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SYNTHESIS, AND P. M. R. AND MASS SPECTRA OF SOME BORONIC ESTERS OF CARBOHYDRATES*

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ABSTRACT

The synthesis of boronic esters of L-fucose, D-glucose, D-fructose, and DL-glyceraldehyde is described. The structures of these compounds and appropriate derivatives, based on p.m.r. and mass-spectral data, are discussed.

INTRODUCTION

Following our observation[1] that certain sugars gave single peaks on g.l.c. after reaction with butaneboronic acid followed by silylation, the synthesis, in high yield, of the butaneboronic and benzeneboronic esters of xylose and arabinose[2] was described. We now report on the boronates of L-fucose, D-glucose, D-fructose, and DL-glyceraldehyde. Although the derivative of choice for g.l.c. was the butaneboronate, the benzeneboronates are more suitable for synthetic and structural studies because of their crystallinity.

RESULTS AND DISCUSSION

The products of synthesis described here may be usefully compared with the previously reported[2] boronates (**1–4**) of xylose and arabinose. Structures have been assigned by comparisons with **1–4** and with acetal derivatives, by examination of molecular models, and from p.m.r., mass-spectral, and i.r. data.

The benzeneboronates were usually crystalline, but pyridine was difficult to remove from the crystals of the 6-deoxy-L-galactose (L-fucose) (**10**) and D-fructose benzeneboronates (**11**) which contained one mole of pyridine of crystallization. α-L-Fucopyranose 1,2:3,4-bis(benzeneboronate) (**10**) was isolated free from pyridine.

The p.m.r. data (first-order analysis) are recorded in Tables I and II. The pyranose derivatives (**9–12**) of D-fructose and L-fucose have spectra similar to that of **2**, and the D-glucofuranose derivatives (**6–8**) have spectra closely related to that of **4**.

The L-fucose boronates, **9** and **10**, show almost identical, vicinal coupling constants. For the benzeneboronate, the shifts of which are consistently to lower

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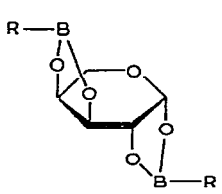
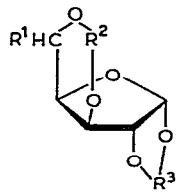
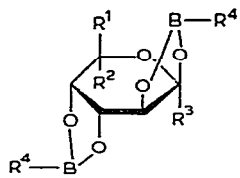


1 R = Bu
2 R = Ph



3 R^1 = H, R^2 = R^3 = B-Bu
4 R^1 = H, R^2 = R^3 = B-Ph
5 R^1 = H, R^2 = B-Ph, R^3 = CMe_2
6 R^1 = CH_2OH, R^2 = R^3 = B-Ph
7 R^1 = CH_2OBz, R^2 = R^3 = B-Ph
8 R^1 = CH_2OH, R^2 = B-Ph, R^3 = CMe_2



9 R^1 = R^3 = H, R^2 = Me, R^4 = Bu
10 R^1 = R^3 = H, R^2 = Me, R^4 = Ph
11 R^3 = CH_2OH, R^1 = R^2 = H, R^4 = Ph
12 R^3 = CH_2OBz, R^1 = R^2 = H, R^4 = Ph

field, the doublet (J 5.9 Hz) at lowest field was assigned to the anomeric proton (H-1), thereby establishing the doublet of doublets (4.35 p.p.m., larger splitting 5.9 Hz) as due to H-2. The signal for the Me protons was identified as the doublet at 1.22 p.p.m. Thus, the doublet–quartet at 3.74 p.p.m. (partially overlapping with the signal for H-4 in the benzeneboronate in benzene-d_6, but well resolved in $CDCl_3$) was from

