CCXXXV.—*The Rotatory Dispersion of Derivatives of Tartaric Acid. Part III. Diacetyltartaric Acid and its Esters.*

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Previous work upon diacetyltartaric acid (Austin and Park, J., 1925, **127**, 1926) revealed some anomalies, which could not be properly interpreted at the time. For instance, the lævorotations of a solution of the pure acid in dry acetone were found to be identical with those obtained when the anhydride was mixed in the same solvent with one molecular proportion of water and the mixture had been kept for 16 days until mutarotation was complete; but the presence of increasing amounts of water led to greatly increased lævorotations, a fact which pointed to some further change in structure. Moreover, the values calculated for the velocity coefficients of the hydration of the anhydride indicated that the reaction could be regarded neither as unimolecular nor as bimolecular. Nevertheless, the measurements of rotatory dispersion corresponded well with the values calculated from a simple one-term Drude formula, although the dispersion constant ($\lambda_0^2 = 0{\cdot}0833$) was unusually high. The result was unexpected and the conclusion was drawn that this acid afforded the first instance of simple dispersion in the tartaric acid series which was independent of ring formation.

This conclusion was regarded with some suspicion, however, in view of the fact that Patterson's value of the ratio $\alpha_{4358}/\alpha_{5461}$ for the *iso*butyl ester (J., 1916, **109**, 1170) is less than the theoretical minimum for a simple dispersion, *viz.*, 1·57 (compare Lowry and Austin, *Phil. Trans.*, 1922, *A*, **222**, 249), so that the rotatory dispersion of this ester is obviously complex. This ester was therefore prepared, and purified by repeated distillation under low pressures. Since the liquid could not be induced to crystallise, its rotatory dispersion was measured without a solvent in a 4-dcm. tube, whereby an undoubted maximum was detected about 56 Å.U. beyond the blue mercury line. The lower esters of the acid were then prepared by the action of an excess of acetic anhydride on the corresponding esters of tartaric acid, in the presence of a few drops of concentrated sulphuric acid. The methyl and *iso*propyl esters were easily crystallised, the ethyl ester somewhat less readily, the *n*-propyl ester only with difficulty, and the *n*-butyl and *iso*butyl esters refused to solidify. Readings were therefore taken of the pure liquid *n*-propyl and the two butyl esters and of solutions in the other cases. The *n*- and *iso*-butyl and -propyl esters gave maxima in the visible region, and a solution of the ethyl ester in acetone showed a reversal of sign in the red ; but the rotatory dispersion of a solution in acetone of the methyl ester was so nearly simple in the visible region that there was at first some uncertainty as to whether the dispersion was simple or complex. The readings in acetone could not be prolonged beyond 3720 Å.U., and the ester is not sufficiently soluble to be examined in ether; the deviations from a simple formula become marked, however, in the early photographic region. Finally, the complexity of the free acid was established by using dry ether in place of dry acetone as solvent, whereupon it was found that photographic readings could be prolonged considerably farther into the ultra-violet region. The fact that the values of $[\alpha]$ are considerably lower in ether than in acetone may be due to a partial interaction between the acid and acetone to form a definite compound, which would presumably give simple dispersion.

The equations used in Tables I—VIII show that, whereas the dispersion of the other esters is anomalous, that of the methyl ester and of the acid is *complex but normal*, since $\lambda_1^2 < \lambda_2^2$ when $k_1^2 < k_2^2$ (compare Lowry, J., 1915, **107**, 1195). The dispersion constants λ_1^2 and λ_2^2 are 0·0507 and 0·0691, respectively, for the acid and its methyl ester, and 0·0457 and 0·0507 for the other esters. Although, therefore, the rotatory dispersion of most of the esters is obviously anomalous, the dispersion constants of the two terms of Drude's equation differ by an amount corresponding to a separation of only about 114 Å.U. between the characteristic frequencies at 2138 and 2252 Å.U. of the higher esters, and of 377 Å.U. between the characteristic frequencies at 2252 and 2629 Å.U. of the acid and its methyl ester. Under these conditions, as Lowry and Dickson pointed out (J., 1913, **103**, 1075; compare also Hunter, J., 1924, **125**, 1203), it is exceptionally difficult to distinguish between a simple and a complex dispersion, and this distinction would have been quite impossible if the terms had been of similar sign. The rotatory dispersion of the free acid is, indeed, so nearly simple that the calculation of the curves of complex rotatory dispersion which are developed during the hydrolysis of the anhydride (Austin and Park, *loc. cit.*) still holds good without alteration.

