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Synthesis of 2- and 4-nitrophenyl β-glycosides of β-(1 → 4)-D-xylo-oligosaccharides of dp 2–4

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Abstract

2- and 4-Nitrophenyl β-D-xylopyranosides (**4** and **5**) were transformed, via dibutyltin oxide-mediated acylation, into the corresponding 2,3-di-*O*-benzoyl derivatives **11** and **15**. Xylobiose and xylotriose were easily isolated by charcoal column chromatography from a commercially available material and converted into the di- and trisaccharide methyl 1-thio-β-glycosides **36** and **37**. The 2- and 4-nitrophenyl β-glycosides of the β-(1 → 4)-D-xylo-oligosaccharides of dp 2–4 were synthesized by *N*-iodosuccinimide–silver triflate-promoted condensation using **11** and **15** as the glycosyl acceptors and ethyl 1-thio-β-D-xylopyranoside triacetate **16**, **36**, and **37** as the glycosyl donors. Also described are an improved preparation of **4** and **5**, and the synthesis of 1-naphthyl β-D-xylopyranoside, as well as an alternative approach to the 2- and 4-nitrophenyl β-xylobiosides.

Keywords: Glycoside; β-(1 → 4)-D-Xylo-oligosaccharides, 2- and 4-Nitrophenyl glycosides; Xylanase; Chromogenic substrate

1. Introduction

A specific chromogenic substrate that is cleaved exclusively at the aglycon chromogenic site by the action of an enzyme is useful for the evaluation of the catalytic activity of the enzyme. As for chromogenic substrates of xylanases, 2-nitrophenyl 4-thio-β-xylobioside [1] and 4-nitrophenyl β-xylobioside (**31**) [2] were recently prepared and shown to be valuable for kinetic studies of several xylanases, but the details of the synthesis of **31**, as well as its physical properties, were not reported. We now report the

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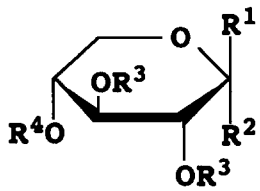
synthesis of 2- and 4-nitrophenyl β-glycosides of the series of β-(1 → 4)-D-xylo-oligosaccharides from xylobiose (**19**) to xylotetraose, namely 2-nitrophenyl β-xylobioside (**29**), **31**, 2- (**42**) and 4-nitrophenyl β-xylotrioside (**43**), and 2- (**48**) and 4-nitrophenyl β-xylotetraoside (**49**). Also described are an improved synthesis of 2- (**4**) and 4-nitrophenyl β-D-xylopyranoside (**5**), as well as the preparation of 1-naphthyl β-D-xylopyranoside (**7**) that may serve as the reagent for assay of the activity of β-xylosidases, as a reddish violet color is developed by the reaction of a diazonium salt [3] with the 1-naphthol liberated from **7** by the action of the enzyme. After this work had been completed, the synthesis of **29** and **31** by a method different from that described herein has been reported [4].

2. Results and discussion

The synthetic methods employed here for the preparation of **29, 31, 42, 43, 48**, and **49** were based on (*a*) the synthesis of suitably protected 2- (**11**) and 4-nitrophenyl β-D-xylopyranoside (**15**) derivatives, both having 4-OH unsubstituted, to be used as the glycosyl acceptors, (*b*) isolation of **19** and xylotriose (**20**) from a commercially obtainable material, conversion of **19** into the corresponding disaccharide α-bromide **26**, and transformation of **19** and **20** into methyl 1-thio-β-xylobioside pentaacetate (**36**) and methyl 1-thio-β-xylotrioside heptaacetate (**37**), as the glycosyl donors, (*c*) condensation of **11** or **15** with each of the mono- to tri-saccharide glycosyl donors, ethyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranoside [5] (**16**), **36**, and **37**, using a combination of *N*-iodosuccinimide (NIS) and silver triflate as a thiophilic activator [6] for all the glycosylation reactions, and (*d*) an alternative route to **29** and **31** by coupling of **26** with 2- or 4-nitrophenol. The following steps were performed.

The nitrophenyl β-D-xylopyranosides **4** and **5** are well known and even commercially available. However, the previous reported syntheses of **2** and **3**, which led to **4** and **5** after *O*-deacetylation, involved condensation of 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide (**1**) with the nitrophenols either in the presence of sodium hydroxide in aqueous acetone [7] or in the presence of methanolic potassium hydroxide in acetone [8], and gave **2** and **3** in low to moderate yields (21–41%). Therefore, the practical synthesis of **2** and **3** was first examined, and this could be achieved by adaptation of the reaction conditions reported by Comtat et al. [1] for the preparation of aryl 4-thioxylobioside and 1,4-dithioxylobiosides. Thus, the reaction of **1** with 2- or 4-nitrophenol in acetone in the presence of potassium carbonate [1] gave **2** and **3** in 65 and 69% yields, respectively. *O*-Deacetylation of **2** and **3** with methanolic sodium methoxide provided **4** and **5**, respectively. Condensation of **1** with 1-naphthol, as above, afforded 58% of 1-naphthyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (**6**), which was *O*-deacetylated to provide crystalline **7**.

Regioselective chloroacetylation of **4** via the dibutylstannylene derivative [9,10] proceeded smoothly to give the 4-*O*-chloroacetyl derivative **8** (70%). Acetylation of **8** with acetyl chloride–pyridine in dichloromethane afforded the 2,3-di-*O*-acetyl-4-*O*-chloroacetyl derivative **9**, the ^{1}H NMR spectrum of which proved [10–12] the position of the chloroacetyl group in **8**. In a similar way, compound **5** was selectively chloroacetylated



	R1	R2	R3	R4		R1	R2	R3	R4
1	H	Br	Ac	Ac	**9**	O-2-NP	H	Ac	CA
2	O-2-NP	H	Ac	Ac	**10**	O-2-NP	H	Bz	CA
3	O-4-NP	H	Ac	Ac	**11**	O-2-NP	H	Bz	H
4	O-2-NP	H	H	H	**12**	O-4-NP	H	H	CA
5	O-4-NP	H	H	H	**13**	O-4-NP	H	Ac	CA
6	O-1-NA	H	Ac	Ac	**14**	O-4-NP	H	Bz	CA
7	O-1-NA	H	H	H	**15**	O-4-NP	H	Bz	H
8	O-2-NP	H	H	CA	**16**	EtS	H	Ac	Ac

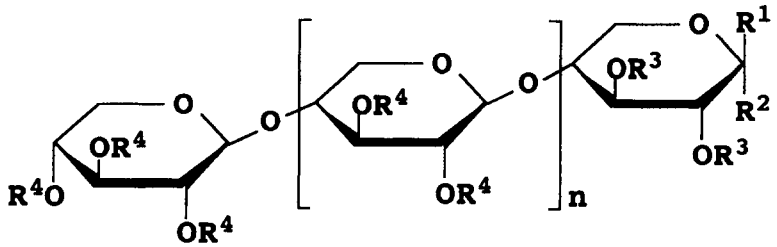
NP: Nitrophenyl; NA: Naphthyl; CA: $ClCH_2CO$

at the 4-position by treatment with dibutyltin oxide, followed by chloroacetyl chloride, giving the 4-*O*-chloroacetyl derivative **12** (73%). Acetylation of **12**, as for **8**, afforded **13**, whose identity was confirmed by ^1H NMR spectroscopy. These results are in sharp contrast to the previous observation that a similar reaction for **4** and **5** resulted in the formation of significant amounts of diacylated products along with unreacted starting material [4]. Benzoylation of **8** with benzoyl chloride–pyridine in dichloromethane afforded the 2,3-di-*O*-benzoyl-4-*O*-chloroacetyl derivative **10** (92%), which was *O*-dechloroacetylated with thiourea [13] to provide the 2,3-di-*O*-benzoyl derivative **11**. Likewise, compound **12** was transformed into **15** by a reaction sequence (→ **14** → **15**) analogous to that described above.

