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Synthesis of (1 → 4)-β-D-xylo-oligosaccharides of dp 4–10 by a blockwise approach

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Abstract

Dibutyltin oxide-mediated regioselective chloroacetylation of methyl 1-thio-β-xylobioside, followed by treatment of the product with 4-methylbenzoyl chloride–pyridine, gave methyl 4-*O*-chloroacetyl-2,3-di-*O*-(4-methylbenzoyl)-β-D-xylopyranosyl-(1 → 4)-2,3-di-*O*-(4-methylbenzoyl)-1-thio-β-D-xylopyranoside (**18**) in 70% yield. Coupling of **18** with benzyl alcohol afforded the disaccharide benzyl β-glycoside, which was *O*-dechloroacetylated to provide methyl 2,3-di-*O*-(4-methylbenzoyl)-β-D-xylopyranosyl-(1 → 4)-2,3-di-*O*-(4-methylbenzoyl)-1-thio-β-D-xylopyranoside (**20**). A homologous series of (1 → 4)-β-D-xylo-oligosaccharides from the tetra- to the deca-saccharide have been synthesized in a blockwise manner by using **20** as the glycosyl acceptor, **18**, methyl 1-thio-β-xylobioside pentaacetate, and methyl 1-thio-β-xylotrioside heptaacetate as the glycosyl donors, and a combination of *N*-iodosuccinimide–silver triflate as the promoter.

Keywords: Oligosaccharides, D-xylo-; Synthesis, blockwise; Glycosidation

1. Introduction

Further extension of our studies of the structural analysis of oligo- and poly-saccharides in solution by small angle X-ray scattering and computer simulation based on the Monte Carlo Method [1] required the preparation of a homologous series of (1 → 4)-β-D-xylo-oligosaccharides from the tetra- to the deca-saccharides. (1 → 4)-β-D-Xylo-oligosaccharides of dp 2–7 have been isolated by chromatographic separation of

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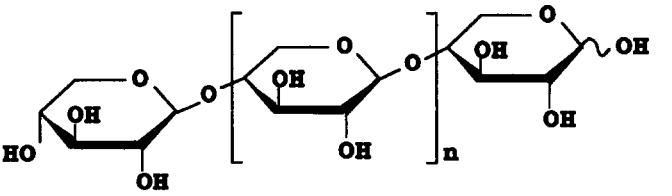
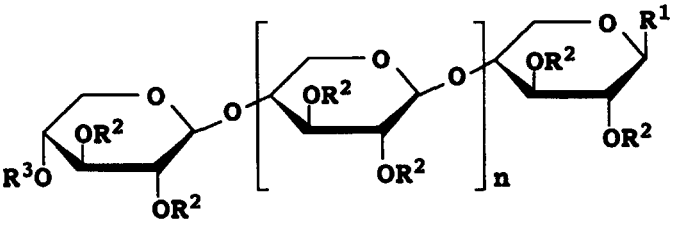
the products from partial acid hydrolysis of plant xylans [2–4], and the chemical syntheses of lower members of the oligosaccharides, namely xylobiose [5–9] (**1**), xylotriose [9,10] (**2**), xylotetraose [9] (**3**), and xylopentaose [9] (**4**), have been undertaken. We have previously reported the synthesis of the derivatives of **3** and xylohexaose (**5**) by using a disaccharide building-block obtained by coupling of two D-xylose synthons [11]. Herein we report an alternative systematic synthesis, by a blockwise approach, of the complete series of (1 → 4)-β-D-xylo-oligosaccharides from **3**, through xylodecaose (compounds **3**–**9**), via their benzyl β-glycosides (compounds **35**–**41**), starting from the di- and tri-saccharide derivatives **10** and **27**, which have been prepared from **1** and **2** in the previous study [12].



	n		n
1	0	**6**	5
2	1	**7**	6
3	2	**8**	7
4	3	**9**	8
5	4		

2. Results and discussion

For the preparation of higher members of (1 → 4)-β-D-xylo-oligosaccharides with dp 5 or higher, we considered that a blockwise elongation of the oligosaccharide chain employing a disaccharide building-block may be more efficient rather than the related stepwise synthesis using monosaccharide synthons [9], as it was reported that the separation by column chromatography of the product obtained by a glycosidation reaction is more difficult with increasing chain length of the oligosaccharides [9]. The above disaccharide building-unit must bear a substituent on O-2 capable of neighboring group participation, and a selective removal protecting group on O-4^2, the site of further chain extension [11]. Therefore, the synthetic methods used here were based on (*a*) conversion of methyl 1-thio-β-xylobioside (**11**) into a properly substituted derivative that is not only suitable for a blockwise insertion of a xylobiose unit into the



	n	R^1	R^2	R^3		n	R^1	R^2	R^3
10	0	SMe	Ac	Ac	**19**	0	OBzl	MBz	CA
11	0	SMe	H	H	**20**	0	OBzl	MBz	H
12	0	SMe	Bz	Bz	**21**	2	OBzl	MBz	CA
13	0	SMe	Bz	CA	**22**	2	OBzl	MBz	H
14	0	OBzl	Bz	CA	**23**	4	OBzl	MBz	CA
15	0	OBzl	Bz	H	**24**	4	OBzl	MBz	H
16	2	OBzl	Bz	CA	**25**	6	OBzl	MBz	CA
17	0	SMe	MBz	MBz	**26**	6	OBzl	MBz	H
18	0	SMe	MBz	CA	**27**	1	SMe	Ac	Ac

CA : $ClCH_2CO$; MBz : 4-Methylbenzoyl

oligosaccharide chain allowing further glycosylation on O-4^2, but can also serve as a precursor to the synthesis of a disaccharide derivative corresponding to the reducing xylobiose unit; (*b*) the use of methyl 1-thio-β-xylobioside pentaacetate [12] (**10**) and methyl 1-thio-β-xylotrioside heptaacetate [12] (**27**) as the glycosyl donors for the construction of terminal nonreducing di- and tri-saccharide units, respectively; (*c*) condensation of the di- and tri-saccharide methyl 1-thio-β-glycoside derivatives mentioned above, using a combination of *N*-iodosuccinimide (NIS) and silver triflate as the promoter [13] for all the glycosylation steps. The following steps were performed.

