Carbohydrate Research, 128 (1984) 217–226
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYNTHESIS OF REDUCING DISACCHARIDES OF D-XYLOPYRANOSE*

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(Received December 20th, 1982; accepted for publication in revised form, November 11th, 1983)

ABSTRACT

Twenty-one derivatives of reducing disaccharides, D-xylopyranosyl-(1→2)-, -(1→3)-, and -(1→4)-α- or -β-D-xylose were synthesized according to the Helferich and Zirner method. Disaccharides having a pyranose reducing unit were prepared by condensation of 2,3,4-tri-*O*-acetyl-, 2,4-di-*O*-acetyl-3-*O*-chloroacetyl-, and 2,3-di-*O*-acetyl-4-*O*-chloroacetyl-α-D-xylopyranosyl bromide with tri-*O*-acetyl-β-D-xylopyranose derivatives; among these, 1,2,4-tri-*O*-acetyl-3-*O*-(2,4-di-*O*-acetyl-β-D-xylopyranosyl)-β-D-xylopyranose and 1,2,3-tri-*O*-acetyl-4-*O*-(2,3-di-*O*-acetyl-β-D-xylopyranosyl)-β-D-xylopyranose having a free hydroxyl group in the nonreducing sugar group were prepared for the synthesis of higher-mol.wt. linear oligomers. Glycosylation of the readily available 5-*O*-chloroacetyl- or 5-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose gave 1,2-*O*-isopropylidene-3-*O*-β-D-xylopyranosyl-D-xylofuranose derivatives, further transformed into hexa-*O*-acetyl-β-(1→3)-xylobiose. Some analogs of α-D-linked disaccharides were formed during glycosylation. The location of the acetyl groups in the reducing and nonreducing residues were identified by comparison of the methyl-proton resonances for solutions in ($^2H_6$)benzene of 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→3)-1,2,4-tri-*O*-acetyl-β-D-xylopyranose and of a hexa-*O*-acetyl disaccharide having deuterated acetyl groups in the reducing residue, obtained by acetylation of 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→3)-D-xylopyranose with ($^2H_6$)acetic anhydride.

INTRODUCTION

D-Xylose is widely distributed in Nature and is commonly found as a constituent of polysaccharides from land plants or marine algae. In our laboratory, for several years, we have developed methods for the synthesis of D-xylose derivatives[1–9], and numerous precursors, such as tri-*O*-acetyl-D-xylopyranoses[2] and 3-*O*-chloroacetyl- (**14**) or 4-*O*-chloroacetyl-α-D-xylopyranosyl bromide[3] (**15**) have been prepared for the synthesis of di- and oligo-xylosaccharides. These precursors are

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0008-6215/84/$ 03.00

invaluable for the stepwise synthesis of oligosaccharides, as they give, at each step, oligomers having a good, temporary protecting group at the terminal, nonreducing glycosyl group. We describe herein the synthesis and caracterization of twenty one disaccharides, some having a D-xylofuranose reducing residue (**21**–**27**), others having a chloroacetyl protecting group in the nonreducing group (**4**, **6**, **9**, and **11**). All these compounds were synthesized according to the method of Helferich and Zirner[10] by condensation of α-D-xylopyranosyl bromide derivatives with D-xylopyranose or -furanose compounds having a free hydroxyl group.

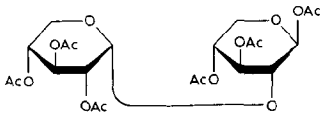
We have reported[4] previously the ^{1}H- and ^{13}C-n.m.r. spectra for **1**–**12**, and the use of these data has been important for the interpretation of the n.m.r. spectra of several D-xylans isolated from land plants[11] or marine sources[12].

RESULTS AND DISCUSSION

In 1961, the preparation of 4-*O*-β-D-xylopyranosyl-D-xylose and 3-*O*-methyl-4-*O*-β-D-xylopyranosyl-D-xylose was described by Aspinall and Ross[13] by way of the condensation of 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide with methyl 2,3-anhydro-β-D-ribopyranoside. At the same time, Myhre and Smith[14] obtained 4-*O*-β-D-xylopyranosyl-D-xylose by treatment of 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide with benzyl 2,3-di-*O*-benzyl-D-xylopyranoside. Ball and Jones[15] isolated, by chromatographic separation from a mixture of oligosaccharides obtained by acid reversion of D-xylose, 4-*O*-β-, 3-*O*-α-, and 2-*O*-α-D-xylopyranosyl-D-xylose. In the preparation of (1→3)-linked disaccharides, Curtis and Jones[16] obtained, by Koenigs–Knorr condensation, 3-*O*-β-D-xylopyranosyl-D-xylose (rhodymenabiose) from 5-*O*-benzoyl-2,4-*O*-benzylidene-D-xylose, and Ferrier and Prasad[17], by the Helferich method, 3-*O*-α- and 3-*O*-β-D-xylopyranosyl-D-xylose from benzyl β-D-xylopyranoside 2,4-phenylboronate. The three (1→1)-D-xylobiose, analogs of trehalose, were obtained by Helferich and Ost[18] by condensation of 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide with 2,3,4-tri-*O*-acetyl-D-xylopyranose.