Condensation of **11** with **16** gave the disaccharide glycoside **17** (80%), which was *O*-deacylated to furnish crystalline **29** [4]. Acetylation of **29** afforded the crystalline pentaacetate **30**, the ^1H NMR of which agreed with that reported [4], but with different mp {113°C; cf. 188°C [4]}. Similarly, compound **15** was coupled with **16** to give **18** (82%), *O*-deacylation of which afforded crystalline **31** [4], which was further characterized as the crystalline pentaacetate **32** [4]. Compound **31** had previously been obtained [4] as a foam.

A mixture of β-(1 → 4)-D-xylo-oligosaccharides [1] [14] appeared to us an attractive

[1] Available commercially from Waco Pure Chem. Ind., Ltd. (tradename; Xylo-oligosaccharides, code 242-00641). According to the manufacturer (Suntory Ltd.), the product contains H_2O (2.6%), D-xylose (2.8%), other monosaccharides (0.3%), and **19** (60.2%), in addition to higher members of the xylo-oligosaccharides (34.0%) composed of **20** and xylotetraose as the major and minor components.



	n	R^1	R^2	R^3	R^4
17	0	O-2-NP	H	Bz	Ac
18	0	O-4-NP	H	Bz	Ac
19	0	-H,OH-		H	H
20	1	-H,OH-		H	H
21	0	OAc	H	Ac	Ac
22	1	OAc	H	Ac	Ac
23	0	H	Br	Ac	Ac
24	0	H	OBz	Bz	Bz
25	0	OBz	H	Bz	Bz
26	0	H	Br	Bz	Bz
27	0	O-2-NP	H	Bz	Bz
28	0	O-4-NP	H	Bz	Bz
29	0	O-2-NP	H	H	H
30	0	O-2-NP	H	Ac	Ac
31	0	O-4-NP	H	H	H
32	0	O-4-NP	H	Ac	Ac
33	1	H	OBz	Bz	Bz
34	1	OBz	H	Bz	Bz
35	1	H	Br	Bz	Bz
36	0	MeS	H	Ac	Ac
37	1	MeS	H	Ac	Ac
38	1	O-2-NP	H	Bz	Ac
39	1	O-4-NP	H	Bz	Ac
40	1	O-2-NP	H	Ac	Ac
41	1	O-4-NP	H	Ac	Ac
42	1	O-2-NP	H	H	H
43	1	O-4-NP	H	H	H
44	2	O-2-NP	H	Bz	Ac
45	2	O-4-NP	H	Bz	Ac
46	2	O-2-NP	H	Ac	Ac
47	2	O-4-NP	H	Ac	Ac
48	2	O-2-NP	H	H	H
49	2	O-4-NP	H	H	H

NP : Nitrophenyl

source for obtaining the substantial amounts of **19** and **20**, since the mixture is composed mainly of **19** and **20**. Indeed, when the mixture (74 g) was subjected to fractionation by chromatography on a column of charcoal, compounds **19** [15] (32.6 g) and **20** [15] (13.2 g) were isolated easily both in crystalline form. Acetylation [16] of **19** and **20** afforded the β-hexaacetate **21** [15] and β-octacetate **22** [15], respectively.

In order to obtain **30** and **32** more efficiently, attempted reaction of **21** with hydrogen

bromide in dichloromethane [17] (→ **23**), followed by condensation with 2- or 4-nitrophenol as for **1**, gave a complex mixture of the products. Altenatively, benzoylation of **19** with benzoyl chloride in pyridine gave a mixture from which the α- (**24**) and β-hexabenzoate **25** were isolated by column chromatography in 42 and 51% yields, respectively. Treatment of **24** or **25** with hydrogen bromide in acetic acid–1,2-dichloroethane gave the corresponding disaccharide α-bromide **26** (86%) in crystalline form. Condensation of **26** with 2- or 4-nitrophenol, as for **1**, afforded the disaccharide glycosides **27** (65%) and **28** (68%), which were *O*-debenzoylated to provide **29** and **31**, respectively. The physical properties of **29** and **31** were in good agreement with those of the compounds obtained by the reaction of **16** with **11** or **15**, followed by *O*-deacetylation. Benzoylation of **20**, as for **19**, gave the α- (**33**, 41%) and β-octabenzoate **34** (49%). Attempted conversion of **33** and **34** into the corresponding trisaccharide α-bromide **35**, as for **24** and **25**, failed.

Treatment of **21** and **22** with methyl tributyltin sulfide in 1,2-dichloroethane in the presence of tin(IV) chloride [18] gave the di- (**36**, 82%) and tri-saccharide methyl 1-thio-β-glycoside **37** (78%). Glycosylation of **11** or **5** with **36** afforded the trisaccharide glycosides **38** (84%) and **39** (85%) which, upon saponification followed by acetylation (to facilitate the isolation of **42** and **43**), afforded the trisaccharide glycoside heptaacetates **40** and **41**, respectively. *O*-Deacetylation of **40** and **41** then furnished **42** and **43**, respectively. Likewise, compounds **11** and **15** were each coupled with **37** to give the tetrasaccharide glycosides **44** (73%) and **45** (78%), which were sequentially *O*-deacylated and acetylated to afford the tetrasaccharide glycoside nonaacetates **46** and **47**, respectively. *O*-Deacetylation of **46** and **47** provided **48** and **49**, respectively. Compounds **29, 31, 42, 43, 48**, and **49** were homogeneous by LC and gave ^{13}C NMR spectra consistent with the structures assigned.

3. Experimental

General methods.—Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were measured at 25°C with an Applied Electronic automatic polarimeter Model MP-1T. NMR spectra (^1H at 90 MHz, ^{13}C at 22.6 MHz) were recorded with a Hitachi R-90H spectrometer for solutions in $CDCl_3$, $(CD_3)_2CO$, and pyridine-d_5 (internal Me_4Si) or D_2O (internal sodium 4,4-dimethyl-3-trimethyl-4-silapentanoate-d_6). ^1H NMR spectra of compounds **9, 13**, and **30** were recorded with a Jeol JNM GX-270 spectrometer for solutions in $CDCl_3$ (internal Me_4Si). The assignment of the signals in the ^{13}C NMR spectra of **29, 31, 42, 43, 48**, and **49** were based on the data reported [19] for methyl β-glycosides of β-(1 → 4)-D-xylo-oligosaccharides. HPLC was performed at 30°C with a Jasco 880-PU instrument equipped with a Shodex SE-61 RI detector and a column of YMC-pack polyamine-II (250 × 4.6 mm, i.d., YMC, Kyoto) using 73:27 (v/v) MeCN–H_2O as eluent. Retention times (t_R) of **29, 31, 42, 43, 48**, and **49** are given relative to those of **4** and **5**, respectively. Organic solutions were dried over anhydrous Na_2SO_4 or $MgSO_4$. Solutions were concentrated at a temperature < 40°C under diminished pressure. TLC

was performed on Silica Gel 60 (No. 7734, E. Merck), with detection by charring with 10% H_2SO_4 in EtOH, followed by heating. Silica-gel column chromatography was performed on Waco Gel C-300 and carbon column chromatography on charcoal (60–150 mesh; No. CHR-30, Nacalai tesque, Kyoto).

