450. *The Interaction of Phenylboronic Acid with Hexosides.*

By R. J. Ferrier.

Methyl α-D-glucopyranoside reacts with phenylboronic acid (1 mol.) to give a crystalline 4,6-cyclic ester which, in turn, forms a 2,3-(diphenylpyroboronate) (containing a 7-membered ring) with an excess of the reagent. Phenylboronic acid (2 mol.) condenses smoothly with methyl α-D-mannopyranoside, to give the 2,3:4,6-diester, but with 1 mol. of the acid this reaction does not give a homogeneous product. Substituted phenylboronate esters of methyl α-D-glucopyranoside, and phenylboronates of other glycosides and related compounds, are reported. All the derivatives described are air-stable solids which readily decompose in water or alcohols. The ester linkages have been shown to be stable to esterifying conditions but unstable during methylation.

The interaction in aqueous solution of boric acid with hydroxylated compounds has been studied extensively,[1] but less attention has been paid to the reactions which take place in non-aqueous solvents. The possibility of triester formation complicates the investigation of the cyclic borates formed from diols, and with carbohydrate derivatives, which concern us here, condensation, with dimerisation, of such diesters has been shown to occur.[2] In an attempt to overcome this difficulty, phenylboronic acid, which is known to condense with polyhydroxy-compounds to give cyclic esters,[3] has been used in model experiments. Some crystalline phenylboronates of hexitols [3] and free sugars [4] have already been reported, but little is known of the kinds of diol system with which the acid will react.

Although methyl α- and β-D-glucopyranoside have been found to react with both boric acid [5] and phenylboronic acid,[6] discrete esters have not been reported and the sites of esterification have not been well defined. We have examined the action of 1 mol. of phenylboronic acid on these glycosides, and by azeotropic distillation in the presence of benzene to remove water have been able to obtain crystalline cyclic esters in high yield. The anhydride of phenylboronic acid (triphenylboroxole) was equally effective in the syntheses.

To determine the stability and sites of the boronate linkages, esterification and etherification of the free hydroxyl groups in the compounds were examined. Sugihara and

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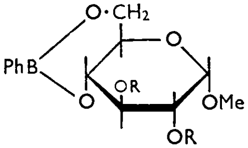
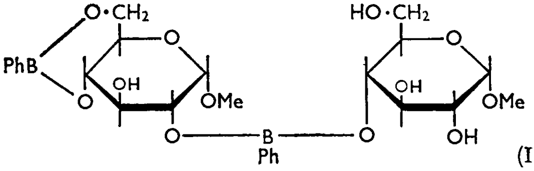
[1] For reviews see Böeseken, *Adv. Carbohydrate Chem.*, 1949, **4**, 189; Foster, *ibid.*, 1957, **12**, 81.
[2] Ferrier, unpublished results; cf. Gerrard, Lappert, and Mountfield, *J.*, 1959, 1529.
[3] Kuivila, Keough, and Soboczenski, *J. Org. Chem.*, 1954, **19**, 780.
[4] Wolfrom and Solms, *J. Org. Chem.*, 1956, **21**, 815.
[5] (*a*) Sugihara and Petersen, *J. Amer. Chem. Soc.*, 1956, **78**, 1760; (*b*) Bell, *J.*, 1935, 175.
[6] Sugihara and Bowman, *J. Amer. Chem. Soc.*, 1958, **80**, 2443.

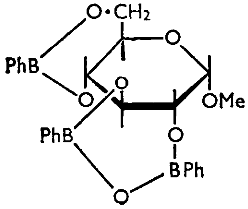
Bowman[6] found that the ester linkages of pyrogallol phenylboronate were stable towards benzoyl chloride in pyridine but unstable towards acetic anhydride in pyridine, as a mono-*O*-benzoate and a tri-*O*-acetate were produced. Smooth benzoylation (benzoyl chloride in pyridine) and acetylation (acetyl chloride in pyridine) of methyl α-D-glucopyranoside phenylboronate yielded a crystalline di-*O*-benzoate and di-*O*-acetate which were, respectively, identical with the compounds (I; R = Bz, Ac) prepared by the action of phenylboronic acid on methyl α-D-glucoside 2,3-dibenzoate and 2,3-diacetate. The product of the initial reaction is therefore methyl α-D-glucopyranoside 4,6-phenylboronate (I; R = H). Thus two *trans*-fused six-membered ring systems (cf. methyl 4,6-*O*-benzylidene-α-D-glucopyranoside) have been formed.



