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Note

Selective benzoylation of methyl α- and β-D-xylopyranoside

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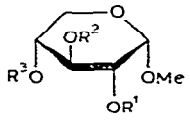
Previously, the selective benzoylation of 1,5-anhydro-D-glucitol[1] and 1,5-anhydroxylitol[2] was reported, and an influence of the methylene group at C-1 on the relative reactivity of the secondary hydroxyl groups was discussed. In connection with those studies, we now describe the selective benzoylation of methyl α- and β-D-xylopyranoside.



	R^1	R^2	R^3
1	H	H	H
2	Bz	Bz	Bz
3	Bz	H	Bz
4	Bz	Bz	H
5	Bz	H	H
6	Bz	Ts	Bz
7	Bz	Bz	Ts
8	Ts	Bz	Bz
9	Bz	Ts	Ts
10	H	H	Ts
11	Ts	H	H

Bz = PhCO
Ts = p-$MeC_6H_4SO_2$

Selective benzoylation of methyl α-D-xylopyranoside (**1**) with 2 molar equivalents of benzoyl chloride in pyridine at −40° gave a mixture of products which was shown by quantitative, t.l.c. analysis to consist of the tribenzoate **2** (11%), the 2,4-dibenzoate **3** (45%), the 2,3-dibenzoate **4** (39%), and the 2-benzoate **5** (5%). After chromatographic fractionation of each component on silica gel, their structures were

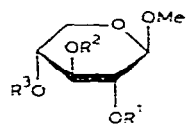
established by p.m.r.-spectral analysis, or by conversion into authentic specimens by unequivocal synthesis, or both.

Assignment of the position of the free hydroxyl groups in the dibenzoates **3** and **4** was proved by p.m.r. spectroscopy. The signals of H-3 of **3** and of H-4 of **4** respectively appeared 1.5 and 1.1 p.p.m. to higher field than those of the corresponding hydrogen atoms of the tribenzoate **2**, because of the lack of the deshielding effect of benzoyl groups on the methine protons attached to the same carbon atoms. The hydroxyl groups of **3** and **4** are, therefore, attached to C-3 and C-4, respectively.

The structure of **4** was further confirmed by tosylation, giving methyl 2,3-di-*O*-benzoyl-4-*O*-tosyl-α-D-xylopyranoside (**7**), which had physical constants in good agreement with those of an authentic sample prepared from methyl 4-*O*-tosyl-α-D-xylopyranoside[4] (**10**) by perbenzoylation.

The structure of **3** was established by conversion into the known methyl 2,4-di-*O*-benzoyl-3-*O*-tosyl-α-D-xylopyranoside[3] (**6**), which was readily distinguishable from the remaining methyl 3,4-di-*O*-benzoyl-2-*O*-tosyl-α-D-xylopyranoside (**8**) obtained by perbenzoylation of the known methyl 2-*O*-tosyl-α-D-xylopyranoside[4] (**11**).

The structure of **5** was proved by preparing the di-*O*-tosyl derivative, which was shown to be methyl 2-*O*-benzoyl-3,4-di-*O*-tosyl-α-D-xylopyranoside (**9**) by comparison of its p.m.r. spectrum with that of **2**. The signals of H-3 and H-4 of **9** appeared at higher field (0.9 p.p.m.) than those of **2**, and the signals of H-2 in the spectra of both compounds **9** and **2** appeared at a similar field. This result indicated that the tosyl groups in **9** are attached to O-3 and O-4, and the benzoyl group to O-2.



	R^1	R^2	R^3
12	H	H	H
13	Bz	Bz	Bz
14	Bz	H	Bz
15	Bz	Bz	H
16	H	Bz	Bz
17	H	Bz	H
18	H	H	Bz
19	Bz	H	H
20	Bz	Ts	Bz
21	Bz	Bz	Ts
22	Ts	Bz	Bz
23	Ts	Bz	Ts
24	Ts	Ts	Bz
25	Bz	Ts	Ts
26	H	Ts	H

Dimolar benzoylation of methyl β-D-xylopyranoside (**12**) with benzoyl chloride in pyridine afforded a complex mixture composed of the tribenzoate **13** (17%), the 2,4-dibenzoate **14** (22%), a mixture of the 2,3-dibenzoate **15** and the 3,4-dibenzoate **16** (53%), the 3-benzoate **17** (4%), and a mixture of the 4-benzoate **18** and the 2-benzoate **19** (4%).

