156. *Boric Acid Derivatives as Reagents in Carbohydrate Chemistry. Part III.*[1] *The Interaction of Phenylboronic Acid with Methyl Xylofuranosides and the Isolation of the Four Methyl Xylosides.**

By R. J. Ferrier, D. Prasad, and A. Rudowski.

Methyl α-D-xylopyranoside, which is normally difficult to obtain, can be isolated simply and in 43% yield from an equilibrated mixture of methyl xylosides by way of its 2,4-phenylboronate from which it is readily recovered. Methyl α- and β-D-xylofuranosides can also be isolated from a furanoside-rich mixture of glycosides by way of their phenylboronates in 21 and 29% yields. These esters are shown to possess 3,5-cyclic structures.

In Part II [1] it was shown that both methyl D-xylopyranosides react under dehydrating conditions with phenylboronic acid to give crystalline 2,4-cyclic esters, and whereas the 3-hydroxyl group in the β-derivative is strongly intramolecularly hydrogen bonded to 1-O, that in the α-compound is free from such bonding. The large difference in the solubilities of these esters (α, 0·07 g./100 ml.; β, 53 g./100 ml. in hot light petroleum), which results from this difference in bonding, facilitates greatly their separation, and so provides a simple means of isolating the hitherto difficultly obtainable methyl α-D-xylopyranoside. This glycoside is normally prepared by removing the β-pyranoside which crystallises from an equilibrium mixture of xylosides and submitting the mother-liquors to tedious fractional crystallisation,[2] or by carrying out a fractional crystallisation on the derived tri-*O*-acetates.[3] Other workers have reported an enzymic synthesis.[4]

An equilibrated mixture of methyl xylosides which Bishop and Cooper [5] have shown to contain 65 and 30% of the α- and β-pyranosides, and 2 and 3% of the α- and β-furanosides,

* A preliminary account of this work has appeared in *Chem. and Ind.*, 1964, 1260.

[1] Part II, Ferrier, Prasad, Rudowski, and Sangster, *J.*, 1964, 3330.
[2] Hudson, *J. Amer. Chem. Soc.*, 1925, **47**, 265.
[3] Lindberg and Wood, *Acta Chem. Scand.*, 1952, **6**, 791.
[4] Bourquelot, *Ann. Chim.* (*France*), 1915, **3**, 298; Phelps and Purves, *J. Amer. Chem. Soc.*, 1929, **51**, 2443.
[5] Bishop and Cooper, *Canad. J. Chem.*, 1963, **41**, 2743.

yielded directly pure crystalline β-pyranoside (19%) in our hands. (Hudson [2] reported a yield of 38% of this isomer but his product must have been highly impure.) The mother-liquors on treatment in boiling benzene [6] with a molar equivalent of phenylboronic acid (as its anhydride) and removal of the water formed, gave a mixture of xyloside boronates from which the poorly soluble methyl α-D-xylopyranoside 2,4-phenylboronate [1] was isolated in quantities equivalent to 46% of the original glycosides. Earlier work [1] showed that the boronate ester groupings could readily be removed from such compounds by the addition of propane-1,3-diol, and with the aid of this reagent the uncrystallised xyloside boronates were de-esterified and yielded further quantities (8%) of the β-pyranoside. The non-crystalline glycosides were reconverted to the phenylboronates and a second crop of the α-pyranoside ester (equivalent to 4% of the glycosides) was obtained. Since methyl α-D-xylopyranoside was recovered in 85% yield from its ester with propane-1,3-diol, this fractionation can be used to obtain the pure α- and β-pyranosides in 43 and 27% yield, respectively.

