# Synthesis of uronic acid-containing xylans found in wood and pulp

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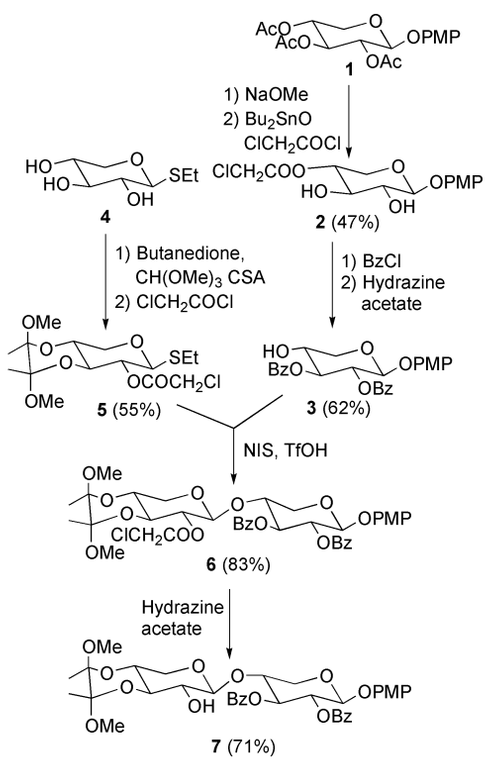
Two uronic acid-containing trisaccharides, (4-deoxy-β-L-*threo*-hex-4-enopyranosyluronic acid)- and (4-*O*-methyl-α-D-gluropyranosyluronic acid)-(1→2)-β-D-xylopyranosyl-(1→4)-D-xylopyranose, found in enzyme hydrolysates from pulp are synthesised. A common dixyloside 2′-OH acceptor, *p*-methoxyphenyl [3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-β-D-xylopyranosyl]-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside, is constructed and coupled with two glucuronate thioglycoside donors differently substituted in the 4-position, *O*-methyl and *O*-mesyl, respectively, to give trisaccharides. DMTST as promoter in diethyl ether gives exclusively the α-linked products in high yield. Treatment of the 4″-*O*-mesyl trisaccharide with DBU then gives the α,β-unsaturated uronic acid derivative. The protection pattern introduced in the acceptor allows continued synthesis of larger oligosaccharides. Removal of the butanedione acetal produces 3′,4′-acceptors, and the *p*-methoxyphenyl glycoside can be transformed into various glycosyl donors, *e.g.* thioglycosides and sugar halides. Complete deprotection gives the two target reducing trisaccharides.

## Introduction

Wood consists mainly of cellulose, lignin and hemicellulose. The several different hemicelluloses found in wood are all small heteropolymers that comprise several hundred monosaccharide units. The amount of hemicellulose in wood is usually between 20 and 30% of the dry weight. The most common hemicellulose in hardwood is a glucuronoxylan. The backbone structure consists of β-(1→4)-linked D-xylopyranose units, about 70% of which have an *O*-acetyl group at either position 2 or 3. In addition, at about every tenth xylose unit there is an α-(1→2)-linked 4-*O*-methylglucuronic acid (MeGlcA) residue.[1] The alkaline conditions used during kraft pulping of the wood cleave the acetate groups of glucuronoxylan. In addition, the MeGlcA side groups are partly converted into hexenuronic acid (HexA) *via* β-elimination and into 4-*O*-methyl-L-iduronic acid via C-5 epimerisation. Partial enzyme hydrolysis of the kraft pulp generates an array of oligosaccharides with different length, preferably with the uronic acid substituent at the non-reducing end.[2–4] To aid in the characterisation of such complex mixtures synthetic oligosaccharide model compounds are useful. Syntheses of the 4-*O*-methylglucuronic acid residue[5] as well as the 4-*O*-Me-α-D-GlcA-(1→2)-β-D-Xyl disaccharide[6] have been published. In this article the syntheses of the MeGlcA- and HexA-containing trisaccharides **17** and **21** are described. The synthetic pathway chosen allows continued synthesis of larger fragments of the glucuronoxylan.




**Scheme 1**

## Results and discussion

Since the target trisaccharides contain a common dixyloside motif, it was decided to first construct this as a common acceptor derivative (**7**, Scheme 1) and then introduce the uronic acid residues. As glycosyl donors thioglycosides were selected, because of our good experiences with such donors, but the choice of anomeric protecting group to be introduced at the reducing end of the acceptor was not obvious. Other things to consider were when to introduce the carboxy function and the unsaturation.

### Preparation of the dixyloside acceptor

The aglycone part in the acceptor xyloside should be easy to remove to give the target reducing trisaccharides, but also should preferably directly function as a donor leaving group or be easily transformed into one to allow the production of larger xylan fragments. The trimethylsilylethyl group, thoroughly investigated by G. Magnusson and co-workers,[7] was considered as well as an allyl group. Finally, a *p*-methoxyphenyl (PMP) glycoside was chosen, which, besides being stable under most coupling and protecting-group-manipulation conditions, is easily hydrolysed to give the hemiacetal, and, furthermore, efficiently can be transformed into halide sugars or thioglycosides, as recently reported by Zhang and Magnusson.[8] Accordingly, the known[9] acetylated *p*-methoxyphenyl xyloside **1** was

