

**223. The Rotatory Dispersion of Organic Compounds. Part XXII. Borotartrates and Boromalates.**

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THE isolation of potassium borotartrate by Lowry (J., 1929, 2853) has not only revived interest in the study of borotartrates but has also confirmed the early view of Biot that the remarkable variations in the character of the rotatory dispersion observed on adding boric acid to aqueous solutions of tartaric acid are due to chemical changes. A further study of such complexes appeared desirable in order to establish their structure, and at the same time to throw new light on the origin of the optical anomalies of tartaric and malic acids: some new boro-complexes have therefore been isolated and examined.

TABLE I.

*Rotatory Dispersion of Ammonium Borotartrate in Water at 20°.*

$$p = 11.74, d_{40}^{20} = 1.0530, a/a_{5461} = 0.2666/(\lambda^2 - 0.0316).$$

$\lambda$ .	$\alpha$ ( $l=2$ ).	$a/a_{5461}$ .				[ $\alpha$ ].	$\lambda$ .	$\alpha$ ( $l=2$ ).	$a/a_{5461}$ .				[ $\alpha$ ].
		Obs.	Calc.	1000 (O-C).					Obs.	Calc.	1000 (O-C).		
Li 6708	+ 9.66°	0.638	0.637	+1	+39.07°	Li 4602	22.36°	1.476	1.479	-3	90.42°		
Li 6104	11.85	0.782	0.782	±	47.93	Hg 4358	25.50	1.683	1.683	±	103.10		
Na 5893	12.76	0.842	0.843	-1	51.62		$\alpha$ ( $l=1$ ).						
Cu 5782	13.30	0.878	0.881	-3	53.79	Hg 5461	7.21	—	—	—	61.19		
Hg 5780	13.35	0.881	0.881	±	53.99	Fe 4272	12.75	1.768	1.767	+1	108.2		
Cu 5700	13.77	0.909	0.909	±	55.69	Fe 4202	13.25	1.838	1.839	-1	112.4		
Hg 5461	15.15	1.000	1.000	±	61.37	Fe 4144	13.75	1.907	1.903	+4	116.6		
Cu 5218	16.73	1.105	1.107	-2	67.66	Fe 3970	15.25	2.115	2.116	-1	129.4		
Cu 5153	17.30	1.142	1.140	+2	69.95	Fe 3826	16.75	2.323	2.323	±	142.1		
Cu 5105	17.63	1.163	1.164	-1	71.28	Fe 3700	18.26	2.533	2.533	±	151.4		
Zn 4811	20.28	1.339	1.334	+5	82.01	Fe 3590	19.76	2.740	2.740	±	167.7		

In Table I\* are set out the values of the rotatory power of *ammonium borotartrate* measured for 20 different wave-lengths, ranging from  $\lambda = 6708$  to 3590. The results clearly show that a condition of simple dispersion is realised when tartaric acid is wholly converted into borotartaric acid in the more stable form of a salt, and in the light of this result there can be little doubt of the correctness of Lowry's view that the complex character of the dispersion of solutions of tartaric and boric acids examined by Lowry and Austin (*Phil. Trans.*, 1922, 222, 249) and later by Descamps (*Compt. rend.*, 1927, 184, 453) and Burgess and Hunter (J., 1929, 2838) is due to uncombined tartaric acid.

On the other hand, discrepancies arose either when free boric acid was added to the borotartrate or when *potassium ethyl borotartrate* was examined. Thus the addition of free boric acid to an aqueous solution of the borotartrate increased both the specific rotation and the dispersion ratio, and a close examination revealed a mutarotation; in view of this, lack of agreement with a one-term Drude equation is not surprising. The underlying cause of this mutarotation remains unknown, but it is reasonable to suppose that further combination takes place with the formation of a compound having a higher rotatory power than the original borotartrate.