*2-Nitrophenyl 2,3,4-tri-*O*-acetyl-β-*D*-xylopyranoside* (**2**).—A solution of **1** [20] (41.2 g, 0.12 mol) in dry Me_2CO (150 mL) was added dropwise during 30 min at room temperature to a stirred solution of 2-nitrophenol (28.7 g, 0.21 mol) in dry Me_2CO (700 mL) containing anhyd powdered K_2CO_3 (57.0 g, 0.41 mmol). After stirring overnight at room temperature, the insoluble material was collected on a Celite pad, washed with Me_2CO, and the combined filtrate and washings were concentrated. A solution of the residue in 2:1 EtOAc–hexane (300 mL) was filtered through a layer of silica gel, which was washed with 2:1 EtOAc–hexane (500 mL). The combined filtrate and washings were concentrated, and the residue was crystallized from 2-PrOH–EtOH to give **2** (31.4 g, 65%): mp 112.5–113.5°C; $[\alpha]_D$ – 53.7° (*c* 1.0, $CHCl_3$); lit. [8] mp 112–114°C; $[\alpha]_D$ – 52.6° (*c* 2, $CHCl_3$).

*4-Nitrophenyl 2,3,4-tri-*O*-acetyl-β-*D*-xylopyranoside* (**3**).—To a mixture of 4-nitrophenol (34.9 g, 0.25 mol) and K_2CO_3 (69.3 g, 0.5 mol) in Me_2CO (900 mL) was added a solution of **1** (50.1 g, 0.15 mol) in Me_2CO (130 mL), and the mixture was processed as just described. The resulting solid was recrystallized from 2-PrOH–EtOH to give **3** (40.5 g, 69%): mp 139.5–141°C; $[\alpha]_D$ – 72.4° (*c* 1.3, $CHCl_3$); lit. mp 142°C [7], mp 149–151°C; $[\alpha]_D$ – 73.5° (*c* 2, $CHCl_3$) [8].

*2-Nitrophenyl β-*D*-xylopyranoside* (**4**).—A solution of **2** (29.6 g) in dry MeOH (300 mL) was treated with a catalytic amount of methanolic NaOMe. The mixture was kept for 5 h at room temperature, made neutral with Amberlite IR-120 (H^+) resin, filtered, and concentrated. The residue was crystallized from EtOH to give **4** (18.6 g, 92%): mp 172–174°C; $[\alpha]_D$ – 79.0° (*c* 0.6, H_2O); lit. [8] mp 170–173°C; $[\alpha]_D$ – 78.6° (*c* 1, MeOH).

*4-Nitrophenyl β-*D*-xylopyranoside* (**5**).—*O*-Deacetylation of **3** (48.8 g) as just described afforded **5** (31.0 g, 93%): mp 141–142°C (from 2-PrOH), 160–161.5°C (from MeOH); $[\alpha]_D$ – 54.2° (*c* 0.6, H_2O); lit. mp 144°C (from H_2O) [7], mp 143°C (from EtOH), 159–161°C (from 95% EtOH), $[\alpha]_D$ – 56.0° (*c* 0.5, H_2O) [8].

*1-Naphthyl 2,3,4-tri-*O*-acetyl-β-*D*-xylopyranoside* (**6**).—A solution of **1** (5.65 g, 15.65 mmol) in Me_2CO (30 mL) was added dropwise to a mixture of 1-naphthol (4.32 g, 30 mmol) and K_2CO_3 (4.14 g, 30 mmol) in Me_2CO (70 mL) and processed as described for the preparation of **2**. Column chromatography (10:1 PhMe–EtOAc) of the residue gave **6** (3.88 g, 58%): mp 163.5–165°C (from EtOH); $[\alpha]_D$ – 100° (*c* 1.07, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.5 and 169.2 (C=O), 152.2–108.8 (Ar C), 98.6 (C-1), 70.5 (C-3), 70.0 (C-2), 68.4 (C-4), 61.8 (C-5), 20.6 ($COCH_3$). Anal. Calcd for $C_{21}H_{22}O_8$: C, 62.68; H, 5.51. Found: C, 62.75; H, 5.57.

*1-Naphthyl β-*D*-xylopyranoside* (**7**).—*O*-Deacetylation of **6** (3.13 g), as described for the preparation of **4**, gave **7** (2.0 g, 93%); mp 161–163°C (from EtOH); $[\alpha]_D$ – 66.7° (*c* 0.2, MeOH); ^{13}C NMR (pyridine-d_5): δ 153.9–110.4 (Ar C), 103.4 (C-1), 78.05 (C-3), 74.6 (C-2), 70.7 (C-4), 67.0 (C-5). Anal. Calcd for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84. Found: C, 65.31; H, 5.81.

2-Nitrophenyl 4-O-chloroacetyl-β-D-xylopyranoside (**8**).—A suspension of **4** (4.13 g, 15.2 mmol) and dibutyltin oxide (4.17 g, 16.7 mmol) in MeOH (120 mL) was boiled under reflux. After ~ 30 min, the mixture became homogeneous, and the heating was continued for a further 1.5 h, during which time the solution was concentrated to half of its original volume using a Dean–Stark condenser. The mixture was cooled to room temperature and concentrated to dryness. To a stirred solution of the residue in anhyd CH_2Cl_2 (70 mL) at 0°C was added dropwise a solution of $ClCH_2COCl$ (1.33 mL, 16.7 mmol) in CH_2Cl_2 (15 mL), and the mixture was stirred for 30 min at 0°C, and then concentrated. Column chromatography (2:1 PhMe–EtOAc) of the residue afforded **8** (3.71 g, 70%): mp 127–128°C (from $CHCl_3$–Et_2O); $[\alpha]_D$ − 114.0° (*c* 1.0, Me_2CO); NMR [$(CD_3)_2CO$]: δ_H 7.88–7.19 (m, 4 H, Ar H), 5.28 (d, 1 H, $J_{1,2}$ 6.6 Hz, H-1), 4.30 (s, 2 H, $ClCH_2CO$); δ_C 167.4 (C=O), 150.25–118.4 (Ar C), 102.4 (C-1), 74.8, 73.7, and 73.6 (C-2,3,4), 63.0 (C-5), 41.5 ($ClCH_2CO$). Anal. Calcd for $C_{13}H_{14}ClNO_8$: C, 44.91; H, 4.06; N, 4.03. Found: C, 45.03; H, 4.16; N, 3.96.

2-Nitrophenyl 2,3-di-O-acetyl-4-O-chloroacetyl-β-D-xylopyranoside (**9**).—To a stirred solution of **8** (0.35 g, 1 mmol) in CH_2Cl_2 (10 mL) containing pyridine (0.98 mL, 12.1 mmol) at 0°C was added a solution of AcCl (0.43 mL, 6 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred for 30 min at room temperature. The mixture was diluted with CH_2Cl_2, poured into ice–water, and then the organic layer was separated, washed successively with dil HCl, aq $NaHCO_3$, and H_2O, dried, and concentrated. Column chromatography (4:1 PhMe–EtOAc) of the product afforded **9** (0.38 g, 88%): mp 109.5–110.5°C (from Et_2O); $[\alpha]_D$ − 59.5° (*c* 1.0, $CHCl_3$); NMR ($CDCl_3$): δ_H 7.81–7.14 (m, 4 H, Ar H), 5.44 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.17 (t, 1 H, $J_{3,4}$ 5.5 Hz, H-3), 5.13 (dd, 1 H, H-2), 5.06 (sx, 1 H, H-4), 4.32 (dd, 1 H, H-5b), 4.10 (s, 2 H, $ClCH_2CO$), 3.72 (dd, 1 H, $J_{4,5a}$ 4.9, $J_{5a,5b}$ 13.0 Hz, H-5a), 2.16 and 2.15 (2 s, each 3 H, 2 OAc); δ_C 169.5, 169.1, and 166.2 (C=O), 148.7–117.8 (Ar C), 97.6 (C-1), 69.0 and 68.0 (2 C) (C-2,3,4), 60.4 (C-5), 40.5 ($ClCH_2CO$), 20.6 ($COCH_3$). Anal. Calcd for $C_{17}H_{18}ClNO_{10}$: C, 47.78; H, 4.20; N, 3.24. Found: C, 47.83; H, 4.29; N, 3.15.,