Benzoylation of **12** with 1 molar equivalent of benzoyl chloride gave **13** (2%), **14** (8%), a mixture of **15** and **16** (19%), **17** (25%), **18** (20%), and **19** (26%), which were quantitatively determined by t.l.c. After chromatographic separation, the structure of **14** was confirmed by tosylation, giving methyl 2,4-di-*O*-benzoyl-3-*O*-tosyl-β-D-xylopyranoside (**20**), the physical and spectral properties of which were in good agreement with those of an authentic sample prepared by perbenzoylation of methyl 3-*O*-tosyl-β-D-xylopyranoside (**26**). Compound **26** was synthesized by a sequence of tosylation and removal of the cyclic, boronic ester, starting from the known methyl β-D-xylopyranoside 2,4-phenylboronate[5].

The mixture of **15** and **16** was difficult to separate by column chromatography. Therefore, in order to ascertain the positions of the benzoyl groups in **15** and **16**, this mixture obtained from dibenzoylation of **12** was converted into its *O*-tosyl derivatives **21** and **22**. The p.m.r. spectrum of this tosylated mixture showed the signals of the methyl proton of the tosyloxy group at τ 7.77 and 7.85 in the ratio of 3:7. Compound **21** readily crystallized from the mixture, and was proved identical with methyl 2,3-di-*O*-benzoyl-4-*O*-tosyl-β-D-xylopyranoside in the following way. Comparison of the p.m.r. spectrum of **21** with that of the tribenzoate **13** showed an upfield shift (~0.7 p.p.m.) of the H-4 resonance of **21**, in agreement with the assigned structure having a tosyloxy group at C-4. Its structure was further established by an unequivocal synthesis from **12**. Isopropylidenation of **12**, followed by tosylation of the acetal, *O*-deisopropylidenation, and perbenzoylation, gave **21**. In the p.m.r. spectrum of **21**, the resonance of the methyl proton of the tosyloxy group appeared at τ 7.85 and, therefore, the resonance at τ 7.77 was assigned to the tosyloxy-methyl proton signal of methyl 3,4-di-*O*-benzoyl-2-*O*-tosyl-β-D-xylopyranoside (**22**). This indicated the ratio of **15** to **16** to be 7:3.

Compound **17** was characterized by comparison with the known methyl 3-*O*-benzoyl-β-D-xylopyranoside[5] reported by Ferrier *et al.* The structure of **17** was further demonstrated, as its ditosylate **23**, by p.m.r. spectroscopy. The H-3 resonance (a triplet) appeared to low field of all other ring-proton resonances, suggesting that this proton must be geminal to the deshielding benzoyloxy group.

Compounds **18** and **19** could not be separated from each other on a column of silica gel. Therefore, the mixture of **18** and **19** was directly tosylated with tosyl chloride, to give the corresponding ditosylates **24** and **25**. Compound **25** readily crystallized from the mixture, and was proved identical with methyl 2-*O*-benzoyl-3,4-di-*O*-tosyl-β-D-xylopyranoside by p.m.r. spectroscopy. In the p.m.r. spectrum of **25**, the signal of H-2 appeared as a quartet well down-field of the H-3 and H-4 resonances, indicating that the benzoyloxy group was on C-2. Accordingly, the ditosylate **24** must be methyl 4-*O*-benzoyl-2,3-di-*O*-tosyl-β-D-xylopyranoside; it was

readily distinguishable from the 2,4- and 3,4-ditosylates (**23** and **25**) by comparison of their spectral and other physical properties.