Solutions of potassium ethyl borotartrate in methyl alcohol exhibited mutarotation even in the absence of free boric acid. Drastic purification of the alcohol failed to arrest

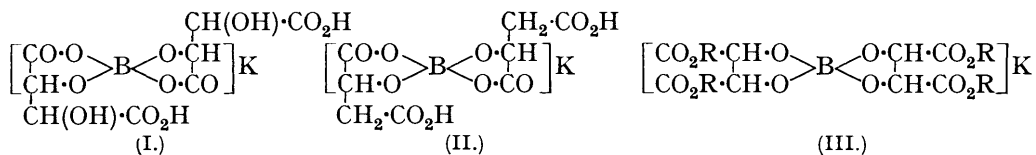
\* The constants of this equation are the same as for potassium borotartrate (Lowry, *loc. cit.*).

this change, while the substitution of a silica polarimeter tube for the ordinary glass tube was without effect. Since the dispersion is complicated by this mutarotation, an exact agreement between the observed and calculated dispersion ratios is hardly to be expected. Nevertheless, the values given in Tables II and III show that, with only small and quite irregular deviations, the dispersion in the visible region can be represented satisfactorily by a one-term equation. In the circumstances, it was useless to extend the measurements to the photographic region. The study of other similar borotartrates was impracticable owing to their low solubilities in the ordinary organic solvents and their instability in aqueous solution.

*Potassium boromalate* was readily obtained as a white crystalline solid from a warm solution of malic and boric acids in aqueous potassium hydroxide, and in order to characterise it a crystallographic study was made. The dispersion ratio for this compound is so low as to suggest that the dispersion is not simple in regions beyond the visible, but the complexity which is thus probably present may well be due to dissociation.

Although borotartrates of different composition have been known for a century (cf. Lowry, *loc. cit.*), there is no evidence that any of them, with the exception of Lowry's potassium borotartrate, are definite chemical compounds. Complex formation has often been assumed on insufficient evidence, whilst many of the so-called compounds isolated have been obtained by evaporating to dryness a solution containing the two acids in the proper proportions. Nevertheless, there appears to have been fairly general agreement that the change in the character of the dispersion of tartaric acid produced by the addition of boric acid is to be attributed to some kind of combination, and Lowry and Austin tentatively suggested in 1922 that the alcoholic hydroxyl groups might be linked together by the  $>B-OH$  group, adding that "it is possible that the simple character of its rotatory dispersion may be due to the bridge between the asymmetric carbon atoms." It is therefore of interest that, whereas the rotatory dispersion of tartaric acid and its esters is markedly altered by addition of boric acid, the dispersion of methylenetartronic acid, in which the hydroxyl groups are no longer free, is unchanged. Comparing the values in Table V with those observed by Austin and Carpenter (J., 1924, 125, 1939) for methylenetartronic acid alone, it is seen that, not only is the dispersion ratio the same, but the rotatory power is almost identical.

The work of Böeseken and his collaborators (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, 27, 174; *Rec. trav. chim.*, 1930, 49, 711) on  $\alpha$ -hydroxy-acids has shown, however, that a carboxyl group in close proximity to a hydroxyl group can take part in complex formation, and in accordance with this view potassium borotartrate has been represented by the formula (I). The isolation of a borotartrate from malic acid with its single hydroxyl



group lends support to this formulation, whilst the isolation from ethyl tartrate of a complex of opposite rotation and very different dispersive power from that obtained from tartaric acid indicates that the structure of these two complexes is dissimilar. Indeed, in view of the evidence (Part XXI; this vol., p. 788) that the formation from a *d*-tartrate of a five-membered ring involving the two alcoholic hydroxyl groups is always accompanied by the production of levorotation, it appears reasonable to formulate potassium boromalate and the potassium alkyl borotartrates as (II) and (III) respectively. This formulation of the complex, potassium borotartrate, receives support from Böeseken's study of the composition and acidity of glycolboric acids. By three methods not involving their separation from solution, these acid complexes are shown to have the composition  $\text{HBD}_2$ , where D represents a diol residue (Böeseken, *loc. cit.*), and Böeseken concludes that the structure and mode of ionisation of these complexes are best represented by the general formula (IV). The structures suggested for these borotartrates, however, are not

in complete agreement with the compositions indicated by analysis. When reporting the isolation of potassium borotartrate, Lowry pointed out that the results of analysis



agreed only approximately with the structure proposed, while Bancroft and Davis (*J. Physical Chem.*, 1930, **34**, 2479) found, from titrations with mannitol, that the equivalent weight of this complex was 91 as against 88.5 reported by Lowry, and hence concluded that the complex is formed from its components by the loss of two molecules of water

TABLE II.

