

CCCXC.—*The Influence of Solvents and of Other Factors on the Rotation of Optically Active Compounds. Part XXVIII. The Rotation Dispersion of Mannitol and Some of its Derivatives. Note on Rotation Dispersion Curves.*

By THOMAS STEWART PATTERSON and ALEXANDER
ROBERTUS TODD.

WHEN the rotation of an optically active compound is plotted against the square of the wave-length of the light used, it sometimes happens, as was first pointed out by Biot, that a curve approximating to a rectangular hyperbola is obtained. Drude ("Lehrbuch der Optik," 1900, 380) modified Biot's expression by writing $\alpha = k/(\lambda^2 - \lambda_0^2)$,

where λ_0 is a wave-length of a supposed absorption band. If, when this expression is used, the approximation to a hyperbola is such that any deviation falls within the limiting experimental error of ordinary polarimetric apparatus, it has become not uncommon to describe the dispersion as "simple," other terms, "complex" and "anomalous," being used to indicate divergences from this type of curve.

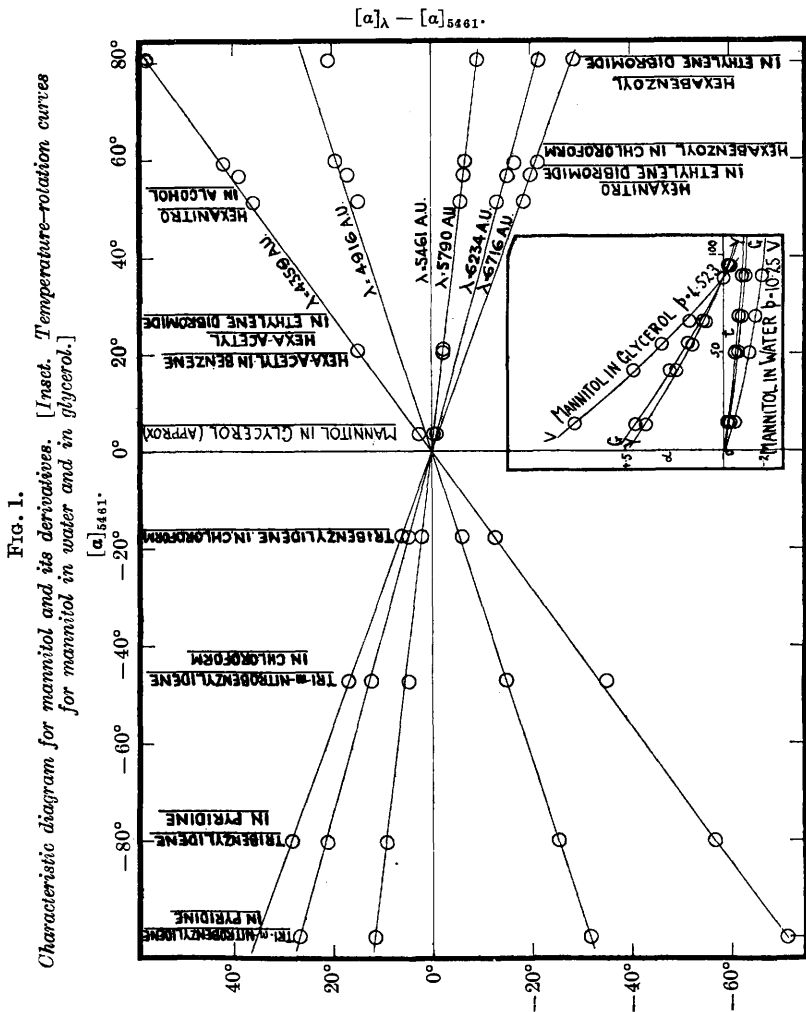
In most substances, what is usually called the coefficient of dispersion is not by any means a constant, but may be caused to assume any value whatsoever by comparatively slight changes (*e.g.*, of temperature, of solvent, or of concentration in a given solvent) in the physical conditions. But, as has been pointed out by one of us, constant values are usually obtained if the dispersion be calculated from a rational zero, this being the point of intersection of the lines for two given colours on a characteristic diagram for the substance in question, or of the two corresponding temperature-rotation curves for one of the derivatives belonging to the series. If the lines on the characteristic diagram happen in any given instance to intersect at zero, then the dispersion coefficients calculated in the ordinary way should also remain constant throughout, or at least over wide changes in physical conditions.