It will be seen that the acetyl derivatives give *two* low-frequency terms, where the corresponding hydroxy-compounds are governed by one term of low frequency and one term of much higher frequency. The increased lævorotations observed on increasing the proportion of water in the mutarotation experiments of diacetyltartaric anhydride (Austin and Park, *loc. cit.*) may therefore be ascribed, as in the case of tartaric acid itself, to an alteration in the equilibrium between two components of opposite sign. The calculation of the true values of the velocity coefficients during mutarotation would then depend on a detailed knowledge, which is not yet available, of the effect of water upon this equilibrium.

An attempt to prolong the region of investigation in the case of diacetyltartaric anhydride by employing ether as solvent was unsuccessful owing to insufficient solubility. The dispersion constant in this case is, however, only 0·0507, and there is no reason to doubt the simple character of the compound on account of the oxygen bridge between the two acid groups.

EXPERIMENTAL.

Preparation of Diacetyltartaric Acid.—In the earlier work great difficulty was experienced in obtaining crystals of the acid which resulted from the slow mutarotation of the anhydride in acetone to which exactly the calculated quantity of water had been added. It is advantageous to concentrate the acetone solution, after mutarotation, by evaporation in a desiccator to a small bulk and to add the residue to boiling benzene, instead of eliminating the acetone. The solubility is thereby greatly increased and much larger crops of crystals can be obtained.

Preparation of the Esters.—These esters have been prepared previously by Anschütz and Pictet (*Ber.*, 1880, **13**, 1175) and by Freundler (*Ann. Chim. Phys.*, 1894, **3**, 454) by the action of acetyl chloride on the tartaric esters. McCrae and Patterson used acetic anhydride with ethyl tartrate and boiled the mixture (J., 1900, **77**, 1098). I have found that the addition of a trace of concentrated sulphuric acid to a mixture of the tartaric ester with a considerable excess of acetic anhydride is sufficient to catalyse the reaction without boiling, since the mixture rapidly becomes hot (compare Chattaway and Parkes, J., 1923, **123**, 663). After standing in the desiccator, the methyl ester soon crystallised, but the ethyl ester crystallised only after several weeks. The methyl ester was washed with ether and recrystallised from the same solvent; m. p. 103°. It is very soluble in acetone. The ethyl ester dissolved readily in both ether and acetone, but could be recrystallised from hot ligroin. As the crystals were slightly coloured, they were melted and the liquid was distilled at 17 mm. pressure; it then boiled at 179°, giving a colourless distillate, which solidified at 67°.

In the remaining cases, the excess of acetic anhydride was carefully distilled off after the mixture had stood for 12 hours, the sulphuric acid neutralised with calcium or barium carbonate, and the distillation continued under reduced pressure. It was found necessary to use flasks with wide side tubes (10—12 mm. diameter) and to heat them in an oil-bath in order to obtain colourless distillates. The first portions were rejected in each case. On cooling, the *iso*propyl ester soon solidified to a mass of crystals, m. p. 31·4°, but the *n*-propyl ester refused to solidify for several months. Eventually crystallisation took place in the polarimeter tube during the course of a set of readings. The substance was then refraction-

TABLE I.

Constants of Diacetyltartaric Acid and its Esters.

	M. p.	B. p.	$d_{4^\circ}^{20^\circ}$.	Liquid examined.	$[\alpha]_D$.	λ_μ Å.U.
Acid	—	—	—	10·83% in acetone	—24·57°	∞
				10·83% in ether	—17·01	∞
Methyl ester	118°	—	—	25% in acetone	—17·87	∞
Ethyl ester	103	179°/17 mm.	—	25% in ether	— 0·50	8531
n-Propyl ester ...	67	181 /10 mm.	1·1114	Supercooled	+11·02	4784
*iso*Propyl ester ...	21·5	167 /11 mm.	—	25% in ether	+ 8·63	5168
n-Butyl ester ...	31·4	205 /15 mm.	1·0823	Liquid ester	+22·20	4821
*iso*Butyl ester ...	—	193 /13 mm.	1·0816	Liquid ester	+67·18	4303

TABLE II.

