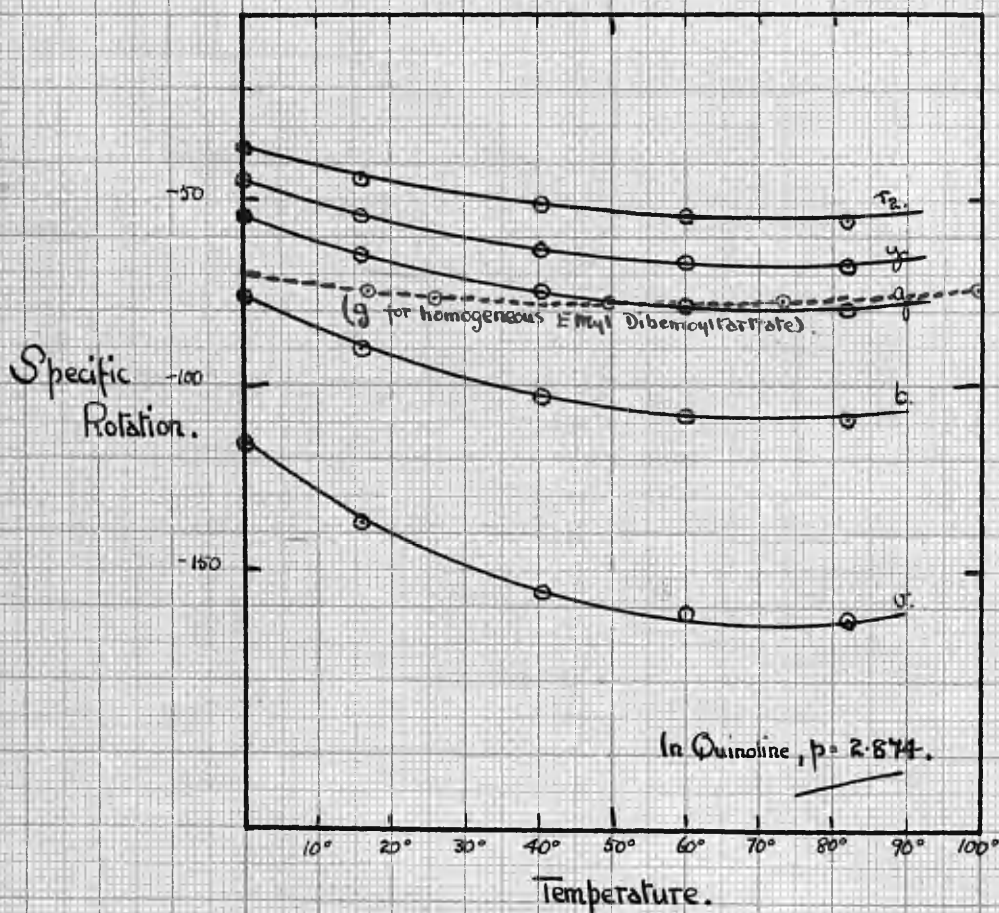


FIG. VII. T-R curves for diethyl dibenzoyl- $\alpha$ -tartrate in quinoline.

Quinoline .....	-53.91°
Homogeneous tartrate .....	-70°( by extrapolation)
Ethylene bromide .....	-74°(by extrapolation)
Pyridine.....	88.06°

From this it seems that pyridine has the greatest negative effect on the rotation of ethyl dibenzoyltartrate, and that quinoline raises the rotation.

Viewing the results with reference to the T-R curves for tartrates (page 31), the sequence of the solvents in accordance with their effect on the form of the T-R curves is the same. Quinoline solution gives the region w x y to the left of that for the homogeneous compound, x y z; there is very little difference between the green line for the homogeneous compound and for the ethylene bromide solution, but since the minimum for the ethylene bromide solution occurs at a greater negative value, the curves for the solution are slightly to the ~~right~~ of those for the homogeneous compound; the curves for the pyridine solution, of the type x y z a, are to be regarded as on the right of those for ethylene bromide.

The solvents are therefore to be regarded as being in the following order of effect on the rotation:-

<sup>w x y</sup>  
 Quinoline....(Benzoyltartrate)..<sup>x y z</sup>Ethylene bromide...<sup>x y z</sup>Pyridine.<sup>x y z a</sup>

