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Carbohydrate Research 309 (1998) 281–286

CARBOHYDRATE RESEARCH

Two novel synthetic methods for 1,4-anhydro-α-D-xylopyranose derivatives

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Received 16 March 1998; accepted 18 May 1998

Abstract

Two novel methods for the syntheses of 1,4-anhydro-3-*O*-benzyl-2-*O*-pivaloyl- (**1**) and 2-*O*-acetyl-1,4-anhydro-3-*O*-benzyl-α-D-xylopyranose (**2**), starting materials for synthesizing stereoregular β-(1→5)-xylofuranan by ring-opening polymerization are reported. Both synthetic routes start from D-xylopyranose, involve nine reaction steps, and give approximately 30–35% overall yields. The key reaction in the novel synthetic routes is the intramolecular nucleophilic attack of C-1 oxyanion on the C-5 position of 3-*O*-benzyl-5-*O*-(*p*-toluenesulfonyl)-α-D-xylofuranose (**10**), resulting in 1,5-acetal bond formation in high yield. The present synthetic routes enable us to prepare 1,4-anhydro-α-D-xylopyranose derivatives having different substituents at the 2-*O*- and the 3-*O*-positions.

Keywords: Ring-opening polymerization; Intramolecular nucleophilic attack; 1,5-Acetal bond formation; 1,4-Anhydro-α-D-xylopyranose derivatives; Stereoregular β-(1→5)-xylofuranan

1. Introduction

Uryu et al. reported the ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose [1]. Stereoregular α-(1→5)-xylofuranan was obtained only when $BF_3 \cdot Et_2O$ was used as catalyst, and a polymer consisting of a mixture of α-(1→5)- and β-(1→5)-xylofuranose linkages was obtained when other Lewis acids were used. Stereoregular β-(1→5)-xylofuranan was never obtained by their method.

We have chemically synthesized cellulose and found that substituents on the monomer played an important role in stereoregularity of the resulting polymer [2–11]. On the basis of this work, we expect that there is a good possibility of synthesizing stereoregular β-(1→5)-xylofuranan by the ring-opening polymerization of 1,4-anhydro-3-*O*-benzyl-2-*O*-pivaloyl- (**1**) and 2-*O*-acetyl-1,4-anhydro-3-*O*-benzyl-α-D-xylopyranose (**2**).

Uryu et al. [1] synthesized 1,4-anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose from 1,4-anhydro-α-D-xylopyranose; the latter was prepared by vacuum pyrolysis of D-xylose according to the method of Köll et al. [12]. This synthetic route is not suitable for the syntheses of compounds **1** and **2** because it is difficult to introduce two different substituents specifically in the 2-*O*- and 3-*O*-positions of 1,4-anhydro-α-D-xylopyranose. Furthermore, vacuum

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0008-6215/98/$—see front matter
PII S0008-6215(98)00135-9

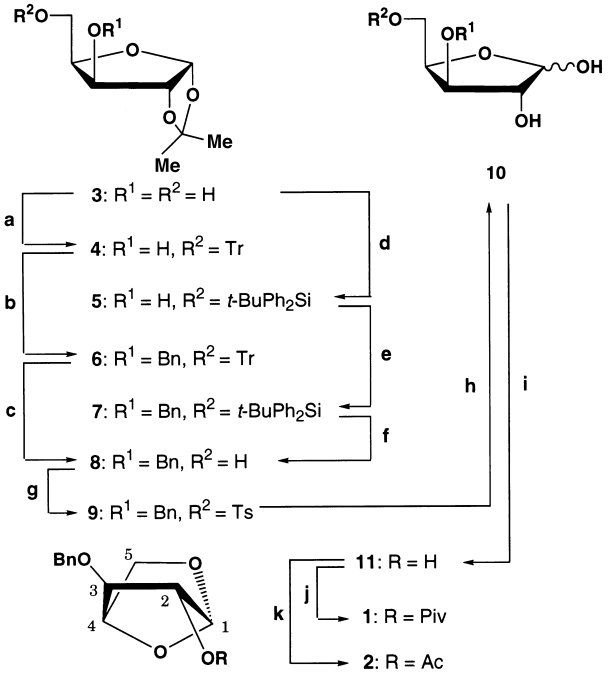
pyrolysis of D-xylose gave 1,4-anhydro-α-D-xylopyranose in only 5% yield, even though only one reaction step was involved.

