CCXIX.—*Anomalous Rotatory Dispersion from the Standpoint of the Drude Equation.*

By Charles Edmund Wood and Sydney Diggary Nicholas.

Although the rotatory dispersion of ethyl and methyl tartrates has been investigated exhaustively (Lowry and Dickson, J., 1915, **107**, 1173; Lowry and Abram, *ibid.*, p. 1187; Patterson, J., 1916, **109**, 1139, *et seq.*; Winther, *Z. physikal Chem.*, 1902, **41**, 177, etc.) both in the homogeneous condition and in solution, yet relatively little research has been done on the dispersion of the simple derivatives of these two esters. A series of derivatives was therefore prepared in order to see whether the anomalous dispersion shown by the parent esters persisted in the derived compounds, or whether the dispersion passed from anomaly to complexity or to simplicity in a definite manner in the two series; also, to gain further information on the relationship of dispersion to relative configuration and their interpretation in terms of the Drude equation.

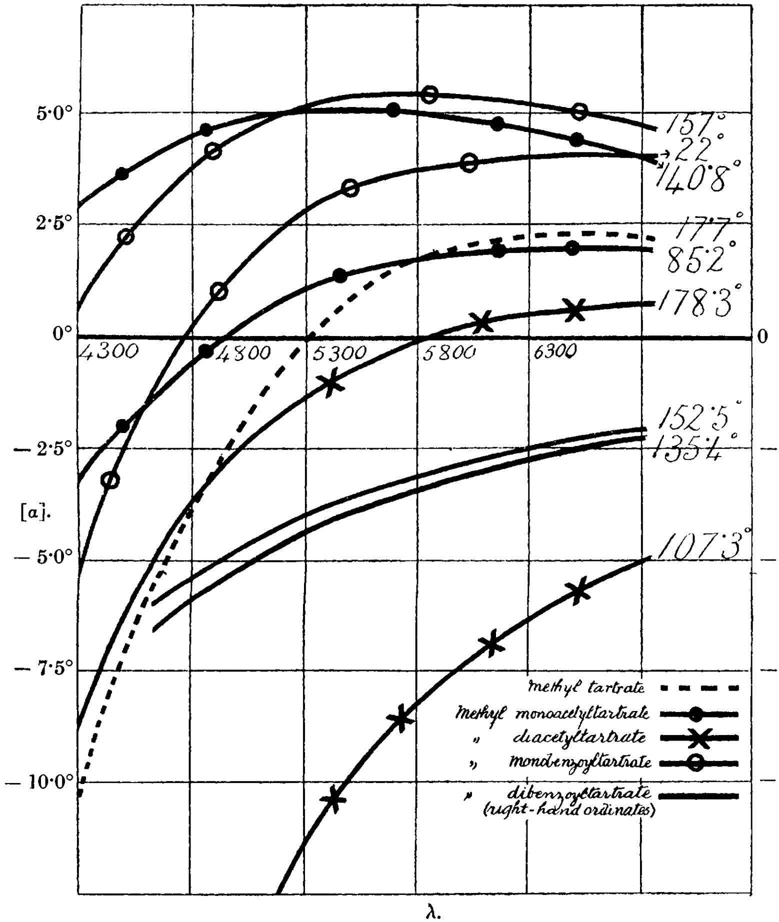
Anomalous Rotatory Dispersion and Relative Configuration.

Examination of the rotatory dispersion curves for the compounds shows that (*a*) both inflexion and maxima are confined to the positive region of rotation, and (*b*) crossing of the axis occurs in one way only, *viz.*, as the wave-length decreases so the rotation decreases, $d\alpha/d\lambda$ being always positive.

Fig. 1 shows that methyl *d*-tartrate and its monoacetyl, diacetyl (at 178·3° only), and monobenzoyl derivatives exhibit visual anomaly in the positive region of rotation, and further, when crossing of the axis occurs, $d\alpha/d\lambda$ is positive. The disposition of the dispersion curves for the dibenzoyl derivative is given on the diagram; they do not show visual anomaly.

Fig. 2 indicates that inflexion of the dispersion curves in the positive region of rotation was realised for the mono- and di-acetyl and monobenzoyl derivatives of ethyl tartrate; inflexion of the dispersion curves for the ester itself occurs at higher temperatures than shown in the diagram. Maxima occur in the positive region for ethyl tartrate and its mono- and di-acetyl and monobenzoyl derivatives. The diacetyl derivative, like the parent ester, shows crossing of the axis. The dispersion curves for the dibenzoyl derivative, for the range of temperature and wave-length examined, are situated in the negative region. On the same diagram is indicated the disposition of the dispersion curves for the thionyltartaric and dichlorosuccinic esters.

FIG. I.



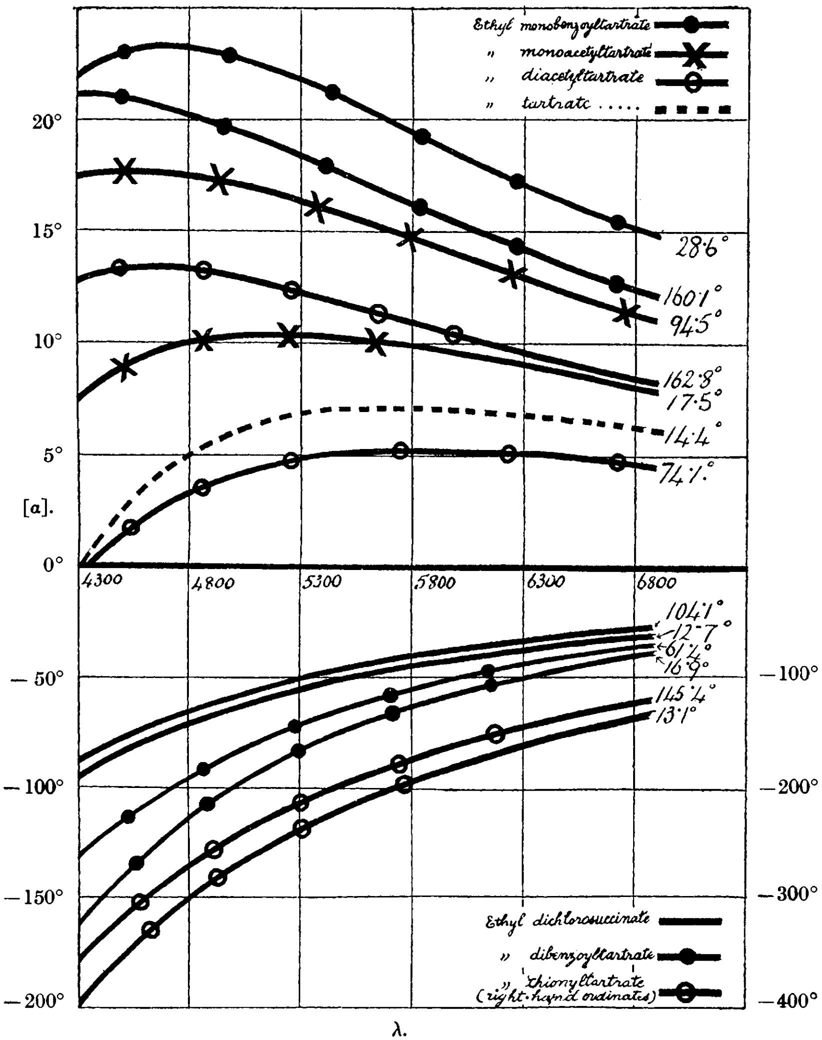
Methyl tartrate and certain derivatives.

The types of dispersion of the compounds examined are given below :

	Dispersion.		Dispersion.
Methyl tartrate	Anomalous	Ethyl tartrate	Anomalous
Monoacetyl derivative	Anomalous	Monoacetyl derivative	Anomalous
Diacetyl derivative ... (at the higher temperature)	Anomalous	Diacetyl derivative ...	Anomalous
Monobenzoyl derivative	Anomalous	Monobenzoyl derivative	Anomalous
Dibenzoyl derivative ...	Complex (negative region)	Dibenzoyl derivative ...	Complex (negative region)
		Thionyl derivative ...	Simple in region of spectrum examined.
		Ethyl dichlorosuccinate	

In general, the dispersions of the simple acetyl and benzoyl derivatives of the two series are closely related, but comparison of

FIG. 2.



Ethyl tartrate and certain derivatives.

the two diagrams shows that the crossing of the axis and, consequently, maxima are removed to a shorter wave-length in passing from methyl tartrate and its derivatives to ethyl tartrate and its derivatives, a fact which is well illustrated by the diacetyl derivatives of the two series.

Lowry (J., 1915, **107**, 1195), having proved conclusively the validity of the Drude equation, quotes inflexion, maxima, and crossing of the axis as visual criteria for anomalous dispersion, but this investigation and a survey of the literature indicate that the above three points are also criteria for relative configuration. Thus for *d*-tartaric acid and its derivatives the mode of crossing the axis is always the same, points of inflexion occur only in the positive region of rotation, and, in all cases, maxima are confined to the positive region.

The dispersion curves for methyl diacetyltartrate are of particular interest; they form a series of curves which approach the axis from the negative side with increasing temperature, and the curve obtained at 178·3° crosses the axis towards the red end of the spectrum. A solution of ethyl tartrate in carbon tetrachloride (Lowry and Dickson, *loc. cit.*) affords a similar case. The curves do not become asymptotic to the zero axis in the negative region.* It is hard to reconcile this phenomenon, which is not confined to these cases, with the founding of a general explanation of optical rotation on a Drude equation with the infra-red term omitted. Although quantitative measurements have justified such procedure, yet the theoretical significance is lost. The infra-red term is associated with the configuration, and should be regarded as the relative configuration term. For a compound of " *d* " configuration it is negative, and for a compound of " *l* " configuration positive. It is this term which prevents dispersion curves in the negative region, for a compound of relative configuration denoted by " *d*," becoming asymptotic to the zero axis in that region towards the red in the visible and non-visible region of the spectrum; and thus, by the influence of the infra-red term, the curve is drawn over the axis into the positive region.

