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Note

A facile synthesis of 4-*O*-allyl-D-xylopyranose and its use in the preparation of xylo-oligosaccharides

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4-*O*-Allyl-2,3-di-*O*-benzoyl-α-D-xylopyranosyl bromide (**8**), the D-xylopyranosyl donor for synthesis of L-serine-linked carbohydrate units in the glycopeptide linkage region of several mammalian proteoglycans, was prepared from D-arabinose in ten steps[1,2]. The most laborious step involved in the sequence[1,2] for practical preparation of 4-*O*-allyl-D-xylopyranose (**5**, precursor to **8**) appears to be the opening of the anhydro ring in benzyl 2,3-anhydro-β-D-ribopyranoside by extended treatment with concentrated alkali at high temperature.

Here we report an alternative, facile synthesis of **5**, along with **8**, starting from the commercially available methyl β-D-xylopyranoside (**1**). Also described is the preparation of xylobiose (**18**), xylotetraose (**20**), and the xylohexaose derivative **22** suitable for complete synthesis of carbohydrate chains of trehalose-containing lipooligosaccharide antigens from *Mycobacterium kansasii* [3], using **8** as the key intermediate.

Acetonation of **1** with 2-methoxypropene in *N*,*N*-dimethylformamide in the presence of a catalytic amount of methanolic hydrogen chloride, by a slight modification[4,5] of the original procedure[6], gave a mixture which, without isolation of the 2,3-*O*-isopropylidene derivative[5] **2**, was alkylated with allyl bromide–sodium hydride in *N*,*N*-dimethylformamide[7], and then treated with dilute acid in acetone. Fractional crystallization of the product provided 47% of pure methyl 4-*O*-allyl-β-D-xylopyranoside[8] (**3**). Acid hydrolysis of **3**, followed by acetylation with acetic anhydride–sodium acetate[9], gave 1,2,3-tri-*O*-acetyl-4-*O*-allyl-D-xylopyranose (**4**, 80%), which was *O*-deacetylated to afford crystalline **5** (94%). The overall yield of **5**, based on **1**, was 35%. Benzoylation of **5** gave 4-*O*-allyl-1,2,3-tri-*O*-benzoyl-D-xylopyranose (**6**, 93%), which was a mixture of the α and β anomer **7** in the ratio 1:2.4 (^{13}C-n.m.r.). Fractional crystallization of **6** afforded 54% of **7**, the m.p. (89°) of which differed significantly from that reported[1] (98°). The benzoate **6** was converted into **8** (94%) by treatment with hydrogen bromide in acetic acid.

Acetonation of ethyl 1-thio-β-D-xylopyranoside[10] (**9**) with 2-methoxypropene, as

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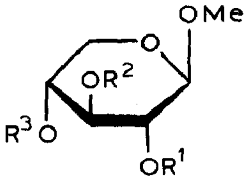
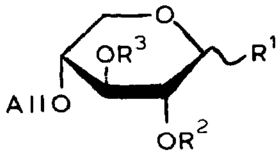
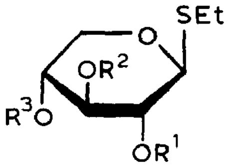
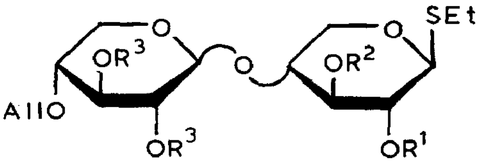


1 $R^1 = R^2 = R^3 = H$
2 $R^1, R^2 = Me_2C$; $R^3 = H$
3 $R^1 = R^2 = H$, $R^3 = All$



4 $R^1 = OAc$, $R^2 = R^3 = Ac$
5 $R^1 = OH$, $R^2 = R^3 = H$
6 $R^1 = OBz$, $R^2 = R^3 = Bz$
7 $R^1 = OBz$ (β), $R^2 = R^3 = Bz$
8 $R^1 = Br$ (α), $R^2 = R^3 = Bz$