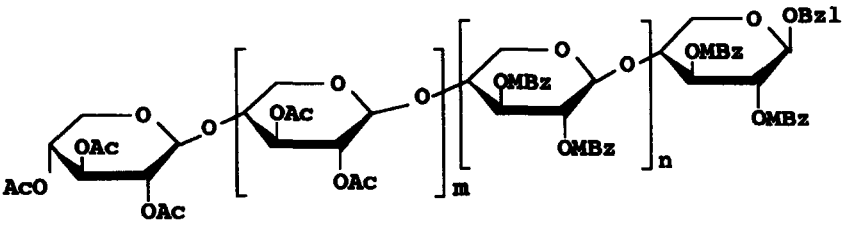
It first appeared to us that methyl 2,3-di-*O*-benzoyl-4-*O*-chloroacetyl-β-D-xylopyranosyl-(1 → 4)-2,3-di-*O*-benzoyl-1-thio-β-D-xylopyranoside (**13**) might fulfil the requirement for the internal xylobiose unit described above in *a*. *O*-Deacetylation of **10** with methanolic sodium methoxide gave the crystalline **11**. Regioselective chloroacetylation of **11** with chloroacetyl chloride in dichloromethane, via the stannylene derivative [12,14,15], followed by benzoylation of the product, in one pot, with benzoyl chloride–pyridine, gave a mixture from which the pentabenzoate **12** and **13** were isolated in 11 and 72% yields, respectively, after column chromatography. The 2D $^1H-^1H$ chemical shift correlation experiment of **13**, obtained by 2D $^1H-^1H$ homonuclear COSY [16], allowed the unambiguous assignment of all the coupled ring-proton pairs in **13**. The most-deshielded ring protons were H-3, H-3′, H-2, and H-2′ (δ 5.65–5.22), in accord with the observation that a ring proton attached to the same carbon as a benzoyloxy

group occurs to low field of the other protons [17]. The H-4′ proton appeared at δ 4.95 as a sextet ($J_{4',5'a}$ 6.8, $J_{4',5'b}$ 4.4 Hz) [18], indicating the position of the chloroacetyl group in **13**. Coupling of **13** with benzyl alcohol afforded the disaccharide benzyl β-glycoside **14** (84%), which was *O*-dechloroacetylated with thiourea [19] to give the disaccharide derivative **15** having HO-4^2 unsubstituted. When compound **15** was subjected to glycosylation with **13** in dichloromethane with a view to obtaining the tetrasaccharide derivative **16**, a highly crystalline product precipitated from the reaction mixture. TLC examination, as well as the ^{13}C NMR spectrum of the crystalline product in pyridine-d_5, showed the presence of **16** as the major component, in addition to the byproducts (experimental, not reported). However, compound **16** could not be isolated pure from the mixture either by column chromatography or by fractional crystallization, because of its sparing solubility in such solvents as acetone, chloroform, ethyl acetate, benzene, toluene and so on. Therefore, an alternative blocking group in place of the benzoyl group in **13** was sought in order to improve the solubility of the derivative of **11** in common solvents that are suitable for purification by column chromatography of the products in glycosylation reactions.

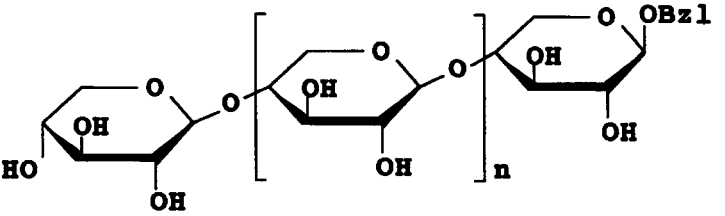
Regioselective chloroacetylation of **11**, mediated by dibutyltin oxide, followed by treatment of the product with 4-methylbenzoyl chloride–pyridine, as described before, afforded the penta(4-methylbenzoyl) derivative **17** and methyl 4-*O*-chloroacetyl-2,3-di-*O*-(4-methylbenzoyl)-β-D-xylopyranosyl-(1 → 4)-2,3-di-*O*-(4-methylbenzoyl)-1-thio-β-D-xylopyranoside (**18**) in 10 and 70% yields, respectively, after column chromatography. The location of the chloroacetyl group in **18** was proved, as for **13**, by the 2D ^{1}H–^{1}H homonuclear COSY. Condensation of **18** with benzyl alcohol gave the disaccharide benzyl β-glycoside **19** (83%), which, on *O*-dechloroacetylation as for **14**, afforded the disaccharide derivative **20** having HO-4^2 unsubstituted.

Glycosylation of **20** with **18** gave the tetrasaccharide benzyl β-glycoside **21** (81%), which was *O*-dechloroacetylated to afford the tetrasaccharide derivative **22** having HO-4^4 unsubstituted. In a similar way, the hexa- (**23** and **24**) and octa- (**25** and **26**) saccharide derivatives were prepared by a sequence involving condensation of **22** with **18** (→ **23**), followed by *O*-dechloroacetylation (→ **24**), coupling with **18** (→ **25**), and *O*-dechloroacetylation (→ **26**).

Having prepared a di- (**20**), a tetra- (**22**), a hexa- (**24**), and an octa-saccharide glycosyl acceptor **26**, we were able to carry out the synthesis of benzyl β-glycosides of the xylo-oligosaccharides by further elongation of the oligosaccharide chain in a blockwise manner, using a di- (**10**) and a tri-saccharide glycosyl donor **27**. Coupling with **20** with **10** or **27** gave the tetra- (**28**) and penta-saccharide derivative **29**, respectively. In an analogous manner, each reaction of **22** with **10** or **27**, **24** with **10** or **27**, and of **26** with **10** afforded the hexa- (**30**), hepta- (**31**), octa- (**32**), nona- (**33**), and deca-saccharide derivative **34**, respectively. *O*-Deacylation of **28**, **29**, **30**, **31**, **32**, **33**, and **34** provided the corresponding benzyl β-glycosides **35**, **36**, **37**, **38**, **39**, **40**, and **41**, respectively; all the compounds being obtained in crystalline form. Catalytic hydrogenolysis (Pd–C) of **35**, **36**, **37**, **38**, **39**, **40**, and **41**, furnished **3**, **4**, **5**, **6**, **7**, **8**, and **9**, respectively, which were homogeneous by HPLC. The physical properties of **3**–**6** agreed with those reported [2–4,9]. The ^{13}C NMR spectra of **3** and **4** were identical to those reported [9,20], and those of **5**–**9** were consistent with the structures assigned.



	n	m		n	m
28	1	1	**32**	5	1
29	1	2	**33**	5	2
30	3	1	**34**	7	1
31	3	2			



	n		n
35	2	**39**	6
36	3	**40**	7
37	4	**41**	8
38	5		

3. Experimental

General methods.—Unless stated otherwise, these were as described [12]. Optical rotations were measured at 25°C. NMR spectra (^{1}H at 90 MHz, ^{13}C at 22.6 MHz) were recorded with a Hitachi R-90H spectrometer for solutions in $CDCl_3$ (internal Me_4Si) or D_2O (internal sodium 4,4-dimethyl-4-silapentanoate-d_6). ^{1}H NMR spectra of compounds **13** and **18** were recorded with a Bruker DMX-500 spectrometer (500 MHz) for solutions in $CDCl_3$ (internal Me_4Si), and the 2D ^{1}H–^{1}H homonuclear COSY experiments were performed to obtain proton assignments. HPLC was performed at 20°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 69:31 (v/v)

MeCN–H_2O as eluent. Retention times (t_R) of **3–9** are given relative to that of D-xylose.

Methyl β-D-xylopyranosyl-(1 → 4)-1-thio-β-D-xylopyranoside (**11**).—A solution of **10** [12] (40.5 g) in dry MeOH (300 mL) was treated with methanolic M NaOMe (2 mL). The mixture was kept for 2 h at room temperature, made neutral with Amberlite IR-120 (H^+) resin, filtered, and concentrated. The residue was crystallized from EtOH to give **11** (22.3 g, 92%): mp 172.5–174°C; $[\alpha]_D$ −72.8° (*c* 1.3, H_2O); ^{13}C NMR (D_2O): δ 104.3 (C-1^2), 88.8 (C-1^1), 78.8, 78.1, 77.7, 75.2, 74.0, 71.7, 69.2 (C-5^1), 67.8 (C-5^2), 14.1 (SMe). Anal. Calcd for $C_{11}H_{20}O_8S$: C, 42.30; H, 6.45. Found: C, 42.36; H, 6.53.

Methyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1 → 4)-2,3-di-O-benzoyl-1-thio-β-D-xylopyranoside (**12**) *and methyl 2,3-di-O-benzoyl-4-O-chloroacetyl-β-D-xylopyranosyl-(1 → 4)-2,3-di-O-benzoyl-1-thio-β-D-xylopyranoside* (**13**).—A mixture of **11** (5.04 g, 16.1 mmol) and Bu_2SnO (4.82 g, 19.4 mmol) in MeOH (300 mL) was boiled under reflux for 2 h, during which time the solution was concentrated to half of its original volume using a Dean–Stark trap. The mixture was cooled to room temperature and concentrated to dryness. To a stirred suspension of the residue in anhyd CH_2Cl_2 (250 mL) at 0°C was added dropwise a solution of $ClCH_2COCl$ (1.41 mL, 17.7 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 30 min at 0°C, then treated with pyridine (26.0 mL, 0.32 mol), followed, dropwise with stirring, by BzCl (14 mL, 0.12 mol), and stirring was continued for a further 5 h at room temperature. The solution was washed successively with cold dil H_2SO_4, aq $NaHCO_3$, H_2O, dried, and concentrated. The residue was subjected to column chromatography (50:1 → 30:1 PhMe–EtOAc, stepwise) to give first **12** (1.48 g, 11%): mp 116–118°C (from MeOH–Me_2CO); $[\alpha]_D$ −18.5° (*c* 1.3, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 165.3–164.8 (C=O), 134.3–127.9 (Ar C), 99.7 (C-1^2), 83.8 (C-1^1), 75.55, 73.5, 70.2, 70.0, 69.7, 68.5, 66.2 (C-5^1), 60.85 (C-5^2), 12.0 (SMe). Anal. Calcd for $C_{46}H_{40}O_{13}S$: C, 66.34; H, 4.84. Found: C, 66.42; H, 4.93.

Eluted second was a mixture of **12** and **13** (1.2 g).

Eluted third was **13** (9.35 g, 72%): mp 139–140.5°C (from MeOH–Me_2CO): $[\alpha]_D$ +5.8° (*c* 1.1, $CHCl_3$); NMR ($CDCl_3$): δ_H 7.98–7.37 (m, 20 H, Ar), 5.65 (t, 1 H, $J_{3,4}$ 8.4 Hz, H-3), 5.48 (t, 1 H, $J_{3',4'}$ 7.2 Hz, H-3'), 5.345 (t, 1 H, $J_{2,3}$ 8.8 Hz, H-2), 5.22 (dd, 1 H, $J_{2',3'}$ 6.9 Hz, H-2'), 4.95 (sx, 1 H, $J_{4',5'a}$ 6.8, $J_{4',5'b}$ 4.4 Hz, H-4'), 4.86 (d, 1 H, $J_{1',2'}$ 5.3 Hz, H-1'), 4.59 (d, 1 H, $J_{1,2}$ 8.7 Hz, H-1), 4.13 (dd, 1 H, $J_{4,5b}$ 5.1, $J_{5a,5b}$ 11.8 Hz, H-5b), 4.07 (m, 1 H, H-4), 3.95 (AB q, 2 H, *J* 14.9 Hz, $ClCH_2CO$), 3.84 (dd, 1 H, $J_{5a',5'b}$ 11.9 Hz, H-5'b), 3.47 (dd, $J_{4,5a}$ 9.2 Hz, H-5a), 3.31 (dd, 1 H, H-5'a), 2.17 (s, 3 H, SMe); δ_C 166.0–164.7 (C=O), 133.4–127.9 (Ar C), 100.0 (C-1^2), 83.8 (C-1^1), 75.7, 73.4, 70.2, 69.9 (2 C), 69.8, 66.2 (C-5^1), 60.7 (C-5^2), 40.3 ($ClCH_2CO$), 12.1 (SMe). Anal. Calcd for $C_{41}H_{37}ClO_{13}S$: C, 61.15; H, 4.63. Found: C, 61.23; H, 4.69.

Benzyl 2,3-di-O-benzoyl-4-O-chloroacetyl-β-D-xylopyranosyl-(1 → 4)-2,3-di-O-benzoyl-β-D-xylopyranoside (**14**).—To a stirred mixture of **13** (3.04 g, 3.8 mmol), benzyl alcohol (0.78 mL, 7.5 mmol), and powdered 4 Å molecular sieves (3 g) in CH_2Cl_2 (50 mL) at −20°C was added NIS (0.97 g, 3.8 mmol), followed, dropwise with stirring, by a solution of silver triflate (0.15 g, 584 μmol) in PhMe (3 mL). After 10 min, the mixture was filtered through a Celite layer into iced H_2O. The filtrate was partitioned, and the organic layer was washed successively with aq $Na_2S_2O_7$, aq $NaHCO_3$, and H_2O, dried, and concentrated. Column chromatography (50:1 → 30:1

PhMe–EtOAc, stepwise) of the product gave **14** (2.75 g, 84%): mp 137–138°C (from MeOH); $[\alpha]_D$ +1.5° (*c* 1.1, $CHCl_3$); NMR ($CDCl_3$): δ 166.0–164.7 (C=O), 136.7–126.8 (Ar C), 99.9 and 99.2 (C-1^1,1^2), 75.5, 71.9, 71.0, 70.2 (2 C), 69.9, 69.7, 62.2 and 60.5 (C-5^1,5^2), 40.3 ($ClCH_2CO$). Anal. Calcd for $C_{47}H_{41}ClO_{14}$: C, 65.24; H, 4.78. Found: C, 65.30; H, 4.88.

*Benzyl 2,3-di-*O*-benzoyl-β-*D*-xylopyranosyl-(1 → 4)-2,3-di-*O*-benzoyl-β-*D*-xylopyranoside* (**15**).—A mixture of **14** (2.03 g, 2.3 mmol) and $(NH_2)_2C=S$ (0.89 g, 11.6 mmol) in MeOH (30 mL) and CH_2Cl_2 (5 mL) was boiled under reflux for 4 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 (10:1 PhMe–EtOAc) of the product afforded **15** (1.70 g, 92%): mp 162–164°C (from MeOH); $[\alpha]_D$ +15.2° (*c* 1.0, $CHCl_3$); NMR ($CDCl_3$): δ 166.6–164.8 (C=O), 136.7–127.6 (Ar C), 100.9 and 99.3 (C-1^1,1^2), 76.0, 75.2, 72.2, 71.1, 70.85, 70.3, 68.1, 64.4 and 62.6 (C-5^1,5^2). Anal. Calcd for $C_{45}H_{40}O_{13}$: C, 68.52; H, 5.11. Found: C, 68.61; H, 5.08.