TABLE I

CHEMICAL SHIFTS OF SOME L-FUCOSE, D-GLUCOSE, AND D-FRUCTOSE DERIVATIVES

Compound	*Chemical shifts* (δ)						
9[a,d]	5.58 d (H-1)	4.17 dd (H-2)	4.55 dd (H-3)	3.85 dd (H-4)	3.53 dq (H-5)	1.20 d (3 H-6)	
10[a,d]	5.67 d (H-1)	4.35 dd (H-2)	4.84 dd (H-3)	3.98 dd (H-4)	3.74 dq (H-5)	1.22 d (3 H-6)	
6[b,e]	6.20 d (H-1)	5.01 d (H-2)	4.71 d (H-3)	4.30 db (H-4)	~4.5 mb (H-5)	3.5-4.1 mb (H-6,6′)	~1.8 b (OH)
6+Eu(FOD)$_3$[c,e]	6.67 d (H-1)	5.47 d (H-2)	6.04 d (H-3)	5.63 db (H-4)	~6.4 mb (H-5)	~7 mbo (H-6,6′)	
7[b,e]	6.25 d (H-1)	5.07 d (H-2)	4.76 do (H-3)	4.39 db (H-4)	~4.7 o (H-5)	~4.6 ddo (H-6)	~4.4 ddo (H-6)
7+Eu(FOD)$_3$[c,e]	6.48 do (H-1)	5.34 d (H-2)	5.44 d (H-3)	4.90 db (H-4)	~5.23 tb (H-5)	6.70 dd (H-6)	~6.49 ddo (H-6)
8[b,d]	5.85 d (H-1)	4.67 d (H-2)	4.57 d (H-3)	1.55 s (C–Me)	1.32 s (C–Me)		
11[a,e,f]	3.81 do (H-1)	3.60 d (H-2)	4.76 d (H-3)	5.07 dd (H-4)	4.64 db (H-5)	3.93 d (H-6)	3.75 ddo (H-6′)
12[b,e]	4.70 do (H-1)	4.39 d (H-1)	4.93 d (H-3)	5.11 dd (H-4)	~4.7 o (H-5)	4.05 d (H-6)	3.81 dd (H-6′)
5[a,d]	5.64 d (H-1)	4.42 d (H-2)	1.40 s (Me)	1.10 s (Me)			

[a]In C_6D_6. [b]In $CDCl_3$. [c]In $CDCl_3$; ~0.6:1 molar ratio of shift reagent:boronate. [d]60 MHz. [e]100 MHz. [f]OH at 3.4 p.p.m. (sb). Key: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad, o, overlapping.

TABLE II

COUPLING CONSTANTS FOR THE COMPOUNDS IN TABLE I

Compound	*Coupling constants (Hz)*									
9	6.0 ($J_{1,2}$)	2.2 ($J_{2,3}$)	8.0 ($J_{3,4}$)	2.0 ($J_{4,5}$)	6.1 ($J_{5,6}$)					
10	5.9 ($J_{1,2}$)	2.2 ($J_{2,3}$)	8.1 ($J_{3,4}$)	1.9 ($J_{4,5}$)	6.4 ($J_{5,6}$)					
6	4.2 ($J_{1,2}$)	~0 ($J_{2,3}$)	2.6 ($J_{3,4}$)	~0 ($J_{4,5}$)[a]	3–4 ($J_{5,6}$)	3–4 ($J_{5,6}$)	11–12 ($J_{6,6'}$)			
7	4.2 ($J_{1,2}$)	~0 ($J_{2,3}$)	2.6 ($J_{3,4}$)	~0 ($J_{4,5}$)[a]	3.9 ($J_{5,6}$)	3.4 ($J_{5,6}$)	12 ($J_{6,6'}$)			
8	3.6 ($J_{1,2}$)	~0 ($J_{2,3}$)	2.5 ($J_{3,4}$)							
11	2.3 ($J_{3,4}$)	8.4 ($J_{4,5}$)	1.8 ($J_{5,6'}$)	<1 ($J_{5,6}$)	13 ($J_{6,6'}$)	12 ($J_{1,1'}$)				
12	2.3 ($J_{3,4}$)	8.5 ($J_{4,5}$)	2.0 ($J_{5,6'}$)	<0.5 ($J_{5,6}$)	13.8 ($J_{6,6'}$)	11.8 ($J_{1,1'}$)				
5	3.7 ($J_{1,2}$)	12 ($J_{5,5'}$)								

[a]Signal broadening indicates a small $J_{4,5}$ coupling.