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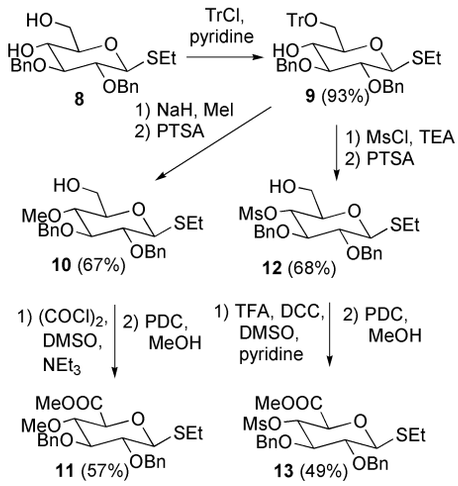
prepared and deacetylated. The selective protection of hydroxy groups in xyloside derivatives is not trivial since all hydroxy groups are secondary, equatorial, and *trans*. However, using stannylene activation a reactivity difference between the three hydroxy groups in a β-xyloside has been observed and the reactivity is known to be OH-4 > OH-3 > OH-2.[10] Thus, subsequent stannylene activation and monochloroacetylation gave the 4-*O*-protected derivative **2** (47%) (Scheme 1). Benzoylation followed by selective removal of the chloroacetyl group by hydrazine acetate treatment then yielded the acceptor **3** (62%). As precursor for the donor, ethyl thioxyloside[11] **4** was selected. Treatment of **4** with butanedione and camphor-10-sulfonic acid (CSA) in the presence of trimethyl orthoformate gave the 3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl) ketal (BDA)[12–14] together with the 2,3-regioisomer, which could easily be separated on a silica gel column. Chloroacetylation of the 3,4-isomer then gave donor **5** (55% overall yield from **4**). An analogue to donor **5** with a 4-*O*-*tert*-butyldimethylsilyl (TBDMS) and a 3-*O*-acetyl group was first prepared and used in couplings to **3** to give a dixyloside.[15] However, when the chloroacetyl goup was removed and the resulting 2′-OH compound was tried as acceptor in couplings with glucuronate donors **11** and **13** no trisaccharides at all were obtained. One explanation for the low reactivity of the 2′-hydroxy group could be the deactivating effect of the 3′-*O*-acetyl group, and consequently another protection pattern was introduced. Coupling between acceptor **3** and donor **5** promoted by *N*-iodosuccinimide–trifluoromethanesulfonic acid (NIS–TfOH) efficiently gave disaccharide **6** (83%), dechloroacetylation of which gave the dixyloside acceptor **7** (71%) (Scheme 1).

### Preparation of the glucuronate donors

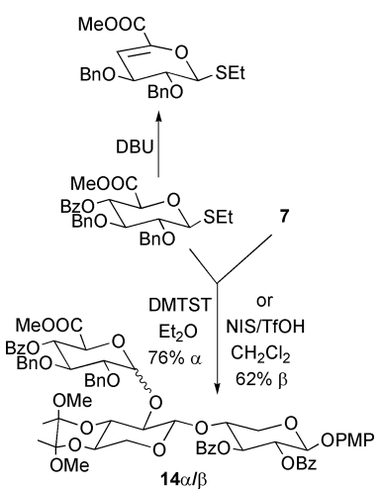
Since the native glucuronic acid is α-linked a non-participating protecting group in the 2-position was necessary. A benzyl group was chosen, which more or less excluded glucuronic acid precursors, since these are difficult to benzylate in good yields. Instead, glucose derivative **8**[16] was selected as starting material and regioselectively tritylated to give **9** (93%) (Scheme 2). Compound **9** was either methylated or mesylated and the trityl group then removed to yield the primary alcohol derivatives **10** (67%) and **12** (68%), respectively. In spite of the large number of oxidation methods available the oxidation of these alcohols to a uronic acid derivative is still not trivial. Often an optimisation has to be performed for each specific compound to find optimum reagents and conditions, and the yield is seldom excellent or even very high, which makes it an advantage to perform the oxidation early in the synthesis. The use of thioglycosides brings in an additional possible complication, *i.e.* oxidation of sulfur, but the use of dimethyl sulfoxide (DMSO)-based oxidation methods usually circumvents this problem. Swern oxidation[17] of **10** followed by pyridinium dichromate (PDC)-oxidation of the intermediate aldehyde in the presence of MeOH[18] gave the methyl ester glucuronate **11** (57%). Swern oxidation of **12**, however, gave mainly the 4,5-unsaturated aldehyde, which proved impossible to oxidise further with PDC. Instead, a Pfitzner–Moffat oxidation[19,20] was tried, to produce the saturated aldehyde, which was then oxidised to the methyl ester derivative **13** (49%) by PDC–MeOH. Originally, compound **13** was designed as the 4-*O*-benzoyl derivative,[15] since an elimination reaction of this using 1,7-diazabicyclo[5.4.0]undec-7-ene (DBU) as base proceeded smoothly at the monosaccharide stage to give the 4,5-unsaturated glucuronic acid as has also been shown by others (Scheme 3).[21] However, at the trisaccharide level it proved impossible to eliminate the benzoate irrespective of the base used.[15] Also, the corresponding *galacto* analogue proved inert in spite of the supposed more favourable *trans*-diaxial arrangement of the groups to be eliminated. In addition a tosyl group was tried as leaving group, but the mesyl group was found to be the best alternative.