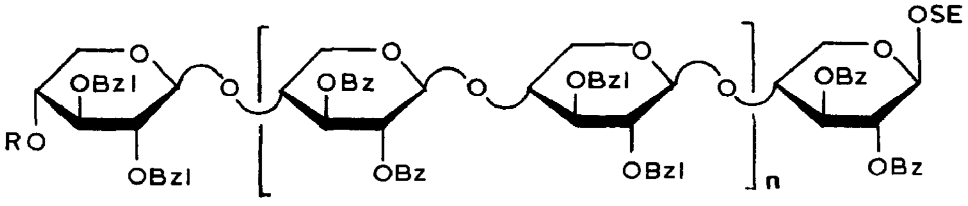


9 $R^1 = R^2 = R^3 = H$
10 $R^1, R^2 = Me_2C$; $R^3 = H$
11 $R^1 = H$; $R^2, R^3 = Me_2C$
12 $R^1, R^2 = Me_2C$; $R^3 = Ac$

13 $R^1, R^2 = Me_2C$; $R^3 = Bz$
14 $R^1, R^2 = Me_2C$; $R^3 = Bzl$
15 $R^1 = R^2 = H$, $R^3 = Bzl$
16 $R^1 = R^2 = Bz$, $R^3 = Bzl$

for **1**, gave the 2,3- (**10**) and 3,4-*O*-isopropylidene derivative **11** in 70 and 18% yields, respectively. Acetylation of **10** gave the 4-*O*-acetyl-2,3-*O*-isopropylidene derivative **12**, the ^{1}H-n.m.r. spectrum of which showed an octet for H-4 at δ 5.04, confirming[4,5] the position of the acetal group in **10**.

Condensation of **10** with **8** in toluene–dichloromethane in the presence of silver triflate and 1,1,3,3-tetramethylurea[11] afforded, after column chromatography, ethyl *O*-(4-*O*-allyl-2,3-di-*O*-benzoyl-β-D-xylopyranosyl)-(1→4)-2,3-*O*-isopropylidene-1-thio-β-D-xylopyranoside (**13**, 80%). The latter was transformed into ethyl *O*-(4-*O*-allyl-2,3-di-*O*-benzyl-β-D-xylopyranosyl)-(1→4)-2,3-di-*O*-benzoyl-1-thio-β-D-xylopyranoside (**16**) by a sequence involving *O*-debenzoylation and subsequent benzylation (→ **14**), de-*O*-isopropylidenation (→ **15**), and benzoylation. Glycosylation of **16** with 2-(trimethylsilyl)ethanol in toluene in the presence of methyl triflate and molecular sieve[12] gave 2-(trimethylsilyl)ethyl *O*-(4-*O*-allyl-2,3-di-*O*-benzyl-β-D-xylopyranosyl)-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (**17**, 92%). Isomerization of the allyl group in **17** to the propenyl ether with the Wilkinson catalyst[13] in the presence of 1,4-



17 n = 0, R = All

18 n = 0, R = H

19 n = 1, R = All

20 n = 1, R = H

21 n = 2, R = All

22 n = 2, R = H

SE : $Me_3Si(CH_2)_2$

diazabicyclo[2.2.2]octane, followed by hydrolysis with dilute acid in aqueous acetone[14], gave **18** having 4^2-OH unsubstituted. Coupling of **18** with **16**, promoted by methyl triflate as before, yielded the tetrasaccharide derivative **19** (84%), *O*-deallylation of which gave **20** having 4^4-OH unsubstituted. Methyl triflate-promoted glycosylation of **20** with **16** gave the hexasaccharide derivative **21** (83%), which was *O*-deallylated to furnish **22** having 4^6-OH unsubstituted.

EXPERIMENTAL

General methods. — Unless stated otherwise, these were as described[4]. N.m.r. spectra (^{1}H, 90 MHz; ^{13}C, 22.6 MHz) for solutions in $CDCl_3$ (internal Me_4Si) or D_2O (internal sodium 4,4-dimethyl-4-silapentanoate-d_4) were recorded with a Hitachi R-90H spectrometer.

Methyl 4-O-allyl-β-D-xylopyranoside (**3**). — 2-Methoxypropene (67.1 mL, 0.7 mol) was added dropwise during 15 min at 5° to a stirred suspension of **1** (50 g, 0.3 mol) in dry *N,N*-dimethylformamide (150 mL) containing 5M HCl in MeOH (0.1 mL). After ~ 5 min, the mixture became clear and the solution was stirred for 1 h at room temperature. T.l.c. (1:1 hexane–EtOAc) then showed the disappearance of **1** and the presence of one major (R_F 0.41) and one minor (R_F 0.68) component. The mixture was diluted with $CHCl_3$ (500 mL) and washed with water (500 mL). The aqueous layer was extracted 3 times with $CHCl_3$ (150 mL). The combined $CHCl_3$ solution was made slightly acidic by addition of 5M HCl in MeOH (0.01 mL). After ~ 10 min, t.l.c. (1:1 hexane–EtOAc) showed conversion of the minor product (R_F 0.68) into the major component (R_F 0.41). The solution was washed successively with aq. $NaHCO_3$, and water, dried, and the solvent evaporated off. The last traces of solvents were removed by repeated evaporation of PhMe. To a stirred solution of the residue in *N,N*-

