The Nature of the Complex Formation between Boric Acid and Organic Polyoxy Compounds.

By Yojiro TSUZUKI.

(Received December 21st, 1940.)

It is a well-known fact that complex compounds are formed between boric acid and polyoxy compounds. The compositions have been estimated by means of various methods, and even definite compounds have been isolated.(1) It has not been elucidated, however, under what conditions the complexes are formed. The author has previously shown that free boric acid forms complexes only in little quantity with diols such as ethyl tartrate, while alkali borates combine with it to a large extent.(2) Thus the author has stated that only borate ion combines with diols, but free boric acid does not, since it gives in aqueous solution only a small quantity of BO_2', and it has been suggested that complexes (similar to boric acid complex) can be formed in general between polyoxy compounds, only when one reactant is in ionic state.

The present work deals with the polarimetric studies on the complex formation between boric acid and polyoxy compounds of various types (mannitol, glucose, tartaric acid, tartrates, gluconate) carried out in order to elucidate the nature of the complex formation.

The experimental results will be described and discussed with each polyoxy organic compound.

Mannitol. It is known that mannitol shows a very feeble laevorotation, which is scarcely changed by the addition of free boric acid,(3) but in the presence of alkali borate, the solution shows strong dextrorotation.(4) It was shown several years ago by Böeseken and Vermaas(5) that, in the solutions of mannitol in water with $NaBO_2$, there exist complex ions of the formula BD' and BD_2', where D represents a molecule of a polyhydric alcohol. The author has now observed the variation in the optical rotation of mannitol with the change of BO_2' concentration in the mannitol-boric acid system. The results are shown in Fig. 1 and described in Table 1.

---

(1) Lowry, *J. Chem. Soc.*, **1929**, 2853; Bancroft and Davis, *J. Phys. Chem.*, **34** (1930), 2479; Lowry, "Optical Rotatory Power," 290, London (1935).

(2) Y. Tsuzuki, this Bulletin, **13** (1938), 337 (by distribution method); Y. Tsuzuki and Y. Kimura, this Bulletin, **15** (1940), 27 (by polarimetric method).

(3) J. M. Braham, *J. Am. Chem. Soc.*, **41** (1919), 1707; F. B. Marti, *Bull. Soc. chim. Belg.*, **39** (1930), 590.

(4) Vignon, *Compt. rend.*, **77** (1873), 1191; *Ann. chim. phys.*, [5], **2** (1874), 440; E. Fischer, *Ber.*, **23** (1890), 385.

(5) J. Böeseken and N. Vermaas, *Rec. trav. chim.*, **54** (1935), 853.

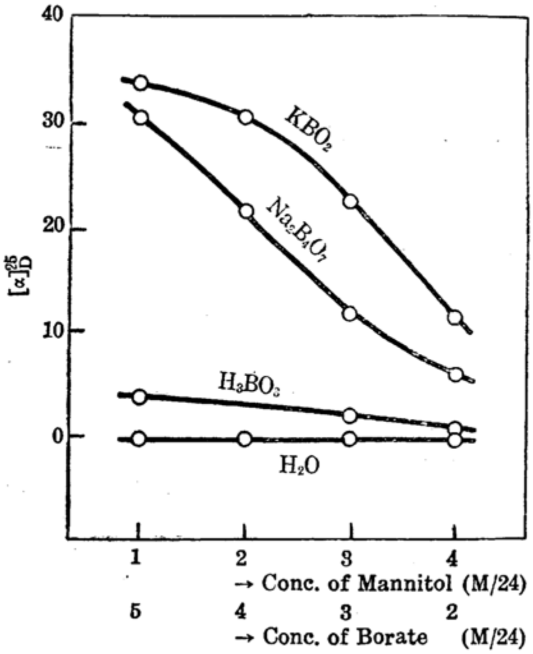
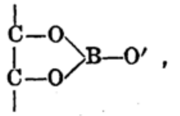


Fig. 1. Effect of Borates on the Optical Rotation of Mannitol.

