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CHARACTERISATION OF BORONIC ESTERS OF ARABINOSE AND XYLOSE*

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ABSTRACT

The benzene- and butane-boronates of arabinose and xylose have been prepared in high yield and shown to be the 1,2:3,4- and 1,2:3,5-diboronic esters, respectively. P.m.r. data indicated conformations similar to those of related acetal derivatives. The mass-spectral data are consistent with the proposed structures.

INTRODUCTION

Boronic esters of some free reducing sugars were first prepared[1] by a fusion technique. Subsequently, benzeneboronates of some glycosides were used in synthesis[2–4]. α-D-Glucofuranose 1,2:3,5-bis(benzeneboronate)[5] has been utilised[6,7] in a convenient route to 6-substituted D-glucose derivatives.

G.l.c.–m.s. of cyclic boronic esters of some 1,2- and 1,3-diols[8–10] and of butaneboronic esters of carbohydrates[11–13] has been described. As a result of the specific, stereochemical requirements for reaction, butaneboronic acid should form constitutional isomers from diastereomers (*e.g.*, xylose and arabinose), thus allowing unequivocal identification by mass spectrometry. This feature of a di-functional substitution was previously commented on by DeJongh and Biemann in studies of isopropylidene derivatives[14]. As part of a continuing study of the potential of boronic esters for analysis and identification of sugars, this paper describes an improved synthesis of L-arabinose and D-xylose benzeneboronates, and compares the mass spectra of these and the previously unreported butaneboronates.

EXPERIMENTAL

General. — Melting points were determined on a micro hot-stage and are corrected. Optical rotations were determined on a Perkin–Elmer 141 spectrometer. Mass spectrometry was carried out on a Dupont 21-490 Mass Spectrometer, using a direct-probe inlet, an ionisation potential of 70 eV, and inlet and source temperatures of 180°. G.l.c. was carried out on a Pye Series 104 Model Chromatograph

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(dual FID) fitted with dual glass columns (5 ft × 0.25 in.) packed with 3% OV-225 on Gas Chrom. Q (80–100 mesh). Samples were injected into a heated inlet (175°) and the column was programmed (5–10°/min) from 100° to ~200°, with a nitrogen flow-rate of 60 ml/min and flame-ionisation detection. Infrared spectra were recorded for solutions in chloroform, using a Beckman IR 20A instrument. All evaporations were carried out under diminished pressure at 37°. Pyridine was dried by refluxing over, followed by distillation from, barium oxide; benzene and light petroleum (b.p. 80–100°) used for recrystallisation were dried over calcium chloride followed by sodium. Analytical figures are given for twice-distilled or recrystallised material. P.m.r. spectra were recorded under frequency-sweep conditions at 100 MHz on a Varian XL-100 and at 60 MHz on a Varian T-60 spectrometer.

For the preparation of butaneboronates, a solution (~2%) of the pentose (1 mol.) in dry pyridine was treated with butaneboronic acid (3 mol.). The solution was refluxed for 15 min and cooled to room temperature, and the pyridine was evaporated. A solution (~2%) of the crude, liquid product in chloroform was thrice extracted with 10% aqueous copper sulphate. The blue–green precipitate at the interface was discarded, and the chloroform layer was washed thrice with distilled water, dried (Na_2SO_4), and concentrated. The products were mobile liquids.

For the preparation of the benzeneboronates, 2 mol. of benzeneboronic acid were used and the extraction step was omitted. The following compounds were thus prepared:

β-L-Arabinopyranose 1,2:3,4-bis(benzeneboronate) (81%), m.p. 165–166° (from light petroleum), $[\alpha]_D^{21}$ +8.8° (*c* 1, benzene), +47.5° (*c* 5, chloroform); lit.[1] m.p. 166°, $[\alpha]_D^{25}$ +8.5° (*c* <5, benzene).

α-D-Xylofuranose 1,2:3,5-bis(benzeneboronate) (93%), m.p. 142–142.5° (from light petroleum), $[\alpha]_D^{26}$ −10° (*c* 5, benzene), +54° (*c* 4.8, chloroform); lit.[1] m.p. 137°, $[\alpha]_D^{25}$ −8.5° (*c*<5, benzene).

β-L-Arabinopyranose 1,2:3,4-bis(butaneboronate) (94%), b.p. 90 ±5° (bath)/0.02 mmHg, $[\alpha]_D^{22}$ +19° (*c* 5, chloroform), $[\alpha]_D^{24}$ +80 (2 min) → +62 (10 min) → +50 (20 min) → +39° (100 h) (*c* 1.74, pyridine–water, 9:1), $[\alpha]_D^{25}$ +50 (2 min) → +71 (10 min) → +66 (20 min) → +46 (80 min) → +18° (100 h) (*c* 1.74, acetone–water, 9:1).