Recently, Kováč and associates have described the synthesis of both 2-*O*-α- and -β-D-xylopyranosyl-D-xylose by condensation of 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide with benzyl 3,4-di-*O*-benzyl-β-D-xylopyranoside[19] and, at the same time, reported the ^{13}C-n.m.r. spectra of thirteen synthesized methyl glycosides of D-xylo-oligosaccharides[20]. Subsequently, they obtained 3-*O*-α- and -β-D-xylopyranosyl-D-xylose from 5-*O*-benzoyl-1,2-*O*-isopropylidene-3-*O*-(2,3,4-tri-*O*-acetyl-α- and -β-D-xylopyranosyl)-α-D-xylofuranose[21], and 2,4-di-*O*-β-D-xylopyranosyl-D-xylopyranose and *O*-α-D-xylopyranosyl-(1→2)-[*O*-β-D-xylopyranosyl-(1→4)]-D-xylopyranose[22]. More recently they have described the sequential synthesis of (1→4)-β-D-xylo-oligosaccharides[23] and their methyl β-D-glycosides[24].

The six hexa-*O*-acetyl-α- and -β-(1→4)-, -(1→3)- and -(1→2)-linked, reducing xylobioses (**1**, **2**, **3**, **5**, **8**, and **10**) were prepared by condensation of 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide (**13**) with the corresponding tri-*O*-acetyl-β-D-xylopyranose[2] (**16**–**18**). In the same manner, condensation of the 3-*O*- or 4-*O*-



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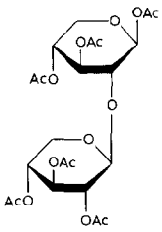

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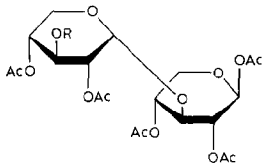
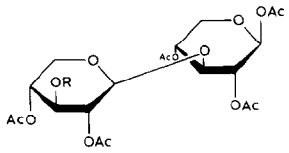
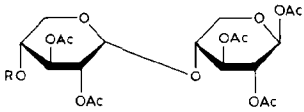


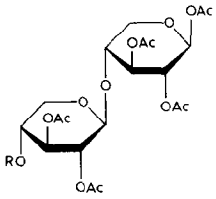
3 R = Ac
4 R = Cl_2CH_2CO



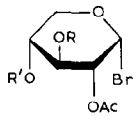
5 R = Ac
6 R = $ClCH_2CO$
7 R = H



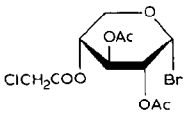
8 R = Ac
9 R = $ClCH_2CO$



10 R = Ac
11 R = $ClCH_2CO$
12 R = H



13 R = R′ = Ac
14 R = $ClCH_2CO$, R′ = Ac



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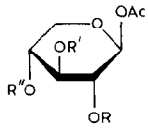
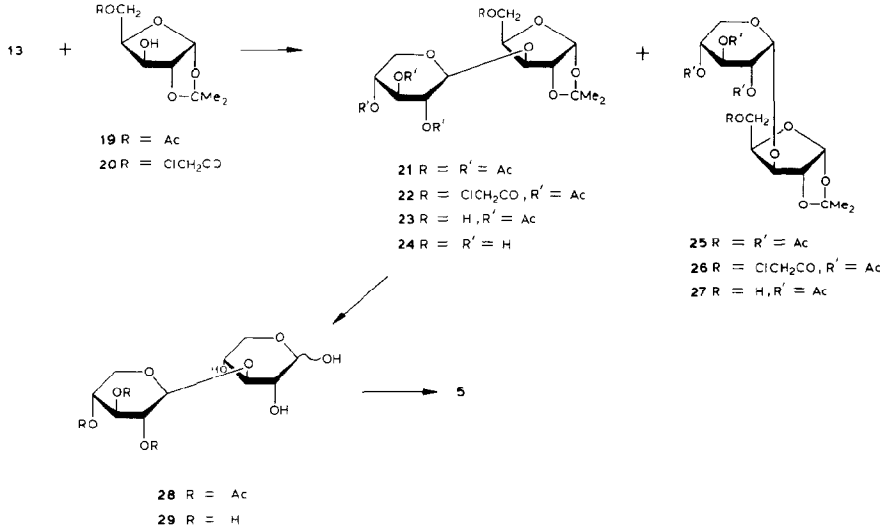


16 R = H, R′ = R″ = Ac
17 R = R″ = Ac, R′ = H
18 R = R′ = Ac, R″ = H

chloroacetyl-substituted α-D-xylopyranosyl bromide **14** and **15**, prepared from the corresponding chloroacetylated tri-*O*-acetyl-D-xylopyranose derivatives[2], respectively with 1,2,4-tri-*O*-acetyl- (**17**) and 1,2,3-tri-*O*-acetyl-β-D-xylopyranose (**18**) afforded disaccharides **4** and **6**, and **9** and **11**, respectively, having a temporary protecting chloroacetyl group in the nonreducing glycosyl group. Compounds **6** and **11** were further transformed into disaccharides **7** and **12** having one free hydroxyl group, which are precursors for the synthesis of higher-mol.-wt. linear oligomers; no attempts were made to deprotect **4** and **9**.