H-5. The $J_{4,5}$ value measured from the splitting in the H-5 signal allowed the signal centred at 3.98 p.p.m. to be assigned to H-4. Likewise, the signal for H-2 could be linked to that at 4.84 p.p.m., which must be due to H-3.

Characteristic doublets for H-1,2,3 in isopropylidenexylohexofuranose derivatives[5,14], and noted[2] for **3** and **4**, were apparent in the spectrum of **6**. The low-field signal (6.20 p.p.m.) for H-1 had the same splitting as the signal at 5.01 p.p.m. (H-2). Irradiation in the region of 4.71 p.p.m. (H-3) collapsed the broad doublet at 4.30 p.p.m. (H-4) to a broad singlet. In experiments with the shift reagent added, the signals for H-1 and H-2 were confirmed by decoupling. Irradiation in the region of the H-4 resonance collapsed the signal assigned to H-3 to a singlet and somewhat sharpened the signal for H-5. The signals for H-5,6,6′ were distinguished by integration, addition of shift reagent, and the effect of benzoylation. In C_6D_6 (results not tabulated), irradiation at ~3.97 p.p.m. (H-4) sharpened the signal for H-5.

Further corroboration of assignments was obtained by examination of **7**, the benzoate of **6**. Three characteristic doublets (H-1,2,3) were observed at 6.25, 5.07, and 4.76 p.p.m., respectively. The signal for H-3 overlapped that for H-5. The signals for H-1,2,3,4 were shifted slightly downfield on benzoylation of **6**, but those for H-5,6,6′ were more affected. The signal for H-6,6′ in **7**, which was an AB quartet further split by H-5, was considerably shifted downfield by addition of shift reagent. Distinction between H-3 and H-4 was difficult, and was made on the basis of comparison with the acetal derivatives[5,14] and **3** and **4**. Further corroboration of these assignments depended upon the $J_{4,5}$ value which resulted in the doublet from H-4 being broadened and which resulted in a slight sharpening of the signal for H-5 when the region of the H-4 resonance was irradiated.

The spectra of the benzeneboronic derivatives **11** and **12** of D-fructose showed similarities to those of **1** and **2**, and **9** and **10**. Thus, $J_{3,4}$ of **11** corresponds to $J_{2,3}$ of **10** or **2**; likewise, $J_{4,5}$ corresponds to $J_{3,4}$, and $J_{5,6'}$ to $J_{4,5}$. In the fructose

derivatives, **11** and **12**, the assignment was based on H-3 (coupled only to H-4). Irradiation in the region of H-3 collapsed the lowest field doublet of doublets to a doublet, identifying this signal as due to H-4. The AB quartets for H-1,1′ and H-6,6′ overlapped in the spectrum of **12** and no HO coupling was observed, possibly because of the presence of pyridine. However, distinction between H-1,1′ and H-6,6′ was made on the basis of coupling to H-5. In the benzoylated derivative, the AB quartet that was not thus further split shifted downfield.

The spectral assignments of **8** and **5** were based on inspection and comparison with the spectra of **4**, **6**, and **7**.