(I)



(II)

(III)


Repeated unsuccessful attempts were made to prepare a crystalline product by the toluene-*p*-sulphonylation of the boronate (I; R = H), but the expected polyester (I; R = p-$C_6H_4Me{\cdot}SO_2$) was obtained by esterification of methyl 2,3-di-*O*-tosyl-α-D-glucopyranoside with phenylboronic acid.

The methyl ether (I; R = Me) was readily prepared from methyl 2,3-di-*O*-methyl-α-D-glucopyranoside and phenylboronic acid but was obtained only in poor yield on methylation of the phenylboronate (I; R = H) with methyl iodide and silver oxide. Chromatographic examination of the hydrolysed methylation products indicated that the boronate ring had ruptured during the reaction. Tri-*O*-methylglucose, together with the expected di-*O*-methylglucose, was detected in significant quantities after acid hydrolysis. No tetra-*O*-methylglucose could be found. Addition of desiccants to the methylation medium did not prevent cleavage of the ring. Obviously caution must be exercised in the interpretation of the results of methylation experiments involving borate esters.[5b]

All the boronates described are air-stable solids which crystallise readily from hydrocarbon solvents [but see methyl α-D-glucopyranoside 2,3-(diphenylpyroboronate) 4,6-phenylboronate]. On addition of water or alcohols to solutions in dry dioxan there is an immediate change in optical rotation. In each case the magnitude of the rotational change is consistent with the occurrence of B–O bond fission with retention of the sugar configuration and regeneration of the parent glycoside. Other borates and boronates have been shown to hydrolyse similarly[7] and, for example, Wolfrom and Solms[4] isolated L-arabinose from the hydrolysate of its di(phenylboronate).

The infrared spectra of the glycoside boronates are characterised by strong absorptions at 1350—1310 cm.$^{-1}$ which have been attributed[8] to the B–O stretching frequency, and much sharper ones at 1440 cm.$^{-1}$ arising from the B–aryl systems.[8]

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[7] Lappert, *Chem. Rev.*, 1956, **56**, 959.

[8] Bellamy, Gerrard, Lappert, and Williams, *J.*, 1958, 2412.

Addition of triphenylboroxole to solutions in dioxan of the glycoside boronate (I; R = H) caused immediate changes in the optical rotations, but solutions of the 2,3-di-*O*-substituted derivatives were unaffected. As stated, alcohols (including cyclohexanol) cause the alcoholysis of the boronate rings. Consequently, it is possible that in solution the ester (I; R = H) might undergo intermolecular reaction to a slight extent, leading to compound (II) and related species. If the changes in rotation were due solely to interaction between the phenylboroxole and molecules of this type, or to changes in equilibria involving them, no effect would be observable in the benzylidene series but 2- and 3-mono-*O*-substituted derivatives of the ester (I; R = H) would be expected to be sensitive. The optical rotation of a solution of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside was, however, markedly decreased by the addition of the boroxole, while its 2,3-di-*O*-substituted derivatives and methyl 2-deoxy-α-D-glycopyranoside 4,6-phenylboronate were unaffected. It is concluded that reaction occurs at, and requires, the *trans*-2,3-diol grouping.

Equimolecular amounts of phenylboronic acid and the ester (I; R = H) were heated in benzene [procedure (*a*)], and from the products approximately 50% of the boronate was recovered. Repetition of the condensation with 2 mol. of phenylboronic acid gave methyl α-D-glucopyranoside 2,3-(diphenylpyroboronate) 4,6-phenylboronate (III) which showed insignificant O–H stretching absorption in the infrared region. The similarity between the interactions of this reagent and acetaldehyde with methyl α-D-glucopyranoside becomes clear.[9]

The 7-membered ring formed is analogous, therefore, to that produced between phenylboronic acid and *trans*-cyclohexane-1,2-diol.[6,10] The compound recrystallised only when moisture was strictly excluded and the relative stabilities of the 6- and the 7-membered ring containing boron were demonstrated by partial hydrolysis of the fully esterified glycoside (III) to the disubstituted derivative (I; R = H) in wet benzene in good yield. The extreme instability of this 7-membered ring does not seem to be a general feature of such cyclic systems, as a compound analogous to the polyester (III) prepared from 1,5-anhydro-D-glucitol could be handled very readily and no product of partial hydrolysis was obtained on treatment with wet benzene.