In addition to the aforementioned synthesis, 1,2,4-tri-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-β-D-xylopyranose (**5**) was prepared *via* a D-xylofuranose intermediate. Treatment of 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide (**13**) with 5-*O*-acetyl-1,2-isopropylidene-α-D-xylofuranose (**19**), or its 5-*O*-chloroacetyl analog[6] (**20**), afforded the β-(1→3)-linked disaccharides **21** or **22**, respectively, and the α-(1→3)-linked isomers **25** and **26**, respectively. The removal of



$ClCH_2CO$-5 of **22** and **26** was achieved in nearly quantitative yield, and gave **23** and **27**, respectively. Only the β-linked disaccharide **23** was further transformed into 3-*O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-D-xylose (**28**) by hydrolysis of the 1,2-acetal group, and acetylation gave the β-(1→3)-linked D-xylobiose hexaacetate (**5**) in high yield. From the 5-*O*-acetyl substituted disaccharides **21** and **25**, only the former was further transformed into **24** by deacetylation with triethylamine–methanol. Removal of the isopropylidene group by acid hydrolysis gave **29** which, on acetylation, gave **5**.

For the application of acetyl group resonances of ^{1}H-n.m.r. spectra for specific structural assignments of hexa-*O*-acetyl-D-xylobioses*, acetylation of 3-*O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-D-xylopyranose (**28**) with ($^2H_6$)acetic anhydride gave a peracetylated disaccharide having deuterated acetyl groups in the reducing residue. Isolation of the crystalline, deuterated disaccharide **5**, 1,2,4-tri-*O*-($^2H_9$-1,2,4)acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-β-D-xylopyranose and comparison of its ^{1}H-n.m.r. spectrum with that of **5** in ($^2H_6$)benzene allowed to differentiate between the two sets of methyl proton resonances in the reducing residue (δ 1.785, 1.705, and 1.667 relative to the signal of Me_4Si) and in the non-reducing group (δ 1.816, 1.741, and 1.621).

EXPERIMENTAL

General methods. — Melting points were determined with a Büchi–Tottoli apparatus and are not corrected. Optical rotations were measured at room temperature with a "Quick" Roussel–Jouan polarimeter for chloroform solutions in a 2-

*For a preliminary report on hexa-*O*-acetyl-β-(1→4)-D-xylobiose, see ref. 25.

cm cell. T.l.c. was performed on silica gel-coated glass-plates (Merck, Darmstadt, Germany, ref. 5721) with 1:1 (v/v) ethyl acetate–hexane, and detection with 9:9:2 (v/v) sulfuric acid–methanol–water at 120°. Column chromatography was carried out on silica gel (Merck Kieselgel 60, mesh 0.063–0.200, ref. 7734). ^{1}H-N.m.r. spectra were recorded with a Cameca spectrometer at 250 MHz, and ^{13}C-n.m.r. spectra at 62.86 MHz, with (^{2}H)chloroform as solvent and tetramethylsilane as the internal standard. Elemental analyses were performed by the Service Central de Microanalyses du C.N.R.S. (France).

*Glycosylation. — (a). With 2,3,4-tri-*O*-acetyl-α-*D*-xylopyranosyl bromide* (**13**). To a solution of monohydroxyl compound (3.46 mmol) in dry acetonitrile (10 mL) were added mercury cyanide (1 g) and mercury bromide (30 mg). The mixture was stirred at room temperature for 10 min. 2,3,4-Tri-*O*-acetyl-α-D-xylopyranosyl bromide[26] (4.7 mmol) was added in two parts at a 3 h-interval, and the solution stirred overnight at room temperature. The mixture was diluted with chloroform (50 mL) and stirred for 10 min, and the suspension filtered. The filtrate was washed successively with a saturated solution of potassium bromide (2 × 150 mL), and then distilled water (150 mL). The aqueous phases were extracted each time with chloroform (50 mL), and all the organic solutions were combined and dried (sodium sulfate). Solvents were evaporated and the residue was dissolved in dry benzene (20 mL). Dry pyridine (0.3 mL) and acetic anhydride (0.2 mL) were added for acetylation of the 2,3,4-tri-*O*-acetyl-D-xylopyranose formed during glycosylation or washing. The mixture was stirred at room temperature and the reaction monitored by t.l.c. (R_F 0.20 for D-xylose triacetate, as compared with R_F 0.41 for tetraacetate) until completion (3 h). The solvents were evaporated under diminished pressure, and toluene was added and evaporated to remove pyridine. A solution of the residual syrup in chloroform was treated with charcoal, and then evaporated. T.l.c. showed the presence of two major products ($0.28 < R_F < 0.38$) and minor products (R_F 0.39, 0.41, and 0.47). The syrup (1.8–2.3 g) was dissolved in toluene and transferred onto a column of silica gel (100 g). Elution with 3:1 (v/v) toluene–ethyl acetate afforded successively side-reaction products, pure fractions of α-linked disaccharide, a mixture of α- and β-linked disaccharides, and pure β-linked disaccharide. The mixture fraction was rechromatographed, and the yields were calculated on the basis of pure disaccharides obtained.