dimethylformamide (350 mL) was added portionwise at 0° NaH (16.5 g; 60% in mineral oil) and the mixture was stirred for 30 min at 0°. Allyl bromide (32 mL) was added dropwise and the mixture was stirred for 2 h at room temperature, whereupon t.l.c. (4:1 benzene–EtOAc) showed complete conversion of the isopropylidene derivative (R_F 0.18) into the product (R_F 0.77). The excess of alkylating reagent was decomposed by addition of MeOH, most of the solvents were evaporated, and a solution of the residue in $CHCl_3$ was washed with water, dried, and the solvent evaporated off. To a solution of the residue in Me_2CO (250 mL) was added M HCl (2 mL). The mixture was boiled under reflux for 10 min, made neutral with solid $NaHCO_3$, filtered through a Celite pad, and the solvent was evaporated off. The residue was dissolved in 2-propanol (250 mL) at 50°, and then hexane was added until a faint turbidity persisted. The crystals formed on cooling to room temperature were filtered off and recrystallized from the same solvent to give **3** (29.2 g, 47%), m.p. 107–108°, $[\alpha]_D^{20}$ $-95°$ (c 1.1, $CHCl_3$); lit.[8] m.p. 106.5–107°, $[\alpha]_D$ $-96°$; R_F 0.39 (t.l.c. in 9:1 benzene–EtOH). The ^{13}C-n.m.r. spectrum was identical to that reported[8].

4-O-Allyl-D-xylopyranose (**5**). — A mixture of **3** (26.5 g) and M HCl (400 mL) was stirred for 3 h at 90°, at which time t.l.c. (9:1 $CHCl_3$–MeOH) showed complete conversion of **3** (R_F 0.8) into **5** (R_F 0.28). The mixture was cooled, the pH was adjusted to 6.0 by addition of solid Li_2CO_3, and the mixture was concentrated to dryness by evaporation of PhMe. The residue was treated[9] with Ac_2O (100 mL) and NaOAc (15 g) under reflux for 30 min. Conventional isolation[9] followed by column chromatography (10:1 benzene–EtOAc) of the crude product, gave amorphous 1,2,3-tri-*O*-acetyl-4-*O*-allyl-D-xylopyranose (**4**, 32.8 g, 80%), R_F 0.5 (t.l.c. in 4:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 92.3 (C-1β) and 89.4 (C-1α) in the ratio 1.6:1.

Anal. Calc. for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37. Found: C, 53.24; H, 6.43.

A solution of **4** (30.4 g) in anhydrous MeOH (200 mL) containing methanolic M NaOMe (2 mL) was kept for 1 h at room temperature, made neutral with Amberlite IR-120 (H^+) resin, filtered, and the solvent evaporated off. Crystallization from EtOAc–Et_2O gave **5** (17.2 g, 94%), m.p. 97–98°, $[\alpha]_D^{23}$ $-22°$ (2 min) $\rightarrow$ $+7°$ (24 h, constant; c 1.3, H_2O); ^{13}C-n.m.r. (D_2O): δ 136.5 and 121.0 ($CH=CH_2$), 99.0 (C-1β), 94.5 (C-1α), 65.8 (C-5β), and 61.6 (C-5α).

Anal. Calc. for $C_8H_{14}O_5$: C, 50.52; H, 7.42. Found: C, 50.56; H, 7.34.

4-O-Allyl-1,2,3-tri-O-benzoyl-β-D-xylopyranose (**7**). — A solution of **5** (12.0 g) in pyridine (80 mL) was treated at 0° with BzCl (29 mL), and the mixture was kept overnight at room temperature. Conventional processing and chromatography (4:1 hexane–EtOAc) gave amorphous 4-*O*-allyl-1,2,3-tri-*O*-benzoyl-D-xylopyranose (**6**) (29.5 g, 93%), R_F 0.71 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 92.8 (C-1β) and 90.2 (C-1α) in the ratio 2.4:1.