From the above results and the observation that *cis*-cyclohexane-1,2-diol reacts smoothly to form a 5-membered boronate ring,[6] it was predicted that methyl α-D-mannopyranoside would yield a 2,3:4,6-di(phenylboronate). Reaction between this glycoside and phenylboronic acid did not occur in boiling benzene, but a hydroxyl-free ester was readily prepared in dioxan [2 mol. of acid; procedure (*b*)]. With 1 mol. of the reagent this glycoside gave rise to a syrup which slowly crystallised. No suitable method of purification was discovered, but condensation with more acid (1 mol.) gave the known crystalline di(phenylboronate). The partially substituted derivative was acetylated and after distillation the syrupy di-*O*-acetyl α-D-mannopyranoside phenylboronate consumed *ca.* 0·7 mol. of periodate. This result, together with the fact that analysis of the syrupy distillate indicated that it was contaminated with small amounts of acetolysed products, shows that phenylboronic acid combined with both the 4,6- and the 2,3-diol groupings of the glycoside, but preferably with the latter. It was shown that the phenylboronic acid liberated on treatment of the glycoside phenylboronates with aqueous periodate did not interfere with the course of the periodate oxidations.

Methyl β-D-galactopyranoside with phenylboronic acid (1 mol.) gives a discrete crystalline product. Preliminary investigations[11] indicate that this compound has the 4,6-cyclic structure.

Other compounds in this series are listed in the Table.

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[9] Appel, Haworth, Cox, and Llewellyn, *J.*, 1938, 793.

[10] Compare the action of simple aldehydes on this compound: Head, *J.*, 1960, 1778.

[11] Ferrier, Hannaford, Overend, and Smith, unpublished results.

Phenylboronates and a diphenylpyroboronate.

Compound	Solvent for crystn.[a]	M. p.	$[\alpha]_D$	Found (%)			Formula	Required (%)		
				C	H	B		C	H	B
1	Benzene	188—189°	−82°	55·8	6·3	3·9	$C_{13}H_{17}BO_6$[b]	55·7	6·1	3·9
2	Benzene	177—178	−91	63·7	6·0	3·0	$C_{19}H_{21}BO_6$	64·0	5·9	3·0
3	Benzene–Pet	142—143	+63	59·0	6·5	4·1	$C_{13}H_{17}BO_5$	59·1	6·4	4·1
4	Benzene	176—177	−80	57·0	6·1	4·2	$C_{12}H_{15}BO_5$	57·6	6·0	4·3
5	Pet	180—181	+265	60·6	4·7		$C_{18}H_{16}BNO_6$[c]	61·2	4·6	
6	Benzene	164—165	+59	49·2	5·2	3·4	$C_{13}H_{16}BClO_6$[d]	49·6	5·1	3·4
7	Benzene	168—169	+49	48·0	5·3	3·4	$C_{13}H_{16}BNO_8$[e]	48·0	5·0	3·3
8	Benzene–Pet	188—189	−121	64·9	5·6	7·3	$C_{24}H_{23}B_3O_6$	65·4	5·3	7·4

Compounds (preparation procedure in parentheses): 1, *methyl β-D-glucopyranoside 4,6-phenylboronate* (*a*); 2, *benzyl β-D-glucopyranoside 4,6-phenylboronate* (*a*); 3, *methyl 2-deoxy-α-D-glucopyranoside 4,6-phenylboronate* (*a*); 4, *1,5-anhydro-D-glucitol 4,6-phenylboronate* (*b*); 5, p-*nitrophenyl 2,3-didehydro-2,3-dideoxy-α-D-glucopyranoside 4,6-phenylboronate* (*a*) (Ferrier, Overend, and Ryan, unpublished work); 6, *methyl α-D-glucopyranoside 4,6-*p-*chlorophenylboronate* (*a*); 7, *methyl α-D-glucopyranoside 4,6-*m-*nitrophenylboronate* (*a*); 8, *1,5-anhydro-D-glucitol 2,3-(diphenylpyroboronate) 4,6-phenylboronate* (*a*).