**Scheme 2**

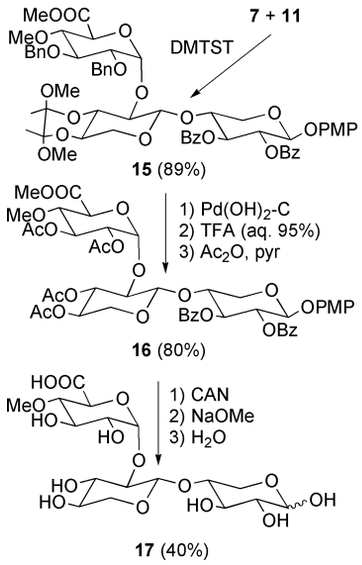
### Trisaccharide synthesis

As had been shown earlier,[22,23] glucuronate thioglycosides proved effective as donors to produce trisaccharides. Primary model couplings with the 4-*O*-benzoyl-protected donor afforded insight into the stereospecific outcome of the reaction, which proved to be very sensitive to changes in the reaction conditions (Scheme 3). Coupling with **7** using dimethyl(methylthio)sulfonium triflate (DMTST) as promoter in diethyl ether, conditions known to promote α-glycosylation,[24] yielded 76% of the α-linked trisaccharide **14α** ($\delta_C$ 96.3, C-1″), whereas NIS as promoter in $CH_2Cl_2$ gave 62% of the β-product **14β** ($\delta_C$ 102.5 or 102.8, C-1″). Thus, good conditions for obtaining the desired α-glycoside were found and these were shown to be general for the other donors as well. Coupling of acceptor **7** with donor **11** with DMTST as promoter gave trisaccharide **15** ($\delta_C$ 97.1, C-1″) in 89% yield, and coupling with donor **13** gave trisaccharide **18** ($\delta_C$ 95.9, C-1″) in 80% yield (Schemes 4 and 5).

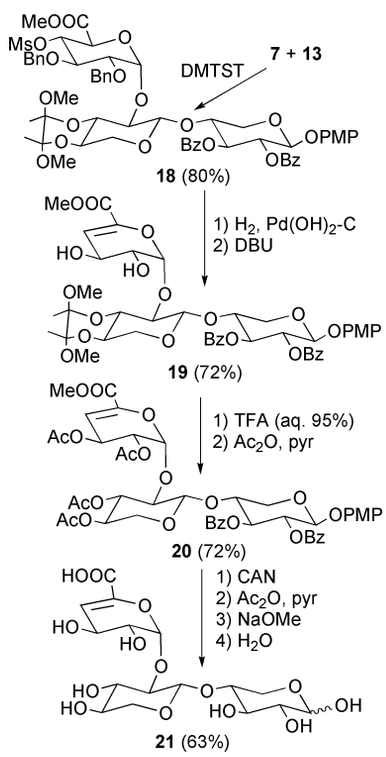



**Scheme 3**

To obtain the unsaturated derivative, trisaccharide **18** was first subjected to catalytic hydrogenolysis to remove the benzyl groups (which removal in the presence of a double bond might have caused problems) and then treated with DBU to accomplish the elimination (→**19**, 72%). Efforts were also made to produce an unsaturated trisaccharide derivative by using an unsaturated glucuronate thioglycoside donor, (as mentioned above) easily obtained by DBU treatment of derivative **13** or its 4-*O*-benzoyl analogue (Scheme 3). This donor, however, turned out to be inert to activation by any thiophilic promoter. Even under rather harsh conditions (DMTST + NIS, TfOH, reflux $CH_2Cl_2$) the unsaturated glucuronate thioglycoside was stable.




**Scheme 4**




**Scheme 5**

This inertness may be due to an inductive effect and/or a torsional 'disarming' effect in the formation of the intermediate oxocarbenium ion, as has been suggested for 4,6-*O*-benzylidene donors,[25] and will have to be investigated.

The two derivatives **15** and **19** are both designed to allow their transformation into new acceptors and donors for continued syntheses of larger glucuronoxylan fragments. After debenzylation (of **15**) and acetylation, removal of the BDA ketal will give 3″,4″-diol acceptors, whereas conversion of the PMP glycoside into halide sugars, trichloroimidates or thioglycosides will produce trisaccharide donors.[8]

### Deprotection

Removal of all the protecting groups except the methyl ester and the *p*-methoxyphenyl group from compounds **15** and **19** proceeded smoothly to give compounds in which the assumed (from $^{13}$C-shift of the anomeric signals in **15** and **18**) anomeric configuration of the glucuronic acid residues could be verified by $^{1}$H NMR [$\delta_H$(acetone-d$_6$) 5.28 (1 H, d, $J_{1,2}$ 3.8 Hz, H-1$^{MeGlcA}$) and $\delta_H$(CDCl$_3$–MeOH) 5.36 (1 H, d, $J_{1,2}$ 2.2 Hz, H-1$^{HexA}$]. However, when removal of the PMP group in these compounds was attempted, hydrolysis of the linkage between the two xylose residues was observed, probably due to the acidity of the reagent, cerium(IV) ammonium nitrate (CAN) in CH$_3$CN–water. For stabilisation and to make the products organic-soluble, the tetraols obtained after removal of the benzyl groups and/or BDA ketals from **15** and **19** were therefore first acetylated to give compounds **16** and **20**. Removal of the PMP group from these derivatives now proceeded in good to excellent yields (64 and 99%, respectively, the HexA trisaccharide isolated as its anomeric acetate) without any detected hydrolysis of the resulting trisaccharides. Finally, deacylation under Zemplén conditions and saponification of the methyl ester gave the target compounds **17** and **21**, whose NMR data were in excellent agreement with those recorded for similar structures obtained through enzymatic degradation of pulp.[4]

## Conclusions

The syntheses of two uronic acid-containing trisaccharide structures found in hemicellulose pulp have been completed. Features of the syntheses are: Use of a BDA ketal to temporarily protect the 3- and 4-hydroxy groups in a xylose residue without lowering the reactivity of the 2-OH group; Use of glucuronate thioglycoside donors with a 2-*O*-nonparticipating group, with which the stereoselectivity in glycosylations can be controlled by the conditions employed. DMTST in diethyl ether gave α-glycosides, whereas NIS in CH$_2$Cl$_2$ yielded β-glycosides; Use of PMP glycosides, which can be either hydrolysed to obtain the target reducing saccharides or converted to a donor for continued synthesis.