Anal. Calc. for $C_{29}H_{26}O_8$: C, 69.31; H, 5.22. Found: C, 69.43; H, 5.31.

Crystallization of **6** (14.4 g) from MeOH afforded **7** (7.8 g, 54%), m.p. 89–91°, $[\alpha]_D^{23}$ $+32.5°$ (c 1.1, $CHCl_3$); lit.[1] m.p. 98–100°, $[\alpha]_D^{32}$ $+32°$; ^{13}C-n.m.r. ($CDCl_3$): δ 165.2, 165.1, and 164.5 (C=O), 133.1 and 117.6 ($CH=CH_2$), 92.8 (C-1), and 63.5 (C-5).

Anal. Found: C, 69.34; H, 5.27.

Ethyl 2,3- (**10**) *and 3,4-O-isopropylidene-1-thio-β-*D*-xylopyranoside* (**11**). — A solution of **9** (7.25 g, 37.3 mmol) in *N,N*-dimethylformamide (20 mL) was treated with 5M HCl in MeOH (0.02 mL) and 2-methoxypropene (8.2 mL, 85.6 mmol) as described for **1**. Column chromatography (9:1 benzene–EtOAc containing 0.1% Et_3N) of the product afforded **10** (6.13 g, 70%) and **11** (1.58 g, 18%).

Compound **10** had m.p. 95.5–96.5° (from Et_2O-petroleum ether), $[\alpha]_D^{23}$ $-64°$ (*c* 1.8, $CHCl_3$); R_F 0.25 (t.l.c. in 4:1 benzene–EtOAc); n.m.r. ($CDCl_3$): ^1H, δ 4.61 (d, 1 H, $J_{1,2}$ 9.0 Hz, H-1), 2.60 (m, 2 H, $SC\mathit{H}_2CH_3$), 1.48 (s, 6 H, $C\mathit{Me}_2$), and 1.32 (t, 3 H, $SCH_2C\mathit{H}_3$); ^{13}C, δ 111.0 ($\mathit{C}Me_2$), 83.3 (C-1), 83.0, 75.7, 69.8 (C-2,3,4), 68.8 (C-5), 26.7 and 26.5 ($C\mathit{Me}_2$), 24.4 ($S\mathit{C}H_2CH_3$), and 15.1 ($SCH_2\mathit{C}H_3$).

Anal. Calc. for $C_{10}H_{18}O_4S$: C, 51.26; H, 7.74. Found: C, 51.22; H, 7.80.

Compound **11** had m.p. 92–93° (from Et_2O–petroleum ether), $[\alpha]_D^{23}$ $-83°$ (*c* 1.4, $CHCl_3$); R_F 0.35 (t.l.c. in 4:1 benzene–EtOAc); n.m.r. ($CDCl_3$): ^1H, δ 4.25 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 2.74 (m, 2 H, $SC\mathit{H}_2CH_3$), 1.47 (s, 6 H, $C\mathit{Me}_2$), and 1.32 (t, 3 H, $SCH_2C\mathit{H}_3$); ^{13}C, δ 111.6 ($\mathit{C}Me_2$), 87.3 (C-1), 82.5, 73.3, and 71.9 (C-2,3,4), 68.3 (C-5), 26.7 and 26.55 ($C\mathit{Me}_2$), 24.9 ($S\mathit{C}H_2CH_3$), and 15.2 ($SCH_2\mathit{C}H_3$).

Anal. Calc. for $C_{10}H_{18}O_4S$: C, 51.26; H, 7.74. Found: C, 51.32; H, 7.77.

