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THE USE OF BORIC AND BENZENEBORONIC ACIDS IN THE PARTIAL ACETONATION OF MONOSACCHARIDES*

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ABSTRACT

The preparation of mono-*O*-isopropylidene derivatives and mono-*O*-isopropylidene benzeneboronates of monosaccharides in one step is described, together with their p.m.r. and mass-spectral characteristics. In particular, the use of boric acid in the synthesis of the new acetal 1,2-*O*-isopropylidene-β-L-arabinopyranose (**8**) is described, together with improved procedures for the preparation of 2,3-*O*-isopropylidene-D-mannofuranose (**5**) and 3,4-*O*-isopropylidene-L-arabinopyranose (**10**). The use of boric acid in the partial hydrolysis of 1,2:3,4-di-*O*-isopropylidene-β-L-arabinopyranose to give the 1,2-acetal is reported.

INTRODUCTION

The reaction of boric acid with hydroxy compounds has been studied mainly *via* physical measurements on the complexes formed in solution. Thus, changes in optical activity[1,2], pH[3,4], and electrophoretic mobility[5,6] have given insight into the structure and stereochemical factors governing the formation and stability of borate complexes. Crystalline boric esters of carbohydrates are not well-known, although Vargha[7] prepared 1,2-*O*-isopropylidene-α-D-glucofuranose 3,5-borate by the concurrent reaction of acetone and boric acid with D-glucose. In contrast, benzeneboronic acid reacts readily with monosaccharides under anhydrous conditions to yield crystalline derivatives[8,9] that are useful, synthetic intermediates, as they are stable to the conditions of glycoside synthesis[10], esterification[11], and certain oxidising conditions[12]. We have applied Vargha's procedure to other reducing sugars as a means of preparing monoisopropylidene acetals in a single stage. We have also replaced boric acid with benzeneboronic acid, not only to facilitate the formation of crystalline derivatives but also to give a novel, direct route to mono-*O*-isopropylidene benzeneboronates that may be useful intermediates in synthesis.

*Dedicated to the memory of Professor Edward J. Bourne.

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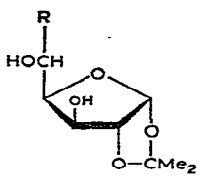
RESULTS AND DISCUSSION

The presence of boric acid in the reaction of acetone with monosaccharides resulted, after codistillation with methanol, in the formation of a mixture of mono- and di-*O*-isopropylidene derivatives that could be separated conveniently only by column chromatography. Relatively low yields of the mono-*O*-isopropylidene acetals were obtained (Table I), varying from 21% for D-glucose to 0.1% for D-mannose. The following known compounds were prepared: 1,2-*O*-isopropylidene-α-D-glucofuranose (**2**), 1,2-*O*-isopropylidene-α-D-xylofuranose (**1**), and 2,3-*O*-isopropylidene-D-mannofuranose (**5**). In general, the method offers no advantage over previously reported means of obtaining these monoacetals, particularly[13] in the case of **5**.



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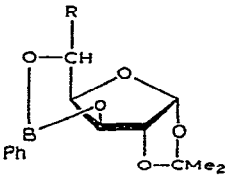
2 R = CH_2OH



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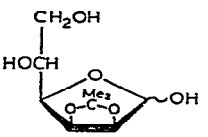

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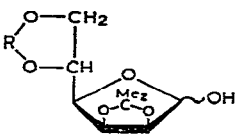
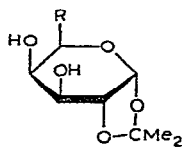
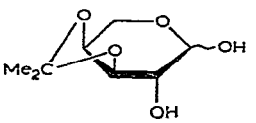


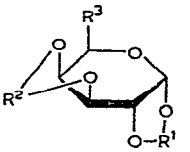
6 R = CMe_2
7 R = BPh



8 R = H
9 R = CH_2OH



10



11 R^1 = CMe_2, R^2 = CMe_2, R^3 = H
12 R^1 = CMe_2, R^2 = BPh, R^3 = H
13 R^1 = BPh, R^2 = CMe_2, R^3 = H
14 R^1 = BPh, R^2 = BPh, R^3 = H
15 R^1 = CMe_2, R^2 = CMe_2, R^3 = CH_2OH
16 R^1 = CMe_2, R^2 = BPh, R^3 = CH_2OH