[a] Pet = light petroleum (b. p. 60—80°). [b] Found: MeO, 11·0. Reqd.: MeO, 11·1%. [c] Found: N, 4·0. Reqd.: N, 4·0%. [d] Found: Cl, 10·8. Reqd.: Cl, 11·3%. [e] Found: N, 4·3. Reqd.: N, 4·3%.

EXPERIMENTAL

The benzene and light petroleum used for recrystallisations of the boronates were dried over sodium wire. The specific rotations are quoted for 1% solutions in dioxan purified by fractional distillation from lithium aluminium hydride. They were measured in a 1 dm. tube at 22° ± 2°. It was shown that methoxyl determination by the infrared method of Anderson and Duncan[12] is satisfactory when applied to compounds containing boron. The author thanks Dr. D. M. W. Anderson (University of Edinburgh) for carrying out these analyses.

General Procedures for the Preparation of Boronate Esters (see Table).—(*a*) The reactants were stirred mechanically in boiling benzene, the water being collected in a Dean and Stark apparatus. The method gives quantitative yields, but is limited in that the water produced during small-scale reactions cannot be determined accurately. (*b*) The reactants were treated in boiling dioxan and the water produced was removed by careful fractional distillation of its azeotrope with the solvent. This method has two advantages over procedure (*a*): the compounds examined have a higher solubility in dioxan and this permits some reactions which do not proceed in benzene, and the water liberated in relatively small-scale experiments can be determined. For example, methyl 2,3-di-*O*-methyl-α-D-glucopyranoside (0·3 g.) was boiled in dioxan (50 ml.) with an excess of triphenylboroxole; the total water of condensation was removed in about 10 ml. of distillate (column packed with glass helices and of about 20 theoretical plates), which was then diluted to 25 ml. with dry dioxan; 5 ml. aliquot parts of this solution were titrated by the Karl Fischer method; 1·0 mol. of water was found.

Methyl α-D-Glucopyranoside 4,6-Phenylboronate.—Methyl α-D-glucopyranoside (9·7 g.) and phenylboronic acid (6·1 g., 1 mol.) in benzene (1·2 l.) were treated according to procedure (*a*), and water (1·8 ml., 100% theor.) was collected. On cooling, crystals (10·0 g.) separated and further material (3·2 g., total 94%) was obtained on concentration of the filtrate. Sublimation, or recrystallisation from benzene, gave pure *methyl α-D-glucopyranoside 4,6-phenylboronate*, m. p. 166—167°, $[\alpha]_D$ +59° (Found: C, 56·0; H, 6·3; B, 3·9; OMe, 11·2%; *M*, 309. $C_{13}H_{17}BO_6$ requires C, 55·7; H, 6·1; B, 3·9; OMe, 11·1%; *M*, 280).

*Methyl 2,3-Di-*O*-benzoyl-α-D-glucopyranoside 4,6-Phenylboronate.*—To methyl α-D-glucopyranoside 4,6-phenylboronate (4·0 g.), dissolved in dry pyridine (30 ml.) at 0°, benzoyl chloride (4·0 ml.) was added slowly with stirring. Stirring was continued for 1 hr. at 0°, then the precipitated pyridine hydrochloride was removed and washed with hot benzene. The combined pyridine and benzene solutions were taken to dryness and the residue was extracted with hot benzene. Evaporation of this extract gave a syrup which crystallised readily on treatment with benzene–light petroleum (b. p. 60—80°). Recrystallisation from the same solvents yielded *methyl 2,3-di-*O*-benzoyl-α-D-glucopyranoside 4,6-phenylboronate* (4·4 g., 64%), m. p. 203—204°, $[\alpha]_D$ +94° (Found: C, 66·9; H, 4·8; B, 2·2; OMe, 6·3. $C_{27}H_{25}BO_8$ requires C, 66·4; H, 5·1; B, 2·2; OMe, 6·3%). The product obtained in quantitative yield from phenylboronic

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[12] Anderson and Duncan, *Talanta*, 1960, **7**, 70.

acid and methyl 2,3-di-*O*-benzoyl-α-D-glucopyranoside (0·006 mole) [procedure (*a*)] had m. p. 203—204° alone or on admixture with the above sample.

