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Note

The mass spectra of benzeneboronate derivatives of some hexopyranosides

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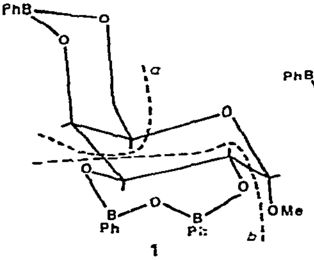
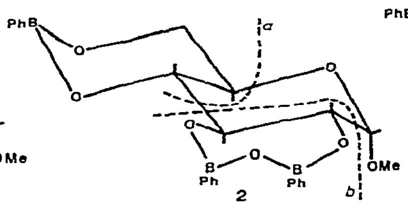
We wish to report the preparation and mass spectrometry of benzeneboronates of methyl α-D-galactopyranoside (**1**), methyl α-D-glucopyranoside (**2**), and methyl α-D-mannopyranoside (**3**). The structures of **2** and **3** have been described[1], but the mass spectra of these derivatives, which may be useful for distinguishing various aldohexoses, have not been reported.



1



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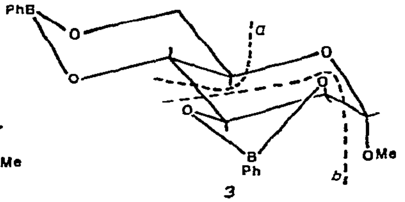

3

For the preparation of the benzeneboronates, dry methyl glycopyranoside (~1.5 mg) was dissolved in *N*,*N*-dimethylformamide (100 μl), to which 2,2-dimethoxypropane (100 μl) containing benzeneboronic acid (4 mg) was added. The solutions were kept in sealed glass-ampoules for ~30 min at 20–22°. The derivatised methyl glycopyranoside (1 μl, ~10 μg) was introduced into an AEI MS-902 mass spectrometer on the direct-insertion probe at a source temperature of 200°. Mass spectra were measured by using an electron beam of 70 eV. The atomic compositions of the ions cited in the following schemes have been verified from computer-processed, high-resolution, mass-spectral data[2], and metastable ions were measured by the "defocused mode" method[3].

The mass-spectral evidence has been derived from a consideration of the molecular ion and some of its major fragment ions (Table I and Fig. 1) which occur through fission of the pyranose rings by processes (*a*) and (*b*) as shown in formulae **1**–**3**. The ion at *m*/*e* 160 is produced from **1**, **2**, and **3** by fission process (*a*) and is consistent with a 4,6-benzeneboronate substituent (a 6-membered boronate ring). The ion at *m*/*e* 250, a 7-membered boronate ring (the 2,3-dibenzenepyroboronate), from both **1** and **2** is generated by fission process (*b*), whereas this process for **3** yields an ion at *m/e* 146 which is a 5-membered boronate ring. However, the ion at *m/e* 250 decomposes further by loss of C_6H_5BO to form the ion at *m/e* 146; therefore, although the ion ($C_{14}H_{12}B_2O_3$) at *m/e* 250 is characteristic of the *trans*-2,3-dibenzenepyroboronate in **1** and **2**, the ion at *m/e* 146 cannot be used on its own to establish the presence of a *cis*-2,3-benzeneboronic ester (the 5-membered boronate ring). However, the absence of an ion at *m/e* 250 in the spectrum of **3** (mol. wt. 366), together with evidence (ion at *m/e* 160) consistent with a 4,6-benzeneboronic ester, leaves only one alternative for the 2,3-diol substituent, *i.e.* a *cis*-2,3-benzeneboronic ester. The spectra of the stereoisomers **1** and **2** are qualitatively similar; however, there are noticeable changes in the intensities of the fragment ions and a pronounced difference in intensity of the molecular ions (Table I), which, apart from being useful diagnostic information, suggests that the galactosyl configuration is capable of conferring stability upon the molecular species.

TABLE I

THE RELATIVE INTENSITIES OF SELECTED IONS IN THE SPECTRA OF BENZENEBORONATES OF THREE METHYL HEXOPYRANOSIDES

	1	**2**	**3**
Mol. wt.	470 ($C_{25}H_{25}B_3O_7$)	470 ($C_{25}H_{25}B_3O_7$)	366 ($C_{19}H_{20}B_2O_6$)
M	7.5	0.2	0.1
M−60	0.6	0.06	0.2
m/e 250 ($C_{14}H_{12}B_2O_3$)	26.0	27.5	—
m/e 160 ($C_9H_9BO_2$)	6.8	14.4	39.4
m/e 146 ($C_8H_7BO_2$)	100.0	100.0	100.0

Confirmatory evidence for the mass-spectral interpretations was obtained from a comparison of the spectra of the benzeneboronic esters of the methyl 4,6-*O*-benzylidene-α-D-glycopyranoside analogues (**1a**–**3a**) of **1**–**3**. The spectra of **1a** and **2a** have molecular ions at *m/e* 472 and contain a fragment ion at *m/e* 250, whereas the spectrum of **3a** has a molecular ion at *m/e* 368 and does not have a fragment ion at *m/e* 250. Furthermore, the relative intensity of the molecular ion of **1a** and **2a** are in the same ratio as those for **1** and **2**.

