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A STUDY OF THE COMPLEXES OF BORATE IONS AND SOME CYCLITOLS USING ^{11}B-N.M.R. SPECTROSCOPY

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ABSTRACT

Complexes between borate ion and cyclohexane-*cis*-1,2-diol, cyclohexane-*cis,cis*-1,3,5-triol, and *myo*- and *epi*-inositol have been investigated by ^{11}B-n.m.r. spectroscopy. Three different complexes of *myo*-inositol have been identified. Formation constants have been determined for the borate complexes of each cyclitol. Where the complex is formed from the less-stable chair conformer, MNDO calculations have been performed to determine the enthalpies of inversion. For *myo*-inositol, an iterative method of calculation gave a set of constants which provided a good match with experimental data and supported the proposed formulation of its borate complexes.

INTRODUCTION

The formation of complexes of borate ions and hydroxy compounds has been studied on the basis of the changes in conductivity[1] or pH[2,3] that occur when boric acid and hydroxy compounds are mixed in solution, and by using electrophoresis[4,5], ionophoresis[6], and ^{11}B-n.m.r. spectroscopy[7].

According to Boeseken[1], the reaction between boric acid and polyols is:

Angyal and McHugh[6] found that 1:1 complexes were formed from *myo*-, *epi*-, and *cis*-inositols and boric acid, and they defined the relevant equilibrium constant as $K = [C^-]/[B^-][C]$, where [C], $[B^-]$, and $[C^-]$ are the concentrations of the inositol, borate, and complex, respectively. These authors stressed that their definition of K did not imply that complexation actually involved borate ions and they considered that, over the pH range used (6.0–9.1), it was much more likely

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that the reacting species was boric acid, not borate ion. The K values reported[6] were 25 for *myo*-inositol, 7×10^3 for *epi*-inositol, and 1.09×10^6 for *cis*-inositol.

cis-Inositol exists in the chair conformation having the 1,3,5-hydroxyl groups axial. The large K value for its 1:1 borate complex shows that this arrangement is particularly favourable for complexation, and the complex is tridentate involving three 6-membered rings. In their stable chair conformations, *myo*- and *epi*-inositol have one and two axial hydroxyl groups, respectively, and form similar 1:1 complexes only after inversion to their less-stable conformers, each of which has the required axial 1,3,5-hydroxyl groups. Although the K values for these complexes reflect the extent of complexation in solution, they are not strictly formation constants, the determination of which requires a knowledge of the concentration of the unstable conformer in the reaction mixture.

Posternak *et al.*[8], using data of Angyal *et al.*[9], estimated the difference in free energy between the more- and less-stable conformers of *scyllo*-, *myo*-, and *epi*-inositol as 38.9, 25.9, and 13.0 $kJ.mol^{-1}$, respectively. From the last two values, equilibrium constants for inversion were calculated, and thence the following formation constants between the unstable conformers and boric acid: *myo*-inositol, 1.0×10^6; *epi*-inositol, 1.4×10^6. A value of 1.1×10^6 was found for the *cis*-inositol complex.

Complexation by axial 1,3,5-hydroxyl groups has been found in the 2:1 borate complex of *scyllo*-inositol isolated[10] as a solid and subjected[11] to X-ray analysis. The more-stable chair conformation of *scyllo*-inositol has six equatorial hydroxyl groups and the less stable has two sets of axial 1,3,5-hydroxyl groups, each of which can form a tridentate complex. Another kind of borate complex involves vicinal *cis*-hydroxyl groups and a 5-membered ring. Many polyols form such 1:1 complexes and, for some compounds, a second polyol molecule is involved to form a 2:1 (spiro) complex.