In order to determine the molar ratio of the monobenzoates **18** and **19**, a mixture of the monobenzoates (fractionated from the monobenzoylation product), in which the ratio of **18** to **19** was 3:4, was tosylated, and the product analyzed by p.m.r. spectroscopy. In the p.m.r. spectrum of the resulting tosylated mixture, the signals of the methyl proton of the methoxyl group appeared at τ 6.70 and 6.82, with relative proton intensities of 8:5. The p.m.r. spectra of **24** and **25** showed the signals of the methyl proton of the methoxyl group at τ 6.82 and 6.70, respectively; this indicated the ratio of **18** to **19** in the mixture to be 5:8. Therefore, the minor monobenzoate **18** was identified as methyl 4-*O*-benzoyl-β-D-xylopyranoside, and the major monobenzoate **19** as methyl 2-*O*-benzoyl-β-D-xylopyranoside.

In the dibenzoylation of methyl α-D-xylopyranoside (**1**), the preponderance of the 2,4-dibenzoate over the 2,3-dibenzoate shows that the relative reactivity of the hydroxyl groups in **1** is in the order: OH-2 > OH-4 > OH-3, which is consistent with the results of selective benzoylation of benzyl α-D-xylopyranoside[6]. On the other hand, the yield of the dibenzoates in the dibenzoylation of the β-D anomer **12** was in the order: 2,3- (37%), 2,4- (22%), and 3,4- (16%) dibenzoates on a relative, molar basis. Therefore, the order of reactivity of the hydroxyl groups in **12** is OH-2 > OH-3 > OH-4. This order is, however, in agreement with the results of monobenzoylation of **12**, in which serious differences in the reactivity of the OH-2 and OH-3 groups are not observed, as they are in dibenzoylation.

The high reactivity of the OH-2 group in **1** could be explained by intramolecular hydrogen-bonding with the *cis*-OR substituent. The finding of the lowest reactivity of the OH-3 group in **1** is in accord with the results of selective benzoylation of benzyl α-D-xylopyranoside reported by Sivakumaran and Jones[6], who attempted to rationalize this behavior from gauche interactions in the sugar molecule substituted at C-2; the OH-3 group has gauche interactions with a benzoyl and a hydroxyl group, whereas OH-4 has interactions with a hydroxyl group and a hydrogen atom. Therefore, the OH-4 group is less sterically hindered, thus causing a preponderance of the 2,4-dibenzoate over the 2,3-dibenzoate. From this viewpoint, however, the preponderance of the 2,3-dibenzoate over the 2,4-dibenzoate in selective benzoylation of **12** cannot be similarly explained; a similar discrepancy was found in selective benzoylation of 1,5-anhydro-D-glucitol[1].

Selective benzoylation of 1,5-anhydroxylitol[2] led us to predict that the gauche interactions in the same steric arrangements should be almost equivalent, and have no significant influence on the differences in the reactivity of the hydroxyl groups. In comparison with the results of selective benzoylation of benzyl α-D-xylopyranoside (having a bulky substituent at C-1), much more of the 2,3-dibenzoate was formed in the dimolar benzoylation of **1**. The foregoing observations suggest that the lowest reactivity of the OH-3 group in **1** is to be interpreted in terms of electronic or steric hindrance from the glycosidic substituent, or both.

In the dibenzoylation of methyl β-D-xylopyranoside (**12**), the OH-2 group is the most reactive of the ring-hydroxyl groups.

Preferential esterification of the OH-2 over the OH-3 group was reported in the selective acetylation of benzyl 4-*O*-methyl-β-D-xylopyranoside[7] with acetyl chloride in pyridine. It is noteworthy that the OH-4 group is the least reactive, because it becomes less sterically hindered than the other hydroxyl groups by its adjacency to the methylene group containing C-5. The enhanced reactivity of the OH-2 group compared with the OH-4 group was confirmed by monobenzoylation of the 3-benzoate **17**. The resulting dibenzoates were converted into tosyl derivatives of the 2,3- and 3,4-dibenzoates in the ratio of 4:1 (shown by p.m.r. spectroscopy, from the relative proton-intensities of the tosyloxy methyl group).

