RAPID COMMUNICATIONS IN MASS SPECTROMETRY
Rapid Commun. Mass Spectrom. **13**, 2406–2415 (1999)

Structural Analysis of Diols by Electrospray Mass Spectrometry on Boric Acid Complexes

Suzanne Z. Ackloo[1], Peter C. Burgers[2], Brian E. McCarry[1] and Johan K. Terlouw[1]*

[1]Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada
[2]Hercules B.V., Hercules European Research Center, P.O. Box 252, 3770 AG Barneveld, The Netherlands

A method is presented to characterize diols using negative ion electrospray (ES) mass spectrometry in combination with collision-induced dissociation tandem mass spectrometry (MS/MS). The analyte diol is added to a solution containing an ethylene glycol/boric acid [2:1] complex and then subjected to infusion ES. The following boric acid complexes are formed: (i) a complex with two ethylene glycol molecules, (ii) a mixed ethylene glycol/analyte complex, and (iii) a complex with two analyte molecules. The first complex serves as a reference for the assessment of the extent of complex formation with the analyte.

The ES mass spectra of acyclic vicinal diols all feature intense mixed complex signals, indicative of efficient complex formation. Chemical fine tuning is achieved by MS/MS experiments. Thus, although the (2*R*,3*R*)-(−)-2,3-butanediol and *meso*-2,3-butanediol stereo-isomers show the same complexation efficiency, MS/MS experiments reveal pronounced structure characteristic differences. By contrast, 1,3- and 1,4-diols are less prone to complex formation as they give only weak signals relative to the reference. For cyclic vicinal diols only the *cis* isomer produces an intense mixed complex, whose MS/MS spectrum is characteristically different from that of the *trans* form. The above procedure does not permit an unambiguous differentiation of acyclic polyhydroxy compounds like mannitol and sorbitol. However, structurally related methyl glycosides show characteristic MS/MS spectra.

Our findings indicate that the above simple procedure may be useful to probe the presence and structure of diols and other polyols in aqueous solutions. Copyright © 1999 John Wiley & Sons, Ltd.

Received 27 August 1999; Revised 6 October 1999; Accepted 8 October 1999

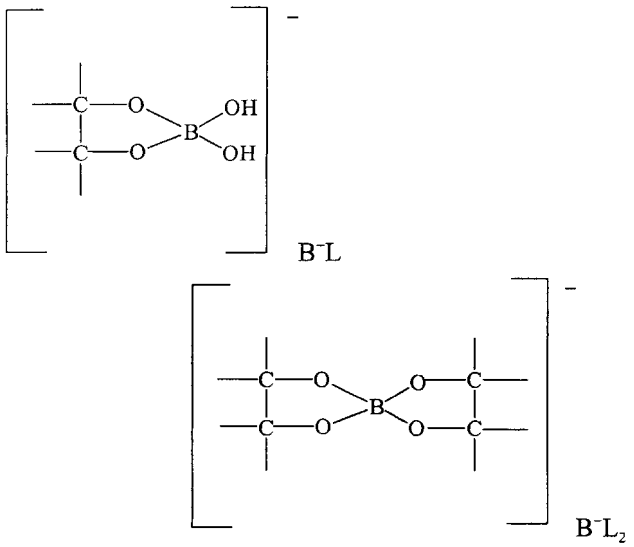
Boron has three valence electrons and forms planar, tricovalent derivatives that are electron deficient. These derivatives act as Lewis acids by accepting two electrons from bases to complete the outer shell octet of boron; the two reactants (the boron derivative and the Lewis base) form stable coordinate covalent complexes, many of which are commercially available. For example, boron trifluoride diethyl etherate [$(C_2H_5)_2O^+$-BF_3^-] is widely used as a catalyst for esterifications and acylations. Any substance having free electron pairs can accommodate a proton and so Lewis bases are identical to Brønsted-Lowry bases. By contrast, Lewis acids are not necessarily proton donors. A case in point is boric acid $B(OH)_3$.[1] An aqueous solution of boric acid is weakly acidic, but not because boric acid deprotonates by itself; rather it can only generate protons after hydration has taken effect:

$$B(OH)_3 + H_2O \rightleftarrows B(OH)_4^- + H^+$$

In fact, the intermediate complex $B(OH)_3OH_2$[2] acts as the Brønsted acid.

It has long been known that boric acid reacts efficiently with certain hydroxy compounds in aqueous solution, leading to a decrease in pH.[3] Over 150 years ago, Biot reported that a solution of boric acid became acidic to litmus upon the addition of sugar.[4,5] In fact, the extent to which the pH of solutions containing boric acid decreases upon addition of a polyhydroxy compound has been used as an indication of the ease of chelate formation. In 1949, Deutsch and Osoling[5] investigated the boric acid–mannitol system. Mannitol (compound **14** in Scheme 1) contains six hydroxyl groups of which two pairs (C2 and C3, and C4 and C5) are *cis* to each other, allowing easy formation of the complex. In solution mannitol does not have restricted movement so it is likely that the terminal hydroxyl groups rotate to a position that allows easy complex formation. This increases the number of combinations of hydroxyl groups which can complex with boric acid. Deutsch and Osoling[5,6] described the formation of two types of complexes:

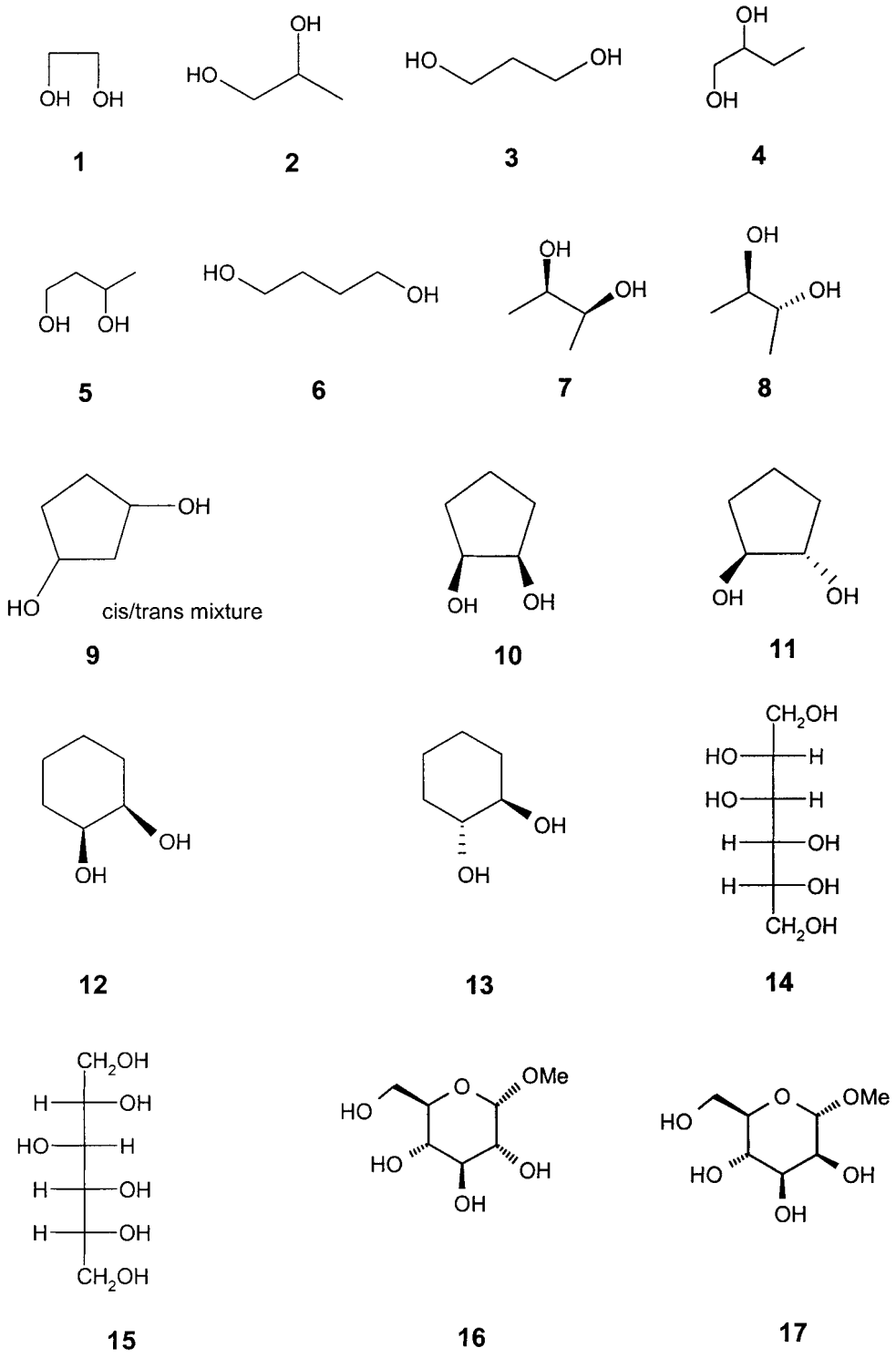
(i) a1:1[1M] complex, also referred to as B^-L complex
(i) a2:1[2M] complex, also referred to as B^-L_2 complex



Titration of a boric acid/mannitol solution with sodium hydroxide showed that the [1M] complex ($K = 3 \times 10^2$) predominates when there is excess boric acid while the [2M] complex ($K = 5 \times 10^4$) is the principal species when there is excess mannitol.

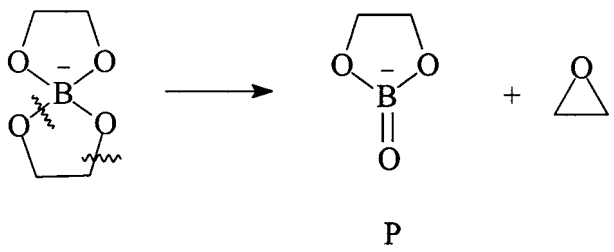
*Correspondence to: J. K. Terlouw, Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4M1, Canada.
E-mail: terlouwj@mcmaster.ca
Contract/grant sponsor: The Natural Sciences and Engineering Research Council of Canada.

CCC 0951–4198/99/232406–10 $17.50



Scheme 1.

Although potentiometry provided initial evidence for the existence of these complexes, conductometry, polarimetry, electrophoresis, refractometry, nuclear magnetic resonance (NMR) spectroscopy[1] and circular dichroism[7] have also been used for their characterization. NMR spectroscopy is one technique that has often been used to characterize borate esters. Carbon-13 (^{13}C), proton (^{1}H), and boron-11 (^{11}B) NMR spectroscopy have been used either in conjunction with each other, or separately, to analyze the complexes. In particular, association constants for many [1M] and [2M] borate esters, including those of 1,2-ethanediol and 1,2-propanediol, have been obtained.[6,7] Further, Chapelle and Verchere used ^{11}B and ^{13}C NMR spectroscopy to show that sugars of the *ribo* series have a higher affinity for boric acid relative to the *xylo* series.[8] In solution, sugars equilibrate between the α/β-furanose and α/β-pyranose forms. *Xylo* sugars exist mainly in the pyranose form which implies that the hydroxyl groups are in a *trans* orientation. As a result



P

Scheme 2.

chelate formation between *xylo* sugars and boric acid is less facile.

Several applications based on affinity chromatography have been reported wherein (stereo) isomeric polyols have been separated. One example is the use of affinity chromatography to separate sugars by using an anion-exchange stationary phase.[9,10]

Mass spectrometry has also been used in studies of boric acid complexes of polyols and carbohydrates using negative ion ES and fast atom bombardment,[11] thermospray[12] and matrix-assisted laser desorption[13] techniques. In addition, Bayer *et al.*, in a recent communication[14] on coordination-ionspray-MS (CIS-MS), have reported that under the conditions selected for CIS-MS, fructose produces a stable [2M] complex whereas glucose does not.

In this contribution we have applied the concept of boric acid complexation to explore structural analysis of isomeric polyols using negative ion ES in conjunction with collision-induced dissociation of the complexes. The selected group of (stereo) isomeric polyhydroxy compounds is listed in Scheme 1.

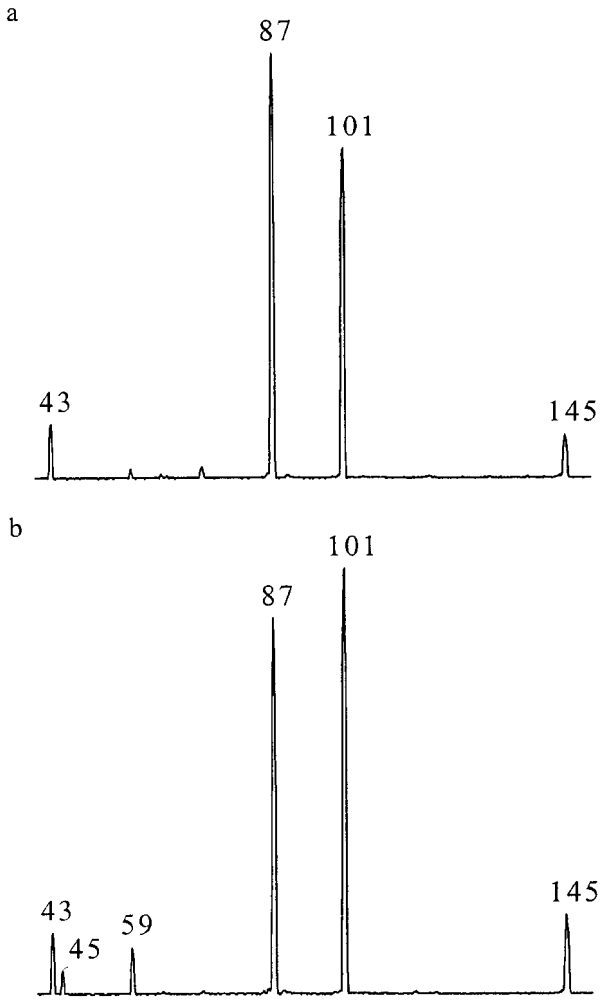


Figure 1. Negative ion ES-MS/MS spectra of the (*m/z* 145) mixed complexes of (a) 1,2-propanediol, ethylene glycol and boric acid and (b) 1,3-propanediol, ethylene glycol and boric acid.