*(b). With 2,4-di-*O*-acetyl-3-*O*-chloroacetyl-* (**14**) *or 2,3-di-*O*-acetyl-4-*O*-chloroacetyl-α-*D*-xylopyranosyl bromide* (**15**). — To a solution of **14** or **15** (2.75 mmol) in dry acetonitrile (7 mL) were added, at the same time and at room temperature, mercury cyanide (750 mg), mercury bromide (30 mg), and tri-*O*-acetyl-β-D-xylopyranose (**17** or **18**) (5.5 mmol). The mixture was stirred overnight at room temperature, and the products were isolated and separated in the manner described for (*a*), except that the step of mild acetylation after glycosylation was not performed before chromatographic purification. Yields were calculated from pure fractions of α- and β-linked disaccharides.

*1,3,4-Tri-*O*-acetyl-2-*O*-[2,3,4-tri-*O*-acetyl-α-* (**1**) *and β-*D*-xylopyranosyl]-β-*D*-*

xylopyranose (**2**). — The total yield of **1** and **2** was 57% (1.054 g), and the ratio of β to α anomer 1.9:1.

Compound **1**. Yield 0.362 g (19.6%), m.p. 178° (ethyl ether), $[\alpha]_D^{20}$ +94° (*c* 1, chloroform); t.l.c. R_F 0.33.

Anal. Calc. for $C_{22}H_{30}O_{15}$: C, 49.44; H, 5.66. Found: C, 49.36; H, 5.75.

Compound **2**. To a solution of chromatographically pure **2** (0.692 g, yield 37.4%) in methanol (20 mL) was added drops of water until turbid. After a few weeks, a crystalline solid appeared. Recrystallization from methanol gave **2**, m.p. 100°, $[\alpha]_D^{20}$ −16° (*c* 0.5, chloroform); t.l.c. R_F 0.30.

Anal. Calc. for $C_{22}H_{30}O_{15}$: C, 49.44; H, 5.66. Found: C, 49.38; H, 5.63.

*1,2,4-Tri-*O*-acetyl-3-*O*-[2,3,4-tri-*O*-acetyl-α-* (**3**) *and -β-*D*-xylopyranosyl]-β-*D*-xylopyranose* (**5**). — The pure disaccharides **3** and **5** were isolated in a total yield of 1.128 g (61%), and the ratio of β to α anomer was 1.6:1.

Compound **3**. Yield 0.434 g (23.5%), m.p. 171° (ethyl ether), $[\alpha]_D^{20}$ +67° (*c* 1, chloroform); t.l.c. R_F 0.31.

Anal. Calc. for $C_{22}H_{30}O_{15}$: C, 49.44; H, 5.66. Found: C, 49.42; H, 5.67.

Compound **5**. Yield 0.694 g (37.5%), m.p. 105–106° (ethyl ether or chloroform–hexane), $[\alpha]_D^{20}$ −56° (*c* 1, chloroform); t.l.c. R_F 0.28.

Anal. Calc. for $C_{22}H_{30}O_{15}$: C, 49.44; H, 5.66. Found: C, 49.38; H, 5.60.

*1,2,4-Tri-*O*-acetyl-3-*O*-[2,4-di-*O*-acetyl-3-*O*-chloroacetyl-α-* (**4**) *and -β-*D*-xylopyranosyl]-β-*D*-xylopyranose* (**6**) *(glycosylation b).* — The total yield **4** and **6** was 60% (0.939 g), and the ratio of β to α anomer 2.7:1. Several minor fractions containing two disaccharides were observed; one of these was identified as **7**, and the second is probably the α-linked analog (total weight 0.150 g).

Compound **4**. Yield 16.2%, m.p. 173° (ethyl ether), $[\alpha]_D^{20}$ +66° (*c* 1, chloroform); t.l.c. R_F 0.36.

Anal. Calc. for $C_{22}H_{29}ClO_{15}$: C, 46.45; H, 5.14; Cl, 6.23. Found: C, 46.42; H, 5.18; Cl, 6.28.

Compound **6**. Yield 43.8%, m.p. 132° (ethyl ether), $[\alpha]_D^{20}$ −54° (*c* 1, chloroform); t.l.c. R_F 0.31.

Anal. Calc. for $C_{22}H_{29}ClO_{15}$: C, 46.45; H, 5.14; Cl, 6.23. Found: C, 46.48; H, 5.09; Cl, 6.32.

*1,2,4-Tri-*O*-acetyl-3-*O*-(2,4-di-*O*-acetyl-β-*D*-xylopyranosyl)-β-*D*-xylopyranose* (**7**). — A solution of **6** (0.15 g) in 20:10:3 (v/v) 1,2 dichloroethane–methanol–pyridine (10 mL) was heated to 50°. After three days, the reaction was complete (t.l.c. R_F 0.16, no side products), and the solvents were evaporated, and toluene was added and evaporated to remove pyridine. A solution of the residual syrup in chloroform was washed with water, dried, treated with charcoal, filtered, and evaporated, to give **7** (90% yield), m.p. 142.5° (ethyl ether–hexane), $[\alpha]_D^{20}$ −57° (*c* 1, chloroform).