The reaction of L-arabinose with boric acid in acetone solution containing sulphuric acid (2% v/v) gave, in addition to 1,2:3,4-di-*O*-isopropylidene-β-L-arabinopyranose (**11**), a monoisopropylidene acetal which differed in its R_F value and infrared spectrum from the known 3,4-*O*-isopropylidene-L-arabinopyranose (**10**). The compound was non-reducing (Fehling's solution) indicating that the acetal linkage involved O-1. The p.m.r. spectrum (methyl sulphoxide; Table II) showed no signal in the region (δ 6.6–5.95) associated[14] with anomeric OH groups, in contrast to the p.m.r. spectrum of **10** which on standing showed doublets centred at δ 6.6 and δ 6.3. The compound was distinguished from 1,2-*O*-isopropylidene-β-L-arabinofuranose[15]

TABLE I

PHYSICAL CONSTANTS OF THE COMPOUNDS PREPARED

Mono-saccharide	*Procedure*	*Product*											
		Structure	*Yield* (%)		*Calc.* (%)			*Found* (%)			*M.p.* (*degrees*)	*Lit. m.p.* (*degrees*)	*Ref.*
					C	*H*	*B*	*C*	*H*	*B*			
D-Glucose	*A*	2[a]	23	$C_9H_{16}O_6$							159–160	160–161	23
	B (0.5, 24 h)[f]	2[a]	21	$C_9H_{16}O_6$							159–160	160–161	23
	C	4[b]	37	$C_{15}H_{19}BO_6$							112–113	113–115	26
D-Mannose	*A*	5[c]	0.1	$C_9H_{16}O_6$							80–82	80–82	13
	B (0.05, 2 h)[f]	5[c]	32	$C_9H_{16}O_6$							80–81	80–82	13
	C	7	41	$C_{15}H_{19}BO_6$	58.8	6.21	3.6	58.95	6.37	3.48	171–173		
D-Galactose	*A*	9[d]	8	$C_9H_{16}O_6$	49.1	7.33		49.2	7.30		92–93	156–157	21
	C	16	16	$C_{15}H_{19}BO_6$	58.8	6.21	3.6	58.9	6.18	3.5	143–145		
L-Arabinose	*A*	8[e]	24	$C_8H_{14}O_5$	50.5	7.37		50.7	7.36		82–83		
	B (0.05, 24 h)[f]	10[b]	39	$C_8H_{14}O_5$							78–80	80	17
	C	12	29	$C_{14}H_{17}BO_5$	61.0	6.16	4.0	60.84	6.16	3.86	130–131		
D-Xylose	*A*	1[a]	22	$C_8H_{14}O_5$							Syrup	41–43	23
	B (2.0, 24 h)[f]	1[a]	19	$C_8H_{14}O_5$							Syrup	41–43	23
	C	3[b]	26	$C_{14}H_{17}BO_5$							127–128	128–129	27

[a]Showed i.r. spectrum identical with lit.[23] data. [b]I.r. spectrum identical with that of an authentic sample. [c]$[\alpha]_D^{20}$ +2.4° (*c* 0.7, water); lit.[13] $[\alpha]_D^{15}$ +4.5° (*c* 2.4, water). [d]Non-reducing; consumption of 0.7 mol. of periodate, no formaldehyde liberated; i.r. spectrum not identical with lit.[23] data. [e]Non-reducing, consumption of 1.0 mol. periodate. [f]Figures in parenthesis after procedure *B* refer to concentration of sulphuric acid (v/v) and time of reaction, respectively.