*Ethyl 4-O-acetyl-2,3-O-isopropylidene-1-thio-β-*D*-xylopyranoside* (**12**). — Acetylation of **10** (0.17 g) with 1:1 Ac_2O–pyridine (3 mL) gave amorphous **12** (0.19 g, 95%), $[\alpha]_D^{23}$ $-93°$ (*c* 1.2, $CHCl_3$); R_F 0.54 (t.l.c. in 2:1 hexane–EtOAc); n.m.r. ($CDCl_3$): ^1H, δ 5.04 (o, 1 H, $J_{4,5e}$ 5.3 Hz, $J_{4,5a}$ 8.1 Hz, H-4), 4.70 (d, 1 H, $J_{1,2}$ 9.0 Hz, H-1), 4.24 (m, 1 H, H-5*e*), 3.74 (t, 1 H, $J_{3,4}$ 9.2 Hz, H-3), 3.40 (t, 1 H, $J_{2,3}$ 9.1 Hz, H-2), 3.23 (m, 1 H, H-5*a*), 2.75 (m, 2 H, $SC\mathit{H}_2CH_3$), 2.09 (s, 3 H, OAc), 1.48 (s, 6 H, $C\mathit{Me}_2$), and 1.31 (t, 3 H, $SCH_2C\mathit{H}_3$); ^{13}C, δ 169.0 (C = 0), 111.5 ($\mathit{C}Me_2$), 83.3 (C-1), 79.3, 76.0, and 70.6 (C-2,3,4), 66.6 (C-5), 26.7 and 26.55 ($\mathit{C}Me_2$), 24.2 ($S\mathit{C}H_2CH_3$), 20.8 ($CO\mathit{C}H_3$), and 15.1 ($SCH_2\mathit{C}H_3$).

Anal. Calc. for $C_{12}H_{20}O_5S$: C, 52.16; H, 7.29. Found: C, 52.25; H, 7.37.

*Ethyl O-(4-O-allyl-2,3-di-O-benzoyl-β-*D*-xylopyranosyl)-(1→4)-2,3-O-isopropylidene-1-thio-β-*D*-xylopyranoside* (**13**). — To a solution of **6** (8.04 g) in CH_2Cl_2 (30 mL) at 0° was added a saturated (at 0°) solution of HBr in AcOH (20 mL). The mixture was stirred for 20 min at 0° and then diluted with CH_2Cl_2. The solution was washed successively with iced water, aq. $NaHCO_3$, and water, dried, and concentrated, to give amorphous 4-*O*-allyl-2,3-di-*O*-benzoyl-α-D-xylopyranosyl bromide (**8**) (6.94 g, 94%), $[\alpha]_D^{22}$ $+167°$ (*c* 1.0, CH_2Cl_2), which was used in the glycosylation step without purification; n.m.r. ($CDCl_3$): ^1H, δ 6.75 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1); ^{13}C, δ 133.05 and 117.75 ($CH = CH_2$), 88.2 (C-1), and 64.2 (C-5).

A solution of **8** (6.68 g, 14.5 mmol) in CH_2Cl_2 (50 mL) was added dropwise at $-20°$ to a stirred solution of **10** (2.61 g, 11.1 mmol) in PhMe (20 mL) and CH_2Cl_2 (50 mL) containing silver triflate (4.09 g, 15.9 mmol) and 1,1,3,3-tetramethylurea (3.81 mL, 31.8 mmol). The mixture was allowed to attain room temperature, and then stirred for 2 h. Insoluble material was collected on a Celite layer, washed with CH_2Cl_2, and the combined filtrate and washings were washed successively with cold water, aq. $NaHCO_3$, and water, dried, and concentrated. Column chromatography (30:1 → 20:1 benzene–EtOAc, stepwise) of the product gave **13** (5.48 g, 80%), $[\alpha]_D^{23}$ $+16°$ (*c* 1.1,

$CHCl_3$); R_F 0.38 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 165.3 and 164.95 (C = O), 133.0 and 117.5 ($CH = CH_2$), 111.0 (CMe_2), 99.1 (C-1^2), 83.2 (C-1^1), 67.5 (C-5^1), 63.0 (C-5^2), 26.8 and 26.5 (CMe_2), 24.2 (SCH_2CH_3), and 15.1 (SCH_2CH_3).

Anal. Calc. for $C_{32}H_{38}O_{10}S$: C, 62.53; H, 6.23. Found: C, 62.68; H, 6.16.