2-Nitrophenyl 2,3-di-O-benzoyl-4-O-chloroacetyl-β-D-xylopyranoside (**10**).—To a stirred solution of **8** (5.90 g, 17 mmol) in CH_2Cl_2 (90 mL) containing pyridine (11.0 mL, 0.14 mol) at −5°C was added dropwise a solution of BzCl (7.88 mL, 68 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 5 h at 0°C and processed as just described. Column chromatography (60:1 PhMe–EtOAc) of the residue afforded amorphous **10** (8.58 g, 91%): $[\alpha]_D$ + 28.0° (*c* 1.0, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 166.1, 164.95 and 164.7 (C=O), 149.0–118.2 (Ar C), 98.2 (C-1), 68.9, 68.4, and 68.1 (C-2,3,4), 60.2 (C-5), 40.5 ($ClCH_2CO$). Anal. Calcd for $C_{27}H_{22}ClNO_{10}$: C, 58.34; H, 3.99; N, 2.52. Found: C, 58.50; H, 3.89; N, 2.44.

2-Nitrophenyl 2,3-di-O-benzoyl-β-D-xylopyranoside (**11**).—A mixture of **10** (7.89 g, 14.2 mmol) and $(NH_2)_2C=S$ (5.40 g, 70.9 mmol) in MeOH (100 mL) was boiled under reflux for 2 h. The mixture was concentrated and the residue was partitioned between CH_2Cl_2 and aq $NaHCO_3$. The organic layer was washed with H_2O, dried, and concentrated. Column chromatography (6:1 PhMe–EtOAc) of the residue afforded amorphous **11** (6.12 g, 90%): $[\alpha]_D$ + 69.7° (*c* 1.3, $CHCl_3$); ^{13}C NMR [$(CD_3)_2CO$)]: δ 166.4 and 164.9 (C=O), 149.3–118.4 (Ar C), 99.1 (C-1), 73.6, 69.7, and 67.4 (C-2,3,4),

64.15 (C-5). Anal. Calcd for $C_{25}H_{21}ClNO_9$: C, 62.63; H, 4.41; N, 2.92. Found: C, 62.50; H, 4.49; N, 2.85.

4-Nitrophenyl 4-O-chloroacetyl-β-D-xylopyranoside (**12**).—Compound **5** (8.5 g, 15.2 mmol) was treated with dibutyltin oxide (8.33 g, 33.5 mmol) in MeOH (120 mL), followed by $ClCH_2COCl$ (2.66 mL, 33.4 mmol) in CH_2Cl_2 as described for the preparation of **8**. The residue was subjected to column chromatography (2:1 PhMe–EtOAc) to afford **12** (7.69 g, 73%): mp 68.5–70°C (from Et_2O); $[\alpha]_D$ – 72.9° (*c* 0.9, Me_2CO); NMR [$(CD_3)_2CO$]: δ_H 7.34–7.19 (m, 4 H, Ar H), 5.27 (d, 1 H, $J_{1,2}$ 6.8 Hz, H-1), 4.32 (s, 2 H, $ClCH_2COCl$); δ_C 167.5 (C=O), 162.8–117.3 (Ar C), 101.4 (C-1), 74.0 (2 C) and 73.7 (C-2,3,4), 63.1 (C-5), 41.55 ($ClCH_2CO$). Anal. Calcd for $C_{13}H_{14}ClNO_8$: C, 44.91; H, 4.06; N, 4.03. Found: C, 44.97; H, 3.93; N, 3.94.

4-Nitrophenyl 2,3-di-O-acetyl-4-O-chloroacetyl-β-D-xylopyranoside (**13**).—Acetylation of **12** (0.38 g), as described for **8**, gave **13** (0.43 g, 91%): mp 145–147°C (from EtOH); $[\alpha]_D$ – 72.2° (*c* 1.0, $CHCl_3$); NMR ($CDCl_3$) δ_H 8.23–7.08 (m, 4 H, Ar H), 5.36 (d, 1 H, $J_{1,2}$ 5.2 Hz, H-1), 5.20 (t, 1 H, $J_{3,4}$ 7.0 Hz, H-3), 5.20 (dd, 1 H, $J_{2,3}$ 7.0 Hz, H-2), 5.07 (sx, 1 H, H-4), 4.26 (dd, 1 H, H-5b), 4.09 (s, 2 H, $ClCH_2CO$), 3.86 (dd, 1 H, $J_{4,5a}$ 6.4, $J_{5a,5b}$ 12.5 Hz, H-5a), 2.12 and 2.10 (2 s, each 3 H, 2 OAc); δ_C 169.4, 169.0, and 166.2 (C=O), 160.8–116.5 (Ar C), 97.3 (C-1), 69.5, 69.4, and 69.05 (C-2,3,4), 61.2 (C-5), 40.4 ($ClCH_2CO$), 20.6 ($COCH_3$). Anal. Calcd for $C_{17}H_{18}ClNO_{10}$: C, 47.78; H, 4.20; N, 3.24. Found: C, 47.69; H, 4.29; N, 3.28.

4-Nitrophenyl 2,3-di-O-benzoyl-4-O-chloroacetyl-β-D-xylopyranoside (**14**).—Benzoylation of **12** (6.88 g), as described for **8**, gave amorphous **14** (10.1 g, 92%): $[\alpha]_D$ – 11.1° (*c* 1.2, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 166.3 and 164.8 (C=O), 160.8–116.4 (*Ar* C), 96.9 (C-1), 69.0 and 68.5 (2 C) (C-2,3,4), 60.55 (C-5), 40.5 ($ClCH_2CO$). Anal. Calcd for $C_{27}H_{22}ClNO_{10}$: C, 58.34; H, 3.99; N, 2.52. Found: C, 58.41; H, 3.89; N, 2.54.

4-Nitrophenyl 2,3-di-O-benzoyl-β-D-xylopyranoside (**15**).—A mixture of **4** (7.89 g, 14.2 mmol) and $(NH_2)_2C=S$ (5.40 g, 70.9 mmol) in MeOH (100 mL) was boiled under reflux for 2 h. The mixture was processed as described for the preparation of **11**. Column chromatography (6:1 PhMe–EtOAc) of the residue afforded **15** (6.12 g, 90%): mp 187–188.5°C (from EtOH); $[\alpha]_D$ + 32.9° (*c* 1.3, $CHCl_3$) ^{13}C NMR ($CDCl_3$): δ 166.35 and 164.9 (C=O), 161.0–116.5 (Ar C), 97.7 (C-1), 73.9, 69.6, and 67.7 (C-2,3,4), and 64.5 (C-5). Anal. Calcd for $C_{25}H_{21}ClNO_9$: C, 62.63; H, 4.41; N, 2.92. Found: C, 62.56; H, 4.49; N, 2.87.