Rotatory Dispersion of Diacetyltartaric Acid in Ether at 20°.

10·8334 g. $C_8H_{10}O_8$ in 100 c.c. of solution; $l = 4$ dcm.; $[\alpha] = 2{\cdot}3077\alpha$.

Simple formula : $[\alpha_1] = \dfrac{4{\cdot}235}{\lambda^2 - 0{\cdot}1009}$ (showing deviations in the ultra-violet).

Complex formula : $[\alpha_2] = \dfrac{14{\cdot}380}{\lambda^2 - 0{\cdot}0507} - \dfrac{18{\cdot}229}{\lambda^2 - 0{\cdot}0691}$.

λ.		$[\alpha]$ obs.	$[\alpha_1]$ calc.	$[\alpha_2]$ calc.	$[\alpha] - [\alpha_2]$.
Li	6708	— 11·82°	— 12·13°	— 11·85°	+0·03°
Li	6104	— 15·35	— 15·59	— 15·39	+0·04
Na	5893	— 17·01	— 17·19	— 17·04	+0·03
Cu	5782	— 18·00	— 18·14	— 18·03	+0·03
Hg	5780	— 18·05	— 18·16	— 18·05	±0·00
Cu	5700	— 18·83	— 18·91	— 18·82	—0·01
Ag	5469	— 21·35	— 21·37	— 21·37	+0·02
Hg	5461	— 21·46	— 21·46	— 21·46	±0·00
Cu	5219	— 24·76	— 24·70	— 24·81	+0·05
Ag	5209	— 24·92	— 24·48	— 24·96	+0·04
Cu	5154	— 25·87	— 25·71	— 25·85	—0·02
Cu	5105	— 26·70	— 26·52	— 26·68	—0·02
Cd	5086	— 27·05	— 26·84	— 27·01	—0·04
Li	4602	— 38·54	— 38·19	— 38·49	—0·05
Hg	4359	— 47·54	— 47·53	— 47·54	±0·00
Fe	*4132*	*— 59·4*	*— 60·6*	*— 59·6*	*+0·2*
Fe	*3860*	*— 81·9*	*— 88·0*	*— 81·9*	*±0·0*
Fe	*3767*	*— 92·3*	*—103·3*	*— 92·7*	*+0·4*
Fe	*3720*	*— 99·2*	*—113·0*	*— 99·1*	*—0·1*
Fe	*3650*	*—109·6*	*—130·6*	*—110·0*	*+0·4*
Fe	*3609*	*—117·7*	*—144·3*	*—117·3*	*—0·4*
Fe	*3581*	*—122·3*	*—154·9*	*—122·8*	*+0·5*
Fe	*3542*	*—131·5*	*—172·4*	*—131·1*	*—0·4*
Fe	*3498*	*—140·8*	*—197·3*	*—141·6*	*+0·8*

ated and crystallised by seeding. It melted at 21·5°,* but observations could be made with the supercooled liquid. For the purpose of comparison with older results, the observed melting points, boiling points, densities, and specific rotations for the sodium line are summarised in Table I, which also shows the wave-lengths λ_μ of maximum rotations.

The remaining tables show the observed and the calculated values of the specific rotations over a wide range of wave-lengths. The concentration of the solution of diacetyltartaric acid in ether (Table II) is the same as that in acetone, given in Part II. 10·8334 G. of the acid are equivalent to 10·0 g. of the anhydride.

TABLE III.

Rotatory Dispersion of Methyl Diacetyltartrate in Acetone at 20°.