^{11}B-N.m.r. spectroscopy affords a direct measure of the amounts of boron in different environments[7] and we have applied this technique to study the borate complexes of cyclitols in aqueous solution. The interactions have been studied at pH ~12, where the preponderant ion is $B(OH)_4^-$ and the equilibrium is

RESULTS AND DISCUSSION

The ^{11}B-n.m.r. spectrum of a solution of sodium borate at pH >11 shows the characteristic narrow resonance at δ 1.7 due to $B(OH)_4^-$ ($\delta = 0$ for the external standard, Et_2OBF_3). In order to minimise possible complications due to the presence of polyborates, which co-exist[12] with $B(OH)_4^-$ in the pH range 5–11, complexation in solutions of pH ~12 was studied.

Cyclohexane-cis-*1,2-diol.* — The presence of a 1:1 complex was indicated by the ^{11}B resonance at δ 5.2 and, in solutions with a high diol–borate ratio, that of a 2:1 diol–borate spiro complex by a second resonance at δ 8.6–8.8.

The following equilibria are involved:

$$D + B(OH)_4^- \overset{K_m}{\rightleftharpoons} DB(OH)_2^- + 2\,H_2O,$$

and

$$2D + B(OH)_4^- \overset{K_s}{\rightleftharpoons} D_2B^- + 4\,H_2O,$$

where D, $DB(OH)_2^-$, and D_2B^- represent the diol, mono complex, and spiro complex, respectively.

From the above equilibria, it follows that

$$K_s = \frac{[D_2B^-][H_2O]^4}{[D]^2[B(OH)_4^-]} \quad \text{and} \quad K_m = \frac{[DB(OH)_2^-][H_2O]^2}{[D][B(OH)_4^-]}.$$

As there is no significant change in either $[H_2O]^2$ or $[H_2O]^4$ on complexation, then

$$K_s' = \frac{[D_2B^-]}{[D]^2[B(OH)_4^-]} \quad \text{and} \quad K_m' = \frac{[DB(OH)_2^-]}{[D][B(OH)_4^-]}.$$

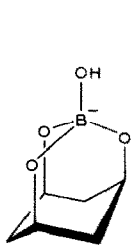
Experimental data and K values are given in Table I. The mean value (1.8) for K_m' agrees well with that (1.9) reported[7]. The value (0.32) of K_s' calculated from data obtained with the highest diol–borate ratio is close to that (0.3) reported[3]. Our data for the other mixture that shows evidence for the presence of the spiro complex are less reliable because of the likely error in measuring accurately its low percentage (1.4%).

TABLE I

EQUILIBRIUM CONCENTRATIONS (M) AND FORMATION CONSTANTS FOR COMPLEXATION OF CYCLOHEXANE-*cis*-1,2-DIOL BY BORATE[a] AT pH ~12

Diol–borate molar ratio	$[B(OH)_4^-]$	$[D]$	$[DB(OH)_2^-]$	$[D_2B^-]$	K_s'	K_m'[b]
15:1	0.027	0.72	0.017	0.0063	0.32	0.9
5:1	0.040	0.24	0.0089	0.0007	0.07	0.9
1:1	0.047	0.047	0.0026			1.2
1:5	0.049	0.0086	0.0014			3.3
1:10	0.049	0.0044	0.0006			2.8

[a]All solutions were 0.05M with respect to boron. [b]Mean value of $K_m' = 1.8$.



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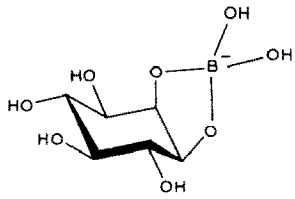

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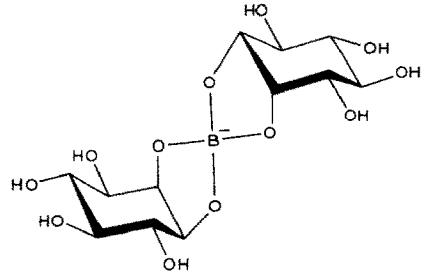

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Cyclohexane-cis,cis-*1,3,5-triol.* — This triol forms[13] a crystalline 1:1 borate complex, and an ionophoretic study[6] gave a value of 32 for the equilibrium constant for its formation in aqueous solution. The stable chair conformation of the triol has three equatorial hydroxyl groups and it is the axial 1,3,5-hydroxyl groups in the less-stable chair conformer which are involved in a 1:1 tridentate complex ("cleisto" structure **1**). This gives rise to the ^{11}B resonance at δ 0.76–0.85 [*cf.* δ 1.7–1.77 for $B(OH)_4^-$].