In the case of a compound of " *d* " configuration in the *positive* region, no instance can be traced where intersection of the zero axis, $d\alpha/d\lambda$ being negative, occurs; the approach, as the curve passes into the red end of the spectrum, appears to be asymptotic in character either to the zero axis, or to an axis parallel to the zero axis in the positive region.

In cases where the dispersion curve does not actually pass over

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* The dispersion curve for the same compound in ethylene dibromide does not cross the axis in the visible region, and extrapolation by means of the two-term equation shows that crossing of the zero axis does not occur, but that the dispersion curve becomes asymptotic to the zero axis in the negative region.

into the negative region, its approach to the zero axis is a sufficient guide for relative configuration, provided that the *approach* is towards the *blue* end of the spectrum. Many instances are given in the two diagrams of experimental results (Figs. 1 and 2).

Methyl and ethyl dibenzoyltartrates, ethyl dichlorosuccinate and ethyl thionyltartrate have rotations removed from the axis on the negative side. The first two compounds have been obtained by simple chemical reactions not prone to give rise to a Walden inversion, hence their relative configuration is taken as " *d*." The configuration of dextrorotatory * dichlorosuccinic acid and its ethyl ester (for comparison of preparation and optical rotation, see Darzens, *Compt. rend.*, 1912, **154**, 1615; Holmberg, *Svensk Kem. Tidsk.*, 1912) has been discussed by Clough (J., 1918, **113**, 526), who, on the basis of the relationship between optically active α-amino- and α-hydroxy-acids, regards this acid as of relative configuration " *l*." The relative configuration of the thionyl ester, which is an intermediate product in the preparation of the dichloro-ester, is assumed to be " *d*."

Experiments with solvents failed to reduce the high rotation of the last two esters sufficiently for observations to be taken in the anomalous region. This is to be expected, for optically active compounds only exhibit great sensitiveness to both temperature and solvents near or in the region of anomalous rotatory dispersion.

Interpretation of Anomaly by the Drude Equation.

In the consideration of the Drude equation, R. W. Wood (" Physical Optics," p. 492), from theoretical considerations, indicates that the anomalous rotatory dispersion of tartaric acid is due to an infra-red lævorotatory electron and an ultra-violet lævorotatory electron. This view has been rejected by Lowry (Lowry and Cutter, J., 1925, **127**, 604), who, from quantitative measurement, expresses the rotatory dispersion " as the sum of two simple partial rotations of which the characteristic frequencies are both in the ultra-violet region," the two partial rotations being of opposite sign. Lowry, however, admits the theoretical possibility of " spurious anomaly " in transparent media.

The view here put forward is that both explanations of the phenomenon are incomplete, and it is considered that anomaly is due to one or more rotations of electronic origin in the ultra-violet, and a rotation of molecular origin, due to atomic oscillations, in the infra-red.

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* The compound investigated was lævorotatory, *i.e.*, of opposite relative configuration.

The total rotation of the plane of polarisation being expressed in the usual way as a summation of terms,

$$\alpha = \sum \frac{k}{\lambda^2 - \lambda_0^2}$$

each term, except the infra-red term, represents the contributary rotation due to ultra-violet electrons, active in rotating light. The infra-red term, however, represents rotation referred to molecular origin. Observations on selective reflexion and absorption have shown that characteristic frequencies in the ultra-violet arise from electrons, whereas those in the infra-red, which in many cases pass into the region of short electric-discharge waves, are referred to atomic oscillations.* The contributary rotation due to this infra-red term, although small in the visible region, is definite, and, being of molecular origin, gives rise to dextrorotatory or lævorotatory dispersion according as the relative configuration is " *d* " or " *l*." The importance of this configuration term as a fundamental part of the Drude equation is considered below.

Case 1. The infra-red term contributes a dextrorotatory dispersion which is of lævorotatory molecular origin, and which manifests itself in the near infra-red through the oscillations of the constituent atoms (or atomic groups),† and the ultra-violet term contributes a dextrorotatory dispersion of a dextrorotatory electron (or system of electrons) :

$$\alpha = \underset{\text{(ultra-violet)}}{\frac{k_1}{\lambda^2 - \lambda_1^2}} - \underset{\text{(infra-red)}}{\frac{k_2}{\lambda^2 - \lambda_2^2}}$$

The condition is shown diagrammatically in Fig. 3, the upper set of curves showing the two simple rotations, and the lower the resultant curve. The dotted lines ‡ represent the unrealisable regions of the spectrum in the red, infra-red, and ultra-violet.

The realisable curve shows no anomaly in the visible spectrum, for minima in the positive region of rotation have not been realised.

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* Compare Haas, " Introduction to Theoretical Physics," Vol. ii, 1925, section on " General theory of spectra and of atomic structure "; Lecomte, " Contribution à l'étude de l'absorption des rayons infra-rouges par les composés organiques," La Lino-Générale, Paris; Baly, " Spectroscopy," Vol. I, p. 217 (1927); Coblentz, " Investigations of infra-red spectra," Carnegie Institution of Washington, 1905, **35**, 117.

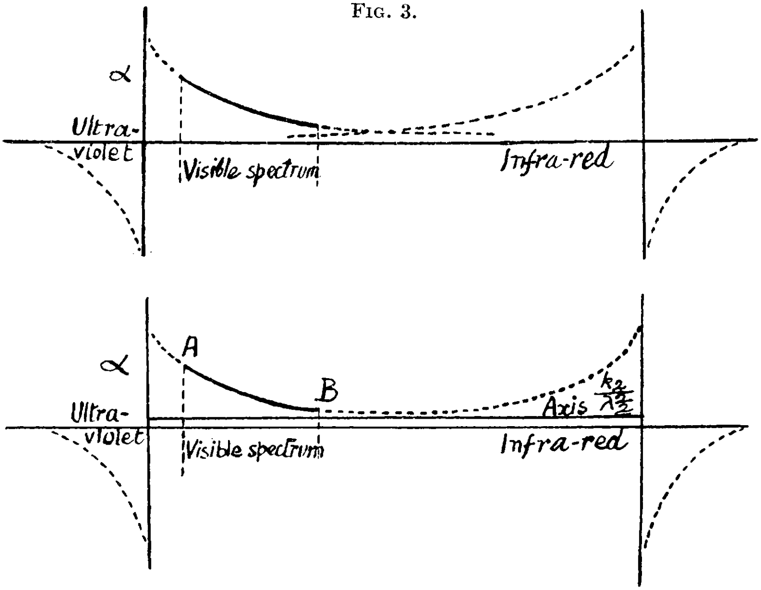
† Compare Bjerrum's theory; also Lorentz, " Lectures on Theoretical Physics," Vol. ii, p. 395 (1927).

‡ The dotted portion of the lower curves for longer wave-lengths in Figs. 3 and 4, if realisable, would represent those parts where the infra-red term is no longer functioning as a constant, the ultra-violet term at the same time passing to a constant value. The complete curve represents, according to the part considered, either simplicity, complexity, or anomaly.

The rotatory dispersion is always positive; the curve tends to become asymptotic and not to cut the axis. Even Ingersoll (*Physical Rev.*, 1917, **9**, No. 4, 257), who investigated the infra-red, did not realise the asymptotic portion of the dispersion curve.

The rotation due to the dextrorotatory electron dies down with increasing wave-length, whilst that due to molecular rotation increases in effect. No apparent deviation from simplicity occurs in the visible spectrum, for

FIG. 3.



$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda_2^2},$$

where k_2/λ_2^2 is a constant representing an axis k_2/λ_2^2 above the zero axis to which the dispersion curve would ultimately tend to become asymptotic.

Case 2. The infra-red term contributes a dextrorotatory dispersion as before, but the ultra-violet term contributes a lævorotatory dispersion due to a lævorotatory electron (or system of electrons):

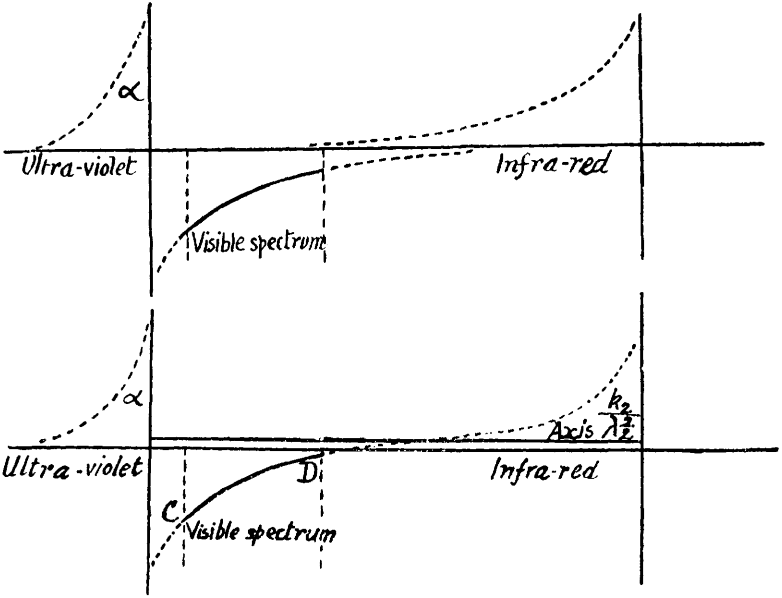
$$\alpha = -\underset{\text{(ultra-violet)}}{\frac{k_1}{\lambda^2 - \lambda_1^2}} - \underset{\text{(infra-red)}}{\frac{k_2}{\lambda^2 - \lambda_2^2}}$$

This condition is shown in Fig. 4. The effect due to the infra-red term is slight, and departure from simplicity cannot be detected. The constant k_2/λ_2^2 represents an axis parallel to the zero axis in the *positive* region; it is the axis to which the curve tends to become asymptotic and which it finally cuts in the unrealisable region on proceeding up to the band.