TABLE II

P.M.R. DATA[a] FOR D-MANNOSE, D-GALACTOSE, AND L-ARABINOSE DERIVATIVES

Compound	*Solvent*	*Chemical shift (δ)*								*Coupling constant (Hz)*					
		H-1	*H-2*	*H-3*	*H-4*	*H-5*	*C-Me*	*B-Ph*	*OH*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5}$	$J_{5,5}$
6[28]	$CDCl_3$	5.38	4.61	4.81			1.49, 1.39 1.33		3.54	<0.5	5.9	3.2			
	Me_2SO-d_6	5.13	4.44	4.70			1.34, 1.27 1.24		6.34	<0.5	5.8	3.2			
7	$CDCl_3$	5.50b	4.90d	5.15dd			1.50s, 1.40s	7.6m	3.4b	<0.5	5.4	3.0			
	Me_2SO-d_6	5.28b	4.80d	5.14dd			1.35b	7.48m	6.73b	<0.5	5.8	3.0			
8	Me_2SO-d_6	5.20d					1.48s, 1.30s		4.8b	<0.5					
9	Me_2SO-d_6	5.66d					1.55s, 1.40s		5.15d, 4.70m	4.5					
10	Me_2SO-d_6	5.00d					1.45s, 1.30s		6.62d, 6.30d, 5.0m	3.75					
11[30]	$CDCl_3$	5.52	4.32	4.60	4.23	3.86, 3.67	1.53, 1.50, 1.44			5.0	2.4	7.8	2.0	1.4	13.0
12	$CDCl_3$	5.60d	4.5ddo	5.0dd	4.65ddo	4.12, 3.8	1.65s, 1.40s	7.6m		5.25	2.25	9.0	1.5	<0.5	12.0
13	$CDCl_3$	6.0d	4.7m	4.7m	4.25	3.60, 3.80	1.55s, 1.40s	7.6m		6.0		7.5	1.5	<0.5	13.5
14[29]	C_6D_6	5.58d	4.32dd	4.64dd	3.92d	3.57d,b 3.29dd				6.0	2.7	8.2	1.9	<0.5	13.5
15[30]	$CDCl_3$	5.60	4.36	4.66	4.29		1.54, 1.46, 1.35		2.78	5.0	2.4	8.0	1.4		
16	$CDCl_3$	5.60d	4.55dd	5.0dd	4.70dd		1.65s, 1.45s	7.6m	2.2b	5.0	2.25	9.0	1.5		

[a]60 MHz; d, doublet; dd, doublet of doublets; m, multiplet; s, singlet; b, broad; o, overlap of signals.

by virtue of melting point and periodate-oxidation studies (consumption of one mol. of periodate). The above data are consistent with a 1,2-acetal linkage on a pyranose ring, *i.e.*, 1,2-*O*-isopropylidene-β-L-arabinopyranose (**8**).

The above result is contrary to previous findings[16] concerning the low reactivity of the diol group involving the anomeric hydroxyl group in isopropylidene acetal formation. This lower reactivity is exemplified by the preparation of **10** using copper sulphate as a mild, Lewis acid catalyst[17]. Examination of this reaction by t.l.c. has indicated no concurrent formation of the 1,2-*O*-isopropylidene derivative **8**. Furthermore, the absence of **8** has also been indicated (t.l.c.) in the reaction of L-arabinose with acetone under mildly acidic conditions (0.1% of sulphuric acid), when the diacetal **11** was the main product together with traces of **10**. The incorporation of boric acid into the latter reaction mixture resulted in the initial formation of **10** and **11**, subsequently giving **8** as an additional product. When copper sulphate was employed as catalyst, **10** was the only product (t.l.c.) and was obtained in higher yield than by Ohle's procedure[17]. These results indicate the possibility that **8** may be formed by the partial hydrolysis of **11** (no evidence has been found for the conversion of **10** into **8** *via* an acetal rearrangement), and when the hydrolysis was carried out in the presence of boric acid (ethyl acetate solution containing 0.5% v/v of sulphuric acid), **8** was the major product. Partial hydrolysis has not been previously successful[18,19] because, under conventional conditions, complete hydrolysis to L-arabinose occurs. Boric acid may prove to be a useful aid for the partial hydrolysis of compounds containing two 1,3-dioxolane rings that do not have greatly differing steric environments.