O-β-D-Xylopyranosyl-(1 → 4)-D-xylopyranose (**19**) *and O-β-D-xylopyranosyl-(1 → 4)-O-β-D-xylopyranosyl-(1 → 4)-D-xylopyranose* (**20**).—The "xylo-oligosaccharides" (74 g), as described before, was dissolved in H_2O (700 mL), and the solution was applied to a column (9.5 × 32 cm) of charcoal (500 g). The column was washed successively with H_2O (10 L), 5% EtOH (12 L), 10% EtOH (6 L), and 15% EtOH (6 L). The sugar composition of the successive effluents from the column was examined by LC, and appropriate fractions containing **19** and **20** were combined in two fractions. Each of the fractions was concentrated and converted by repeated addition of EtOH and continued evaporation to a solid foam, which was crystallized. The yields of **19** and **20** obtained in crystalline form were 32.6 g and 13.2 g, respectively.

Compound **19** had mp 184.5–186°C (from MeOH); $[\alpha]_D$ −25.0° (*c* 1.1, H_2O, equil.); lit. [15] mp 185–186°C; $[\alpha]_D$ −25.5° (H_2O).

Compound **20** had mp 216–218°C (from aq EtOH); $[\alpha]_D$ −47.5° (*c* 1.0, H_2O, equil.); lit. [15] mp 205–206°C; $[\alpha]_D$ −47.0° (H_2O).

The ^{13}C NMR spectra of **19** and **20** were identical to those reported [21].

O-(2,3,4-Tri-O-acetyl-β-D-xylopyranosyl)-(1 → 4)-1,2,3-tri-O-acetyl-β-D-xylopyranose (**21**).—Compound **19** (24.4 g) was acetylated [16] with Ac_2O (120 mL) and NaOAc (20 g) under reflux for 30 min. Crystallization from the product from EtOH afforded **21** (38.3 g, 83%); mp 154–155°C; $[\alpha]_D$ −74.2° (*c* 1.1, $CHCl_3$); lit. [22] mp 154–155°C; $[\alpha]_D$ −74.5° (*c* 0.9, $CHCl_3$); the ^{13}C NMR spectrum was identical to that reported [21].

O-(2,3,4-Tri-O-acetyl-β-D-xylopyranosyl)-(1 → 4)-O-(2,3-di-O-acetyl-β-D-xylopyranosyl)-(1 → 4)-1,2,3-tri-O-acetyl-β-D-xylopyranose (**22**).—Acetylation of **20** (12.4 g), as just described, gave **22** (17.7 g, 79%); mp 108–109.5°C (from MeOH); $[\alpha]_D$ −84.2° (*c* 1.1, $CHCl_3$); lit. [22] mp 109–110°C; $[\alpha]_D$ −84.3° (*c* 0.6, $CHCl_3$); the ^{13}C NMR spectrum was identical to that reported [21].

O-(2,3,4-Tri-O-benzoyl-β-D-xylopyranosyl)-(1 → 4)-1,2,3-tri-O-benzoyl-α- and -β-D-xylopyranose (**24** and **25**).—Compound **19** (2.02 g, 7.15 mmol) was dissolved in boiling pyridine (50 mL), and the solution was cooled to 0°C, then treated dropwise with BzCl (9.1 mL, 78.4 mmol), and stirred for 5 h at room temperature. The mixture was processed as described for the preparation of **9**, and the residue was subjected to column chromatography (70:1 → 50:1 PhMe–EtOAc, stepwise) to give first **25** (3.32 g, 51%): mp 171–172.5°C (from MeOH); $[\alpha]_D$ −39.9° (*c* 0.9, $CHCl_3$); NMR ($CDCl_3$): δ_H 6.15 (d, 1 H, $J_{1,2}$ 5.9 Hz, H-1); δ_C 99.6 (C-1′), 92.7 (C-1), 74.5, 71.4, 70.1, 69.6 (2 C), 68.5, 62.7 and 60.9 (C-5,5′). Anal. Calcd for $C_{52}H_{42}O_{15}$: C, 68.95; H, 4.67. Found: C, 68.97; H, 4.61.

Eluted next was **24** (2.72 g, 42%); mp 204–206°C (from MeOH–Me_2CO); $[\alpha]_D$ +75.9° (*c* 0.6, $CHCl_3$); NMR ($CDCl_3$): δ_H 6.70 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1); δ_C 100.15 (C-1′), 90.0 (C-1), 76.0, 70.7 (2 C), 70.2, 69.6, 68.4, 61.8 and 60.9 (C-5,5′). Anal. Found: C, 68.94; H, 4.70.

O-(2,3,4-Tri-O-benzoyl-β-D-xylopyranosyl)-(1 → 4)-2,3-di-O-benzoyl-α-D-xylopyranosyl bromide (**26**).—To a chilled solution of **25** (2.06 g) in 1,2-dichloroethane (3 mL) at 0°C was added a saturated (at 0°C) solution of HBr in AcOH (1.2 mL). The mixture was stirred for 30 min at room temperature and then diluted with CH_2Cl_2. The solution was washed successively with iced H_2O, aq $NaHCO_3$, H_2O, dried, and concentrated. Crystallization of the residue from CH_2Cl_2–hexane gave **26** (1.69 g, 86%): mp 134–135°C; $[\alpha]_D$ +50.1° (*c* 0.95, CH_2Cl_2); NMR ($CDCl_3$): δ_H 6.71 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1); δ_C 99.5 (C-1′), 87.7 (C-1), 75.1, 71.8, 70.9, 69.85, 68.9, 68.1, 63.6 and 60.5 (C-5,5′). Anal. Calcd for $C_{45}H_{37}BrO_{13}$: C, 62.44; H, 4.31. Found: C, 62.37; H, 4.47.

Compound **26** was also obtainable from **24** or from a mixture of **24** and **25**.

O-(2,3,4-Tri-O-benzoyl-β-D-xylopyranosyl)-(1 → 4)-O-(2,3-di-O-benzoyl-β-D-xylopyranosyl)-(1 → 4)-1,2,3-tri-O-benzoyl-α- and -β-D-xylopyranose (**33** and **34**).—Benzoylation of **20** (1.17 g, 2.8 mmol) with BzCl (4.0 mL, 34.5 mmol) in pyridine (30 mL), as described for **19**, followed by column chromatography (50:1 → 30:1 PhMe–EtOAc) of the product, gave **33** (1.46 g, 41%) and **34** (1.71 g, 49%).

Compound **33** had mp 201–203°C (from MeOH–Me_2CO); $[\alpha]_D$ +52.6° (*c* 1.1, $CHCl_3$); NMR ($CDCl_3$): δ_H 6.63 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1); δ_C 101.4 and 99.3 (C-1′,1″), 89.9 (C-1), 76.6, 74.7, 71.95, 71.5, 70.9, 70.5, 70.0, 69.5, 68.4, and 62.1, 61.7, and 60.8 (C-5,5′,5″). Anal. Calcd for $C_{71}H_{58}O_{21}$: C, 68.37; H, 4.69. Found: C, 68.47; H, 4.77.

Compound **34** had mp 222–224°C (from MeOH–Me_2CO); $[\alpha]_D$ −39.6° (*c* 0.8, $CDCl_3$); NMR ($CDCl_3$): δ_H 6.14 (d, 1 H, $J_{1,2}$ 5.7 Hz, H-1); δ_C 100.8 and 99.3 (C-1′,1″), 92.7 (C-1), 74.9, 74.7, 71.9, 71.4 (2 C), 70.0, 69.6 (2 C), 68.4, and 63.0, 62.1, and 60.7 (C-5,5′,5″). Anal. Found: C, 68.50; H, 4.62.