---



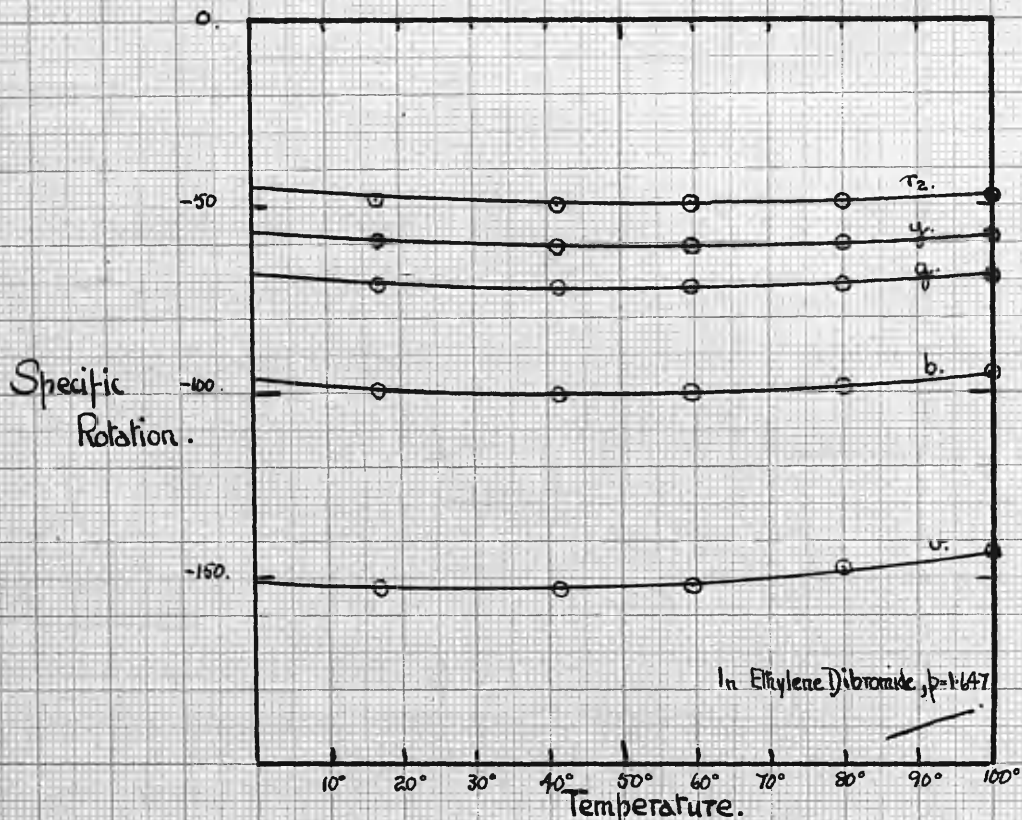


FIG. VIII. T-R curves for di-*n*-butyl dibenzoyl-*d*-tartrate in ethylene bromide.

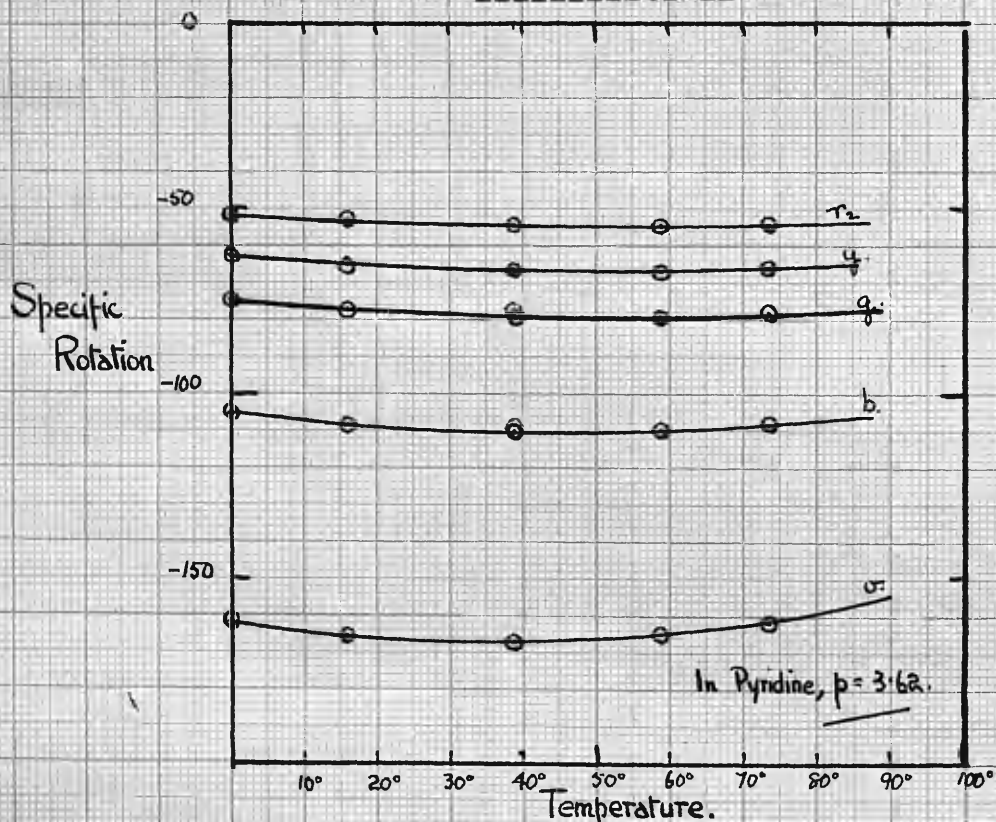


FIG. IX. T-R curves for di-*n*-butyl dibenzoyl-*d*-tartrate in pyridine.



