THE EFFECT OF CERTAIN SUGAR ALCOHOLS AND THEIR ANHYDRIDES ON THE DISSOCIATION OF BORIC ACID

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INTRODUCTION

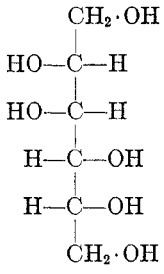
The use of the polyhydric alcohols in the titration of boric acid with alkalies is a well-established analytical procedure. The increase of the dissociation constant of the acid in the presence of various polyhydric alcohols and phenols was studied extensively by Böeseken (1). The subject was studied further and comprehensively reviewed by Mellon and Norris (2). The authors became interested in the fate of certain sugar alcohols and their anhydrides in the animal body (3, 4) and in bacterial culture media (5). The differences in effect were so striking that a comparison of the influences of these substances on the titration curves of boric acid suggested itself. Previously van Romburgh and van der Burg (6) have measured the difference between the electrical conductivity of boric acid in mannitol, mannitan, and isomannide solutions.

MATERIALS

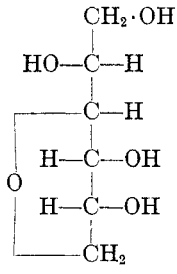
The mannitol used in this investigation was supplied through the courtesy of Merck and Company, Inc., Rahway, N. J. The aqueous solution of the compound (1:10) is neutral to litmus and very slightly dextrorotatory. The mannitan was prepared from mannitol by a slight modification of the method of Vignon (7), in which the dehydration is accomplished by means of sulfuric acid. The compound was acetylated and the resulting ester distilled *in vacuo*. The fraction distilling between 200–210°C. at 10 mm. was saponified. The calculated percentage of acetic acid is 72.31; that found was 71.70. The mannide was prepared by the method devised by Liebermann (8). Analysis gave: C, 48.37 per cent; H, 7.32 per cent. The calculated values are: C, 49.27 per cent; H, 6.90 per cent. The isomannide was prepared by Fauconnier's method (9). The compound melted sharply at 87°C. (uncorrected).

The dulcitol employed was Pfanstiehl's C.P. product, m.p. 188°C., free from galactose. The dulcitan was prepared by Berthelot's method (10). Analysis gave the following composition: C, 43.79 per cent; H, 7.20 per cent. The calculated values are: C, 43.87 per cent; H, 7.37 per cent.

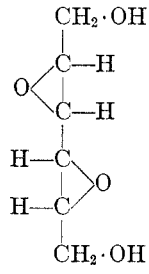
The following formulas indicate the structural relationships existing among the compounds.



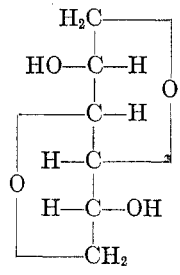
Mannitol



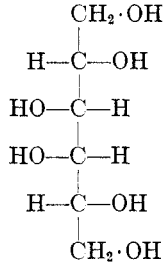
Mannitan



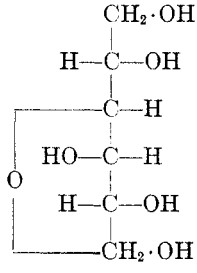
Mannide



Isomannide



Dulcitol



Dulcitan

METHOD

The solutions of the various compounds used contained 4 g. of compound in 100 cc. of 0.1 molar boric acid. To 10-cc. portions was added 0.1 normal sodium hydroxide in quantities varying from 1 cc. to 11 cc. Immediately after the addition of the alkali the pH of the solution was determined electrometrically at 25 $\pm$0.5°C., using a Wilson (11) type hydrogen electrode. The results are set forth in figure 1.

DISCUSSION

It will be observed that the two hexahydric alcohols have practically the same dissociation-potentiating capacity on solutions of boric acid. The second anhydride of mannitol, namely isomannide, with two ring structures in the molecule, does not possess the capacity to influence the dissociation of boric acid, and the titration curve for the acid containing isomannide is practically identical with that of the acid alone. The curves for the two first anhydrides lie intermediate between the values obtained for the alcohols and those obtained for pure boric acid.

The curve for the double anhydride of mannitol, mannide, shows this

substance to have a greater potentiating influence on the dissociation of boric acid than the first anhydrides. A comparison of this fact with the structure assigned to mannide by Liebermann (8) is incompatible with the hypothesis of Böeseken (1), namely, that the strongly dissociating complexes of boric acid are formed when two hydroxyl groups are situated on the same side of adjacent carbon atoms to which they are bound. The authors observed the rather rapid conversion of mannide into mannitol in the presence of alkali. It is possible that the partial conversion of this

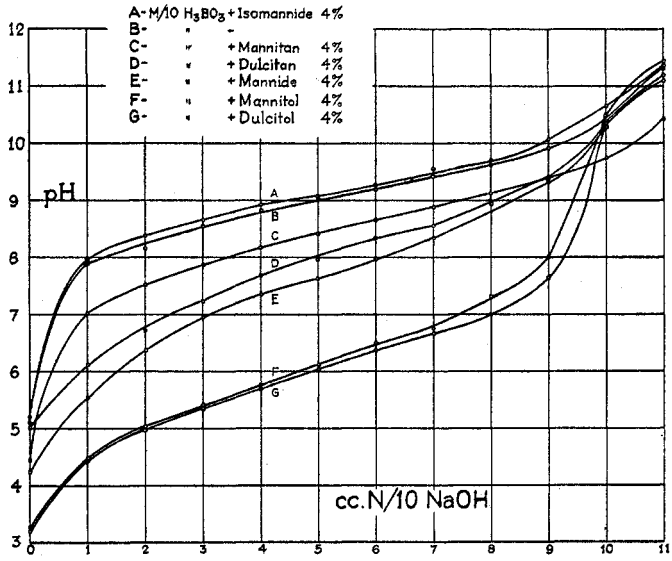


FIG. 1. Titration curves of boric acid in the presence of certain sugar alcohols and their anhydrides

double anhydride into the polyhydric alcohol is responsible for the observed effect on the titration curve.

SUMMARY

The influence of two polyhydric alcohols, mannitol and dulcitol, on the titration curve of boric acid has been studied. This effect has been compared with the action of the anhydrides mannitan, mannide, isomannide, and dulcitan.

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