Carbohydrate Research, 35 (1974) 165–173

THE STEREOCHEMISTRY OF COMPLEX FORMATION OF POLYOLS WITH BORATE AND PERIODATE ANIONS, AND WITH METAL CATIONS*

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(Received December 10th, 1973; accepted for publication, February 10th, 1974)

ABSTRACT

In alkaline solution, periodate ions form complexes with three consecutive hydroxyl groups in an axial–equatorial–axial arrangement but not with three *syn*-axial hydroxyl groups. Borate ions form complexes with three *syn*-axial hydroxyl groups but not with the *ax–eq–ax* sequence. Accordingly, *cis*-inositol gives a 1,2,3-periodate and a 1,3,5-borate complex. Cations form complexes with either type of conformation, but complex formation provides little energy towards achieving it by ring inversion. Lanthanide ions have been used to establish the sites of complex formation.

INTRODUCTION

It has recently been established that metal cations form complexes in aqueous solution with sugars and cyclitols which have a sequence of three hydroxyl groups in the axial–equatorial–axial arrangement.[1–3] The *ax–eq–ax* arrangement has also been postulated as the site for tridentate complexing with periodate ions in alkaline solution[4,5], and with molybdate and tungstate ions[6]. On the other hand, borate ions are known to form tridentate complexes† only with three *syn*-axial hydroxyl groups[8] (or one amino and two hydroxyl groups[9]). The purpose of the present work was to confirm and explain this stereospecificity and to search for other possible types of complexing sites.

In 1959, Barker and Shaw found[4] that, in solutions buffered to pH 7 or higher, the periodate ion reacts with certain cyclic *cis-cis*-1,2,3-triols to form complexes which decompose only slowly. It was assumed that the formation of such complexes requires the adoption of the conformation of the six-membered ring in which two of the participating oxygen atoms occupy axial positions. A study[5] of the periodate oxidation

*Dedicated to Dr. Horace S. Isbell, in honour of his 75th birthday.

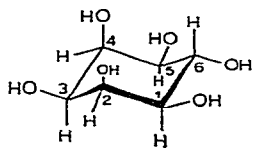
†Only tridentate complexes (those involving three oxygen atoms of the polyol) are discussed in this paper. Bidentate periodate esters are the important, but unstable, intermediates in glycol fission; bidentate borate esters are widely known and used; metal cations form only very weak complexes with two oxygen atoms of a polyol[7].

of the inositols subsequently supported this assumption but direct evidence for the *ax–eq–ax* attachment was not produced.

Such direct evidence has now been obtained by the study of n.m.r. spectra.

RESULTS AND DISCUSSION

When one equiv. of sodium periodate and one of sodium carbonate are added to a solution of *epi*-inositol (**1**) in deuterium oxide, a substantial change is noted in the n.m.r. spectrum. The coupling constants remained unaltered, indicating no change in the conformation of the molecule, but all the signals had shifted downfield, H-1, H-5 by 0.07, H-2, H-4 by 0.19, H-3 by 0.55, and H-6 by 0.195 p.p.m. These shifts are in the same relative proportion as those caused[10] by complexing with a metal cation at the *ax–eq–ax* site, O-2, O-3, O-4; H-3 is most affected because its bond with C-3 points approximately towards the complexing ion[1]. Complex formation is slow on the n.m.r. time-scale: when less than one equiv. of periodate is added, the spectra of the complexed and uncomplexed cyclitol are both observed. The complex is reasonably stable: the spectrum was still clearly distinguishable one day later.