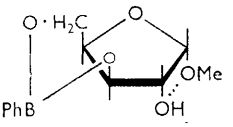
In view of the likelihood that the xylofuranosides would react to give 3,5-esters with phenylboronic acid and that these, because of profound differences in the intramolecular bonding of the unreacted hydroxyl groups, would have markedly different solubilities, an attempt was made to isolate them from a mixture of methyl xylosides which was rich in furanosides. [The corresponding bonding differences in the methyl 3,5-*O*-isopropylidene xylofuranosides render them readily separable by distillation (b. p.s: α- 85°/0·1 mm.; β- 108°/0·1 mm.).[7]] This furanoside mixture, prepared by heating xylose in refluxing methanol containing hydrochloric acid (0·012%),[8] on treatment with a molar equivalent of phenylboronic acid, did yield two new methyl xyloside phenylboronates (β and α) which were separated by fractional crystallisation, and which on treatment with anion exchange resin gave the known crystalline methyl β- and α-xylofuranoside, respectively. These xylofuranosides have previously been obtained in 45 and 22% yields by fractionation of a furanoside-rich mixture on a column of cellulose powder; [8] the phenylboronate method afforded them in 29 and 21% yields. Gas chromatography of furanoside-rich mixtures also showed that the β-isomer predominates.[5]

An alternative method of fractionating methyl glycoside mixtures involving chromatography on anion exchange columns has been described [9] but has not been applied in the xylose series.

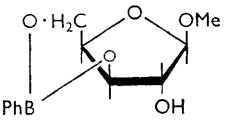
The infrared absorption of the furanoside esters at 3500—3650 cm.$^{-1}$ was consistent with their having the 3,5-cyclic structures (I and II).[10] The β-isomer (II) showed an absorption for an unbonded hydroxyl group (O–H stretching frequency 3623 cm.$^{-1}$), and low solubility (0·64 g./100 ml. in hot light petroleum); the α-ester (I) absorbed at 3543 cm.$^{-1}$ indicating that an intramolecular hydrogen bond involving $O_{(1)}$ is present, and was consequently more soluble (17·3 g./100 ml.). The frequency of a bonded hydroxyl group of *cis*-1,2-diols on five-membered rings varies extensively with ring conformation.[11] When the hydroxyl groups are eclipsed as in camphane-2,3-*cis*-diol [12] or bicyclo[2,2,1]heptane-2,3-*cis*-diol [13] the frequency is near 3530 cm.$^{-1}$, whereas in the more puckered cyclopentane-1,2-*cis*-diol [10a] and tetrahydrofuran-2,3-*cis*-diol [10c] the hydrogen bonds are weaker and the corresponding absorptions occur at 3572 and 3585 cm.$^{-1}$, respectively. The observed absorption frequency for the α-glycoside boronate (I) indicates that the $C_{(1)}$–$O_{(1)}$ and $C_{(2)}$–$O_{(2)}$ bonds contain a projected angle of 25°,[11] and examination of molecular models

[6] Ferrier, *J.*, 1961, 2325.
[7] Baker, Schaub, Joseph, and Williams, *J. Amer. Chem. Soc.*, 1954, **76**, 4044.
[8] Augestad and Berner, *Acta Chem. Scand.*, 1954, **8**, 251.
[9] Austin, Hardy, Buchanan, and Baddiley, *J.*, 1963, 5350.
[10] (*a*) Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492; (*b*) *ibid.*, 1954, **76**, 4323; (*c*) Brimacombe, Foster, Stacey, and Whiffen, *Tetrahedron*, 1958, **4**, 351.
[11] Brutcher and Bauer, *J. Amer. Chem. Soc.*, 1962, **84**, 2236.
[12] Angyal and Young, *J. Amer. Chem. Soc.*, 1959, **81**, 5467.
[13] Kwart and Vosburgh, *J. Amer. Chem. Soc.*, 1954, **76**, 5400.

reveals that the T_2^3 or T_3^2 conformations [14] are amongst those probable for the furanoid ring.



(I)



(II)

Chemical methods were applied to confirm the structure of the furanoside boronates. The α-isomer (I), on conversion into the *N*-phenylcarbamate, removal of the boronate ester groups, and methylation, gave the crystalline methyl 3,5-di-*O*-methyl-α-D-xylofuranoside 2-*N*-methyl-*N*-phenylcarbamate which on reduction yielded the dimethyl glycoside and thence 3,5-di-*O*-methyl-D-xylose. The melting point of the *p*-bromophenylosazone of this sugar was in poor agreement with the recorded value [15] but identical to that of a sample prepared by an independent synthesis involving 1,2-*O*-isopropylidene-α-D-xylofuranose which was readily purified through its crystalline 3,5-phenylboronate. 3,5-Di-*O*-methyl-D-xylose also formed a crystalline phenylboronate.