*Methyl 2,3,4-tri-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)-2,3-di-*O*-(4-methylbenzoyl)-1-thio-β-*D*-xylopyranoside* (**17**) *and methyl 4-*O*-chloroacetyl-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)-2,3-di-*O*-(4-methylbenzoyl)-1-thio-β-*D*-xylopyranoside* (**18**).—Compound **11** (5.0 g, 16 mmol) was treated with Bu_2SnO (4.78 g, 19.2 mmol) in MeOH (300 mL), followed by $ClCH_2COCl$ (1.40 mL, 17.6 mmol) in CH_2Cl_2, and then with pyridine (26.0 mL) and 4-methylbenzoyl chloride (16.9 mL, 0.13 mol), as described for the preparation of **12** and **13**. Column chromatography (100:1 → 30:1 PhMe–EtOAc, stepwise) of the product gave **17** (1.45 g, 10%) and **18** (9.65 g, 70%).

Compound **17** had mp 131–133°C (from MeOH–Me_2CO): $[\alpha]_D$ +4.8° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 165.2–162.3 (C=O), 145.3–126.2 (Ar C), 100.0 (C-1^2), 83.9 (C-1^1), 75.7, 73.4, 70.2, 69.8 (2 C), 68.6, 66.5 (C-5^1), 61.1 (C-5^2), 21.6 (aryl CH_3), 11.95 (SMe). Anal. Calcd for $C_{51}H_{50}O_{13}S$: C, 67.84; H, 5.58. Found: C, 67.92; H, 5.62.

Compound **18** had mp 165.5–166.5°C (from MeOH): $[\alpha]_D$ +37.9° (*c* 1.1, $CHCl_3$); NMR ($CDCl_3$): δ_H 7.88–7.16 (m, 16 H, Ar), 5.61 (t, 1 H, $J_{3,4}$ 8.5 Hz, H-3), 5.43 (t, 1 H, $J_{3',4'}$ 7.0 Hz, H-3′), 5.31 (t, 1 H, $J_{2,3}$ 8.7 Hz, H-2), 5.175 (dd, 1 H, $J_{2',3'}$ 7.05 Hz, H-2′), 4.92 (sx, 1 H, $J_{4',5'a}$ 8.9, $J_{4',5'b}$ 6.6 Hz, H-4′), 4.84 (d, 1 H, $J_{1',2'}$ 5.15 Hz, H-1′), 4.55 (d, 1 H, $J_{1,2}$ 8.8 Hz, H-1), 4.11 (dd, 1 H, $J_{4,5b}$ 5.1, $J_{5a,5b}$ 11.8 Hz, H-5b), 4.045 (m, 1 H, H-4), 3.96 (AB q, 2 H, *J* 14.9 Hz, $ClCH_2CO$), 3.86 (dd, 1 H, $J_{5a',5'b}$ 12.5 Hz, H-5′b), 3.44 (dd, $J_{4,5a}$ 9.4 Hz, H-5a), 3.30 (dd, 1 H, H-5′a), 2.39 and 2.37 (2 s, each 12 H, 4 aryl CH_3), 2.16 (s, 3 H, SMe); δ_C 166.0–162.3 (C=O), 145.1–126.4 (Ar C), 100.0 (C-1^2), 83.9 (C-1^1), 75.8, 75.6, 73.3, 69.8 (3 C), 66.4 (C-5^1), 60.6 (C-5^2), 40.4 ($ClCH_2CO$), 21.6 (aryl CH_3), 12.0 (SMe). Anal. Calcd for $C_{45}H_{45}ClO_{13}S$: C, 62.75; H, 5.27. Found: C, 62.80; H, 5.20.

*Benzyl 4-*O*-chloroacetyl-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranoside* (**19**).—A mixture of **18** (8.20 g, 9.5 mmol), benzyl alcohol (1.97 mL, 19 mmol), NIS (2.12 g, 9.5 mmol), and powdered 4A molecular seives (5 g) in CH_2Cl_2 (200 mL) was treated with a solution of silver triflate (0.49 g, 1.9 mmol) in PhMe (10 mL), and processed as described for the preparation of

14. Column chromatography (50:1 → 25:1, PhMe–EtOAc, stepwise) of the residue afforded **19** (7.28 g, 83%): mp 115–117°C (from MeOH–Me_2CO); $[\alpha]_D$ +32.9° (*c* 1.3, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 165.1–164.7 (C=O), 144.1–126.0 (Ar C), 99.8 and 99.3 (C-1^1,1^2) 75.55, 71.9, 70.9, 69.8 (4 C), 62.4 and 60.5 (C-5^1,5^2), 40.4 (Cl*C*H_2CO), 21.6 (Ar CH_3). Anal. Calcd for $C_{51}H_{49}ClO_{14}$: C, 66.48; H, 5.36. Found: C, 66.59; H, 5.38.

*Benzyl 2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranoside* (**20**).—A mixture of **19** (8.52 g) and $(NH_2)_2C=S$ (3.52 g) in MeOH (150 mL) and CH_2Cl_2 (50 mL) was boiled under reflux for 5 h and processed as described for **14**. Column chromatography (10:1 PhMe–EtOAc) of the residue gave **20** (7.11 g, 91%): mp 112–113°C (from EtOH); $[\alpha]_D$ +60.1° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 165.7–165.1 (C=O), 143.85–126.4 (Ar C), 100.95 and 99.45 (C-1^1,1^2), 76.1, 75.2, 72.2, 70.7 (2 C), 70.15, 68.2, 64.4 and 62.8 (C-5^1,5^2), 21.5 (Ar CH_3). Anal. Calcd for $C_{49}H_{48}O_{13}$: C, 69.66; H, 5.73. Found: C, 69.79; H, 5.80.

*Benzyl 4-*O*-chloroacetyl-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)-bis[2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)]-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranoside* (**21**).—The product obtained by reaction of **20** (4.98 g, 5.9 mmol) with **18** (6.09 g, 7.1 mmol), as described for the preparation of **14**, was subjected to column chromatography (20:1 PhMe–EtOAc) to afford **21** (7.91 g, 81%): mp 205–207°C (from MeOH–CH_2Cl_2); $[\alpha]_D$ +23.2° (*c* 1.2, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 166.0–164.85 (C=O), 144.0–125.95 (Ar C), 100.5, 100.1, and 99.3 (C-1^1,1^2,1^3,1^4), 75.55, 74.7, 71.6, 71.2, 70.1, 69.7, and 62.5, 62.0, and 60.4 (C-5^1,5^2,5^3,5^4), 40.4 (Cl*C*H_2CO), 21.5 (Ar CH_3). Anal. Calcd for $C_{93}H_{89}ClO_{26}$: C, 67.37; H, 5.41. Found: C, 67.40; H, 5.34.

*Benzyl 2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)-bis[2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)]-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranoside* (**22**).—*O*-Dechloroacetylation of **21** (7.05 g), as described for **14**, followed by column chromatography (10:1 PhMe–EtOAc) of the product, gave **22** (6.19 g, 92%): mp 215–217°C (from EtOH); $[\alpha]_D$ +35.5° (*c* 1.4, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 166.8–164.85 (C=O), 143.5–126.0 (Ar C), 100.4 and 99.3 (C-1^1,1^2,1^3,1^4), 75.5, 75.4, 74.7, 71.8, 71.2, 70.9, 70.3, 70.2, 68.2, 64.2 and 62.2 (C-5^1,5^2,5^3,5^4), 21.55 (Ar CH_3). Anal. Calcd for $C_{91}H_{88}O_{25}$: C, 69.10; H, 5.61. Found: C, 69.24; H, 5.53.