Few cases—if indeed any—of the latter behaviour have been observed, perhaps the most definite being the benzenesulphonates, naphthalene- α - and - β -sulphonates of menthol (J., 1927, 353) and of borneol (J., 1928, 2472) examined by Patterson and McAlpine, the dispersion coefficients of which are practically constant.

Now, in these, and in most, cases, the zero of the diagram is an interpolated point and does not represent actual experimental data; but it has been observed that mannitol, which contains four asymmetric carbon atoms all supposed to be acting in the same sense, is a compound possessed of so little optical activity that the real existence of rotatory power was only established with some difficulty. Vignon (*Compt. rend.*, 1873, 77, 1191) enhanced the rotation by the addition of boric acid and sodium borate, Bichat (*ibid.*, p. 1192), presumably under Pasteur's direction, detected the rotation of an aqueous solution of mannitol directly, using a tube 4 m. long, and Bouchardat found that ordinary mannitol in aqueous solution ($c = 15$) has a rotation for sodium light of approximately -1.1° in a tube 3 m. long (*ibid.*, 1875, 80, 120). The addition of other inorganic substances, such as salts of molybdic acid (Gernez, *ibid.*, 1891, 112, 1360; Tanret, *ibid.*, 1921, 172, 1500) or an alkaline solution of chromium nitrate (Grossmann and Loeb, *Z. physikal. Chem.*, 1910, 72, 112), develops the activity markedly.

It follows from these facts that, on a characteristic diagram

constructed for derivatives of mannitol, the data for mannitol itself will lie almost exactly upon the zero point, which, obviously, would lend special precision to this region. *A priori*, the dispersion



coefficients for mannitol derivatives, calculated in the ordinary manner, might be expected to show a very general constancy.

Mannitol is, unfortunately, little soluble in most of the convenient solvents, but we were able to examine its optical activity in aqueous solution and in glycerol. The temperature-rotation curves obtained are shown in the small inset diagram of Fig. 1. It will be observed

that in 10% aqueous solution at the ordinary temperature, mannitol has a very slight, but observable, negative rotation, which would become zero, apparently for all colours of light, at a temperature of about -3° . When the solution is heated, the negative rotation is intensified, reaching, however, only the value of -0.2° in a 100 mm. tube for light of $\lambda = 4359 \text{ \AA.U.}$ at a temperature of 100° .

We had expected that, since mannitol and glycerol are substances of similar character, they might be easily miscible with one another; this, however, is not the case, for the solubility of mannitol is only about 5% at the ordinary temperature. With a solution of approximately this concentration we obtained the results shown on the diagram in Fig. 1. At the ordinary temperature in this solvent, the rotation is distinctly positive and, with rise of temperature, it diminishes for the three colours of light used, in such a way that the temperature-rotation curves would intersect exactly, as far as can be judged, on the zero axis. At a temperature of 88° the observed rotation became zero, and at 95° we were just able to detect a slight negative rotation for all three colours of light; the observations were not pushed further. It is quite clear, however, that these curves for mannitol in glycerol show a distinct temperature coefficient, and that their curvature is convex towards the point of origin of the diagram, as is also the case with the aqueous solution. The solvent influence of glycerol, as compared with water, is to displace the region of intersection through 91° of temperature—from -3° to $+88^{\circ}$.

The rotatory dispersion of the hexa-acetyl, the hexabenzoyl, and the hexanitro-derivatives, and also the tribenzylidene and tri-*m*-nitrobenzylidene derivatives of mannitol, were then examined, with the numerical results given on p. 2888. These substances all have rotations considerably different from that of mannitol itself—as was for the most part already known—so that the compensation of the rotational effects of the several asymmetric carbon atoms does not persist in the derivatives of mannitol. The data obtained are shown on the characteristic diagram, Fig. 1, drawn as described in J., 1916, 109, 1181. Hexa-acetyl mannitol, both in benzene and in ethylene dibromide, has a specific rotation of just above 20° for mercury green, hexanitromannitol in ethylene dibromide has a rotation of 56.75° , and hexabenzoyl mannitol has, in ethylene dibromide, a rotation of 80.32° . The last-mentioned is therefore fairly high: these all lie on the positive side of the diagram. On the other hand, tribenzylidene- and tri-*m*-nitrobenzylidene-mannitol in chloroform have negative specific rotations, for mercury green, of approximately -17.52° and -47.22° , and in pyridine -80.4° and -100.1° , respectively. Substitutions in the mannitol

molecule thus produce derivatives having positive and also negative rotations of considerable magnitude.