In this paper, we describe two new synthetic methods for compounds **1** and **2**. As expected, these two monomers were found to induce stereoselective β-glycosidic bond formation by the neighboring-group participation of the 2-*O*-acyl group to give β-(1→5)-xylofuranan as will be reported in a separate paper [13].

2. Results and discussion

General considerations.—The two methods synthesize compounds **1** and **2** from D-xylopyranose in nine steps. Both methods involve a common starting intermediate, 1,2-*O*-isopropylidene-α-D-xylofuranose (**3**), which is synthesized from D-xylose in two steps according to the method of Levene and Raymond [17]. The two methods also share a common final four steps starting from 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**8**). Thus, the two methods differ from each other only by the three-step synthesis of compound **8** from compound **3** as shown in Scheme 1. We shall first describe the two different methods, A and B, for the synthesis of compound **8** from compound **3**. This is to be followed by description of the common final four steps from compound **8** to compounds **1** and **2**.

Synthesis of compound **8** *from compound* **3**.—*Method A* (reaction steps: a–c in Scheme 1). 1,2-*O*-Isopropylidene-α-D-xylofuranose (**3**) was treated with triphenylmethyl chloride and triethylamine in dry 1,4-dioxane to afford 1,2-*O*-isopropylidene-5-*O*-triphenylmethyl-α-D-xylofuranose (**4**) in 78% yield (reaction step a in Scheme 1). However, purification of compound **4** was difficult because triphenylmethyl alcohol, which is a byproduct, has almost the same R_f value as that of compound **4** on the TLC plate developed with a number of organic solvents and solvent mixtures, for example with 1:2 EtOAc–*n*-hexane. Compound **4** was converted to 3-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-triphenylmethyl-α-D-xylofuranose (**6**) by benzylation (reaction step b in Scheme 1). Detriphenylmethylation of compound **6** was performed with formic acid in diethyl ether to give 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**8**) in 77% yield (reaction step c in Scheme 1), but a side reaction also occurred because the isopropylidene group was not stable under the acidic conditions.



Scheme 1. Reagents and conditions: (a) TrCl, Et_3N, anhydrous dioxane, 100 °C, 3 h, 78%; (b, e) BnBr, NaH, Bu_4NI, THF, r.t., overnight, 98%; (c) formic acid, diethyl ether, r.t., 30 min, 77%; (d) *t*-$BuPh_2SiCl$, imidazole, DMF, r.t., overnight, 99%; (f) Bu_4NF, THF, r.t., overnight, 79%; (g) TsCl, pyridine, 60 °C, overnight, 99%; (h) trifuruoroacetic acid, H_2O, r.t., 3 h, 80%; (i) Me_4NOH, DMF, 60 °C, 3 h, 93%; (j) PivCl, pyridine, 80 °C, overnight, 78%; (k) Ac_2O, pyridine, r.t., overnight, 86%.

Method B (Reaction steps: d–f in Scheme 1). The *tert*-butyldiphenylsilyl group, which can be selectively removed with tetrabutylammonium fluoride, was introduced onto the 5-OH of compound **3** to give 5-*O*-*tert*-butyldiphenylsilyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**5**) in 99% yield (reaction step d in Scheme 1). Compound **5** was converted to 3-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**7**) by benzylation (reaction step e in Scheme 1), and subsequent de-*tert*-butyldiphenylsilylation of compound **7** gave compound **8** in 79% yield without any side reactions (reaction step f in Scheme 1).