Methyl O-*(2,3,4-tri*-O-*acetyl-β*-D-*xylopyranosyl)-(1 → 4)-2,3-di*-O-*acetyl-1-thio-β*-D-*xylopyranoside* (**36**).—A solution of $SnCl_4$ (2.65 mL, 22.6 mmol) in 1,2-dichloroethane (20 mL) was added dropwise at 0°C to a stirred solution of **21** (11.0 g, 20.6 mmol) and Bu_3SnSMe (7.63 g, 22.6 mmol) in 1,2-dichloroethane (100 mL). The mixture was stirred for 1 h at room temperature, poured into ice–aq $NaHCO_3$–aq KF, and filtered through a Celite layer, which was washed with CH_2Cl_2. The combined filtrate and washings were partitioned, and the organic layer was washed with H_2O, dried, and concentrated. Column chromatography (2:1 PhMe–EtOAc) of the residue afforded **36** (8.82 g, 82%): mp 132–133.5°C (from EtOH); $[\alpha]_D$ −86.0° (*c* 1.2, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.5–168.8 (C=O), 99.5 (C-1), 83.6 (C-1), 74.8, 73.5, 70.4 (2 C), 69.45, 68.3, 66.7 (C-5), 61.5 (C-5′), 20.6 ($COCH_3$), 11.6 (SMe). Anal. Calcd for $C_{21}H_{30}O_{13}S$: C, 48.27; H, 5.79. Found: C, 48.40; H, 5.67.

Methyl O-*(2,3,4-tri*-O-*acetyl-β*-D-*xylopyranosyl)-(1 → 4)*-O-*(2,3-di*-O-*acetyl-β*-D-*xylopyranosyl)-(1 → 4)-2,3-di*-O-*acetyl-1-thio-β*-D-*xylopyranoside* (**37**).—A mixture of **22** (3.50 g, 4.7 mmol) and Bu_3SnSMe (7.63 g, 5.1 mmol) in 1,2-dichloroethane (50 mL) was treated with a solution of $SnCl_4$ (0.60 mL, 5.1 mmol) in 1,2-dichloroethane (5 mL). Processing of the mixture, followed by column chromatography (4:1 PhMe–EtOAc) of the product, as just described, afforded amorphous **37** (2.68 g, 78%): $[\alpha]_D$ −92.4° (*c* 1.5, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.5–168.85 (C=O), 100.3 and 99.4 (C-1′,1″), 83.5 (C-1), 75.4, 74.15, 73.5, 71.9, 71.0, 70.4 (2 C), 69.4, 68.3, 66.8 (C-5), 62.4 and 61.5 (C-5′,5″), 20.6 ($COCH_3$), 11.6 (SMe). Anal. Calcd for $C_{30}H_{42}O_{19}S$: C, 48.78; H, 5.73. Found: C, 48.90; H, 5.61.

Glycosylation of **11** *or* **15** *with* **16**, **36**, *or* **37**.—To a stirred mixture of **11** (1.76 g, 3.7 mmol), **16** (1.53 g, 4.8 mmol), and powdered 4 Å molecular sieves in CH_2Cl_2 (30 mL) at 0°C was added NIS (1.06 g, 4.8 mmol), followed, dropwise, by a solution of silver triflate (0.19 g, 739 μmol) in PhMe (5 mL). After 10 min, the mixture was filtered through a Celite layer into iced water, and the filtrate was partitioned. The organic layer was washed successively with aq $Na_2S_2O_3$, aq $NaHCO_3$, and H_2O, dried, and concentrated. Column chromatography (10:1 PhMe–EtOAc) of the product afforded 2-nitrophenyl *O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (**17**) (2.17 g, 80%): mp 175–176°C (from MeOH); $[\alpha]_D$ +10.5° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.7–165.0 (C=O), 149.2–118.1 (Ar C), 100.0 and 98.7 (C-1,1′), 73.4, 70.8, 70.5, 69.85, 69.3, 68.2, 61.5 and 61.4 (C-5,5′). Anal. Calcd for $C_{36}H_{35}NO_{16}$: C, 58.62; H, 4.78; N, 1.90. Found: C, 58.70; H, 4.77; N, 1.95

Similar reaction of **11** with **36** or **37** and of **15** with **16**, **36**, or **37**, followed by column chromatography of each product with the mixture of appropriately adjusted porarity consisting of PhMe and EtOAc, gave the following compounds:

4-Nitrophenyl *O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (**18**), 82%: mp 177.5–179°C (from EtOH); $[\alpha]_D$ −44.5° (*c* 1.2, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.7–164.9 (C=O), 161.0–116.4 (Ar C), 99.9 and 97.5 (C-1,1'), 73.6, 70.6, 70.3 (2 C), 69.4, 68.1, 61.8 and 61.5 (C-5,5'), 20.6 ($COCH_3$). Anal. Cald for $C_{36}H_{35}NO_{16}$: C, 58.62; H, 4.78; N, 1.90. Found: C, 58.55; H, 4.70; N, 1.84

2-Nitrophenyl *O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)-*O*-(2,3-di-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (**38**), 84%, amorphous solid: $[\alpha]_D$ −38.4° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.6–164.9 (C=O), 149.2–118.1 (Ar C), 100.7, 99.6, and 98.7 (C-1,1',1''), 74.3, 73.75, 72.0, 71.2, 70.6, 70.4, 69.8, 69.2, 68.4, and 62.35, 61.6, and 61.4 (C-5,5',5''), 20.55 ($COCH_3$). Anal. Calcd for $C_{45}H_{47}NO_{18}$: C, 66.98; H, 4.48; N, 1.32. Found: C, 67.10; H, 4.40; N, 1.22.

4-Nitrophenyl *O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)-*O*-(2,3-di-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (**39**), 85%: mp 245–246.5°C (from MeOH–CH_2Cl_2); $[\alpha]_D$ −70.8° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.6–164.9 (C=O), 161.0–116.4 (Ar C), 100.8, 99.6, and 97.5 (C-1,1',1''), 74.2 (2 C), 72.0, 71.1, 70.6, 70.3 (2 C), 69.3, 68.4, and 62.4, 61.9, and 61.6 (C-5,5',5''), 20.6 ($COCH_3$). Anal. Calcd for $C_{45}H_{47}NO_{18}$: C, 66.98; H, 4.48; N, 1.32. Found: C, 66.90; H, 4.40; N, 1.25.

2-Nitrophenyl *O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)-bis[*O*-(2,3-di-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)]-2,3-di-*O*-benzoyl-β-D-xylopyranoside (**44**), 73%, amorphous solid: $[\alpha]_D$ −54.5° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.6–164.9 (C=O), 149.1–118.1 (Ar C), 100.5, 100.4, 99.4, and 98.7 (C-1,1',1'',1'''), 74.8, 74.2, 73.7, 72.0 (2 C), 71.0, 70.9, 70.3 (2 C), 69.9, 69.3, 68.3, and 62.5, 62.4, and 61.5 (2 C) (C-5,5',5'',5'''), 20.7 and 20.6 ($COCH_3$). Anal. Calcd for $C_{54}H_{59}NO_{28}$: C, 55.43; H, 5.08; N, 1.20. Found: C, 55.60; H, 5.13; N, 1.13.

4-Nitrophenyl *O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)-bis[*O*-(2,3-di-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)]-2,3-di-*O*-benzoyl-β-D-xylopyranoside (**45**), 78%: mp 231–232.5°C (from MeOH–CH_2Cl_2): $[\alpha]_D$ −80.1° (*c* 0.9, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.5–164.8 (C=O), 161.0–116.4 (Ar C), 100.6, 100.4, 99.4, and 97.5 (C-1,1',1'',1'''), 74.7, 74.1 (2 C), 71.9 (2 C), 70.9 (2 C), 70.3 (3 C), 69.3, 68.3, and 62.4 (2 C), 61.9, and 61.5 (C-5,5',5'',5'''), 20.6 ($COCH_3$). Anal. Calcd for $C_{54}H_{59}NO_{28}$: C, 55.43; H, 5.08; N, 1.20. Found: C, 55.36; H, 5.17; N, 1.15.