EXPERIMENTAL

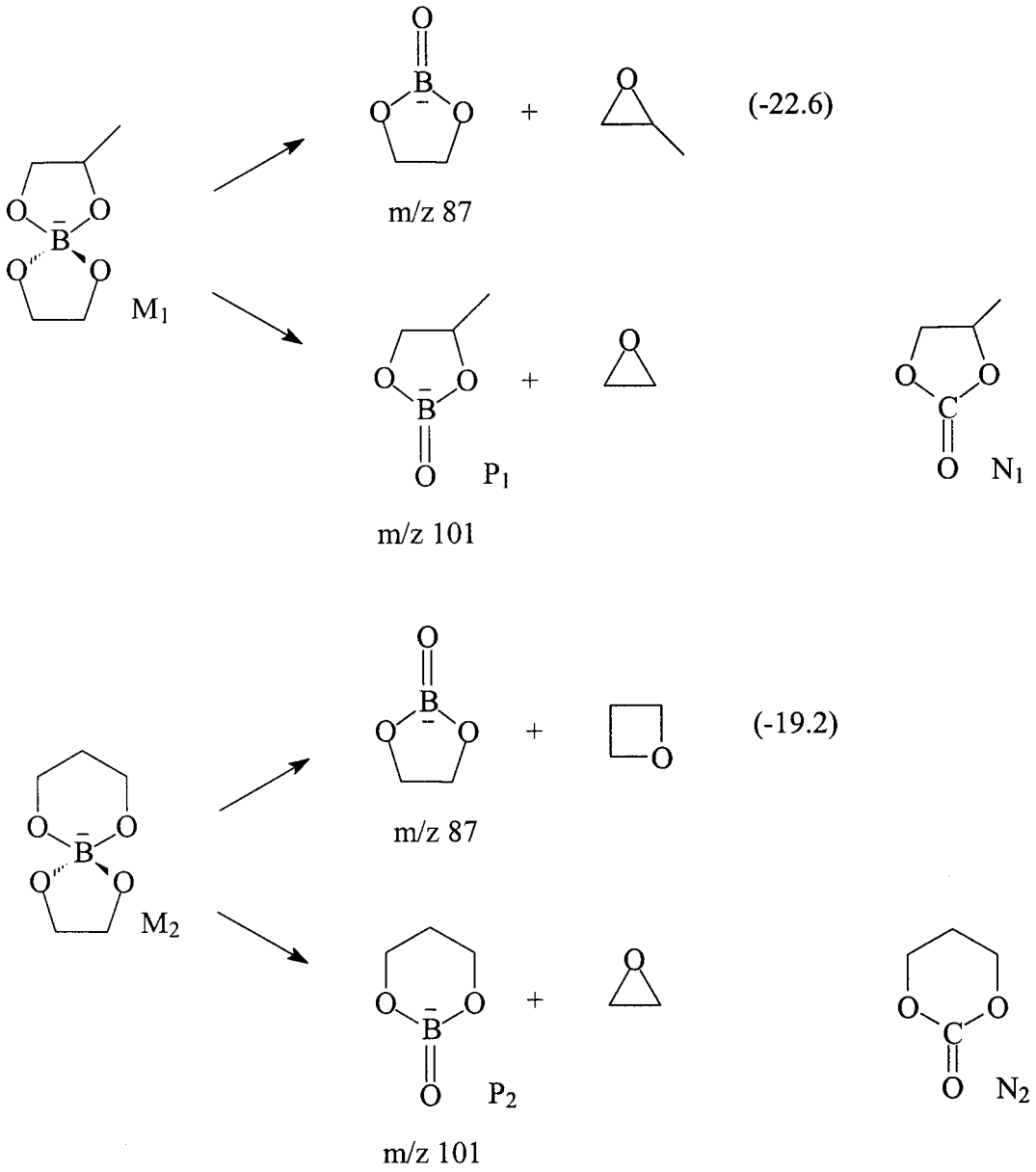
Boric acid was obtained from CP Baker while ^{10}B-boric acid was purchased from Sigma-Aldrich. For all experiments HPLC-grade methanol and distilled de-ionised water was used. The compounds listed in Scheme 1, 1,2-ethanediol (ethylene glycol) (**1**), 1,2-propanediol (**2**), 1,3-propanediol (**3**), 1,2-butanediol (**4**), 1,3-butanediol (**5**), 1,4-butanediol (**6**), *meso*-2,3-butanediol (**7**), (2*R*,3*R*)-(−)-2,3-butanediol (**8**), 1,3-cyclopentanediol [mixture of *cis* and *trans* isomers] (**9**), *cis*-1,2-cyclopentanediol (**10**), *trans*-1,2-cyclopentanediol (**11**), *cis*-1,2-cyclohexanediol (**12**), *trans*-1,2-cyclohexanediol (**13**), D-mannitol (**14**), D-sorbitol (**15**), α-methyl-D-glucopyranoside (**16**) and α-methyl-D-mannopyranoside (**17**) were purchased from Sigma-Aldrich and used without further purification. The deuterium-labelled 1,2-propanediol isotopologues were a gift from Dr A. Milliet (Ecole Polytechnique, Palaiseau, France).

Negative ion ES-MS and MS/MS experiments were performed on a McMaster Quattro LC (Micromass, England) triple quadrupole instrument. Normal mass spectra were acquired with the cone set at 30 V, the capillary at 4 kV, the high voltage lens at 0.2 kV, and the multiplier at 700 V. Product ion spectra were obtained using Argon as the collision gas. Typically, a collision energy of 22 eV was used with a gas cell pressure of 2.5×10^{-3} mBar and the multiplier at 800 V. The analyte was infused via a pneumatically assisted Rheodyne 7010 injector equipped with a 20 μL injection loop. In all experiments a CH_3OH/H_2O (1:1) mobile phase was delivered at a flow rate of 10 μL/min via a Brownlee pump (Advanced Biosystems, Canada). All spectra were acquired for 2 min.

RESULTS AND DISCUSSION

Preliminary experiments

Preliminary experiments indicated that 1,2-diols such as 1,2-ethanediol (ethylene glycol), 1,2-propanediol and mannitol complexed easily with boric acid. Ethylene glycol is the simplest dihydroxy compound that can form a complex with boric acid and therefore it was chosen as an internal standard in comparative experiments. The idea was that if we mix a particular diol [B] and ethylene glycol [A] in a ratio of 1:1 and find a [2M] complex of boric acid and ethylene glycol [AA], a mixed complex of boric acid, the diol and ethylene glycol [AB], and a [2M] complex of boric acid and the diol [BB] in a ratio of 1:2:1, then complex formation of the diol occurs at the same rate as for ethylene glycol. In addition, MS/MS



Scheme 3.

experiments on the mixed complex [AB] would allow us to obtain information as to the configuration of the hydroxyl groups of the diol [B]. Unfortunately, we found that boric acid tends to remain adsorbed in the analyte delivery system, leading to memory effects and irreproducible results. However, we also found that boric acid memory effects do not occur when the infused samples contain ethylene glycol in a two-fold excess. Therefore, in all experiments we used a molar ratio of the diol to ethylene glycol to boric acid of 1:2:1. Because borate formation is reversible, a stock solution of boric acid and ethylene glycol may be prepared and used in comparative experiments. The analyte was prepared as follows. From 1% (w/v) solutions of boric acid or its ^{10}B isotopomer in CH_3OH/H_2O (1:1), stock solutions were prepared containing boric acid and ethylene glycol in a 1:2 molar ratio. To an aliquot of this solution the analyte was added such that the molar ratio of the resulting analyte/ethylene glycol/boric acid mixture was 1:2:1. In a typical experiment 2–10 μmoles of analyte were infused.