D-Galactose reacted with acetone (2% of sulphuric acid) in the presence of boric acid to give a crystalline, non-reducing compound in low yield, which had an elemental analysis corresponding to a mono-*O*-isopropylidene derivative. The compound consumed 0.7 mol. of periodate with no formaldehyde being liberated. P.m.r. spectroscopy showed the absence of signals in the region associated with anomeric OH signals, confirming the non-reducing property. These data are consistent with structure **9**; however, data previously recorded for 1,2-*O*-isopropylidene-α-D-galactopyranose[20–22] (m.p. and i.r. spectrum[23]) differ considerably from those obtained in the present study. Peaks at ν_{max} 920, 830, 815, and 765 cm^{-1} were exclusive to compound **9**, while the peak at 850 cm^{-1} was exclusive to the spectrum recorded by Tipson *et al.*[23]; the spectra were also different in absorption strength and shape of peaks. Moreover, the tri-*O*-methyl-D-galactose prepared by Levene and Meyer[21] differs in its specific rotation from that recorded for 3,4,6-tri-*O*-methyl-D-galactose[24], but is in good agreement with that recorded for 3,5,6-tri-*O*-methyl-D-galactose[25].

A modification of the acetone–boric acid reaction, involving initial formation of borate complexes of monosaccharides, has resulted in an improved procedure for the synthesis of some mono-*O*-isopropylidene derivatives. D-Mannose gave **5** in yields of up to 32%, with a work-up procedure simpler than that used by Iwadare[13]. L-Arabinose formed **10** in relatively high yield and with a reaction time considerably shorter than that for the established procedure involving copper sulphate[17]. For D-glucose and D-xylose, no improvement in yield of mono-*O*-isopropylidene derivatives

was obtained, compared with the above acetone–boric acid reaction. D-Galactose yielded mainly the di-*O*-isopropylidene derivative (t.l.c.), and only trace amounts of a mono-*O*-isopropylidene derivative.

The reaction of various monosaccharides with acetone in the presence of benzeneboronic acid gave crystalline, mixed acetal boronates in moderately high yield. Thus, 1,2-*O*-isopropylidene-α-D-glucofuranose 3,5-benzeneboronate (**4**) and 1,2-*O*-isopropylidene-α-D-xylofuranose 3,5-benzeneboronate (**3**) were prepared directly from D-glucose and D-xylose, respectively, whereas previous syntheses[26,27] involved the intermediate preparation of the respective monoacetal. D-Mannose, L-arabinose, and D-galactose gave 2,3-*O*-isopropylidene-α-D-mannofuranose 5,6-benzeneboronate (**7**), 1,2-*O*-isopropylidene-β-L-arabinopyranose 3,4-benzeneboronate (**12**), and 1,2-*O*-isopropylidene-α-D-galactopyranose 3,4-benzeneboronate (**16**), respectively. The structures **7** and **12** were established by comparison with the products obtained in the reaction of the appropriate mono-*O*-isopropylidene derivative with benzeneboronic acid. The structure of **16** was established by p.m.r. and mass-spectral data only.

The apparent absence of 3,4-*O*-isopropylidene-β-L-arabinopyranose 1,2-benzeneboronate (**13**) from the reaction mixture of L-arabinose with acetone–benzeneboronic acid prompted its preparation directly from 3,4-*O*-isopropylidene-L-arabinopyranose (**10**). Compound **13** was extremely soluble in organic solvents, and had the same R_F value as **12**, leaving open the possibility that both compounds may be formed in the acetone–benzeneboronic acid reaction (in the analogous acetone–boric acid reaction, the 1,2-*O*-isopropylidene derivative was the major monoacetal obtained).

The p.m.r. data of the compounds prepared in this study are given in Table II, together with the literature data on 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose[28] (**6**), 1,2:3,4-di-*O*-isopropylidene-β-L-arabinopyranose[30] (**11**), β-L-arabinopyranose 1,2:3,4-bis(benzeneboronate)[29] (**14**), and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose[30] (**15**). The use of methyl sulphoxide to assign the anomeric configuration of **8**, **9**, and **10** has been described earlier. Other than the signal for H-1, the ring protons of **8**, **9**, and **10** resonated as complex multiplets centred at δ 3.6, 4.0, and 4.0, respectively. The addition of shift reagent $Eu(FOD)_3$ to **8** did not give a clear separation of the multiplet, and an unequivocal assignment of ring protons was not possible.