Synthesis of compounds **1** *and* **2** *from compound* **8**.—Compound **8** was treated with *p*-toluenesulfonyl chloride in pyridine to afford 3-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-(*p*-toluenesulfonyl)-α-D-xylofuranose (**9**). Compound **9** was then treated with 9:1 trifluoroacetic acid–H_2O to give 3-*O*-benzyl-5-*O*-(*p*-toluenesulfonyl)-α-D-xylofuranose (**10**). An overall yield of 80% was obtained in these two steps starting from compound **8**. Compound **10** was treated with tetramethylammonium hydroxide

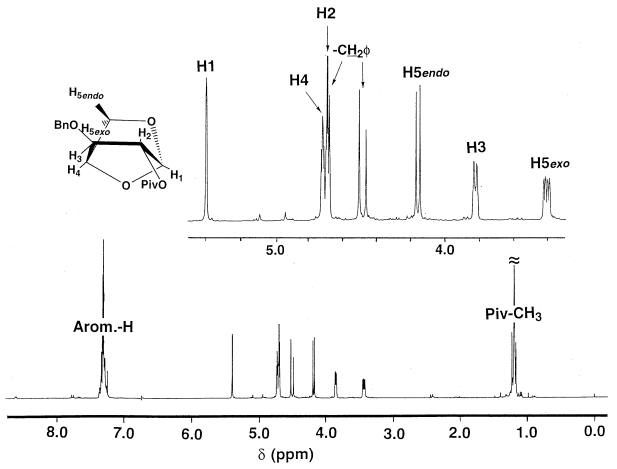


Fig. 1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 1,4-anhydro-3-*O*-benzyl-2-*O*-pivaloyl-α-D-xylopyranose (**1**).

in DMF at 60 °C for 3 h to afford 1,4-anhydro-3-*O*-benzyl-α-D-xylofuranose (**11**) in a 93% yield. Pivaloylation or acetylation of compound **11** gave compound **1** or compound **2**, respectively.

Compounds **1** and **2** are synthesized in seven reaction steps from compound **3** by either method A or method B. Comparing the two methods, method B is preferred over method A for higher overall yield, simpler purification steps, and less complicated reactions. The key step of these novel synthetic routes is the formation of a 1,5-acetal bond resulting from elimination of the *p*-toluenesulfonyl group at 5-*O*-position by the backside attack of the C-1 oxyanion of compound **10** (reaction step i in Scheme 1) [15].

The ^{1}H NMR spectrum of compound **1** is shown in Fig. 1. The anomeric proton appears at δ 5.4 ppm, which is in agreement with its having a dihedral angle of ~90° with H-2. The *endo* proton H-5 appears as a broad doublet (*J* 6.64 Hz) at δ 4.18 ppm as a result of having a dihedral angle of ~90° with H-4 [15]. The observed long-range couplings of the anomeric proton with H-4 and of H-3 with the *exo* proton H-5 also support the strained 1,4-anhydro structure. The spectrum of compound **2** was almost the same as that of compound **1**.

3. Conclusions

We have developed two novel synthetic methods for 1,4-anhydro-3-*O*-benzyl-2-*O*-pivaloyl- (**1**) and 2-*O*-acetyl-1,4-anhydro-3-*O*-benzyl-α-D-xylopyranose (**2**). For large-scale preparations, we found that method B may be preferred over method A. Compounds **1** and **2** were obtained from D-xylose by our synthetic route (especially method B) in 32.1 and 35.5% overall yield, respectively. The present synthetic methods are extremely useful for the two secondary hydroxyl groups, as the C-2 and C-3 positions in 1,4-anhydro-α-D-xylopyranose may be substituted with different substituents.

4. Experimental

General methods.—^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC 300 FT-NMR (300 MHz) spectrometer, in chloroform-*d* with tetramethylsilane (Me_4Si) as an internal standard. Chemical shifts (δ) and coupling constants (*J*) are given in δ-values (ppm) and Hz, respectively. Some chemical shift assignments were assigned using a decoupling method; others were assigned by comparing with literature data and with model compounds. Optical rotations were measured at 25 °C using a JASCO Dip-1000 digital polarimeter. A standard workup procedure was employed in each synthesis step. The procedure included diluting the mixture with ethyl acetate, washing with aqueous $NaHCO_3$ and brine, drying the organic extract over Na_2SO_4, and evaporating the solvents *in vacuo*.