Dissociation of the [2M] complex of boric acid and ethylene glycol, the reference diol

MS/MS experiments on the complex of boric acid and ethylene glycol at *m/z* 131 show that this [2M] complex dissociates largely by loss of 44 Da to form *m/z* 87. It will be shown below that the neutral species lost corresponds to C_2H_4O. The simplest way to envisage C_2H_4O loss is multiple simple bond cleavage without rearrangement to generate ion P in Scheme 2, where boron is doubly bonded to oxygen. In this scenario the neutral lost would be ethylene oxide whose heat of formation (ΔH_f) is −22.6 kcal/mol.[15] However, we cannot exclude the

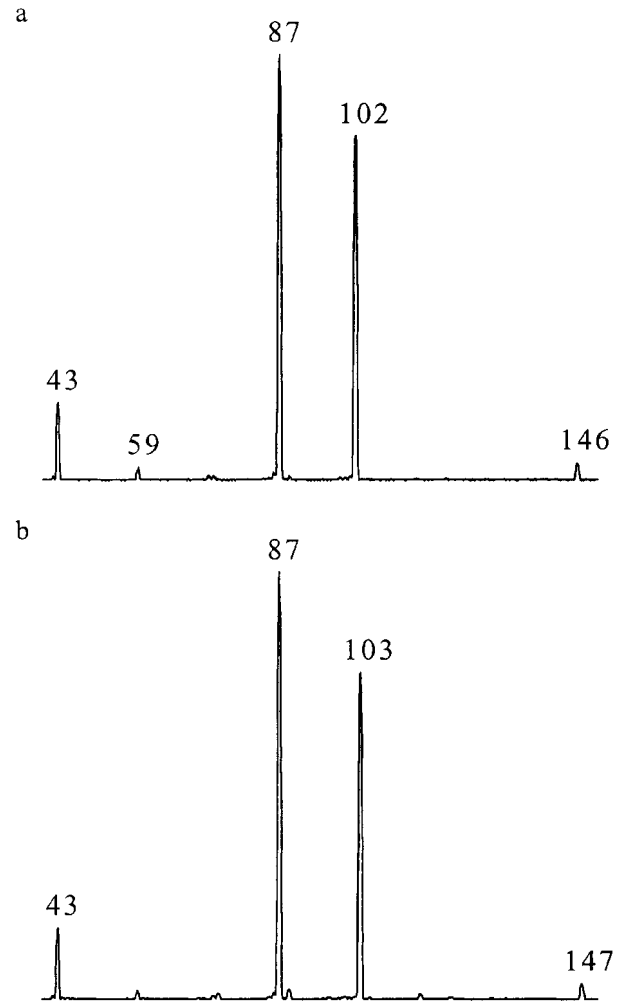


Figure 2. Negative ion ES-MS/MS spectra of the mixed complexes of (a) 1,2-propanediol-2-d_1, ethylene glycol and boric acid and (b) 1,2-propanediol-1,1-d_2, ethylene glycol and boric acid.

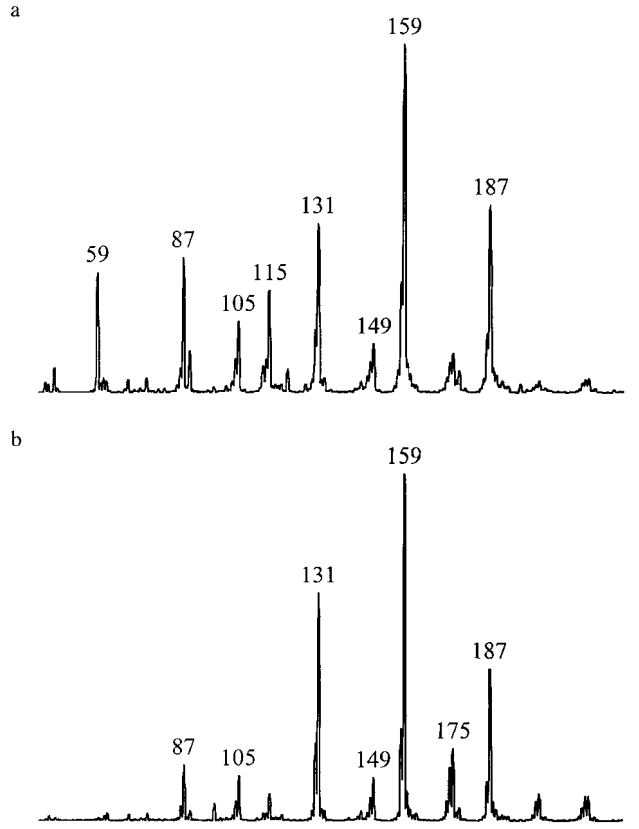


Figure 3. Negative ion ES mass spectra of (1:2:1) solutions of (a) (2*R*,3*R*)-(−)-2,3-butanediol, ethylene glycol and boric acid and (b) *meso*-2,3-butanediol, ethylene glycol and boric acid.

possibility that a 1,2-H shift takes effect prior to this dissociation to generate the more stable acetaldehyde isomer for which ΔH_f is −39.6 kcal/mol.[15] Such a hydrogen shift does account for the presence of a significant peak at *m/z* 59 in the MS/MS spectrum which, as confirmed by a ^{10}B-labelling experiment, corresponds to $[C_2H_3O_2]^-$.

The vicinal diols studied competed efficiently with ethylene glycol for complex formation with boric acid. In solutions containing a straight chain vicinal diol as the analyte, negative ion ES-MS showed peaks corresponding to the [2M] complex with ethylene glycol, the mixed complex and the [2M] complex with the analyte, in a 1:2:1 intensity ratio.

By contrast, ES-MS of solutions containing a 1,3-diol as the analyte showed a base peak corresponding to the [2M] ethylene glycol complex. A similar result was obtained when the 1,3-diol was replaced with a 1,4-diol. Therefore, as the hydroxyl groups move further apart in the diol, complex formation with boric acid and thus competition with ethylene glycol becomes more difficult. In the following, ES-MS/MS experiments were performed on the mixed complexes using naturally occurring boric acid and ^{10}B-boric acid.