The data obtained, since they lie both on the positive and the negative side, are very suitable for the construction of a characteristic diagram, and it will be seen in Fig. 1 that the experimental points lie very closely on straight lines. In one or two cases there is a slight divergence, particularly for hexabenzoyl mannitol in ethylene dibromide for the blue line, but since this is rather a difficult colour to read, the discrepancy is probably due chiefly to experimental error. Since all of these substances are but little soluble in the solvents which we tried, the influence of change of concentration and the effect of change of temperature were not examined. As regards change of solvent, it will be seen that the rotations of hexa-acetyl mannitol in benzene and in ethylene dibromide are nearly equal, but those of hexabenzoyl mannitol in chloroform and in ethylene dibromide show a difference of rather more than 20° for green.

The lines of the characteristic diagram pass, as we had anticipated on account of the behaviour of mannitol, through the point of origin, and it follows that the dispersion ratios throughout this diagram are approximately constant. This is seen in Table I, the average dispersion ratios between violet and green being 1.704, and between green and yellow 0.885.

TABLE I.

Substance.	Solvent.	Dispersion coefficients, $[\alpha]_{\lambda}^*/[\alpha]_g$.				
		v*/g.	b/g.	y/g.	r ₂ /g.	r ₁ /g.
Hexa-acetyl mannitol	C_6H_6	1.703	—	0.886	—	—
	$C_2H_4Br_2$	1.724	—	0.888	—	—
Hexabenzoyl mannitol	$CHCl_3$	1.704	1.328	0.888	0.717	0.640
	$C_2H_4Br_2$	1.716	1.256	0.884	0.732	0.645
Hexanitro-mannitol	$C_2H_4Br_2$	1.676	1.297	0.891	0.730	0.648
	C_2H_5OH	1.690	1.282	0.887	0.746	0.634
Tribenzylidene-mannitol	$CHCl_3$	1.703	1.352	0.884	0.730	0.648
	C_5H_5N	1.710	1.315	0.883	0.741	0.648
Tri- <i>m</i> -nitrobenzyl-idenemannitol	$CHCl_3$	1.705	1.308	0.882	0.743	0.641
	C_5H_5N	1.711	1.319	0.883	0.731	—

* For wave-lengths used, see p. 2887.

It is, of course, quite impossible to decide definitely the shape of a curve determined by only six experimental points, and we are not prepared to say that our data for six colours of light when plotted against λ^2 lie upon rectangular hyperbolæ,* but if any set of these points does lie on such a curve, then (experimental error apart) all the other sets must also lie upon similar curves and ought all there-

* When $1/a$ was plotted against λ^2 , a line approximately straight was obtained; but this is quite an insufficient criterion.

fore to be represented by an expression of the form $\alpha(\lambda^2 - c)^* = k$, where c might possibly be zero.

To determine the constants k and c , we find, from our experiments, that when the rotation of any compound related to mannitol like those we have examined (and in any circumstances of solvent and temperature), for mercury green light, is 80° , the rotation of this substance for light of $\lambda = 0.4359 \mu$ will be 136.8° , and for light of $\lambda = 0.5790 \mu$, it will be 70.7° ; whence we have

$$136.8(0.4359^2 - c) = k, \text{ and } 70.7(0.5790^2 - c) = k,$$

from which $c = 0.04$ (to a close approximation), and $k = 20.8$.

Similarly, from data corresponding to $[\alpha]_{0.5461} = 40^\circ$, c has the same value as before, but $k = 10.4$. The value of k is therefore directly proportional to the value of the rotation for the reference colour; or $k = K[\alpha]_{0.5461}$, whence $K = 20.8/80 = 0.26$. Therefore, as covering the whole behaviour of the mannitol derivatives, we have the equation

$$[\alpha]_{\lambda}(\lambda^2 - 0.04) = K \times [\alpha]_{0.5461} = 0.26 \times [\alpha]_{0.5461}.$$

As far as we are aware, this is the first time that the rotational behaviour of a whole series of compounds has been given by a single expression, containing two constants, and shown to depend, otherwise, merely on the rotational value for one selected colour.