The experiments indicate that complex formation proceeds with the increase of the concentration of borate ion. Borate ion enhances the rotation of mannitol because it gives a complex with the cyclic structure, which is assumed to have a large optical rotation, since the free rotation of the OH groups in the molecule is inhibited. The quantity of this complex compound will be increased if the concentration of BO_2' becomes greater, inasmuch as equilibrium exists between these substances.



$$\underset{\text{feeble rotation}}{C_6H_{12}O_6 + BO_2'} \rightleftharpoons \underset{\text{strong rotation}}{\text{Mannito-borate} + H_2O}\ .$$

It is, therefore, due to the greater concentration of BO_2' that KBO_2 has a stronger effect than borax of the same molar concentration with respect to B-atom.

Mention should be made here to the well-known fact that boric acid can be titrated with alkali in the presence of mannitol (as well as glycerol), although it is in itself a very weak acid. It appears, therefore, that free boric acid can form complex compounds of a strongly acidic character with these polyhydric alcohols, but this fact is to be explained in the following way. In the titration of boric acid in the presence of mannitol, mannito-boric acid is formed from mannitol and borate ion. This complex which has a strongly acidic character can be formed in a measurable quantity, only after adding a certain amount of alkali, and the quantity of this complex is gradually increased with the progress of titration, thus in the presence of excess mannitol, all the boric acid can be titrated, since it can then be totally converted into strongly acidic complex acid.

Glucose. Darmois and Peyroux⁽⁶⁾ have shown that H_3BO_3 even at saturation is without effect on the rotation of glucose, but that sodium borates have a large effect. Murgier and Darmois⁽⁷⁾ came to the con-

---

(6) Darmois and Peyroux, *Compt. rend.*, **193** (1931), 1182.

(7) Murgier and Darmois, *Angew. Chem.*, **51** (1938), 753, X International Congress for Chemistry in Rome, May 1938.

clusion by examining optical rotation that H_3BO_3 gives with hexoses a very small amount of complexes, while $NaBO_2$ gives a well characterized compound.

The author has examined the effects of boric acid and its alkali salts on the rotation of glucose by varying the ratio Borate/Glucose (Fig. 2 and Table 2) as in the case of mannitol.

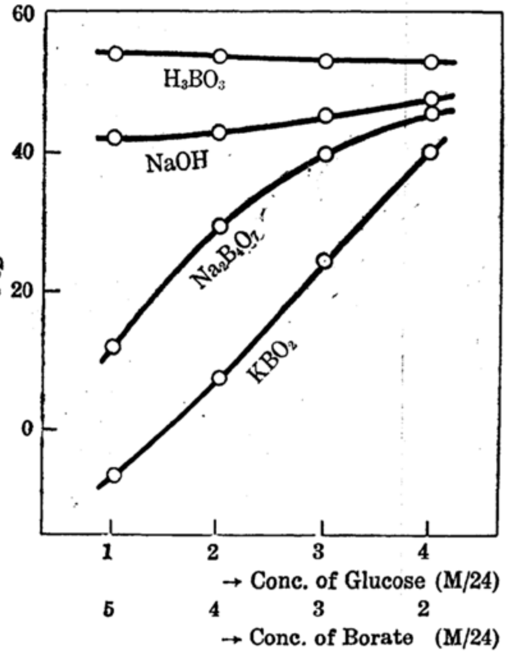


Fig. 2. Effect of Borates on the Optical Rotation of Glucose.