Anal. Calc. for $C_{20}H_{28}O_{14}$: C, 48.78; H, 5.73. Found: C, 48.82; H, 5.72.

*1,2,3-Tri-*O*-acetyl-4-*O*-[2,3-di-*O*-acetyl-4-*O*-chloroacetyl-α-* (**9**) *and -β-*D-

xylopyranosyl]-β-D-*xylopyranose* (**11**) *(glycosylation b).* — Crude **9** and **11** were obtained in 70% overall yield; the ratio of β to α anomer was 2.2:1.

Compound **9**. Yield 22%, m.p. 146° (ethyl ether), $[\alpha]_D^{20}$ +36° (*c* 1, chloroform); R_F 0.42.

Anal. Calc. for $C_{22}H_{29}ClO_{15}$: C, 46.45; H, 5.14; Cl, 6.23. Found: C, 46.44; H, 5.12; Cl, 6.30.

Compound **11**. Yield 48%, m.p. 137° (ethyl ether), $[\alpha]_D^{20}$ −60° (*c* 1, chloroform); R_F 0.38.

Anal. Calc. for $C_{22}H_{29}ClO_{15}$: C, 46.45; H, 5.14; Cl, 6.23. Found: C, 46.48; H, 5.10; Cl, 6.35.

1,2,3-Tri-O-*acetyl-4*-O-*(2,3-di*-O-*acetyl*-β-D-*xylopyranosyl)*-β-D-*xylopyranose* (**12**). — Hydrolysis of the chloroacetyl group of **11** was performed for 48 h as described for **7**, t.l.c. showing one spot (R_F 0.14), yield 85–90%, m.p. 181° (ethyl ether), $[\alpha]_D^{20}$ −54° (*c* 1, chloroform).

Anal. Calc. for $C_{20}H_{28}O_{14}$: C, 48.78; H, 5.73. Found: C, 48.86; H, 5.70.

2,4-Di-O-*acetyl-3*-O-*chloroacetyl*-α-D-*xylopyranosyl bromide* (**14**). — This compound was prepared from 1,2,4-tri-*O*-acetyl-3-*O*-chloroacetyl-β-D-xylopyranose[2] in the same manner as that described for bromide[3] **15**, m.p. 77–78° (ethyl ether), $[\alpha]_D^{20}$ +190° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 2.08, 2.12 (OAc), 3.90 (t, $J_{4,5b} = J_{5a,5b}$ 11.25 Hz, H-5b), 4.03 (s, CH_2Cl), 4.09 (dd, $J_{4,5a}$ 6.0 Hz, H-5a), 4.84 (dd, $J_{1,2}$ 4.0, $J_{2,3} = J_{3,4}$ 9.75 Hz, H-2), 5.10 (m, H-4), 5.61 (t, H-3), and 6.19 (d, H-1); ^{13}C-n.m.r. ($CDCl_3$): δ 20.564 ($OCOCH_3$), 40.362 ($ClCH_2$), 62.508 (C-5), 67.814 (C-4), 70.621 (C-2), 71.539 (C-3), and 87.306 (C-1).

Anal. Calc. for $C_{11}H_{14}BrClO_7$: C, 35.37; H, 3.78; Br, 21.39; Cl, 9.49. Found: C, 35.48; H, 3.90; Br, 20.62; Cl, 9.58.

5-O-*Acetyl-1,2*-O-*isopropylidene*-α-D-*xylofuranose* (**19**). — This compound was prepared by the method of Levene and Raymond[27]; ^{13}C-n.m.r. ($CDCl_3$): δ 20.189 ($COCH_3$), 26.117 and 26.789 [$C(CH_3)_2$], 61.640 (C-5), 74.601, 78.377, 85.163 (C-2,3,4), 104.809 (C-1), and 111.850 [$C(CH_3)_2$].

5-O-*Chloroacetyl-1,2*-O-*isopropylidene*-α-D-*xylofuranose* (**20**). — This compound has been obtained previously[6]; ^{13}C-n.m.r. ($CDCl_3$): δ 26.232 and 26.840 [$HC(CH_3)_2$], 40.778 ($ClCH_2$), 63.541 (C-5), 74.922, 78.148, 85.391 (C-2,3,4), 104.989 (C-1), 112.171 [$C(CH_3)_2$], and 167.983 ($ClCH_2CO$).

5-O-*Acetyl-1,2*-O-*isopropylidene-3*-O-[*2,3,4-tri*-O-*acetyl*-α- (**25**) *and* -β-D-*xylopyranosyl*]-α-D-*xylofuranose* (**21**). — Total yield 62%; the ratio of β to α anomer was 1.94:1.