Comparison of the p.m.r. spectra of 1,2-*O*-isopropylidene-β-L-arabinopyranose 3,4-benzeneboronate (**12**) and 3,4-*O*-isopropylidene-β-L-arabinopyranose 1,2-benzeneboronate (**13**) with that of **11** showed that signals of pyranose ring protons involved in a boronate ring are shifted downfield relative to the signals of the corresponding protons involved a 1,3-dioxolane ring. Thus, the H-1 and H-2 signals of **12** showed a very slight shift downfield, whereas the corresponding signals in **13** showed a large downfield shift (Table II). Similarly, the chemical shifts for H-3 and H-4 showed no change for **13**, but a marked downfield shift for **12** was observed.

In view of the limitations[31] in the application of the Karplus equation with a single set of parameters to a cyclic structure such as a pyranose ring, detailed conformational analysis based on coupling constants was not attempted. The coupling

constants of vicinal protons in **11** and **14** have been interpreted as indicating a skew conformation[29,30] for the pyranose ring. Similar coupling constants have now been found for **12** and **13**, indicating that the pyranose rings here may also be in a skew conformation. The observation[29] that larger coupling constants could be expected from the vicinal protons engaged in a 1,3,2-dioxaborolane ring, compared with a 1,3-dioxolane ring, was substantiated by the larger values of $J_{1,2}$ for **13**, and $J_{3,4}$ for **12**, when compared with the corresponding coupling constants for **11**.

The spectrum of **16** showed clear similarities with that[30] of **15**, close agreement being found in the chemical shifts of H-1, H-2, and the complex multiplet assigned to H-5 and H-6. However, the signals due to H-3 and H-4 for **16** were shifted downfield. Furthermore, the coupling constants of **16**, when compared with those of **15**, showed a significantly larger value for $J_{3,4}$; otherwise, the coupling constants were in good agreement. The above evidence is consistent with the proposed structure **16**. Additional evidence for the acetal linkage across C-1 and C-2 and the benzeneboronate linkage across C-3 and C-4 was obtained by comparison of the spectrum of **16** with those of **12** and **13**; similar chemical shifts and coupling constants were observed for **16** and **12**, rather than for **16** and **13**.

The p.m.r. spectrum of **7** was comparable with that obtained[28] from **6**, but for **7** the chemical shifts were slightly downfield and the coupling constants slightly smaller. The low value of $J_{1,2}$ for **7** is evidence[28] for the presence of the α anomer. No definitive evidence for the structure of **7** could be obtained, other than the similarity of the spectrum to that of the diacetal, and the negative inference that no large increase in coupling constant together with downfield chemical shift was observed for H-1, H-2, or H-3, indicating that these protons are not attached to the boronate ring.

The mass-spectral characteristics of some of the compounds investigated are given in Table III. Characteristic peaks for *O*-isopropylidene derivatives[32] were observed: M−15 peaks that gave confirmation of the molecular weight of the proposed structures, M−15−60 peaks (loss of acetic acid) with relative abundances 3, 8, and 10% for structures **7**, **10**, and **13**, respectively, together with peaks at *m/e* 85, 59, and 43, were common to all spectra.

The mass spectra of the mono-*O*-isopropylidene derivatives (**8** and **10**) of L-arabinose showed the effect on fragmentation pattern of differing positions of a 1,3-dioxolane ring on a pyranose ring. Of particular diagnostic value may be the loss of water from the M−15 peak (metastable peak at *m/e* 141; calc. 140.9) in the spectrum of **8**, whereas the spectrum of **10** had peaks at *m/e* 173 (relative abundance 1%, indicative of an unsubstituted hemiacetal hydroxyl group[32]) and 159 (M−31). Whether the loss of water in the fragmentation of **8** is *via* a mechanism involving 1,2-elimination or 1,4-elimination (which may be expected[33–35]) could not be ascertained with certainty without high-resolution data and deuterium labelling. Examination of molecular models of **8** and **10** showed no clear difference for a 1,2-elimination of either a *cis* or *trans* nature. However, if a 1,4-elimination is postulated, then HO-4 in **8** has the possibility of elimination with the anomeric proton unique to structure **8**.