Two equilibria represent the reactions in solution, namely, the inversion process whereby the stable conformer, T_s, is converted into the unstable conformer, T_u,

$$T_s \overset{K_i}{\rightleftharpoons} T_u,$$

and complexation,

$$T_u + B(OH)_4^- \overset{K_c}{\rightleftharpoons} T_uB(OH)^- + 3\ H_2O.$$

Hence,

$$\frac{K_iK_c}{[H_2O]^3} = \frac{[T_uB(OH)^-]}{[T_s][B(OH)_4^-]}.$$

The constant, K_c', is defined as $K_c/[H_2O]^3$; the data and values for K_iK_c' are given in Table II.

In order to calculate K_c', the formation constant of the cleisto complex, an estimate of K_i is needed and this has been obtained from MNDO calculations, which give directly the enthalpies of formation of T_s and T_u. The difference $(\Delta H_s - \Delta H_u)$ is the enthalpy of inversion of the two conformers as isolated molecules. If it is assumed that the enthalpies of hydration and the entropies of formation of the conformers are identical, then $(\Delta H_s - \Delta H_u)$ may be equated with the free-energy change, ΔG_i, accompanying inversion, and K_i can then be calculated. The results

TABLE II

EQUILIBRIUM CONCENTRATIONS (M) AND FORMATION CONSTANT FOR COMPLEXATION OF CYCLOHEXANE-*cis,cis*-1,3,5-TRIOL BY BORATE[a] AT pH ~12

Triol–borate molar ratio	$[B(OH)_4^-]$	$[T_s]$	$[T_uB(OH)^-]$	K_iK_c'[b]
2.11:1	0.046	0.231	0.120	11.3
1.52:1	0.059	0.144	0.102	12.0
1:1	0.069	0.070	0.092	19.0
1:1.46	0.094	0.042	0.070	17.7
1:2.01	0.112	0.029	0.053	16.3
1:4.79	0.139	0.010	0.024	17.3

[a]All solutions were 0.16M with respect to boron. [b]Mean value 15.6.

of the MNDO calculations are given in Table VI; for the triol, $K_i = 0.0267$ and, since $K_iK_c' = 15.6$, $K_c' = 584$.

The reported[6] value of 32 for the formation constant should be properly compared with the value of K_iK_c'. The difference is almost certainly due to different concentrations of $Na_2B_4O_7$ (2.5mM by Angyal and McHugh and 0.16M in the present work). The values represent the conditional constants defined in terms of concentration, and their magnitude is expected to vary with concentration.

myo-*Inositol*. — The ^{11}B-n.m.r. spectra of a series of mixtures in which the inositol–borate molar ratio varied between 15:1 and 1:5 showed four resonances (Fig. 1). On the basis of the work of Henderson *et al.*[7], three complexes can be identified as monocyclic (δ 5.27–5.69), spirocyclic (δ 9.3–9.5), and cleisto (δ −0.33–0.0); $B(OH)_4^-$ gave a resonance at δ 1.44–1.78.

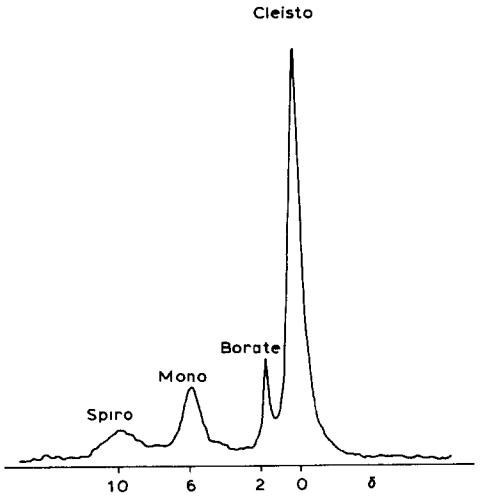

Fig. 1. ^{11}B-N.m.r. spectrum (28.75 MHz) of an aqueous solution of *myo*-inositol–borate (ratio 12:1) at pH 12.