Di-n-propyl Dibenzoyl-d-tartrate.

The results of the polarimetric observations are given in Figs. VIII, IX, and X), from which it will be seen that in general the curves are similar to those for diethyl dibenzoyltartrate solutions.

The ethylene bromide solution (  $p = 1.647$ , Fig. VIII) gives curves showing minima of rotation. The minimum for mercury-green having the value of  $-72^\circ$  occurs at  $55^\circ\text{C}$ .

The pyridine solution (  $p = 3.62$ , Fig. IX) as before gives a region of minima at lower temperatures and higher values than for ethylene bromide. The minimum in the curve for green occurs at a temperature of  $50^\circ\text{C}$ . and has a value of  $-80^\circ$ .

The quinoline solution (  $p = 3.27$ , Fig. X) shows no direct minima within the experimental range of temperature, but by continuation of the curves minima make their appearance at the high-temperature ends of the curves. The value in specific rotation for the minimum for green is  $-67^\circ$  ; the temperature is approximately  $80^\circ\text{C}$ .

The values of the specific rotations for green at  $0^\circ\text{C}$  are :-

Quinoline .....	$-36^\circ$
Ethylene bromide.....	$-68^\circ$ (by extrapolation)
Pyridine .....	$-75^\circ$

These values show that when magnitude of rotation is considered pyridine depresses the rotation most. This order is the same as that for the ethyl homologue (page 65).

Referring to the shape of the T-R curves, the quinoline solution gives curves that are typical of the region v w x (y) of the fundamental T-R curves (page 31, Part I). The curves for ethylene bromide are for the region of minima itself, the region x y z, whilst those for pyridine must be regarded as slightly to the right of this region. The sequence of the solvents according to magnitude of rotation or form of the curves is therefore the same for this compound.

-----

#### Di-n-butyl Dibenzoyl-d-tartrate.

From the T-R curves for this compound in the three solvents ( Figs., XI, XII, and XIII) it can be seen that they are similar to those for the diethyl and di-n-propyl derivatives.

The solution in ethylene bromide still gives a region of negative minima between the temperatures of 0° and 100°C. (  $p$ , of solution, = 1.705, Fig. XI). The value of the specific rotation at the minimum in the green curve is  $-62^\circ$ , at a temperature of 60° ; these being lower values