Propanediol series

A solution containing a 1:2:1 mole ratio of 1,2-propanediol to ethylene glycol to boric acid showed an intensity ratio of 1:2:1 for the [2M] complex with ethylene glycol (*m/z* 131), the mixed complex (*m/z* 145), and the [2M] complex with the analyte (*m/z* 159), respectively. However, a 1:0.25:0.05 intensity ratio was observed for the same ions when 1,2-propanediol was replaced by 1,3-propanediol, showing that complex formation for the 1,3-diol is much less efficient (by a factor of 4.5, compare the relative association constant of **3** derived from NMR experiments[6]). The MS/MS spectra of the mixed complexes of 1,2-propanediol and 1,3-propanediol are shown in Fig. 1. The intensity differences that are observed are reproducible. It is seen that the mixed complex with 1,2-propanediol (M_1 in Scheme 3) loses C_3H_6O (methyl-oxirane) more abundantly than C_2H_4O (oxirane), while the reverse is true for the mixed complex with 1,3-propanediol (M_2 in Scheme 3). In the absence of thermochemical data it is difficult to rationalize these differences, but a brief discussion in terms of possible product structures is nevertheless useful.

Scheme 3 gives the product structures for the dissociations leading to *m/z* 87 and 101, assuming that these reactions do not involve hydrogen shifts. The numbers refer to established heats of formation (kcal/mol) from Ref. 15. There are two ways of looking at these data. The more

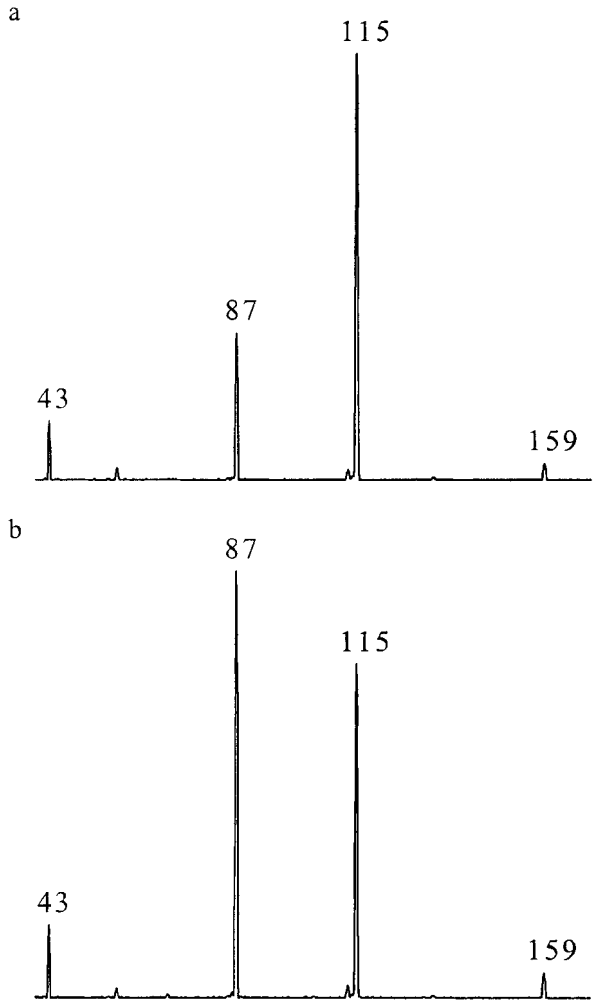


Figure 4. Negative ion ES MS/MS of the mixed complex (*m/z* 159) with (a) (2*R*,3*R*)-(−)-2,3-butanediol, ethylene glycol and boric acid, and (b) *meso*-2,3-butanediol, ethylene glycol and boric acid.

intense *m/z* 87 signal in Fig. 1(a) could be attributed to the formation of a more stable C_3H_6O neutral for M_1 compared to M_2; neutral methyloxirane has a lower heat of formation than oxetane (note that the ring strain energies of three and four membered rings are similar[16]). Conversely, if the same neutral is formed in both these reactions, then the increased intensity of *m/z* 101 in Fig. 1(b) indicates that the product ion P_2 is more stable than P_1. Localizing the electron on boron, the stability difference between P_1 and P_2 may be approximated by considering the isoelectronic neutrals N_1 and N_2. Although the heat of formation of N_1 has been accurately measured,[15] that for N_2 is unknown. However, both heats of formation can be estimated from Benson's additivity scheme.[16] We then find that N_2 is more stable than N_1, by 2.3 kcal/mol, and equate this to the difference in the heat of formation of P_2 and P_1. Thus it is not possible to say whether formation of *m/z* 87 in Fig. 1(b) becomes unfavourable because of a less stable neutral, or that *m/z* 101 becomes more favourable because of a more stable ion. It is entirely possible that a delicate balance exists between the two.

We also examined the ES-MS and MS/MS mass spectra of solutions containing 1,2-propanediol-2-d_1 and 1,2-propanediol-1,1-d_2 as the analyte. Both isotopomers cleanly generated mixed complex ions at *m/z* 146 and 147, respectively. Their MS/MS spectra are presented in Fig. 2. Note that for the *m/z* 147 species, see Fig. 2(b), the spectrum displays a peak at *m/z* 103, which is two mass units higher than that observed for the unlabelled counterpart, see Fig. 1(a), whereas *m/z* 87 remains unchanged. These observations confirm that the neutrals lost in these dissociations are C_2H_4O and C_3H_6O.

Butanediol series

A series of butanediols was also investigated by the above method. Here, too, only the vicinal diols showed ions corresponding to the [2M] ethylene glycol complex at *m/z* 131, [A], the mixed complex at *m/z* 159, [B], and the [2M] analyte complex at *m/z* 187, [C], with an intensity ratio of 1:2:1. For 1,3- and 1,4-butanediol, the normal mass spectra showed peaks corresponding to [A], [B] and [C] in an intensity ratio of 1:0.5:0.25, paralleling observations made for 1,2- and 1,3-propanediol, *vide supra*.

The ES mass spectra of solutions containing (2*R*,3*R*)-(−)-2,3- and *meso*-2,3-butanediol as analytes are presented in Fig. 3. These spectra are similar but not identical which becomes even more manifest when the MS/MS spectra of the mixed complexes are considered, see Fig. 4.