The percentage of total boron in each species, calculated from the peak area, was used to determine the formation constants. A set of self-consistent constants from which experimental percentages could be matched well with those calculated could be determined only if it was assumed that the cleisto complex was a 1:2 inositol–borate complex. The nature of this complex is discussed later, but for the purpose of analysing data, it was formulated as $M_uB_2(OH)_3^{2-}$, where M_u represents the less-stable conformer of *myo*-inositol. The mono- and spiro-cyclic complexes are formed from the stable conformer, M_s, with boron co-ordinated in bidentate fashion with the vicinal *cis*-hydroxyl groups of one and two molecules of *myo*-inositol, respectively, and formulated as $M_sB(OH)_2^-$ (**2**) and $(M_s)_2B^-$ (**3**).

For the formation of the three complexes, four equilibria can be considered, namely,

$$M_s + B(OH)_4^- \overset{K_m}{\rightleftharpoons} M_sB(OH)_2^- + 2\,H_2O,$$

$$2M_s + B(OH)_4^- \overset{K_s}{\rightleftharpoons} (M_s)_2B^- + 4\,H_2O,$$

$$M_s \overset{K_i}{\rightleftharpoons} M_u,$$

and

$$M_u + 2B(OH)_4^- \overset{K_c}{\rightleftharpoons} M_uB_2(OH)_3^{2-} + 5\,H_2O.$$

Using these equations, the percentage of boron in various forms can be expressed as:

$$\%B \text{ as } B(OH)_4^- = 100 \Big/\left(1 + \frac{K_m[M_s]}{[H_2O]^2} + \frac{K_s[M_s]^2}{[H_2O]^4} + \frac{2K_cK_i[M_s][B(OH)_4^-]}{[H_2O]^5}\right)$$

$$\%B \text{ as } M_sB(OH)_2^- = 100K_m[M_s]/[H_2O]^2 \Big/\left(1 + \frac{K_m[M_s]}{[H_2O]^2} + \frac{K_s[M_s]^2}{[H_2O]^4} + \frac{2K_cK_i[M_s][B(OH)_4^-]}{[H_2O]^5}\right)$$

$$\%B \text{ as } (M_s)_2B^- = 100K_s[M_s]^2/[H_2O]^4 \Big/\left(1 + \frac{K_m[M_s]}{[H_2O]^2} + \frac{K_s[M_s]^2}{[H_2O]^4} + \frac{2K_cK_i[M_s][B(OH)_4^-]}{[H_2O]^5}\right)$$

$$\%B \text{ as } M_uB_2(OH)_3^{2-} = (200K_cK_i[M_s][B(OH)_4^-]/[H_2O]^5) \Big/\left(1 + \frac{K_m[M_s]}{[H_2O]^2} + \frac{K_s[M_s]^2}{[H_2O]^4} + \frac{2K_cK_i[M_s][B(OH)_4^-]}{[H_2O]^5}\right)$$

TABLE III

COMPOSITION OF *myo*-INOSITOL–BORATE[a] MIXTURES AT pH ~12[b]

Inositol–borate molar ratio	*%B as*			
	$B(OH)_4^-$	$M_sB(OH)_2^-$	$(M_s)_2B^-$	$M_uB_2(OH)_3^-$
15:1	5.0	29.0	23.7	42.3
10:1	6.4	25.4	12.0	56.2
3:1	8.5	22.3	7.2	62.0
1:1.5	35.0	6.7	—	58.2
1:2	44.7	6.9	—	48.4
1:3	49.7	6.0	—	44.2
1:3.5	56.8	6.0	—	37.2
1:4	61.9	2.3	—	35.8
1:5	62.5	2.8	—	34.6

[a]Concentrations in the range 0.4–0.67M with respect to boron. [b]Calculated equilibrium constants: K'_m = 0.75; K'_s = 0.069; $K_iK'_c$ = 17.93.