*1,2-*O*-Isopropylidene-5-*O*-triphenylmethyl-*α*-D-xylofuranose* (**4**).—To a solution of 1,2-*O*-isopropylidene-α-D-xylofuranose (**3**) (3 g, 15.8 mmol) in dioxane dried over 4Å MS (100 mL) triphenylmethyl chloride (6.9 mg, 17.4 mmol) and triethylamine (22 mL, 0.2 mmol) were added, and then the reaction mixture was heated to 100 °C. After 3 h, the reaction mixture was worked up by the standard procedure to afford an orange syrup. Compound **4** was purified on a silica gel column (Wakogel C-200) eluted with 1:9 ethyl acetate–*n*-hexane and 1:1 ethyl acetate–*n*-hexane to give a yellow syrup (5.3 g, 78.0% yield): $[\alpha]_D^{25}$ +6.32° (*c* 2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.97 (d, 1 H, $J_{1,2}$ 3.72 Hz, H-1), 4.49 (d, 1 H, $J_{2,3}$ 0 Hz, H-2), 4.24–4.28 (H-3, H-4), 3.55 (dd, 1 H, $J_{4,5a}$ 5.11 Hz, H-5a), 3.46 (dd, 1 H, J_{gem} 10.3 Hz, $J_{4,5b}$ 3.89 Hz, H-5b), 7.22–7.45 (Ar), 1.48, 1.30 (s, 3 H, respectively, CH_3); ^{13}C NMR ($CDCl_3$): δ 105.0 (C-1), 87.5, 85.1, 78.5, 76.3, 61.8 [C-2, C-3, C-4, C-5, $\underline{C}(C_6H_5)_3$], 26.8, 26.2 (CH_3), 111.5 [$(CH_3)_2\underline{C}(O\text{-})_2$], 143.2, 128.5, 128.1, 127.3 (Ar). Anal. Calcd for $C_{27}H_{28}O_5$: C, 74.98; H, 6.52. Found: C, 74.78; H, 6.53.

5-O-tert-*Butyldiphenylsilyl-1,2*-O-*isopropylidene*-α-D-*xylofuranose* (**5**).—To a solution of 1,2-*O*-isopropylidene-α-D-xylofuranose (**3**) (3 g, 15.8 mmol) in DMF (20 mL), *tert*-butyldiphenylsilyl chloride (5.47 mL, 19.0 mmol) and imidazole (2.58 g, 37.9 mmol) were added, and the mixture was kept at room temperature. After 1 day, the reaction mixture was worked up by the standard procedure. Compound **5** was purified on a silica gel column (Wakogel C-200) eluted with 1:9 ethyl acetate–*n*-hexane to give a colorless syrup (6.7 g, 99.3% yield): $[\alpha]_D^{25}$ −1.93° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 6.00 (d, 1 H, $J_{1,2}$ 3.67 Hz, H-1), 4.54 (d, 1 H, $J_{2,3}$ 0 Hz, H-2), 4.02 (d, 1 H, $J_{3,4}$ 3.14 Hz, H-3), 4.37 (t, 1 H, $J_{4,5a}$ 0 Hz, H-4), 4.10–4.14 (overlapped, 2 H, H-5a, H-5b), 7.40–7.44, 7.66–7.73 (Ar), 1.47, 1.33 (s, 3 H, respectively, CH_3), 1.05 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR ($CDCl_3$): δ 105.0 (C-1), 85.5, 78.4, 76.9, 62.8 (C-2, C-3, C-4, C-5), 26.8, 26.7 (CH_3), 19.1 [$(CH_3)_2\underline{C}(O\text{-})_2$], 127.9, 130.1, 135.5, 135.7 (Ar). Anal. Calcd for $C_{24}H_{32}O_5Si$: C, 67.26; H, 7.53; O, 18.66. Found: C, 67.07; H, 7.53.