The constant in both cases is positive and is the "*d*" configuration constant. The above two cases represent simplicity in the positive and negative regions, respectively.

The two compounds mentioned below are examples of Case 2. They were found to be simple over a wide range of temperature. Under the experimental conditions the small constant infra-red contribution could not be differentiated. The rotational constant for the thionyl ester decreases numerically with increase of temperature, but the constant for the dichlorosuccinate passes through a maximum. Very little variation of λ_0^2 was observed with temperature, the tendency (except at 145·4° for the thionyl ester) being a slight movement of the ultra-violet absorption band towards a greater wave-length with increase of temperature.

FIG. 4.



Ethyl thionyltartrate.		
Temp.	λ_0^2.	*k*.
13·1°	0·04264	56·18
20·3	0·04350	55·46
42·3	0·04356	54·09
56·9	0·04326	53·33
82·6	0·04448	51·96
116·9	0·04452	51·08
125·2	0·04440	50·56
145·4	0·04318	50·28

Ethyl dichlorosuccinate.		
Temp.	λ_0^2.	*k*.
12·7°	0·04992	12·61
22·6	0·04950	12·66
41·4	0·04979	12·67
62·4	0·04991	12·51
87·0	0·05141	12·13
104·1	0·05165	11·88

The introduction of another ultra-violet term of the same sign into equations under Cases 1 and 2 gives the condition for complexity. The dispersion curve in the visible region now represents the summation of three simple curves, although the contribution by the infra-red term may not be detectable quantitatively. The dispersion curves in the negative and positive regions, respectively, take corresponding paths in the infra-red, *via* an axis k/λ_2^2 similar to those taken by the curves expressing simplicity. This directive molecular influence, though of little magnitude in the visible region, dominates the final direction of the dispersion curve.

Figs. 3 and 4 illustrate complexity when AB and CD represent the summation of two simple electronic curves of like sign, together with the small molecular contribution.

The introduction of an ultra-violet term of opposite sign into Cases 1 and 2 gives rise to anomaly; the positive term must, however, be associated with the high-frequency constant. The compounded curve produces under certain conditions the three cases of visible anomaly. In all cases the curves eventually take a path, *via* the axis k_2/λ_2^2, up to the band.

Curves wholly in the positive region never touch the zero axis. Curves in the negative region cross the zero axis.

Anomaly is illustrated by Fig. 5, EF being the compounded curve obtained by the introduction of a term of opposite sign. This curve shows that crossing of the zero axis occurs in one way only, $d\alpha/d\lambda$ being positive, and that anomaly (maxima and inflexion) is confined to the positive region. Curves crossing the axis ($d\alpha/d\lambda$ negative) or showing maxima or inflexion in the negative region could only arise from a compound of "*l*" configuration, for the electronic and molecular dispersion curves form one continuous function, and reversal of the electronic part implies reversal of the molecular portion of the dispersion curve. Such curves belong to a general type of curve represented by the mirror image of the curve in Fig. 5.

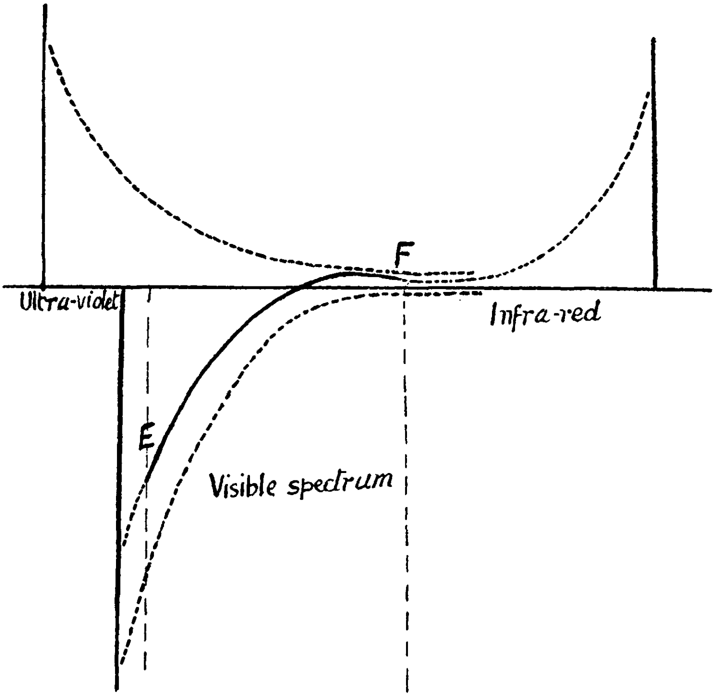
Although quantitative measurements show that the infra-red term is practically negligible in the visible region, yet its importance must not be under-rated, for it determines the path to the infra-red band. This restriction to a particular path places upon the occurrence of anomaly those limitations which are such valuable criteria for the determination of relative configuration.

Methyl diacetyltartrate is an interesting example of visual anomaly occurring towards the red end of the spectrum. From 107·3° to 171·5°, inclusive, the dispersion curves lie wholly in the negative region, whilst at 178·3° crossing of the axis from the negative to the positive region takes place between λ 5893 and λ 5590. Increase of temperature has caused the crossing to move from infra-red into the visible region; the approach to the zero axis of the curves in the negative region is not asymptotic in character.

The further movement of crossing from the visible spectrum into the ultra-violet is shown by methyl monobenzoyltartrate :

Temp.	22·0°	57·0°	80·8°
Crossing of zero axis at λ...	4861—4678	4678—4455	4455—4359

FIG. 5.



For higher temperatures the curves lie wholly in the positive region, the crossing having moved into the ultra-violet. Simultaneously with the movement of the crossing there occur the development and then the movement of maxima (see Experimental). Crossing and maxima form part of a continuous curve, the maxima always occurring at a greater wave-length than the crossing.

Lowry (J., 1915, **107**, 1195) has discussed the limiting condition for anomalous dispersion on the assumption that an infra-red band is absent. From the foregoing considerations it follows that the limiting condition requires modification, *viz.*, the high-frequency term may have the rotation constant *k* not only greater than but also equal to k_1, the rotational constant of the low-frequency ultra-violet term. When $k = k_1$ the curve may cut the zero axis in the visible region, for the contribution due to the molecular rotation, though small, is of appreciable magnitude. The importance of the infra-red term is that it prevents such dispersion curves becoming asymptotic to the zero axis.

In all cases of anomaly the smaller ultra-violet dispersion constant (high frequency), regardless of the value of k, is associated with the positive ultra-violet term for a compound of " *d* " configuration, and with the negative ultra-violet term for a compound of " *l* " configuration. Reference to the sign of the infra-red term is only necessary for determining configuration in the cases of simplicity and complexity.

The Infra-red Term and the Relative Configuration of Quartz.

Quartz affords an interesting example, since the infra-red term has been included in the equation expressing its dispersion (Lowry, *Phil. Trans.*, 1913, *A*, **212**, 261). The term is positive for left-handed quartz; this variety is accordingly configuratively related to *l*-tartaric acid.

The configuration can be deduced, however, without considering the infra-red term; the high-frequency constant (omitted on account of its small magnitude) is associated with the negative ultra-violet term. Similar reasoning, from data given by Lowry and Cutter (J., 1925, **127**, 604) for *d*-camphor, shows that it is configuratively related to left-handed quartz.

The wave-length of the " Reststrahlen " from quartz, as determined by Porter (*Astrophys. J.*, 1905, **22**, 227), is 8·28 μ; Rubens and Nichols (*Ann. Physik*, 1897, **60**, 418) found that reflexion took place at three points of the spectrum, 8·5 μ, 9·02 μ, and 20·75 μ; Lowry, in the application of the Drude equation to the rotatory power of quartz, gives $(8{\cdot}84)^2$ μ as the dispersion constant in the infra-red term and states that " the infra-red absorption is an essential factor in determining the optical rotation in quartz both in the infra-red and in the visible region of the spectrum." Waves whose frequencies differ little from a characteristic frequency are strongly reflected and absorbed; further, infra-red frequencies are referred to atomic oscillations.

Physical Interpretation of the Infra-red Term and Anomaly.

Thomson (*Phil. Mag.*, 1920, **40**, 720) has deduced a general expression for the rotation of the plane of polarisation, due to the scattering of light by electrons, on the assumptions that (1) the whole molecule rotates as a rigid body, and (2) there is no displacement of the electrons relative to the atoms in the molecule. He shows that molecules representing enantiomorphs rotate in opposite directions, and calculates the contribution, due to the rotation of the molecule, to the optical rotation. This calculated rotation is less than 12′ specific rotation per cm., thus the molecular contribution is only a small part of the optical rotation generally observed. The contribution to the rotation of quartz by the infrared term for λ 5896 is 10·3′ per mm. (compare Lowry, *loc. cit.*).

Since the whole molecule, rotating as a rigid body, does not give sufficient movement to account for the rotation produced by optically active compounds, Thomson regards the molecule as made up of two parts : (1) the atomic tetrahedron formed by the atoms or groups round the asymmetric carbon atom, and (2) the electronic tetrahedron formed by the structural electrons round the asymmetric carbon atom. The displacement of the atomic tetrahedron in response to light waves in the visible spectrum will be small in comparison with that of the much lighter tetrahedral arrangement of the electrons.

A system of electrons, α, β, γ, and δ, is considered, each electron being situated at the corner of a tetrahedron. If the restoring forces for α and β are large compared with those for γ and δ, the two electrons γ and δ would rotate round the axis $\alpha\beta$ when acted on by light. The rotation due to this single electronic tetrahedron is found to give values comparable with the rotation given by optically active compounds. The volume of the tetrahedron, which measures the optical rotation of a single molecule, vanishes in the following cases : (1) $\gamma\delta$ is parallel to $\alpha\beta$; (2) $\gamma\delta$ intersects $\alpha\beta$; (3) $\gamma\delta$ is at right angles to $\alpha\beta$ (regular tetrahedron). A shift in the position of one or both of the electrons $\gamma\delta$ might change the sign of the optical rotation produced by the molecule. A compound, by temperature or solvent action, may change its sign of rotation owing to electronic displacements, but not the sign of the contributary molecular rotation unless change of configuration takes place.