TABLE IV

COMPOSITION OF *myo*-INOSITOL–BORATE[a] MIXTURES AT pH ~12[b]

Inositol–borate molar ratio	*%B as*			
	$B(OH)_4^-$	$M_sB(OH)_2^-$	$(M_s)_2B^-$	$M_uB_2(OH)_3^-$
12:1	8.7	19.2	13.2	59.0
10:1	9.2	17.0	9.7	64.1
8:1	10.5	16.4	8.7	64.3
7:1	12.2	15.6	8.1	64.0
3.5:1	19.3	15.2	4.1	61.4
2.5:1	21.7	11.9	2.7	63.7
1.5:1	27.0	6.4	0.5	65.6

[a]All solutions were 0.081M with respect to boron. [b]Calculated equilibrium constants: K'_m = 0.31; K'_s = 0.027; $K_iK'_c$ = 7.758.

As for the triol, $K'_c = K_c/[H_2O]^5$, $K'_m = K_m/[H_2O]^2$, and $K'_s = K_s/[H_2O]$. Experimental results for relatively high (0.4–0.67M) and much lower (0.081M) concentrations of borate are given in Tables III and IV, respectively. Computer-calculated values of K'_cK_i, K'_m, and K'_s are also given.

MNDO calculations showed ($\Delta H_s - \Delta H_u$) for *myo*-inositol to be −13.46 kJ.mol^{-1} (Table VI). With the same assumptions as before, $K_i = 4.11 \times 10^3$. Experimental values and theoretically computed curves for the components present in these solutions at different polyol–borate ratios are shown in Fig. 2. For the more dilute borate solutions, $K'_c = 1.78 \times 10^3$. Fig. 3 shows a comparison between experimental and theoretical data. There is generally satisfactory agreement, and the proposed equilibria provide a self-consistent set to explain experimental observations.

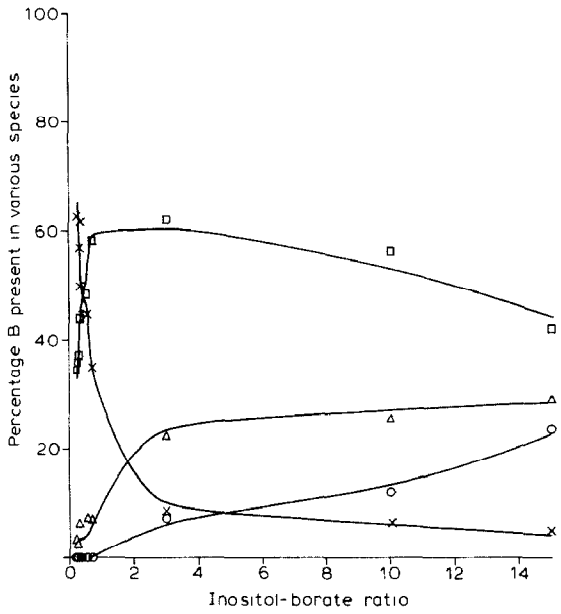

Fig. 2. Comparison of calculated and experimental values of the amounts of different species present in *myo*-inositol–borate mixtures as a function of inositol–borate ratio (boron concentration in the range 0.4–0.67M): ⊙, spiro; ⊡, cleisto; △, mono; ×, borate; ——, theoretical.