In the preparation of the unsaturated structure it was experienced that the usually easy β-elimination reaction required a very good leaving group when performed at the trisaccharide stage. It was also found that a 4-deoxyhex-4-enuronate thioglycoside donor was inert towards activation even with strong thiophilic promoters.

## Experimental

### General

TLC was carried out on Merck precoated 60 F$_{254}$ plates using UV light and/or 8% sulfuric acid for visualisation. Column chromatography was performed on silica gel (0.040–0.063 mm, Amicon). NMR spectra were recorded in CDCl$_3$ (internal Me$_4$Si, $\delta = 0.00$) or D$_2$O (internal acetone; $\delta_C = 31.0$, $\delta_H = 2.21$) at 25 °C on a Varian 300 MHz or 400 MHz instrument. Optimal rotations were measured on a Perkin-Elmer 241 polarimeter; $[a]_D$-values are given in units of $10^{-1}$ deg cm$^2$ g$^{-1}$. Organic phases were dried over Na$_2$SO$_4$ before evaporation, which was performed under reduced pressure.

### *p*-Methoxyphenyl 2,3-di-*O*-benzoyl-β-D-xylopyranoside 3

A solution of **1**[9] (13 g, 34.4 mmol) in MeOH (250 ml) was treated with a catalytic amount of 1 M methanolic NaOMe at room temperature overnight. Dowex 50 (H$^+$) ion-exchange resin was added until neutral pH and the mixture was then filtered and concentrated. The deacetylated material and dibutyltin oxide (9.0 g, 36.1 mmol) were suspended in toluene (500 ml) and the mixture was refluxed overnight in a flask equipped with a Dean–Stark trap. The resulting clear solution was cooled to −40 °C under Ar and chloroacetyl chloride (3 ml, 37.8 mmol) was added dropwise. After the addition was complete, the reaction mixture was allowed to attain room temperature (4 h). The crude mixture was concentrated, the residue was dissolved in MeCN, and the solution was washed

twice with light petroleum (40–65 °C). Evaporation of the solvent followed by silica gel chromatography (toluene–EtOAc 1 : 3) afforded *p*-methoxyphenyl 4-*O*-chloroacetyl-β-D-xylopyranoside **2** (5.3 g, 47%) as a white solid, $\delta_C(CDCl_3)$ 40.7 ($ClCH_2CO$), 55.8 (OMe), 61.4 (C-5), 72.1, 72.3 and 72.7 (C-2–4), 101.7 (C-1).

Benzoyl chloride (318 μl, 2.74 mmol) was added to a solution of **2** (225 mg, 0.69 mmol) in $CH_2Cl_2$–pyridine (15 : 1; 16 ml) at 0 °C. After being stirred overnight at room temperature the mixture was washed successively with water, 1 M HCl and saturated aq. $NaHCO_3$, dried, filtered and concentrated. Purification of the residue by silica gel chromatography (toluene–EtOAc 6 : 1) gave the dibenzoylated material, which was dissolved in MeOH (15 ml), and hydrazine acetate (59 mg, 0.64 mmol) was added. After 6 h at room temperature the reaction mixture was concentrated, and purified by silica gel chromatography (toluene–EtOAc 3 : 1) to give **3** (203 mg, 62%); $[a]_D$ +70 (*c* 0.1 in $CHCl_3$) (Found: C, 67.05; H, 5.21. Calc. for $C_{26}H_{24}O_8$: C, 67.23; H, 5.21%); $\delta_C(CDCl_3)$ 55.6 (OMe), 64.6, 68.4, 70.4 and 75.2 (C-2–5), 99.9 (C-1), 114.6–155.5 (Ph), 165.2 and 167.0 (Ph*C*O).

### Ethyl 2-*O*-chloroacetyl-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-1-thio-β-D-xylopyranoside 5

CSA (420 mg, 1.8 mmol) was added to a solution of **4**[12] (3.5 g, 18 mmol), butanedione (1.74 ml, 19.8 mmol), and trimethyl orthoformate (5.93 ml, 54 mmol) in dry MeOH (100 ml). The mixture was refluxed for 2 h and then neutralised with $NEt_3$ (0.5 ml), concentrated, and purified by silica gel chromatography (toluene–EtOAc 3 : 1) to give the 3,4-BDA derivative (3.3 g, 59%) and 1.9 g (34%) of the 2,3-BDA isomer.

Chloroacetyl chloride (179 μl, 2.24 mmol) was added to a solution of the 3,4-BDA derivative (393 mg, 1.12 mmol) in $CH_2Cl_2$–pyridine (15 : 1; 16 ml) at 0 °C. The reaction mixture was stirred for 3 h at room temperature, then diluted with toluene, concentrated, and purified by silica gel chromatography (toluene–EtOAc 9 : 1) to afford **5** (381 mg, 92%); $[a]_D$ +110 (*c* 1 in $CHCl_3$) (Found: C, 46.69; H, 6.59. Calc. for $C_{15}H_{25}ClO_7S$: C, 46.81; H, 6.55%); $\delta_C(CDCl_3)$ 14.8 (SEt), 17.5 and 17.6 (BDA), 23.6 (SEt), 40.7 ($ClCH_2CO$), 47.8 and 48.0 (BDA), 65.9, 67.8, 70.7 and 71.9 (C-2–5), 84.2 (C-1), 99.6 and 100.0 (BDA), 165.9 ($ClCH_2CO$).