Compound **25**. M.p. 113° (ethyl ether–hexane), $[\alpha]_D^{20}$ +67° (*c* 1.04, chloroform); R_F 0.41; ^{1}H-n.m.r. ($CDCl_3$): δ 1.32 and 1.49 (CMe_2), 2.01–2.08 (OAc), 3.63 (t, $J_{4',5'} = J_{5'a,5'b}$ 10.75 Hz, H-5'b), 3.90 (q, $J_{4',5'a}$ 6.0 Hz, H-5'a), 4.13 (d, $J_{3,4}$ 2.5 Hz, H-3), 4.21 (q, $J_{4,5b}$ 4.75, $J_{5a,5b}$ 10.25 Hz, H-5b), 4.35 (q, $J_{4,5a}$ 6.75 Hz, H-5a), 4.40 (m, H-4), 4.63 (d, $J_{1,2}$ 3.75 Hz, H-2), 4.85 (q, $J_{2',3'}$ 10.25, $J_{1',2'}$ 3.75 Hz, H-2'), 4.98 (m, $J_{3',4'}$ 10.25 Hz, H-4'), 5.07 (d, H-1'), 5.41 (t, H-3'), and 5.99 (d, H-1); ^{13}C-n.m.r. ($CDCl_3$): δ 20.682 ($COCH_3$), 26.338 and 26.847 [$C(CH_3)_2$], 59.229 (C-

5'), 61.584 (C-5), 69.182 (C-4',3'), 70.662 (C-2'), 77.920 (C-4), 82.872 (C-3), 83.649 (C-2), 97.947 (C-1'), 105.156 (C-1), and 112.220 [$C(CH_3)_2$].

Anal. Calc. for $C_{21}H_{30}O_{13}$: C, 51.43; H, 6.17. Found: C, 51.56; H, 6.15.

Compound **21**. Syrup, $[\alpha]_D^{20}$ −44° (*c* 1, chloroform); R_F 0.34; ^{1}H-n.m.r. data ($CDCl_3$): δ 1.32 and 1.49 (CMe_2), 2.05–2.09 (OAc), 3.45 (q, $J_{4',5'b}$ 7.25, $J_{5'a,5'b}$ 12.0 Hz, H-5'b), 4.11 (q, $J_{4',5'a}$ 4.5 Hz), 4.22 (q, $J_{4,5b}$ 7.5, $J_{5a,5b}$ 11.75 Hz, H-5b), 4.31 (d, $J_{3,4}$ 3.50 Hz, H-3), 4.35 (q, $J_{4,5a}$ 7.5 Hz, H-5a), 4.44 (m, H-4), 4.50 (d, $J_{1,2}$ 3.75 Hz, H-2), 4.69 (d, $J_{1',2'}$ 5.5 Hz, H-1'), 4.81 (q, $J_{2',3'} = J_{3',4'}$ 7.25 Hz, H-2'), 4.89 (m, H-4'), 5.11 (t, H-3'), and 5.90 (d, H-1); ^{13}C-n.m.r. data ($CDCl_3$): δ 20.706 ($COCH_3$), 26.313 and 26.847 [$C(CH_3)_2$], 61.317 (C-5'), 62.409 (C-5), 68.089 (C-4'), 69.861 (C-2'), 70.031 (C-3'), 77.750 (C-4), 79.814 (C-3), 82.557 (C-2), 97.849 (C-1'), 105.180 (C-1), and 112.171 [$C(CH_3)_2$].

Anal. Calc. for $C_{21}H_{30}O_{13}$: C, 51.43; H, 6.17. Found: C, 51.36; H, 6.15.

5-O-Chloroacetyl-1,2-O-isopropylidene-3-O-[2,3,4-tri-O-acetyl-α- (**26**) *and -β-*D*-xylopyranosyl]-α-*D*-xylofuranose* (**22**). — Total yield 58%; the ratio of β to α anomer was 3.2:1.

Compound **26**. Yield 13.8%, syrup, $[\alpha]_D^{20}$ +34° (*c* 1, chloroform); t.l.c. R_F 0.44; ^{1}H-n.m.r. ($CDCl_3$): δ 1.32 and 1.49 (CMe_2), 2.05, 2.06, 2.10 (OAc), 3.80 (t, $J_{5'a,5'b}$ 10.75, $J_{4',5'b}$ 10.75 Hz, H-5'b), 3.90 (q, $J_{4',5'a}$ 6.0 Hz, H-5'a), 4.10 (s, CH_2Cl), 4.15 (d, $J_{3,4}$ 2.50 Hz, H-3), 4.33 (q, $J_{4,5b}$ 4.0, $J_{5a,5b}$ 10.0 Hz, H-5b), 4.41 (m, H-4), 4.46 (q. $J_{4,5a}$ 6.25 Hz, H-5a), 4.63 (d, $J_{2,3}$ ~0, $J_{1,2}$ 3.50 Hz, H-2), 4.84 (q, $J_{2',3'}$ 10.0 Hz, H-2'), 4.97 (m, $J_{3',4'}$ 10.0 Hz, H-4'), 5.10 (d, $J_{1',2'}$ 3.75 Hz, H-1'), 5.40 (t, H-3'), and 6.00 (d, $J_{1,2}$ 3.50 Hz, H-1); ^{13}C-n.m.r. ($CDCl_3$): δ 19.225 ($COCH_3$), 26.313 and 26.823 [$C(CH_3)_2$], 40.684 ($ClCH_2$), 59.253 (C-5'), 63.307 (C-5), 69.084 (C-4'), 69.182 (C-3'), 70.687 (C-2'), 77.605 (C-4), 83.018 (C-3), 83.552 (C-2), 98.019 (C-1'), 105.180 (C-1), and 112.317 [$C(CH_3)_2$].