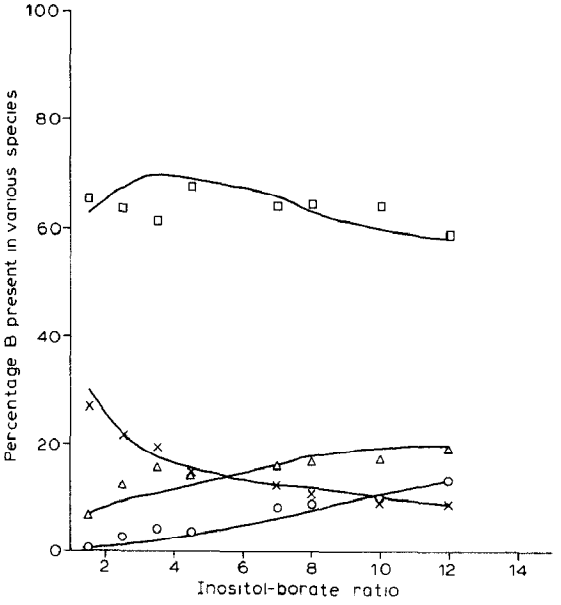

Fig. 3. Comparison of calculated and experimental values of the amounts of different species present in *myo*-inositol–borate mixtures as a function of inositol–borate ratio (all solutions were 0.081M with respect to boron): ⊙, spiro; ⊡, cleisto; △, mono; ×, borate; ——, theoretical.

The formulation of the cleisto complex as a 1:2 inositol–borate species was necessary because, when the data were processed on the assumption that this was a 1:1 complex, no constancy was reached for the equilibrium constants as defined. In the cleisto complex, one boron would be expected to be in tridentate co-ordination with the less-stable conformer of *myo*-inositol, as with cyclohexane-*cis,cis*-1,3,5-triol. The manner of co-ordination of the second boron is open to speculation. Bidentate co-ordination involving the 4,6-positions is sterically possible as in the borate complexes of 1,3-diols. The boron atom would then be in a 6-membered ring. The 1:1 complexes[7] between propane-1,3-diol or butane-1,3-diol and boron have chemical shifts in the range δ 1.6–1.9, *i.e.*, close to the region where resonance due to the cleisto boron occurs. The ^{11}B resonance of the *myo*-inositol cleisto complex is much broader than that found for the cleisto complex of cyclohexane-*cis,cis*-1,3,5-triol and could result from two nearly coincident resonances. If this is so, then it would not be possible to determine from our spectra the proportions of the 1:2 complex and its precursor, the 1:1 cleisto structure.

Comparison of our results with published data on *myo*-inositol–borate systems is not fruitful because the pH and borate concentrations were much lower than those used here and the reactions involved boric acid, not borate ion. Also, we have identified three complexes, whereas only the formation of a 1:1 cleisto complex was considered hitherto.

epi-*Inositol*. — Angyal and McHugh[6] proposed that *epi*-inositol gave a 1:1 complex with boric acid, in which its less-stable conformer forms a tridentate complex. The ^{11}B-n.m.r. results, summarised in Table V, reveal only the cleisto complex (δ −0.07 to −0.14) with $B(OH)_4^-$ resonating at δ 1.70.

TABLE V

EQUILIBRIUM CONCENTRATIONS AND EQUILIBRIUM CONSTANTS FOR COMPLEXATION OF *epi*-INOSITOL[a] BY BORATE AT pH ~12

Inositol–borate molar ratio	$[B(OH)_4^-]$	$[E_s]$	$[E_uB(OH)^-]$	K_tK_c'
9.71:1	—	0.030	0.0035	
4.78:1	—	0.026	0.0069	
1.94:1	0.002	0.017	0.014	411
1:1.04	0.013	0.012	0.016	103
1:1.71	0.026	0.008	0.018	88.9
1:2.07	0.033	0.008	0.015	56.8
1:3.13	0.050	0.008	0.012	34.3
1:4.14	0.061	0.006	0.012	32.8
1:5.52	0.073	0.005	0.010	27.4
1:8.3	0.089	0.004	0.008	22.5
1:16.6	0.112	0.003	0.004	11.9

[a]Initial concentration 0.034–0.007M (and 0.0035–0.116M for boron).