A similar, low reactivity of the hydroxyl group which is adjacent to a hydroxyl group and hydrogen atoms, and is less sterically hindered, had been observed in the selective benzoylation of 1,5-anhydro-D-glucitol[1] and its *O*-benzylidene derivative[8]. A remarkable difference in the reactivity of the hydroxyl groups in **12** towards benzoyl chloride was found in the dibenzoylation (rather than in the monobenzoylation). This difference would be explained in terms of the enhancement[9,10] of reactivity due to substitution, indicating that the dibenzoylation of **12** proceeds in a considerably complicated manner. However, the results obtained in the monobenzoylation of the 3-benzoate **17** suggest the presence of a certain activating effect, on the OH-2 group, of the glycosidic substituent.

EXPERIMENTAL

General methods. — Melting points were determined on a Yanagimoto hot-stage microscope and are uncorrected. Quantitative, thin-layer chromatography was performed on quartz rods sintered with 1:2 silica gel H (Merck)–glass powder, and the spots were detected with an Iatron chromatoscanner TH-10 equipped with a hydrogen-flame ionization-detector. Percentages are expressed on a relative, molar basis. Preparative, column chromatography was conducted on silica gel 60 (Merck; 70–230 mesh). Optical rotations were measured with a Yanagimoto OR-50 polarimeter, and p.m.r. spectra were recorded with a Hitachi R-24, 60-MHz instrument, using chloroform-*d*, with tetramethylsilane as the internal standard.

Dimolar benzoylation of methyl α-D-xylopyranoside (**1**). — To a solution of **1** (1 g) in distilled pyridine (40 mL) at −40° was added benzoyl chloride (1.5 mL, 2.1 mol) dropwise during 15 min, with stirring. The bath temperature was kept for 3 h at −20° and for 2 days at 0°, and then the mixture was stirred for a further 2 days at room temperature. Water was added, the mixture extracted with chloroform, and the extract washed successively with dilute hydrochloric acid, saturated sodium hydrogencarbonate, and water, dried (sodium sulfate), and evaporated to a syrup which was chromatographed on silica gel (150 g). Elution with 9:1 benzene–ethyl acetate gave the 2,3,4-tribenzoate **2**, which crystallized from methanol; m.p. 116–118°, $[\alpha]_D^{28}$ +57° (*c* 1.0, chloroform); p.m.r. data: τ 3.80 (t, 1 H, $J_{2,3} = J_{3,4} = 8$ Hz,

H-3), 4.57 (sex, 1 H, $J_{4,5a}$ 10, $J_{4,5e}$ 6 Hz, H-4), 4.65 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.75 (q, 1 H, H-2), 5.87 (q, 1 H, $J_{5a,5e}$ 10 Hz, H-5*e*), 6.27 (q, 1 H, H-5*e*), and 6.53 (s, 3 H, OCH_3).

Anal. Calc. for $C_{27}H_{24}O_8$: C, 68.05; H, 5.04. Found: C, 67.93; H, 4.95.

Elution with 4:1 benzene–ethyl acetate gave the 2,4-dibenzoate **3**, which crystallized from methanol; m.p. 161–163°, $[\alpha]_D^{28}$ +62° (*c* 1.2, chloroform); p.m.r. data: τ 4.82 (sex, 1 H, $J_{4,5a}$ 10, $J_{4,5e}$ 6 Hz, H-4), 4.97 (q, 1 H, $J_{1,2}$ 3 Hz, H-2), 5.01 (d, 1 H, H-1), 5.60 (broad t, 1 H, $J_{2,3} = J_{3,4} = 9$ Hz, H-3), 6.02 (q, 1 H, $J_{5a,5e}$ 10 Hz, H-5*e*), 6.32 (t, 1 H, H-5*a*), 6.62 (s, 3 H, OCH_3), and 6.82 (broad s, 1 H, exchanges in D_2O).

Anal. Calc. for $C_{20}H_{20}O_7$: C, 64.50; H, 5.42. Found: C, 64.41; H, 5.52.