*Benzyl 4-*O*-chloroacetyl-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)-tetrakis[2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)]-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranoside* (**23**).—The product obtained by reaction of **22** (4.70 g, 3.0 mmol) with **18** (3.07 g, 3.6 mmol), as described for the preparation of **14**, was subjected to column chromatography (20:1 PhMe–EtOAc) to afford **23** (5.70 g, 80%): mp 252–254°C (from MeOH–CH_2Cl_2); $[\alpha]_D$ +20.1° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 166.0–165.1 (C=O), 143.6–126.65 (Ar C), 100.0, and 99.3 (C-1^1,1^2,1^3,1^4,1^5,1^6), 75.55, 74.6, 71.5, 71.1, 69.7, 61.95 and 60.4 (C-5^1,5^2,5^3,5^4,5^5,5^6), 40.4 (Cl*C*H_2CO), 21.6 (Ar CH_3). Anal. Calcd for $C_{135}H_{129}ClO_{38}$: C, 67.71; H, 5.43. Found: C, 67.60; H, 5.29.

*Benzyl 2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)-tetrakis[2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)]-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranoside* (**24**).—*O*-Dechloroacetylation of **23** (5.17 g), as described for **14**, followed by column chromatography (8:1 PhMe–EtOAc) of the product, gave **24** (4.40 g, 88%): mp

256–258°C (from EtOH); $[\alpha]_D$ +26.6° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 166.8–164.6 (C=O), 144.1–126.0 (Ar C), 100.5, 100.3, 99.9, and 99.3 (C-1^1,1^2,1^3,1^4,1^5,1^6), 75.4, 75.1, 74.5, 71.8, 71.5, 71.2, 71.0, 70.85, 70.3, 70.2, 68.2, and 64.2, 62.4, and 62.0 (C-5^1,5^2,5^3,5^4,5^5,5^6), 21.5 (Ar CH_3). Anal. Calcd for $C_{133}H_{128}O_{37}$: C, 68.90; H, 5.57. Found: C, 68.74; H, 5.47.

Benzyl 4-O-chloroacetyl-2,3-di-O-(4-methylbenzoyl)-β-D-xylopyranosyl-(1 → 4)-hexakis[2,3-di-O-(4-methylbenzoyl)-β-D-xylopyranosyl-(1 → 4)]-2,3-di-O-(4-methylbenzoyl)-β-D-xylopyranoside (**25**).—The product obtained by reaction of **24** (2.09 g, 0.9 mmol) with **18** (0.93 g, 1.1 mmol), as described for the preparation of **14**, was subjected to column chromatography (15:1 PhMe–EtOAc) to afford **25** (2.20 g, 78%): mp 256–258°C (from MeOH–CH_2Cl_2); $[\alpha]_D$ +26.5° (*c* 1.2, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 166.0–164.75 (C=O), 144.0–126.5 (Ar C), 100.5, 100.0, and 99.3 (C-1^1,1^2,1^3,1^4,1^5,1^6,1^7,1^8), 75.55, 74.5, 71.8, 71.5, 71.0, 70.1, 69.1, 61.95 (C-5^1,5^2,5^3,5^4,5^5,5^6,5^7,5^8), 40.3 (Cl*C*H_2CO), 21.6 (Ar CH_3). Anal. Calcd for $C_{177}H_{169}ClO_{50}$: C, 67.89; H, 5.44. Found: C, 68.01; H, 5.58.

Benzyl 2,3-di-O-(4-methylbenzoyl)-β-D-xylopyranosyl-(1 → 4)-hexakis[2,3-di-O-(4-methylbenzoyl)-β-D-xylopyranosyl)-(1 → 4)]-2,3-di-O-(4-methylbenzoyl)-β-D-xylopyranoside (**26**).—*O*-Dechloroacetylation of **25** (1.33 g), as described for **14**, followed by column chromatography (8:1 PhMe–EtOAc) of the product, gave **26** (1.07 g, 82%): mp 270–272°C (from MeOH–Me_2CO); $[\alpha]_D$ +23.6° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 166.8–164.7 (C=O), 144.1–126.0 (Ar C), 100.4, 100.25, 100.2, 100.0, and 99.3 (C-1^1,1^2,1^3,1^4,1^5,1^6,1^7,1^8), 75.4, 75.1, 74.9, 74.45, 71.8, 71.5, 71.25, 71.0, 70.4, 70.1, 68.2, and 64.3, 64.2, 62.4, and 61.95 (C-5^1,5^2,5^3,5^4,5^5,5^6,5^7,5^8), 21.55 (Ar CH_3). Anal. Calcd for $C_{175}H_{168}O_{49}$: C, 68.80; H, 5.54. Found: C, 68.97; H, 5.43.

Benzyl 2,3,4-tri-O-acetyl-β-D-xylopyranosyl-(1 → 4)-2,3-di-O-acetyl-β-D-xylopyranosyl-(1 → 4)-2,3-di-O-(4-methylbenzoyl)-β-D-xylopyranosyl-(1 → 4)-2,3-di-O-(4-methylbenzoyl)-β-D-xylopyranoside (**28**).—A mixture of **10** (1.04 g, 2 mmol), **20** (1.40 g, 1.7 mmol), NIS (0.44 g, 2 mmol), and powdered 4A molecular sieves in CH_2Cl_2 (25 mL) was treated with a solution of silver triflate (102 mg, 389 μmol) in PhMe (3 mL) as described for the preparation of **14**. Column chromatography (6:1 PhMe–EtOAc) of the product gave **28** (1.84 g, 84%): mp 231–233.5°C (from MeOH–CH_2Cl_2); $[\alpha]_D$ −13.3° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.6–165.0 (C=O), 143.7–126.5 (Ar C), 100.7, 100.5, 99.7, and 99.4 (C-1^1,1^2,1^3,1^4), 75.9, 75.1, 74.4, 72.1, 71.8, 71.6, 70.9, 70.6, 70.4, 70.15, 68.35, and 62.6, 62.1, and 61.6 (C-5^1,5^2,5^3,5^4), 21.6 (Ar CH_3), 20.6 and 20.4 (CO*C*H_3). Anal. Calcd for $C_{69}H_{74}O_{26}$: C, 62.82; H, 5.65. Found: C, 62.77; H, 5.60.

Similar glycosylation of **20** with **27**, **22** with **10** or **27**, **24** with **10** or **27**, and of **26** with **10**, followed by column chromatography of each product with the mixture of appropriately adjusted polarity of PhMe and EtOAc, gave the following compounds **29**–**34**.