Methyl 2,3-*Di*-O-*acetyl*-α-D-*glucopyranoside* 4,6-*Phenylboronate.*—Methyl α-D-glucopyranoside 4,6-phenylboronate (2·0 g.) in dry pyridine (20 ml.) was treated with acetyl chloride (5·0 ml.). Working up as for the benzoyl derivative, followed by distillation, gave a pale yellow viscous syrup (1·7 g., 65%), b. p. 154°/0·17 mm., which crystallised completely on trituration with light petroleum (b. p. 60—80°). Recrystallisation from this solvent gave *methyl* 2,3-*di*-O-*acetyl*-α-D-*glucopyranoside* 4,6-*phenylboronate*, m. p. 116—117°, $[\alpha]_D$ +74° (Found: C, 56·6; H, 6·0; B, 2·9; OMe, 8·5. $C_{17}H_{21}BO_8$ requires C, 56·1; H, 5·8; B, 3·0; OMe, 8·5%). The m. p. on admixture with the compound (m. p. 115—116°) obtained in high yield by reaction of phenylboronic acid and methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside (0·01 mole) [procedure (*a*)] was 115—116°.

Methyl 2,3-*Di*-O-*tosyl*-α-D-*glucopyranoside* 4,6-*Phenylboronate.*—(*a*) Reaction of equimolecular amounts (0·005 mole) of phenylboronic acid and methyl 2,3-di-*O*-tosyl-α-D-glucopyranoside [procedure (*a*)] gave *methyl* 2,3-*di*-O-*tosyl*-α-D-*glucopyranoside* 4,6-*phenylboronate* in good yield; recrystallised from dry, alcohol-free chloroform–light petroleum (b. p. 60—80°), this had m. p. 180—181°, $[\alpha]_D$ −15° (Found: C, 55·5; H, 4·7; B, 1·8; OMe, 5·3; S, 11·0. $C_{27}H_{29}BO_{10}S_2$ requires C, 55·1; H, 5·0; B, 1·8; OMe, 5·3; S, 10·9%). (*b*) Toluene-*p*-sulphonyl chloride reacted with the glycoside phenylboronate (I; R = H) in dry pyridine, to liberate pyridine hydrochloride, but no crystalline glycoside derivative was obtained.

Methyl 2,3-*Di*-O-*methyl*-α-D-*glucopyranoside* 4,6-*Phenylboronate.*—(*a*) Methyl 2,3-di-*O*-methyl-α-D-glucopyranoside (0·01 mole) and phenylboronic acid (0·01 mole) gave [procedure (*a*)] the 4,6-*phenylboronate* [from light petroleum (b. p. 60—80°)] in quantitative yield, with m. p. 119—121°, $[\alpha]_D$ +61° (Found: C, 58·7; H, 6·8; OMe, 29·6; B, 3·5. $C_{15}H_{21}BO_6$ requires C, 58·5; H, 6·9; OMe, 30·2; B, 3·5%). (*b*) Methyl α-D-glucopyranoside 4,6-phenylboronate (2·0 g.) was heated under reflux in methyl iodide (50 ml.) with silver oxide (3·0 g.) for 6 hr. The solids were removed and the solvent evaporated. Chromatographic analysis of the hydrolysate (2N-hydrochloric acid at 100° for 2 hr.) of the syrupy residue revealed mixtures of tri-, di-, and mono-*O*-methylglucose. The tri-*O*-methyl ethers were present in considerable quantity. Three successive such methylations resulted in increased amounts of di- and tri-*O*-methylglucose and less mono-*O*-methyl ether in the hydrolysate. No tetra-*O*-methylglucose could be detected. Addition of calcium chloride or Drierite to the methylation mixtures caused no observable change in products. The syrup obtained after one methylation of the boronate (4·0 g.) with methyl iodide (100 ml.) and silver oxide (12 g.) in the presence of Drierite (10 g.) was distilled. Redistillation of the crude product gave a viscous syrup from which crystals (0·1 g.) were obtained on trituration with light petroleum (b. p. 60—80°). Recrystallisation from this solvent gave methyl 2,3-di-*O*-methyl-α-D-glucopyranoside 4,6-phenylboronate, m. p. 120—122°, identical (mixed m. p.) with the product of reaction (*a*).