The equilibria to be considered are similar to those for complexation with cyclohexane-*cis,cis*-1,3,5-triol, namely,

$$E_s \overset{K_t}{\rightleftharpoons} E_u$$

and

$$E_u + B(OH)_4^- \overset{K_c}{\rightleftharpoons} E_uB(OH)^- + 3\,H_2O,$$

from which

$$\frac{K_tK_c}{[H_2O]^3} = \frac{[E_uB(OH)^-]}{[E_s][B(OH)_4^-]},$$

where E_s and E_u represent the more- and less-stable conformers of *epi*-inositol, respectively.

As before, $K_c' = K_c/[H_2O]^3$, and the values of K_tK_c' shown in Table V increase monotonically as the proportion of inositol in the mixture increases and as the total molarity of the solute decreases. There are several possible explanations for this finding. First, the total molarity (mol of *epi*-inositol plus mol of borate) was not maintained constant because of solubility restrictions, so that the changing concentration may affect the magnitude of K_c'. Second, the proposed model of a 1:1 complex may be incorrect. However, when other chemically feasible compositions, *e.g.*, 2:1 or 1:2 inositol–borate ratios, were used to calculate K_tK_c', the variation in its value was much greater. Third, no allowance was made for the possible formation of polyborates. Although these are absent from solutions of borate alone at such a high pH, it is possible that some polymeric structures involving *epi*-inositol may develop during complexation.

From MNDO calculations, $(\Delta H_s - \Delta H_u)$ was shown to be -4.097 kJ.mol^{-1} and so $K_t = 1.92 \times 10^{-1}$. Estimates of K_c' varied from 2140 ($K_tK_c' = 411$) to 62.0 ($K_tK_c' = 11.9$), and there is no meaningful single value for this formation constant. Probably, the reaction scheme is too simple and other, more complicated reactions such as polyborate formation also occur.

MNDO Calculations. — The heats of formation of the more- and less-stable chair conformers of cyclohexane-*cis,cis*-1,3,5-triol and of *scyllo*-, *myo*-, and *epi*-inositol have been determined by MNDO LCAO SCF MO calculations with complete geometry optimisation[14], and the results are summarised in Table VI. The difference between the heat of formation for the more-stable (ΔH_s) and less-stable (ΔH_u) conformer is a measure of the overall energy change accompanying inversion of the molecule, whereby axial and equatorial hydroxyl groups are interconverted.

TABLE VI

HEAT OF FORMATION (ΔH/kJ.mol^{-1}) FOR STABLE AND UNSTABLE CONFORMERS OF *scyllo*-INOSITOL, *myo*-INOSITOL, CYCLOHEXANE-*cis,cis*-1,3,5-TRIOL, AND *epi*-INOSITOL, FROM MNDO CALCULATIONS

	ΔH_s	ΔH_u	$(\Delta H_s - \Delta H_u)$/kJ.mol^{-a}
scyllo-Inositol	−1156.49	−1120.98	−35.51
myo-Inositol	−1151.15	−1137.69	−13.46
Cyclohexane-*cis,cis*-1,3,5-triol	−645.44	−636.46	−8.98
epi-Inositol	−1152.43	−1148.33	−4.1

For *scyllo*-inositol, ($\Delta H_s - \Delta H_u$) is 35.5 kJ.mol^{-1}. This is the energy required to convert all six equatorial into axial hydroxyl groups. For *myo*-inositol, inversion generates four axial hydroxyl groups and the ($\Delta H_s = \Delta H_u$) value (−13.46 kJ.mol^{-1}) is much smaller. For cyclohexane-*cis,cis*-1,3,5-triol, inversion generates three axial hydroxyl groups, which requires −8.98 kJ.mol^{-1}. For the inversion of *epi*-inositol, there is a net increase of two axial hydroxyl groups, which requires −4.1 kJ.mol^{-1}.

