OPTICAL ROTATORY DISPERSION OF SOME BRIDGED DERIVATIVES OF ALKYLTARTRATES.*

By Yojiro TSUZUKI.

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In marked contrast to tartaric acid and its esters whose rotatory dispersion is anomalous⁽¹⁾, many of the bridged derivatives of tartaric acid are known to exhibit simple rotatory dispersion⁽²⁾, i. e. the dispersion in the transparent region can be expressed by a single term of Drude's equation, $\alpha = k / (\lambda^2 - \lambda_0)$, which was first demonstrated by Austin and Carpenter⁽³⁾ in the cases of dimethylene tartrate, in which the bridging takes place between the hydroxyl and carboxyl groups (type A) and of monomethylene tartaric acid, where the two alcoholic hydroxyl groups are linked together (type B), and then by Austin and Parker⁽⁴⁾ in the case of diacetyl tartaric anhydride, in which the bridging is performed between the two carboxyl groups (type C). Of the B type, two more bridged derivatives were added on the list later by Brynmor Jones⁽⁵⁾, namely dimethyl and diethyl benzylidene-tartrates.

Recently the author obtained some bridged derivatives of alkyltartrates of the B type such as diethyl isopropylidene-tartrate (I)⁽⁶⁾, dimethyl isopropy-

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* Studies on the synthesis of bridged derivatives of tartaric acid and their optical activity. Paper III.

(1) Lowry and Austin, *Trans. Roy. Soc.* (London), **222 A** (1922), 293; Lowry and Cutter, *J. Chem. Soc.*, **121** (1922), 532; Bruhat, *Trans. Faraday Soc.*, **26** (1930), 400.

(2) Lowry and Dickson, *Trans. Faraday Soc.*, **10** (1914), 96.

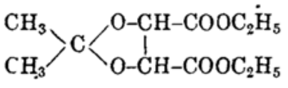
(3) *J. Chem. Soc.*, **125** (1924), 1939.

(4) *J. Chem. Soc.*, **127** (1925), 1926.

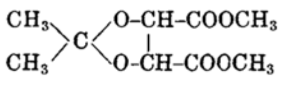
(5) *J. Chem. Soc.*, **1933**, 788.

(6) Tsuzuki, this Bulletin, **10** (1935), 255.

lidene-tartrate (II), diethyl ethylidene-tartrate (III), dimethyl ethylidene-tartrate (IV) and diethyl methylene-tartrate (V)⁽⁷⁾.



(I)



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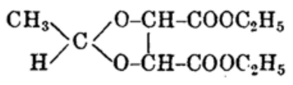

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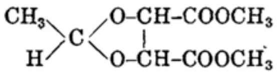

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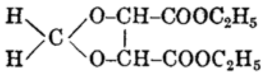

(V)

These compounds are all liquid substances, in contrast to the hitherto examined compounds which are all in the solid state and whose rotatory dispersion was necessarily observed in solution, which induces the author to take interest in examining the rotatory dispersion of these compounds whether the dispersion is really simple or complex, especially when the following fact is recalled that ethyl tartrate in pure liquid state shows the characteristics of anomalous dispersion in the visible region, i. e. inflection maximum and reversal of sign in the curve of the $\alpha-\lambda$ diagram. And if the dispersion be actually shown to be simple, it may be of no small interest further to inquire into the characteristic wave length λ_0 by comparing its value with those of similar compounds. As already recognized, the anomalous rotatory dispersion of tartaric acid and its esters mentioned above is considered to be due to two partial rotations with opposite signs, and actually the dispersion has been proved to conform to two terms of Drude's equation: $\alpha = k_1/(\lambda^2-\lambda_1^2)-k_2/(\lambda^2-\lambda_2^2)$. This is attributed, on the other hand, to the free rotation of the two halves of the molecule about the central bond, since it has been observed that simple rotatory dispersion is associated with ring formation⁽⁸⁾, by which process the free rotation must be impeded⁽⁹⁾. It may therefore be admitted that with ring formation one of the two terms of Drude's equation appears to become negligibly small, thus leaving in the derivative of the type A only a negative term and in those of the type B as well as C a positive term. These considerations direct us to an interesting problem about the relation between the chemical structure and the optical activity or optically active absorption band, particularly about "identity of structure" and

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(7) Tsuzuki, this Bulletin, **11** (1936), 362.

(8) Austin, *J. Chem. Soc.*, **125** (1924), 1941; **127** (1925), 1926; *Trans. Faraday Soc.*, **26** (1930), 415.

(9) The impedance of free rotation may also be caused by the introduction of bulky substituents as in diacetyl-tartaric acid which exhibits simple dispersion. Austin, *J. Chem. Soc.*, **1928**, 1828.

"persistence of absorption". The present paper aims also to deal with this problem.

The experimental results are shown in Tables 1–5.