The L-fucose and D-fructose boronates, **9**–**12**, show J values similar to those of **1** and **2**, and probably have similar conformations[2]. The coupling constants for the protons at the bridgehead of the boronic ester and pyranoid rings are slightly larger than the corresponding constants of 1,2:3,4-di-*O*-isopropylidene-β-L-arabinopyranose[15]. Thus, $J_{1,2}$ and $J_{3,4}$ for the isopropylidene derivative and a number of related structures were 5.0 and 7.8–7.9 Hz, respectively. The boronic esters **1**, **2**, **9**, and **10** had $J_{1,2}$ 5.9–6.0, and $J_{3,4}$ 7.9–8.2 Hz (**11** and **12** had $J_{4,5}$ 8.4–8.5 Hz). Although this trend to higher J values may be a result of other than stereochemical factors, the result is consistent with the view[2] that the trigonal, planar nature of the boron causes a somewhat flatter ring. Comparison of a dioxolane ring with a cyclic carbonate ester containing a trigonal carbonyl carbon showed a similar effect[16].

It is possible to identify the signals for the ring methylene protons of the D-fructose and L-arabinose[2] derivatives **11**, **12**, **1**, and **2** by comparison with the L-fucose derivatives, **9** and **10**, where there is only one proton at this position in the pyranose ring, *trans* to the 3,4-boronate group ($J_{4,5}$ 2.0 Hz). In the fructose derivatives, **11** and **12**, this identified H-6′ as *trans* to the 4,5-boronate group, and in the L-arabinose derivatives[2] **1** and **2**, H-5 is *trans* to the 3,4-boronate ring. Therefore, it is the methylene proton to higher field that is further split by the vicinal ring proton and which is *trans* to the boronate ring.

Examination of molecular models and reference to the acetal analogues[17] suggests that two possible structures might be expected for the bis(benzeneboronic) ester of D-fructose, namely the 2,3:4,5- or 1,2:4,5-bis(boronate); the p.m.r. evidence favours the former structure. The similarity of the p.m.r. spectra of **11**, **12**, and **2**, already discussed, closely parallels that of the spectra of 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose and 1,2:3,4-di-*O*-isopropylidene-β-L-arabinopyranose[17]. The easy preparation and high yield of the D-fructose bis(boronate) make it an attractive synthetic intermediate (*cf.* D-glucose, refs. 3 and 4).

α-D-Glucofuranose 1,2:3,5-bis(benzeneboronate) (**6**) has been previously characterized[3,4], but the p.m.r. spectrum has not been discussed, and the benzoate derivative is new. Comparison of **6** with the boronic esters **3** and **4** of xylose[2] and with some 1,2:3,5-di-*O*-benzylidene-α-D-glucofuranose derivatives[5] suggests similar conformations for the furanoid ring. Thus, Coxon[5] reported $J_{1,2}$ 3.6–3.7, $J_{2,3}$ <0.4, and $J_{3,4}$ 2.3–2.5 Hz for the benzylidene derivatives. Compounds **3**, **4**, **6**, and **7** show similar values, but $J_{1,2}$ (4.0–4.2 Hz) is consistently larger. The effect is numerically

less marked than for **1**, **2**, **9**, **10**, **11**, and **12** as already discussed, but may similarly be interpreted as due to a slight flattening of the ring at the C-1–C-2 bridgehead as a result of the fusion of the 1,2-boronic ester ring. The corresponding 1,2-*O*-isopropylidene 3,5-benzeneboronate derivatives, **8** and **5**, showed the same values for $J_{1,2}$ as reported by Coxon[5], and, by analogy, a conformation approaching that of an envelope (^3E) is suggested for **6–8**.

The major, mass-spectral peaks are shown in Table III. The data are consistent with the structures proposed. The molecular ions of both boronates (**9** and **10**) of L-fucose are easily detected and this, in combination with elemental analysis and i.r. data (absence of OH absorptions), establishes the bis(boronic ester) structure.