3-O-*Benzyl-1,2*-O-*isopropylidene-5*-O-*triphenylmethyl*-α-D-*xylofuranose* (**6**).—Compound **4** (5.3 g, 12.3 mmol) was dissolved in THF (60 mL) and sodium hydride (1 g, 24.5 mmol, 60% in mineral oil), tetrabutylammonium iodide (453 mg) and benzyl bromide (2.19 mL, 18.4 mmol) were added. The mixture was stirred at room temperature. After 15 h, methanol was added to the reaction mixture to decompose excess benzyl bromide. The reaction mixture was worked up by the standard procedure to give a yellow oil. Compound **6** was purified on a silica gel column (Wakogel C-200) eluted with 1:4 ethyl acetate–*n*-hexane to give a yellow syrup (6.25 g, 97.6% yield): $[\alpha]_D^{25}$ −30.8° (*c* 2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.89 (d, 1 H, $J_{1,2}$ 3.81 Hz, H-1), 4.56 (d, 1 H, $J_{2,3}$ 0 Hz, H-2), 3.96 (d, 1 H, $J_{3,4}$ 3.12 Hz, H-3), 4.38 (m, 1 H, $J_{4,5a}$ 5.76 Hz, H-4), 3.54 (dd, 1 H, J_{gem} 9.35 Hz, H-5a), 3.31 (dd, 1 H, $J_{4,5b}$ 6.81 Hz, H-5b), 4.57, 4.42 (d, 1 H, respectively, *J* 12.0 Hz, $C\underline{H}_2C_6H_5$) 7.23–7.43 (Ar), 1.52, 1.31 (s, 3 H, respectively, CH_3); ^{13}C NMR ($CDCl_3$): δ 105.0 (C-1), 86.9, 82.4, 81.6, 79.4, 72.0, 64.3 [C-2, C-3, C-4, C-5, $\underline{C}H_2C_6H_5$, $\underline{C}(C_6H_5)_3$], 26.8, 26.2 (CH_3), 111.5 [$(CH_3)_2\underline{C}(O\text{-})_2$], 143.8, 137.4, 127.0–128.7 (Ar). Anal. Calcd for $C_{34}H_{34}O_5$: C, 78.14; H, 6.56. Found: C, 78.31; H, 6.53.

3-O-*Benzyl-5*-O-tert-*butyldiphenylsilyl-1,2*-O-*isopropylidene*-α-D-*xylofuranose* (**7**).—The procedure used for benzylation of compound **5** (6.7 g, 15.7 mmol) to compound **7** was identical to that used for the benzylation of compound **4** as described in the above section for the preparation of compound **6**. Compound **7** was then purified on a silica gel column (Wakogel C-200) eluted with 1:9 ethyl acetate–*n*-hexane to give a colorless syrup (7.91 g, 97.6% yield): $[\alpha]_D^{25}$ −21.9° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.89 (d, 1 H, $J_{1,2}$ 3.78 Hz, H-1), 4.60 (d, 1 H, $J_{2,3}$ 0 Hz, H-2), 4.06 (d, 1 H, $J_{3,4}$ 3.16 Hz, H-3), 4.32 (m, 1 H, $J_{4,5a}$ 7.76 Hz, H-4), 3.99 (dd, 1 H, J_{gem} 9.99 Hz, H-5a), 3.91 (dd, 1 H, $J_{4,5b}$ 5.36 Hz, H-5b), 4.67, 4.57 (d, 1 H, respectively, *J* 11.8 Hz, $C\underline{H}_2C_6H_5$), 7.26–7.40, 7.63–7.66 (Ar), 1.49, 1.31 (s, 3 H, respectively, CH_3), 1.07, 1.06, 1.04 [s, 3 H, respectively, $C(CH_3)_3$]; ^{13}C NMR ($CDCl_3$): δ 105.1 (C-1), 82.6, 81.6, 80.6, 72.3, 60.8 (C-2, C-3, C-4, C-5, $\underline{C}H_2C_6H_5$,), 26.9, 26.6, 26.4 [$\underline{C}H_3$, $C(\underline{C}H_3)_3$], 19.2 [$\underline{C}(CH_3)_3$], 111.7 [$(CH_3)_2\underline{C}(O-)_2$], 127.5-137.7 (Ar). Anal. Calcd for $C_{31}H_{38}O_5Si$: C, 71.78; H, 7.38; O, 15.42. Found: C, 71.80; H, 7.38.