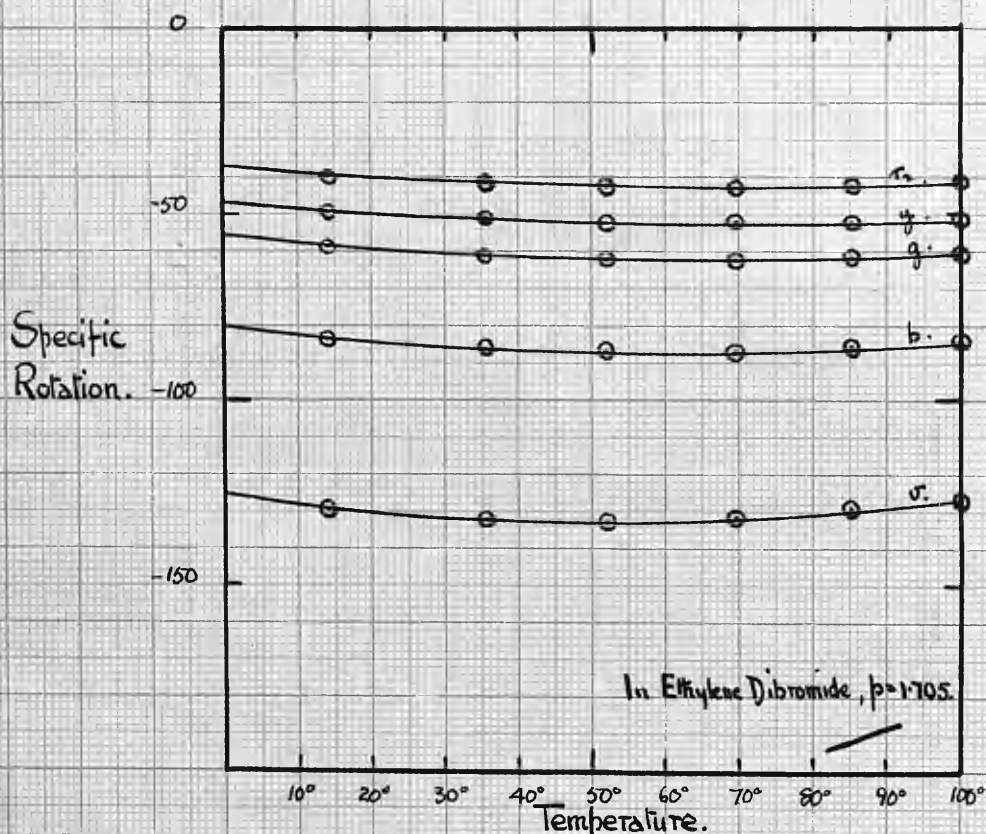


FIG. XI. T-R curves for di-n-propyl dibenzoyl-d-tartrate in ethylene bromide

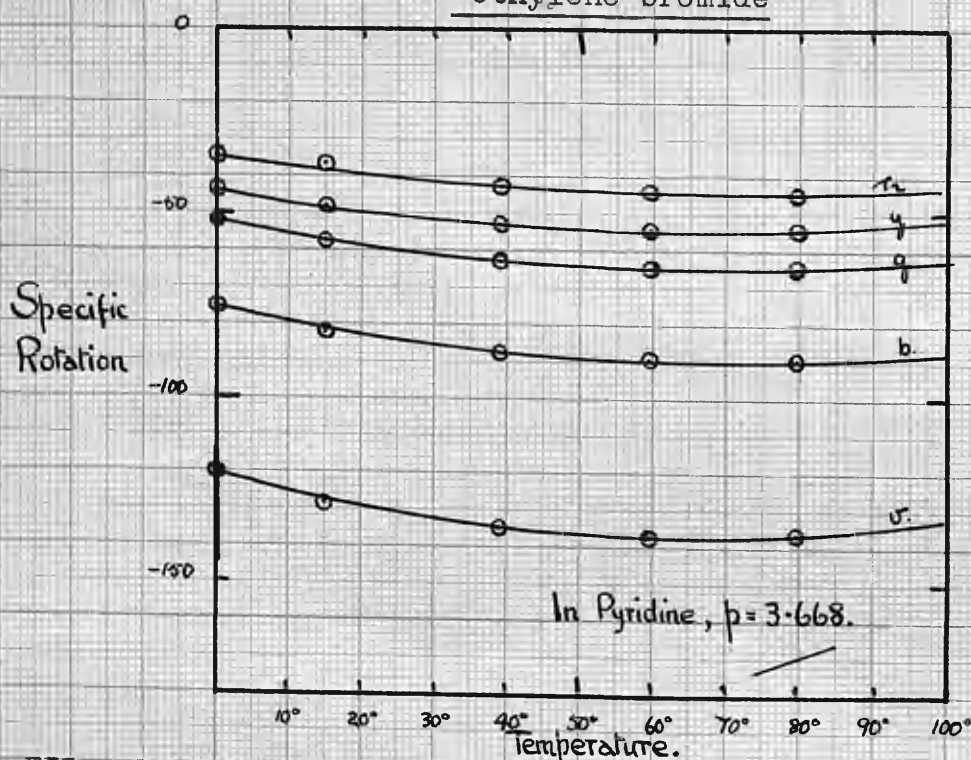


FIG. XII. T-R curves for di-n-propyl dibenzoyl-d-tartrate in pyridine.

than for the propyl homologue in the same solvent.

In the curves for the pyridine solution (  $p = 3.668$ , Fig. XII) the region of minima occurs almost at the same temperatures and for almost the same rotational values as for the ethylene bromide solution. Towards the low-temperature ends of the graphs, there is quite a difference between the T-Rs of the two solutions.; the pyridine curves have a more decided rotation-temperature gradient,  $\frac{d[\alpha]}{dT}$ , falling from higher rotational values to the minimum values. The minimum for mercury-green occurs at a temperature of 70°C. and has the value -65°.

In this instance, the T-R curves for the quinoline solution(  $p = 3.353$ , Fig.XIII) all, with the exception of that for violet which has a very small negative value, pass through positive rotations at 0°C into the negative region of rotation with increase of temperature. From the trend of the curves themselves there is every indication that at a temperature but a little lower than 0°C, a region of visible anomaly is to be found -- a region similar to that obtained for the quinoline solution of di-o-nitrobenzyl dibenzoyl-d-tartrate (pages 29 - 31, Fig.XVII -Part I). This result confirms the existence of such a region of anomaly for tartrates in general, even though the region is not fully revealed for this solution.

There are no actual negative minima in the curves,

but the shape of the curves suggests that they are tending towards such a region, which quite probably exists at 100°C.

The specific rotation values for green light at 0°C. are :-

Quinoline.....	+ 5.5°
Pyridine.....	-52°
Ethylene bromide.....	-56° (by extrapolation)

The quinoline solution gives curves corresponding to the region u v w x of the fundamental T-R curves (Part I, page 31 ), and the curves for pyridine and ethylene bromide occupy very similar positions in the middle of the negative minima region, x y z.

The sequence of the solvents according to their effect on rotation is almost the same as for the propyl homologue. There is not, however, such a decided difference between the curves for pyridine and ethylene bromide solutions.

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### Characteristic Diagrams.

