CCXXXVI.—*The Rotatory Dispersion of Derivatives of Tartaric Acid. Part IV. Propyl and Butyl Tartrates.*

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SINCE the investigation of the esters of diacetyltartaric acid recorded in Part III (preceding paper) involved the preparation of *n*-propyl, *iso*propyl, *n*-butyl, and *iso*butyl tartrates, measurements of the rotatory dispersions of these esters were made in order that they might be compared with values previously obtained by Lowry and Abram for methyl tartrate (J., 1915, **107**, 1187) and by Lowry and Cutter for the ethyl ester (J., 1922, **121**, 542). It has been found that in every case the rotatory dispersion is both complex and anomalous, but although the same dispersion constants are used throughout the series, no simple relation appears to exist between the rotation constants. These are recorded in Table I, which also shows the melting points, boiling points, and densities, where ascertained, and the wave-lengths λ_μ calculated for maximum rotations. For comparison, the published values for the methyl and ethyl esters are included. The value of λ_μ for methyl tartrate is exceptionally high.

TABLE I.

Constants of the Esters at 20°.

Ester.	M.p.	B. p.	$d_4^{20°}$.	k_1.	k_2.	λ_μ, Å.U.	Liquid examined.
Methyl	48° & 61·5°*	—	—	22·576	22·079	15436	Supercooled.
Ethyl	18·7	—	1·2028	25·005	20·678	5629	,,
n-Propyl	—	177°/17 mm.	1·1186	22·139	17·124	4957	Pure ester.
*iso*Propyl	—	152°/12 mm.	1·1136	27·680	20·140	4548	,,
n-Butyl	21·8	182°/11 mm.	1·0909	21·436	16·687	5009	Supercooled.
*iso*Butyl	66	171°/11 mm.	—	24·985	18·741	5374	25% in ether.

* Dimorphous.

Preparation of the Esters.—The preparation of the propyl esters was more troublesome than that of the butyl esters, since in the latter case the boiling points of the alcohols are sufficiently high to enable one to eliminate the water produced by slowly distilling off a constant-boiling mixture of the alcohol and water through a long fractionating column. When the propyl alcohols were used, it was necessary to use a dehydrating agent. Hydrogen chloride was first used, but in order to avoid possible contamination of the final product with chlorinated compounds (compare Lowry and Cutter, *loc. cit.*), calcium chloride was substituted later. The solubility of calcium chloride in the alcohol renders its subsequent removal troublesome, but fairly satisfactory yields could be obtained. The powdered tartaric acid dissolved much more rapidly in *n*-butyl than in *iso*butyl alcohol. The esters were carefully distilled and fractionated under low pressure. An oil-bath was used for heating the distillation flasks. This was particularly necessary in the case of *iso*propyl tartrate, which decomposes somewhat readily.

The results are in the following tables. The rotations are all positive, except the one case recorded.

TABLE II.

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

$d_4^{20°} = 1·1186$; $l = 2$ dcm.; $[\alpha] = 0·447a$.

Complex formula: $[\alpha_1] = \frac{22·139}{\lambda^2 - 0·030} - \frac{17·124}{\lambda^2 - 0·056}$.

λ.	[α] obs.	[α₁] calc.	[α] − [α₁].	λ.	[α] obs.	[α₁] calc.	[α] − [α₁].
Li 6708	9·26°	9·25°	+0·01°	Cd 5086	12·32°	12·33°	−0·01°
Cd 6438	9·80	9·81	−0·01	Cd 4800	12·28	12·29	−0·01
Li 6104	10·55	10·54	+0·01	Cd 4678	12·07	12·08	−0·01
Na 5893	10·99	10·99	±0·00	Li 4602	11·86	11·87	−0·01
Cu 5782	11·23	11·22	+0·01	Hg 4359	10·58	10·58	±0·00
Hg 5780	11·27	11·27	±0·00	*Fe 4132*	*8·05*	*8·06*	*−0·01*
Cu 5700	11·38	11·39	−0·01	*Fe 4046*	*6·57*	*6·59*	*−0·02*
Ag 5469	11·83	11·83	±0·00	*Fe 3978*	*5·14*	*5·15*	*−0·01*
Hg 5461	11·85	11·85	±0·00	*Fe 3956*	*4·65*	*4·63*	*+0·02*
Cu 5219	12·20	12·20	±0·00	*Fe 3930*	*3·93*	*3·96*	*−0·03*
Ag 5209	12·21	12·21	±0·00	*Fe 3879*	*2·46*	*2·51*	*−0·05*
Cu 5154	12·29	12·27	+0·02	*Fe 3856*	*1·79*	*1·78*	*+0·01*
Cu 5105	12·31	12·31	±0·00	*Fe 3799*	*−0·22*	*−0·22*	*±0·00*

TABLE III.

Rotatory Dispersion of iso*Propyl Tartrate at* 20°.

$d_4^{20°} = 1{\cdot}1136$; $l = 2$ dcm.; $[\alpha] = 0{\cdot}449a$.

Complex formula: $[\alpha_1] = \frac{27{\cdot}680}{\lambda^2 - 0{\cdot}030} - \frac{20{\cdot}140}{\lambda^2 - 0{\cdot}056}$.