Table 1. Rotatory Dispersion of Diethyl Isopropylidenetartrate (I).

$$\alpha = \frac{-17.775}{\lambda^2 - 0.03110}, \qquad [\alpha]^{20} = 0.8948\,\alpha,$$

$$d^{20} = 1.1175, \qquad t = 20^\circ, \qquad l = 1\ \mathrm{dm}.$$

λ	$\alpha_{obs.}$	$\alpha_{calc.}$	Difference
6362	− 47.49°	− 47.56°	+ 0.07°
6234	− 49.76	− 49.71	− 0.05
5893	− 56.23	− 56.23	±
5461	− 66.43	− 66.54	+ 0.11
5219	− 73.66	− 73.68	+ 0.02
5086	− 78.28	− 78.12	− 0.16
4916	− 84.33	− 84.41	+ 0.08
4680	− 94.64	− 94.58	− 0.06
4358	−111.70	−111.90	+ 0.20

Table 2. Rotatory Dispersion of Dimethyl Isopropylidenetartrate (II).

$$\alpha = \frac{-19.847}{\lambda^2 - 0.03012}, \qquad [\alpha]^{20} = 0.8025\,\alpha,$$

$$d^{20} = 1.1900, \qquad t = 20^\circ, \qquad l = 1\ \mathrm{dm}.$$

λ	$\alpha_{obs.}$	$\alpha_{calc.}$	Difference
6708	− 47.40°	− 47.27°	− 0.13°
6438	− 51.74	− 51.63	− 0.11
6234	− 55.24	− 55.36	+ 0.12
5893	− 62.68	− 62.59	− 0.09
5461	− 74.06	− 74.06	±
5218	− 81.78	− 81.95	+ 0.17
5086	− 86.70	− 86.84	− 0.14
4916	− 93.85	− 93.85	±
4799	− 99.17	− 99.10	− 0.07
4358	−124.0	−124.2	+ 0.2

Table 3. Rotatory Dispersion of Diethyl Ethylidenetartrate (III).

$$\alpha = \frac{-25.150}{\lambda^2 - 0.04400}, \quad t = 16^\circ, \quad l = 1\,\mathrm{dm}.$$

$$d^{16} = 1.1520, \qquad [\alpha]^{16} = 0.8680\,\alpha$$

λ	$\alpha_{obs.}$	$\alpha_{calc.}$	Difference
6708	− 61.72°	− 61.95°	+ 0.23°
6438	− 67.55	− 67.87	+ 0.32
6234	− 72.95	− 72.97	+ 0.02
5893	− 83.20	− 82.94	− 0.26
5461	− 98.75	− 98.94	+ 0.19
5218	−110.45	−110.17	− 0.28
5086	−117.00	−117.17	+ 0.17
4916	−127.08	−127.23	+ 0.15
4799	−134.89	−134.94	+ 0.05
4358	−172.45	−172.32	− 0.13

Table 4. Rotatory Dispersion of Dimethyl Ethylidenetartrate (IV).

$$\alpha = \frac{-15.427}{\lambda^2 - 0.04324}, \quad t = 16^\circ, \quad l = 0.5\,\mathrm{dm}.$$

$$d^{16} = 1.2450, \qquad [\alpha]^{16} = 1.6065\,\alpha$$

λ	$\alpha_{obs.}$	$\alpha_{calc.}$	Difference
6708	− 37.79°	− 37.93°	+ 0.14°
6438	− 41.60	− 41.55	− 0.05
6234	− 44.65	− 44.65	±
5893	− 50.65	− 50.75	+ 0.10
5461	− 60.52	− 60.52	±
5218	− 67.61	− 67.35	− 0.26
5086	− 71.50	− 71.61	+ 0.11
4916	− 77.73	− 77.75	+ 0.02
4799	− 82.61	− 82.43	− 0.18
4358	−105.05	−105.16	+ 0.11

Table 5. Rotatory Dispersion of Diethyl Methylenetartrate (V).

$$\alpha = \frac{-13.748}{\lambda^2 - 0.04585}, \quad t = 20^\circ, \quad l = 0.5\,\text{dm}.$$

$$d^{20} = 1.1958, \quad [\alpha]^{20} = 1.6725\,\alpha.$$

λ	$\alpha_{obs.}$	$\alpha_{calc.}$	Difference
6708	− 33.93°	− 34.02°	+ 0.09°
6438	− 37.21	− 37.29	+ 0.08
6234	− 40.25	− 40.11	− 0.14
5893	− 45.90	− 45.62	− 0.28
5461	− 54.48	− 54.49	+ 0.01
5218	− 60.83	− 60.71	− 0.12
5086	− 64.62	− 64.62	±
4916	− 70.18	− 70.21	+ 0.03
4799	− 74.52	− 74.50	− 0.02
4358	− 95.25	− 95.41	+ 0.16

As shown in the tables, the rotatory dispersions of these compounds can be expressed by a one-term Drude equation, so they are apparently simple in the visible region, which may be further confirmed by the dispersion ratio and the optically active absorption band calculated from the dispersion constant λ_0^2 (Table 6).

Table 6. Dispersion Ratio and Absorption Band of Bridged Derivatives of Tartaric Acid.