2-Nitrophenyl *O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-(1 → 4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (**27**).—To a mixture of 2-nitrophenol (0.83 g, 6 mmol) and K_2CO_3 (1.65 g, 11.9 mmol) in Me_2CO (30 mL) was added dropwise a solution of **26** (2.58 g, 3 mmol) in Me_2CO (20 mL), and the mixture was processed as described for the preparation of **2**. Column chromatography (50:1 PhMe–EtOAc) of the product gave **27** (1.79 g, 65%): mp 204–205°C (from MeOH–Me_2CO); $[\alpha]_D$ −22.9° (*c* 1.0, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 165.25–164.9 (C=O), 149.15–118.0 (Ar C), 99.3 and 98.6 (C-1,1'), 73.3, 70.15, 70.0, 69.7, 69.5, 68.5, 60.9 (2 C, C-5,5'). Anal. Calcd for $C_{51}H_{41}NO_{16}$: C, 66.30; H, 4.47; N, 1.52. Found: C, 66.20; H, 4.54; N, 1.46.

4-Nitrophenyl *O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-(1 → 4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (**28**).—A solution of **26** (2.54 g, 2.9 mmol) in Me_2CO was added to a mixture of 4-nitrophenol (0.82 g, 5.9 mmol) and K_2CO_3 (1.65 g, 11.7 mmol) in Me_2CO, as described for the preparation of **2**. Column chromatography of the product,

as just described, gave **28** (1.84 g, 68%): mp 220–21.5°C (from MeOH–Me_2CO); $[\alpha]_D$ – 63.1° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 165.1 (C=O), 161.0–116.5 (Ar C), 99.6 and 97.6 (C-1,1′), 73.8, 70.6, 70.3, 69.7 (2 C), 68.5, 61.6, and 61.1 (C-5,5′). Anal. Calcd for $C_{51}H_{41}NO_{16}$: C, 66.30; H, 4.47; N, 1.52. Found: C, 66.22; H, 4.44; N, 1.44.

2-Nitrophenyl *O*-β-D-xylopyranosyl-(1 → 4)-β-D-xylopyranoside (**29**).—(*a*) A solution of **17** (1.02 g) in MeOH (20 mL) and CH_2Cl_2 (5 mL) was treated with M methanolic NaOMe (0.5 mL), and processed, as described for the preparation of **4**, to give **29** (0.85 g, 83%): mp 95–97.5°C (from EtOH) and 104–105.5°C (from CH_3CN); $[\alpha]_D$ – 82.6° (*c* 0.7, MeOH); LC: t_R 1.17; lit. [4] mp 113–115°C (from CH_3CN); $[\alpha]_D$ – 81.3° (*c* 0.9, MeOH); ^{13}C NMR ($CDCl_3$): δ 151.8, 142.5, 137.7, 128.0, 125.6, and 120.25 (*Ar* C), 104.45 (C-1), 103.7 (C-1′), 78.7 (C-4), 78.3 (C-3′), 75.9 (C-3), 75.4 (C-2), 74.9 (C-2′), 71.8 (C-4′), 67.9 (C-5′), 65.6 (C-5). Anal. Calcd for $C_{16}H_{21}NO_{11}$: C, 47.65; H, 5.25; N, 3.47. Found: C, 47.77; H, 5.31; N, 3.35. (*b*) Compound **27** (1.53 g) was treated with methanolic sodium methoxide in MeOH and CH_2Cl_2, as just described, to give **29** (0.55 g, 82%): mp and mixed mp 95–97.5°C (from EtOH); $[\alpha]_D$ – 82.0° (*c* 1.0, MeOH).

2-Nitrophenyl *O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)-2,3-di-*O*-acetyl-β-D-xylopyranoside (**30**).—A solution of **29** (0.27 g) in 2:3 (v/v) Ac_2O–pyridine (3 mL) was kept overnight at room temperature, and the solvents were removed with the aid of repeated additions and evaporation of PhMe. Crystallization of the residue from EtOH gave **30** (0.38 g, 93%): mp 113–115°C (from EtOH); $[\alpha]_D$ –79.0° (*c* 1.0, $CHCl_3$); lit. [4] mp 188°C (from EtOAc–hexane); ^{13}C NMR ($CDCl_3$): δ 169.7–168.9 (C=O), 148.9–118.0 (*Ar* C), 99.8 and 98.7 (C-1,1′), 73.5, 70.85, 70.6, 70.1, 69.2, 68.4, 61.8 and 61.7 (C-5,5′), 20.6 ($COCH_3$). Anal. Calcd for $C_{26}H_{31}NO_{16}$: C, 50.90; H, 5.09; N, 2.28. Found: C, 51.03; H, 5.15; N, 2.33. The ^1H NMR spectrum was identical with that reported [4].

4-Nitrophenyl *O*-β-D-xylopyranosyl-(1 → 4)-β-D-xylopyranoside (**31**).—(*a*) *O*-Deacylation of **18** (2.55 g), as for **17**, afforded **31** (1.26 g, 91%): mp 121–123°C (from H_2O) and 115–117°C (from EtOH–Me_2CO); $[\alpha]_D$ –92.2° (*c* 1.2, MeOH); LC: t_R 1.15; lit. [4] $[\alpha]_D$ –88.8° (*c* 1, MeOH); ^{13}C NMR (D_2O): δ 164.15, 144.7, 128.4, and 118.9 (*Ar* C), 104.5 (C-1), 102.6 (C-1′), 78.7 (C-4), 78.3 (C-3′), 76.1 (C-3), 75.4 (2 C, C-2,2′), 71.9 (C-4′), 68.0 (C-5′), 65.7 (C-5). Anal. Calcd for $C_{16}H_{21}NO_{11}$: C, 47.65; H, 5.25; N, 3.47. Found: C, 47.74; H, 5.38; N, 3.39. (*b*) *O*-Debenzoylation of **28** (2.41 g), as for **27**, gave **31** (0.97 g, 92%): mp and mixed mp 121–123°C (from H_2O); $[\alpha]_D$ –92.0° (*c* 1.0, MeOH).

4-Nitrophenyl O-*(2,3,4-tri*-O-*acetyl*-β-D-*xylopyranosyl)-(1 → 4)-2,3-di*-O-*acetyl*-β-D-*xylopyranoside* (**32**).—Acetylation of **31** (0.30 g), as described for **29**, gave **32** (0.42 g, 91%): mp 188–190°C (from EtOH); $[\alpha]_D$ –92.6° (*c* 1.2, $CHCl_3$); lit. [4] mp 182–184°C (from EtOAc–hexane); ^{13}C NMR ($CDCl_3$): δ 169.7–168.9 (C=O), 161.0–116.5 (*Ar* C), 99.7 and 98.0 (C-1,1′), 74.0, 71.3, 70.6, 70.5, 70.15, 68.35, 62.5 and 61.7 (C-5,5′), 20.6 ($COCH_3$); the ^1H NMR spectrum was identical with that reported [4].