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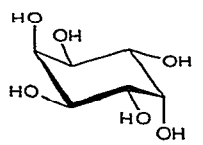

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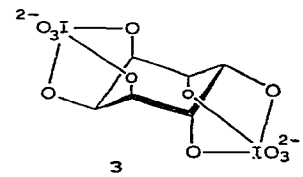

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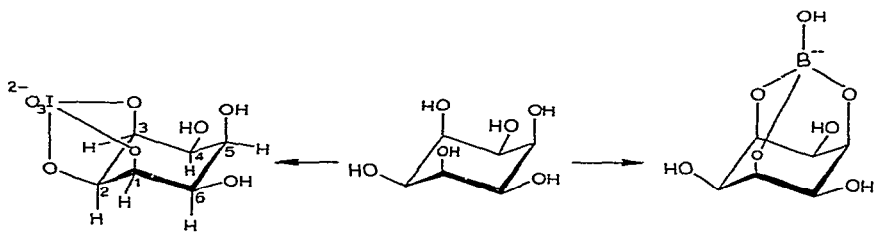
A more-informative case is that of *neo*-inositol (**2**). In its more stable conformation, it has no *ax–eq–ax* sequence, but inversion to the other chair form (which requires an estimated 13.0 kJ.mole^{-1} of free energy[11]) produces two such sequences. From his titration data, Barker concluded[5] that *neo*-inositol forms a complex (**3**) with two periodate ions. The n.m.r. spectra confirm this conclusion. The spectrum of *neo*-inositol consists of a doublet at δ 3.72 (J 1 Hz, axial H) and a triplet at 4.05 (equatorial H). When less than 2 equiv. of periodate are added, the spectrum of the complex is obtained, as well as that of the cyclitol. With more than 2 equiv. of periodate, two singlets (or one doublet) appear at δ 4.35 and 4.37. If the chair inverts to form *ax–eq–ax* complexes (**3**), and the shielding effect of the periodate ion is the same as in the *epi*-inositol complex, both proton signals would be expected to be near δ 4.35. Since it has no free hydroxyl groups which could be attacked by periodate, this complex is particularly stable.

In contrast to their behaviour with periodate ion, *neo*-inositol forms no tridentate complex with the borate ion, and *epi*-inositol inverts to its alternative chair form (which requires $\sim$13.0 kJ.mole^{-1} of free energy[11]) and forms a triaxial borate complex[8].

N.m.r. spectroscopy has been used once before to determine the structure of a tridentate periodate complex, namely, that formed from 1,2-*O*-isopropylidene-α-D-

glucofuranose[12]. This is not an *ax–eq–ax* complex; the ester is formed at O-3, O-5, and O-6, and, accordingly, the signals of H-3, H-5, H-6, and H-6′ are shifted downfield in the complex. Complexing here involves a change in the conformation of the molecule, which also alters the chemical shifts; in addition, one of the negatively charged oxygen atoms linked to the iodine atom is close in the complex to H-2 and causes its n.m.r. signal to shift upfield.

cis-Inositol (**4**) provides more information on the stereospecificity of complex formation. *cis*-Inositol is a unique molecule which contains three *syn*-axial hydroxyl groups in each of its equivalent chair conformations. Recent X-ray crystallographic analysis[13] has shown that each axial oxygen atom is equidistant from four others (2 axial, 2 equatorial). There are three *ax–eq–ax* sequences in addition to the *syn*-axial group of three oxygen atoms; the *ax–eq–ax* and the *syn*-axial oxygen atoms form similar geometrical arrangements but their reactivity towards complex-forming reagents is different.



6 **4** **5**

The spectrum of *cis*-inositol at room temperature consists of two peaks which are not completely separated; at 0°, they are fully separated and narrow. These represent the axial and equatorial hydrogen atoms, respectively. Because each hydroxyl group has to pass between two other hydroxyl groups during ring inversion, this inversion is slow on the n.m.r. time-scale, and the coalescence temperature of the two signals is above ambient temperature. (*cf.* ref. 14). The signal at δ 3.68 is assigned to the axial, and that at 4.03 to the equatorial, hydrogen atom by comparison with those of H-3 (3.70) and H-2 (4.05) of *epi*-inositol (**1**), which are in the same environment. On addition of sodium tetraborate, the two signals remain but become sharper and shift slightly upfield to δ 3.49 and 3.95 (Fig. 1). In the borate complex, therefore, the equivalence of all equatorial and of all axial hydrogen atoms has been retained; the complex (**5**) must be triaxial. On addition of one equivalent of sodium periodate and one equivalent of sodium carbonate, the spectrum changes completely (Fig. 1) and shows four signals. A 2-proton signal (δ 3.78) and a 1-proton signal (δ 4.00) remain close to their original positions: these must be due to H-4,6 and H-5, respectively. A 2-proton signal at δ 4.32 must be that of H-1,3, and a 1-proton signal much shifted downfield (δ 5.43) must be that of H-2. The complex therefore is of the *ax–eq–ax* type (**6**), as postulated by Barker[5]; it is worth noting that the downfield shift of the central hydrogen atom is much larger than in the case of *epi*- and *neo*-inositol. The