The expression which Thomson obtains for the rotations of each tetrahedron, electronic and atomic, we regard as representing the ultra-violet and infra-red terms, respectively, of the Drude equation. An extension of this view, considering eight electrons instead of four round the asymmetric carbon atom, would give rise to two electronic tetrahedra and would afford a physical insight into the meaning of complexity and anomaly, as expressed by the Drude equation. The displacement of the electronic tetrahedra in opposite directions would give rise to anomaly; in the same direction, to complexity; in the same direction and acting as a single tetrahedron, to simplicity. On this view, one asymmetric centre in a molecule is sufficient to account for the various classes of dispersion.

Tschugaeff (*Trans. Faraday Soc.*, 1914, **10**, 35) states that "it is by no means necessary that the electrons in the four radicals and in the central atom should rotate in the same direction. Consequently it seems to be possible that certain bodies containing but one asymmetric carbon atom can exhibit anomalous rotatory dispersion."

Drude ("Optics," p. 415) states that "in general every active substance must show anomalous * rotatory dispersion in certain regions of vibration, but these regions do not necessarily lie within the limits of the vibrations which can be produced experimentally," and this statement occurs immediately after reference to cases of anomalous rotatory dispersion mentioned by Landolt ("Das optische Drehungsvermögen").

It is important to summarise the classes of anomaly:

(1) True anomalous rotatory dispersion occurring at the crossing of an absorption band which is of optically active electronic origin.

(2) Anomalous rotatory dispersion due to the superposition of two simple rotations of opposite sign, the characteristic frequencies being both in the ultra-violet.

(3) Spurious anomalous rotatory dispersion, *i.e.*, dispersion occurring between two bands.

(4) Type discussed in paper on co-ordination compounds (this vol., p. 1727).

Discussion of Different Types of Anomalous Rotatory Dispersion.

The view that a single asymmetric centre can give rise to anomaly makes class (*f*) (ii) (Lowry and Cutter, *loc. cit.*) ("existence of two natural frequencies in a single molecule") a fundamental class. The recognition of this class is regarded by the above authors as a matter of pure speculation, in spite of the increasing number of cases in which a single asymmetric centre shows anomaly, this conclusion being based on the fact that there is no experimental proof of a single asymmetric centre, having two frequencies, giving rise to two absorption bands.

Such a demand is unjustifiable, since no case is known (even when more than one asymmetric centre is in a single molecule), where two bands, corresponding to a high and a low frequency and satisfying the demands of the Drude equation, have been located experimentally. In those cases in which the low-frequency band has actually been determined, the high-frequency band, in the case of anomalous or complex compounds, has been inferred. Accord-

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* "Anomalous" should be interpreted to include also "spurious anomalous," which is defined by Frankland (*Trans. Faraday Soc.*, 1914, **10**, 91).

ingly, the experimental determination of the low-frequency and the inference of the presence of the high-frequency band for a single molecule with one asymmetric centre, is sufficient (and the only available) proof to satisfy the demand.

(*a*) *d*-γ-Nonyl nitrite (Pickard and Hunter, J., 1923, **123**, 434) with absorption band λ 3670—3720, though not anomalous, has a single asymmetric centre which possesses two natural frequencies, giving rise to two bands.

(*b*) For potassium chromium oxalate, $[Cr(C_2O_4)_3]K_3$ (Jaeger and Thomas, *Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 693), the molecular rotation passes through a maximum about λ 5200 and through a minimum about λ 5700 in passing through the band. The compound thereafter shows visual anomaly to the right of the band, *viz.*, on the long wave-length side of the band.

Asymmetric centres of the same relative configuration occurring in a single molecule give rise to the same phenomenon as class (*f*) (ii) the dispersion exhibited being a summation effect; instances are methyl and ethyl *d*-tartrates and *l*-β-octyl oxalate (Lowry and Richards, J., 1924, **125**, 1593). The bands are far removed in the ultra-violet and have not been determined experimentally, but the dispersion has been measured and the results expressed by equations involving two terms of opposite sign (Lowry and collaborators, *locc. cit.*). In these cases the two centres of activity are of identical type. Methyl and ethyl diacetyl-*d*-tartrates are further examples since they show visual anomaly. Methyl and ethyl monoacetyl- and monobenzoyl-tartrates are examples of compounds having two centres of " *d* " configuration with different rotatory power, showing visual anomaly.

When the two asymmetric centres are of different configuration, the resulting anomaly expresses the configuration of the dominant centre. When more than two centres are present, the dispersion curve represents a summation effect.

d-*sec*.-Butyl *d*-lactate (Wood, Such, and Scarf, J., 1926, 1928) exhibits anomaly in the negative region, the dominant centre being the lactate radical. A case of historical interest, though the radicals involved are both of the same relative configuration (" *l* "), is menthyl camphor-β-sulphonate, the dispersion of which was investigated by Tschugaeff (*Ber*., 1911, **44**, 2023). Menthyl triphenylacetate (*idem*, *ibid*., 1912, **45**, 2759) is anomalous in the negative region of rotation; camphor-β-sulphonic acid is potentially anomalous (Lowry, J., 1925, **127**, 1503), the high-frequency term being negative. The ester menthyl camphor-β-sulphonate is anomalous, and, as would be expected, in the negative region (" *l* " configuration).

For over ten years, it has been the convention to assign compounds containing one asymmetric centre and compounds containing asymmetric centres of identical type, showing anomaly, to class (*c*): "Formation of two molecular types from one optically active compound." The origin of this class can be traced to the view, put forward by Arndtsen in 1858, explaining the anomalous rotatory dispersion of solutions of *d*-tartaric acid. The present tendency, however, is to seek a cause for a partial rotation of opposite sign in the molecule itself. Such centres of opposite sign have been assumed, on the theory that an unsaturated group in an asymmetric molecule may acquire an induced asymmetry [type (*e*), "induced asymmetry in unsaturated molecules," Lowry, *loc. cit.*].

The necessity for seeking, either by isomeric change or by induced asymmetry, a centre giving rise to an opposite partial rotation is due to the non-recognition that a single asymmetric centre can give rise to two electronic components (two electronic tetrahedra) which may contribute rotations of the same or opposite sign.

The carbonyl group in camphor is considered optically active by induced asymmetry, and the rotation contributed by this hypothetical centre is 71·05° (*d*-camphor in acetone, λ 5893). This is the contribution due to the low-frequency term, whereas the high-frequency term only contributes 20·54°. A theory which attaches importance to a hypothetical centre needs scrutiny. More serious than the assumption of a rotational value is the point that the carbonyl group has been considered asymmetric in order that it might be a decisive factor with respect to determining the relative configuration of the molecule.

The carbonyl group need not be regarded as an asymmetric centre but rather as causing a deflecting and disturbing action on the electronic system round the asymmetric centre. The nearer the carbonyl group is to the asymmetric centre the greater will be the effect on the electronic tetrahedra (compare Tschugaeff's views on rotatory dispersion, *Trans. Faraday Soc., loc. cit.*, p. 35, with regard to the influence of the electrons attached to the radicals and the asymmetric carbon atom).

Quartz has been placed provisionally in class (*f*) (i) ("Crystals with two natural frequencies"), since class (*f*) (ii) has been discarded. On the view here expressed, quartz falls naturally into this class. Thomson (*loc. cit.*) has applied the same general equation to quartz as to organic compounds. Molecules, in the crystalline condition, can be optically active, owing to distortion, although inactive when fused or in solution. This distortion will be reflected in the arrangement of a system of electrons round the silicon atoms, and anomaly may result.

In β-quartz, Bragg and Gibbs (*Proc. Roy. Soc.*, 1925, **109**, 405) find that the oxygen atoms are placed almost exactly in a tetrahedral arrangement round the silicon atom, and they consider that silicon, being a quadrivalent atom, is probably striving for such an arrangement. In addition, Gibbs (*ibid.*, 1926, **110**, 443) has pointed out that, in passing from β- to α-quartz, the tetrahedrally arranged oxygens have been twisted and slightly distorted with consequent loss of symmetry, which is in accordance with the rotation data (for sodium light) :

$$\underset{21{\cdot}7^\circ\ (20^\circ\text{C.})}{\alpha\text{-Quartz}} \xleftrightarrow{575^\circ} \underset{2{\cdot}52^\circ\ (600^\circ\text{C.})}{\beta\text{-Quartz}}$$

The explanation offered of the pyro- and piezo-electric effects of quartz by the suggested structure rests on the assumption of electric doublets, one corresponding to each valency. This is in harmony with the assumption that the eight structural electrons round the silicon atom form two tetrahedral arrangements.

EXPERIMENTAL.

Ethyl Tartrate.—The ester was prepared by the continuous esterification process (Aston and Frankland, J., 1901, **79**, 511) and fractionated ten times in a vacuum. After the seventh distillation the ester exhibited a transient yellow colour and the distillates in the subsequent fractionations behaved similarly. B. p. 155—156°/15 mm. Rotations were taken in a 3-dcm. tube.