### *p*-Methoxyphenyl [3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-β-D-xylopyranosyl]-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside 7

A mixture of **3** (3.00 g, 6.52 mmol) and **5** (3.61 g, 9.77 mmol) in dry $CH_2Cl_2$ (150 ml) containing powdered molecular sieves (4 Å) was stirred under Ar at room temperature for 30 min. The solution was then cooled to 0 °C, NIS (2.20 g, 9.77 mmol) and triflic acid (288 μl, 3.2 mmol) were added, and the mixture was stirred for 1 h. The reaction was quenched with the addition of $NEt_3$ (0.5 ml). The mixture was stirred for 10 min and then filtered through Celite. The filtrate was washed successively with $Na_2S_2O_3$ (10% aq.), $NaHCO_3$ (saturated aq.) and water, dried and concentrated. The residue was purified by silica gel chromatography (toluene–EtOAc 6 : 1) to yield *p*-methoxyphenyl [2-*O*-chloroacetyl-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-β-D-xylopyranosyl]-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside **6** (4.25 g, 83%). $\delta_C(CDCl_3)$ 17.4 and 17.6 (BDA), 40.5 ($ClCH_2CO$), 47.7 and 47.9 (BDA), 55.6 (OMe), 62.3, 63.8, 65.3, 70.2, 70.3, 71.4, 72.7 and 75.8 (C-2–5, 2′–5′), 99.5, 99.6, 99.7 and 102.4 (C-1, -1′, BDA), 114.6–155.5 (Ph), 165.2, 165.3 and 165.5 (Ph*C*O, $ClCH_2CO$).

Hydrazine acetate (724 mg, 7.87 mmol) was added to a solution of **6** (4.13 g, 5.25 mmol) in MeOH (100 ml) and the mixture was stirred overnight. Additional hydrazine acetate (200 mg, 2.17 mmol) was added and after 2 h the solution was diluted with $CHCl_3$, washed with water, dried and concentrated. Silica gel chromatography (toluene–EtOAc 3 : 1) of the residue yielded **7** (2.65 g, 71%) (Found: C, 62.35; H, 6.09. Calc. for $C_{37}H_{42}O_{14}$: C, 62.53; H, 5.96%); $\delta_C(CDCl_3)$ 17.5 and 17.6 (BDA), 47.8 and 47.9 (BDA), 55.6 (OMe), 62.3, 63.9, 65.5, 70.3, 70.9, 71.4, 72.2 and 75.0 (C-2–5, 2′–5′), 99.4, 99.5, 99.7 and 104.1 (C-1, -1′, BDA), 114.6–155.4 (Ph), 165.3 and 165.5 (Ph*C*O); $\delta_H(CDCl_3)$ 4.37 (1 H, d, $J_{1,2}$ 6.6 Hz, H-1′), 5.30 (1 H, d, $J_{1,2}$ 5.5 Hz, H-1).

### Methyl (ethyl 2,3-di-*O*-benzyl-4-*O*-methyl-1-thio-β-D-glucopyranosid)uronate 11

Chlorotriphenylmethane (2.27 g, 8.14 mmol) was added to a solution of **8**[16] (3.00 g, 7.42 mmol) in pyridine (16 ml) at room temperature. After being stirred overnight at 55 °C the mixture was diluted with toluene and concentrated. Co-evaporation twice from toluene gave a crude product, which was purified by silica gel chromatography (toluene–EtOAc 19 : 1) to yield ethyl 2,3-di-*O*-benzyl-6-*O*-triphenylmethyl-1-thio-β-D-glucopyranoside **9** (4.46 g, 93%); $\delta_C(CDCl_3)$ 15.2 (SEt), 24.7 (SEt), 64.4 (C-6), 72.2, 75.4, 75.5, 78.0, 81.3, 84.7, 86.1 and 87.0 (C-1–5, $Ph_3C$, $PhCH_2$), 126.7–143.7 (Ph).

Sodium hydride (60% dispersion in oil; 92 mg, 2.32 mmol) was washed with dry light petroleum (40–65 °C). DMF (5 ml) was added and subsequently a solution of **9** (1.0 g, 1.55 mmol) in DMF (10 ml) dropwise at 0 °C. After 1 h, a solution of methyl iodide (135 μl, 2.16 mmol) in DMF (3 ml) was added and the solution was allowed to attain room temperature. After 3 h, MeOH (1 ml) was carefully added and the mixture was diluted with toluene, washed three times with water, dried, and concentrated *in vacuo*. The residue was dissolved in $CHCl_3$–MeOH (2 : 1; 75 ml) and the pH was adjusted to 2 by addition of toluene-*p*-sulfonic acid (PTSA). After 2 h, the mixture was washed successively with water and saturated aq. $NaHCO_3$, dried, concentrated, and purified on a silica gel column (toluene–EtOAc 6 : 1) to give ethyl 2,3-di-*O*-benzyl-4-*O*-methyl-1-thio-β-D-glucopyranoside **10** (435 mg, 67%); $\delta_C(CDCl_3)$ 15.1 (SEt), 25.2 (SEt), 60.8, 62.1 (OMe, C-6), 75.6, 75.7, 79.3, 79.9, 81.6, 85.2 and 86.3 (C-1–5. $PhCH_2$), 127.7–138.5 (Ph).