The importance of the characteristic diagram in revealing a deep-seated regularity of behaviour does not seem to be adequately appreciated. Such a diagram is an expression of the fact that, if, by altering the circumstances of an active compound (*e.g.*, by change of solvent, of temperature, or of concentration), its rotation for one colour of light can be made the same as that of some related compound for the same colour of light, then, under these particular conditions, the rotation of both compounds for all other colours will also be the same; and, further, that "visibly anomalous" dispersion, if it occur at all, will occur in the same rotational region for all these compounds.

No theory hitherto propounded accounts successfully for this behaviour. The suggestion that the anomalousness of so many dispersion curves is due to the existence of the active compound in two different forms has not been substantiated, in spite of the ingenuity displayed in inventing elusive isomerides, which—*simply ex hypothesi*—should bring about the desired result. The further great difficulty now arises that, even if it were possible to make dual personality account for the behaviour of a whole group of compounds the data for which lie on a characteristic diagram showing

* To write this expression in the form $\alpha(\lambda^2 - \lambda_0^2) = k$, would imply acceptance of Drude's views, which, at present, are not part of our scientific faith.

“anomalous” dispersion, the problem would still remain of explaining a set of compounds showing “simple” dispersion, such as the mannitol group, for which—*ex eadem hypothesisi*—the supposed isomerides are absent.

Our own view is that “anomalous” rotation dispersion is the normal behaviour; that on the very large majority of characteristic diagrams the lines for the different colours of light would intersect over a range, and that only in quite exceptional cases, such as that of mannitol, will these lines pass through the zero point of the diagram, and thereby cause the individual dispersion curves (α plotted against $\lambda^2 - c$) to be (perhaps) genuine hyperbolæ. In those cases (*e.g.*, tartar emetic) where a substance belonging to a group having a characteristic diagram indicating “anomalous” dispersion, gives a dispersion curve which can be represented by a single-term equation of the form $[\alpha] = k/(\lambda^2 - c)$, there is nothing to show that this is not merely because the high values of the rotation mask the anomalousness of the curve.

Note [added November 14th, 1929].—In a paper published since the above was written, Lowry and Lloyd (this vol., p. 1789), referring to characteristic diagrams, say: “These devices are merely a graphical expression of Biot’s mixture rule, according to which the rotatory power of a binary mixture for any wave-length can be calculated by simple proportion from the rotatory powers of the two components for the same wave-length.” Now, it is true that the inventors of the characteristic diagram, Armstrong and Walker (*Proc. Roy. Soc.*, 1913, *A*, **88**, 392), did develop it as a composition diagram, but this is a special way of looking at the matter, which involves the quite arbitrary assumption, upheld by Lowry, that the changes which characterise optical rotatory power are necessarily due to the presence of two or more components, and of which, in spite of abundant experimental material, no valid proof has hitherto been adduced.

But even apart from the complete absence of experimental proof, there are very serious objections to Lowry and Lloyd’s way of regarding the matter. The characteristic diagram has, in fact, a fundamentally different significance from that attributed to it by them. On a characteristic diagram the rotation values for other colours of light are plotted relative to those for some one colour regarded as standard—a procedure free from any kind of theory whatever. When data are thus plotted, it is generally found that the values for the different colours of light lie along lines which are straight or approximately so. The conclusion to be drawn from this, and one again entirely free from any assumption, is that the dispersion—the separation—of any two colours is proportional to the

distance (measured in rotational value) from that point (rotation) at which their values are identical—the rational zero. Moreover, not only does this hold for one individual substance, but it is found that the relative data for many, if not all, derivatives of that substance fit, in a most surprising manner, upon the same diagram. This, although not universal, appears to hold very widely, and is of the utmost importance.

Consider this from the point of view of Arendtsen's hypothesis, and imagine a compound A, which could exist in two forms, A_1 and A_3 ; and suppose further, that in, say, aqueous solution, only molecules of the former were present. The dispersion must then, by hypothesis, be represented by the expression $\alpha = k_1/(\lambda^2 - c_1)$. Again, suppose that in alcoholic solution, the dispersion, being wholly due to molecules A_3 , is represented by $\alpha = -k_3/(\lambda^2 - c_3)$. Then let these rotation data be plotted on a characteristic diagram as shown in Fig. 4, and lie on the vertical lines A_1A_1 and A_3A_3 . Now if an active compound such as A shows, either in the homogeneous condition or in any given solvent, a dispersion represented by a one-term equation, it must be impossible for it to have, in any other circumstances, rotation values higher or lower respectively than these; and it is therefore clear, in the first place, that such a diagram must be limited towards the right and the left by the lines A_1A_1 and A_3A_3 , since the dispersion cannot be more "simple," in Lowry's sense, than in either of these cases. Also, no data lying on the lines of the diagram between A_1A_1 and A_3A_3 can be represented by a rectangular hyperbola. If, then, in some other solvent, a higher rotation than A_1A_1 or a lower rotation than A_3A_3 should be reached as at A_2A_2 and A_4A_4 and the dispersion appears to be "simple," it would follow that the one-term expressions for the data at A_1A_1 or A_2A_2 , as the case may be, are necessarily wrong; they cannot all be simple and lie on the lines of the same characteristic diagram. It must be clear, therefore, that any finality is impossible. It could never be known when a characteristic diagram was complete; it could never be known that some hitherto untried solvent might not produce a still higher rotation than any previously observed, and thus disprove the "simpleness" of the dispersions already recorded.