Methyl β-D-xylofuranoside phenylboronate was converted into the crystalline *O*-acetyl derivative and the phenylboronic acid was removed by distillation with excess of propane-1,3-diol. N.m.r. spectroscopy revealed that the syrupy product, which did not reduce periodate, bore the acetoxy-group at $C_{(2)}$ since the ester was secondary and the ring ester proton did not have a *cis*-neighbouring hydrogen. [The signal from this proton appeared as a singlet so that coupling with both neighbours was very small ($J^s < 1$ c./sec.); this condition is the only one which permits configurational assignment with furanosides.[16]] Further proof of the site of acetylation was obtained by heating the derived crystalline methyl 2-*O*-acetyl-3,5-di-*O*-toluene-*p*-sulphonyl-β-D-xyloside with sodium benzoate in dimethylformamide [17] and removing the acetyl and benzoyl groupings and the aglycone in the product by acidic hydrolysis. The only new sugar present was ribose (a minute trace of xylose remained) which was identified by two-dimensional cochromatography with [^{14}C]ribose. This indicates that tosyloxy-displacement involved an inversion at $C_{(3)}$ only [17] (apparently the neighbouring acetoxy-group did not influence the course of the reaction).

Marked variations exist between the stabilities of the different xyloside phenylboronates. While the removal of the ester groupings from all of the pyranoside derivatives was simply and effectively carried out with propane-1,3-diol,[1] none of the furanoside compounds could be freed from phenylboronic acid by the addition of a molar proportion of the diol to their solutions, followed by removal of the solvent and extraction of the residue with light pretroleum. Repetition of this process was partially successful in the cases of the α-furanoside boronate and its 3-*N*-phenylcarbamate but was quite ineffective with the β-furanoside boronate and its 2-*O*-acetyl derivative. Two alternative methods of removing phenylboronic acid were found to be applicable to even the most stable esters: (*a*) the repeated addition of excess of diol followed by vacuum distillation, and (*b*) the application of ion exchange on basic resins.

The relative stabilities of the methyl xyloside boronates were determined by adding small quantities of water to solutions of the boronates in dioxan and noting the volumes necessary to cause complete hydrolysis (determined polarimetrically): α-pyranoside, *ca.* 1%; β-pyranoside, *ca.* 3%; α-furanoside, *ca.* 9%; β-furanoside, *ca.* 30%. The high stability of the last ester was further reflected by the observation that only methyl β-D-xylofuranoside showed increased mobility when phenylboronic acid was added to

[14] Hall, *Chem. and Ind.*, 1963, 950.
[15] Levene and Raymond, *J. Biol. Chem.*, 1933, **102**, 331.
[16] Lemieux and Lineback, *Ann. Rev. Biochem.*, 1963, **32**, 155; Lemieux and Lown, *Canad. J. Chem.*, 1963, **41**, 889.
[17] Cf. Foster, Harrison, Lehmann, and Webber, *J.*, 1963, 4471.

chromatographic solvents. The stability of different carbohydrate phenylboronates will be discussed in a later communication.

Experimental

Optical rotations were measured at room temperature in a 1 dm. tube and at concentrations within the range 0·7—1·4%. The solvent was dry dioxan unless specified. Light petroleum had b. p. 60—80°.

High resolution infrared spectra were measured at room temperature in carbon tetrachloride solution at concentrations in the range 0·003—0·005M on the Unicam S.P. 700 spectrophotometer. N.m.r. spectra were measured in carbon tetrachloride solution using tetramethylsilane as internal reference on the Varian A-60 instrument.

The solubilities of the phenylboronates were measured by heating excess of the esters in boiling light petroleum, withdrawing an aliquot portion of the saturated solution and determining the solute content by weight.