A stirred solution of oxalyl dichloride (348 μl, 4.06 mmol) in $CH_2Cl_2$ (5 ml) in a 50 ml round-bottomed flask equipped with a pressure-equalising dropping funnel was cooled to −60 °C. A mixture of DMSO (655 μl, 9.23 mmol) in $CH_2Cl_2$ (5 ml) was added dropwise to the stirred oxalyl dichloride solution, followed by dropwise addition of a solution of **10** (1.54 g, 3.69 mmol) in $CH_2Cl_2$ (10 ml). Stirring was continued for 15 min, $NEt_3$ (1.69 ml, 12.18 mmol) was added and the reaction mixture was stirred for 5 min more at −60 °C and then allowed to attain room temperature. 1 M HCl (30 ml) was added, the phases were separated, and the aqueous layer was reextracted with $CH_2Cl_2$ (30 ml). The combined organic layers were washed with saturated aq. NaCl (50 ml), dried and concentrated. The crude aldehyde was dissolved in dry DMF (40 ml) containing MeOH (0.9 ml, 22.1 mmol) and the solution was cooled on ice for 30 min in a vessel covered to exclude light. PDC (8.3 g, 22.1 mmol) was added in one portion. The mixture was allowed to attain room temperature and react overnight and was then poured into a beaker containing EtOAc in order to precipitate chromium salts. The mixture was filtered through Celite, concentrated, and purified on a silica gel column (toluene–EtOAc 12 : 1) to give **11** (934 mg, 57%), mp 67–68 °C; $[a]_D$ +4 (*c* 1 in $CHCl_3$) (Found: C, 64.55; H, 6.75. Calc. for $C_{24}H_{30}O_6S$: C, 64.55; H, 6.77%); $\delta_C(CDCl_3)$ 14.9 (SEt), 25.1 (SEt), 52.4 (6-OMe), 60.6 (4-OMe), 75.4, 75.6, 77.8, 80.8, 81.0, 85.5 and 85.7 (C-1–5, $PhCH_2$), 127.5–138.1 (Ph), 168.5 (C-6).

### Methyl (ethyl 2,3-di-*O*-benzyl-4-*O*-methylsulfonyl-1-thio-β-D-glucopyranosid)uronate 13

$NEt_3$ (1.47 ml, 10.5 mmol) and methanesulfonyl chloride (818 μl, 10.5 mmol) were added to a solution of **9** (2.27 g, 3.5 mmol) in EtOAc (50 ml) at 0 °C. The mixture was stirred for 1 h, then

diluted with EtOAc (50 ml), washed successively with water and 1 M HCl, dried and concentrated. The residue was dissolved in $CHCl_3$–MeOH (2 : 1; 75 ml) and the pH was adjusted to 2 by addition of PTSA. After 2 h, the mixture was washed successively with water and saturated aq. $NaHCO_3$ (aq, sat), dried, concentrated and purified on a silica gel column (toluene–EtOAc 2 : 1) to give ethyl 2,3-di-*O*-benzyl-4-*O*-methylsulfonyl-1-thio-β-D-glucopyranoside **12** (1.15 g, 68%); $\delta_C(CDCl_3)$ 15.0 (SEt), 25.2 (SEt), 38.3 (OMs), 61.0 (C-6), 75.4, 75.6, 78.1, 81.8, 83.1 and 85.1 (C-1–5, Ph*C*$H_2$), 127.4–137.1 (Ph).

Pyridine (192 μl, 2.38 mmol), $CF_3COOH$ (89 μl, 1.19 mmol) and dicyclohexylcarbodiimide (DCC) (1.72 g, 8.35 mmol) were added to a solution of **12** (1.15 g, 2.38 mmol) in DMSO (30 ml) at room temperature. The mixture was stirred overnight. Oxalic acid (1 g) dissolved in MeOH (25 ml) was added to the reaction mixture in order to precipitate formed *N*,*N*-dicyclohexylurea, and after 30 min the mixture was filtered. Toluene and saturated aq. NaCl were added to the filtrate and the phases were separated. The organic phase was washed successively with water, saturated aq. $NaHCO_3$ and water. After drying and concentration of the organic phase, the obtained crude aldehyde was dried on a pump and used for the next oxidation without further purification. The crude aldehyde was dissolved in dry DMF (25 ml) containing MeOH (0.55 ml, 14.28 mmol) and the solution was cooled on ice for 30 min in a vessel covered to exclude light. PDC (5.4 g, 14.28 mmol) was added in one portion. The mixture was allowed to attain room temperature and react overnight and then poured into a beaker containing EtOAc in order to precipitate chromium salts. The mixture was filtered through Celite and the solvents were evaporated. Further purification was accomplished through silica gel chromatography (toluene–EtOAc 10 : 1) and recrystallisation to give **13** (526 mg, 49%), mp 82–83 °C (from EtOAc–hexane); $[a]_D$ +3 (*c* 1 in $CHCl_3$) (Found: C, 55.60; H, 5.98. Calc. for $C_{24}H_{30}O_8S_2$: C, 56.45; H, 5.92%); $\delta_C(CDCl_3)$ 14.9 (SEt), 25.0 (SEt), 38.5 (OMs), 52.7 (6-OMe), 75.2, 75.5, 76.5, 77.7, 81.0, 82.5 and 85.2 (C-1–5, Ph*C*$H_2$), 127.5–137.2 (Ph), 166.8 (C-6).