Methyl α-D-*Glucopyranoside* 2,3-(*Diphenylpyroboronate*) 4,6-*Phenylboronate.*—Methyl α-D-glucopyranoside 4,6-phenylboronate (6·7 g.) and triphenylboroxole (2·5 g., 0·33 mol.) were caused to react by procedure (*a*) (700 ml. of benzene); water was eliminated. Unchanged ester (3·1 g., 46%) was recovered and was the only crystalline material obtained. The condensation was repeated [procedure (*b*)] with double quantity of triphenylboroxole. Removal of the dioxan gave, in quantitative yield, a product which crystallised on trituration with light petroleum (b. p. 60—80°; dried by lithium aluminium hydride), m. p. 161—163°. Recrystallisation from the same solvent gave *methyl* α-D-*glucopyranoside* 2,3-(*diphenylpyroboronate*) 4,6-*phenylboronate*, m. p. 162—163°, $[\alpha]_D$ −31° (Found: C, 64·0; H, 5·5; B, 6·8. $C_{25}H_{25}B_3O_7$ requires C, 63·9; H, 5·4; B, 6·9%). All samples studied had slight O–H stretching absorptions in the infrared region, but the magnitudes of these absorptions indicated that the molecular structure was devoid of hydroxyl groupings. The spectrum of the analogous compound derived from 1,5-anhydro-D-glucitol (see Table 1) lacked absorption in this region.

The polyester (10 g.) was dissolved in benzene (250 ml.), water (0·8 ml.) was added, and the mixture was shaken. Overnight precipitation occurred of methyl α-D-glucopyranoside 4,6-phenylboronate (4·7 g., 79%), m. p. and mixed m. p. 166—167°, $[\alpha]_D$ +60°.

Methyl α-D-*Mannopyranoside Phenylboronate.*—Methyl α-D-mannopyranoside (2·0 g.) with phenylboronic acid (1·2 g., 1 mol.) [procedure (*b*)] gave a syrup (2·8 g.) which slowly crystallised. The solid was insoluble in benzene and no suitable solvent for recrystallisation could be found;

it had m. p. (after draining on porcelain tile) 106—108°, $[\alpha]_D$ $-52°$ (Found: C, 56·6; H, 6·1; B, 3·9. $C_{13}H_{17}BO_6$ requires C, 55·7; H, 6·1; B, 3·9%). Treatment of this solid (0·2 g.) with phenylboronic acid (0·09 g., 1 mol.) yielded *methyl* α-D-*mannopyranoside* 2,3:4,6-*di(phenylboronate)* (0·16 g., 60%), m. p. 112—115°; recrystallised from light petroleum (b. p. 60—80°) it had m. p. 116—117°, $[\alpha]_D$ $-118°$, devoid of OH infrared absorption (Found: C, 61·9; H, 5·6; B, 5·8. $C_{19}H_{20}B_2O_6$ requires C, 62·3; H, 5·5; B, 5·9%). This compound had undepressed m. p. on admixture with that readily obtained from methyl α-D-mannopyranoside and 2 mol. of phenylboronic acid [procedure (*b*)].

The methyl α-D-mannopyranoside phenylboronate (2·6 g.) was acetylated under the conditions used to prepare methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside 4,6-phenylboronate, to give a syrup (2·5 g., 74%) part of which (0·6 g.) was distilled. The resulting glassy *product* (0·35 g.), $[\alpha]_D$ $-5·4°$, consumed 0·73 mol. of periodate (see below) (Found: C, 55·6; H, 6·0; Ac, 27·0; B, 2·8. $C_{17}H_{21}BO_8$ requires C, 56·1; H, 5·8; Ac, 23·6; B, 3·0%).

Periodate Oxidation of Glycoside Boronates.—The oxidations were carried out with aqueous sodium metaperiodate containing dioxan (5%) (added initially to dissolve the esters). The consumption of reagent was followed spectrophotometrically,[13] any absorptions due to the esters or solvent being nullified by incorporation of these in the blank cells.

Results. Consumptions of periodate were: methyl α-D-glucopyranoside 4,6-phenylboronate 1·95 mol. (5 hr. const.); methyl α-D-mannopyranoside 2,3:4,6-di(phenylboronate) 1·95 mol. (5 hr. const.); methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside 4,6-phenylboronate, no uptake during 3 days; methyl di-*O*-acetyl-α-D-mannopyranoside phenylboronate 0·73 mol. (5 hr. const.).

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[13] Aspinall and Ferrier, *Chem. and Ind.*, 1957, 1216.