Since the solutions in pyridine and in ethylene bromide are generally confined to the actual region of minima of rotation, characteristic diagrams constructed from

these results cannot be expected to show any regularities. Such a point was brought forward in the case of di-o-nitrobenzyl dibenzoyl-d-tartrate for similar curves ( Part I, page 32). The curves for the quinoline solutions, having greater variation in shape and showing a more decided change in rotation with change in temperature, indicate that the dispersion data for these solutions would be most suitable for characteristic diagrams.

Fig. XIV contains the characteristic diagrams for the quinoline solutions of the four compounds, and the violet line for ethyl tartrate has been plotted for purposes of comparison. It is seen that, for all lines but violet, the results for all four compounds are collinear for each wave-length. There is a little irregularity for the methyl dibenzoyltartrate results , but it must be remembered that the curves for this solution are for the high-temperature side of the negative minimum, x y z; some such irregularity is thus to be expected.

The variation in the position of the violet line markedly shows the difference in the dispersion relationships of the compounds. For methyl dibenzoyltartrate this line is not regular ,as has been pointed out above. For the ethyl and propyl derivatives, the same line serves to summarise the change of the rotation for violet with variation in the value of green, and in general the results for the latter compound are nearest the rational zero, which

has a value of  $+21^{\circ}$ . For the n-butyl dibenzoyltartrate in quinoline, there is a slight difference in the violet line from that for the ethyl and propyl solutions. The line is parallel and only a little displaced. The rational zero is now  $+18^{\circ}$ . The rational zero of ethyl tartrate is  $+14.27^{\circ}$  (Patterson, J.C.S., 1916, 109, 1191), and the violet line for this compound is also parallel to those for the dibenzoyltartrates in quinoline solution.

It has been said (page 68) that the T-R curves obtained for the quinoline solution of di-n-butyl dibenzoyl-d-tartrate are confirmatory of the existence for tartrates in general of the new anomalous region as revealed by a quinoline solution of di-o-nitrobenzyl dibenzoyl-d-tartrate (Part I, pages 29 - 31 ; Fig. XVII). The characteristic diagrams are not the least similar, however. The dissimilarity is indicated in the rational zero values; that for the butyl compound, as given above, is  $+18^{\circ}$ , whilst the zero for the other is  $+40^{\circ}$ . This enormous difference is inexplicable if the curves are really for similar regions, except on the assumption that the nitro-group in the nitrobenzyl compound causes considerable dispersion distortion. Such an assumption is quite feasible, since it has been shown that there is some difference in the characteristic diagrams for the meta- and the para-compounds, and that the diagram cannot be utilised at all in connexion with

the ortho-derivatives. In further support of this supposition, Pickard and Kenyon (J.C.S., 1915, 107, 35) found that the specific rotatory powers of l-menthol and of many derivatives can be coordinated on one characteristic diagram, but that the results for the nitrobenzoic esters give a different characteristic diagram, on which the results for the ortho-compound do not fit very well. They, Pickard and Kenyon, attribute the dissimilarity of the characteristic diagrams to the presence of the nitro-grouping; they also suggest that this variation is due to the fact that the nitro-substituted acids may contain either the grouping  $\text{-N} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{O} \end{smallmatrix}$  or  $\text{-N} \begin{smallmatrix} \text{O} \\ \text{=O} \end{smallmatrix}$ . Without any discussion of this "explanation," it is evident that the presence of the nitro-group does modify the dispersion relationships to a considerable degree. It can thus be taken that the results for the quinoline solution of di-n-butyl dibenzoyl-d-tartrate do confirm the existence of such a region of anomalous dispersion for tartrates as revealed by the nitrobenzyl dibenzoyltartrate and as suggested on the amended fundamental T-R diagram (page 31).

From the trend of the results on the characteristic diagram with ascent of the homologous series, it is extremely possible that the results for a higher homologue will in the same solvent reveal the whole anomalous region.

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### General Discussion.

It has previously been suggested (Part I, pages 34 - 35) that magnitude of rotation is not so decisive in correlating the effect of solvents on rotatory power as the presence, or proximity, of an easily identifiable region in T-R curves. Where the dibenzoyltartrates are concerned, all the T-R curves exhibit negative minima or by their form indicate that a region of such minima is near, and thus comparison of solvent effect is easily made.

It is a curious fact that for every ethylene bromide solution the T-R curves possess negative minima, lying almost symmetrically between 0° and 100°C.; the temperatures at which the minimum appears in the curves for green are, progressively, 50°, 55°, 55°, and 60°. The same feature is evident for the ethylene bromide solutions of iso-butyl dibenzoyl-d-tartrate (Patterson and Moudgill, Proc. Roy. Soc. Edin., 1918-19, 39, 26 - Fig.3), and also of di-o-nitrobenzyl dibenzoyl-d-tartrate (Part I, page 27 and Fig. XV). This illustrates very well the depressant effect that this solvent has upon the rotation of these dibenzoyltartrates, and seems to suggest that the ethylene bromide solutions of other simple dibenzoyltartrates will produce T-R curves with negative minima.