TABLE III

MASS-SPECTRAL DATA

Compound	*Major fragment ions (relative abundance, %)*
9	126(100), 70(29), 125(26), 113(15), 43(9), 69(8), 170(8), 55(7), 56(6), 83(5).
10	146(100), 145(27), 55(26), 57(22), 43(20), 41(18), 69(17), 105(15), 83(13), 97(12).
6	159(100), 147(85), 146(64), 175(30), 352(27), 158(26), 104(26), 91(22), 55(15), 351(15), 188(14), 160(14), 145(14), 206(11), 201(11), 103(11).
7	105(100), 146(27), 159(27), 334(16), 77(15), 188(12), 147(12), 160(11), 106(10), 145(8), 104(7).
8	43(100), 159(93), 59(54), 105(51), 147(35), 41(35), 104(25), 57(25), 291(25), 55(22), 91(19), 85(18).
11[a]	105(100), 321(91), 159(61), 173(52), 320(45), 104(43), 146(43), 39(40), 91(36), 44(20).
12	105(100), 321(59), 159(37), 77(37), 320(31), 173(28), 104(24), 160(17), 78(14), 51(14).
5	43(100), 159(54), 105(48), 160(45), 104(39), 261(32), 91(23), 59(19), 158(15), 77(15).
13	147(100), 105(79), 91(76), 104(68), 159(62), 146(48), 160(41), 77(29), 51(25), 103(23).

[a]Peaks for pyridine have been removed from the spectrum.

The prominent base-peak at *m/e* 126 (146), previously commented upon[2,6], probably arises from the ion $[C_2H_2O_2BR]^+$ (R = butyl or phenyl). The shift of 20 mass units (126–146) between the butaneboronate and the benzeneboronate indicates the presence of the butyl and phenyl radical, respectively. The ratios of the intensities of ions 126:125 and 146:145 indicate the presence of boron in the fragment, which is consistent with the proposed structures for **9** and **10**. The ions at *m/e* 127 (147) are present at 8–10% of the base peak and are thus mainly accountable in terms of ^{13}C and ^2H isotope peaks from the fragment at *m/e* 126 (146). The peaks at *m/e* 139 (159) are also very small (2–4% of base). Since the mass spectra of the other boronates reported here and previously[2] all possess one or both of these peaks, it seems reasonable to propose that the lack of a methylene group in **9** and **10** affects fragmentation mechanisms in such a way as to hinder the formation of these ions.

The benzeneboronate (**6**) of D-glucose has a prominent molecular ion and a low intensity (2%) peak at *m/e* 321 (M−31) which is indicative of the CH_2OH group.

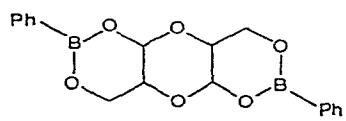
The molecular ion of the benzoate **7** is of low intensity (2%), and the first, major fragmentation ion occurs at *m/e* 334 (loss of benzoic acid). A metastable peak between *m/e* 244 and 245 was detected for this fragmentation process (theoretical, *m/e* 244.6). The rather simple spectrum has the base peak at *m/e* 105, which is probably mainly the ion $[PhCO]^+$. However, all benzeneboronates (*e.g.*, **11**) studied to date contain ions at *m/e* 104 and 105, consequently, the peak at *m/e* 105 must represent at least three fragment ions; the ion at *m/e* 104, which has been identified[7] as $[PhBO]^{\ddagger}$, will contribute ^{13}C and ^{2}H isotope peaks at 105, and the ion $[C_8H_9]^+$ is also formed in benzeneboronates[18].

The molecular ion of β-D-fructopyranose 2,3;4,5-bis(benzeneboronate) (**11**) was weak. A prominent M−31 peak was observed, however, as would be expected since formation of a major fragment ion from scission of the C-1–C-2 bond is characteristic of the 2-hexuloses[8], where the CH_2OH group is attached to an acetal carbon rather than an ether carbon atom as in the aldohexoses[9]. Such a cleavage would be unlikely as a major fragmentation process if C-1 were involved in a 1,2- or 1,3-boronic ester linkage. The benzoate **12** also shows a weak molecular ion (1%) and, like the glucose derivative, there is a prominent M−122 peak at *m/e* 334 (loss of benzoic acid). Again, scission of the C-1–C-2 bond gives a prominent fragment at *m/e* 321.

