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Double Tridentate Complex of Triquinoyl with Boric Acid

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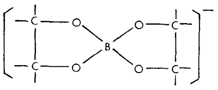
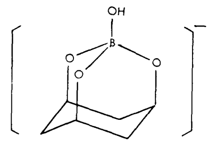
Synopsis. Triquinoyl forms with boric acid a strongly acid double-tridentate complex, dipotassium salt of which is almost insoluble in water. The formation of this complex supports dodecahydroxycyclohexane structure for triquinoyl.

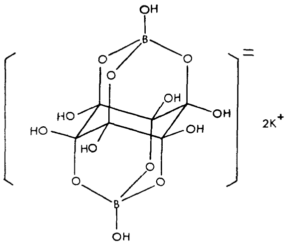
It is well known that some polyol compounds form borate complexes,[1-3] which cause the increased acidity and conductivity of boric acid solutions after the addition of the polyols.[4] There are two types of the borate complexes. One type (**A**), which is usually called as Böeseken complex, is believed to involve *cis*-1,2-diol structures[2] and the borate-polyol reactions forming this type of complexes are usually reversible. Another type is seen in some borate–cyclitol complexes. Cyclitols having three *cis*-1,3,5-hydroxyl groups form complexes by a three-point attachment as in **B**, which are referred to as tridentate complexes.[5,6] The complexes are usually stable and strong acids.[5] *cis*-Phloroglucitol makes tridentate complex (**B**) from its less stable chair form. *cis*-Inositol with three axial hydroxyl groups on the same side of the ring in either chair form, forms by far the firmest complex. Scyllitol in its all equatorial conformation cannot form a tridentate complex and hence forms no borate complex under mild conditions,[5] but under forced conditions it could form a double tridentate complex with borate.[7]



A



B



I

We found that triquinoyl also forms a stable complex with borate in a 1 : 2 ratio. When 1 M KCl solution (10 ml) was added to an aqueous 0.5 M boric acid solution (20 ml) of triquinoyl (60 mg) white precipitate appeared immediately, which was collected by centrifugation and washed with water (pH of the supernatant was 2.4). When the borate solution of triquinoyl was slowly titrated with 0.1 M KOH solution two equivalents of KOH per 1 mol of triquinoyl were consumed and crystalline precipitate was formed. The precipitate shows no definite mp, no UV absorption, and apparent pK_a at *ca.* 2.6, and is almost insoluble in water and usual organic solvents, but soluble in conc. HCl; IR spectrum is shown in Fig. 1.

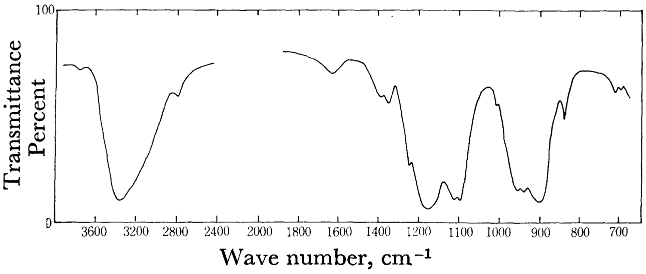


Fig. 1. Infrared spectrum of I.

Found: B, 5.20; K, 19.3%. Calcd for $C_6H_8O_{14}$-B_2K_2: B, 5.36; K, 19.35%. The complex is assigned to have the double tridentate structure (**I**) from its elemental analysis, titration equivalent, apparent pK_a, and by analogy from other tridentate complexes.[8]

Böeseken and Meuwissen[9] observed that triquinoyl increases the electronic conductivity of boric acid. They had suggested the structure of triquinoyl as the completely hydrated form, dodecahydroxycyclohexane [$C_6(OH)_{12}\cdot 2H_2O$], which was later confirmed by IR spectroscopic analysis.[10] The formation of the double tridentate borate complex supports this structure.

References

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8) Leuconic acid also forms insoluble barium salt of its borate complex. Alkaline titration indicated 1 : 1 ratio of leuconic acid and borate. Elemental analysis indicates the composition of $C_5H_6O_{10}BBa_{0.5}\cdot 5$—6 H_2O (Found: Ba, 17.4; B, 2.64%. Calcd for $C_5H_6O_{10}BBa_{0.5}\cdot 5H_2O$: Ba, 17.36; B, 2.73; for $C_5H_6O_{10}BBa_{0.5}\cdot 6H_2O$: Ba, 16.60; B, 2.62%); removal of water by heating causes gradual decomposition. Polymer structures similar to Böeseken complex **A** may be assumed for this complex.
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