Considering the curves for the ethylene bromide,

pyridine, and the quinoline solutions, it is to be noticed that they are not in the same sequence for every compound. For methyl dibenzoyltartrate, ethylene bromide gives curves in the region of negative minima, x y z, the pyridine curves show a displacement to the right of this region, and quinoline gives a further displacement in this direction. For all the other compounds, the quinoline solution gives T-R curves of a form more to the left of the negative minimum, as revealed by ethylene bromide solutions, whilst the curves for pyridine are towards the right.

Further, it is to be noticed that, in passing from the methyl to the n-butyl homologue, the difference between the curves for ethylene bromide and for the corresponding solution in pyridine becomes less marked; for the n-butyl compound there is some difficulty in distinguishing the relation between the two.

It has thus been demonstrated that, for this homologous series of the dibenzoyltartrates, the relative effects of the solvents on the rotatory power is not constant. This being the case, the results are in disagreement with any theory which attempts to correlate the rotatory power of a solution with a physical property of the pure solvent. Although Rule and McLean (J.C.S., 1931, 674) have shown that for l-menthyl methyl benzoate there is a relationship between

the rotation and the dipole moments of solvents, no such connexion is observed for the dibenzoyltartrates . The dipole moments of the three solvents are :-

<u>Moment x <math>10^{18}</math> e.s.u.</u>	
Quinoline.....	2.184 (Le Fevre and Smith, J.C.S.,1932, 2811)
Pyridine .....	2.21 ( Engel and Meyer, Ber.,1932, <u>65</u> ,446)
Ethylene bromide	0.8 - 1.05 (Smyth and Kammerlung, J.A.C.S., 1931, <u>53</u> , 2988).

According to Rule's views, ethylene bromide being the least polar solvent should give the greatest rotation values. This is not the case for methyl dibenzoyltartrate, where the quinoline solution possesses the greatest rotation values. On the whole, no parallelism can be seen to exist between the moments for the pure solvents and their effect on rotation, there being no fixed regularity of effect throughout the dibenzoyltartrate series.

Rule and McLean(J.C.S.,1932, 1409) observing similar irregularities offer the explanation that the polar solvents tend to enter into combination or dipole association with the solute. In an investigation with the 1-menthyl dialkylmalonates, Rule and Ritchie (J.C.S., 1932, 2332) demonstrate once again a lack of relationship, and postulate the existence of some disturbing factor which operates in all cases except for the dipropyl and dibutylmalonates. The hypothesis meets with many exceptions.

Singh and Biswas (J.C.S., 1924, 125, 1895) tried to correlate dielectric constant of the solvent and rotatory power, showed that no relationship existed, and suggested that it would be more rational to attempt the correlation with the dielectric constant of the corresponding solutions. A similar conclusion ought to be made with regard to the dipolemoment theory.

The T-R curves for the quinoline solutions, more than for the pyridine solutions, show a progressive change in passing from one compound to the other in the homologous series. It has been shown that the curves for the methyl compound are comparable to the region y z a of the fundamental curves for tartrates (page 63). For the ethyl derivative, the curves are of the form w x y (page 65) and for the n-propyl compound they are intermediate with the latter region and that for the n-butyl homologue, the region u v w x ( pages 67 and 69). The increase in molecular weight seems to mean a displacement of the T-R curves towards the low-temperature region, s t u v, of the fundamental T-R curves for tartrates (Part I, page 31).

In conclusion, it has to be claimed that the results of this investigation have demonstrated the usefulness of Professor Patterson's hypothesis of periodicity in T-R curves ; indeed, they emphasize its indispensability.

EXPERIMENTAL.

For this series of compounds, the following five wave-lengths were used for the examinations of rotatory power :-

$\lambda$ (A.U)	$r_D$	$\gamma$	$g$	$b$	$v$
	6234	5790	5461	4916	4358

-----

Methyl Dibenzoyl-d-tartrate.

This compound was prepared by the method of Frankland and Wharton (J.C.S., 1896, 69, 1585). The excess benzoyl chloride having been distilled off under reduced pressure, the distillate at 180 - 220°C. under a pressure of 0.6mm. of Hg was collected. This was recrystallised four times from absolute alcohol.

M.pt. 135° : c.f. 135.5° ( Frankland and Wharton, loc. cit.)

and 135.5° (Wood and Nicholas, J.C.S., 1928, 1689)

Starting with 15g. of methyl tartrate, 12.7g. of the dibenzoyltartrate were obtained. Yield, 32%.

For a solution of 2.466% in pyridine,  $[\alpha]_{546}^{20} = \underline{-109.3^\circ}$ .

In ethylene bromide,  $p = 0.9616$ .