Bridged derivative	Dispersion ratio $\alpha_{4358}/\alpha_{5461}$	λ_0 (Å)
Diethyl isopropylidenetartrate (I)	1.681	1763
Dimethyl isopropylidenetartrate (II)	1.674	1735
Diethyl ethylidenetartrate (III)	1.742	2102
Dimethyl ethylidenetartrate (IV)	1.736	2080
Diethyl methylenetartrate (V)	1.748	2141

The values of the dispersion ratio and the absorption band are those which may be expected to occur in those compounds whose rotatory dispersions are simple. It may therefore be safely concluded that the rotatory dispersions of these compounds are not only normal, but very probably simple.

From Table 6 it is also noticed that a perceptible difference exists between the characteristic wave length of the derivatives formed by the condensation of aldehydes (III, IV, V) and that of those obtained from acetone (I, II): viz. the former compounds possess the characteristic frequency at about 2100 Å, while those of the latter are located at about 1750 Å.

For the comparison, the values of the dispersion ratio and the characteristic wave length of several saturated aliphatic compounds (including some with aromatic radical) exhibiting simple rotatory dispersion is cited, (Table 7).

Table 7. Dispersion Ratio and Characteristic Wave Length of Aliphatic Compounds.

	Dispersion ratio $\alpha_{4358}/\alpha_{5461}$	Characteristic wave length (Å)	Author
Primary amyl alcohol	1.700	1880	Lowry and Dickson(10)
Isovaleric acid	1.710	1940	
Ethyl isovalerate	—	1710	Levene, Rothen and Marker(11)
Methylene-tartaric acid (in water)	1.740	2100	Austin and Carpenter(3)
Dimethyl benzylidene-tartrate (in ethyl-acetate)	1.739	2087	Jones(5)
Diethyl benzylidene-tartrate (in methyl-alcohol)	1.739	2087	

It is clearly seen from Table 7 that all the bridged derivatives of tartaric acid formed by the condensation of aldehydes possess the characteristic wave length at about 2100 Å, but the compounds derived from acetone (Table 6) considerably shorter wave lengths which are just coincident with that of carboxylic ester, but are somewhat shorter than those of free carboxylic acid as well as of primary amyl alcohol. Although it is a tempting task to elucidate the relation between the absorption band and the chemical structure, it is still a doubtful question whether this latter wave length (1750 Å) corresponds with the absorption band of saturated aliphatic carboxylic ester, for the rotatory dispersion of pure ethyl tartrate can be expressed by the equation

$$[\alpha] = 25.005/(\lambda^2-0.03)-20.678/(\lambda^2-0.056),$$ (12)

which possesses the two characteristic wave lengths λ_1 and λ_2 at 1730 Å and 2370 Å respectively, and the former wave length (1730 Å) has practically the

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(10) *J. Chem. Soc.*, **103** (1913), 1067.
(11) *J. Chem. Physics*, **1** (1933), 662.
(12) Lowry and Cutter, *J. Chem. Soc.*, **121** (1922), 532.

same numerical value as the characteristic wave length of the compounds from acetone, but of opposite sign, and the latter negative term of this equation will presumably be attributed to the carboxyl group.(13)

Finally it will be remarked that the above-mentioned characteristic frequency of the bridged derivatives from aldehydes (2100 Å) can neither be identified with that of the positive nor that of the negative term of the rotatory dispersion of ethyl tartrate (and of tartaric acid(13)). To interpret this may be quite difficult. But it will be permitted to suppose that in the present case the absorption maximum may be displaced to a more or less extent through the bridging of the hydroxyl groups by means of chromophoric molecules, although the optically active absorption band of a substituent may generally be retained in the derivatives. The author wishes to further the studies of the rotatory dispersion of similar compounds touching this point.

The measurements of the rotatory dispersion have been enabled by the kindness of Dr. T. Higashi and Dr. H. Shiba of the Institute of Physical and Chemical Research, Tokyo, to whom the author wishes to express his grateful acknowledgements.

Summary.

(1) Rotatory dispersions in the region from 6708 Å to 4358 Å of diethyl and dimethyl isopropylidene-tartrates, diethyl and dimethyl ethylidene-tartrates and diethyl methylene-tartrate, bridged derivatives of alkyl-tartrates, in which both the hydroxyls are linked with the rest of the carbonyl compounds have been measured, all with no solvent, and shown to be expressed by one term of Drude's equation.

(2) It is pointed out that the absorption bands of the condensation products from ketone are located at about 1750 Å, whereas those of the compounds derived from aldehydes at about 2100 Å, and the relation between these values and the chemical constitution is discussed.

(3) Considering the fact that the dispersion ratio $\alpha_{4358} / \alpha_{5461}$ and the characteristic wave length λ_0 range from 1.674 to 1.748 and from 1735 Å to 2141 Å respectively, the rotatory dispersion of these compounds is concluded to be very probably simple.

Musashi Higher School, Nakaarai, Tokyo.

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(13) It will be noted also that Bruhat has located the two characteristic frequencies of the anomalous rotatory dispersion of aqueous solutions of tartaric acid at 1750 Å and 2330 Å, *Trans. Faraday Soc.*, **26** (1930), 400.