Anal. Calc. for $C_{13}H_{24}B_2O_5$: C, 55.38; H, 8.58. Found: C, 55.86; H, 8.16.

α-D-Xylofuranose 1,2:3,5-bis(butaneboronate) (87%), b.p. 90 ±5° (bath)/0.02 mmHg, $[\alpha]_D^{25}$ +34° (*c* 5, chloroform), was a pale-yellow liquid. G.l.c. of this product revealed two minor impurity peaks (each ~2% of the main peak) believed to be from the reagent.

Anal. Calc. for $C_{13}H_{24}B_2O_5$: C, 55.38; H, 8.58. Found: C, 55.83; H, 8.46.

RESULTS AND DISCUSSION

The use of pyridine as a solvent gives greatly improved yields in the synthesis of the benzeneboronates of L-arabinose and D-xylose. (80–90% compared[1] to 40–45%). Previous workers used fusion techniques[1], or solvents such as anhydrous benzene and removed water from the reaction by azeotropic distillation[2-4]. More recently, 2-methoxyethanol[6,7] has been successfully used as a solvent for formation of the boronic ester of D-glucose. Robinson *et al.*[15] used 2,2-dimethoxypropane as a water scavenger in the micro-preparation of benzeneboronates of some glycosides.

Both substrate and reagent are soluble in pyridine. As previously reported[11], the pyridine reaction mixture may be directly used for g.l.c. The present results show that the products can be isolated from pyridine solutions in high yield. The hydrolytic instability of cyclic boronic esters is well established[1,16], but comparison of the stabilities of the isolated reaction products in aqueous pyridine and acetone, based on changes in optical rotation, showed no evidence for pyridine stabilisation of product.

Attempts to prepare the butaneboronate of L-arabinose by refluxing with 2 mol. of butaneboronic acid yielded a product which, after two distillations, was highly impure. However, when a chloroform solution of the reaction mixture obtained from an optimal[17] 3:1 molar ratio of butaneboronic acid to sugar was extracted with 10% aqueous copper sulphate, both residual pyridine and, apparently, the excess boronic acid were removed. Vacuum distillation then yielded mobile liquids of acceptable purity. Cyclic boronates are known to hydrolyse easily[1,16] and alkyl boronates are also susceptible to oxidation[18]. It was found that distillation at lower temperatures yielded products showing satisfactory elemental analysis, whereas higher temperatures appeared to cause some breakdown.

P.m.r. data for the boronates are shown in Tables I and II. Confirmation of the arabinose assignments was obtained as follows. Irradiation at δ 5.58 (H-1, doublet) collapsed the doublet of doublets at 4.32 to a doublet (2.8 Hz) confirming this as the signal from H-2. Irradiation at δ 4.64 collapsed the doublet of doublets at 4.32 to a doublet (6.0 Hz), and collapsed the broad doublet centred at 3.92 to a broad singlet (width at half-height, ~2 Hz) confirming this as the H-4 signal. Irradiation at δ 3.92 collapsed the signal centred at 3.29 to a widely spaced doublet (14.0 Hz; one half of an AB quartet) confirming this as the signal due to one of the methylene protons (H-5'), leaving the other half of the AB quartet (δ 3.57) as the signal from H-5.

TABLE I

CHEMICAL SHIFTS (δ, P.P.M.) OF PROTONS OF BORONATES OF L-ARABINOSE AND D-XYLOSE IN C_6D_6

Sample	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-5'*
Butaneboronate of arabinose[a]	5.56 (*d*)[d]	4.19 (*q*)	4.50 (*q*)	3.94 (*d*, *b*)	3.60 (*d*, *b*)	3.27 (*q*)
Benzeneboronate of arabinose[b]	5.58 (*d*)	4.32 (*q*)	4.64 (*q*)	3.92 (*d*, *b*)	3.57 (*d*, *b*)	3.29 (*q*)
Butaneboronate of xylose[a]	5.75 (*d*)	4.36 (*d*)	3.90 (*d*)	~3.6 (*o*)	3.95 (*o*)	3.39 (*o*)
Benzeneboronate of xylose[b]	5.72 (*d*)	4.52 (*d*)	4.02 (*d*)	~3.48 (*o*)	4.01 (*d*, *b*)	3.40 (*q*)
Benzeneboronate of xylose+$Eu(FOD)_3$[b,c]	6.03 (*d*)	4.69 (*d*)	4.14 (*d*, *o*)	3.68 (*s*, *b*)	4.11 (*d*, *b*, *o*)	3.49 (*q*)

[a] 60 MHz; [b] 100 MHz; [c] ~0.8:1 molar ratio of shift reagent to boronate derivative. [d] *s* = singlet, *d* = doublet, *q* = doublet of doublets, *o* = overlapping signals, *b* = broad signals (see text).