The estimates of Posternak *et al.*[8] quoted above represent a linear relationship between the free energy of inversion for *scyllo*-, *myo*-, and *epi*-inositol and the net increase in the number of axial hydroxyl groups. Provided that the assumptions made earlier about enthalpies of hydration and entropies of formation are valid, the MNDO calculations show that the relationship is not linear (Fig. 4). The values of the inversion energies of *myo*- and *epi*-inositol are much lower than hitherto supposed. Consequently, relatively little energy may be required for the formation

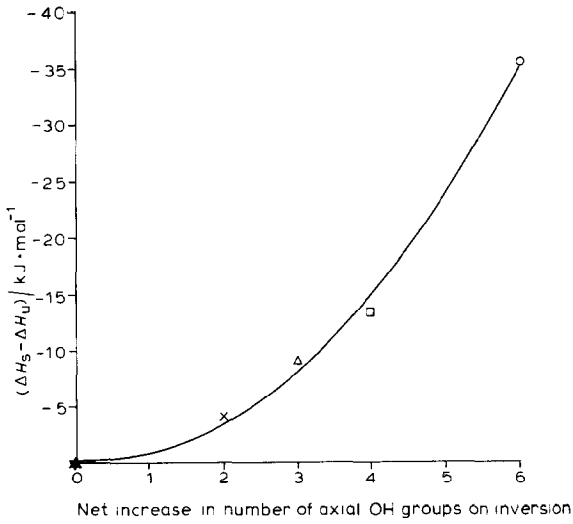

Fig. 4. Relationship between ($\Delta H_s - \Delta H_u$)/kJ.mol^{-1} and the net change in number of axial hydroxyl groups on inversion; ⊙, *scyllo*-inositol; ⊡, *myo*-inositol; △, cyclohexane-*cis,cis*-1,3,5-triol; ×, *epi*-inositol; ★, *cis*-inositol.

of their borate complexes and this may be of some significance in plants where borate–cyclitol interactions are likely. However, MNDO data relate to isolated molecules and must be used with caution to interpret energy changes in solution.

EXPERIMENTAL

myo-Inositol (Sigma) and cyclohexane-1,2-diol (Aldrich) were commercial materials. The latter was shown by g.l.c. to consist of a mixture in which the *cis–trans* ratio was 1.082:1. *epi*-Inositol was prepared by oxidation[15] of *myo*-inositol to *epi*-inosose followed by reduction[16] with $NaBH_4$. Cyclohexane-*cis,cis*-1,3,5-triol was prepared by a modified high-pressure hydrogenation[13,17] of phloroglucinol in the presence of a rhodium/alumina catalyst.

^{11}B-N.m.r. spectra at 28.75 MHz were recorded at 30° with a Jeol FX 90Q FT spectrometer, and the Et_2OBF_3 complex was used as the external reference.

Solutions of weighed quantities of boric acid and the polyol in distilled water were mixed, the pH was raised to ~12 by the addition of aqueous sodium hydroxide, and the final volume was adjusted to 20 mL.

Calculation of equilibrium constants for myo*-inositol–borate complexes.* — The sum of the squares of the errors between experimental and calculated points for each of the four curves was taken as the parameter to be optimised when calculating equilibrium constants. Initial, guessed values were assigned to the three constants K'_s, K'_m, and K'_cK_i, and the error sum was calculated. A random number generator was then used to select one of these constants and the estimate was increased by a small amount, Δk, the error sum calculated and, if this led to a reduction in the sum, the new value of the constant was stored. If not, the value of the constant was reduced by a small increment, Δk, and the error sum checked. If there was an improvement, the new value of the constant was stored. If not, the constant was set at its original value and a new constant (to be varied in the manner described above) was picked out by the random number generator. This procedure was carried out iteratively until there was no further change >0.0001 in any of the three constants generated.

The resulting constants provided the best fit of experimental data, in a least-squares sense, to the proposed model. Convergence to a unique set of equilibrium constants was checked by inputting initial (guessed) constants which were both greater and smaller than the converged value. This algorithm was implemented in BASIC on a microcomputer.

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