The spectra of 1,2-*O*-isopropylidene-α-D-xylofuranose 3,5-benzeneboronate (**5**) and the equivalent D-glucose derivative (**8**) showed expected features of both acetal and boronic ester derivatives. Thus, the molecular ion was comparatively weak, but a prominent M−15 peak was observed, corresponding to the loss of a methyl radical from the isopropylidene function. The ion at *m/e* 159, the base peak in the bis(benzeneboronic) derivatives, remained prominent. In addition, in **5**, a prominent ion at *m/e* 160, not present in the isopropylidene[10], and generally less prominent in the benzeneboronic series was observed. This may represent a direct cleavage of the 3,5-boronic ring to give a fragment $[C_3H_4O_2BPh]^{\ddagger}$, as opposed to $[C_3H_3O_2BPh]^+$, postulated[2] for the fragment of *m/e* 159. A fragment at *m/e* 160 corresponding to $[C_3H_4O_2BPh]^{\ddagger}$ has been reported in the mass spectra of 4,6-benzeneboronic esters of methyl pyranosides[6]. The postulated structure for **13** also possesses a 6-membered boronic ring containing a methylene group, and the mass spectrum similarly shows a relatively prominent ion at *m/e* 160. However, other boronates reported here show an ion at *m/e* 160, and benzoylation appears to increase the abundance of this ion relative to the ion *m/e* 159. Consequently, more than one mechanism may be operating, and more than one ion present at *m/e* 160. The peaks at *m/e* 201 (xylose) and 231 (glucose) probably correspond to the C-fragments of the isopropylidene derivatives. The F_2 ion, *m/e* 85, is also present, but the ion at *m/e* 100 (F_1) is small (5% for glucose) or not observed (xylose). Isopropylidene derivatives form a prominent M−15 peak by elimination of a methyl radical[10]; the low probability of boron carrying a positive charge prevents the formation of a similar ion at the boronic ester group. This evidently results in major differences in the preferred fragmentation pathways. Detailed discussion of these processes would require high-resolution and/or labelling

studies. As emphasised in our previous report[2], although the use of chemical labelling (butyl and phenyl radical) and comparisons with the literature allow tentative proposals to be made concerning ion composition, only high-resolution studies can provide indisputable evidence.

A number of stereoisomers are possible for the dimer of DL-glyceraldehyde and, consequently, a number of benzeneboronates may be formed. These may have been limited by steric requirements (fusion of two 6-membered boronate rings to a central 1,4-dioxolane ring) and further purification may have occurred during crystallization. However, the wide sublimation range and the appearance of the p.m.r. spectra (60 MHz; broad, unresolved envelope of signals) suggested a mixture of products, the elemental analysis of which was consistent with the postulated structure **13**. The mass spectrum provided some evidence in favour of the proposed structure. The highest mass peak observed (*m/e* 352, 2% of base) corresponds to the molecular ion. Characteristic ions for benzeneboronic esters at *m/e* 159, 147 and 146 were observed.



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Peaks characteristic of benzeneboronates were also observed at *m/e* 105, 104, and 91. The mass spectra of the benzeneboronates of ethylene glycol and propane-1,3-diol are reported[11,19] to show peaks for the tropylium ion at *m/e* 91, which decomposes to *m/e* 65 with the formation of a metastable peak at *m/e* 46.4. The mass spectrum of **13** shows a metastable peak between *m/e* 46 and 47. Thus, the ion at *m/e* 91 (observed in the other benzeneboronates reported here) is probably the tropylium ion, although the daughter ion at *m/e* 65 is very weak. Under the conditions used in this study, metastable peaks could only rarely be identified. However, for **13** an intense, metastable peak at *m/e* 122 was observed. This could correspond to the decomposition of the ion *m/e* 177 (8%) to form the ion *m/e* 147. A metastable peak between *m/e* 56 and 57 probably represents the formation of *m/e* 77 from the ion at *m/e* 104 (theoretical *m/e* 56.9; see ref. 11). A further metastable peak at *m/e* ~72 may arise from the formation of *m/e* 159 from the molecular ion (theoretical, *m/e* 71.8).