(Fig. II)

t.	d.	$[\alpha]_{r_2}$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
15.5°	2.174	-61.98	-75.44	-89.54	-124.0	-187.8
35	2.133	63.59	77.13	90.93	125.8	188.7
50	2.104	63.96	77.71	91.60	126.0	187.4
64	2.074	63.48	76.54	90.33	124.7	185.7
83	2.033	62.18	75.67	88.86	122.7	180.3
100	1.999	61.37	73.55	87.04	118.7	175.4

---

In pyridine,  $p = 2.118$ .

(Fig. III)

0°	*1.0065	-76.37	-93.46	-110.4	-150.8	-224.6
16.5	0.9906	77.32	93.17	110.3	151.5	223.9
36.5	0.9705	75.25	92.04	108.6	147.8	218.6
51	0.9561	73.57	89.19	106.0	144.3	214.6
66	0.9410	72.18	86.76	103.4	140.5	206.6
81	0.9253	69.10	82.75	98.22	133.9	198.6

---

In quinoline,  $p = 1.419$ .

(Fig. IV)

16°	1.099	-79.50	-96.47	-113.3	-154.9	-227.8
36	1.083	76.98	94.17	111.3	150.5	221.3
54	1.069	77.52	92.39	108.8	148.5	218.2
73	1.054	73.53	88.90	105.3	143.0	208.9
90.5	1.040	-	86.58	101.8	-	-

---

\* All densities are experimental except those marked with \*.

Ethyl Dibenzoyl-d-tartrate.

The diethyl dibenzoyltartrate was prepared by the method of Frankland and Wharton (loc. cit.). On fractionation under reduced pressure, it was collected at 218 - 220°C. at 0.3mm. Hg. The jelly thus obtained crystallised on standing in the refrigerator for a few days. The solid obtained was repeatedly recrystallised from aqueous alcohol. 17.5 g. of ethyl tartrate yielded 6.5 g., the yield was therefore 18.5%.

M.pt. 63.5°C. : c.f. 62.5° (Frankland and Wharton, l.c.).

63.5 (Wood and Nicholas, l.c.).

For a solution of 2.15% in pyridine  $[\alpha]_{5461}^{20} = \underline{-90.84^\circ}$

-----

In ethylene bromide.  $p = 1.984.$

(Fig. V)

t.	d.	$[\alpha]_F$	$[\alpha]_Y$	$[\alpha]_G$	$[\alpha]_B$	$[\alpha]_V$
15.5°	*2.16	-52.93	-65.30	-77.94	-109.1	-166.3
35.5	2.122	55.12	66.94	79.79	111.0	168.7
50.75	2.091	55.58	67.84	80.41	111.4	167.7
74.75	2.042	55.21	67.25	79.54	110.3	165.1
100	1.986	53.70	64.89	76.98	106.4	157.3

-----

In pyridine,  $p = 4.13$ .

(Fig. VI)

t.	d.	$[\alpha]_x$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
0°	*1.069	-60.50	-74.18	-88.06	-122.6	-186.6
12.25	0.9970	62.20	75.97	90.01	125.2	188.8
35.5	0.9743	63.22	77.34	91.49	126.2	189.8
51.25	0.9585	63.54	76.74	91.05	124.9	187.8
65.75	0.9441	62.75	76.17	89.80	123.8	185.1
78.75	0.9307	61.49	74.92	88.33	121.3	181.0

---

In quinoline,  $p = 2.874$ .

(Fig VII)

0°	*1.112	-36.15	-44.36	-53.91	-75.93	-117.7
16	1.099	44.08	54.13	64.43	90.07	137.2
40.5	1.081	51.24	63.08	74.49	102.8	155.8
60	1.065	54.11	66.33	78.54	108.0	161.4
82	1.047	55.30	67.61	79.34	109.1	163.0

---

Di-n-propyl Dibenzoyl-d-tartrate.

This ester was prepared by the same method as the methyl and ethyl compounds. Propyl tartrate (23g.) was heated with excess benzoyl chloride (50g.) to 140 - 150°C. for four hours. The excess benzoyl chloride was distilled off under reduced pressure and the residue distilled



in high vacuum. The solid obtained at 234°C, under a pressure of 7mm. Hg was spread on a porous plate to remove any oily material. This was dissolved in methylated spirits and, after standing for several days, crystals were obtained. After three recrystallisations from aqueous alcohol, the product was obtained as fine white needle crystals, m.pt.

44.5°C. 6.5 g. were obtained, yield was 15.0%..

| Found: C, 64.63 ; H, 6.305. Calculated: C, 64.86 ; H, 6.306%)

For a 2.162% solution in pyridine  $[\alpha]_{5461}^{17.5} = - \underline{78.16^\circ}$ .

This compound is much more soluble in the various solvents, alcohol, ethylene bromide, pyridine, benzene, etc., than the methyl and ethyl compounds. For example a 7% solution in ethylene bromide is possible.

In ethylene bromide,  $p = 1.647$ .