*Rotatory Dispersion of Potassium Ethyl Borotartrate in Methyl Alcohol at 20°.* (Glass polarimeter tube.)

$$p = 32.38, d_{44}^{20} = 0.9220, a/a_{5461} = 0.2205/(\lambda^2 - 0.07782).$$

$\lambda$ .	$\alpha$ ( $l=2$ ).	$a/a_{5461}$ .			[ $\alpha$ ].	$\lambda$ .	$\alpha$ ( $l=2$ ).	$a/a_{5461}$ .			[ $\alpha$ ].
		Obs.	Calc.	1000 (O-C).				Obs.	Calc.	1000 (O-C).	
Li 6708	-8.49°	0.593	0.593	±	-14.23°	Hg 5461	14.31°	1.000	1.000	±	23.97°
Zn 6363	9.71	0.673	0.674	-1	16.26	Cu 5218	16.20	1.132	1.134	-2	27.13
Li 6104	10.68	0.746	0.749	-2	17.89	Cu 5153	16.75	1.171	1.174	-3	28.05
Na 5893	11.74	0.820	0.818	+2	19.67	Cu 5105	17.22	1.204	1.206	-2	28.84
Cu 5782	12.24	0.856	0.859	-3	20.50	Zn 4811	20.60	1.439	1.436	+3	34.51
Hg 5780	12.28	0.858	0.860	-2	20.57	Zn 4722	21.81	1.524	1.519	+5	36.53
Cu 5700	12.79	0.894	0.892	+2	21.43	Hg 4358	28.11	1.965	1.965	±	47.09

TABLE III.

*Rotatory Dispersion of Potassium Ethyl Borotartrate in Methyl Alcohol at 20°.* (Silica polarimeter tube.)

$$p = 33.13, d_{44}^{20} = 0.9238, a/a_{5461} = 0.2205/(\lambda^2 - 0.07782).$$

$\lambda$ .	$\alpha$ ( $l=2$ ).	$a/a_{5461}$ .			[ $\alpha$ ].	$\lambda$ .	$\alpha$ ( $l=2$ ).	$a/a_{5461}$ .			[ $\alpha$ ].
		Obs.	Calc.	1000 (O-C).				Obs.	Calc.	1000 (O-C).	
Li 6708	-8.94°	0.593	0.593	±	14.61°	Cu 5218	17.11°	1.135	1.135	±	27.95°
Cd 6439	9.88	0.655	0.656	-1	16.13	Cu 5153	17.74	1.177	1.176	+1	28.98
Zn 6363	10.19	0.676	0.676	±	16.64	Zn 4811	21.69	1.439	1.438	+1	35.44
Li 6104	11.29	0.749	0.749	±	18.44	Zn 4722	22.93	1.521	1.521	±	37.47
Na 5893	12.34	0.818	0.819	-1	20.15	Cd 4678	23.64	1.568	1.566	+2	38.62
Hg 5780	12.98	0.861	0.862	-1	21.22	Li 4602	24.82	1.647	1.648	-1	40.56
Cu 5700	13.47	0.893	0.893	±	22.00	Hg 4358	29.71	1.970	1.970	±	48.54
Hg 5461	15.08	1.000	1.000	±	24.63						

TABLE IV.

*Rotatory Dispersion of Potassium Boromaleate in Water at 20°.*

$$p = 27.29, d_{44}^{20} = 1.1390, a/a_{5461} = 0.2897/(\lambda^2 - 0.008542).$$

$\lambda$ .	$\alpha$ ( $l=4$ ).	$a/a_{5461}$ .			[ $\alpha$ ].	$\lambda$ .	$\alpha$ ( $l=4$ ).	$a/a_{5461}$ .			[ $\alpha$ ].
		Obs.	Calc.	1000 (O-C).				Obs.	Calc.	1000 (O-C).	
Li 6708	-5.28°	0.655	0.656	-1	-4.246°	Cu 5218	8.85°	1.098	1.098	±	7.116°
Cd 6439	5.74	0.712	0.714	-2	4.616	Cu 5105	9.26	1.149	1.149	±	7.446
Zn 6363	5.90	0.732	0.731	+1	4.745	Cd 5086	9.33	1.158	1.158	±	7.503
Li 6104	6.42	0.796	0.796	±	5.163	Zn 4811	10.48	1.130	1.130	±	8.427
Na 5893	6.88	0.854	0.855	-1	5.533	Zn 4722	10.87	1.349	1.351	-2	8.744
Hg 5780	7.17	0.890	0.890	±	5.766	Li 4602	11.48	1.424	1.425	-1	9.232
Ag 5466	8.05	0.999	0.998	-1	6.474	Hg 4358	12.87	1.597	1.597	±	10.35
Hg 5461	8.06	1.000	1.000	±	6.481						

TABLE V.