Only **6**, **8**, and **11** showed significant i.r. absorption for HO; B-aryl (~1440 cm^{-1}) absorptions were observed in the appropriate derivatives, and bands attributable[21] to the B–O stretching frequency were observed in the region 1360–1310 cm^{-1}.

Elemental composition and mass-spectral data, which showed the molecular ion and provided no evidence of pyroboronate structures[6], established a diboronic ester structure (**5** and **8** excepted), which was confirmed where appropriate by the lack of significant i.r. absorption for HO.

Comparison of the p.m.r. data in this and our previous report[2] with published

data on acetal derivatives[5,14,15] provided strong evidence for closely related, fused-ring systems, since the vicinal coupling constants were very similar. Variations may be logically interpreted in terms of stereochemical differences between trigonal boron and tetrahedral carbon. Thus, except for **5** and **8** (where, as expected, the $J_{1,2}$ values are the same as for previously reported acetals[5,14]), a 1,2-boronic ester structure is present.

An important inference from the mass spectra is the resistance of the fused carbohydrate–boronate ring systems to fragmentation (thus allowing easy identification of the molecular ion). When ring cleavage does occur, it appears that many rearrangements must be taking place and no unique ions diagnostic of a particular structure have been identified, although in the absence of evidence of a pyroboronate, the presence of an ion at *m/e* 146 (126) is good evidence of a 1,2-boronate structure. The mass spectra were useful in identifying free, primary hydroxyl groups in **6** and **11**.

Examination of molecular models revealed no structures, other than those assigned, which were consistent with the above facts.

^{13}C-N.m.r. studies[20] of **2**, **4**, and **8** have further confirmed the assigned structures. The size of the boronic ester rings may be recognized from the shift values of the *ortho*-^{13}C signals in the aromatic rings.

These and previous[1,2] studies indicate the potential usefulness of boronic esters for identification of some carbohydrates, either at the micro level by g.l.c.–m.s. of the butaneboronic derivatives (silylated if necessary) or by means of the crystalline benzeneboronates.

EXPERIMENTAL

General methods have been previously described[2]. Benzeneboronates were prepared by heating a solution of the appropriate sugar derivative in pyridine with 1 mol. of benzeneboronic acid for each diol group to be esterified. Butaneboronates were prepared by using a 3:1 molar excess of butaneboronic acid followed by extractions with chloroform.

α-L-Fucopyranose 1,2:3,4-bis(butaneboronate) (**9**). — The crude liquid product (74%), when twice distilled, had b.p. 70 ±5° (bath)/0.01 mmHg, $[\alpha]_D^{25}$ +24° (*c* 2.6, chloroform), +46° (*c* 1.3, benzene).

Anal. Calc. for $C_{14}H_{26}B_2O_5$: C, 56.81; H, 8.86. Found: C, 56.61; H, 8.67.

α-L-Fucopyranose 1,2:3,4-bis(benzeneboronate) (**10**). — Crystallization of the crude product from light petroleum gave material (65% corrected for solvation) which contained pyridine and had m.p. 55–75°, which was not improved by two further crystallizations.

Anal. Calc. for $C_{18}H_{18}B_2O_5 \cdot C_5H_5N$: C, 66.74; H, 5.58; N, 3.38. Found: C, 66.32; H, 5.64; N, 3.44.