Elution with 2:1 benzene–ethyl acetate gave the 2,3-dibenzoate **4**, which crystallized from ethanol; m.p. 128–129°, $[\alpha]_D^{19}$ +16° (*c* 1.4, chloroform); p.m.r. data: τ 4.27 (t, 1 H, $J_{3,4} = J_{4,5} = 8$ Hz, H-3), 4.83 (q, 1 H, $J_{1,2}$ 3, $J_{2,3}$ 10 Hz, H-2), 4.94 (d, 1 H, H-1), 5.6–6.4 (m, 4 H, H-4,5*a*, 5*e*, OH), and 6.63 (s, 3 H, OCH_3).

Anal. Calc. for $C_{20}H_{20}O_7$: C, 64.50; H, 5.42. Found: C, 64.57; H, 5.50.

Elution with ethyl acetate gave the 2-benzoate **5** as a syrup that could not be crystallized; $[\alpha]_D^{22}$ +97° (*c* 1.1, chloroform).

*Methyl 2,4-di-*O*-benzoyl-3-*O*-tosyl-α-*D*-xylopyranoside* (**6**). — The 2,4-dibenzoate **3** (150 mg) in pyridine (2 mL) was treated with tosyl chloride (230 mg) for 4 days at room temperature, with stirring. The mixture was extracted with chloroform, and purified as already described, to give a crystalline product. Recrystallization from chloroform–ethanol gave **6** (164 mg, 77%); m.p. 117–118°, $[\alpha]_D^{28}$ +56° (*c* 1.4, chloroform) {lit.[3] m.p. 147–148°, $[\alpha]_D^{25}$ +58° (*c* 1, chloroform)}; p.m.r. data: τ 5.93 (q, 1 H, $J_{4,5e}$ 6, $J_{5a,5e}$ 10 Hz, H-5*e*), 6.25 (t, 1 H, H-5*a*), 6.55 (s, 3 H, OCH_3), and 7.93 (s, 3 H, $SO_2C_6H_4CH_3$).

*Methyl 2,3-di-*O*-benzoyl-4-*O*-tosyl-α-*D*-xylopyranoside* (**7**). — (*a*). The dibenzoate **4** (147 mg) was tosylated with tosyl chloride (224 mg) in pyridine (2 mL) for 2 days to afford the sulfonate **7** (200 mg, 97%), which crystallized from chloroform–ethanol; m.p. 185–186°, $[\alpha]_D^{21}$ +115° (*c* 1.5, chloroform); p.m.r. data: τ 4.10 (t, 1 H, $J_{2,3} = J_{3,4} = 10$ Hz, H-3), 4.92 (q, 1 H, $J_{1,2}$ 3 Hz, H-2), 4.95 (d, 1 H, H-1), 5.30 (sex, 1 H, $J_{4,5a}$ 10, $J_{4,5e}$ 6 Hz, H-4), 5.99 (q, 1 H, $J_{5a,5e}$ 10 Hz, H-5*e*), 6.18 (t, 1 H, H-5*a*), 6.62 (s, 3 H, OCH_3), and 7.85 (s, 3 H, $SO_2C_6H_4CH_3$).

Anal. Calc. for $C_{27}H_{26}O_9S$: C, 61.58; H, 4.99; S, 6.09. Found: C, 61.75; H, 5.00; S, 6.35.

(*b*). A solution of **10** (40 mg) in pyridine (1 mL) was treated with benzoyl chloride (0.05 mL) at 0°, and stirred overnight at room temperature. The usual processing, followed by crystallization from chloroform–ethanol, gave **7** (61 mg, 92%), m.p. 186–187°, identical with the material prepared as described in (*a*).

*Methyl 2-*O*-benzoyl-3,4-di-*O*-tosyl-α-*D*-xylopyranoside* (**9**). — Treatment of the monobenzoate **5** (226 mg) with tosyl chloride (642 mg) gave the sulfonate **9** (383 mg, 79%), which crystallized from chloroform–petroleum ether; m.p. 160°, $[\alpha]_D^{28}$ +145° (*c* 1.7, chloroform); p.m.r. data: τ 4.73 (t, 1 H, $J_{2,3} = J_{3,4} = 8$ Hz, H-3), 5.07 (q,

1 H, $J_{1,2}$ 4 Hz, H-2), 5.17 (d, 1 H, H-1), 5.53 (sex, 1 H, $J_{4,5a}$ 10, $J_{4,5e}$ 5 Hz, H-4), 6.05 (q, 1 H, $J_{5a,5e}$ 10 Hz, H-5*e*), 6.33 (t, 1 H, H-5*a*), 6.68 (s, 3 H, OCH_3), and 7.62 and 7.82 (2 s, 6 H, 2 $SO_2C_6H_4CH_3$).