λ.	[α] obs.	[α₁] calc.	[α]−[α₁].	λ.	[α] obs.	[α₁] calc.	[α]−[α₁].
Li 6708	14·79°	14·79°	±0·00°	Cd 5086	21·69°	21·68°	+0·01°
Cd 6438	15·79	15·81	−0·02	Cd 4800	22·64	22·64	±0·00
Li 6104	17·17	17·18	−0·01	Cd 4678	22·90	22·90	±0·00
Na 5893	18·09	18·10	−0·01	Li 4602	23·02	22·99	+0·03
Cu 5782	18·59	18·59	±0·00	Hg 4359	22·70	22·70	±0·00
Hg 5780	18·59	18·60	−0·01	*Fe 4132*	*21·10*	*21·15*	*−0·05*
Cu 5700	18·97	18·96	+0·01	*Fe 4045*	*19·98*	*20·01*	*−0·03*
Ag 5469	19·99	20·01	−0·02	*Fe 3971*	*18·72*	*18·72*	±0·00
Hg 5461	20·05	20·05	±0·00	*Fe 3872*	*16·39*	*16·38*	*+0·01*
Cu 5219	21·13	21·12	+0·01	*Fe 3807*	*14·37*	*14·37*	±0·00
Ag 5209	21·17	21·17	±0·00	*Fe 3790*	*13·78*	*13·77*	+0·01
Cu 5154	21·40	21·40	±0·00	*Fe 3749*	*12·21*	*12·18*	*+0·03*
Cu 5105	21·60	21·60	±0·00				

TABLE IV.

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

Supercooled to 20°; setting point 21·8°; $d_4^{20°} = 1{\cdot}0909$; $l = 4$ dcm.; $[\alpha] = 0{\cdot}2292a$.

Complex formula: $[\alpha_1] = \frac{21{\cdot}436}{\lambda^2 - 0{\cdot}030} - \frac{16{\cdot}687}{\lambda^2 - 0{\cdot}056}$.

λ.	[α] obs.	[α₁] calc.	[α]−[α₁].	λ.	[α] obs.	[α₁] calc.	[α]−[α₁].
Li 6708	8·66°	8·68°	−0·02°	Cu 5105	11·39°	11·40°	−0·01°
Cd 6438	9·22	9·20	+0·02	Cd 5086	11·44	11·41	+0·03
Li 6104	9·85	9·86	−0·01	Cd 4800	11·35	11·28	+0·07
Na 5893	10·26	10·27	−0·01	Cd 4678	11·00	11·04	−0·04
Cu 5782	10·46	10·48	−0·02	Li 4602	10·80	10·80	±0·00
Hg 5780	10·48	10·48	±0·00	Hg 4359	9·44	9·44	±0·00
Cu 5700	10·63	10·63	±0·00	*Fe 4132*	*6·87*	*6·87*	±0·00
Ag 5469	11·04	11·02	+0·02	*Fe 4064*	*5·72*	*5·73*	*−0·01*
Hg 5461	11·03	11·03	±0·00	*Fe 4046*	*5·39*	*5·39*	±0·00
Cu 5219	11·33	11·32	+0·01	*Fe 3978*	*3·91*	*3·94*	*−0 03*
Ag 5209	11·32	11·33	−0·01	*Fe 3879*	*1·26*	*1·30*	*−0·04*
Cu 5154	11·35	11·37	−0·02	*Fe 3860*	*0·69*	*0·71*	*−0·02*

TABLE V.

Rotatory Dispersion of iso*Butyl Tartrate in Ether at* 20°.

25 g. $C_{12}H_{22}O_6$ in 100 c.c. of solution; $l = 4$ dcm.; $[\alpha] = a$.

Complex formula: $[\alpha_1] = \frac{24{\cdot}985}{\lambda^2 - 0{\cdot}030} - \frac{18{\cdot}741}{\lambda^2 - 0{\cdot}056}$.

λ.	α=[α] obs.	[α₁] calc.	[α]−[α₁].	λ.	α=[α] obs.	[α₁] calc.	[α]−[α₁].
Li 6708	11·92°	11·92°	±0·00°	Cu 5105	16·76°	16·75°	+0·01°
Cd 6438	12·69	12·70	−0·01	Cd 5086	16·80	16·79	+0·01
Li 6104	13·72	13·73	−0·01	Cd 4800	17·22	17·21	+0·01
Na 5893	14·43	14·41	+0·02	Cd 4678	17·22	17·22	±0·00
Cu 5782	14·77	14·76	+0·01	Li 4602	17·16	17·14	+0·02
Hg 5780	14·77	14·77	±0·00	Hg 4359	16·30	16·30	±0·00
Cu 5700	15·00	15·03	−0·03	*Fe 4177*	*14·70*	*14·75*	*−0·05*
Ag 5469	15·76	15·76	±0·00	*Fe 4045*	*12·80*	*12·84*	*−0·04*
Hg 5461	15·78	15·78	±0·00	*Fe 3978*	*11·50*	*11·53*	*−0·03*
Cu 5219	16·49	16·47	+0·02	*Fe 3878*	*9·00*	*8·99*	*+0·01*
Ag 5209	16·50	16·50	±0·00	*Fe 3860*	*8·50*	*8·44*	*+0·06*
Cu 5154	16·74	16·74	±0·00				

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