Crystals of **10** (22%), obtained from the mother liquors of a third recrystallization, had m.p. 108.5–109.5°, $[\alpha]_D^{25}$ −6° (*c* 2.5, chloroform), +29° (*c* 1.1, benzene); lit.[12] m.p. 109.5°, $[\alpha]_D^{25}$ +29.4° (*c* <5, benzene).

α-D-Glucofuranose 1,2:3,5-bis(benzeneboronate) (**6**). — The crude product was crystallized from benzene–light petroleum to give **6** (~100%), m.p. 159–162°, $[\alpha]_D^{25}$ +25° (*c* 1.6, benzene); lit.[4] m.p. 161–162°.

6-O-Benzoyl-α-D-glucofuranose 1,2:3,5-bis(benzeneboronate) (**7**). — Benzoyl chloride (2 ml) was added dropwise with stirring to a solution of **6** (1.6 g) in dry pyridine (50 ml) at 5°. After 2 h, the solution was brought to room temperature and, after a further 30 min, concentrated to dryness. The residue was stored overnight *in vacuo* over phosphorus pentaoxide–potassium hydroxide and then extracted with refluxing benzene (100 ml). The extract was decolourized with charcoal and concentrated, the residue was extracted with boiling, light petroleum, and the extract was decolourized with charcoal. The crude product (82%) was recrystallized from light petroleum to give **7**, m.p. 142–144°, $[\alpha]_D^{26}$ +81° (*c* 1.5, benzene).

Anal. Calc. for $C_{25}H_{22}B_2O_7$: C, 65.83; H, 4.86. Found: C, 66.05; H, 4.98.

β-D-Fructopyranose 2,3:4,5-bis(benzeneboronate) (**11**). — Crystallization of the crude product from light petroleum–benzene gave material (92%) containing 1 mole of pyridine per mole of benzeneboronate. Attempts to remove the pyridine were unsuccessful. Recrystallization from toluene gave a colourless, crystalline product, m.p. 89–98°, $[\alpha]_D^{23}$ −17° (*c* 1.08, benzene).

Anal. Calc. for $C_{18}H_{18}B_2O_6 \cdot C_5H_5N$: C, 64.08; H, 5.38; N, 3.25. Found: C, 63.74; H, 5.64; N, 3.35.

1-O-Benzoyl-β-D-fructopyranose 2,3:4,5-bis(benzeneboronate) (**12**). — Compound **11** (2 g) was treated with benzoyl chloride, as described above, to give **12** (74%), m.p. 139–142° (from light petroleum), $[\alpha]_D^{23}$ −26° (*c* 1.1, benzene).

Anal. Calc. for $C_{25}H_{22}B_2O_7$: C, 65.84; H, 4.86. Found: C, 66.00; H, 4.89.

1,2-O-Isopropylidene-α-D-xylofuranose 3,5-benzeneboronate (**5**). — The crude product (97%, from benzene) was recrystallized from light petroleum to give **5**, m.p. 128–129°, $[\alpha]_D^{25}$ −1° (*c* 2.5, chloroform).

Anal. Calc. for $C_{14}H_{17}BO_5$: C, 60.90; H, 6.16. Found: C, 61.60; H, 6.28.

1,2-O-Isopropylidene-α-D-glucofuranose 3,5-benzeneboronate (**8**). — The crude product (88%, from light petroleum) was recrystallized to give **8**, m.p. 116–117°, $[\alpha]_D^{25}$ +14° (*c* 2.4, chloroform); lit.[13] m.p. 113–115°.

DL-*Glyceraldehyde benzeneboronate* (**13**). — The crude product (34%, from light petroleum), on recrystallization from toluene, gave **13** which sublimed at 260–274°. From the mother liquors, an additional yield (26%) of crystals was obtained which sublimed at 250–265°.

Anal. Calc. for $C_{18}H_{18}B_2O_6$: C, 61.42; H, 5.15. Found: C, 61.87; H, 5.07.

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