25 g. of $C_{10}H_{14}O_8$ in 100 c.c. of solution; $l = 4$ dcm.; $\alpha = [\alpha]$.

$$\text{Complex formula : } [\alpha_1] = \frac{10{\cdot}200}{\lambda^2 - 0{\cdot}0507} - \frac{14{\cdot}551}{\lambda^2 - 0{\cdot}0691}.$$

	λ.	$[\alpha]$ obs.	$[\alpha_1]$ calc.	$[\alpha]-[\alpha_1]$.		λ.	$[\alpha]$ obs.	$[\alpha_1]$ calc.	$[\alpha]-[\alpha_1]$.
Li	6708	−12·64°	−12·66°	+0·02°	Cu	5105	−27·34°	−27·39°	+0·05°
Cd	6438	−14·06	−14·09	+0·03	Cd	5086	−27·74	−27·71	−0·03
Li	6104	−16·28	−16·26	−0·02	Cd	4800	−33·39	−33·45	+0·06
Na	5893	−17·87	−17·92	+0·05	Cd	4678	−36·56	−36·52	−0·04
Cu	5782	−18·88	−18·90	+0·02	Li	4602	−38·80	−38·66	−0·14
Hg	5780	−18·93	−18·92	−0·01	Hg	4359	−47·14	−47·14	±0·00
Cu	5700	−19·68	−19·69	+0·01	*Fe*	*4132*	*−58·0*	*−58·2*	*+0·2*
Ag	5469	−22·25	−22·20	−0·05	*Fe*	*4046*	*−63·5*	*−63·6*	*+0·1*
Hg	5461	−22·30	−22·30	±0·00	*Fe*	*3978*	*−68·5*	*−68·4*	*−0·1*
Cu	5219	−25·60	−25·57	−0·03	*Fe*	*3879*	*−76·5*	*−76·6*	*+0·1*
Ag	5209	−25·69	−25·72	+0·03	*Fe*	*3860*	*−78·5*	*−78·4*	*−0·1*
Cu	5154	−26·55	−26·58	+0·03	*Fe*	*3720*	*−93·5*	*−93·7*	*+0·2*

TABLE IV.

Rotatory Dispersion of Ethyl Diacetyltartrate in Ether at 20°.

25 g. of $C_{12}H_{18}O_8$ in 100 c.c. of solution; $l = 4$ dcm.

$$\text{Complex formula : } \alpha = [\alpha] = \frac{86{\cdot}666}{\lambda^2 - 0{\cdot}0457} - \frac{85{\cdot}400}{\lambda^2 - 0{\cdot}0507}.$$

	λ.	$[\alpha]$ obs.	$[\alpha_1]$ calc.	$[\alpha]-[\alpha_1]$.		λ.	$[\alpha]$ obs.	$[\alpha_1]$ calc.	$[\alpha]-[\alpha_1]$.
Li	6708	+0·49°	+0·49°	±0·00°	Cu	5105	− 3·56°	− 3·58°	+0·02°
Cd	6438	+0·24	+0·25	−0·01	Cd	5806	− 3·71	− 3·70	−0·01
Li	6104	−0·19	−0·19	±0·00	Cd	4800	− 5·99	− 6·01	+0·02
Na	5893	−0·58	−0·58	±0·00	Cd	4678	− 7·36	− 7·36	±0·00
Cu	5782	−0·83	−0·83	±0·00	Li	4602	− 8·35	− 8·34	−0·01
Hg	5780	−0·84	−0·84	±0·00	Hg	4359	−12·47	−12·47	±0·00
Cu	5700	−1·05	−1·04	−0·01	*Fe*	*4132*	*−18·30*	*−18·30*	*+0·00*
Ag	5469	−1·78	−1·79	+0·01	*Fe*	*4046*	*−21·30*	*−21·29*	*−0·01*
Hg	5461	−1·82	−1·82	±0·00	*Fe*	*3978*	*−24·00*	*−24·03*	*+0·03*
Cu	5219	−2·90	−2·91	+0·01	*Fe*	*3879*	*−28·80*	*−28·77*	*−0·03*
Ag	5209	−2·99	−2·97	−0·02	*Fe*	*3799*	*−33·40*	*−33·41*	*+0·01*
Cu	5154	−3·29	−3·28	−0·01	*Fe*	*3720*	*−38·90*	*−38·89*	*−0·01*

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* Freundler gives 31° as the m. p., but this could not be confirmed.