TABLE II

COUPLING CONSTANTS (±0.3 Hz) OF PROTONS OF BORONATES OF L-ARABINOSE AND D-XYLOSE

Sample	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$
Butaneboronate of arabinose	6.0	2.5	7.9	<0.5	2.0	13.4
Benzeneboronate of arabinose	6.0	2.7	8.2	<0.5	1.9	13.4
Butaneboronate of xylose	4.1	<1	2.2	—	~2.0	~12.5
Benzeneboronate of xylose	4.1	<0.5	2 3	$\leqslant 1.5$[a]	2 2	13 6

[a] Half width at half height.

Confirmation of the xylose assignments was also straightforward, although overlap of the signals for H-3 and H-5, and H-4 and H-5′, in the xylose boronates prevented immediate assignment of coupling constants and chemical shifts. However, the characteristic doublets for H-1, H-2, and H-3, known from previous work on isopropylidene derivatives with the xylohexofuranose structure[19,20], were immediately obvious when C_6D_6 was used as the solvent. Addition of the shift reagent $Eu(FOD)_3$ to the C_6D_6 solution of the benzeneboronate produced major, downfield shifts in H-1 and H-4, and lesser and quite similar shifts in H-2, H-3, H-5, and H-5′, but did not significantly affect the coupling constants. Thus, only the H-4 and H-5′ overlap was resolved, but this allowed a complete analysis, on a first-order basis.

Decoupling experiments on C_6D_6 solutions, both with and without shift reagent, confirmed the various xylose assignments. Thus, irradiation in the region of H-2 collapsed the low-field (H-1) signal to a singlet. Irradiation in the region of the broad signal assigned to H-4 collapsed the H-5′ signal to a broad doublet (12.8 Hz; one half of an AB quartet), and the doublet assigned to H-3 to a singlet (still overlapped by part of the H-5 signal).

Examination of the p.m.r. data allows some conclusions to be made regarding both conformation and structure of these derivatives. Calculation of dihedral angles and detailed conclusions regarding conformation will not be attempted here in view of the potential error in the first-order analysis and the known limitations of the Karplus equation[21,22]. However, a number of qualitative conclusions are possible, and particularly valuable are the comparisons with certain previously reported acetal derivatives. The data show that there is little difference in either ring structure or conformation between the butane- and benzene-boronates.

The spectra of the arabinose boronates show some close similarities to the spectra of the di-*O*-isopropylidene derivative[23], with the exception that the boronates show slightly larger values for $J_{1,2}$ and $J_{3,4}$, and also have $J_{4,5}$ close to zero.

A chair form was ruled out for the isopropylidene derivative and can similarly be rejected for the boronate. The $^4C_1$ chair would require a higher value of $J_{2,3}$, whereas the $^1C_4$ chair would require a similarly high value for $J_{4,5}$ or $J_{4,5'}$ (coupling constants of vicinal, diaxial hydrogens are usually in the range 8.6–11.5 Hz).

The larger values of $J_{1,2}$ suggest a greater "flattening" of the pyranose ring by the boronate function, *i.e.*, a smaller bridgehead dihedral angle. This is also true for the 3,4-bridgehead, the effect being particularly marked for the benzeneboronate. Although this trend may be due in part to the influence of boron on the coupling constants, the result is not unexpected because the trigonal, planar nature of the boron would be expected to cause a somewhat flatter ring. This effect would be similar to that noted by Anet[24] when comparing a dioxolane ring with a cyclic carbonate that contains the trigonal carbonyl carbon. The greater flattening of the ring is also, presumably, responsible for the major difference in the coupling constants between H-4 and H-5,5′. H-4 apparently divides the angle between H-5 and H-5′ in the boronate derivatives less equally than in the acetal. However, use of the Karplus equation[21] to calculate the angle between the two methylene protons, $\phi_{5,5'}$ ($= \phi_{4,5'} - \phi_{4,5}$), in the boronate derivatives leads to a value of 137°, in considerable disagreement with the expected value of 120° (a similar calculation for the acetals gave[23] $\phi_{5,5'} = 125°$). Such discrepancies are, however, well known[25] and have resulted in a number of modifications to the Karplus equation[21] based on the assumption that the angle between the geminal hydrogens should be 120°.