Anal. Calc. for $C_{21}H_{29}ClO_{13}$: C, 48.05; H, 5.57; Cl, 6.75. Found: C, 48.10; H, 5.74; Cl, 6.60.

Compound **22**. This compound was isolated either by chromatographic separation (yield 44.2%) or by direct crystallization from ethyl ether (25–30% overall yield), and recrystallized from ethyl ether or chloroform–hexane, m.p. 97°, $[\alpha]_D^{20}$ −57° (*c* 1, chloroform); t.l.c. R_F 0.36; ^{1}H-n.m.r. data ($CDCl_3$): δ 1.32 and 1.49 (CMe_2), 2.08 (OAc), 3.43 (q, $J_{5'a,5'b}$ 12.0, $J_{4',5'b}$ 7.5 Hz, H-5'b), 4.11 (q, $J_{4',5'a}$ 4.5 Hz, H-5'a), 4.12 (s, $ClCH_2$), 4.33 (d, $J_{2,3}$ ~0, $J_{3,4}$ 3.25 Hz, H-3), 4.34 (q, $J_{4,5b}$ 8.50, $J_{5a,5b}$ 12.50 Hz, H-5b), 4.49 (d, $J_{4,5a}$ 7.50 Hz, H-5a), 4.49 (m, H-4), 4.51 (d, $J_{1,2}$ 3.75 Hz, H-2), 4.69 (d, $J_{1',2'}$ 5.75 Hz, H-1'), 4.83 (q, $J_{2',3'}$ 7.5 Hz, H-2'), 4.91 (m, $J_{3',4'}$ 7.5 Hz, H-4'), 5.14 (t, H-3'), and 5.90 (d, H-1); ^{13}C-n.m.r. ($CDCl_3$): δ 20.705 ($COCH_3$), 26.338 and 26.896 [$C(CH_3)_2$], 40.781 ($ClCH_2$), 61.705 (C-5'), 63.938 (C-5), 68.235 (C-4'), 70.128 (C-2'), 70.420 (C-3'), 77.459 (C-4), 80.008 (C-3), 82.702 (C-2), 98.236 (C-1'), 105.229 (C-1), and 112.390 [$C(CH_3)_2$].

Anal. Calc. for $C_{21}H_{29}ClO_{13}$: C, 48.05; H, 5.57; Cl, 6.75. Found: C, 48.22; H, 5.52; Cl, 6.90.

1,2-O-Isopropylidene-3-O-[2,3,4-tri-O-acetyl-α- (**27**) *and -β-*D*-xylopyrano-*

syl]-α-D-*xylofuranose* (**23**). — The chloroacetyl group of **22** or **26** was labile when a solution of the product (0.15 g, 10 mL) in 20:10:3 (v/v) 1,2-dichloroethane–methanol–pyridine was heated for several days at +50°. For **22**, the reaction was completed (t.l.c.) within 3 days and gave pure **23** in nearly quantitative yield. For **27**, one week was necessary to complete the reaction. The solvents were evaporated, and toluene was added and evaporated to remove pyridine. A solution of the residual syrup in chloroform was washed with water, dried, and treated with charcoal, and the suspension was filtered and evaporated.

Compound **27**. Yield 90–95%, m.p. 139° (ethyl ether–hexane), $[\alpha]_D^{20}$ +78° (*c* 1, chloroform); t.l.c. R_F 0.19; ^{1}H-n.m.r. data ($CDCl_3$): δ 1.33 and 1.49 (CMe_2), 2.02, 2.03, 2.08 (OAc), 3.64 (t, $J_{4',5'b} = J_{5'a,5'b}$ 10.75 Hz, H-5'b), 3.82 (q, $J_{4,5b}$ 6.5, $J_{5a,5b}$ 11.5 Hz, H-5b), 3.90 (q, $J_{4',5'a}$ 5.75 Hz, H-5'a), 3.94 (q, $J_{4,5a}$ 4.5 Hz, H-5a), 4.18 (d, $J_{2,3}$ ~0, $J_{3,4}$ 3.5 Hz), 4.35 (m, H-4), 4.67 (d, $J_{1,2}$ 3.75 Hz, H-2), 4.89 (q, $J_{2',3'}$ 10, $J_{1',2'}$ 3.75 Hz, H-2'), 5.00 (m, $J_{3',4'}$ 10.0 Hz, H-4'), 5.16 (d, H-1'), 5.43 (t, H-3'), and 5.99 (d, H-1); ^{13}C-n.m.r. data ($CDCl_3$): δ 20.657 ($COCH_3$), 26.362 and 26.799 [$C(CH_3)_2$], 59.181 (C-5'), 59.836 (C-5), 69.036 (C-4'), 69.279 (C-3'), 70.735 (C-2'), 80.129 (C-4), 83.285 (C-3), 83.673 (C-2), 97.704 (C-1'), 105.010 (C-1), and 112.234 [$C(CH_3)_2$].

Anal. Calc. for $C_{19}H_{28}O_{12}$: C, 50.89; H, 6.29. Found: C, 50.92; H, 6.36.