When an attempt is made to account for the fact that the derivatives of the mother substance A also give rotation data lying along the lines of the same characteristic diagram, and that their rotations for two given colours of light become identical always at the same rotation value, the matter is, on the isomeride hypothesis, so complex and speculative as not, at present at least, to merit discussion.

Finally, there is the consideration referred to on p. 2881. Characteristic diagrams show a general resemblance and change

gradually from the somewhat extreme form for the tartrates, where the lines intersect over a fairly wide range, to that in which the lines intersect at the zero point of the diagram. On account of the gradual nature of this change, there does not seem to be the slightest reason to assume a different mechanism in these cases, and if the behaviour of the tartrates is due to dynamic isomerism, so is that of mannitol. But since the lines on the mannitol diagram pass through the zero, anomalous rotation is impossible, and the dispersion must be simple throughout. Thus we are confronted with the dilemma that, since the characteristic diagram is "merely an expression of Biot's mixture rule," the behaviour of mannitol must be due to an equilibrium of isomerides,* which—since the dispersion is simple—cannot be present. Hence, there seems to be sound justification for refusing to accept Arendtsen's view of anomalous rotation dispersion, and, in consequence, also the extension of it, advocated by Lowry, to Drude's equations.

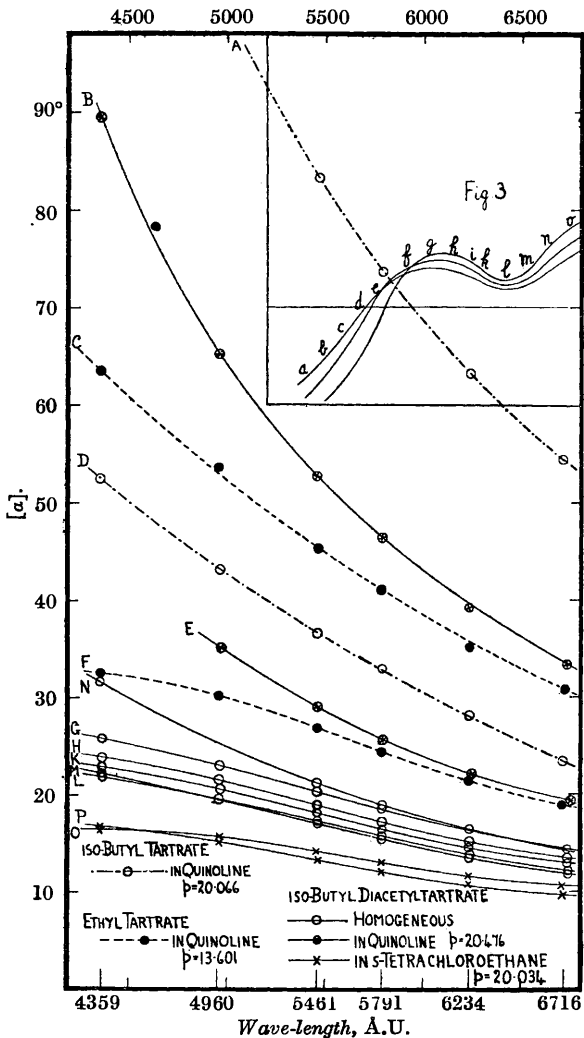
Note on Rotation Dispersion Curves.—Wood and Nicholas (J., 1928, 1671, 1696, 1712, 1727, and, with Chrisman, 2180) have given interesting data which take into account the change, not only of temperature, but also of solvent, of concentration, and of wavelength, and they seem inclined to divide temperature-rotation curves into four different types. This is unfortunate, for although it is not easy to examine the rotation of a compound through any very wide range of temperature, there is no doubt that the rotation of most optically active substances changes when they are heated, and that, if it were possible to heat them beyond the limits which we can at present attain, this change would continue. The experiments of Frankland, Winther, Patterson, and others appear to render it very probable that the four types into which Wood and Nicholas divide their temperature-rotation curves are merely parts of the general curve discussed in J., 1916, 109, 1141 (Fig. 1, D), and now reproduced as Fig. 3 (inset in Fig. 2).