The solvents used for paper chromatography were organic phases of: (*A*) butan-1-ol–benzene–pyridine–water (5 : 1 : 3 : 3), (*B*) butan-1-ol–ethanol–water (4 : 1 : 5), (*C*) butan-2-one saturated with water.

Fractionation of Methyl Xylopyranosides.—D-Xylose (100 g.) was heated in boiling methanol (1 l.) containing hydrochloric acid (1%) for 6 hr. by which time equilibrium had been established. The acid was neutralised with lead carbonate, the solvent was removed, and a portion of the residual syrup (94 g.) on trituration with ethyl acetate afforded methyl β-D-xylopyranoside which was recrystallised from ethanol, 17·7 g. (19%), m. p. 156—157°, $[\alpha]_D$ −65° (H_2O). The noncrystalline fraction was heated in boiling benzene (2 l.) with triphenylboroxole (48·3 g., 0·33 mol.), and the liberated water (8·3 ml., 100%) was collected.[6] The benzene solution was decanted from a small amount of insoluble material and on cooling deposited methyl α-D-xylopyranoside 2,4-phenylboronate (60·2 g.), m. p. 174—175°, $[\alpha]_D$ +9·7°.[1] Further quantities of this ester were collected after half of the solvent had been removed (3·4 g.), and then on the addition of light petroleum (150 ml.) to the supernatant when it had been concentrated to 300 ml. (3·7 g.).

The mother-liquors were taken to dryness, the residual syrup (40·7 g.) was dissolved in acetone (250 ml.) and propane-1,3-diol (12·4 g., 1·0 mol.) was added with stirring.[1] Removal of the acetone gave a syrup from which methyl β-D-xylopyranoside (6·9 g., total yield 27%), m. p. 157—158°, $[\alpha]_D$ −65° (H_2O), was obtained by trituration with ethyl acetate. The noncrystalline fraction was taken to dryness and extracted with boiling light petroleum to remove the propane-1,3-diol phenylboronate, but it was found that appreciable quanties of carbohydrate material were also dissolved out. Later work suggested that the α-furanoside would be preferentially removed by this process. The insoluble residue (10·9 g.) was again treated with triphenylboroxole (6·9 g., 0·33 mol.) in boiling benzene and a further amount of the α-pyranoside ester (4·3 g.) was obtained. The total yield was 71·6 g. (equivalent to 50% of the original glycoside mixture). Under the conditions of paper chromatography phenylboronates hydrolyse completely. An examination (solvent *C*[8]) of the residual syrup showed it to contain appreciable amounts of all four xylosides and it was not examined further.

The α-pyranoside ester (15 g.) was dissolved in acetone (150 ml.), and propane-1,3-diol (4·6 g., 1·0 mol.) was added with stirring. The solvent was removed and trituration of the residue with light petroleum gave a crude solid (9·6 g., 98%) which on recrystallisation from butan-2-one gave methyl α-D-xylopyranoside (8·3 g., 85%), m. p. 90—92°, $[\alpha]_D$ +153° (H_2O).

Fractionation of Methyl Xylofuranosides.—D-Xylose (20 g.) was heated in boiling methanol (1 l.) containing hydrochloric acid (0·012%) for 6 hr.[8] On neutralisation and removal of the solvent a syrup, $[\alpha]_D$ +27° (H_2O), was obtained, part of which (18 g.) was heated in boiling benzene (1·6 l.) with triphenylboroxole (11·4 g., 0·33 mol.). Removal of the liberated water (2·0 ml., 100%) and of the solvent gave a syrup from which two fractions were obtained by crystallisation from light petroleum. Fraction I was purified by recrystallisation from benzene to give *methyl* β-D-*xylofuranoside* 3,5-*phenylboronate* (8·0 g., 29%), m. p. 122—123°, $[\alpha]_D$ −158° (Found: C, 57·2; H, 6·0; B, 4·3; OMe, 11·8. $C_{12}H_{15}BO_5$ requires C, 57·6; H, 6·0; B, 4·3; OMe, 12·4%). Fraction II after recrystallisation from light petroleum gave *methyl* α-D-*xylofuranoside* 3,5-*phenylboronate* (4·7 g., 17%), m. p. 83—84°, $[\alpha]_D$ +21° (Found: C, 57·8; H, 6·3; B, 4·3; OMe, 12·2%). By sublimation from the non-crystalline fraction further quantities (1·0 g., 4%) of the α-ester were obtained. The residue was shown by paper chromatographic analysis (solvent *C*) to contain large amounts of all four xylosides and was not examined further.