Ethyl O-(4-O-allyl-2,3-di-O-benzyl-β-D-xylopyranosyl)-(1→4)-2,3-O-isopropylidene-1-thio-β-D-xylopyranoside (**14**). — To a solution of **13** (8.47 g) in MeOH (70 mL) was added methanolic M NaOMe (0.5 mL) and the mixture was processed as described for the preparation of **5**. A solution of the residue in *N,N*-dimethylformamide (30 mL) was treated with NaH (1.54 g; 60% in mineral oil) and $PhCH_2Br$ (4.2 mL). Processing of the mixture as described for the preparation of **3**, followed by column chromatography (20:1 benzene–EtOAc) of the product, gave **14** (7.27 g, 90%), m.p. 89–90° (from EtOH), $[\alpha]_D^{23}$ +27° (*c* 1.6, $CHCl_3$); R_F 0.46 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 138.5 and 138.3 (aromatic C-1), 134.55 and 117.1 ($CH = CH_2$), 111.1 (CMe_2), 102.2 (C-1^2), 83.3 (C-1^1), 67.5 (C-5^1), 63.9 (C-5^2), 26.8 and 26.5 (CMe_2), 24.2 (SCH_2CH_3), and 15.1 (SCH_2CH_3).

Anal. Calc. for $C_{32}H_{42}O_8S$: C, 65.51; H, 7.22. Found: C, 65.44; H, 7.32.

*Ethyl O-(4-O-allyl-2,3-di-O-benzyl-β-D-xylopyranosyl)-(1→4)-1-*thio*-β-D-xylopyranoside* (**15**). — To a solution of **14** (6.88 g) in Me_2CO (70 mL) was added M HCl (1 mL). The mixture was stirred for 1 h at room temperature, made neutral with solid $NaHCO_3$, filtered through a Celite layer, and the filtrate was concentrated. A solution of the residue in CH_2Cl_2 was washed with water, dried, and concentrated. Crystallization of the residue from Et_2O–petroleum ether gave **15** (5.83 g, 91%), m.p. 88–89°, $[\alpha]_D^{23}$ −26° (*c* 1.05, $CHCl_3$); R_F 0.28 (t.l.c. in 2:1 hexane–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 138.4 and 138.0 (aromatic C-1), 134.4 and 117.3 ($CH = CH_2$), 104.1 (C-1^2), 83.5 (C-1^1), 67.2 (C-5^1), 64.0 (C-5^2), 24.3 (SCH_2CH_3), and 15.2 (SCH_2CH_3).

Anal. Calc. for $C_{29}H_{38}O_8S$: C, 63.72; H, 7.01. Found: C, 63.65; H, 7.12.

Ethyl O-(4-O-allyl-2,3-di-O-benzyl-β-D-xylopyranosyl)-(1→4)-2,3-di-O-benzoyl-1-thio-β-D-xylopyranoside (**16**). — Benzoylation of **15** (5.51 g), as described for **5**, afforded **16** (6.98 g, 92%), m.p. 76–77° (from Et_2O–petroleum ether), $[\alpha]_D^{23}$ +3° (*c* 1.2, $CHCl_3$); R_F 0.57 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 165.3 and 165.1 (C = O), 138.5 and 138.3 (aromatic C-1), 134.5 and 116.95 ($CH = CH_2$), 103.6 (C-1^2), 65.85 (C-5^1), 63.5 (C-5^2), 24.5 (SCH_2CH_3), and 14.8 (SCH_2CH_3).

Anal. Calc. for $C_{43}H_{46}O_{10}S$: C, 68.42; H, 6.14. Found: C, 68.53; H, 6.11.

2-(Trimethylsilyl)ethyl O-(4-O-allyl-2,3-di-O-benzyl-β-D-glucopyranosyl)-(1→4)-2,3-di-O-benzoyl-β-D-xylopyranoside (**17**). — A mixture of **16** (2.02 g, 2.7 mmol), 2-(trimethylsilyl)ethyl alcohol (0.77 mL, 5.4 mmol), and powdered 4A molecular sieve (10 g) in PhMe (27 mL) was stirred under argon for 30 min at room temperature. Methyl triflate (1.51 mL, 13.3 mmol) was injected through a rubber septum and the mixture was stirred for 2 h at 40°. Triethylamine (3.7 mL) was added and the mixture was filtered through a Celite layer, which was washed with PhMe. The combined filtrate and washings were concentrated and the residue was subjected to column chromatography (30:1 benzene–EtOAc), to give **17** (2.0 g, 92%), $[\alpha]_D^{23}$ +5° (*c* 1.3, $CHCl_3$); R_F 0.54 (t.l.c. in 15:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 165.3 and

165.0 (C = O), 138.5 and 138.3 (aromatic C-1), 134.5 and 116.9 (CH = CH$_2$), 103.6 (C-1^2), 100.3 (C-1^1), 66.95 (*C*H$_2$CH$_2$SiMe$_3$), 63.5 and 62.9 (C-5^1,5^2), 18.0 (CH$_2$*C*H$_2$SiMe$_3$), and −1.5 (SiMe$_3$).