The experiment is in harmony with the statement of Darmois and his collaborators⁽⁸⁾. The specific rotation of glucose, whose large value is due to the cyclic structure of glucoside formula, suffers great changes in the presence of alkali borates, and indeed even negative rotation appears with the increase of the concentration of alkali borate. It is not improbable that the cyclic structure of glucose suffers some modifications by the alkalinity of borate salts, thus the strong dextro-rotation being depressed, but the actual effect of weak alkali on the rotation of glucose is very small (Table 2) and even stronger alkali such as NaOH does not exercise a remarkable influence (Fig. 2). We should, therefore, assign the radical change of the rotation to the complex formation between borate ion and glucose. The cyclic nature of the complex is responsible to the depression of the specific rotation of glucose. The general behaviours of glucose with respect to the change of optical rotation are very similar to that of mannitol, although it is in the opposite direction. This is, no doubt, due to the lack of carboxyl group.

Tartaric Acid and Alkali Tartrates. In these cases free boric acid has remarkable influence, in contrast to polyhydric alcohols. The complex formation between boric acid and tartaric acid and alkali tartrates, is due to the union of COO′ and $B(OH)_3$. Here the latter does not act as an ion, but as an undissociated polyoxy compound.

The reaction of these complex formations has been already examined, thus Darmois⁽⁹⁾ has concluded from his polarimetric measurements that

---

(8) The author could not confirm the observation of P. S. Tang and P. N. Sung with regard to the effect of boric acid on glucose that the rotation of glucose shows the minimum value of $[\alpha]_D = +47°$ in the region of 0.2 M H_3BO_3. *Nature*, **137** (1936), 275.

(9) Darmois, *J. Chim. phys.*, **23** (1926), 649.

a complex $B(OH)_3 \cdot 2C_4H_6O_6$ exists in the mixture of tartaric-boric acid. On the other hand he observed that in strong alkaline solution boric acid gives a laevo-rotatory complex salt.

The present author's observations on the effects of boric acid and borates on the rotation of tartaric acid are shown in Fig. 3 and Table 3.

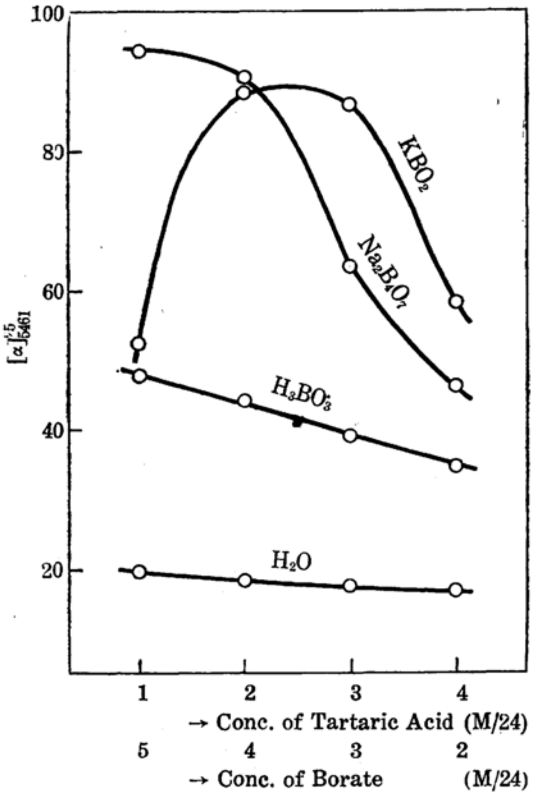


Fig. 3. Effect of Borates on the Optical Rotation of Tartaric Acid.

The results are apparently complicated, hence one must be cautious to draw from these figures some conclusions with respect to complex formation. It is noticed, however, that dextro-rotation is elevated as the ratio $H_3BO_3/C_4H_6O_6$ increases. This phenomenon is to be explained as follows. Boric acid combines with the COO′ group of tartaric acid, giving a complex with a cyclic structure. Since all the cyclic derivatives of tartaric acid formed by fixing its carboxyl groups are strongly dextro-rotatory, borotartaric acid now under consideration is expected to show enhanced dextro-rotation. According to the author's view⁽¹⁰⁾ the COOH group of *d*-tartaric acid is a contributor of its laevo-partial rotation, and its characteristic (i.e. partial rotatory contribution) is enfeebled when it forms a cyclic structure, hence the dextro-partial rotation originating in the OH group predominates. Now the actions of borax on the rotation of tartaric acid (Table 3) are in fact similar to those of H_3BO_3 on sodium tartrate (Table 4). Of course this is due to the circumstances that in aqueous solution there takes place the following exchange reaction between these substances:

$$Na_2B_4O_7 + C_4H_6O_6 + 5H_2O = 4H_3BO_3 + C_4H_4O_2Na_2 .$$

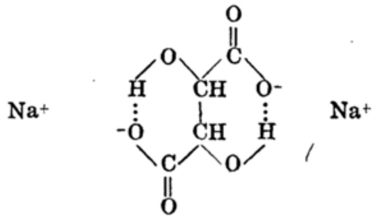
Since these mixtures are always acidic, undissociable OH group is present in an appreciable quantity either in tartaric or in boric acid, and thus combination occurs between anion and OH group, leading to the formation of complexes, similar in structure to those of the free tartaric-boric acid system, but these complexes dissociate more strongly than the latter, so

---

(10) Y. Tsuzuki, *Sci. Pap. Inst. Phys. Chem. Res.*, **35** (1939), 425.

that the complex formation proceeds further, and thus strong dextro-rotation appears. With the increase of the ratio Borax/Tartrate, the concentration of alkali becomes greater. Hence the concentration of borate ion will be raised with the result that dextro-rotation is enhanced.

It is known that alkali tartrates show none of the optical anomalies of the acid⁽¹¹⁾ and exhibit considerably high specific rotation (Tables 4 and 5). This may be due to the formation of a somewhat fixed cyclic structure:



As already shown by the author⁽¹⁰⁾ the (negative) partial rotation of the COOH group is enfeebled in a ring compound of this sort, and the (positive) partial rotation of the OH group becomes predominant; consequently the molecule shows strong dextro-rotation.

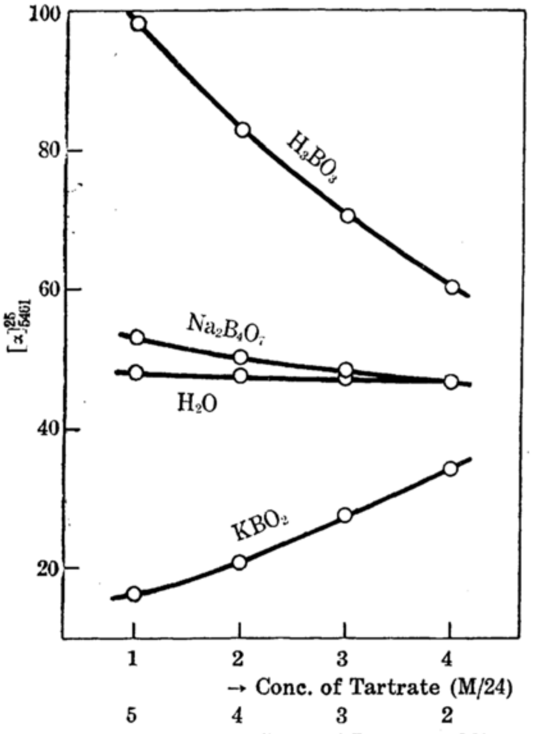


Fig. 4. Effect of Borates on the Optical Rotation of Sodium Tartrate.