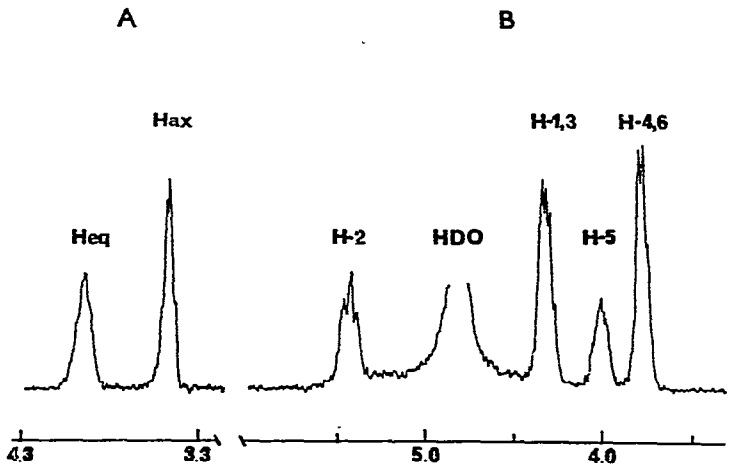


Fig. 1. The 100-MHz n.m.r. spectrum of A, *cis*-inositol borate-complex; B, *cis*-inositol periodate-complex.

spectrum is hardly changed after 24 hours but the signal of formic acid is then visible at δ 8.43.

The choice of complexing site by the two anions is quite specific. This explains also why *cis*-1,3,5-cyclohexanetriol forms a triaxial complex with borate[8] but none with periodate ion. Most of the known tridentate borate complexes are triaxial, with the possible exception of the complexes formed with 2,4-di-*O*-methyl-D-mannose[15] and with 1,2-*O*-isopropylidene-α-D-glucofuranose (the tridentate nature of which has not been definitely established)[15].

It appears that borate ion requires a triaxial site because, with the short B–O distance (1.36 Å), this will provide tetrahedral bond-angles at the oxygen and boron atoms. At the *ax–eq–ax* site, the bond angles would have to be considerably diminished to allow complex formation. By contrast, the long I–O bond (1.85 Å) and the octahedral bonding of the iodine atom fit into the *ax–eq–ax* site without distortion; much distortion would be required to fit the periodate into the triaxial site.

The co-ordinate bonds of the metal complexes are much less sensitive to (or probably independent of) bond angles. The *ax–eq–ax* site complexes well with metal cations[1] having an ionic radius larger than ~0.8 Å. *cis*-Inositol provides evidence that the triaxial site complexes even better with cations. Addition of europium nitrate to its solution causes a shift of both signals upfield; addition of praseodymium chloride moves both signals downfield; in each case, that of the equatorial hydrogen atoms shifts to a greater extent. Numerous examples have shown[16,17] that europium ion shifts the signal of the central hydrogen atom in the *ax–eq–ax* sequence upfield but that of the neighbouring hydrogen atoms downfield; the praseodymium-induced shifts are in the opposite direction. The differing behaviour of *cis*-inositol indicates that the preponderant complex is not of the *ax–eq–ax* type; therefore it must be

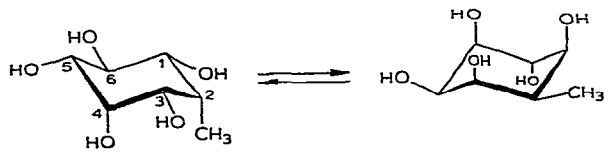
triaxial. When a hydrogen atom is so located in the cation –O–C–H sequence that the C–H bond is antiparallel to the O-cation bond, the signal of the hydrogen atom is strongly shifted upfield by europium, and downfield by praseodymium ion[17]. The equatorial hydrogen atoms in the triaxial complexes of *cis*-inositol are thus located.