Thus, the p.m.r. spectra of both arabinose boronates are consistent with 1,2:3,4-diester structures having similar conformations to, but slightly more planar rings than, the 1,2:3,4-di-*O*-isopropylidene derivative.

The values of $J_{1,2}$, $J_{2,3}$, and $J_{3,4}$ for the xylose boronates are similar to the coupling constants reported by Coxon[20] for some 1,2:3,5-di-*O*-benzylidene-α-D-glucofuranose derivatives, and an identical conformation is suggested (envelope ^3E) for the furanose ring. The higher value for $J_{1,2}$ indicates a slightly greater flattening of the furanose ring by the boronate as compared to the benzylidene group, similar to that noted for arabinose. The values of the coupling constants $J_{4,5}$ and $J_{4,5'}$ are also consistent with the structure proposed, and are self-consistent since calculation with the Karplus equation[21] leads to a value of 118° for $\phi_{5,5'}$ ($= \phi_{4,5} - \phi_{4,5'}$), close to the theoretical 120° expected for the H-5,5′ geminal protons. However, the error in $J_{4,5}$ is likely to be large.

Mass-spectral data (peaks of 10% or greater relative abundance) are shown in Table III. It can be seen that the arabinose boronates give somewhat simpler mass spectra than the corresponding xylose boronates and, in turn, the benzeneboronates give simpler spectra than the butaneboronates. However, no fragment exclusive to one sugar is observed in either the butaneboronate or benzeneboronate derivatives, although in some instances the intensity differences are considerable and consistent under the described conditions. Most of the major fragments may be tentatively assigned structures on the basis of comparison of the benzeneboronate and butaneboronate masses, and by reference to the mass spectra of the structurally related D-xylose and L-arabinose acetals. The difference of 20 mass units between the butyl and phenyl radical permits identification of fragments containing these groups. However, it is emphasised that identifications of fragments must remain tentative in the absence of high-resolution data to confirm atomic composition.

The first step in the fragmentation of isopropylidene derivatives, proposed by DeJongh and Biemann[14], is the formation of a stable, tertiary carbonium ion by

TABLE III

MASS-SPECTRAL DATA (m/e VALUES[a]) FOR BORONATES OF ARABINOSE AND XYLOSE[b]

1	2	3	4	4	4
322 (11)	323 (16)	152 (44)	253 (23)	139 (100)	99 (23)
172 (20)	322 (70)	151 (12)	252 (12)	138 (32)	98 (11)
159 (28)	321 (36)	139 (42)	197 (13)	127 (71)	97 (32)
147 (15)	172 (30)	138 (11)	182 (10)	126 (55)	96 (20)
146 (100)	160 (20)	127 (26)	169 (15)	125 (33)	87 (17)
145 (31)	159 (100)	126 (100)	168 (11)	124 (14)	84 (12)
105 (20)	158 (24)	125 (30)	167 (17)	114 (10)	83 (29)
104 (12)	147 (40)	100 (13)	157 (23)	113 (29)	82 (11)
	146 (83)	97 (18)	156 (14)	112 (16)	81 (23)
	145 (22)	96 (11)	155 (23)	111 (24)	71 (11)
	105 (55)	83 (14)	154 (14)	110 (11)	70 (28)
	104 (34)	70 (64)	153 (18)	101 (10)	69 (24)
	103 (13)	69 (19)	152 (31)	100 (14)	57 (17)
	91 (38)	56 (16)	151 (10)		56 (16)
	89 (11)	55 (18)	141 (19)		55 (22)
	77 (14)	44 (24)	140 (22)		43 (19)
	43 (18)	43 (21)			

[a] Relative abundance given in brackets; peaks with ≥ 10% relative abundance are recorded. [b] β-L-Arabinopyranose 1,2:3,4-bis(benzeneboronate) (**1**), α-D-xylofuranose 1,2·3,5-bis(benzeneboronate) (**2**), β-L-arabinopyranose 1,2·3,4-bis(butaneboronate) (**3**), α-D-xylofuranose 1,2·3,5-bis(butaneboronate) (**4**).

elimination of a methyl group from the 2,2-dimethyl-1,3-dioxolane or -1,3-dioxane ring. Thus, a prominent M−15 peak is observed. A similarly stabilised, initial fragment is not possible for the boronic esters. Thus, the low probability of boron carrying a positive charge is responsible for the major differences in preferred fragmentation pathways.