The furanoside boronates (0·5 g. of each) were dissolved in water and passed through a column of anionic resin (De-Acidite FF, OH form). The eluates gave negative tests for boron and on evaporation of the water yielded the xylofuranosides (0·33 g., 100% in both cases). Crystallised from dry ethyl acetate, the α-isomer had m. p. 85—85·5°, $[\alpha]_D$ +180° (H_2O), and the β- m. p. 43—44°, $[\alpha]_D$ −86° (H_2O). Augestad and Berner [8] give m. p. 84°, $[\alpha]_D$ +182° (H_2O); m. p. 45°, $[\alpha]_L$ −89·5° (H_2O), for these compounds. Particular care had to be taken to protect the β-glycoside from moisture during crystallisations.

Methyl α-D-*Xylofuranoside* 3,5-*Phenylboronate* 2-N-*phenylcarbamate*.—The α-furanoside boronate (4·5 g.) was dissolved in dry benzene (250 ml.), phenyl isocyanate (2 ml., 1·0 mol.) was added, and the solution was heated under reflux for 6 hr. The solvent was removed, final traces of volatile materials were eliminated at 0·1 mm., and the residual solid on recrystallisation from benzene gave *methyl* α-D-*xylofuranoside* 3,5-*phenylboronate* 2-N-*phenylcarbamate* (4·6 g., 70%), m. p. 215—216°, $[\alpha]_D$ +97° (Found: C, 61·2; H, 5·6; B, 3·1; N, 4·0; OMe, 7·9. $C_{19}H_{20}BNO_6$ requires C, 61·8; H, 5·4; B, 2·9; N, 3·8; OMe, 8·4%).

Methyl α-D-*Xylofuranoside* 2-N-*Phenylcarbamate*.—The boronate carbanilate (4·0 g.) was dissolved in acetone (200 ml.) and propane-1,3-diol (0·82 g., 1·0 mol.) was added. After the removal of the acetone the crystalline residue (3·1 g.) was washed with light petroleum but could not be freed from boron by this means. Recrystallisation from light petroleum–ethyl acetate afforded *methyl* α-D-*xylofuranoside* 2-N-*phenylcarbamate* (1·85 g.), m. p. 174—175°, $[\alpha]_D$ +159° (Found: C, 54·5; H, 6·0; N, 5·3; OMe, 10·7. $C_{13}H_{17}NO_6$ requires C, 55·1; H, 6·0; N, 4·9; OMe, 10·9%). The mother-liquors from the crystallisation were taken to dryness, redissolved in acetone, and treated with a second portion of propane-1,3-diol (0·2 g.) to give further quantities of the carbanilate (0·8 g., total yield 2·65 g., 85%).

Methyl 3,5-*Di*-O-*methyl*-α-D-*xylofuranoside* 2-N-*Methyl*-N-*phenylcarbamate*.—The α-furanoside carbanilate (1·7 g.) was dissolved in dry dimethylformamide (40 ml.) and methyl iodide (5·6 g.) and stirred with silver oxide (6 g.) and " Hi-Drite " (3 g.) for 18 hr. After the removal of the solids and the solvent, the syrup was dissolved in chloroform which was then washed with water and dried. The syrup remaining after removal of the chloroform was shown by thin-layer chromatography to contain incompletely methylated compounds and was remethylated by a similar process. On distillation (bath temp. 150°; 0·05 mm.) the product crystallised partially and the non-crystalline portion after sublimation *in vacuo* also solidified. Recrystallisation from light petroleum gave *methyl* 3,5-*di*-O-*methyl* α-D-*xylofuranoside* 2-N-*methyl*-N-*phenylcarbamate* (0·75 g., 38%), m. p. 56—57°, $[\alpha]_D$ +76° (Found: C, 58·8; H, 7·0; N, 4·4; OMe, 26·9. $C_{16}H_{23}NO_6$ requires C, 59·1; H, 7·1; N, 4·3; OMe, 28·6%).