It is evident from the literature that, in general, benzeneboronic esters can be prepared easily from small amounts of material[4], are amenable to sequential derivatisation[4,5], and give mass spectra containing clearly distinguishable, molecular ion groups (^{10}B:^{11}B = 1:4.2)[5–7]. The mass spectra shown in Fig. 1 have been obtained by subtraction of the mass spectrum of the reagent which showed major ions at *m/e* 312, 164, and 104, representing the anhydride triphenylboraxole, PhBPh, and PhBO, respectively. The triphenylboraxole, which may be the esterifying agent[1], we believe to be formed from benzeneboronic acid by dehydration in the water-scavenging solvent 2,2-dimethoxypropane.

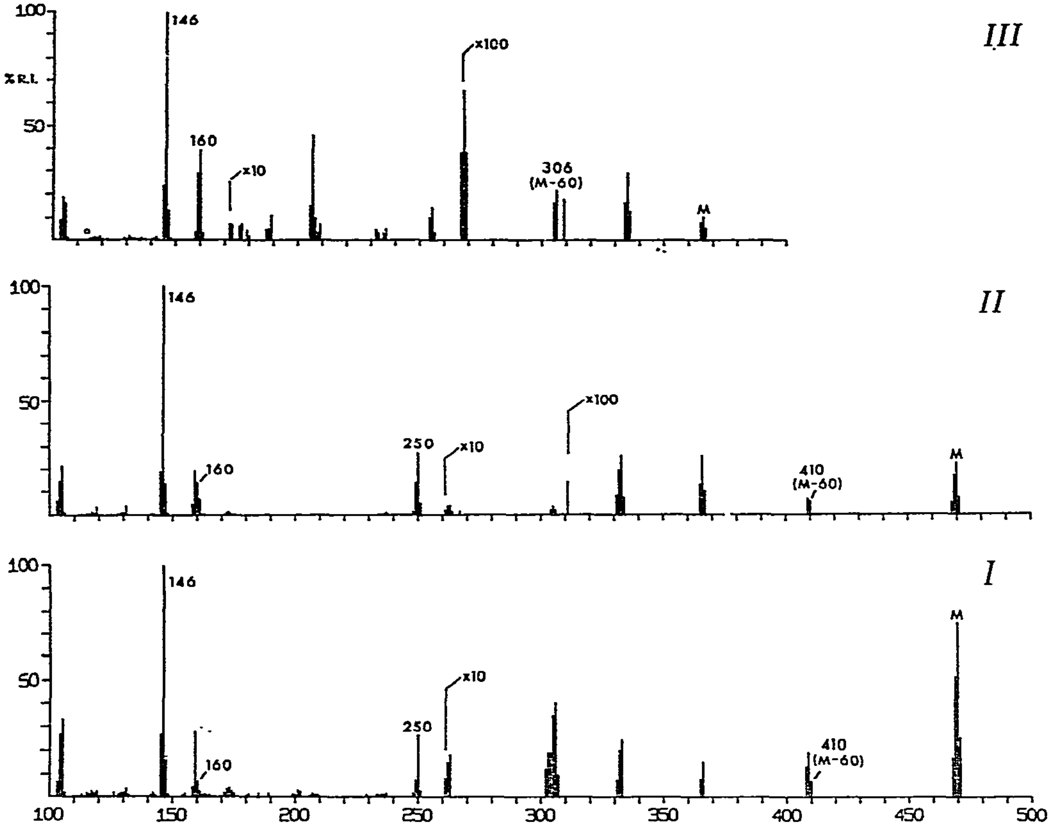

Fig. 1. Mass spectra of the benzeneboronates. I, Methyl α-D-galactopyranoside; II, methyl α-D-glucopyranoside; III, methyl α-D-mannopyranoside.

These studies have substantiated the structures of **2** and **3** proposed by Ferrier[1] and indicate that an analogous structure (**1**) for the per(benzeneboronic ester) of methyl α-D-galactopyranoside may be proposed.

From the mass spectra of the per(benzeneboronates) of the three glycosides and their analogous benzylidene derivatives, it seems that the 2,3-*trans*- and -*cis*-diol groups and the 4,6-diol group, as found in compounds **1**–**3**, form a 7-membered dibenzenepyroboronate ring, and a 5- and 6-membered benzeneboronate ring, respectively. Herein, it has been demonstrated that the 1,2-*trans* and 1,2-*cis* isomers of the three methyl glycopyranosides can be identified by the study of the mass spectra of their benzeneboronates, in contrast to the studies of the mass spectra of their methyl ethers and peracetates[8] which indicate the sequential loss of substituent groups and which show, to a lesser extent, ring-cleavage processes. Further work is required to establish whether a 1,2-*trans*-diol group in other sugars always forms a 7-membered dibenzenepyroboronate ring and to determine which benzeneboronate rings are preferentially formed in other polyhydroxy compounds. Application to deoxy sugars and disaccharides, which will be described later, indicates that some simple rules for the reactivity of various hydroxyl groups present in carbohydrates can be formulated, and that the techniques should provide a useful adjunct for microanalytical, structural analysis of oligosaccharides in mucosubstances.

The mass spectra of all compounds discussed in this paper will be sent to the Mass Spectral Data Centre, Aldermaston.

ACKNOWLEDGMENT

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