Densities determined :

t°	0·2	28·06	61·51	106·9	149·45
$d_{4^\circ}^{t^\circ}$	1·2246	1·1961	1·1621	1·1155	1·0720

$d_{4^\circ}^{0\cdot8^\circ}$ 1·2239.		$d_{4^\circ}^{14\cdot4^\circ}$ 1·2101.		$d_{4^\circ}^{20^\circ}$ 1·2044.		$d_{4^\circ}^{40^\circ}$ 1·1840.	
λ.	$[\alpha]_\lambda^{0\cdot8^\circ}$.	λ.	$[\alpha]_\lambda^{14\cdot4^\circ}$.	λ.	$[\alpha]_\lambda^{20^\circ}$.	λ.	$[\alpha]_\lambda^{40^\circ}$.
6438	+5·28°	6152	7·01°	5893	7·83°	5590	10·22°
6364	5·31	5893	7·16	5700	7·90	5461	10·35
6152	5·31	5770	7·18	5613	7·90	5344	10·40
5893	5·31	5700	7·19	5590	7·91	5334	10·41
5770	5·31	5639	7·19	5538	7·90	5323	10·41
5700	5·28	5590	7·18	5324	7·78	5292	10·40
5590	5·12	5461	7·10			5086	10·27

$d_{4^\circ}^{60^\circ}$ 1·1635.		$d_{4^\circ}^{80^\circ}$ 1·1430.		$d_{4^\circ}^{100^\circ}$ 1·1226.		$d_{4^\circ}^{120^\circ}$ 1·1022.		$d_{4^\circ}^{140^\circ}$ 1·0817.	
λ.	$[\alpha]_\lambda^{60^\circ}$.	λ.	$[\alpha]_\lambda^{80^\circ}$.	λ.	$[\alpha]_\lambda^{100^\circ}$.	λ.	$[\alpha]_\lambda^{120^\circ}$.	λ.	$[\alpha]_\lambda^{140^\circ}$.
5324	12·40°	5086	14·57°	4861	16·23°	4722	17·76°	4678	18·78°
5154	12·52	4964	14·68	4786	16·30	4678	17·80	4587	18·86
5105	12·55	4926	14·70	4722	16·31	4587	17·81	4510	18·87
5086	12·55	4861	14·72	4678	16·31	4510	17·76	4472	18·85
4926	12·54	4786	14·69	4587	16·24				
4861	12·46	4678	14·61						

Ethyl Monoacetyltartrate.—This derivative was prepared by a modification of the method given by Patterson (J., 1900, **77**, 1099). Acetyl chloride (14 g.; slightly less than the calculated amount), in three times its volume of benzene, was added 1 c.c. at a time to 40 g. of ethyl tartrate dissolved in 30 c.c. of benzene. After each addition the mixture was shaken vigorously and heated to 80° until hydrogen chloride ceased to be evolved, then cooled to ordinary temperature, and the process repeated. After all the acetyl chloride had been added the benzene was removed, the residue distilled under diminished pressure, and the distillate collected at 165—170°/15 mm. The distillate was shaken with 5 c.c. of water and separated. This was repeated eight times in order to remove ethyl tartrate. The residual oil was dissolved in a large volume of water and cooled to 0°; the ethyl diacetyltartrate which separated was filtered off and the filtrate extracted with chloroform. The extract was dehydrated over anhydrous sodium sulphate and the solvent removed at the ordinary temperature. The above purification process was repeated three times and the ester gave $[\alpha]_D^{31\cdot2°}$ + 12·41° (Patterson gives $[\alpha]_D^{31\cdot2°}$ + 11·60°). The rotation remained unchanged after repetition of the purification process.

Estimation of the acetyl group by the method of Sudborough and Thomas (J., 1905, **87**, 1752) gave 17·2% (Calc.: 17·34) (Found: C, 48·28; H, 6·6. Calc. for $C_{10}H_{16}O_7$: C, 48·37; H, 6·5%). The rotations were taken through a 2-dcm. length, except at the highest temperature for which a 1-dcm. tube was employed. The ester exhibits anomaly; the temperature–rotation curves intersect. Rotations taken above 100° indicated decomposition of the compound.

Densities determined:

$t°$	14·3	34·5	46·5	56·6	90·7	94·5
$d_{40°}^{t°}$	1·1876	1·1676	1·1554	1·1456	1·1118	1·1078

	$d_{4°}^{17\cdot5°}$ = 1·1845.	$d_{4°}^{25\cdot1°}$ = 1·1768.	$d_{4°}^{29\cdot5°}$ = 1·1724.	$d_{4°}^{44\cdot5°}$ = 1·1576.	$d_{4°}^{59\cdot6°}$ = 1·1426.	$d_{4°}^{76\cdot8°}$ = 1·1255.	$d_{4°}^{94\cdot5°}$ = 1·1078.
λ.	$[\alpha]_\lambda^{17\cdot5°}$.	$[\alpha]_\lambda^{25\cdot1°}$.	$[\alpha]_\lambda^{29\cdot5°}$.	$[\alpha]_\lambda^{44\cdot5°}$.	$[\alpha]_\lambda^{59\cdot6°}$.	$[\alpha]_\lambda^{76\cdot8°}$.	$[\alpha]_\lambda^{94\cdot5°}$.
6708	+8·30°	8·61°	8·82°	9·45°	10·08°	10·82°	11·61°
6563	8·62	8·95	9·15	9·79	10·47	11·26	12·09
6438	8·95	9·27	9·48	10·13	10·79	11·62	12·52
6152	9·46	9·84	10·07	10·83	11·59	12·52	13·52
5893	9·82	10·27	10·51	11·41	12·31	13·35	14·46
5590	10·19	10·70	10·99	12·01	13·03	14·23	15·50
5461	10·39	10·90	11·22	12·23	13·30	14·60	15·96
5324	10·46	11·02	11·33	12·47	13·59	14·94	16·40
5086	10·44	11·06	11·44	12·68	13·97	15·48	17·08
4861	10·26	10·95	11·31	12·68	14·11	15·76	17·49
4678	9·85	10·57	10·97	12·46	13·97	15·76	17·67
4455	8·87	9·68	10·12	11·81	13·55	15·61	17·78
4359	8·25	9·12	9·62	11·44	13·29	15·45	17·71

Ethyl Diacetyltartrate.—This ester, prepared by the method of McCrae and Patterson (J., 1900, **77**, 1098), distilled at 163°/10—11 mm. It was fractionated three times and recrystallised from aqueous alcohol five times. Further distillation and recrystallisation caused no change in rotation (Found : C, 49·56; H, 6·29. Calc. for $C_{12}H_{18}O_8$: C, 49·66; H, 6·21%). The compound is anomalous; the temperature–rotation curves intersect. The rotation was found to be slightly higher than the values given by the above authors. Rotations were taken in a 1-dcm. tube.

	$\alpha_D^{67\cdot6^\circ}$.	$[\alpha]_D^{67\cdot6^\circ}$.	M. p.
McCrae and Patterson give	+5·28	4·75	67—68°
The authors find	5·44	4·85	67·7° (corr.)

Densities determined :

t°	66	116·1	149·9	182·4
$d_{4^\circ}^{t^\circ}$	1·1149	1·0627	1·0274	0·9934

	$d_{4^\circ}^{74\cdot1^\circ}$ = 1·1059.	$d_{4^\circ}^{87\cdot5^\circ}$ = 1·0920.	$d_{4^\circ}^{101\cdot3^\circ}$ = 1·0779.	$d_{4^\circ}^{122\cdot2^\circ}$ = 1·0562.	$d_{4^\circ}^{142\cdot8^\circ}$ = 1·0350.	$d_{4^\circ}^{162\cdot8^\circ}$ = 1·0139.
λ.	$[\alpha]_\lambda^{74\cdot1^\circ}$.	$[\alpha]_\lambda^{87\cdot5^\circ}$.	$[\alpha]_\lambda^{101\cdot3^\circ}$.	$[\alpha]_\lambda^{122\cdot2^\circ}$.	$[\alpha]_\lambda^{142\cdot8^\circ}$.	$[\alpha]_\lambda^{162\cdot8^\circ}$.
6708	+4·67°	5·10°	5·62°	6·58°	7·61°	8·61°
6563	4·78	5·26	5·81	6·80	7·92	8·94
6364	4·93	5·44	6·03	7·12	8·27	9·39
6152	5·04	5·57	6·22	7·43	8·69	9·91
5893	5·13	5·74	6·48	7·80	9·26	10·65
5590	5·08	5·83	6·68	8·20	9·88	11·47
5461	5·01	5·76	6·70	8·36	10·16	11·84
5324	4·85	5·68	6·68	8·44	10·39	12·18
5086	4·29	5·39	6·47	8·44	10·67	12·75
4861	3·51	4·81	6·05	8·23	10·62	13·21
4678	2·64	3·96	5·46	7·92	10·50	13·39
4359	0·09	1·74	3·65	6·76	9·93	13·08

Ethyl Monobenzoyltartrate.—This ester was prepared by a modification of Frankland and McCrae's method (J., 1898, **73**, 307). To 40 g. of anhydrous ethyl tartrate, heated and mechanically stirred in an oil-bath (130—135°), 19 g. of freshly distilled benzoyl chloride were added, drop by drop, during 2 hours. The purification was carried out in accordance with their method, except that anhydrous sodium sulphate was used in place of potassium carbonate as drying agent. The compound was recrystallised four times from light petroleum (b. p. 40—60°); yield 24 g. (Found : C, 57·93; H, 5·87. Calc. for $C_{15}H_{18}O_7$: C, 58·04; H, 5·83%); m. p. 66·2° (corr.); $[\alpha]_D^{24^\circ}$ 19·13°; $[\alpha]_D^{135^\circ}$ 16·68° (compare Frankland and McCrae : yield, 23 g. from 60 g. of ester; m. p. 66—66·5°; $[\alpha]_D^{24^\circ}$ 20·71°; $[\alpha]_D^{135^\circ}$ 16·36°). The ester exhibits anomalous rotatory dispersion, and the temperature–rotation curves for short wavelengths intersect. Rotations relate to a 1-dcm. column.