Further evidence is provided by complexing of smaller cations. Magnesium and zinc complex very weakly with *ax–eq–ax* sites[3], but electrophoresis shows that they complex reasonably well with *cis*-inositol[18]; the complexes must be triaxial. Complexing is also shown by the n.m.r. spectra: addition of magnesium or zinc ions shifts both signals downfield This behaviour differs characteristically from that caused by larger ions, indicating that the complexing site is different: whereas lanthanum ion shifts the axial-proton signal to a slightly greater extent than the equatorial one, zinc or magnesium ions cause a much larger shift of the equatorial-proton signal. The reason why smaller ions prefer the triaxial site is probably because the effective distances between axial oxygen atoms can easily be diminished (and complexing then diminishes the interaction between them); those in the *ax–eq–ax* sequence are not so easily diminished. Still smaller ions do not form complexes with either site: addition of aluminum or lithium salts causes no change in the spectrum of *cis*-inositol.

Neither *neo*-inositol nor *cis*-1,3,5-cyclohexanetriol form strong complexes with metal ions: the energy of complex formation with cations appears insufficient for the required chair–chair inversion. It is surprising, therefore, that DL-2-deoxy-2-methyl-*epi*-inositol[18] (7) forms a complex nearly as readily as does *epi*-inositol (M_i 0.34, compared to 0.42 for *epi*-inositol*). The predominant conformation of this cyclitol (7) contains neither a triaxial nor an *ax–eq–ax* site; ring inversion to the less-stable chair form (8) provides both, but the energy required for this process is calculated to be about the same as for the inversion of *neo*-inositol. That inversion occurs on complex formation is shown by the shift of the signal of H-2 upfield (from δ 2.31 to 2.08, *eq* to *ax*) and of the methyl group downfield (from δ 1.05 to 1.14, *ax* to *eq*) on addition of 6.0 equiv. of calcium chloride. Both the triaxial and the *ax–eq–ax* site are involved in complex formation, as shown by the following evidence: (*i*) in the spectrum of the complex formed with lanthanum ion, all the signals appear at higher field than in the spectrum of the calcium complex. Lanthanum induces larger shifts than calcium[3], but when complexed at O-3, O-4, O-5, it would not shift the signal of H-1 and H-2 to a greater extent. (*ii*) Magnesium (5.35 equiv.) also causes ring inversion, shifting H-2 to δ 2.23 and the methyl group to δ 1.09; its complexing ability appears to be about a third of that of calcium. This complexing must occur at the triaxial site because magnesium ion forms only very weak complexes with the *ax–eq–ax* sequence[3]. (*iii*) Addition of even very small amounts (0.01 equiv.) of europium nitrate broadens the signals of H-1, H-3, and H-5. Larger amounts cause considerable, upfield shifts of these signals and also of that of H-4; H-2 shifts slightly upfield, and only H-6 remains unaffected and sharp. Complexing at O-1, O-3, O-5 alone would not cause an upfield

*Electrophoretic mobilities were determined[9], relative to that of *cis*-inositol, in 0.2M solution of calcium acetate containing 0.2M acetic acid.

shift of H-4, nor would complexing at O-3, O-4, O-5 alone cause an upfield shift of H-1. Similarly, addition of praseodymium chloride shifts all signals (except possibly that of H-6) downfield, proving that complexing occurs at both sites.



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2-Deoxy-2-methyl-*epi*-inositol readily complexes also with borate and periodate ions, with ring inversion. The borate ion reacts with the three axial hydroxyl groups[19], and periodate forms an *ax–eq–ax* complex, as shown by the downfield shift of the signal of H-4.