Compound **23**. Yield 85%, m.p. 179° (ethyl ether–hexane), $[\alpha]_D^{20}$ −44° (*c* 1, chloroform); R_F 0.16; ^{1}H-n.m.r. ($CDCl_3$): δ 1.33 and 1.49 (CMe_2), 2.05–2.08 (OAc), 3.42 (q, $J_{4',5'b}$ 8.5, $J_{5'a,5'b}$ 12.0 Hz, H-5'b), 3.83 (dd, $J_{5a,5b}$ ~0, $J_{4,5a}$ 5.0, H-5a, $J_{4,5b}$ 5.0 Hz, H-5b), 4.15 (q, $J_{4',5'a}$ 5.0 Hz, H-5'a), 4.31 (d, $J_{3,4}$ 3.75 Hz, H-3), 4.32 (m, H-4), 4.45 (d, $J_{1,2}$ 3.75 Hz, H-2), 4.66 (d, $J_{1',2'}$ 6.5 Hz, H-1'), 4.85 (q, $J_{2',3'}$ 8.0 Hz, H-2'), 4.93 (m, $J_{3',4'}$ 8.0 Hz, H-4'), 5.16 (t, H-3'), 5.89 (d, H-1); ^{13}C-n.m.r. ($CDCl_3$): δ 20.657 ($COCH_3$), 26.386 and 26.847 [$C(CH_3)_2$], 59.909 (C-5), 61.924 (C-5'), 68.162 (C-4'), 70.332 (C-2'), 70.687 (C-3'), 79.644 (C-4), 81.149 (C-3), 83.212 (C-2), 99.039 (C-1'), 105.010 (C-1), and 112.171 [$C(CH_3)_2$].

Anal. Calc. for $C_{19}H_{28}O_{12}$: C, 50.89; H, 6.29. Found: C, 50.98; H, 6.40.

*1,2-O-Isopropylidene-3-O-β-*D-*xylopyranosyl-α-*D-*xylopyranose* (**24**). — A solution (3 mL) of **21** or **22** (180 mg) in 1:9 (v/v) triethylamine–methanol was heated for 3 days at 40° (the reaction was complete according to t.l.c.). The solvents were evaporated, and a solution of the residue in methanol was treated with charcoal, filtered, and evaporated to give a nearly quantitative yield of **24**, syrup, $[\alpha]_D^{20}$ −30° (*c* 1, methanol); R_F (9:1, v/v, ethyl acetate–95% ethanol) 0.20; ^{13}C-n.m.r. ($CDCl_3$): δ 26.459 and 26.847 [$C(CH_3)$], 59.860 (C-5), 65.832 (C-5'), 69.691, 72.556, 76.270 (C-2',3',4'), 79.935, 80.445, 83.431 (C-2,3,4), 101.952 (C-1'), 105.107 (C-1), and 112.113 [$C(CH_3)_2$].

Anal. Calc. for $C_{13}H_{22}O_9$: C, 48.44; H, 6.88. Found: C, 48.52; H, 6.72.

*3-O-β-*D-*Xylopyranosyl-*D-*xylopyranose* (**29**). — A solution of **24** (700 mg) in 9:1 (v/v) trifluoroacetic acid–water (7 mL) was stirred for 20 min at room temperature. The solvents were evaporated after addition of toluene and ethyl acetate to give **29** in quantitative yield, pure according to t.l.c. [R_F (ethyl acetate) 0.85]. Con-

ventional acetylation of **29** with sodium acetate and acetic anhydride gave **5** in nearly quantitative yield.

3-O-(2,3,4-Tri-O-acetyl-β-D-xylopyranosyl)-D-xylopyranose (**28**). — A solution of **23** in trifluoroacetic acid–water was treated in the same way as described for **24** to give syrupy **28**, pure according to t.l.c. Conventional acetylation of **28** gave **5** in nearly quantitative yield; ^{1}H-n.m.r. data ($CDCl_3$): δ 3.25–4.19 (H-3,4,5,4′,5′), 4.54 (d, $J^{\beta}_{1,2}$ 6.87 Hz, H-1β), 4.634 (d, $J^{\alpha}_{1',2'}$ 7.70 Hz, H-1′α), 4.66 (d, $J^{\beta}_{1',2'}$ 7.70 Hz, H-1′β), 4.96–5.02 (2 dd, H-2′β,2′α), 5.15 (d, $J^{\alpha}_{1,2}$ 3.16 Hz, H-1α), 5.25 (2 t, $J^{\alpha}_{2',3'} = J^{\beta}_{2',3'}$ 9.35 Hz, H-3′α,β).

Acetylation of **28** *with* ($^2H_6$)*acetic anhydride*. — To a solution of syrupy **28** (10 mg) in dry pyridine (1 mL) was added 1.2 time the stoichiometric quantity of ($^2H_6$)acetic anhydride. The mixture was kept for one day at 50°, and the solvent was coevaporated with distilled toluene. The solution of the residue in chloroform was washed with water, dried, and stirred and stored with charcoal. The suspension was filtered, and the filtrate evaporated. The residue crystallized from ethyl ether. The ^{1}H-n.m.r. spectrum of the product showed features for the cyclic protons identical with those of **5**.

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