2-Nitrophenyl O-*(2,3,4-tri*-O-*acetyl*-β-D-*xylopyranosyl)-(1 → 4)*-O-*(2,3-di*-O-*acetyl*-β-D-*xylopyranosyl)-(1 → 4)-2,3-di*-O-*acetyl*-β-D-*xylopyranoside* (**40**).—*O*-Deacylation of **38** (1.80 g) as described for the preparation of **29**, followed by acetylation as described for the preparation of **30**, and column chromatography (4:1 PhMe–EtOAc) of

the product, afforded **40** (1.15 g, 81%): mp 153–155°C (from EtOH); $[\alpha]_D$ −85.9° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.6–168.9 (C=O), 148.9–118.0 (Ar C), 100.3, 99.5, and 98.5 (C-1,1′,1″), 74.3, 73.6, 72.1, 71.1, 70.5, 70.4, 69.9, 69.0, 68.3, 62.7 and 61.55 (2 C) (C-5,5′,5″), 20.7 and 20.6 ($COCH_3$). Anal. Calcd for $C_{35}H_{43}NO_{22}$: C, 50.67; H, 5.22; N, 1.69. Found: C, 50.77; H, 5.18; N, 1.60.

The sequence of reactions used for **38** was applied to **39**, **44**, and **45** to give the following compounds:

4-Nitrophenyl *O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)-*O*-(2,3-di-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)-2,3-di-*O*-acetyl-β-D-xylopyranoside (**41**), 83%: mp 224–226°C (from EtOH); $[\alpha]_D$ −104.7° (*c* 1.0, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.55 (C=O), 161.0–116.5 (Ar C), 100.5, 99.5, and 97.9 (C-1,1′,1″), 74.4 (2 C), 72.0, 71.2 (2 C), 70.4 (3 C), 68.3, 62.2 (2 C) and 61.6 (C-5,5′5″), 20.7 ($COCH_3$). Anal. Calcd for $C_{35}H_{43}NO_{22}$: C, 50.67; H, 5.22; N, 1.69. Found: C, 50.75; H, 5.30; N, 1.73.

2-Nitrophenyl *O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)-bis[*O*-(2,3-di-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)]-2,3-di-*O*-acetyl-β-D-xylopyranoside (**46**), 85%: mp 224–226°C (from EtOH); $[\alpha]_D$ −103.1° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.5–168.8 (C=O), 148.9–118.0 (Ar C), 100.3 (2 C), 99.45, and 98.6 (C-1,1′,2″,1‴). 74.9, 74.2, 73.6, 72.1, 71.9, 71.0 (2 C), 70.5 (2 C), 70.0, 69.05, 68.3, and 62.7, 62.6, 62.5, and 61.55 (C-5,5′,5″,5‴), 20.7 and 20.6 ($COCH_3$). Anal. Calcd for $C_{44}H_{55}NO_{28}$: C, 50.53; H, 5.30; N, 1.40. Found: C, 50.75; H, 5.23; N, 1.34.

4-Nitrophenyl *O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)-bis[*O*-(2,3-di-*O*-acetyl-β-D-xylopyranosyl)-(1 → 4)]-2,3-di-*O*-acetyl-β-D-xylopyranoside (**47**), 83%: mp 257–258.5°C (from $CHCl_3$–EtOH); $[\alpha]_D$ −96.7° (*c* 1.2, CH_2Cl_2); ^{13}C NMR ($CDCl_3$): δ 169.5–169.1 (C = O), 160.95–116.4 (Ar C), 100.2 (2 C), 99.4, and 97.9 (C-1,1′,1″,1‴), 74.6, 74.2 (2 C), 71.9 (2 C), 71.2, 70.9 (2 C), 70.4 (2 C), 70.0, 68.3, 62.5 (3 C) and 61.5 (C-5,5′,5″,5‴), 20.6 ($COCH_3$). Anal. Calcd for $C_{44}H_{55}NO_{28}$: C, 50.53; H, 5.30; N, 1.40. Found: C, 50.61; H, 5.35; N, 1.31.

O-Deacetylation of **40**, **41**, **46**, and **47**, as described for the preparation of **29**, afforded the following compounds:

2-Nitrophenyl *O*-β-D-xylopyranosyl-(1 → 4)-*O*-β-D-xylopyranosyl)-(1 → 4)-β-D-xylopyranoside (**42**), 92%, amorphous solid: $[\alpha]_D$ −84.1° (*c* 1.0, H_2O); LC: t_R 1.41; ^{13}C NMR (D_2O): δ 151.8, 142.5, 137.75, 128.2, 125.8, and 120.3 (*Ar* C), 104.5 (C-1), 104.3 (C-1″), 103.7 (C-1′), 79.1 (C-4′), 78.7 (C-4), 78.3 (C-3″), 76.3 (C-3′), 75.95 (C-3), 75.4 (2 C, C-2,2′), 74.9 (C-2″), 71.9 (C-4″), 67.9 (C-5″), 65.7 (2 C, C-5,5′). Anal. Calcd for $C_{21}H_{29}NO_{15}$: C, 47.11; H, 5.46; N, 2.62. Found: C, 46.91; H, 5.59; N, 2.54.

4-Nitrophenyl *O*-β-D-xylopyranosyl-(1 → 4)-*O*-β-D-xylopyranosyl-(1 → 4)-β-D-xylopyranoside (**43**), 95%, amorphous solid: $[\alpha]_D$ −96.5° (*c* 1.0, H_2O); LC: t_R 1.39; ^{13}C NMR (D_2O): δ 164.15, 144.9, 128.5, and 119.1 (*Ar* C), 104.5 (2 C, C-1,1′), 102.6 (C-1″), 79.1 (C-4′), 78.75 (C-4), 78.3 (C-3″), 76.3 (C-3′), 76.1 (C-3), 75.4 (3 C, C-2,2′,2″), 71.9 (C-4″), 67.9 (C-5″), 65.8 (2 C, C-5,5′). Anal. Calcd for $C_{21}H_{29}NO_{15}$: C, 47.11; H, 5.46; N, 2.62. Found: C, 46.96; H, 5.61; N, 2.57.

2-Nitrophenyl *O*-β-D-xylopyranosyl-(1 → 4)-bis[*O*-β-D-xylopyranosyl-(1 → 4)]-β-D-xylopyranoside (**48**), 92%, amorphous solid: $[\alpha]_D$ −91.2° (*c* 1.05, H_2O); LC: t_R 1.78; ^{13}C NMR (D_2O): δ 151.8, 142.6, 137.8, 128.2, 125.8, and 120.4 (*Ar* C), 104.5 (C-1), 104.3 (2 C, C-1″,1‴), 103.7 (C-1′), 79.0 (2 C, C-4′,4″), 78.7 (C-4), 78.3 (C-3‴), 76.3 (2

C, C-3′,3″), 75.95 (C-3), 75.3 (3 C, C-2,2′,2″), 74.9 (C-2‴), 71.8 (C-4‴), 67.9 (C-5‴), 65.7 (3 C, C-5,5′,5″). Anal. Calcd for $C_{26}H_{37}NO_{19}$: C, 46.78; H, 5.59; N, 2.10. Found: C, 46.86; H, 5.66; N, 2.05.

4-Nitrophenyl *O*-β-D-xylopyranosyl-(1 → 4)-bis[*O*-β-D-xylopyranosyl-(1 → 4)]-β-D-xylopyranoside (**49**), 91%, amorphous solid: $[\alpha]_D$ −102.6° (*c* 1.0, H_2O); LC: t_R 1.75; ^{13}C NMR (D_2O): δ 164.15, 144.9, 128.6, and 119.1 (*Ar* C), 104.4 (3 C, C-1,1′,1″), 102.6 (C-1‴), 79.1 (3 C, C-4,4′,4″), 78.3 (C-3‴), 76.3 (3 C, C-3,3′,3″), 75.3 (4 C, C-2,2′,2″,2‴), 71.9 (C-4‴), 67.9 (C-5‴), and 65.7 (3 C, C-5,5′,5″). Anal. Calcd for $C_{21}H_{29}NO_{15}$: C, 46.78; H, 5.59; N, 2.10. Found: C, 46.88; H, 5.67; N, 2.02.

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