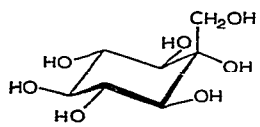
It is not clear why 2-deoxy-2-methyl-*epi*-inositol should form complexes so readily with metal ions. Possibly, complexing with three *syn*-axial oxygen atoms provides more energy than complexing at other sites, by diminishing the repulsive interactions between these atoms; and complexing at the *ax–eq–ax* site may lessen the triaxial interactions by diminishing the electron density on the oxygen atoms involved in complex formation. The explanation will have to wait until a compound containing only a *syn*-axial complexing site is investigated.

In order to estimate the magnitude of the driving force provided by complex formation with periodate, 1,2,3,5/4-cyclohexanepentol was investigated. This compound has the same structure and configuration as 2-deoxy-2-methyl-*epi*-inositol, except that it lacks the methyl group. Chair inversion provides an *ax–eq–ax* and a triaxial site, but this inversion requires ~21 kJ.mole^{-1} of free energy[11]. It forms a complex with periodate ion but its equilibrium constant is smaller than that of the other complexes discussed. When 1.3 equiv. of periodate were added, only 75% of the cyclitol was converted into the complex (as estimated from the n.m.r. spectrum), but after the addition of 4.2 equiv. the signals of the uncomplexed compound were no longer visible in the spectrum.

Attempts have been made to find other sites, besides the *ax–eq–ax* and triaxial ones, for complexing with cations. A vicinal *cis–cis* triol on a five-membered ring complexes well[1,3], but this is essentially the same arrangement as the *ax–eq–ax* grouping on a six-membered ring. Alditols will complex to the extent that they can take up a conformation similar to the *ax–eq–ax* arrangement[19]. An interesting grouping, because it occurs in ketopyranoses, consists of a geminal hydroxyl and hydroxymethyl group and a vicinal, equatorial hydroxyl group; these oxygen atoms can also take up a conformation similar to the *ax–eq–ax* arrangement. *C*-Hydroxymethyl-*scyllo*-inositol[20] (**9**) was used to study this arrangement. It migrates fairly well in 0.02M calcium acetate solution (M_i 0.12), and addition of europium nitrate to its solution in deuterium oxide causes a substantial, upfield shift of the signal of the

methylene group, and a smaller, downfield shift of that of H-2,6. This is in accordance, as found in the study of alditols[19], with complexing occurring at C-1, C-1′, and C-2 (and C-1, C-1′, and C-6).

The C-1 epimer, 2-*C*-hydroxymethyl-*myo*-inositol[20] (**10**) also complexes with cations, but rather weakly (M_i 0.08). When the hydroxymethyl group is axial (as in **9**), all the three staggered conformations of the hydroxyl group are subject to unfavourable interactions; hence, attainment of the conformation suitable for complexing (C-1′–O-1′ parallel to C-2–O-2) requires little energy. When the hydroxymethyl group is equatorial (as in **10**), it has one relatively unhindered, rotational conformation, and complex formation requires the expenditure of more energy. It appears that this arrangement is of little importance for complex formation in ketoses; in neither of the two crystalline adducts of calcium chloride with β-D-fructopyranose is the cation found[21] to be in a tridentate position.



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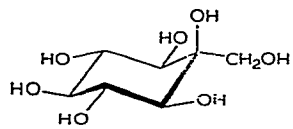

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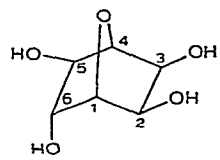

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The O-3, O-5, O-6 grouping of hexofuranoses, which allows the ready formation of tridentate periodate[12], orthoformate[22], and probably borate[15] esters, does not form stable complexes with cations. In solution, the side chain of 1,2-*O*-isopropylidene-α-D-glucofuranose is in the extended zig-zag form, in which O-3 and O-6 are not close to each other; addition of calcium chloride does not change this conformation ($J_{4,5}$ remains unchanged at 8.5 Hz, whereas in the periodate complex it drops[12] considerably). Addition of europium ions, a very sensitive test of complex formation, causes only minor changes in the chemical shifts. Apparently, the energy required for this conformational change (in contrast to that required when the three hydroxyl groups are contiguous) is too large for complex formation with cations.