Anal. Calc. for $C_{27}H_{28}O_{10}S_2$: C, 56.23; H, 4.90; S, 11.12. Found: C, 56.33; H, 4.87; S, 10.84.

*Methyl 3,4-di-*O*-benzoyl-2-*O*-tosyl-α-*D*-xylopyranoside* (**8**). — The 2-tosylate[4] **11** (100 mg) was benzoylated, to give **8** (124 mg, 75%) as fine needles; m.p. 175–176° (from ethanol), $[\alpha]_D^{23}$ +19° (*c* 0.6, chloroform); p.m.r. data: τ 4.10 (t, 1 H, $J_{2,3} = J_{3,4}$ = 10 Hz, H-3), 4.82 (sex, 1 H, $J_{4,5a}$ 10, $J_{4,5e}$ 6 Hz, H-4), 5.01 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 5.93 (q, 1 H, $J_{5a,5e}$ 10 Hz, H-5*e*), 6.28 (t, 1 H, H-5*a*), 6.53 (s, 3 H, OCH_3), and 7.80 (s, 3 H, $SO_2C_6H_4CH_3$).

Anal. Calc. for $C_{27}H_{26}O_9S$: C, 61.58; H, 4.99; S, 6.09. Found: C, 61.51; H, 4.88; S, 6.13.

*Selective benzoylation of methyl β-*D*-xylopyranoside* (**12**). — A solution of **12** (1 g) in pyridine (40 mL) was treated with benzoyl chloride (1.5 mL, 2.1 mol; or 0.6 mL, 0.8 mol) as described for the α anomer. Chromatographic separation of the products on silica gel gave five fractions. The syrupy compound eluted first was identified as the tribenzoate **13**, and it crystallized from ethanol; m.p. 96–98°, $[\alpha]_D^{23}$ −23° (*c* 1.7, chloroform); p.m.r. data: τ 4.22 (t, 1 H, $J_{2,3} = J_{3,4}$ = 8 Hz, H-3), 4.63 (q, 1 H, $J_{1,2}$ 6 Hz, H-2), 4.68 (sex, 1 H, $J_{4,5a}$ 7, $J_{4,5e}$ 4 Hz, H-4), 5.25 (d, 1 H, H-1), 5.53 (q, 1 H, $J_{5a,5e}$ 10 Hz, H-5*e*), 6.30 (q, 1 H, H-5*a*), and 6.48 (s, 3 H, OCH_3).

Anal. Calc. for $C_{27}H_{24}O_8$: C, 68.05; H, 5.01. Found: C, 67.79; H, 5.01.

The 2,4-dibenzoate **14** was obtained as a syrup, $[\alpha]_D^{20}$ −61° (*c* 1.8, chloroform); p.m.r. data: τ 4.8–5.2 (m, 2 H, H-2,4), 5.25 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.67 (q, 1 H, $J_{4,5a}$ 4, $J_{4,5e}$ 3 Hz, H-5*e*), 6.32 (q, 1 H, $J_{5a,5e}$ 12 Hz, H-5*a*), 6.50 (s, 3 H, OCH_3), and 7.95 (broad s, 1 H, OH exchanges in D_2O).

The mixture of 2,3-dibenzoate **15** and 3,4-dibenzoate **16** was obtained as a syrup that could not be resolved.

The 3-benzoate **17** crystallized from chloroform–petroleum ether; m.p. 138–139°, $[\alpha]_D^{18}$ −10° (*c* 0.7, chloroform) {lit.[5] $[\alpha]_D$ −15° (*c* 1, 1,4-dioxane)}; p.m.r. data: τ 4.97 (t, 1 H, $J_{2,3} = J_{3,4}$ = 7 Hz, H-3), 5.70 (d, 1 H, $J_{1,2}$ 6 Hz, H-1), and 6.55 (s, 3 H, OCH_3).