TABLE V.

Rotatory Dispersion of n-*Propyl Diacetyltartrate at* 20°.

$d^{20°} = 1·1114$; $[\alpha] = 0·4499\alpha$; $l = 4$ dcm.

$$\text{Complex formula : } [\alpha_1] = \frac{87·828}{\lambda^2 - 0·0457} - \frac{83·099}{\lambda^2 - 0·0507}.$$

	λ.	$[\alpha]$ obs.	$[\alpha_1]$ calc.	$[\alpha]-[\alpha_1]$.		λ.	$[\alpha]$ obs.	$[\alpha_1]$ calc.	$[\alpha]-[\alpha_1]$.
Li	6708	+ 9·13°	+ 9·12°	+0·01°	Cu	5154	+12·70°	+12·71°	−0·01°
Cd	6438	+ 9·72	+ 9·73	−0·01	Cu	5105	+12·80	+12·79	+0·01
Li	6104	+10·51	+10·52	−0·01	Cd	5086	+12·81	+12·82	−0·01
Na	5893	+11·02	+11·03	−0·01	Cd	4800	+13·09	+13·08	+0·01
Cu	5782	+11·31	+11·31	±0·00	Cd	4678	+13·05	+13·04	+0·01
Hg	5780	+11·31	+11·31	±0·00	Li	4602	+12·93	+12·94	−0·01
Cu	5700	+11·50	+11·51	−0·01	Hg	4359	+12·10	+12·10	±0·00
Ag	5469	+12·08	+12·06	+0·02	*Fe*	*4062*	*+ 9·18*	*+ 9·17*	*+0·01*
Hg	5461	+12·08	+12·08	±0·00	*Fe*	*4045*	*+ 8·91*	*+ 8·89*	*+0·02*
Cu	5219	+12·59	+12·59	±0·00	*Fe*	*4005*	*+ 8·19*	*+ 8·21*	*−0·02*
Ag	5209	+12·62	+12·61	+0·01	*Fe*	*3957*	*+ 7·24*	*+ 7·26*	*−0·02*

TABLE VI.

Rotatory Dispersion of iso*Propyl Diacetyltartrate in Ether at* 20°.

25 g. of $C_{14}H_{22}O_8$ in 100 c.c. of solution; $l = 4$ dcm.

$$\text{Complex formula : } \alpha = [\alpha_1] = \frac{91·392}{\lambda^2 - 0·0457} - \frac{87·310}{\lambda^2 - 0·0507}.$$

	λ.	$[\alpha]$ obs.	$[\alpha_1]$ calc.	$[\alpha]-[\alpha_1]$.		λ.	$[\alpha]$ obs.	$[\alpha_1]$ calc.	$[\alpha]-[\alpha_1]$.
Li	6708	+7·40°	+7·39°	+0·01°	Cu	5154	+9·30°	+9·32°	−0·02°
Cd	6438	+7·80	+7·81	−0·01	Cu	5105	+9·30	+9·32	−0·02
Li	6104	+8·34	+8·34	±0·00	Cd	5086	+9·32	+9·31	+0·01
Na	5893	+8·63	+8·65	−0·02	Cd	4800	+8·96	+8·95	+0·01
Cu	5782	+8·83	+8·81	+0·02	Cd	4678	+8·60	+8·58	+0·02
Hg	5780	+8·81	+8·81	±0·00	Li	4602	+8·25	+8·26	−0·01
Cu	5700	+8·95	+8·92	+0·03	Hg	4359	+6·57	+6·57	±0·00
Ag	5469	+9·15	+9·17	−0·02	*Fe*	*4062*	*+2·20*	*+2·20*	*±0·00*
Hg	5461	+9·18	+9·18	±0·00	*Fe*	*4005*	*+0·90*	*+0·89*	*+0·01*
Cu	5219	+9·30	+9·32	−0·02	*Fe*	*3967*	*−0·10*	*−0·09*	*−0·01*
Ag	5209	+9·31	+9·32	−0·01					

TABLE VII.

Rotatory Dispersion of n-*Butyl Diacetyltartrate at* 20°.