The two axial oxygen atoms on C-2 and C-4, and the ring-oxygen atom in 1,6-anhydro-β-D-glucopyranose are in a similar geometrical arrangement to those in an *ax–eq–ax* sequence. Nevertheless, only a weak complex is formed (M_i 0.07), possibly because the electron density on the ring-oxygen atoms is lower than on the others[23], or because the distance between O-2 and O-4 is larger (3.3 Å) than in monocyclic pyranoses[24]. Complex formation of this and of related compounds is being studied with the aid of lanthanide ions.

At the suggestion of Dr. J. A. Mills, 1,4-anhydro-*epi*-inositol[25] (**11**) was investigated; it appeared possible that cations would complex with O-2, O-3, and the oxygen atom in the bridge. It was found to form a rather weak complex (M_i 0.08). On addition of europium nitrate, the signals of H-2 and H-3 in the n.m.r. spectrum move upfield, whereas those of the other hydrogen atoms move downfield. This is in accordance with the postulated structure in which Eu, O-2, C-2 and H-2 are in a plane,

and Eu, O-3, C-3, and H-3 are also in a plane. This molecule therefore contains a different type of complexing site, but the complexes formed are weaker than those at *ax–eq–ax* sites. It is not certain that the ring–oxygen atom takes part in complex formation; camphane-2,*endo*-3,*endo*-diol and camphane-2,*exo*-3,*exo*-diol[26], which also have two eclipsed hydroxyl groups, show induced shifts of similar magnitude on addition of europium nitrate.

EXPERIMENTAL

N.m.r. data. — N.m.r. spectra were run on a JNM-4H-100 spectrometer in deuterium oxide solution at 25°; chemical shifts were measured from sodium 4,4-dimethyl-4-silapentane-1-sulphonate as internal standard. Cations were added as chlorides or nitrates in several aliquots to allow the shift of each proton to be followed.

The n.m.r. spectrum of *epi*-inositol has been published[2,27]: δ 3.55 (H-1,5), 3.70 (H-3), 3.83 (H-6), 4.05 (H-2,4). Periodate complex: δ 3.62 (H-1,5), 4.02 (H-6), 4.24 (H-2,4), 4.25 (H-3). For borate complex, see ref. 27.

cis-Inositol: δ 3.68 (*ax*), 4.03 (*eq*). Inositol (0.05M) + $LaCl_3$ (0.23M): 3.85 and 4.15. Inositol (0.28M) + $MgSO_4$ (2.45M): 3.79 and 4.24. Inositol (0.16M) + $Zn(NO_3)_2$ (0.88M): 3.80 and 4.30. Inositol (0.125M) + $Eu(NO_3)_3$ (13mM): 3.48 and 3.58. Inositol (0.11M) + $PrCl_3$ (56mM): 3.86 and 4.41.

DL-2-Deoxy-2-methyl-*epi*-inositol[19]: δ 1.05 (*d*, $J_{2,Me}$ 7.5 Hz, Me), 2.31 (*m*, H-2), 3.48 (*d* of *d*, $J_{4,5}$ 3.2, $J_{5,6}$ 9 Hz, H-5), 3.58 (*d* of *d*, $J_{1,2}$ 4.8, $J_{1,6}$ 10 Hz, H-1), 3.78 (*t*, $J_{5,6}$ 9 Hz, H-6), 3.80 (*t*, $J_{2,3}$ 4, $J_{3,4}$ 3.5 Hz, H-3), 4.03 (*t*, H-4). Borate complex, see ref. 19. Periodate complex: δ 1.22 (*d*, Me), 2.09 (*m*, H-2), 3.64 (broad *s*, H-1), 4.15 (broad, H-3,6), 4.35 (*t*, *J* 2.75 Hz, H-5), 5.33 (*t*, H-4). The last two signals were assigned by comparison with the spectrum of *cis*-inositol periodate, the others by decoupling: irradiation at δ 3.64 and 4.15 caused collapse of the signal at 2.09. Cyclitol (0.36M) + $CaCl_2$ (2.15M): δ 1.14 (Me), 2.08 (H-2), 3.72 (H-1), 3.93–4.03 (3H), 4.11 (H-6 or H-5). Cyclitol (0.40M) + $LaCl_3$ (1.89M): 1.165 (Me), 2.17 (H-2), 3.83 (H-1), 4.02–4.12 (3H), 4.22 (H-6). Cyclitol (0.47M) + $MgCl_2$ (2.49M): 1.09 (Me), 2.23 (H-2), Cyclitol (0.29M) + $Eu(NO_3)_3$ (0.09M): 1.06 (Me), 2.19 (H-2), 2.5–4.0 (4H), 4.03 (H-4). Cyclitol (0.36M) + $PrCl_3$ (0.08M): 1.15 (Me), 2.50 (H-2), >4.0 (5H).