Anal. Calc. for $C_{46}H_{54}O_{11}Si$: C, 68.13; H, 6.71. Found: C, 68.25; H, 6.80.

2-(Trimethylsilyl)ethyl O-*(2,3-di-*O-*benzyl-β-*D-*xylopyranosyl)-(1→4)-2,3-di-*O-*benzoyl-β-*D-*xylopyranoside* (**18**).— A mixture of **17** (1.85 g), $(Ph_3P)_3Rh(I)Cl$ (0.3 g) and 1,4-diazabicyclo[2.2.2.]octane (0.7 g) in 10:3:1 EtOH–PhMe–water (70 mL) was boiled for 9 h under reflux, concentrated to dryness, and the residue extracted with CHCl$_3$. The extract was washed successively with cold dil. HCl, aq. NaHCO$_3$, and water, dried, and concentrated. To a solution of the residue in 9:1 Me$_2$CO–water (20 mL) was added M HCl (0.1 mL). The mixture was boiled for 10 min under reflux, neutralized with solid NaHCO$_3$, filtered, and concentrated. Column chromatography (4:1 benzene–EtOAc) gave **18** (1.50 g, 85%), $[\alpha]_D^{23}$ −9.5° (*c* 0.9, CHCl$_3$); R_F 0.14 (t.l.c. in 15:1 benzene–EtOAc); ^{13}C-n.m.r. (CDCl$_3$): δ 165.4 and 165.0 (C = O), 138.2 and 137.9 (aromatic C-1), 102.7 (C-1^2), 100.4 (C-1^1), 67.0 (*C*H$_2$CH$_2$SiMe$_3$), 64.4 and 62.8 (C-5^1,5^2), 18.0 (CH$_2$*C*H$_2$SiMe$_3$), and −1.5 (SiMe$_3$).

Anal. Calc. for $C_{43}H_{50}O_{11}Si$: C, 66.99; H, 6.54. Found: C, 67.13; H, 6.64.

2-(Trimethylsilyl)ethyl O-*(4-*O-*allyl-2,3-di-*O-*benzyl-β-*D-*xylopyranosyl)-(1→4)-*O-*(2,3-di-*O-*benzoyl-β-*D-*xylopyranosyl)-(1→4)-*O-*(2,3-di-*O-*benzyl-β-*D-*xylopyranosyl)-(1→4)-2,3-di-*O-*benzoyl-β-*D-*xylopyranoside* (**19**). — A mixture of **16** (1.74 g, 2.3 mmol), **18** (1.37 g, 1.8 mmol), and powdered 4A molecular sieve (10 g) in PhMe (30 mL) was treated with methyl triflate (1.3 mL, 11.5 mmol), and processed as described for the preparation of **17**. Column chromatography (20:1 benzene–EtOAc) gave **19** (2.18 g, 84%), m.p. 79–80° (from Et$_2$O–petroleum ether), $[\alpha]_D^{24}$ −1° (*c* 1.1, CHCl$_3$); R_F 0.37 (t.l.c. in 15:1 benzene–EtOAc); ^{13}C-n.m.r. (CDCl$_3$): δ 165.3, 165.0, and 164.9 (C = O), 138.5 and 138.2 (aromatic C-1), 134.5 and 116.95 (CH = CH$_2$), 103.6, 103.3, 100.3, and 99.9 (C-1^1,1^2,1^3,1^4), 66.9 (*C*H$_2$CH$_2$SiMe$_3$), 63.5 and 62.8 (C-5^1,5^2,5^3,5^4), 18.0 (CH$_2$*C*H$_2$SiMe$_3$), and −1.5 (SiMe$_3$).

Anal. Calc. for $C_{84}H_{90}O_{21}Si$: C, 68.93; H, 6.20. Found: C, 69.14; H, 6.28.