TABLE III

MASS-SPECTRAL DATA (*m/e* VALUES[a]) FOR D-MANNOSE, D-GALACTOSE, AND L-ARABINOSE DERIVATIVES

7	8	9	10	12	13	16
43 (44)	43 (100)	43 (100)	43 (48)	43 (91)	43 (38)	43 (63)
57 (10)	45 (14)	44 (19)	57 (15)	59 (16)	105 (10)	57 (10)
83 (10)	55 (56)	45 (38)	59 (100)	85 (16)	146 (31)	59 (17)
101 (100)	57 (14)	55 (80)	60 (12)	91 (13)	159 (12)	71 (61)
105 (15)	59 (98)	56 (20)	69 (33)	104 (16)	173 (11)	83 (18)
146 (12)	60 (20)	57 (56)	71 (10)	105 (45)	260 (21)	85 (54)
147 (10)	69 (10)	58 (12)	73 (48)	146 (17)	261 (100)	91 (11)
159 (14)	71 (10)	59 (99)	85 (17)	147 (20)		100 (100)
291 (72)	73 (91)	60 (73)	86 (10)	158 (23)		101 (11)
	83 (10)	61 (31)	131 (14)	159 (100)		104 (14)
	85 (21)	69 (16)	159 (10)	171 (15)		105 (41)
	86 (24)	71 (95)	175 (45)	172 (54)		146 (16)
	97 (23)	72 (11)		173 (10)		147 (17)
	101 (28)	73 (98)		186 (10)		158 (18)
	115 (25)	74 (20)		187 (45)		159 (86)
	131 (20)	85 (95)		189 (10)		160 (11)
	157 (44)	86 (11)		201 (14)		187 (14)
	175 (34)	97 (47)		233 (10)		201 (15)
		98 (10)		260 (10)		202 (49)
		99 (25)		261 (54)		231 (27)
		100 (95)		276 (18)		273 (13)
		101 (63)				291 (41)
		109 (23)				
		113 (12)				
		127 (55)				
		129 (44)				
		131 (45)				
		145 (25)				
		159 (28)				
		162 (10)				
		187 (37)				
		205 (66)				

[a]Relative abundance given in brackets; peaks with $\geq$ 10% relative abundance are recorded.

In common with **8**, the mono-*O*-isopropylidene derivative (**9**) of D-galactose showed a strong peak corresponding to M−15−18 (*m/e* 187), but the presence of a primary hydroxyl group complicates a direct comparison of the spectrum of **9** with those of **8** and **10**. Common peaks at *m/e* 187, 127, 113, and 100 were observed in the spectra of **9** and the di-*O*-isopropylidene derivative[32] **15**, but the previous interpretation[32] of the peaks at *m/e* 187, 127, and 100 has necessitated the presence of two 1,3-dioxolane rings in the parent structure. However, the peaks at *m/e* 187 and 127 in the spectrum of **9** may possibly be accounted for by the loss of water and acetic acid, respectively, *i.e.*, M−15−18 and M−15−18−60.

The peaks characteristic of benzeneboronates (*m/e* 104, 105, 146, 147, 159, and 172) were observed in the spectra of the mono-*O*-isopropylidene benzeneboronates

reported here, although they were of low, relative abundances in the spectra of **7** and **13**.

The isomeric mono-*O*-isopropylidene-β-L-arabinopyranose benzeneboronates **12** and **13** showed significant fragmentation differences in terms of relative abundances. Peaks at *m/e* 233 (M−46) and 187 (M−69), together with a metastable peak at *m/e* 150 (calc. 150.1), in the spectrum **12** were not found in the spectrum of **13**.