Benzyl 2,3,4-tri-O-acetyl-β-D-xylopyranosyl-(1 → 4)-bis[2,3-di-O-acetyl-β-D-xylopyranosyl]-(1 → 4)-2,3-di-O-(4-methylbenzoyl)-β-D-xylopyranosyl-(1 → 4)-2,3-di-O-(4-methylbenzoyl)-β-D-xylopyranoside (**29**).—86%: mp 264–265.5°C (from MeOH–CH_2Cl_2); $[\alpha]_D$ −27.1° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.6–164.85 (C=O), 143.75–126.5 (Ar C), 100.8, 100.4, 100.3, and 99.4 (C-1^1,1^2,1^3,1^4,1^5), 76.0, 74.9, 74.8,

74.2, 72.1, 72.0, 71.7, 70.9, 70.4, 70.2, 68.3, and 62.6, 62.1, and 61.5 (C-5^1,5^2,5^3,5^4,5^5), 21.6 (Ar CH_3), 20.7 and 20.4 ($COCH_3$). Anal. Calcd for $C_{78}H_{86}O_{32}$: C, 61.01; H, 5.65. Found: C, 61.17; H, 5.56.

*Benzyl 2,3,4-tri-*O*-acetyl-β-*D*-xylopyranosyl-(1 → 4)-2,3-di-*O*-acetyl-β-*D*-xylopyranosyl-(1 → 4)-tris[2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)]-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranoside* (**30**).—81%: mp 211–213.5°C (from MeOH–Me_2CO); $[\alpha]_D$ −5.0° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.7–164.8 (C=O), 143.7–126.5 (Ar C), 100.4, 100.3, 100.1, 99.7, and 99.3 (C-1^1,1^2,1^3,1^4,1^5,1^6), 75.0, 74.7, 74.6, 74.3, 71.8, 71.4, 71.3, 71.2, 70.8, 70.4, 70.2, 68.3, and 62.5, 62.4, 62.0, 61.7, and 61.6 (C-5^1,5^2,5^3,5^4,5^5,5^6), 21.6 (Ar CH_3), 20.6 and 20.4 ($COCH_3$). Anal. Calcd for $C_{111}H_{114}O_{38}$: C, 68.84; H, 5.59. Found: C, 68.96; H, 5.69.

*Benzyl 2,3,4-tri-*O*-acetyl-β-*D*-xylopyranosyl)-(1 → 4)-bis[2,3-di-*O*-acetyl-β-*D*-xylopyranosyl-(1 → 4)]-tris[2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)]-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranoside* (**31**).—78%: mp 188.5–191°C (from MeOH–CH_2Cl_2); $[\alpha]_D$ −15.1° (*c* 1.3, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.6–164.8 (C=O), 143.6–126.7 (Ar C), 100.3, 99.9, and 99.4 (C-1^1,1^2,1^3,1^4,1^5,1^6,1^7), 75.1, 74.8, 71.8, 71.7, 71.5, 70.9, 70.7, 70.4, 70.3, 68.3, and 62.6, 62.4, 62.1, and 62.0 (C-5^1,5^2,5^3,5^4,5^5,5^6,5^7), 21.6 (Ar CH_3), 20.6 ($COCH_3$). Anal. Calcd for $C_{120}H_{126}O_{44}$: C, 63.43; H, 5.59. Found: C, 63.53; H, 5.66.

*Benzyl 2,3,4-tri-*O*-acetyl-β-*D*-xylopyranosyl)-(1 → 4)-2,3-di-*O*-acetyl-β-*D*-xylopyranosyl)-(1 → 4)-pentakis[2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)]-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranoside* (**32**).—80%: mp 236–238°C (from MeOH–CH_2Cl_2); $[\alpha]_D$ −0.7° (*c* 1.2, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.6–164.8 (C=O), 143.6–126.7 (Ar C), 100.5, 100.4, 100.2, 100.0, 99.6, and 99.3 (C-1^1,1^2,1^3,1^4,1^5,1^6,1^7,1^8), 75.4, 74.9, 74.5, 74.3, 71.7, 71.55, 71.2, 71.0, 70.9, 70.6, 70.3, 70.1, 68.3, and 62.5, 62.4, 62.0, 61.95, and 61.7 (C-5^1,5^2,5^3,5^4,5^5,5^6,5^7,5^8), 21.6 (Ar CH_3), 20.4 ($COCH_3$). Anal. Calcd for $C_{153}H_{154}O_{50}$: C, 65.80; H, 5.56. Found: C, 65.75; H, 5.64.

*Benzyl 2,3,4-tri-*O*-acetyl-β-*D*-xylopyranosyl-(1 → 4)-bis[2,3-di-*O*-acetyl-β-*D*-xylopyranosyl-(1 → 4)]-pentakis[2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)]-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranoside* (**33**).—80%: mp 241.5–243°C (from MeOH–CH_2Cl_2); $[\alpha]_D$ −8.4° (*c* 1.3, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.5–164.7 (C=O), 143.6–126.5 (Ar C), 100.3, 100.1, 100.0, and 99.4 (C-1^1,1^2,1^3,1^4,1^5,1^6,1^7,1^8,1^9), 74.7, 74.5, 74.3, 74.2, 71.6, 71.0, 70.4, 68.3, and 62.5 and 61.5 (C-5^1,5^2,5^3,5^4,5^5,5^6,5^7,5^8,5^9), 21.6 (Ar CH_3), 20.6 ($COCH_3$). Anal. Calcd for $C_{162}H_{166}O_{56}$: C, 64.66; H, 5.56. Found: C, 64.75; H, 5.69.

*Benzyl 2,3,4-tri-*O*-acetyl-β-*D*-xylopyranosyl-(1 → 4)-2,3-di-*O*-acetyl-β-*D*-xylopyranosyl-(1 → 4)-heptakis[2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranosyl-(1 → 4)]-2,3-di-*O*-(4-methylbenzoyl)-β-*D*-xylopyranoside* (**34**).—82%: mp 262.5–264°C (from MeOH–CH_2Cl_2); $[\alpha]_D$ +1.5° (*c* 1.0, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 169.6–164.7 (C=O), 143.6–126.5 (Ar C), 100.4, 100.3, 100.0, 99.6, and 99.3 (C-1^1,1^2,1^3,1^4,1^5,1^6,1^7,1^8,1^9,1^{10}), 74.9, 74.5, 71.7, 71.5, 71.3, 71.0, 70.6, 70.4, 70.15, 68.3, and 62.5, 62.0, 61.7, and 61.6 (C-5^1,5^2,5^3,5^4,5^5,5^6,5^7,5^8,5^9,5^{10}), 21.6 (Ar CH_3), 20.6, 20.55, and 20.4 ($COCH_3$). Anal. Calcd for $C_{195}H_{194}O_{62}$: C, 66.36; H, 5.54. Found: C, 66.46; H, 5.60.

Benzyl β-D-xylopyranosyl-(1 → 4)-bis[β-D-xylopyranosyl-(1 → 4)]-β-D-xylopyranoside (**35**).—A solution of **28** (1.61 g) in MeOH (20 mL) and CH_2Cl_2 (5 mL) was treated with methanolic M NaOMe (0.5 mL) and processed as described for the preparation of **11**. The residue was triturated with Et_2O, and the resulting solid was recrystallized from MeOH to afford **35** (0.71 g, 91%): mp 186–188°C; $[\alpha]_D$ −88.9° (*c* 1.1, H_2O); ^{13}C NMR (D_2O): δ 104.5 (C-1^1), 100.4 (C-1^4), 104.2 (C-1^2,1^3), 78.9 (C-4^1,4^2,4^3), 78.2 (C-3^4), 76.25 (C-3^1,3^2,3^3), 75.2 (C-2^1,2^2,2^3,2^4), 71.7 (C-4^4), 67.8 (C-5^4), 65.5 (C-5^1,5^2,5^3). Anal. Calcd for $C_{27}H_{40}O_{17}$: C, 50.94; H, 6.63. Found: C, 50.87; H, 6.58.