$d^{20°}_{4°} = 1·0823$; $l = 2$ dcm.; $[\alpha] = 0·462\alpha$.

$$\text{Complex formula : } [\alpha_1] = \frac{83·803}{\lambda^2 - 0·0457} - \frac{79·374}{\lambda^2 - 0·0507}.$$

	λ.	$[\alpha]$ obs.	$[\alpha_1]$ calc.	$[\alpha]-[\alpha_1]$.		λ.	$[\alpha]$ obs.	$[\alpha_1]$ calc.	$[\alpha]-[\alpha_1]$.
Li	6708	+ 8·50°	+ 8·49°	+0·01°	Cu	5154	+11·75°	+11·74°	+0·01°
Cd	6438	+ 9·05	+ 9·05	±0·00	Cu	5105	+11·80	+11·81	−0·01
Li	6104	+ 9·78	+ 9·77	+0·01	Cd	5806	+11·83	+11·84	−0·01
Na	5893	+10·26	+10·25	+0·01	Cd	4800	+12·02	+12·02	±0·00
Cu	5782	+10·49	+10·50	−0·01	Cd	4678	+11·96	+11·95	+0·01
Hg	5780	+10·51	+10·50	+0·01	Li	4602	+11·85	+11·83	+0·02
Cu	5700	+10·68	+10·68	±0·00	Hg	4359	+10·94	+10·95	−0·01
Ag	5469	+11·18	+11·18	±0·00	*Fe*	*4085*	*+ 8·32*	*+ 8·36*	*−0·04*
Hg	5461	+11·19	+11·19	±0·00	*Fe*	*4046*	*+ 7·85*	*+ 7·77*	*+0·08*
Cu	5219	+11·63	+11·64	−0·01	*Fe*	*3997*	*+ 6·93*	*+ 6·93*	*±0·00*
Ag	5209	+11·63	+11·66	−0·03	*Fe*	*3971*	*+ 6·47*	*+ 6·43*	*+0·04*

TABLE VIII.

Rotatory Dispersion of iso*Butyl Diacetyltartrate at* 20°.

$d^{20^\circ}_{4^\circ} = 1{\cdot}0816$; $l = 4$ dcm.; $[\alpha] = 0{\cdot}2311\alpha$.

Complex formula : $[\alpha_1] = \dfrac{85{\cdot}584}{\lambda^2 - 0{\cdot}0457} - \dfrac{79{\cdot}557}{\lambda^2 - 0{\cdot}0507}$.

	λ.	$[\alpha]$ obs.	$[\alpha_1]$ calc.	$[\alpha]-[\alpha_1]$.		λ.	$[\alpha]$ obs.	$[\alpha_1]$ calc.	$[\alpha]-[\alpha_1]$
Li	6708	+12·46°	+12·44°	+0·02°	Cu	5105	+19·22°	+19·22°	±0·00°
Cd	6438	+13·37	+13·38	−0·01	Cd	5086	+19·32	+19·32	±0·00
Li	6104	+14·65	+14·66	−0·01	Cd	4800	+20·64	+20·64	±0·00
Na	5893	+15·53	+15·54	−0·01	Cd	4678	+21·17	+21·15	+0·02
Cu	5782	+16·03	+16·02	+0·01	Li	4602	+21·38	+21·42	−0·04
Hg	5780	+16·04	+16·03	+0·01	Hg	4359	+21·97	+21·97	±0·00
Cu	5700	+16·38	+16·39	−0·01	*Fe*	*4185*	*+21·87*	*+21·91*	*−0·04*
Ag	5469	+17·48	+17·47	+0·01	*Fe*	*4177*	*+21·84*	*+21·82*	*+0·02*
Hg	5461	+17·50	+17·50	±0·00	*Fe*	*4155*	*+21·77*	*+21·78*	*−0·01*
Cu	5219	+18·66	+18·67	−0·01	*Fe*	*4132*	*+21·73*	*+21·70*	*+0·03*
Ag	5209	+18·72	+18·72	±0·00	*Fe*	*4076*	*+21·45*	*+21·43*	*+0·02*
Cu	5154	+19·00	+18·99	+0·01					

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