For such a substance as ethyl tartrate, the dispersion rotation curves corresponding to the point *b* of Fig. 3 lie upon a curve which resembles a hyperbola in the fourth quadrant, whereas those corresponding to points between *g* and *h* resemble hyperbolæ lying in the first quadrant, and in both cases these may be taken, and have been taken, to show "simple" dispersion. On the other hand, dispersion rotation curves corresponding to points near the region *ef* show marked characteristics of so-called "anomalous" dispersion. It seems to us, however, that the anomalousness is just as much inherent in dispersion rotation curves pertaining to other regions of

* Apparently these would be optical antipodes, since the rotation and dispersion are exactly equal and opposite.

the general temperature-rotation curves, although it is not so easily detected. We have already made it clear that "simple" dispersion is likely to be found for the whole mannitol series (p. 2880); similarly,

FIG. 2.
Dispersion rotation curves for various tartrates.

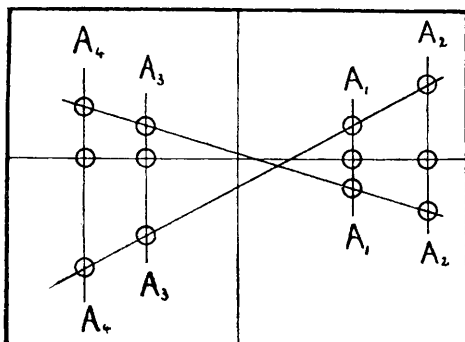


"anomalous" dispersion should be expected for the whole series of tartrates.

We have recently re-examined data published by one of us some

years ago, and wish to put on record a point not previously referred to. We have already mentioned the alteration in shape suffered by dispersion rotation curves when drawn to correspond to different regions of the general temperature-rotation curve, varying from a minimum through a region of intersection to a maximum. The question now relates to the change of shape of dispersion rotation curves in passing, on the general temperature-rotation curves, from one maximum to another maximum through a minimum, *i.e.*, from the region *h* to *o* in Fig. 3. The latter curves for solutions in quinoline of ethyl tartrate, $p = 13$ (J., 1916, **109**, 1145), *isobutyl tartrate*, $p = 20$ (*loc. cit.*, p. 1147), and of *isobutyl diacetyltartrate*, $p = 20$ (*loc. cit.*, p. 1155), clearly belong to the region *ikl* of Fig. 3;

FIG. 4.



whereas those for homogeneous *isobutyl diacetyltartrate* (*loc. cit.*, p. 1155) and for that ester in *s*-tetrachloroethane, $p = 20$ (*loc. cit.*, p. 1156), equally clearly belong to the region *klm*.

In Fig. 2 are reproduced a number of dispersion rotation curves drawn from the data in the paper referred to. It will be seen that the two uppermost curves, A and B, representing *isobutyl tartrate* in quinoline ($p = 20$, $t = 0^\circ$) and *isobutyl diacetyltartrate* in quinoline ($p = 20$, $t = 0^\circ$), and belonging to the region *ik* of Fig. 3, are not visibly anomalous. The curves C (ethyl tartrate in quinoline, $p = 13$, $t = 0^\circ$) and D (*isobutyl tartrate* in quinoline, $p = 20$, $t = 147.5^\circ$) tend to become distinctly flatter towards the violet. Curve E for *isobutyl diacetyltartrate* in quinoline ($p = 20$, $t = 103.3^\circ$) is somewhat similar, but, unfortunately, could not be carried into the dark blue region. These belong to the region *kl* of Fig. 3; and curve F, for ethyl tartrate in quinoline ($p = 20$, $t = 65.1^\circ$)—immediately before the minimum in the temperature-rotation curves (*loc. cit.*, p. 1145)—shows distinct anomalousness, somewhat similar to that found in homogeneous ethyl tartrate at $t = 170^\circ$.