Similar *O*-deacylation of **29–34** afforded the following compounds **36–41**.

Benzyl β-D-xylopyranosyl-(1 → 4)-tris[β-D-xylopyranosyl-(1 → 4)]-β-D-xylopyranoside (**36**).—90%: mp 220–221.5°C (aq MeOH); $[\alpha]_D$ −91.2° (*c* 1.1, H_2O); ^{13}C NMR (D_2O): δ 104.6 (C-1^1), 104.4 (C-1^5), 104.2 (C-1^2,1^3,1^4), 78.9 (C-4^1,4^2,4^3,4^4), 78.2 (C-3^5), 76.2 (C-3^1,3^2,3^3,3^4), 75.2 (C-2^1,2^2,2^3,2^4,2^5), 71.7 (C-4^5), 67.8 (C-5^5), 65.55 (C-5^1,5^2,5^3,5^4). Anal. Calcd for $C_{32}H_{48}O_{21}$: C, 50.00; H, 6.29. Found: C, 49.90; H, 6.35.

Benzyl β-D-xylopyranosyl-(1 → 4)-tetrakis[β-D-xylopyranosyl-(1 → 4)]-β-D-xylopyranoside (**37**).—86%: mp 255–258.5°C (aq MeOH); $[\alpha]_D$ −92.8° (*c* 1.2, H_2O); ^{13}C NMR (D_2O): δ 104.15 (C-1^1,1^2,1^3,1^4,1^5,1^6), 78.9 (C-4^1,4^2,4^3,4^4,4^5), 78.1 (C-3^6), 76.2 (C-3^1,3^2,3^3,3^4,3^5), 75.2 (C-2^1,2^2,2^3,2^4,2^5,2^6), 71.7 (C-4^6), 67.7 (C-5^6), 65.5 (C-5^1,5^2,5^3,5^4,5^5). Anal. Calcd for $C_{37}H_{56}O_{25}$: C, 49.33; H, 6.27. Found: C, 49.43; H, 6.21.

Benzyl β-D-xylopyranosyl-(1 → 4)-pentakis[β-D-xylopyranosyl-(1 → 4)]-β-D-xylopyranoside (**38**).—87%: mp 297–300°C (aq MeOH); $[\alpha]_D$ −94.7° (*c* 1.1, H_2O); ^{13}C NMR (D_2O): δ 104.2 (C-1^1,1^2,1^3,1^4,1^5,1^6,1^7), 79.0 (C-4^1,4^2,4^3,4^4,4^5,4^6), 78.2 (C-3^7), 76.3 (C-3^1,3^2,3^3,3^4,3^5,3^6), 75.3 (C-2^1,2^2,2^3,2^4,2^5,2^6,2^7), 71.8 (C-4^7), 67.8 (C-5^7), 65.6 (C-5^1,5^2,5^3,5^4,5^5,5^6). Anal. Calcd for $C_{42}H_{64}O_{29}$: C, 48.83; H, 6.25. Found: C, 48.89; H, 6.31.

Benzyl β-D-xylopyranosyl-(1 → 4)-hexakis[β-D-xylopyranosyl-(1 → 4)]-β-D-xylopyranoside (**39**).—85%: mp 311–313°C (aq MeOH); $[\alpha]_D$ −96.1° (*c* 0.6, H_2O); ^{13}C NMR (D_2O): δ 104.2 (C-1^2,1^3,1^4,1^5,1^6,1^7,1^8), 79.0 (C-4^1,4^2,4^3,4^4,4^5,4^6,4^7), 78.2 (C-3^8), 76.3 (C-3^1,3^2,3^3,3^4,3^5,3^6,3^7), 75.3 (C-2^1,2^2,2^3,2^4,2^5,2^6,2^7,2^8), 71.8 (C-4^8), 67.8 (C-5^8), 65.6 (C-5^1,5^2,5^3,5^4,5^5,5^6,5^7). Anal. Calcd for $C_{47}H_{72}O_{33}$: C, 48.45; H, 6.23. Found: C, 48.61; H, 6.34.

Benzyl β-D-xylopyranosyl-(1 → 4)-heptakis[β-D-xylopyranosyl-(1 → 4)]-β-D-xylopyranoside (**40**).—84%: mp 325–327°C (aq MeOH); $[\alpha]_D$ −96.8° (*c* 0.7, H_2O); ^{13}C NMR (D_2O): δ 104.3 (C-1^1,1^2,1^3,1^4,1^5,1^6,1^7,1^8,1^9), 79.0 (C-4^1,4^2,4^3,4^4,4^5,4^6,4^7,4^8), 78.3 (C-3^9), 76.3 (C-3^1,3^2,3^3,3^4,3^5,3^6,3^7,3^8), 75.4 (C-2^1,2^2,2^3,2^4,2^5,2^6,2^7,2^8,2^9), 71.9 (C-4^9), 67.9 (C-5^9), 65.7 (C-5^1,5^2,5^3,5^4,5^5,5^6,5^7,5^8). Anal. Calcd for $C_{52}H_{80}O_{37}$: C, 48.15; H, 6.22. Found: C, 48.24; H, 6.28.

Benzyl β-D-xylopyranosyl-(1 → 4)-octakis[β-D-xylopyranosyl-(1 → 4)]-β-D-xylopyranoside (**41**).—87%: mp 310–314°C (aq MeOH); $[\alpha]_D$ −97.6° (*c* 0.6, H_2O); ^{13}C NMR (D_2O): δ 104.4 (C-1^1,1^2,1^3,1^4,1^5,1^6,1^7,1^8,1^9,1^{10}), 79.1 (C-4^1,4^2,4^3,4^4,4^5,4^6,4^7,4^8,4^9), 78.4 (C-3^{10}), 76.4 (C-3^1,3^2,3^3,3^4,3^5,3^6,3^7,3^8,3^9), 75.4 (C-2^1,2^2,2^3,2^4,2^5,2^6,2^7,2^8,2^9,2^{10}), 71.9 (C-4^{10}), 68.0 (C-5^{10}), 65.7 (C-

$5^1,5^2,5^3,5^4,5^5,5^6,5^7,5^8,5^9$). Anal. Calcd for $C_{57}H_{88}O_{41}$: C, 47.89; H, 6.21. Found: C, 48.09; H, 6.17.

β-D-Xylopyranosyl-(1 → 4)-bis[β-D-xylopyranosyl-(1 → 4)]-D-xylopyranose (**3**).—A solution of **35** (0.53 g) in H_2O (30 mL) was hydrogenated in the presence of 10% Pd–C (0.1 g) at normal pressure overnight at room temperature. The insoluble material was collected on a Celite pad and washed with hot H_2O, and the combined filtrate and washings were concentrated. The residue was crystallized from MeOH to give **3** (0.41 g, 91%): mp 220–222°C; $[\alpha]_D$ −59.1° (equil; *c* 1.0, H_2O); t_R 1.47; lit. mp 219–220°C, $[\alpha]_D$ −60.0° [2]; mp 223.5–225.5°C, $[\alpha]_D$ −58° [9].