3-O-*Benzyl-1,2*-O-*isopropylidene*-α-D-*xylofuranose* (**8**).—(From compound **6**.) To a solution of compound **6** (4 g, 7.67 mmol) in diethyl ether (15 mL), formic acid (19.2 mL) was added. The reaction mixture was stirred for 15 min at room temperature. The reaction mixture was worked up by the standard procedure to give a yellow oil. Compound **8** was purified on a silica gel column (Wakogel C-200) eluted with 1:4 ethyl acetate–*n*-hexane and 1:1 ethyl acetate–*n*-hexane to give a yellow syrup (1.7 g, 77.3% yield) after evaporation.

(From compound **7**.) To a solution of compound **7** (4 g, 7.72 mmol) in THF (5 mL), tetrabuthylammonium fluoride (16.3 mL, 15.4 mmol) was added. The reaction mixture was stirred at room temperature overnight. The reaction mixture was diluted with ethyl acetate, washed with N HCl and brine, dried over Na_2SO_4, and evaporated *in vacuo* to give a yellow oil. Compound **8** was purified on a silica gel column (Wakogel C-200) eluted with 1:9 ethyl acetate–*n*-hexane, 1:4 ethyl acetate–*n*-hexane and 1:1 ethyl acetate–*n*-hexane to give a yellow syrup (1.71 g, 79.2% yield): $[\alpha]_D^{25}$ −63.6° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.98 (d, 1 H, $J_{1,2}$ 3.83 Hz, H-1), 4.63 (d, 1 H, $J_{2,3}$ 0 Hz, H-2), 4.00 (d, 1 H, $J_{3,4}$ 3.49 Hz, H-3), 4.27 (m, 1 H, H-4), 3.84–3.96 (overlapped, 2 H, H-5a, H-5b), 4.74, 4.49 (d, 1 H, respectively, *J* 12.1 Hz, $C\underline{H}_2C_6H_5$) 7.30–7.35 (Ar), 1.48, 1.32 (s, 3 H, respectively, CH_3); ^{13}C NMR ($CDCl_3$): δ 105.0 (C-1), 82.5, 82.4, 80.2, 71.8, 60.8 (C-2, C-3, C-4, C-5, $\underline{C}H_2C_6H_5$), 26.7, 26.1 (CH_3), 137.1, 137.3, 132.2, 128.5, 128.0, 127.6 (Ar).

Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.40; H, 6.97.

3-O-*Benzyl-1,2*-O-*isopropylidene-5*-O-*(*p-*toluenesulfonyl)*-α-D-*xylofuranose* (**9**).—To a solution of compound **8** (1.7 g, 6.07 mmol) in pyridine (20 mL), *p*-toluenesulfonyl chloride (1.27 g, 6.68 mmol) was added. The reaction mixture was stirred at 60 °C overnight. The reaction mixture was worked up by the standard procedure to give a yellow oil. Compound **9** was purified on a silica gel column (Wakogel C-200) eluted with $CHCl_3$ to give a yellow syrup (2.62 g, 99.4% yield): $[\alpha]_D^{25}$ −22.3° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.86 (d, 1 H, $J_{1,2}$ 3.72 Hz, H-1), 4.56 (d, 1 H, $J_{2,3}$ 0 Hz, H-2), 3.96 (d, 1 H, $J_{3,4}$ 3.18 Hz, H-3), 4.35 (m, 1 H, $J_{4,5b}$ 5.96 Hz, H-4), 4.29 (dd, 1 H, $J_{4,5a}$ 6.02 Hz, H-5a), 4.18 (dd, 1 H, J_{gem} 9.80 Hz, H-5b), 4.61, 4.46 (d, 1 H, respectively, *J* 11.8 Hz, $C\underline{H}_2C_6H_5$) 7.79, 7.76, 7.26–7.32 (Ar), 2.42 (s, 3 H, *p*-$C\underline{H}_3C_6H_4SO_2$), 1.44, 1.29 (s, 3 H, respectively, CH_3); ^{13}C NMR ($CDCl_3$): δ 105.2 (C-1), 82.1, 81.2, 77.6, 72.1, 67.0 (C-2, C-3, C-4, C-5, $\underline{C}H_2C_6H_5$), 26.8, 26.3 (CH_3), 21.6 ($\underline{C}H_3C_6H_4SO_2$), 137.0, 144.9, 127.7–132.7 (Ar). Anal. Calcd for $C_{23}H_{28}O_7S$: C, 61.59; H, 6.29; S, 7.15. Found: C, 61.84; H, 6.19; S, 7.09.