This behaviour is repeated in the curves G, H, K, and L, which are for homogeneous *isobutyl* diacetyltartrate at temperatures of -18° , 0° , 4° , and 42.2° , respectively. These carry us to the minimum in the temperature-rotation curves, and the next dispersion curve, M, for the same ester at $t = 72.5^{\circ}$, since it cuts L, is obviously tending to show less anomalousness, whilst in curve N, for the same ester at 200° , corresponding to some point about *m* in Fig. 3, the visible anomalousness has largely or entirely disappeared. Curves O and P, for *isobutyl* diacetyltartrate in *s*-tetrachloroethane ($p = 20$) at $t = 0^{\circ}$ and 99.7° , respectively, show a similar behaviour.

There is thus a tendency for visible anomalousness to develop in dispersion curves corresponding to the region *kl* of the general temperature-rotation curve, whilst, in dispersion rotation curves corresponding to regions beyond this minimum of the general temperature-rotation curve, the anomalousness becomes less apparent.

EXPERIMENTAL.

The wave-lengths (in Å.U.) of the light used are denoted by the following letters :

r_1 .	r_2 .	y.	g.	b.	v.
6716	6234	5790	5461	4916	4359

Mannitol in Water.— $p = 10.25$; $l = 160$ mm.

<i>t</i>	14.5°	50°	69°	89.5°
<i>d</i>	1.0358	1.0232	1.0034	0.9940
<i>y</i>	{ <i>a</i>	-0.02°	-0.06°	-0.08°	-0.095°
	{ [<i>a</i>]	-0.12	-0.36	-0.49	-0.58
<i>g</i>	{ <i>a</i>	-0.03	-0.07	-0.09	-0.11
	{ [<i>a</i>]	-0.18	-0.42	-0.55	-0.675
<i>v</i>	{ <i>a</i>	-0.055	-0.13	-0.16	-0.19
	{ [<i>a</i>]	-0.32	-0.775	-0.97	-1.165

Mannitol in Glycerol.— $p = 4.523$; $l = 160$ mm.

<i>t</i>	13.8°	41.0°	54.5°	66.5°	88.0°	95.0°
<i>a_y</i>	+0.40°	+0.24°	+0.16°	+0.09°	0.00°	-0.02°
<i>a_z</i>	+0.45°	+0.27°	+0.18°	+0.10°	0.00°	-0.02°
<i>a_v</i>	+0.76°	+0.46°	+0.31°	+0.17°	0.00°	-0.03°

Hexa-acetyl mannitol was prepared in theoretical yield by Franchimont's method (*Ber.*, 1879, **12**, 2059), acetic anhydride being used in presence of fused zinc chloride as acetylating agent. The crude product, of m. p. 119° , after two recrystallisations had m. p. 126° (literature gives 119°) (Found, by Perkin's method: $\text{CH}_3\cdot\text{CO}$, 59.5. Calc. for $\text{C}_{18}\text{H}_{26}\text{O}_{12}$: $\text{CH}_3\cdot\text{CO}$, 59.45%). Acetylation with acetyl chloride in presence of a few drops of pyridine also gave a theoretical yield, m. p. 126° .

Rotations. (1) In benzene : $c = 2.1405$; $t = 22^\circ$.

$[\alpha]_{\lambda}^{22^\circ}$	y. 18.22°	g. 20.55°	v. 35.04°
---------------------------------------	--------------	--------------	--------------

(2) In ethylene dibromide : $c = 1.389$; $t = 22^\circ$.

$[\alpha]_{\lambda}^{22^\circ}$	18.53°	20.87°	35.99°
---------------------------------------	--------	--------	--------

Hexabenzoyl mannitol was prepared by Panormov's general method for polyhydric alcohols (*J. Russ. Phys. Chem. Soc.*, 1891, **23**, 375). 10 G. of mannitol were added to a mixture of 60 g. of benzoyl chloride with 480 c.c. of 20% caustic soda solution, stirred at 0° for $1\frac{1}{2}$ hours, and kept over-night; the white resinous product which separated was washed with water and dissolved in benzene, excess of benzoyl chloride being removed from this solution by shaking with dilute potassium carbonate solution. When the benzene was removed, the syrup which remained slowly solidified to a white mass of hexabenzoyl mannitol, which was recrystallised from methylated spirit, forming very fine needles, m. p. $147-148^\circ$; yield 65%.

Rotations. (1) In chloroform : $c = 1.1850$; $t = 22^\circ$.