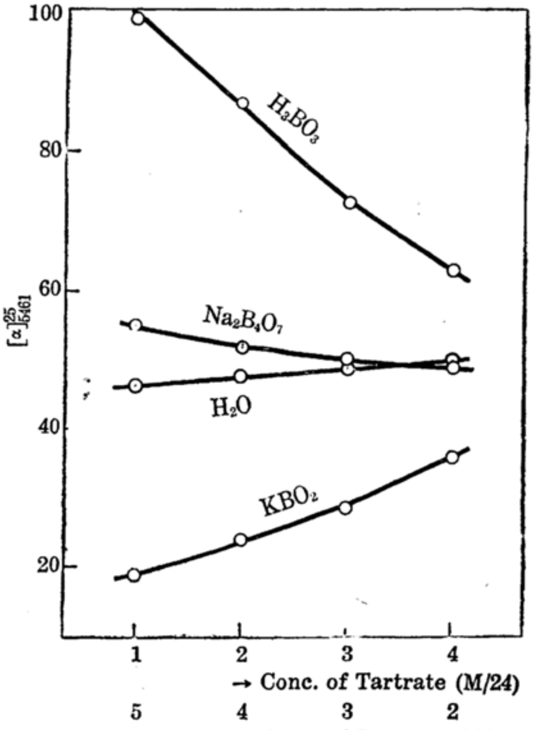
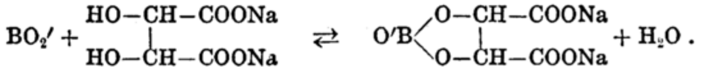


Fig. 5. Effect of Borates on the Optical Rotation of Potassium Tartrate.

---

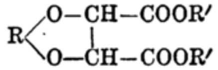
(11) Lowry and Austin, Bakerian Lecture, *Phil. Trans.* A, **222** (1922), 249.

The action of KBO_2 on alkali tartrates depresses the high dextro-rotations of these salts, and indeed the effect becomes stronger as the concentration of BO_2' increases. (Fig. 4 and 5, Tables 4 and 5). This can be explained in the following way. Since BO_2' can not unite with the COO′ group of tartrates, it combines with their OH groups, the reaction being represented as follows:



$$BO_2' + \begin{array}{c} HO-CH-COONa \\ | \\ HO-CH-COONa \end{array} \rightleftarrows O'B\left\langle \begin{array}{c} O-CH-COONa \\ | \\ O-CH-COONa \end{array} \right. + H_2O\ .$$

Seeing that cyclic compounds of the type



$$R\left\langle \begin{array}{c} O-CH-COOR' \\ | \\ O-CH-COOR' \end{array} \right.$$

show strong laevo-rotation,⁽¹²⁾ it will be understood that, with increasing concentration of KBO_2, the concentration of the complex with laevo-rotatory character will be raised, and hence the system becomes less dextro-rotatory. Thus in the system, $KBO_2 : C_4H_6O_6 = 20 : 10$ (Fig. 3, Table 3), which is equivalent to the system, $H_3BO_3 : C_4H_4O_6K_2 = 20 : 10$ (Fig. 5, Table 5) the specific rotation reaches the maximum value $[\alpha]^{25}_{5461} = +87.84°$ at this point, and by adding BO_2' further to this mixture, the high dextro-rotation of this system will be lowered.

Borax is nearly without effect on the rotation of alkali tartrates (Fig. 4 and 5, Tables 4 and 5). This phenomenon appears rather curious, but the author considers that borax reacts with tartaric ion in two ways: on one hand the portion of undissociated boric acid $B(OH)_3$ in borax combines with the COO′ group of the tartrate forming a strongly dextro-rotatory complex, and on the other hand the dissociable portion in borax (BO_2') forms a rather laevo-rotatory complex. The two opposite effects cancel each other, so that the total rotation remains almost unaffected.