Methyl 3,5-*Di*-O-*methyl*-α-D-*xylofuranoside*.—The methylated carbanilate (0·8 g.) was heated under reflux in dry tetrahydrofuran (40 ml.) with aluminium lithium hydride (0·2 g.) for 3·5 hr. when the excess of hydride was destroyed with moist ethanol and then water. Phosphoric acid was added to pH 7, the solids were removed by filtration and the filtrate after treatment with decolourising charcoal was taken to dryness. The residue was distilled (bath temp. 70—75°; 0·06 mm.) to give *methyl* 3,5-*di*-O-*methyl*-α-D-*xylofuranoside* (0·44 g., 93%), $[\alpha]_D$ +105° ($CHCl_3$) (Found: C, 48·9; H, 8·6; OMe, 44·2. $C_8H_{16}O_5$ requires C, 50·0; H, 8·3; OMe, 48·4).

3,5-*Di*-O-*methyl*-D-*xylose*.—Hydrolysis of the glycoside (0·34 g.) with hydrochloric acid (0·05N, 2 hr. at 100°) afforded 3,5-di-*O*-methyl-D-xylose (0·21 g.), $[\alpha]_D$ +23° (H_2O), +11° ($CHCl_3$) (Laidlaw [18] gives 25°, 11°). The derived *p*-bromophenylosazone had m. p. 97—99°, $[\alpha]_D$ −48° ⟶ −29° (const.; pyridine–ethanol 2 : 3). [Levene and Raymond [15] give m. p. 107—108°, $[\alpha]_D$ −46° ⟶ −30° (same solvent) for this compound.] A sample of this sugar prepared by methylation of 1,2-*O*-isopropylidene-α-D-xylofuranose which had been purified by way of its crystalline 3,5-phenylboronate, had $[\alpha]_D$ +23° (H_2O), +14° ($CHCl_3$). The derived *p*-bromophenylosazone had m. p. 98—100°, undepressed on admixture with the first sample.

1,2-O-*Isopropylidene*-α-D-*xylofuranose* 3,5-*Phenylboronate*.—Impure 1,2-*O*-isopropylidene-α-D-xylofuranose (3·9 g.) gave the 3,5-phenylboronate (4·9 g., 88%) m. p. 126—127°, $[\alpha]_D$ −14° (Found: C, 61·0; H, 6·4; B, 3·9. $C_{14}H_{17}BO_5$ requires C, 60·9; H, 6·2; B, 3·9%) on treatment with triphenylboroxole (2·13 g., 0·33 mol.) in boiling benzene (450 ml.) followed by recrystallisation from light petroleum.

The ester grouping was removed with the aid of anion exchange resin and gave pure 1,2-*O*-isopropylidene-α-D-xylofuranose, $[\alpha]_D$ −17° (H_2O).

3,5-*Di*-O-*methyl*-α-D-*xylofuranose* 1,2-*Phenylboronate*.—The dimethylxylose (0·5 g.) on heating

[18] Laidlaw, *J.*, 1952, 2941.

in boiling benzene with triphenylboroxole (0·29 g., 0·33 mol.) and on removal of the liberated water and the solvent gave a syrup which on distillation yielded crystalline 3,5-*di*-O-*methyl*-α-D-*xylofuranose* 1,2-*phenylboronate* (0·42 g., 57%), m. p. 54—55°, $[\alpha]_D$ −9° (Found: C, 59·5; H, 6·3; B, 3·9; OMe, 23·2. $C_{13}H_{17}BO_5$ requires C, 59·1; H, 6·4; B, 4·1; OMe, 23·5%).