3-O-*Benzyl*-*5*-O-*(*p-*toluenesulfonyl)*-D-*xylofuranose* (**10**).—Compound **9** (2.62 g, 6.04 mmol) was dissolved in 9:1 trifluoroacetic acid–H_2O (20 mL). The mixture was stirred at room temperature for 1.5 h. The reaction mixture was evaporated *in vacuo* at 40 °C to remove the solvents. The resulting oil was diluted with ethyl acetate, washed with satd aq $NaHCO_3$ and brine, dried over anhydrous sodium sulfate, and concentrated to dryness. Compound **10** was purified on a silica gel column (Wakogel C-200) eluted with 1:1 ethyl acetate–*n*-hexane to give a yellow syrup (1.9 g, 80.0% yield): $[\alpha]_D^{25}$ +10.2° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.54 (d, 1 H, $J_{1,2}$ 2.42 Hz, H-1α), 5.17 (s, 1 H, $J_{1,2}$ 0 Hz, H-1b), 4.04–4.61 (H-2, H-3, H-4, H-5a, H-5β), 4.59, 4.39 (d, 1 H, respectively, *J* 11.8 Hz, $C\underline{H}_2C_6H_5$) 7.72, 7.69, 7.20–7.27 (Ar), 2.37 (s, 3 H, *p*-$C\underline{H}_3C_6H_4SO_2$); ^{13}C NMR ($CDCl_3$): δ 96.9 (C-1β), 82.7, 76.4, 75.1, 72.1, 69.2 (C-2β, C-3β, C-4β, C-5β, $\underline{C}H_2C_6H_5\beta$), 103.3 (C-1α), 82.0, 78.6, 72.8, 68.9, 60.5 (C-2α, C-3α, C-4α, C-5α, $\underline{C}H_2C_6H_5\alpha$), 21.6 ($\underline{C}H_3C_6H_4SO_2$), 132.4, 136.7, 145.1, 124.4–132.2 (Ar). Anal. Calcd for $C_{20}H_{24}O_7S$: C, 58.81; H, 5.92; S, 7.85. Found: C, 58.72; H, 6.18.

1,4-Anhydro-3-O-*benzyl*-α-D-*xylopyranose* (**11**).—To a solution of compound **10** (1.9 g, 4.82 mmol) in DMF (5 mL), Me_4NOH (10.6 mL, 9.64 mmol) was added. The reaction mixture was stirred at 60 °C. After 3 h, the reaction mixture was neutralized by AcOH and evaporated *in vacuo*. Compound **11** was purified on a silica gel column (Wakogel C-200) eluted with 1:1 ethyl acetate–*n*-hexane to give a yellow syrup (839 mg, 92.8% yield): $[\alpha]_D^{25}$ −7.64° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.34 (d, 1 H, $J_{1,4}$ 0.94 Hz, H-1), 3.81 (s, 1 H, $J_{2,3}$ 0 Hz, H-2), 3.76 (m, 1 H, $J_{3,4}$ 4.83 Hz, H-3), 4.72 (dd, 1 H, $J_{4,5b}$ 3.23 Hz, H-4), 4.09 (d, 1 H, $J_{4,5a}$ 0 Hz, H-5a), 3.41 (m, 1 H, J_{gem} 6.60 Hz, H-5b), 4.67, 4.56 (d, 1 H, respectively, *J* 11.7 Hz, $C\underline{H}_2C_6H_5$) 7.35–7.37 (Ar); ^{13}C NMR ($CDCl_3$): δ 104.3 (C-1), 85.9, 78.0, 76.0, 72.9, 62.5 (C-2, C-3, C-4, C-5, $\underline{C}H_2C_6H_5$), 137.3, 127.0–128.5 (Ar). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.62; H, 6.36.