Anal. Calc. for $C_{13}H_{16}O_6$: C, 58.19; H, 6.02. Found: C, 58.13; H, 5.91.

The final fraction was a mixture of the 4-benzoate **18** and the 2-benzoate **19** which could not be separated from each other.

*Methyl 2,4-di-*O*-benzoyl-3-*O*-tosyl-β-*D*-xylopyranoside* (**20**). — (*a*). Tosylation of the 2,4-dibenzoate **14** (231 mg) gave the 3-tosylate **20** (310 mg, 95%); m.p. 150–152° (from ethanol), $[\alpha]_D^{21}$ −36° (*c* 1.7, chloroform); p.m.r. data: τ 6.60 (s, 3 H, OCH_3) and 7.90 (s, 3 H, $SO_2C_6H_4CH_3$).

Anal. Calc. for $C_{27}H_{26}O_9S$: C, 61.58; H, 4.99; S, 6.09. Found: C, 61.70; H, 5.08; S, 6.34.

(*b*). Methyl β-D-xylopyranoside 2,4-phenylboronate[5] (500 mg) was tosylated with tosyl chloride (1 g) in pyridine (10 mL) for 2 days at room temperature. The

mixture was extracted with chloroform, and the extract was evaporated, to yield the syrupy 3-tosylate (596 mg, 71%). A portion (174 mg) of the syrup was dissolved in acetone (6 mL) and treated with 1,3-propanediol (0.03 mL) to remove the boronic ester. Chloroform extraction, followed by crystallization from isopropyl alcohol–petroleum ether, afforded methyl 3-*O*-tosyl-β-D-xylopyranoside **26** (74 mg, 53%); m.p. 148–149°, $[\alpha]_D^{20}$ −6° (*c* 1.3, chloroform).

Anal. Calc. for $C_{13}H_{18}O_7S$: C, 49.04; H, 5.71; S, 10.07. Found: C, 49.02; H, 5.89; S, 9.89.

Benzoylation of **26** (173 mg), followed by crystallization from ethanol, gave compound **20** (188 mg, 66%); m.p. 151–152°, which was identical with the product prepared in (*a*).

*Methyl 2,3-di-*O*-benzoyl-4-*O*-tosyl-β-*D*-xylopyranoside* (**21**). — (*a*). Treatment of the mixture of the 2,3-dibenzoate **15** and the 3,4-dibenzoate **16** (185 mg) with tosyl chloride, followed by crystallization from chloroform–ethanol, gave the 4-tosylate **21** (158 mg, 61%); m.p. 139–141°, $[\alpha]_D^{21}$ +32.3° (*c* 1.5, chloroform); p.m.r. data: τ 4.48 (t, 1 H, $J_{2,3} = J_{3,4}$ = 8 Hz, H-3), 4.83 (q, 1 H, $J_{1,2}$ 6 Hz, H-1), 5.33 (sex, 1 H, $J_{4,5a}$ 8, $J_{4,5e}$ 5 Hz, H-4), 5.45 (d, 1 H, H-1), 5.67 (q, 1 H, $J_{5a,5e}$ 12 Hz, H-5*e*), 6.40 (q, 1 H, H-5*a*), 6.60 (s, 3 H, OCH_3), and 7.85 (s, 3 H, $SO_2C_6H_4CH_3$).

Anal. Calc. for $C_{27}H_{26}O_9S$: C, 61.58; H, 4.99; S, 6.09. Found: C, 61.49; H, 4.91; S, 6.32.

(*b*). A solution of **12** (500 mg) in *N*,*N*-dimethylformamide (5 mL) containing *p*-toluenesulfonic acid monohydrate (25 mg) was boiled under reflux for 2 h with 2,2-dimethoxypropane (1.5 mL). The acid was neutralized with Amberlite IRA-400 (OH^-) resin, the mixture filtered, the filtrate evaporated *in vacuo*, and the residue extracted with chloroform. Tosylation of the resulting, crude syrup, followed by *O*-de-isopropylidenation in acetic acid (3 mL), and perbenzoylation of the product, afforded a crude solid. Recrystallization from ethanol gave compound **21** (252 mg, 16%), m.p. 139–140°, identical with the product described in (*a*).