$[\alpha]_{\lambda}^{22^\circ}$	r_1 . 37.98°	r_2 . 42.62°	y. 52.75°	g. 59.4°	b. 78.9°	v. 101.2°
---------------------------------------	-------------------	-------------------	--------------	-------------	-------------	--------------

(2) In ethylene dibromide : $c = 0.9650$; $t = 22^\circ$.

$[\alpha]_{\lambda}^{22^\circ}$	51.82°	58.82°	71.0°	80.32°	100.9°	137.8°
---------------------------------------	--------	--------	-------	--------	--------	--------

Hexanitromannitol was prepared as described by Sokoloff (*J. Russ. Phys. Chem. Soc.*, 1879, **11**, 136), the mannitol being stirred into fuming nitric acid cooled in ice. Ice-cold concentrated sulphuric acid was then slowly added with stirring, and, after standing in ice for a few minutes, the semi-solid mass was poured into ice-water and filtered; the white precipitate of hexanitromannitol was washed with water and a little dilute caustic soda solution, and recrystallised from dilute alcohol until pure, forming white, silky needles, m. p. $112-113^\circ$. Yield 75%.

Rotations. (1) In ethylene dibromide : $c = 0.3260$; $t = 22.2^\circ$.

$[\alpha]_{\lambda}^{22^\circ}$	r_1 . 36.8°	r_2 . 41.4°	y. 50.6°	g. 56.75°	b. 73.6°	v. 95.2°
---------------------------------------	------------------	------------------	-------------	--------------	-------------	-------------

(2) In alcohol : $c = 1.3770$; $t = 22^\circ$.

$[\alpha]_{\lambda}^{22^\circ}$	32.7°	38.5°	45.8°	51.6°	66.1°	87.2°
---------------------------------------	-------	-------	-------	-------	-------	-------

Tribenzylidenemannitol (Fischer, *Ber.*, 1895, **28**, 1979) was prepared by shaking together a mixture of 10 g. of mannitol, 20 g. of benzaldehyde, and 30 c.c. of concentrated hydrochloric acid (30%). The benzylidene compound began to separate at once and in a few

minutes the mass went solid. After standing for $\frac{1}{2}$ hour, the mixture was filtered and the crude tribenzylidenemannitol was recrystallised several times from absolute alcohol, in which it is very sparingly soluble, being obtained as a felted mass of fine white needles, m. p. 218—219°. Yield 70%.

Rotations. (1) In chloroform : $c = 1.0562$; $t = 25.0^\circ$.

	r_1 .	r_2 .	y.	g.	b.	v.
$[\alpha]_{\lambda}^{25^\circ}$	-11.4°	-12.8°	-15.5°	-17.5°	-23.7°	-29.8°

(2) In pyridine : $c = 1.008$; $t = 23^\circ$.

$[\alpha]_{\lambda}^{23^\circ}$	-52.1°	-59.4°	-70.9°	-80.4°	-105.65°	-137.4°
---------------------------------------	--------	--------	--------	--------	----------	---------

Tri-*m*-nitrobenzylidenemannitol (De Bruyn and Van Ekenstein, *Rec. trav. chim.*, 1900, **19**, 178) was made in the same way as the preceding compound, but the reaction was complete only when the mixture of mannitol (5 g.), *m*-nitrobenzaldehyde (14 g.), and concentrated hydrochloric acid (20 c.c.) had stood, with occasional shaking, for about a week. The product was recrystallised from acetone, in which it is slightly soluble, and resembled the preceding compound in appearance. M. p. 248—249°. Yield 60%.

Rotations. (1) In chloroform : $c = 0.413$; $t = 25^\circ$; $l = 200$ mm.

	r_1 .	r_2 .	y.	g.	b.	v.
$[\alpha]_{\lambda}^{25^\circ}$	-30.3°	-35.1°	-42.6°	-47.2°	-61.7°	-82.4°

(2) In pyridine : $c = 1.019$; $t = 22^\circ$; $l = 200$ mm.

$[\alpha]_{\lambda}^{22^\circ}$	—	-73.1°	-88.3°	-100.1°	-132.0°	-171.3°
---------------------------------------	---	--------	--------	---------	---------	---------

One of the authors (A. R. T.) desires to express his gratitude to the Carnegie Trustees for the Universities of Scotland for a Research Scholarship which enabled him to take part in this research.

ORGANIC CHEMISTRY DEPARTMENT,
UNIVERSITY OF GLASGOW.

[Received, July 30th, 1929.]