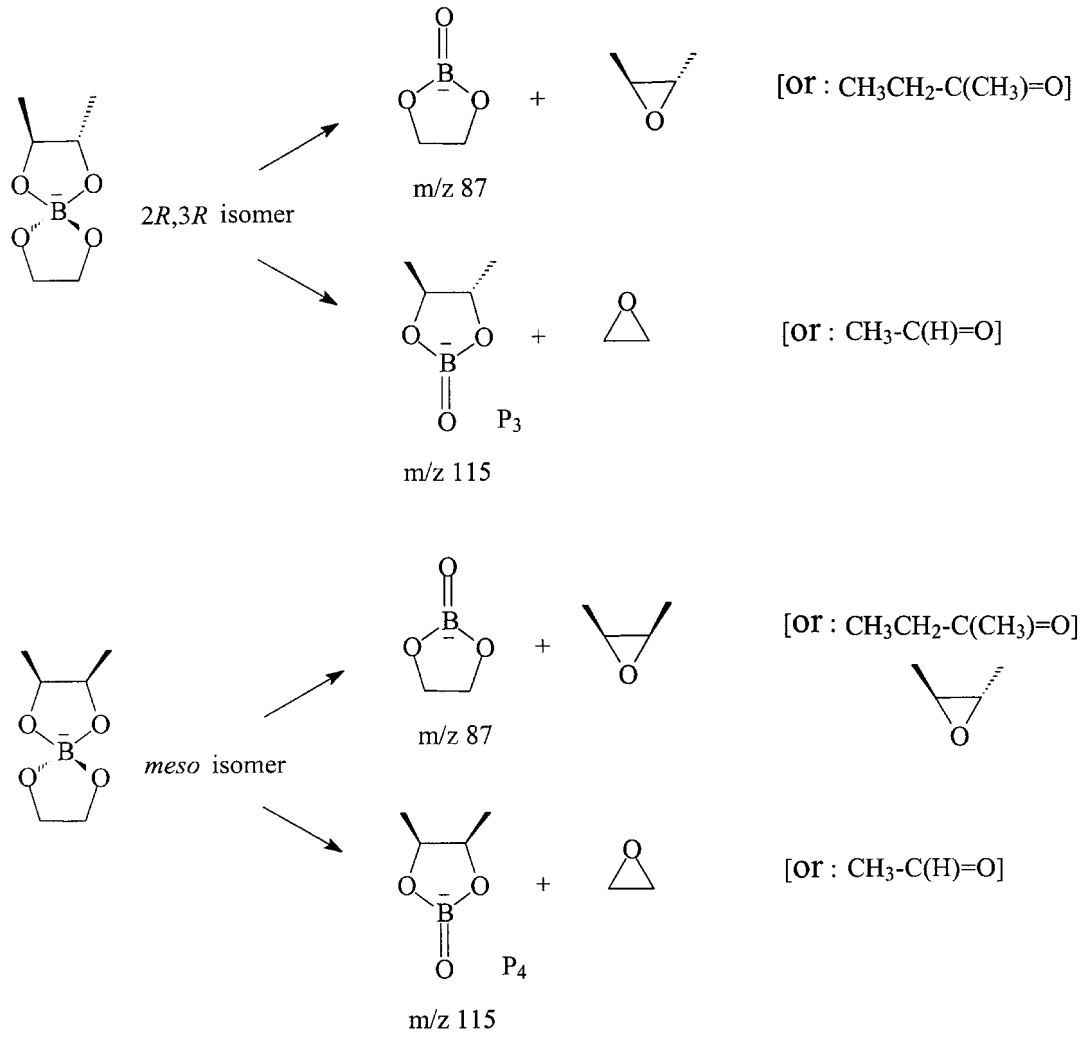
The MS/MS spectra are well reproducible and spectra acquired upon alternately infusing solutions of the (2*R*,3*R*)- and *meso*-2,3- stereoisomers showed no discernable variations in the relative intensity of the MS/MS peaks. Scheme 4 shows the various reaction channels and plausible product structures. Again most heats of formation values are not available. We begin our interpretation by proposing that the stereochemistry is conserved in both the ionic and the neutral products. (This is a valid assumption for the ionic products since the reactive center is in the other ring, but for the neutral expelled stereochemical differentiation may be lost.) Now it follows from Scheme 4 that for the *meso* complex both the formation of *m/z* 87 and 115 may suffer from steric hindrance. For the formation of *m/z* 87 this hindrance would manifest itself in the neutral but this is not observed, only *m/z* 115 suffers from steric hindrance, compare Figs 4(a) and 4(b). This is entirely reasonable because, as stated above, even for the *meso* compound the neutral 1,2-dimethyloxirane may well have the more stable *trans* configuration (and of course, if the neutral is 2-butanone, no stereoisomers exist at all). *Thus, we now have a probe for stereochemical differentiation.*

Finally, the most significant difference between the MS/MS spectra of *meso*-2,3- and 1,2-butanediol was that the mixed complex formed with 1,2-butanediol yielded a tell-tale peak at *m/z* 57 ($C_2HO_2^-$).

Cyclopentanediols and cyclohexanediols

Next, complex formation with *cis*-1,2-, *trans*-1,2- and 1,3-cyclopentanediol (mixture of *cis* and *trans*) was investigated. Of these analytes, only *cis*-1,2-cyclopentanediol readily formed a [2M] complex with boric acid while the *trans*-1,2-cyclopentanediol and the 1,3-cyclopentanediol formed a [1M] complex.

The MS/MS spectra of the mixed complexes, see Fig. 5, are characteristically different. Especially interesting is that



Scheme 4.

the spectra of the complexes of *cis*- and *trans*-1,2-cyclopentanediol, see Figs 5(b) and 5(c), show an 'all-or-nothing' effect in that *m/z* 87 is absent in the former. Thus, the mixed complex with the *cis* isomer readily loses C_2H_4O (oxirane) whereas the *trans* compound readily loses C_5H_8O. This is the opposite behaviour of that found for the 2,3-butanediols. Interestingly, the complex with 1,3-cyclopentanediol does not show a preference for loss of either oxirane or C_5H_8O. Thus, ES-MS/MS allows differentiation between the *cis* and *trans* isomers of 1,2-cyclopentanediol and 1,3-cyclopentanediol.

Similar results were obtained for the *cis* and *trans* isomers of 1,2-cyclohexanediol. MS/MS experiments on the mixed complexes, see Fig. 6, showed that the *cis* isomer loses C_2H_4O (oxirane) rather than $C_6H_{10}O_2$ while the converse is true for the *trans* isomer.

Mannitol and sorbitol

Mannitol was one of the first polyhydroxy compounds shown to decrease the pH of a solution of boric acid. When a solution having a 1:2:1 mole ratio of mannitol to ethylene glycol to boric acid was analyzed by ES-MS, the ion corresponding to the [2M] complex between mannitol and boric acid (*m/z* 371) was the base peak in the spectrum, see Fig. 7(a).

This result is in keeping with the potentiometric observations which showed a substantial increase in conductance of a boric acid solution in the presence of mannitol. The fact that the [2M] complex at *m/z* 371 dominates the ES mass spectrum shows that mannitol competes very effectively with ethylene glycol for complexation with boric acid. This may be due in part to statistical effects, i.e. the number of vicinal hydroxyl groups available for complexation.

The stereoisomer sorbitol (**15** in Scheme 1) was similarly analyzed and again the base peak in the ES mass spectrum was the [2M] complex with boric acid, see Fig. 7(b). However, there is also a substantial signal at *m/z* 181 for the $[M\text{-}H]^-$ ion showing that complexation is less effective in sorbitol than in mannitol. This is not unexpected considering that mannitol, see Scheme 1, has more vicinal *cis* hydroxyl groups available for efficient complexation.