1,4-Anhydro-3-O-*benzyl-2*-O-*pivaloyl*-α-D-*xylopyranose* (**1**).—To a solution of compound **11** (500 mg, 2.25 mmol) in pyridine (5 mL) was added pivaloyl chloride (693.5 μL, 5.63 mmol), and the mixture was heated to 80 °C and kept overnight. Then 0.1 mL MeOH was added, and the mixture was worked up by the standard procedure. Compound **1** was purified on a silica gel column (Wakogel C-200) eluted with 1:4 ethyl acetate–*n*-hexane to give a colorless oil (535.5 mg, 77.7% yield): $[\alpha]_D^{25}$ −36.3° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.40 (d, 1 H, $J_{1,4}$ 0.86 Hz, H-1), 4.70 (d, 1 H, $J_{2,3}$ 1.57 Hz, H-2), 3.85 (m, 1 H, $J_{3,4}$ 4.93 Hz, H-3), 4.54 (m, 1 H, $J_{4,5endo}$ 0 Hz, H-4), 4.18 (d, 1 H, J_{gem} 6.64 Hz, H-5*endo*), 3.44 (m, 1 H, $J_{4,5exo}$ 2.38 Hz, H-5*exo*), 1.20 (s, 9 H, $C{=}OC(C\underline{H}_3)_3$), 4.71, 4.50 (d, 1 H, *J* 11.9 Hz, respectively, $C\underline{H}_2C_6H_5$), 7.31–7.33 (Ar); ^{13}C NMR ($CDCl_3$): δ 102.2 (C-1), 82.2, 78.5, 75.8, 72.6, 62.8 (C-2, C-3, C-4, C-5, $\underline{C}H_2C_6H_5$), 26.9 [$C(\underline{C}H_3)_3$], 38.4 [$\underline{C}(CH_3)_3$], 137.1, 128.4, 127.9, 127.8 (Ar), 177.3 (C=O). Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.36; H, 7.26.

2-O-*Acetyl-1,4-anhydro-3*-O-*benzyl*-α-D-*xylopyranose* (**2**).—To a solution of compound **11** (300 mg, 1.35 mmol) in pyridine (2 mL), acetic anhydride (2 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was evaporated *in vacuo*. Compound **2** was purified on a silica gel column (Wakogel C-200) eluted with 1:2 ethyl acetate–*n*-hexane to give a yellow oil (306.5 mg, 86.0% yield): $[\alpha]_D^{25}$ −43.9° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.44 (d, 1 H, $J_{1,4}$ 0.92 Hz, H-1), 4.69 (d, 1 H, $J_{2,3}$ 1.45 Hz, H-2), 3.90 (m, 1 H, $J_{3,4}$ 4.95 Hz, H-3), 4.73 (m, 1 H, $J_{4,5endo}$

0 Hz, H-4), 4.17 (d, 1 H, J_{gem} 6.65 Hz, H-5*endo*), 3.44 (m, 1 H, $J_{4,5exo}$ 2.30 Hz, H-5*exo*), 2.08 (s, 3 H, Ac-C$\underline{H}_3$), 4.70, 4.52 (d, 1 H, J 11.8 Hz, respectively, C$\underline{H}_2C_6H_5$), 7.31–7.33 (Ar); ^{13}C NMR ($CDCl_3$): δ 102.3 (C-1), 82.5, 79.0, 76.0, 73.0, 63.0 (C-2, C-3, C-4, C-5, $\underline{C}H_2C_6H_5$), 20.9 (CH_3), 127.9-128.5 (Ar), 170.0 (C=O). Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.76; H, 6.19.

Acknowledgements

The authors are indebted to Dr. Hou-min Chang, Professor at North Carolina State University, for his critical reading of the manuscript. This investigation was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan (No. 09460076).

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