*Rotatory Dispersion of Methylene-tartaric Acid in an Aqueous Boric Acid Solution at 20°.*Molecular proportions,  $C_5H_6O_6 : H_3BO_3 = 1 : 1$ . $p = 4.237$ ,  $d_{20}^{20} = 1.0195$ ,  $\alpha/\alpha_{5461} = 0.2547/(\lambda^2 - 0.04356)$ .

$\lambda$ .	$\alpha$ ( $l=2$ ).	$\alpha/\alpha_{5461}$ .			[ $\alpha$ ].	$\lambda$ .	$\alpha$ ( $l=2$ ).	$\alpha/\alpha_{5461}$ .			[ $\alpha$ ].
		Obs.	Calc.	1000 (O-C).				Obs.	Calc.	1000 (O-C).	
Zn 6363	-5.66°	0.707	0.706	+1	-65.56°	Cu 5218	8.89°	1.110	1.114	-4	103.0°
Li 6104	6.20	0.774	0.774	±	71.82	Cu 5153	9.19	1.147	1.147	±	106.5
Hg 5780	7.02	0.877	0.877	±	81.30	Zn 4811	10.87	1.357	1.356	+1	125.9
Cu 5700	7.23	0.903	0.903	±	83.73	Hg 4358	13.93	1.740	1.740	±	161.7
Hg 5461	8.01	1.000	1.000	±	92.76						

and not three, as an equivalent of 88.5 would indicate. Previous to the appearance of this correction, this discrepancy had been investigated in the course of the present work, and from the ultimate analyses and other quantitative estimations it was concluded that each complex contains a molecule of water. It is difficult to represent such complexes by any but co-ordination formulæ, and it would seem that (V) and (III, with  $1H_2O$ ) are at present the least open to criticism.

In view of the definite proof given of the simple character of the dispersion, this co-ordination formula for potassium borotartrate is of particular interest since it appears that the rotation about the single bond joining the two asymmetric carbon atoms which should be still possible is in some way inhibited. It is conceivable that this is due to the mutual influence of the negatively charged boron atom and the polar carboxyl group.

## EXPERIMENTAL.

*Ammonium Borotartrate.*—A mixture of tartaric acid (128 g.), ammonium tartrate (53 g.), and boric acid (37 g.) was dissolved by boiling in water (80 c.c.). On cooling, a white solid separated, which caked in a few hours. This was recrystallised four times from distilled water.

Solutions in water were strongly dextrorotatory, and the specific rotations of an aqueous solution ( $p = 11.74$ ) were practically identical with those of a potassium borotartrate solution ( $p = 33.54$ ) (cf. Lowry, *loc. cit.*). Addition of free boric acid to an aqueous solution increased both the specific rotation and the dispersion ratio. Thus a solution of approximately the same concentration as that in Table I but containing 1 mol. of free boric acid showed an increase of 14% in  $\alpha_{5461}$  and a rise from 1.683 to 1.706 in the dispersion ratio.

Analysis points to the presence of one molecule of water (Found: C, 27.0, 27.24; H, 4.21, 4.23; M, by electrometric titration, 340, 344, 345.  $C_8H_{12}O_{12}NB$  requires C, 29.56; H, 3.72%; M, 325.  $C_8H_{12}O_{12}NB, H_2O$  requires C, 28.0; H, 4.11%; M, 343).

*Potassium Ethyl Borotartrate.*—To a solution of potassium hydrogen carbonate (10 g.) and boric acid (6.2 g.) in 15 c.c. of water, ethyl tartrate (42 g.) was added slowly and with good stirring. Carbon dioxide was liberated, and after the addition of all the ester 47 g. of a white crystalline solid separated. The specimens used for dispersion measurements were recrystallised four times from 80% ethyl alcohol. The salt (Found: C, 40.27; H, 5.54; K, 8.18.  $C_{16}H_{24}O_{12}BK$  requires C, 41.92; H, 5.28; K, 8.53.  $C_{16}H_{24}O_{12}BK, H_2O$  requires C, 40.34; H, 5.46; K, 8.21%) is only sparingly soluble in water, the solutions being dextrorotatory.