The MS/MS spectra of the [2M] *m/z* 371 ions in Figs 7(a) and 7(b) were also obtained. The spectra appeared to be closely similar and thus the MS/MS procedure cannot differentiate these stereoisomeric sugar alcohols. This is

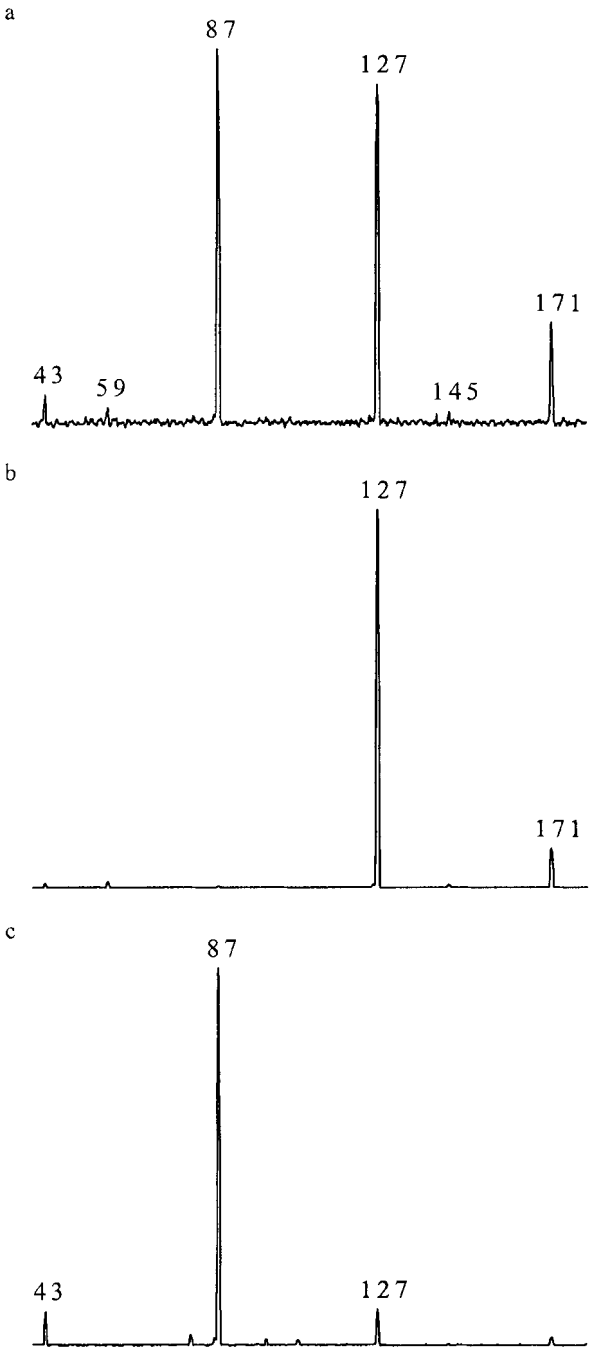


Figure 5. Negative ion ES-MS/MS spectra of the (*m/z* 171) mixed complexes of ethylene glycol and boric acid with (a) (*cis/trans*)-1,3-cyclopentanediol, (b) *cis*-1,2-cyclopentanediol and (c) *trans*-1,2-cyclopentanediol.

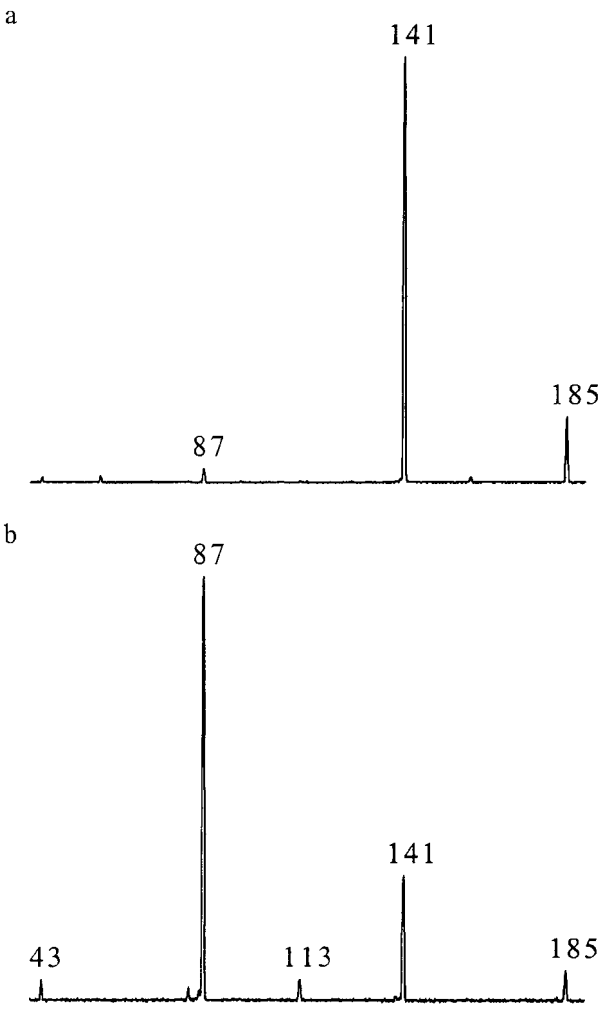


Figure 6. Negative ion ES-MS/MS spectra of the (*m/z* 185) mixed complexes with (a) *cis*-1,2-cyclohexanediol, ethylene glycol and boric acid and (b) *trans*-1,2-cyclohexanediol, ethylene glycol and boric acid.

perhaps not too surprising considering that the hydroxyl groups of these acyclic polyhydroxy compounds may freely rotate in solution allowing the vicinal hydroxyl groups of the two sugar alcohols to adopt closely similar configurations for efficient complex formation.

Methyl glycosides

Sugars in the hemiacetal/hemiketal form undergo mutarotation. This implies that they interconvert between their α/β-furanose and α/β-pyranose forms. Methylating the anomeric hydroxyl prevents mutarotation and ensures that the anomeric hydroxyl group cannot participate in complex formation. A better assessment of the use of the boric acid/ethylene glycol procedure for probing the stereochemistry of sugars is then obtained.

The normal mass spectra showed that α-methylmannopyranoside (**17** in Scheme 1) forms the mixed complex more readily than α-methylglucopyranoside (**16** in Scheme 1). The MS/MS spectrum of the ion representing the mixed complex with the α-methyl-mannopyranoside is characteristically different from that of the α-methylglucopyranoside, compare Figs 8(a) and 8(b). Loss of a mass 32 neutral (CH_3OH) uniquely characterizes the mixed complex with α-methylmannopyranoside by the peak at *m/z* 231, see Fig. 8(a). If the complex formation involves the hydroxyl groups on C3 and C6 in the glucopyranoside and those on C2 and C3 in the mannopyranoside, the MS/MS results can be rationalized by proposing that CH_3OH represents the mass 32 neutral lost from C6 in the mixed complex with the mannopyranoside. This hydroxyl group is bonded to B in the mixed complex with α-methyl-glucopyranoside, preventing the loss of CH_3OH.