Densities determined :

$t°$ ……………	28·6	78·0	124·6	161·9	192·0
$d_{4°}^{t°}$ ……………	1·1943	1·1489	1·1061	1·0719	1·0424

	$d_{4°}^{28·6°}=$ 1·1943.	$d_{4°}^{49·0°}=$ 1·1754.	$d_{4°}^{67·7°}=$ 1·1582.	$d_{4°}^{85·1°}=$ 1·1423.	$d_{4°}^{103·9°}=$ 1·1251.	$d_{4°}^{124·7°}=$ 1·1060.	$d_{4°}^{142·8°}=$ 1·0891.	$d_{4°}^{160·1°}=$ 1·0734
λ.	$[\alpha]_{\lambda}^{28·6°}$.	$[\alpha]_{\lambda}^{49·0°}$.	$[\alpha]_{\lambda}^{67·7°}$.	$[\alpha]_{\lambda}^{85·1°}$.	$[\alpha]_{\lambda}^{103·9°}$.	$[\alpha]_{\lambda}^{124·7°}$.	$[\alpha]_{\lambda}^{142·8°}$.	$[\alpha]_{\lambda}^{160·1°}$.
6708	+15·52°	15·30°	14·93°	14·62°	14·23°	13·70°	13·29°	12·79°
6563	16·11	15·88	15·50	15·15	14·78	14·25	13·83	13·34
6364	16·90	16·69	16·33	15·95	15·55	15·03	14·61	14·11
6152	17·89	17·63	17·24	16·82	16·43	15·86	15·39	14·90
5893	19·10	18·81	18·42	17·98	17·52	16·94	16·46	15·93
5590	20·57	20·26	19·84	19·43	18·93	18·37	17·85	17·28
5461	21·19	20·87	20·47	20·01	19·53	18·94	18·42	17·82
5324	21·81	21·48	21·06	20·67	20·19	19·57	19·04	18·38
5086	22·68	22·45	22·03	21·66	21·27	20·60	19·95	19·37
4678	23·42	23·43	23·24	22·98	22·62	22·01	21·43	20·67
4472	23·02	23·29	23·33	23·24	23·02	22·47	21·89	21·17
4359	22·48	22·91	23·10	23·18	23·09	22·59	22·03	21·31

Ethyl Dibenzoyltartrate.—This ester was prepared by the method of Frankland and Wharton (J., 1896, **69**, 1583), and after it had stood for a few days in a vacuum desiccator crystals began to form. When crystallisation was almost complete, the mass was dissolved in absolute alcohol, allowed to stand, and then seeded. The major part of the ester then crystallised over-night, and was recrystallised eight times from absolute alcohol (Found : C, 63·80; H, 5·40. Calc. for $C_{22}H_{22}O_8$: C, 63·73; H, 5·36%); m. p. 63·5° (corr.); $[\alpha]_D^{18°}$ − 59·30° (Frankland and Wharton give m. p. 62·5°; $[\alpha]_D^{18°}$ − 59·36°). Its rotatory dispersion is complex and shows minima in the temperature-rotation curves (compare Frankland and Wharton). Rotations were taken in a 1-dcm. column.

Densities determined :

$t°$ ……………	16·3	73·95	126·3	158·9	192·9
$d_{4°}^{t°}$ ……………	1·1988	1·1498	1·1046	1·0767	1·0477

	$d_{4°}^{16·9°}=$ 1·1984.	$d_{4°}^{26°}=$ 1·1905.	$d_{4°}^{49·5°}=$ 1·1702.	$d_{4°}^{73·2°}=$ 1·1499.	$d_{4°}^{39·4°}=$ 1·1275.	$d_{4°}^{119·1°}=$ 1·1105.	$d_{4°}^{136·8°}=$ 1·0960.	$d_{4°}^{161·4°}=$ 1·0746.
λ.	$[\alpha]_{\lambda}^{16·9°}$.	$[\alpha]_{\lambda}^{26°}$.	$[\alpha]_{\lambda}^{49·5°}$.	$[\alpha]_{\lambda}^{73·2°}$.	$[\alpha]_{\lambda}^{99·4°}$.	$[\alpha]_{\lambda}^{119·1°}$.	$[\alpha]_{\lambda}^{136·8°}$.	$[\alpha]_{\lambda}^{161·4°}$.
6708	−40·97°	−42·50°	−43·69°	−43·57°	−42·33°	−40·63°	−39·34°	−36·49°
6563	43·54	45·11	46·33	46·17	44·73	43·00	41·51	38·70
6438	45·98	47·63	48·82	48·73	47·09	45·21	43·63	40·87
6152	52·21	53·99	55·26	55·00	53·21	51·10	49·24	46·06
5893	58·91	60·81	62·18	61·95	59·82	57·52	55·27	51·94
5590	69·23	71·23	72·75	72·13	69·61	66·67	64·19	60·51
5324	80·16	82·28	83·98	83·22	80·24	76·76	73·91	69·72
5086	93·25	95·51	97·39	95·76	92·24	88·34	84·87	79·76
4861	107·39	109·8	111·86	110·41	106·00	101·10	97·44	91·21
4678	122·40	125·0	127·27	125·10	119·47	114·10	109·40	102·48
4455	144·60	147·4	150·0	146·0	137·70	131·56	125·70	117·74

Ethyl Thionyltartrate.—The most satisfactory method investigated for the preparation of this compound was that given by Schiller (*Ber.*, 1909, **42**, 2017). The following method of purification was adopted. The mixture, after reaction, was washed repeatedly with water, shaken eight times with 1% sodium carbonate solution, again washed repeatedly with water, dried in ether (anhydrous sodium sulphate) and fractionated in a vacuum. After 9 fractionations, a 3-dcm. column of the compound on comparison with a 3-dcm. column of ethyl tartrate, showed practically no colour (Found : C, 37·91; H, 4·72; S, 12·8. Calc. for $C_8H_{12}O_7S$: C, 38·07; H, 4·80; S, 12·71%).

The data available for this ester are as follows :

	B. p.		
McKenzie and Barrow (J., 1911, **99**, 1910) ...	160°/12 mm.	$\alpha_D^{19\cdot5^\circ}$ −244·3°	$[\alpha]_D^{19\cdot5^\circ}$ −183·8°
Schiller (*loc. cit.*)	169°/11·5 mm.		$[\alpha]_D^{17\cdot5-18^\circ}$ −56·71°
Lee (Thesis, University of Birmingham, 1912)	164°/14 mm.	$\alpha_D^{20\cdot3^\circ}$ −241·5°	
Present authors	159°/11 mm.	$\alpha_D^{20\cdot3^\circ}$ −241·36°	$[\alpha]_D^{20\cdot3^\circ}$ −182·56°

On standing, the oil acquires a yellow colour and shows a decrease in rotation. The ester shows simple rotatory dispersion. Rotations at lower temperatures were taken in a 3-dcm. tube, and those at higher temperatures in a 2-dcm. tube. The formula used for calculating [α] at each temperature is given at the foot of the appropriate columns, and the difference (observed—calculated) is shown in the column headed " Diff."

Densities determined :

t°	11·8	61·01	106·4	148	174·2
$d_{4^\circ}^{t^\circ}$	1·3320	1·2749	1·2225	1·1738	1·1423

	$d_{4^\circ}^{13\cdot1^\circ} = 1\cdot3305.$		$d_{4^\circ}^{20\cdot3^\circ} = 1\cdot3221.$		$d_{4^\circ}^{42\cdot3^\circ} = 1\cdot2966.$	
λ.	$[\alpha]_\lambda^{13\cdot1^\circ}$.	Diff.	$[\alpha]_\lambda^{20\cdot3^\circ}$.	Diff.	$[\alpha]_\lambda^{42\cdot3^\circ}$.	Diff.
6869·5	−130·85°	−0·01	−129·45°	+0·01	−126·27°	+0·01
6708			136·48	+0·04		
6563	144·79	+0·02	143·21	−0·01	139·69	−0·01
6364			153·40	−0·01		
6152	167·31	+0·02	165·54	−0·03	161·49	−0·01
5893	184·42	±0	182·56	±0	178·07	−0·02
5590	208·26	+0·05	206·22	+0·03	201·16	+0·02
5461			217·70	−0·02		
5324			231·22	+0·09	225·54	+0·06
5086	260·08	+0·01	257·73	−0·02	251·40	−0·05
4861	290·11	−0·01	287·63	−0·05	280·59	−0·06
4678	318·91	+0·06	316·29	−0·01	308·55	−0·04
4472	357·15	+0·10	354·45	−0·13	345·80	+0·03
4359	381·20	−0·03	378·56	+0·04	369·30	−0·03

$$[\alpha]_\lambda^{13\cdot1^\circ} = -\frac{56\cdot183}{\lambda^2 - 0\cdot042642} \quad [\alpha]_\lambda^{20\cdot3^\circ} = -\frac{55\cdot46}{\lambda^2 - 0\cdot043495} \quad [\alpha]_\lambda^{42\cdot3^\circ} = -\frac{54\cdot089}{\lambda^3 - 0\cdot43556}$$

$d_{4^\circ}^{56\cdot9^\circ} = 1\cdot2796.$ $d_{4^\circ}^{82\cdot8^\circ} = 1\cdot2496.$ $d_{4^\circ}^{106\cdot9^\circ} = 1\cdot2216.$

λ.	$[\alpha]_\lambda^{56\cdot9^\circ}$.	Diff.	$[\alpha]_\lambda^{82\cdot8^\circ}$.	Diff.	$[\alpha]_\lambda^{106\cdot9^\circ}$.	Diff.
6869·5	−124·43°	+0·03	−121·54°	±0	−119·52°	+0·01
6708						
6563	137·66	+0·02	134·42	−0·09	132·27	+0·00
6364			144·17	+0·06		
6152	159·09	−0·01	155·51	−0·05	152·94	−0·03
5893	175·42	±0	171·55	−0·03	168·71	−0·02
5590	198·14	+0·04	193·88	+0·01	190·66	+0·02
5461						
5324	222·14	+0·10	217·47	+0·05	213·88	+0·08
5086	247·66	+0·08	242·52	−0·05	238·51	−0·03
4861	276·28	−0·01	270·89	−0·03	266·34	−0·04
4678	303·77	+0·03			293·05	+0·01
4472	340·40	−0·12	334·09	−0·01	328·66	+0·09
4359	363·40	+0·01	357·00	−0·01	351·10	−0·01

$$[\alpha]_\lambda^{56\cdot9^\circ} = -\frac{53\cdot331}{\lambda^2 - 0\cdot04326} \qquad [\alpha]_\lambda^{82\cdot8^\circ} = -\frac{51\cdot955}{\lambda^2 - 0\cdot04448} \qquad [\alpha]_\lambda^{106\cdot9^\circ} = -\frac{51\cdot083}{\lambda^2 - 0\cdot04452}$$