### *p*-Methoxyphenyl (methyl 4-*O*-benzoyl-2,3-di-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-[3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-β-D-xylopyranosyl]-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside 14β

A mixture of methyl (ethyl 4-*O*-benzoyl-2,3-di-*O*-benzyl-1-thio-β-D-glucopyranosid)uronate (100 mg, 0.19 mmol) and **7** (89 mg, 0.12 mmol) in dry $CH_2Cl_2$ (10 ml) containing powdered molecular sieves (4 Å) was stirred under Ar at room temperature for 30 min. The solution was cooled to 0 °C, NIS (42 mg, 0.19 mmol) and triflic acid (5.5 μl, 0.06 mmol) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was quenched with the addition of $NEt_3$ (0.1 ml), stirred for 10 min, and filtered through Celite. The filtrate was washed successively with 10% aq. $Na_2S_2O_3$, saturated aq. $NaHCO_3$, and water, dried and evaporated. The residue was purified by silica gel chromatography (toluene–EtOAc 9 : 1) to yield **14β** (92 mg, 62%); $\delta_C(CDCl_3)$ 17.5 and 17.7 (BDA), 47.8 and 47.9 (BDA), 52.5 (6″-OMe), 55.5 (PMP-OMe), 62.0, 63.5, 65.1, 70.3, 71.7, 72.7, 73.9, 74.9, 75.1, 78.1, 81.4 and 82.0 (C-2–5, -2′–5′, -2″–5″, Ph*C*$H_2$), 99.1, 99.4, 99.5, 102.5 and 102.8 (C-1, -1′, -1″, BDA), 114.3–155.1 (Ph), 165.0 (Ph*C*O), 167.7 (C-6″).

### *p*-Methoxyphenyl (methyl 4-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-glucopyranosyluronate)-(1→2)-[3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-β-D-xylopyranosyl]-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside 14α

A solution of methyl (ethyl 4-*O*-benzoyl-2,3-di-*O*-benzyl-1-thio-β-D-glucopyranosid)uronate (500 mg, 0.93 mmol) and **7** (442 mg, 0.62 mmol) in dry diethyl ether (10 ml) containing powdered molecular sieves (4 Å) was stirred at 0 °C in an Ar atmosphere for 30 min. To the mixture was added DMTST (642 mg, 2.48 mmol) and the stirring was continued for 1.5 h. After neutralisation with $NEt_3$ (0.5 ml), the mixture was filtered through Celite and concentrated. The residue was purified on a silica gel column (toluene–EtOAc 6 : 1) to yield the **14α** (560 mg, 76%); $\delta_C(CDCl_3)$ 17.2 and 17.5 (BDA), 47.7 and 47.8 (BDA), 52.3 (6″-OMe), 55.6 (PMP-OMe), 61.5, 63.4, 65.5, 68.4, 69.9, 70.6, 70.9, 72.0, 73.3, 73.7, 74.1, 75.0, 77.9 and 78.7 (C-2–5, -2′–5′, -2″–5″, Ph*C*$H_2$), 96.3, 99.0, 99.2, 99.8 and 103.0 (C-1, 1′, 1″, BDA), 114.3–155.2 (Ph), 164.9 and 165.0 (Ph*C*O), 169.0 (C-6″).

### *p*-Methoxyphenyl (methyl 2,3-di-*O*-benzyl-4-*O*-methyl-α-D-glucopyranosyluronate)-(1→2)-[3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-β-D-xylopyranosyl]-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside 15

A solution of **7** (120 mg, 0.28 mmol) and **11** (114 mg, 0.42 mmol) in dry diethyl ether (10 ml) containing powdered molecular sieves (4 Å) was stirred at 0 °C in an Ar atmosphere for 30 min. To the mixture was added DMTST (174 mg, 1.12 mmol) and stirring was continued for 6 h. After neutralisation with $NEt_3$ (0.5 ml), the mixture was filtered through Celite and concentrated. The residue was purified on a silica gel column (toluene–EtOAc 6 : 1) to yield **15** (165 mg, 89%); $[a]_D$ +61 (*c* 0.7 in $CHCl_3$) (Found: C, 64.55; H, 6.16. Calc. for $C_{59}H_{66}O_{20}$: C, 64.71; H, 6.07); $\delta_C(CDCl_3)$ 17.8 and 17.9 (BDA), 48.1 and 48.5 (BDA), 52.5 (6″-OMe), 56.0 (PMP-OMe), 61.0, 61.8, 63.8, 65.0, 70.3, 70.4, 71.1, 71.2, 73.5, 74.0, 74.8, 75.7, 79.2, 81.4 and 82.8 (4″-OMe, C-2–5, -2′–5′, -2″–5″, Ph*C*$H_2$), 97.1, 99.4, 99.7, 100.2 and 103.4 (C-1, 1′, 1″, BDA), 114.7–155.5 (Ph), 165.2 and 165.3 (Ph*C*O), 171.1 (C-6″).