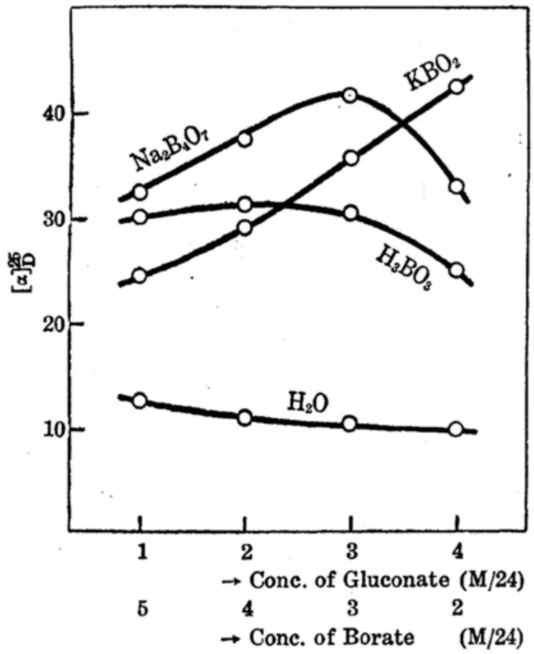


Fig. 6. Effect of Borates on the Rotation of Calcium Gluconate.

Calcium Gluconate. Although free boric acid shows a very feeble ability for complex formation with polyhydric alcohols, such as mannitol and glucose, it exerts a remarkable influence on polyoxy compounds with carboxyl group. This is well illustrated with gluconic acid (Fig. 6 and Table 6).

---

(12) Y. Tsuzuki, this Bulletin, **15** (1940), 27; *Sci. Pap. Inst. Phys. Chem. Res.*, **35** (1939), 425, 466; **36** (1939), 31.

As will be easily understood from the examples of tartrates, this phenomenon must be attributed to the presence of complexes formed between COO′ and H_3BO_3. Calcium gluconate also shows somewhat complicated behaviours with alkali borates as in the cases of tartaric acid and its salts. It is remarkable that the dextro-rotation is lowered with the increase of KBO_2 concentration. This may, however, be explained as follows. In alkaline medium BO_2' unites no more with COO′, but reacts with alcoholic hydroxyl groups, so that it is natural that the rotation suffers alteration in the other direction.

In conclusion it should be remarked that these reactions of complex formation arrive at equilibrium almost instantaneously. This is probably due to exchange reaction. In this connexion mention should be made further that heteropoly acids as well as isopoly acids in inorganic field are perhaps of the nature similar to the present cases, thus they may be explained from the point of view above stated.

Experimental Part.

Polarimetric measurements were made on the mixtures of the following compositions:

	No. 1	No. 2	No. 3	No. 4
M/4-Optically active compound c.c.	5	10	15	20
M/4-H_3BO_3, $\frac{Na_2B_4O_7}{4}$ or KBO_2 c.c.	25	20	15	10

Hence the concentrations in the mixtures are:

		No. 1	No. 2	No. 3	No. 4
Optically active compound	M/24	1	2	3	4
Borate or other substances	M/24	5	4	3	2

The numerical values are given in the following tables. The length of the observation tube is 2.2 dm. The specific rotation of tartaric acid and its salts is given for tartrate ion $C_4H_4O_6''$, and that of gluconate for gluconate ion $C_6H_{11}O_7'$.

Table 1. Mannitol.

No.	α				$[\alpha]_D^{25}$			
	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2
1	−0.001	+0.06	+0.510	+0.564	−0.06	+3.59	+30.55	+33.78
2	−0.003		+0.722	+1.02	−0.09		+21.62	+30.54
3	−0.009	+0.09	+0.583	+1.13	−0.18	+1.80	+11.64	+22.56
4	−0.012	+0.05	+0.387	+0.746	−0.24	+0.60	+ 5.79	+11.17

Table 2. Glucose.

No.	α					$[\alpha]^{30}_{D}$				
	H_3BO_3	$Na_2B_4O_7$	KBO_2	K_2CO_3	NaOH	H_3BO_3	$Na_2B_4O_7$	KBO_2	K_2CO_3	NaOH
1	+0.888	+0.196	−0.107	+0.833	+0.696	+53.77	+11.87	− 6.48	+50.74	+42.14
2	+1.782	+0.979	+0.249	+1.683	+1.421	+53.94	+29.64	+ 7.54	+50.94	+43.02
3	+2.611	+1.97	+1.405	+2.528	+2.235	+52.70	+39.76	+24.36	+51.02	+45.10
4	+3.49	+3.002	+2.683	+3.385	+3.132	+52.83	+45.45	+40.25	+51.25	+47.41

Table 3. Tartaric Acid.