The presence of two metastable peaks at *m/e* 256 and 195 indicates that the 1,2-*O*-isopropylidene-α-D-galactopyranose 3,4-benzeneboronate (**16**) loses acetic acid by a two-stage process, *m/e* 291→273 (calc. metastable 256.1) and *m/e* 273→231 (calc. metastable 195.5). Previous workers[32] have postulated a one-step loss of acetic acid for **15**, from a 1,3-dioxolane ring, but it may be that the boronate ring confers a degree of stability[29] sufficient to allow the detection of the intermediate stage in **16**. Further comparison between the spectra of **15** and **16** shows the absence from the latter of loss of acetone, which would require two 1,3-dioxolane rings, also the absence from **16** of a peak D[32] at *m/e* 127, formed from **15** as a consequence of the disruption of the remaining 1,3-dioxolane ring, presumably again reflecting the greater stability of the boronate ring. The peak at *m/e* 100 has been interpreted[32] as indicative of di-isopropylidene acetals; thus, the presence of this ion (base peak) in the spectrum of **16** presents some difficulties. A metastable ion at *m/e* 72 indicates the breakdown of the ion at *m/e* 100→85 (calc. metastable 72.25), giving rise to the possibility that the ions are F_1 and F_2[32].

Fragmentation of **7** would be expected to occur by scission[32] between C-4 and C-5, yielding ions of *m/e* 147 and 159. However, both ions are characteristic of benzeneboronates, and thus of no diagnostic value in deciding the positions of the acetal and boronate rings in **7**.

EXPERIMENTAL

Solutions were concentrated at 40° under diminished pressure. Melting points were determined on a Kofler block and are uncorrected. I.r. spectra were measured as Nujol mulls on a Perkin–Elmer Model 237 spectrometer, and were calibrated against the 1603 cm^{-1} band of a polystyrene film. T.l.c. was performed on Kieselgel HF_{254} (Merck) with (*A*) ethyl acetate–light petroleum (b.p. 60–80°) (3:1) and (*B*) chloroform–methanol (4:1); detection was by u.v. light (where appropriate), or by spraying with 5% ethanolic sulphuric acid followed by charring. Acetone was purified by refluxing with potassium permanganate, standing over calcium sulphate, and then fractional distillation. Benzene and light petroleum (b.p. 60–80°) were dried over calcium chloride followed by sodium. Standard procedures were used for the quantitative determination of periodate[36] and formaldehyde (chromotropic acid method[37]). The p.m.r. spectra were recorded at 60 MHz with tetramethylsilane as internal reference. Mass spectra were recorded by P.M.C.U., Harwell, using an A.E.I. MS-902 instrument operating at 70 eV with a direct-insertion system.

Reaction of monosaccharides with acetone in the presence of boric acid (*Procedure*

A). — The monosaccharide (0.01 ml) was stirred with dry acetone (100 ml) containing boric acid (0.01 mol), conc. sulphuric acid (2 ml) was added, and stirring was continued for 24 h. The solution was neutralised by stirring with anhydrous sodium carbonate, filtered, and concentrated. Methanol (3 × 50 ml) was distilled from the residue, and the resulting syrup was fractionated on a column of silica gel with solvent *B*.

Reaction of monosaccharide borate complexes with acetone (*Procedure* B). — The monosaccharide (0.01 mol) was refluxed in dry acetone (100 ml) containing boric acid (0.02 mol) for 24 h. After filtration, conc. sulphuric acid (Table I) was added with stirring and the solution was kept at room temperature. Samples (1 ml) were removed at intervals, neutralised by shaking with sodium carbonate (anhydrous), and examined by t.l.c. When the presence of the di-*O*-isopropylidene derivative was just evident, the whole of the reaction mixture was neutralised by stirring with sodium carbonate. After filtration, the solution was concentrated, and methanol (4 × 50 ml) was distilled from the residue, which was then triturated with light petroleum, where necessary. The solid product was extracted with ether (3 × 15 ml), and stored at 5° for 24 h to yield the monoacetal. A second crop could be obtained by the extraction of any remaining residue with ethyl acetate (2 × 15 ml), addition of light petroleum (10 ml), and storage at 5°.

The reaction of monosaccharides with acetone in the presence of benzeneboronic acid (*Procedure* C). — The reaction was effected as in Procedure *A*, replacing boric acid with benzeneboronic acid. After neutralisation with sodium carbonate, followed by filtration, the solution was concentrated and the resulting syrup extracted with light petroleum (3 × 15 ml). The solid product obtained after storage at 5° for 24 h was recrystallised from light petroleum.

Physical characteristics of the compounds prepared by Procedures *A*, *B*, and *C* are given in Table I.