Methyl 2-O-*Acetyl*-β-D-*xylofuranoside* 3,5-*Phenylboronate*.—The β-furanoside boronate (3·0 g.) was dissolved in dry pyridine (45 ml.) and after cooling to 5° acetyl chloride (2·5 ml.) was added with stirring during 1 hr. The stirring was continued for a further 2 hr., the solution was filtered and the filtrate taken to dryness. The residue was extracted with hot benzene and the extract on evaporation gave a solid which was recrystallised from benzene–light petroleum to give *methyl* 2-O-*acetyl*-β-D-*xylofuranoside* 3,5-*phenylboronate* (2·4 g., 68%), m. p. 99—100°, $[\alpha]_D$ −88° (Found: C, 57·7; H, 6·2; B, 3·9; OMe, 10·4. $C_{14}H_{17}BO_6$ requires C, 57·6; H, 5·8; B, 3·7; OMe, 10·6%).

Methyl 2-O-*Acetyl*-β-D-*xylofuranoside*.—The acetylated phenylboronate (1·36 g.) was dissolved in acetone (6 ml.) and propane-1,3-diol (3·5 ml., predistilled) was added. The acetone was removed at the water pump and the diol and its boronate ester by distillation at 0·02 mm. (bath temp. 60—70°). The process was repeated with a second volume of propane-1,3-diol (3 ml.) and the combined distillates were found to contain all of the boron originally present. The syrupy residue (0·82 g., 85%), $[\alpha]_D$ −63°, was shown by n.m.r. spectroscopy to contain only traces of propane-1,3-diol and to be the β-*furanoside* 2-*acetate* (Found: C, 45·0; H, 7·0; OMe, 14·7. $C_8H_{14}O_6$ requires C, 46·6; H, 6·8; OMe, 15·0%). It did not reduce the periodate ion (spectrophotometric determination [19]).

Methyl 2-O-*Acetyl*-3,5-*di*-O-*toluene*-p-*sulphonyl*-β-D-*xylofuranoside*.—The xyloside acetate (0 37 g.) was dissolved in dry pyridine (5 ml.), cooled to 5°, and toluene-*p*-sulphonyl chloride (1·2 g.) in pyridine (5 ml.) was added during 20 min. The solution was left at room temperature for 3 days, when the bulk of the pyridine was removed and the resulting syrup was poured into ice-water which was extracted with chloroform. The extract after washing, drying, and removal of the solvent gave a syrup which solidified on trituration with light petroleum. Recrystallisation from ethyl acetate–light petroleum gave *methyl* 2-O-*acetyl*-3,5-*di*-O-*toluene*-p-*sulphonyl*-β-D-*xylofuranoside* (0·4 g., 43%), m. p. 117—118°, $[\alpha]_D$ −16° (Found: C, 51·3; H, 5·0; S, 12·6; OMe, 5·8. $C_{22}H_{26}O_{10}S_2$ requires C, 51·4; H, 5·1; S, 12·5; OMe, 6·0%).

Toluene-p-*sulphonate Displacement*.—The tosylate (0·1 g.) was heated in dimethylformamide (5 ml.) at 140° in the presence of sodium benzoate (0·3 g.) and the reaction, which was found to be complete in 18 hr., was followed by examining samples on thin-layer chromatograms (silica gel adsorbent, benzene–methanol 9 : 1). Water (15 ml.) was added, the solution was extracted with methylene chloride, and the extract was washed with water and dried. Removal of the solvent left a syrup which was hydrolysed with hydrochloric acid in aqueous dioxan. Simple chromatographic examination of the neutralised hydrolysate indicated the presence of ribose together with a minute trace of xylose. Arabinose was absent. The ribose was further identified by two-dimensional cochromatography with [^{14}C]ribose (0·1 μc) [solvents *A* (24 hr.) and *B* (36 hr.)]. The inactive sugar was detected with an ammoniacal silver nitrate spray and the radioactive by radioautography. Mr. L. R. Hatton kindly performed this experiment.

Hydrolysis of the Xyloside Phenylboronates.—Solutions of the boronates (1%) in dry dioxan were introduced into a centre-filling polarimeter tube (1 dm.) which was sealed with a serum cap. Small volumes of water were added by injection using an " Agla " syringe, and changes in the optical rotation of the solutions were followed to equilibrium. Further quantities were added until hydrolysis was complete.

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[*Received, May 5th*, 1964.]

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