*Methyl 3-*O*-benzoyl-2,3-di-*O*-tosyl-β-*D*-xylopyranoside* (**23**). — Treatment of the 3-benzoate **17** (144 mg) with tosyl chloride gave the 2,4-ditosylate **23** (233 mg, 76%); m.p. 148° (from ethanol), $[\alpha]_D^{19}$ −11° (*c* 2.0, chloroform); p.m.r. data: τ 4.55 (t, 1 H, $J_{2,3} = J_{3,4}$ = 8 Hz, H-3), 5.35 (q, 1 H, $J_{1,2}$ 6 Hz, H-2), 5.42 (sex, 1 H, $J_{4,5a}$ 10, $J_{4,5e}$ 6 Hz, H-4), 5.58 (d, 1 H, H-1), 5.77 (q, 1 H, $J_{5a,5e}$ 12 Hz, H-5*e*), 6.52 (q, 1 H, H-5*a*), 6.67 (s, 3 H, OCH_3), and 7.78 and 7.85 (2 s, 6 H, 2 $SO_2C_6H_4CH_3$).

Anal. Calc. for $C_{27}H_{28}O_{10}S_2$: C, 56.23; H, 4.90; S, 11.12. Found: C, 56.11; H, 4.82; S, 10.87.

*Methyl 2-*O*-benzoyl-3,4-di-*O*-tosyl-β-*D*-xylopyranoside* (**25**) *and methyl 4-*O*-benzoyl-2,3-di-*O*-tosyl-β-*D*-xylopyranoside* (**24**). — A mixture of the 2- and 4-benzoates (**19** and **18**, 272 mg) in pyridine (1 mL) was treated with tosyl chloride (200 mg) for 7 days at room temperature. The usual processing, followed by two recrystallizations from ethanol, yielded **25** (130 mg, 25%) as long needles, m.p. 122–124°, $[\alpha]_D^{29}$ +51° (*c* 1.3, chloroform); p.m.r. data: τ 5.08 (q, 1 H, $J_{1,2}$ 6, $J_{2,3}$ 8 Hz, H-2), 5.18 (t, 1 H, $J_{3,4}$ 8 Hz, H-3), 5.4–5.8 (m, 2 H, H-1,4), 5.82 (q, 1 H, $J_{4,5e}$ 4, $J_{5a,5e}$ 12 Hz, H-5*e*),

6.55 (q, 1 H, $J_{4,5a}$ 7 Hz, H-5*a*), 6.70 (s, 3 H, OCH_3), and 7.62 and 7.80 (2 s, 6 H, 2 $SO_2C_6H_4CH_3$).

Anal. Calc. for $C_{27}H_{28}O_{10}S_2$: C, 56.23; H, 4.90; S, 11.12. Found: C, 56.07; H, 4.81; S, 11.02.

The 4-benzoate **24** could not be isolated in pure form from the mother liquor by fractional recrystallization. The crystalline mixture obtained from the mother liquor contained two types of material, namely, long needles and a white, amorphous substance. Therefore, the amorphous material was collected by picking it out of the mixture; it crystallized from ethanol, affording **24** as fine needles (42 mg, 8%), m.p. 135–136°, $[\alpha]_D^{29}$ 0° (*c* 0.8, chloroform); p.m.r. data: τ 5.85 (q, 1 H, $J_{4,5e}$ 4, $J_{5a,5e}$ 12 Hz, H-5*e*), 6.50 (q, 1 H, $J_{4,5a}$ 5 Hz, H-5*a*), 6.82 (s, 3 H, OCH_3), and 7.60 and 7.67 (2 s, 6 H, 2 $SO_2C_6H_4CH_3$).

Anal. Calc. for $C_{27}H_{28}O_{10}S_2$: C, 56.23; H, 4.90; S, 11.12. Found: C, 56.23; H, 4.81; S, 11.25.

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