Reaction of monoisopropylidene acetals with benzeneboronic acid. — A solution of the appropriate acetal (0.001 mol) in benzene (50 ml) was refluxed in the presence of benzeneboronic acid (0.001 mol) for 8 h using a Dean and Stark apparatus. The clear solution was concentrated and the residue crystallised from light petroleum. The following compounds were thus prepared:

2,3-*O*-Isopropylidene-α-D-mannofuranose 5,6-benzeneboronate (**7**, 74%), m.p. 172–173°, identical (m.p., i.r. spectrum) with the sample obtained by Procedure *C*.

1,2-*O*-Isopropylidene-β-L-arabinopyranose 3,4-benzeneboronate (**12**, 81%), m.p. 130–131°, identical (m.p., i.r. spectrum) with the sample obtained by Procedure *C*.

3,4-*O*-Isopropylidene-β-L-arabinopyranose 1,2-benzeneboronate (**13**, 92%; by evaporation of light petroleum), m.p. 80–82°.

Anal. Calc. for $C_{14}H_{17}BO_5$: C, 61.0; H, 6.2. Found: C, 60.8; H, 6.25.

3,4-O-Isopropylidene-L-arabinopyranose (**10**). — The method of Ohle[17] was used to give **10** (16%), m.p. 78–80°. There was no evidence for the presence of **8** in the reaction mixture (t.l.c., solvent *A*). Incorporation of an equimolar amount of boric

acid into the above reaction gave **10** (24%), m.p. 80–81°; lit.[17] m.p. 80°. No evidence of **8** was observed (t.l.c., solvent *A*).

Reaction of L-*arabinose with acetone under the conditions of mild, acid catalysis.* — (*a*) *Without boric acid.* L-Arabinose (1.5 g) was stirred with acetone (100 ml) containing conc. sulphuric acid (0.1 ml). Samples were removed at 10-min intervals and neutralised with sodium carbonate. Examination by t.l.c. (solvent *A*) indicated a major component, R_F 0.85 (**11**), together with traces of a compound having R_F (0.2) identical with that of **10**.

(*b*) *With boric acid.* A mixture of L-arabinose (1.5 g) and boric acid (0.62 g) was stirred in acetone (100 ml) containing conc. sulphuric acid (0.1 ml) for 24 h. Neutralisation with sodium carbonate, filtration, and concentration, followed by distillation of methanol (3 × 50 ml) from the residue, gave a syrup containing three components, R_F 0.20, 0.33, and 0.85 (solvent *A*). Chromatography on a column of silica gel (250 g; solvent *A*) gave the following fractions.

Fraction 1 (R_F 0.85, 0.6 g) crystallised to give **11**, m.p. 40–41°; lit.[38] m.p. 41.5–43°; with an i.r. spectrum identical with literature data[23].

Fraction 2 (R_F 0.33) was recrystallised from ethyl acetate–light petroleum to give **8** (0.15 g), identical (m.p., i.r. spectrum) with the sample obtained by Procedure *A*.

Fraction 3 (R_F 0.20), recrystallised from ether–light petroleum, yielded **10** (0.25 g) identical (m.p., i.r. spectrum) with the sample obtained by Procedure *B*.

*Partial hydrolysis of 1,2:3,4-di-*O*-isopropylidene-β-*L*-arabinopyranose* (**11**). — A mixture of **11** (2 g) and boric acid (0.62 g) in ethyl acetate (100 ml) containing sulphuric acid (0.5 ml) was stirred overnight, neutralised with sodium carbonate, filtered, and concentrated. Methanol (3 × 50 ml) was distilled from the syrupy residue, which was then fractionated on a column of silica gel (solvent *A*) to give **8** (0.2 g), identical (R_F, i.r. spectrum, m.p.) with the sample obtained by Procedure *A*.

Attempted rearrangement of monoisopropylidene acetals of L-*arabinopyranose.* — Dry ethyl acetate (50 ml) containing toluene-*p*-sulphonic acid (50 mg) was stirred with **10** (0.2 g) for 2 days. No change was observed by t.l.c. (solvent *A*). Replacement of **10** by **8** in the above procedure again gave no rearrangement, as observed by t.l.c. (solvent *A*).

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