Determinations of the rotatory dispersion of solutions in methyl alcohol were complicated by a mutarotation—a small increase in rotatory power occurring (see p. 951). In order to limit this change, all the measurements were carried out without a break while the values of  $\alpha_{5461}$  and  $\alpha_{4358}$  were determined at intervals during the course of the measurements. The values of  $\alpha$  recorded for the other wave-lengths, however, are corrected as far as possible to the values before mutarotation by multiplying by the ratio of  $\alpha_{5461}$  at the beginning of the measurements and at the time when the actual reading of the second wave-length was taken. Since the specimens had been recrystallised from 80% alcohol, a solvent in which it was later found that mutarotation occurred, attempts were made to find a more suitable solvent, but these were unsuccessful. The effect on the specific rotations of further crystallisations is indicated by the fact that  $\alpha_{5461}$  after four and six crystallisations from 80% alcohol were  $-23.9^\circ$  and

— 24·6° respectively. Thus, although the specific rotations observed are probably a little high, the measurements recorded in Tables II and III show that in the visible region the dispersion can be satisfactorily represented by a one-term Drude equation.

*Potassium Methyl Borotartrate.*—This was prepared by a similar method to the ethyl compound. Measurements of the rotatory power could not be made owing to its low solubility in the organic solvents tried, and its instability in aqueous solution (Found: C, 34·23; H, 4·02. Calc. for  $KBC_{12}H_{16}O_{12}$ : C, 35·83, H, 4·01. Calc. for  $KBC_{12}H_{16}O_{12} \cdot H_2O$ : C, 34·30; H, 4·28%).

*Potassium Boromalate.*—A mixture of malic acid (13·4 g.) and boric acid (3·1 g.) was added to a solution of potassium hydroxide (2·8 g.) in 8 c.c. of water. On cooling, a thick syrup was formed which solidified (8 g.) on standing. On addition of a further quantity of the two acids and the alkali to the mother-liquor, a better yield was obtained, 27 g. of malic acid giving 21 g. of the *boromalate* (Found: C, 29·00, 29·06; H, 3·09, 3·02; K, 11·82.  $KBC_8H_8O_{10}$  requires C, 30·58; H, 2·57; K, 12·44.  $KBC_8H_8O_{10} \cdot H_2O$  requires C, 28·92; H, 3·04; K, 11·78%). Attempts to prepare a solid piperidine borotartrate failed.

*Crystallography.* I am indebted to Dr. W. A. Wooster for the following data.

The substance crystallises in the monoclinic system, axial angle  $\beta = 82^\circ 20'$  and axial ratios  $a : b : c = 0.828 \pm 0.003 : 1 : ?$ . The habit was a simple combination of the forms (001) and (110), being tabular with (001) large.

The angles measured were:  $110 : \bar{1}\bar{1}0 = 78^\circ 46' \pm 15'$ ,  $110 : 001 = 84^\circ 5' \pm 15'$ .

As the reflexions from the faces were poor and some doubt remained as to whether the substance was actually monoclinic a Laue photograph was taken with the X-ray beam perpendicular to (001). The well-marked plane of symmetry enables the crystal to be placed with certainty in the monoclinic system. They had  $d$  1·69, and the following observations were made on the optical properties:

The extinctions on the face (001) are parallel to 010 and 100, and on the face (110) parallel to 001.

The optic axial plane is parallel to (010), the acute bisectrix being inclined at an angle of  $8^\circ 38' \pm 7'$  to the normal to (001), and the optic axial angle  $2\bar{V} = 87^\circ 32' \pm 9'$ . No dispersions could be observed. The mean refractive index was  $1.51 \pm 0.05$ . The principal refractive indices ( $\pm 0.05$ ) are  $\alpha = 1.482$ ,  $\beta = 1.51$ ,  $\gamma = 1.536$ . The double refractions ( $\pm 0.0008$ ) are  $\beta - \gamma = 0.0280$ ,  $\gamma - \beta = 0.0256$ , and the sign of the double refraction is negative.

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