In contrast to the acetal derivatives, the molecular ions for each boronate derivative are easily detected and, for the benzeneboronates, are prominent. Thus, the molecular ion of α-D-xylofuranose 1,2:3,5-bis(benzeneboronate) is the third most-prominent peak at 70% of the base peak. ^{10}B isotope peaks of 53–56% of the molecular ion were obtained, except for β-L-arabinopyranose 1,2:3,4-bis(benzeneboronate) which showed a 37% relative abundance. This is somewhat low, but otherwise the values are consistent, within the limits of instrumentation errors, with each molecule containing two boron atoms. The isotopic ratio of ^{11}B:^{10}B is 4.3.1.

Both butaneboronates produce fragments at M−29, presumably from loss of an ethyl radical. This peak is quite prominent for the xylose derivative (19% of base). Further peaks for loss of the propyl and butyl radicals are also present.

The ion at m/e 152 (172 for the benzeneboronates) is a major, characteristic fragment, an equivalent of which is not reported for the acetals[14]. This ion may arise by loss of formaldehyde[26] and RBO_2 (R = butyl or phenyl) to give the fragment $C_4H_4O_2BR^{\cdot +}$.

Fragment ions, for which formation probably follows mechanisms similar to those proposed for isopropylidene derivatives[14], are observed at m/e 139 and 126 for the butaneboronates, and at 20 mass units higher for the benzeneboronates. These prominent and characteristic fragments of boronic esters of carbohydrates probably have the composition $C_3H_3O_2BR^+$ and $C_2H_2O_2BR^+$, where R = butyl or phenyl. The fragment at *m/e* 146 in the benzeneboronate series has previously been identified for methyl hexopyranoside derivatives[15].

As previously mentioned, the mass spectra of the arabinose and xylose boronates do not show any prominent fragment ion exclusive to just one of the sugars. This is in contrast to the acetal derivatives, where a fragment ion of *m/e* 129 distinguishes[14] the xylose from the arabinose derivative. The equivalent fragment in the boronate series would be *m/e* 155 (175). An ion of this mass number is present in the spectrum of each sugar (very weak for the benzeneboronate of arabinose) and thus is not of similar, diagnostic value. However, a major, distinguishing feature in the boronate series is the relatively greater intensity of the peaks at *m/e* 127 (147) for the xylose derivative. The intensity ratio for 126:127 was ~0.8:1 for xylose and ~4.3:1 for arabinose, and the equivalent ratio in the benzeneboronates, 146:147, was ~2.1:1 for xylose and ~6.8:1 for arabinose. This distinctively more-prominent fragment at *m/e* 127 (147) in the xylose boronates possibly arises from the boronic ester at the primary C-5 group. The intensity difference is consistent, is apparent in both the benzeneboronates and butaneboronates, and occurs between peaks separated by just one mass unit. This is good evidence that the difference is of structural significance and of diagnostic value.

Both benzeneboronates show prominent ions at *m/e* 105 and 104. The latter ion, tentatively identified as $C_6H_5BO^+$, has been reported previously[27,28]. To our knowledge, the former more-prominent ion has not been previously described, although it is observed in the mass spectrum of benzeneboronic anhydride[17,28].

Both benzeneboronates give an ion at *m/e* 91, which is probably the tropylium ion. A mechanism has been proposed for the formation of this ion from the benzeneboronates of some 1,2- and 1,3-diols[27]. As expected from this mechanism (requiring the Ph–B–O–CH_2-grouping), the ion *m/e* 91 is much more prominent for the xylose benzeneboronate (38% of base) than for the arabinose derivative (6% of base). The absence of an ion at *m/e* 91 in the butaneboronates is further evidence for the assignment of this fragment as the tropylium ion.

Thus, comparisons with the isopropylidene derivatives of arabinose and xylose, and the substituent-labelling of fragment ions by the phenyl or butyl radicals have allowed some of the major ions in the mass spectra of the boronic esters of arabinose and xylose to be tentatively identified.

Both the mass-spectral and p.m.r. data are consistent with a 1,2:3,4-diboronate structure for L-arabinose and a 1,2:3,5-diboronate structure for D-xylose, as expected from examination of molecular models and by analogy with the isopropylidene derivatives. In addition, differences in the mass spectra, and the ease of formation and suitability for g.l.c.[11,12] of their butaneboronates, allow a simple and sensitive identification of arabinose and xylose.

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