Similar catalytic hydrogenolysis of **36–41** gave the following compounds **4–9**.

β-D-Xylopyranosyl-(1 → 4)-tris[β-D-xylopyranosyl-(1 → 4)]-D-xylopyranose (**4**).—90%: mp 231–233°C; $[\alpha]_D$ −70.5° (*c* 1.1, H_2O); t_R 1.70; lit. mp 231–232°C, $[\alpha]_D$ −66.0° [2]; mp 231–233°C, $[\alpha]_D$ −71.4° [9].

β-D-Xylopyranosyl-(1 → 4)-tetrakis[β-D-xylopyranosyl-(1 → 4)]-D-xylopyranose (**5**).—88%: mp 231–233°C; $[\alpha]_D$ −73.1° (*c* 1, H_2O); lit. mp 236–237°C, $[\alpha]_D$ −72.8° [2]; $[\alpha]_D$ −71.4° [4]; t_R 1.98; ^{13}C NMR (D_2O): δ 104.2 (C-1^2,1^3,1^4,1^5,1^6), 99.1 (C-$1^1\beta$), 94.6 (C-$1^1\alpha$), 79.0 (C-4^1,4^2,4^3,4^4,4^5), 78.2 (C-3^6), 76.5 (C-$3^1\beta$, C-$2^1\beta$), 76.25 (C-3^2,3^3,3^4,3^5) 75.3 (C-2^2,2^3,2^4,2^5,2^6), 74.0 and 73.6 (C-$3^1\alpha$, C-$2^1\alpha$), 71.8 (C-4^6), 67.8 (C-5^6), 65.6 (C-$5^1\beta$, 5^2,5^3,5^4,5^5), 61.5 (C-$5^1\alpha$).

β-D-Xylopyranosyl-(1 → 4)-pentakis[β-D-xylopyranosyl-(1 → 4)]-D-xylopyranose (**6**).—89%: mp 241–243°C (from aq EtOH) after changing to brown at 235°C; $[\alpha]_D$ −75.1° (*c* 1, H_2O); lit. mp 240–242°C, $[\alpha]_D$ −74° [2]; $[\alpha]_D$ −71.3° [4]; t_R 2.33; ^{13}C NMR (D_2O): δ 104.3 (C-1^2,1^3,1^4,1^5,1^6,1^7), 99.1 (C-$1^1\beta$), 94.6 (C-$1^1\alpha$), 79.0 (C-4^1,4^2,4^3,4^4,4^5,4^6), 78.2 (C-3^7), 76.3 (C-$3^1\beta$, C-$2^1\beta$, C-3^2,3^3,3^4,3^5,3^6) 75.3 (C-2^2,2^3,2^4,2^5,2^6,2^7), 74.1 and 73.6 (C-$3^1\alpha$, C-$2^1\alpha$), 71.8 (C-4^7), 67.8 (C-5^7), 65.6 (C-$5^1\beta$, 5^2,5^3,5^4,5^5,5^6), 61.55 (C-$5^1\alpha$).

β-D-Xylopyranosyl-(1 → 4)-hexakis[β-D-xylopyranosyl-(1 → 4)]-D-xylopyranose (**7**).—87%: mp 276–278°C (from aq MeOH) after changing to brown at 240°C; $[\alpha]_D$ −81.6° (*c* 0.6, H_2O); t_R 2.75; ^{13}C NMR (D_2O): δ 104.3 (C-1^2,1^3,1^4,1^5,1^6,1^7,1^8), 99.15 (C-$1^1\beta$), 94.6 (C-$1^1\alpha$), 79.0 (C-4^1,4^2,4^3,4^4,4^5,4^6,4^7), 78.3 (C-3^8), 76.55 (C-$3^1\beta$, C-$2^1\beta$), 76.3 (C-3^2,3^3,3^4,3^5,3^6,3^7), 75.3 (C-2^2,2^3,2^4,2^5,2^6,2^7,2^8), 74.0 and 73.6 (C-$3^1\alpha$, C-$2^1\alpha$), 71.8 (C-4^8), 67.9 (C-5^8), 65.6 (C-$5^1\beta$, 5^2,5^3,5^4,5^5,5^6,5^7), 61.55 (C-$5^1\alpha$). Anal. Calcd for $C_{40}H_{66}O_{33}$: C, 44.70; H, 6.19. Found: C, 44.60; H, 6.26.

β-D-Xylopyranosyl-(1 → 4)-heptakis[β-D-xylopyranosyl-(1 → 4)]-D-xylopyranose (**8**).—85%: mp 279–282°C (from aq MeOH) after changing to brown at 245°C; $[\alpha]_D$ −83.6° (*c* 0.6, H_2O); t_R 3.22; ^{13}C NMR (D_2O): δ 104.3 (C-1^2,1^3,1^4,1^5,1^6,1^7,1^8,1^9), 99.2 (C-$1^1\beta$), 94.7 (C-$1^1\alpha$), 79.1 (C-4^1,4^2,4^3,4^4,4^5,4^6,4^7,4^8), 78.3 (C-3^9), 76.6 (C-$3^1\beta$, C-$2^1\beta$), 76.4 (C-3^2,3^3,3^4,3^5,3^6,3^7,3^8), 75.4 (C-2^2,2^3,2^4,2^5,2^6,2^7,2^8,2^9), 74.1 and 73.7 (C-$3^1\alpha$, C-$2^1\alpha$), 71.9 (C-4^9), 67.9 (C-5^9), 65.7 (C-$5^1\beta$, 5^2,5^3,5^4,5^5,5^6,5^7,5^8), 61.6 (C-$5^1\alpha$). Anal. Calcd for $C_{45}H_{74}O_{37}$: C, 44.78; H, 6.18. Found: C, 44.69; H, 6.25.

β-D-Xylopyranosyl-(1 → 4)-octakis[β-D-xylopyranosyl-(1 → 4)]-D-xylopyranose (**9**).—86%: mp 294–296°C (from aq MeOH) after changing to brown at 244°C; $[\alpha]_D$ −86.3° (*c* 0.6, H_2O); t_R 3.72; ^{13}C NMR (D_2O): δ 104.4 (C-1^2,1^3,1^4,1^5,1^6,1^7,1^8,1^9,1^{10}), 99.2 (C-$1^1\beta$), 94.8 (C-$1^1\alpha$), 79.1 (C-4^1,4^2,4^3,4^4,4^5,4^6,4^7,4^8,4^9), 78.35 (C-3^{10}), 76.65 (C-$3^1\beta$, C-$2^1\beta$), 76.4 (C-3^2,3^3,3^4,3^5,3^6,3^7,3^8,3^9), 75.4 (C-2^2,2^3,2^4,2^5,2^6,2^7,2^8,2^9,2^{10}),

74.1 and 73.7 (C-3$^1\alpha$, C-2$^1\alpha$), 71.9 (C-4^{10}), 68.0 (C-5^{10}), 65.7 (C-5$^1\beta$, 5^2,5^3,5^4,5^5,5^6,5^7,5^8,5^9), 61.65 (C-5$^1\alpha$). Anal. Calcd for $C_{50}H_{82}O_{41}$: C, 44.85; H, 6.17. Found: C, 44.73; H, 6.26.

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