( Fig. VIII)

t.	d.	$[\alpha]_{r_2}$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_{vv}$
17°	2.154	-48.18	-59.26	-70.84	-99.51	-152.4
41.5	2.105	49.60	60.71	72.18	100.6	152.9
59.5	2.068	49.64	61.03	71.91	99.93	151.7
80	2.026	48.87	59.75	70.87	98.47	147.6
100	*1.984	47.28	57.99	68.82	94.71	142.7

In pyridine,  $p = 3.62$ .

(Fig. IX)

t.	d.	$[\alpha]_{r_2}$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
0°	*1.0073	-52.22	-62.44	-74.76	-105.0	-161.4
16	0.9917	52.90	65.43	77.61	108.6	165.5
38.75	0.9692	54.50	66.73	79.41	110.0	167.0
58.75	0.9493	54.70	67.19	79.34	109.7	164.9
73.5	0.9342	53.87	66.01	77.89	108.0	162.2

---

In quinoline,  $p = 3.27$ .

(Fig. X)

0°	*1.1114	-23.25	-29.70	-36.20	-52.83	-85.94
14.5	1.100	31.78	38.71	47.07	67.25	104.4
37.5	1.082	40.05	49.26	58.99	82.77	126.4
51.75	1.071	43.24	52.88	63.45	88.59	135.0
68	1.058	45.61	56.33	66.49	92.23	139.9
80.5	1.048	46.52	56.76	67.76	93.53	141.2

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Di-n-butyl Dibenzoyl-d-tartrate.

This compound was prepared by the usual method. The n-butyl tartrate (35 g.) was heated to 140 -150°C. with excess benzoyl chloride (70 g.).

The solid of b.pt. 245 - 250°C. at 1.2mm. melted

at 41 - 43°C. This ester could not be recrystallised from any of the usual solvents and had therefore to be purified by fractionation under reduced pressure. The portion boiling at 250° at 1.3mm. was taken. This solidified on standing to a white crystalline solid of m.p. 43°C.

(Found : C, 66.27; H, 6.16. Calc.: C, 66.39; H, 6.38%)

The yield was 18 g., i.e., 28.7%.

For a solution of 3.64% in pyridine  $[\alpha]_{5461}^{15} = -57.62^{\circ}$

This compound is soluble in most solvents - alcohol, benzene, from which it is not precipitated by petroleum ether, carbon tetrachloride, acetone, chloroform, ether. It is insoluble in water.

In ethylene bromide,  $p = 1.705$ .

(Fig. XI)

t.	d.	$[\alpha]_{r_2}$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
14°	2.158	-39.92	-49.38	-58.83	-83.73	-129.5
35.5	2.114	41.79	51.31	61.19	86.18	131.9
52	2.081	42.59	52.41	62.20	86.76	132.6
69.5	2.045	42.80	52.28	62.32	87.02	131.4
85.25	*2.0125	42.31	52.02	61.45	85.61	128.9
100	1.982	41.59	51.40	60.59	83.92	127.0

In pyridine,  $p = 3.668$ .

(Fig. XII)

t.	d.	$[\alpha]_{r_2}$	$[\alpha]_y$	$[\alpha]_g$	$[\alpha]_b$	$[\alpha]_v$
0°	*1.007	-34.64	-43.49	-52.22	-75.09	-120.0
15	0.9924	38.50	47.95	57.62	81.98	128.3
39	0.9685	42.53	52.58	62.47	87.76	134.9
59.5	0.9477	44.21	54.28	64.54	89.30	137.4
79.5	0.9272	44.33	54.48	64.59	89.41	136.4

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In quinoline,  $p = 3.353$ .

(Fig. XIII)

0°	*1.1105	+6.631	+6.497	+5.776	+2.92	-4.65
15	1.099	-5.241	-7.665	-10.14	-18.24	-34.61
36.5	1.082	17.91	22.69	28.28	41.72	67.08
51	1.071	23.85	29.68	36.36	52.11	81.87
65	1.059	28.19	34.76	41.91	59.81	92.62
82.25	1.046	31.89	39.04	46.89	65.79	100.80

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### CONCLUSION.

CONCLUSION.

In the researches just described, much use has been made of Professor Patterson's suggestion of periodicity in the temperature-rotation curves for optically active compounds to bring results, widely varied in some cases, into harmony with one another. The application has been attended by no small measure of success, and the continuities in rotatory power thus observed are convincingly in support of the hypothesis.

In Part I (page 31), an extension to the fundamental T-R curves for tartrates has been made on the recognition of a new region of visible anomaly, wherein intersection of the T-R curves and decrease of rotation occur with rise in temperature. This extension is confirmed in Part II (pages 68, and 71 - 72).

As an outcome of this work on the effect of solvents on the rotatory power of related compounds, it cannot be said that any simple relationship exists between the nature of the solvent and its effect on rotatory power. Certain regularities have been observed, however, but no generalisations can be founded thereon.