$d_{4^\circ}^{125\cdot2^\circ} = 1\cdot2003.$ $d_{4^\circ}^{145\cdot4^\circ} = 1\cdot1768.$

λ.	$[\alpha]_\lambda^{125\cdot2^\circ}$.	Diff.	$[\alpha]_\lambda^{145\cdot4^\circ}$.	Diff.
6869·5	−118·27°	±0	−117·28°	+0·03
6708			123·63	+0·04
6563	130·89	−0·01	129·72	±0
6364			138·95	±0
6152	151·40	−0·03	149·95	+0·01
5893	166·94	−0·03	165·33	+0·01
5590	188·65	+0·01	186·76	+0·07
5461			197·12	±0
5324	211·60	+0·04	209·34	+0·10
5086	235·98	−0·05	233·28	−0·03
4861	263·51	−0·05	260·34	−0·01
4678	289·87	−0·06	286·21	±0
4472	325·12	−0·06	320·72	+0·11
4359	347·38	−0·03	342·30	−0·11

$$[\alpha]_\lambda^{125\cdot2^\circ} = -\frac{50\cdot564}{\lambda^2 - 0\cdot04444} \qquad [\alpha]_\lambda^{145\cdot4^\circ} = -\frac{50\cdot275}{\lambda^2 - 0\cdot04318}$$

At 149° a decrease of rotation $\alpha_{5086} = 0\cdot03^\circ$ was noted.

Ethyl Dichlorosuccinate.—This ester was prepared by the method given by Lee (*loc. cit.*) from the ethyl thionyl ester, using pyridine hydrochloride as a catalyst (1 mol. thionyl ester, freshly prepared; 1 mol. thionyl chloride; and 2 mols. pyridine hydrochloride; heated together for 8 hours on a water-bath at 100°). The resulting oil was washed repeatedly with water, taken up in ether, dried over sodium sulphate, and fractionated in a vacuum eight times; b. p. 128°/12—13 mm.; $\alpha_D^{20^\circ}$ − 52·54° (Found: Cl, 28·7. Calc. for $C_8H_{12}O_4Cl_2$: Cl, 29·18%). On standing, racemisation or loss of hydrogen chloride takes place and the rotation decreases; the ester cannot then be brought up to its original rotation by vacuum fractionation. The ester shows simple rotatory dispersion. Rotations were taken in a 2-dcm. tube.

Densities determined :

t°	9·1	61·4	110·6	148·4
$d_{4^\circ}^{t^\circ}$	1·2495	1·1902	1·1346	1·0908

$d_{4^\circ}^{12\cdot7^\circ} = 1\cdot2454.$ $d_{4^\circ}^{22\cdot6^\circ} = 1\cdot2343.$ $d_{4^\circ}^{41\cdot4^\circ} = 1\cdot2130.$

λ.	$[\alpha]_\lambda^{12\cdot7^\circ}$.	Diff.	$[\alpha]_\lambda^{22\cdot6^\circ}$	Diff.	$[\alpha]_\lambda^{41\cdot4^\circ}$.	Diff.
6869·5	−29·89°	+0·01	−29·97°	±0	−30·02°	+0·01
6708	31·54	+0·02	31·62	±0	31·75	+0·09
6563	33·12	+0·01	33·23	+0·02	33·26	±0
6364	35·52	+0·01	35·59	−0·03	35·69	+0·02
6152	38·36	−0·02	38·47	−0·02	38·53	−0·02
5893	42·40	−0·01	42·52	±0	42·58	−0·02
5590	48·02	−0·01	48·24	+0·09	48·29	+0·06
5461	50·77	−0·02	50·87	−0·04	51·01	+0·01
5324	54·00	±0	54·11	−0·02	54·27	+0·05
5086	60·39	−0·02	60·51	−0·03	60·66	±0
4861	67·64	−0·03	67·78	−0·01	67·91	−0·03
4678	74·62	−0·04	74·75	−0·03	74·97	+0·02
4472	84·04	+0·01	84·12	−0·03	84·37	+0·02
4359	90·02	±0	90·14	+0·02	90·36	±0

$$[\alpha]_\lambda^{12\cdot7^\circ} = -\frac{12\cdot611}{\lambda^2 - 0\cdot04992} \quad [\alpha]_\lambda^{22\cdot6^\circ} = -\frac{12\cdot663}{\lambda^2 - 0\cdot04950} \quad [\alpha]_\lambda^{41\cdot4^\circ} = -\frac{12\cdot67}{\lambda^2 - 0\cdot04979}$$

$d_{4^\circ}^{62\cdot4^\circ} = 1\cdot1892.$ $d_{4^\circ}^{87^\circ} = 1\cdot1613.$ $d_{4^\circ}^{104\cdot1^\circ} = 1\cdot1420.$

λ.	$[\alpha]_\lambda^{62\cdot4^\circ}$.	Diff.	$[\alpha]_\lambda^{87^\circ}$.	Diff.	$[\alpha]_\lambda^{104\cdot1^\circ}$.	Diff.
6869·5	−29·63°	−0·01	−28·84°	−0·01	−28·26°	+0·01
6708	31·26	−0·01	30·46	+0·02	29·83	+0·02
6563	32·84	−0·01	31·98	±0	31·34	+0·01
6364	35·20	−0·02	34·31	±0	33·62	+0·01
6152	38·04	−0·03	37·15	+0·06	36·34	±0
5893	42·05	−0·01	41·01	+0·01	40·17	±0
5590	47·74	+0·10	46·48	+0·01	45·55	+0·03
5461	50·35	−0·02	49·16	+0·01	48·16	±0
5324	53·57	+0·01	52·30	+0·02	51·25	+0·02
5086	59·90	−0·02	58·53	±0	57·39	+0·03
4861	67·11	±0	65·61	−0·01	64·34	+0·02
4678	74·05	+0·01	72·46	±0	71·03	±0·00
4472	83·36	+0·02	81·68	+0·03	80·07	±0·00
4359	89·31	+0·03	87·53	±0	85·81	−0·03

$$[\alpha]_\lambda^{62\cdot4^\circ} = -\frac{12\cdot508}{\lambda^2 - 0\cdot04991} \quad [\alpha]_\lambda^{87^\circ} = -\frac{12\cdot131}{\lambda^2 - 0\cdot05141} \quad [\alpha]_\lambda^{104\cdot1^\circ} = -\frac{11\cdot876}{\lambda^3 - 0\cdot05165}$$

At 122·9° an increase of rotation $\alpha_{5154} = 0\cdot33^\circ$ was noted, which indicated decomposition, and comparison of observed with calculated values showed the rotatory dispersion still to be simple.

Methyl Tartrate.—This ester was prepared from Kahlbaum's methyl alcohol by the continuous esterification process mentioned under ethyl tartrate (150 g. tartaric acid; 14 hrs.; oil-bath at 120—125°). It was fractionated in vacuum six times, and had b. p. 165—166°/11·5 mm., m. p. 48°. Rotations were taken in a 2-dcm. tube.

Densities determined :

t°	29·5	53·3	67·8	88·3	122·9	138·9	170
$d_{4^\circ}^{t^\circ}$	1·3232	1·2985	1·2836	1·2624	1·2263	1·2093	1·1770

	$d_{4^\circ}^{17\cdot7^\circ}$ (extrapolated) = 1·3356.	$d_{4^\circ}^{34\cdot9^\circ}$ = 1·3180.	$d_{4^\circ}^{59\cdot8^\circ}$ = 1·2921.
λ.	$[\alpha]_{\lambda}^{17\cdot7^\circ}$.	$[\alpha]_{\lambda}^{34\cdot9^\circ}$.	$[\alpha]_{\lambda}^{59\cdot8^\circ}$.
6708	+2·32°	3·45°	4·53°
6563	2·36	3·49	4·62
6438	2·34	3·49	4·67
6152	2·19	3·45	4·75
5893	1·87	3·28	4·73
5590	1·21	2·84	4·56
4359	−9·17	−5·81	−2·24

	$d_{4^\circ}^{81\cdot2^\circ}$ = 1·2698.	$d_{4^\circ}^{95\cdot3^\circ}$ = 1·2549.	$d_{4^\circ}^{100\cdot8^\circ}$ = 1·2495.	$d_{4^\circ}^{124\cdot9^\circ}$ = 1·2246.	$d_{4^\circ}^{144\cdot8^\circ}$ = 1·2033.	$d_{4^\circ}^{162\cdot1^\circ}$ = 1·1853.
λ.	$[\alpha]_{\lambda}^{81\cdot2^\circ}$.	$[\alpha]_{\lambda}^{95\cdot3^\circ}$.	$[\alpha]_{\lambda}^{100\cdot8^\circ}$.	$[\alpha]_{\lambda}^{124\cdot9^\circ}$.	$[\alpha]_{\lambda}^{144\cdot8^\circ}$.	$[\alpha]_{\lambda}^{162\cdot1^\circ}$.
6708	+5·18°	5·54°	5·67°	6·08°	6·33°	6·51°
6152	5·57	6·02	6·21	6·79	7·18	7·43
5893	5·68	6·16	6·36	7·02	7·52	7·87
5590	5·62	6·21	6·43	7·22	7·75	8·15
5324	5·38	5·99	6·30	7·16	7·74	8·15
5086		5·55		6·86	7·59	8·05
4359	−0·02	1·21	1·65	3·40	4·55	

Methyl Monoacetyltartrate.—The ester was prepared similarly to the ethyl analogue, and purified as follows: The benzene was removed and the residual oil shaken with 5 c.c. of water and separated. This was repeated twice. The oil was then dissolved in a large volume of water and cooled to 0°; the diacetyltartrate which separated was filtered off, the filtrate extracted with ether, the extract dehydrated over sodium sulphate, the solvent removed, and the residual monoacetyl ester crystallised from benzene to constant rotation and m. p., 82·4°. Estimation of acetyl group by Sudborough and Thomas's method (*loc. cit.*) gave 19·3 (Calc., 19·54%) (Found: C, 43·55; H, 5·6. Calc. for $C_8H_{12}O_7$: C, 43·62; H, 5·49%). Rotations were taken in 1-dcm. tube. The ester exhibits anomalous rotatory dispersion.