DL-1,2,3,5/4-Cyclohexanepentol: δ 1.55–2.12 (*m*, CH_2), 3.39–3.59 (*m*, H-3,4,5), 3.79 (X part of ABX pattern, $J_{1,6}$ 11.5, $J_{1,6'}$ 5.0, $J_{1,2}$ 3.0 Hz, H-1), 4.01 (broad *s*, H-2). Periodate complex: δ 2.07, 2.40 (pairs of broad *s*, J_{gem} ~15 Hz, CH_2), 3.83 (H-5), 4.20–4.34 (H-1,3,4), 5.37 (H-2), by analogy with 2-deoxy-2-methyl-*epi*-inositol.

C-Hydroxymethyl-*scyllo*-inositol[20]: δ 3.31 (*t*, $J_{3,4}$ 9.0 Hz, H-4), 3.45 (*d*, $J_{2,3}$ 9.5 Hz, H-2,6), 3.65 (*d* of *d*, H-3,5), 3.79 (*s*, CH_2). In a solution 0.116M in cyclitol and 38mM in europium nitrate, the induced shifts were: H-4, 0.035; H-2,6, 0.07; H-3,5, 0.02; CH_2, —0.085 p.p.m.

1,4-Anhydro-*epi*-inositol[25]: δ 3.63 (*d*, $J_{5,6}$ 1.6 Hz, H-5), 3.93 (*d* of *t*, $J_{1,6}$ 5.2, $J_{4,6}$ 1.4 Hz, H-6), 4.01 (*d*, $J_{2,3}$ 6.4 Hz, H-3), 4.16 (*t*, $J_{1,4}$ 1.4 Hz, H-4), 4.35 (*d* of *d*, H-1), 4.37 (*d*, H-2). In a solution 0.57M in the cyclitol and 0.125M in europium nitrate,

the induced shifts were: H-5, 0.02; H-6, 0.01; H-3, —0.18; H-4, 0.07; H-1, 0.06, and H-2, —0.18 p.p.m. As an aid to the assignment of the signals, the spectrum of 5,6-di-*O*-acetyl-1,4-anhydro-*epi*-inositol[25] was determined in deuterichloroform: δ 2.10, 2.13 (*s*, Me), 3.58 (*s*, OH), 4.13 (H-3), 4.26 (H-2), 4.31 (H-4), 4.56 (H-1), 4.62 (H-5), 4.90 (H-6); the multiplicities and coupling constants were the same as those of the parent cyclitol. The downfield shift of $\sim$1 p.p.m. on acetylation identifies the signals of H-5 and H-6.

Camphane-2,*endo*-3,*endo*-diol[26]: n.m.r. spectrum, see ref. 28. On addition of 0.47 equiv. of europium nitrate to its solution in acetone–deuterium oxide (1:1), the signal of H-2 shifted 0.46, and that of H-3 0.65 p.p.m., upfield. Camphane-2,*exo*-3,-*exo*-diol[26,28]: on addition of 0.77 equiv. of europium nitrate to its solution in acetone, the signal of H-2 shifted 0.75 p.p.m. downfield, but that of H-3 did not shift. The three methyl signals also shifted downfield, one particularly strongly.

ACKNOWLEDGMENTS

This research was supported by a grant from the Australian Research Grants Committee. The authors thank Dr. J. A. Mills for determining the electrophoretic mobilities, and for valuable discussions.

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