2-(Trimethylsilyl)ethyl O-*(2,3-di-*O-*benzyl-β-*D-*xylopyranosyl)-(1→4)-*O-*(2,3-di-*O-*benzoyl-β-*D-*xylopyranosyl)-(1→4)-*O-*(2,3-di-*O-*benzyl-β-*D-*xylopyranosyl)-(1→4)-2,3-di-*O-*benzoyl-β-*D-*xylopyranoside* (**20**). — *O*-Deallylation of **19** (1.88 g), as described for **17**, followed by column chromatography (8:1 benzene–EtOAc) afforded **20** (1.50 g, 82%), $[\alpha]_D^{24}$ −17° (*c* 1.1, CHCl$_3$); R_F 0.2 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. (CDCl$_3$): δ 165.4, 165.0, and 164.9 (C = O), 138.5, 138.2, 137.8, and 137.6 (aromatic C-1), 103.3, 102.6, 100.3, and 100.0 (C-1^1,1^2,1^3,1^4), 67.0 (*C*H$_2$CH$_2$SiMe$_3$), 64.3 and 62.8 (C-5^1,5^2,5^3,5^4), 18.0 (CH$_2$*C*H$_2$SiMe$_3$), and −1.5 (SiMe$_3$).

Anal. Calc. for $C_{81}H_{86}O_{21}Si$: C, 68.34; H, 6.09. Found: C, 68.42; H, 6.20.

2-(Trimethylsilyl)ethyl O-*(4-*O-*allyl-2,3-di-*O-*benzyl-β-*D-*xylopyranosyl)-(1→4)-bis[*O-*(2,3-di-*O-*benzoyl-β-*D-*xylopyranosyl)-(1→4)-(2,3-di-*O-*benzyl-β-*D-*xylopyranosyl)-(1→4)]-2,3-*di-O-*benzoyl-β-*D-*xylopyranoside* (**21**). — The crude product obtained by treatment of a mixture of **16** (0.75 g, 994 μmol), **20** (1.09 g, 766 μmol), and powdered 4A molecular sieve (5 g) in PhMe (20 mL) with methyl triflate (0.56 mL, 4.9 mmol), as described for the preparation of **17**, was chromatographed (15:1 benzene–EtOAc), to give **21** (1.34 g, 83%), m.p. 129–131° (from Et_2O–petroleum ether), $[\alpha]_D^{24}$ $-15°$ (*c* 1.2, $CHCl_3$); R_F 0.43 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 165.3, 165.0, and 164.9 (C–O), 138.5, 138.2, and 138.1 (aromatic C-1), 134.5 and 117.0 ($C=CH_2$), 103.6, 103.2 (2 C), 100.3, and 99.8 (2 C) (C-$1^1,1^2,1^3,1^4,1^5,1^6$), 67.0 ($CH_2CH_2SiMe_3$), 63.5, 62.8, 62.7, and 62.6 (C-$5^1,5^2,5^3,5^4,5^5,5^6$), 18.0 ($CH_2CH_2SiMe_3$), and -1.5 ($SiMe_3$).

Anal. Calc. for $C_{122}H_{126}O_{31}Si$: C, 69.24; H, 6.00. Found: C, 69.31; H, 6.08.

2-(Trimethylsilyl)ethyl O-*(2,3-di-*O*-benzyl-β-*D*-xylopyranosyl)-(1→4)-bis*[O-*(2,3-di-*O*-benzoyl-β-*D*-xylopyranosyl)-(1→4)-(2,3-di-*O*-benzyl-β-*D*-xylopyranosyl)-(1→4)*]*-2,3-di-*O*-benzoyl-β-*D*-xylopyranoside* (**22**). — *O*-Deallylation of **21** (1.09 g) as described for **17**, followed by chromatography (8:1 benzene–EtOAc), gave **22** (0.86 g, 80%), m.p. 119–120° (from MeOH–Me_2CO), $[\alpha]_D^{24}$ $-23°$ (*c* 1.1, $CHCl_3$); R_F 0.56 (t.l.c. in 4:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 165.3, 165.0, and 164.8 ($C=O$), 138.5, 138.2, 138.1, and 137.8 (aromatic C-1), 103.2 (2 C), 102.6, 100.3, and 99.9 (2 C) (C-$1^1,1^2,1^3,1^4,1^5,1^6$), 67.0 ($CH_2CH_2SiMe_3$), 64.2, 62.7, and 62.6 (C-$5^1,5^2,5^3,5^4,5^5,5^6$), 18.0 ($CH_2CH_2SiMe_3$), and -1.5 ($SiMe_3$).

Anal. Calc. for $C_{119}H_{122}O_{31}Si$: C, 68.84; H, 5.92. Found: C, 68.90; H, 6.06.

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