No.	α				$[\alpha]^{25}_{5461}$			
	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2
1	+0.271	+0.652	+1.28	+0.711	+19.97	+48.03	+94.32	+52.38
2	+0.501	+1.20	+2.45	+2.385	+18.45	+44.19	+90.24	+87.84
3	+0.719	+1.59	+2.58	+3.50	+17.66	+39.04	+63.36	+85.94
4	+0.898	+1.88	+2.50	+3.16	+16.55	+34.62	+46.05	+58.20

Table 4. Sodium Tartrate.

No.	α				$[\alpha]^{25}_{5461}$			
	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2
1	+0.650	+1.35	+0.72	+0.22	+47.89	+98.0	+53.1	+16.2
2	+1.295	+2.25	+1.36	+0.57	+47.70	+82.9	+50.1	+21.0
3	+1.927	+2.88	+1.96	+1.14	+47.32	+70.8	+48.2	+28.0
4	+2.562	+3.28	+2.53	+1.88	+47.19	+60.5	+46.6	+34.6

Table 5. Potassium Tartrate.

No.	α				$[\alpha]^{25}_{5461}$			
	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2
1	+0.625	+1.34	+0.75	+0.26	+46.04	+99.0	+55.3	+19.1
2	+1.280	+2.36	+1.40	+0.66	+47.16	+86.9	+51.6	+24.3
3	+1.989	+2.94	+2.04	+1.17	+48.84	+72.2	+50.0	+28.8
4	+2.722	+3.40	+2.65	+1.96	+50.13	+62.7	+48.8	+36.2

Table 6. Calcium Gluconate.

No.	α				$[\alpha]_D^{25}$			
	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2
1	+0.226	+0.544	+0.580	+0.44	+12.64	+30.42	+32.44	+24.61
2	+0.394	+1.13	+1.34	+1.05	+11.02	+31.59	+37.47	+29.36
3	+0.555	+1.64	+2.24	+1.92	+10.35	+30.56	+41.76	+35.80
4	+0.706	+1.99	+2.37	+3.04	+ 9.87	+24.82	+33.09	+42.50

Summary.

By polarimetric observations with regard to the effects of H_3BO_3, $Na_2B_4O_7$ and KBO_2 on various polyoxy compounds the following results and conclusion were obtained.

Boric acid has a very feeble ability for complex formation with non-ionizable polyoxy compounds, such as mannit and glucose, while alkali borates show strong activity upon them. The order of the strengths is $H_3BO_3 \ll Na_2B_4O_7 < KBO_2$. Complex is formed between borate ion and polyhydric alcohols. Its quantity increases with increasing BO_2'.

The effects of boric acid and alkali borates on ionizable polyoxy compounds, like tartaric acid and its salts, appear somewhat complicated. In this case complex formation is possible to a large extent between free boric acid and free tartaric acid (complex I). Complexes are also formed between alkali borate and alkali tartrates (complex II), but they (II) are different in structure from those formed in acidic medium (I). The complex I is formed by the action between BO_2' and alcoholic OH groups, but complex II between $B(OH)_3$ molecule and COO' ion.

Calcium gluconate behaves toward boric acid and borates like alkali tartrates. H_3BO_3 combines with the COO' group of the gluconate, while BO_2' reacts with its alcoholic OH groups.

Thus it has been shown that the complex formation is in general based upon the reaction between molecule and ion, and not between neutral molecules nor between ions.

The author wishes to express his hearty thanks to Mr. Y. Kimura and Mr. T. Yamana for assistance with the experiments and to the Department of Education for a grant.

Musashi Higher School, Tokyo, Nakaarai.