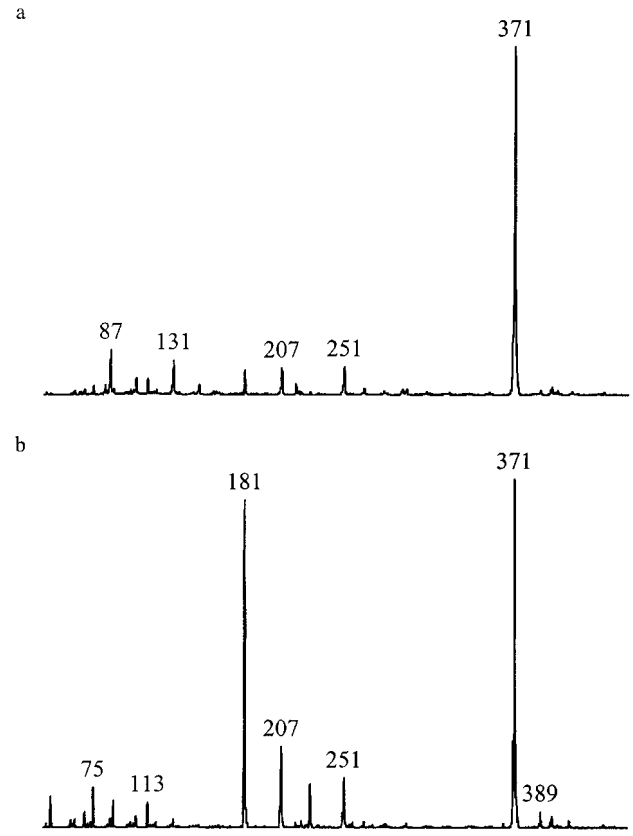


Figure 7. Negative ion ES mass spectrum of a (1:2:1) solution of (a) mannitol, ethylene glycol and boric acid and (b) sorbitol, ethylene glycol and boric acid.

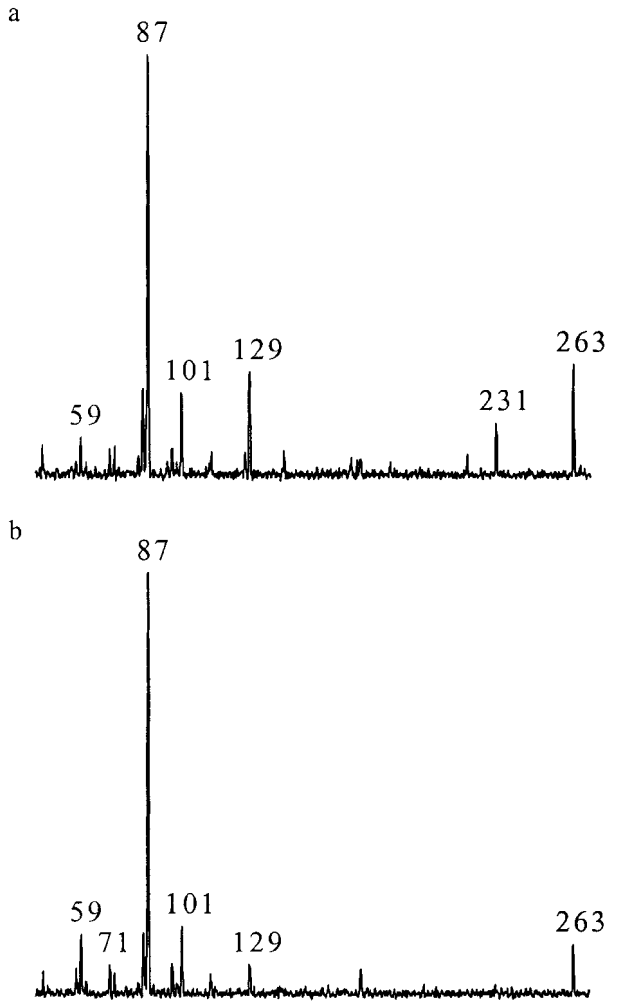


Figure 8. Negative ion ES-MS/MS spectra of the (*m/z* 263) mixed complexes with (a) α-methyl-D-mannopyranoside, ethylene glycol and boric acid and (b) α-methyl-D-glucopyranoside, ethylene glycol and boric acid.

CONCLUSIONS

By adding a measured quantity of a diol of unknown composition to a methanol/water solution containing a preformed ethylene glycol/boric acid [2M] complex, the extent of complex formation between boric acid and the analyte can be assessed. The relative ease of complex formation is derived from the relative intensity of the [2M] complex between ethylene glycol and boric acid and the [2M] complex between the analyte and boric acid.

For vicinal *cis*- and *trans*-cyclic diols it is shown that simple ES-MS is sufficient to differentiate between the two isomers. MS/MS experiments show that the *cis* isomer readily loses C_2H_4O (oxirane), whereas the *trans* isomer characteristically loses the cyclic diol epoxide.

Stereoisomer differentiation between *meso*-2,3- and (2*R*,3*R*)-(−)-2,3-butanediol is also possible but only using MS/MS experiments. Steric interactions between the two methyl groups in the mixed complex with *meso*-2,3-butanediol promote a facile loss of the butanediol portion of the mixed complex. In contrast, with (2*R*,3*R*)-(−)-2,3-butanediol, the ethanediol portion of the complex is more readily lost.

The above procedure does not permit an unambiguous differentiation of acyclic polyhydroxy compounds like the sugar alcohols mannitol and sorbitol. This is likely because these stereoisomers form structurally closely similar complexes with the boric acid/ethylene glycol mixture as witnessed by their virtually identical MS/MS spectra. However, when the structurally related sugars have been methylated on the anomeric hydroxyl group, characteristic MS/MS spectra are readily obtained.

The results obtained so far warrant a more extensive and detailed study of the use of borate complexes for the analysis of polyols in aqueous solutions.

Acknowledgements

Continuous financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

REFERENCES

1. Ferrier RJ. *Adv. Carbohydr. Chem. Biochem.* 1978; **35**: 31.
2. van Duin M, Peters JA, Kieboom APG, van Bekkum H. *Tetrahedron* 1984; **40**: 2901.
3. Oi T, Takeda T, Kakihana H. *Bull. Chem. Soc. Jpn.* 1992; **65**: 1903.
4. Biot JB. *Compt. Rend.* 1842; **14**: 49.
5. Deutsch A, Osoling S. *J. Am. Chem. Soc.* 1949; **71**: 1637.
6. van Duin M, Peters JA, Kieboom APG, van Bekkum H. *Tetrahedron* 1985; **41**: 3411.
7. Shiomi Y, Kondo K, Saisho M, Harada T, Tsukagoshi K, Shinkai S. *Supramol. Chem.* 1993; **2**: 11.
8. Chapelle S, Verchere J. *Carbohydr. Res.* 1989; **191**: 63.

9. Brooks CJW, Cole WJ. *J. Chromatogr.* 1987; **399**: 207.
10. Bergold A, Scouten WH. *Chem. Anal. (N Y)* 1983; **66**: 149.
11. Rose ME, Wycherley D, Preece SW. *Org. Mass Spectrom.* 1992; **27**: 876.
12. Liptak M, Dinya Z, Herczegh P. *Org. Mass Spectrom.* 1993; **28**: 780.
13. Penn SG, Hu H, Brown PH, Lebrilla CB. *Anal. Chem.* 1997; **69**: 2471.
14. Bayer E, Gfrorer P, Rentel C. *Angew. Chem. Int. Ed.* 1999; **38**: 992.
15. Lias S, Bartmess JE, Liebman JF, Holmes JL, Levin RD, Mallard WG. *J. Phys. Chem. Ref. Data*, 1988; **17**: Suppl.
16. Cohen N, Benson SW. *Chem. Rev.* 1993; **93**: 2419.