Densities determined:

t°	87·2	100·5	132	144·5
$d_{4^\circ}^{t^\circ}$	1·2131	1·1987	1·1639	1·1503

	$d_{4^\circ}^{85\cdot2^\circ}$ = 1·2156.*	$d_{4^\circ}^{105\cdot4^\circ}$ = 1·1931.	$d_{4^\circ}^{124\cdot4^\circ}$ = 1·1724.	$d_{4^\circ}^{140\cdot8^\circ}$ = 1·1546.
λ.	$[\alpha]_{\lambda}^{85\cdot2^\circ}$.	$[\alpha]_{\lambda}^{105\cdot4^\circ}$.	$[\alpha]_{\lambda}^{124\cdot4^\circ}$.	$[\alpha]_{\lambda}^{140\cdot8^\circ}$.
6708	+2·06°	3·19°	3·88°	4·19°
6563	2·04	3·25	3·99	4·38
6438	2·02	3·32	4·09	4·53
6152	1·94	3·37	4·28	4·81
5893	1·80	3·35	4·39	5·00
5590	1·54	3·23	4·38	5·11
5461	1·39	3·12	4·32	5·10
5324	1·15	2·95	4·23	5·08
5086	0·51	2·50	3·96	4·94
4861	−0·33	1·90	3·51	4·59
4678	−1·14	1·27	2·99	4·20
4455	−2·21	0·35	2·26	3·53
4359	−2·80	−0·05	1·86	3·21

* **Extrapolated.**

Methyl Diacetyltartrate.—The ester was prepared by heating methyl tartrate and acetic anhydride for 3 hours and finally raising it to its boiling point. The excess of acetic anhydride was removed under reduced pressure and the residue poured into water. The compound was purified by vacuum distillation and recrystallisation from aqueous alcohol; m. p. 106·5°; $\alpha_D^{107·3°}$ – 9·01° (Found : C, 45·65; H, 5·23. Calc. for $C_{10}H_{14}O_8$: C, 45·8; H, 5·38%). Freundler (*Compt. rend.*, 1892, **115**, 509; *Bull. Soc. chim.*, 1894, [3], **11**, 305) gave m. p. 103° and determined the rotation in alcoholic solution. The dispersion curves are complex and anomalous; crossing of the zero axis takes place towards the red end of the spectrum for the highest temperature. Rotations were taken in a 1-dcm. tube.

Densities determined :

$t°$	113	134·1	143·5	157	181
$d_{4°}^{t°}$	1·1407	1·1150	1·1034	1·0868	1·0575

	$d_{4°}^{107·3°}$ = 1·1480.*	$d_{4°}^{128·3°}$ = 1·1220.	$d_{4°}^{143·3°}$ = 1·1036.	$d_{4°}^{171·5°}$ = 1·0689.	$d_{4°}^{178·3°}$ = 1·0609.
λ.	$[\alpha]_\lambda^{107·3°}$.	$[\alpha]_\lambda^{128·3°}$.	$[\alpha]_\lambda^{143·3°}$.	$[\alpha]_\lambda^{171·5°}$.	$[\alpha]_\lambda^{178·3°}$.
6708	–5·20°	–3·96°	–2·85°	–0·12°	+0·75°
6563	5·53	4·27	3·06	0·19	+0·70
6463	5·87	4·54	3·28	0·23	+0·59
6152	6·83	5·35	3·91	0·52	+0·39
5893	7·85	6·22	4·65	0·84	+0·10
5590	9·32	7·41	5·72	1·64	–0·56
5324	11·14	8·89	6·98	2·48	–1·24
5086	13·21	10·62	8·42	3·46	–2·16
4861	15·83	12·75	10·06	4·74	–3·33
4678	18·21	14·85	11·92	6·10	–4·57
4455	21·67	17·99			–6·76

* Extrapolated.

Methyl Monobenzoyltartrate.—This was prepared by slowly adding benzoyl chloride (1 equiv.) to a stirred mixture of methyl tartrate and petroleum ether (b. p. 60—80°), the mixture then being boiled under reflux for 5 days. The petroleum ether was decanted and the layer of residual oil dissolved in benzene, treated with sodium carbonate solution, washed with water, dried over anhydrous sodium sulphate, and the benzene removed. The oil thus obtained was extracted with hot water and the solution filtered. The cold aqueous solution of the required ester was then extracted with ether, and when the latter was removed, the product solidified and was recrystallised from benzene; m. p. 78° (Found : C, 55·22; H, 4·8. Calc. for $C_{13}H_{14}O_7$: C, 55·3; H, 4·99%). Rotations were taken in a 1-dcm. tube. The ester exhibits anomalous rotatory dispersion.

Densities determined :

t° ……	50·5	79·6	93·5	127·4	146·1	158
$d_{4^\circ}^{t^\circ}$ ……	1·2487	1·2204	1·2065	1·1729	1·1533	1·1418

	$d_{4^\circ}^{22^\circ}$ = 1·2780.	$d_{4^\circ}^{57^\circ}$ = 1·2430.	$d_{4^\circ}^{80 \cdot 8^\circ}$ = 1·2192.	$d_{4^\circ}^{125 \cdot 3^\circ}$ = 1·1744.	$d_{4^\circ}^{157^\circ}$ = 1·1427.
λ.	$[\alpha]_\lambda^{22^\circ}$.	$[\alpha]_\lambda^{57^\circ}$.	$[\alpha]_\lambda^{80 \cdot 8^\circ}$.	$[\alpha]_\lambda^{125 \cdot 3^\circ}$.	$[\alpha]_\lambda^{157^\circ}$.
6708	+4·13°	4·63°	4·99°	4·91°	4·90°
6563	4·13	4·73	5·09	5·06	5·05
6438	4·10	4·80	5·18	5·18	5·16
6152	4·01	4·87	5·27	5·35	5·36
5893	3·85	4·78	5·21	5·40	5·44
5589	3·51	4·51	5·00	5·40	5·45
5461	3·30	4·33	4·84	5·30	5·37
5324	2·93	4·06	4·65	5·14	5·22
5086	1·85	3·15	3·91	4·56	4·73
4861	0·41	2·01	2·80	3·67	4·03
4678	−1·05	0·48	1·31	2·63	3·19
4455	−3·46	−1·65	−0·60	1·04	1·91
4359	−4·38	−2·48	−1·40	0·20	1·21

Methyl Dibenzoyltartrate.—This was prepared by the method described by Frankland and Wharton (J., 1896, **69**, 1583). (Found : C, 62·1 ; H, 4·78. Calc. for $C_{20}H_{18}O_8$: C, 62·15 ; H, 4·7%). Comparative data are :

	Frankland and Wharton.	Present authors.
M. p.	135·5°	135·5°
$d_{4^\circ}^{150^\circ}$	1·1285	1·1306
$d_{4^\circ}^{160^\circ}$	1·1191	1·1223
$[\alpha]_D^{137^\circ}$	−66·84°	−64·2°

Rotations were taken in a 1-dcm. tube. The ester exhibits complex rotatory dispersion.

Densities determined :

t°	140·6	153·7	166·2
$d_{4^\circ}^{t^\circ}$	1·1384	1·1276	1·1171

	$d_{4^\circ}^{135 \cdot 4^\circ}$ = 1·1428.	$d_{4^\circ}^{152 \cdot 5^\circ}$ = 1·1285.
λ.	$[\alpha]_\lambda^{135 \cdot 4^\circ}$.	$[\alpha]_\lambda^{152 \cdot 5^\circ}$.
6708	−45·78°	−43·03°
6563	48·23	45·51
6438	50·88	47·78
6152	57·42	53·95
5893	64·51	60·59
5590	74·69	69·95
5461	79·96	74·79
5324	85·76	80·34
5086	97·95	91·57
4861	112·18	104·60
4678	126·13	118·01
4455	145·68	137·88
4359	153·5	147·11

Summary.

(1) Inflexion and maxima are confined to the positive region of rotation, and crossing of the axis, $d\alpha/d\lambda$, is positive for methyl and

ethyl *d*-tartrates and those derivatives of the two esters which exhibit anomalous rotatory dispersion.

(2) The occurrence of anomalous rotatory dispersion is an indication of the relative configuration.

(3) The explanation of anomaly by consideration of ultra-violet terms only is incomplete. A view has been put forward postulating an infra-red term in the Drude equation. The term is negative for a compound of relative configuration "*d*." This term, though its contribution may be small compared with rotation of electronic origin, is necessary, for it controls (*a*) the association of the high-frequency constant with the positive ultra-violet term, and (*b*) the final course of the path to the infra-red band in the positive region.

(4) The consideration of anomaly involves both the superposition rule (Lowry, *loc. cit.*), and also Wood's interpretation of Drude's view of spurious anomaly; for the dispersion occurs between two bands, the low-frequency band in the ultra-violet, and the infra-red band, and not merely outside the ultra-violet bands (longer wave-length side), the infra-red band being neglected.

(5) Quartz is taken as an illustration of the importance of the infra-red term.

(6) By an extension of Thomson's view, a single asymmetric centre can give rise to anomaly.

(7) Different classes of anomalous rotatory dispersion are discussed.

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UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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