### (4-*O*-Methyl-α-D-glucopyranosyluronic acid)-(1→2)-D-xylopyranosyl-(1→4)-D-xylopyranose 17

To a solution of **15** (72 mg, 0.07 mmol) in EtOAc–MeOH–water–HOAc 4 : 4 : 1 : 1 (5 ml) was added $Pd(OH)_2$ on activated carbon powder and the mixture was hydrogenolyzed at 100 psi for 24 h. The mixture was then filtered through Celite and the filter washed with $CH_2Cl_2$ (50 ml). The filtrate was concentrated to 5 ml, diluted with EtOAc (20 ml), washed successively with water and saturated aq. $NaHCO_3$, dried and concentrated. The residue was dissolved in $CH_3CN$ (1 ml) and cooled in ice. $CF_3COOH$ (aq. 95%; 2 ml) was added and the mixture was stirred for 1 h, then diluted with toluene and concentrated to give the crude tetraol. This was stirred overnight at room temperature in acetic anhydride–pyridine (1 : 1; 5 ml). The mixture was diluted with toluene and concentrated. Co-evaporation of the residue twice from toluene followed by silica gel chromatography (toluene–EtOAc 1 : 1) gave *p*-methoxyphenyl (methyl 2,3-di-*O*-acetyl-4-*O*-methyl-α-D-glucopyranosyluronate)-(1→2)-(3,4-di-*O*-acetyl-β-D-xylopyranosyl)-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside **16** (64 mg, 80%); $\delta_C(CDCl_3)$ 20.6, 20.7 and 20.8 (*Me*CO), 52.5 (6″-OMe), 55.5 (PMP-OMe), 60.1, 60.1, 62.3, 69.2, 69.3, 69.8, 69.9, 70.2, 71.2, 72.1, 73.2, 74.2 and 78.8 (4″-OMe, C-2–5, -2′–5′, -2″–5″), 95.5, 98.0 and 101.7 (C-1, -1′, -1″), 114.4–155.0 (Ph), 164.8 and 165.0 (Ph*C*O), 169.0, 169.3, 169.6 and 169.9 (Me*C*O and C-6″).

CAN (65 mg, 0.12 mmol) was added at 0 °C to a solution of **16** (64 mg, 0.06 mmol) in $CH_3CN$–water (2 : 1; 6 ml). The mixture was stirred for 10 min, then diluted with EtOAc (20 ml) and washed successively with water and brine. The organic phase was dried and concentrated. Silica gel chromatography (toluene–EtOAc 1 : 1) afforded the hemiacetal (35 mg, 61%); $\delta_C(CDCl_3)$ 21.0, 21.2 and 21.3 (*Me*CO), 53.0 (6″-OMe), 59.7, 60.5, 62.6, 69.5, 70.5, 70.6, 71.3, 71.4, 72.5, 72.9, 75.4, 76.0, 77.5 and 79.4 (4″-OMe, C-2–5, -2′–5′, -2″–5″), 90.8, 96.9 and 101.5 (C-1, -1′, -1″), 128.5–133.5 (Ph), 165.8 and 166.0 (Ph*C*O), 169.5, 170.1, 170.2 and 170.7 (Me*C*O and C-6″).

1 M NaOMe (5 drops) was added to a solution of the hemiacetal (35 mg, 0.040 mmol) in MeOH (2 ml). After 2 h, water (1 ml) was added to saponify the methyl ester. The mixture was

stirred for 3 h, then neutralised with 0.1 M HCl and concentrated. The residue was dissolved in water, washed successively with diethyl ether and EtOAc, and subsequently purified on a Bio-Gel P-2 column to give **17** (12 mg, 64%) after freeze-drying; $[\alpha]_D$ +40 (*c* 0.4 in $H_2O$); $\delta_C(D_2O)$ 60.7 (4″-OMe), 62.0, 64.5, 64.9, 67.0, 71.5, 71.9, 73.0, 73.3, 74.3, 75.9, 76.3, 78.2, 78.3, 78.9, 83.7 (C-2–5, -2′–5′, -2″–5″), 93.9, 98.4, 99.7, 103.4 and 103.5 (C-1, -1′, -1″), 175.9 (C-6″); *m*/*z* 497.1 $[M + Na]^+$.

### *p*-Methoxyphenyl (methyl 2,3-di-*O*-acetyl-4-deoxy-β-L-*threo*-hex-4-enopyranosyluronate)-(1→2)-(3,4-di-*O*-acetyl-β-D-xylopyranosyl)-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside 20

A solution of **7** (186 mg, 0.26 mmol) and **13** (200 mg, 0.39 mmol) in dry diethyl ether (15 ml) containing powdered molecular sieves (4 Å) was stirred at 0 °C in an Ar atmosphere for 30 min. To the mixture was added DMTST (270 mg, 1.04 mmol) and stirring was continued for 6 h. After neutralisation with $NEt_3$ (0.5 ml), the mixture was filtered through Celite and concentrated. The residue was purified on a silica gel column (toluene–EtOAc 6 : 1) to yield *p*-methoxyphenyl (methyl 2,3-di-*O*-benzyl-4-*O*-methylsulfonyl-α-D-glucopyranosyluronate)-(1→2)-[3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-β-D-xylopyranosyl]-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside **18** (244 mg, 80%); $[\alpha]_D$ +42 (*c* 1 in $CHCl_3$); $\delta_C(CDCl_3)$ 17.2 and 17.5 (BDA), 38.4 (OMs), 47.7 and 48.0 (BDA), 52.4 (6″-OMe), 55.5 (PMP-OMe), 61.3, 63.6, 65.5, 69.0, 69.8, 70.6, 70.8, 72.5, 73.2, 74.6, 75.5, 78.1, 78.8 and 79.3 (C-2–5, -2′–5′, -2″–5″, Ph*C*$H_2$), 95.9, 98.9, 99.3, 100.0 and 102.4 (C-1, -1′, -1″, BDA), 114.3–155.2 (Ph), 164.9 and 165.0 (Ph*C*O), 168.5 (C-6″).

Compound **18** (298 mg, 0.26 mmol) in EtOAc–MeOH–water–HOAc 4 : 4 : 1 : 1 (10 ml) was hydrogenolyzed over $Pd(OH)_2$ on activated carbon powder at 100 psi for 24 h. Additional catalyst was added and the mixture was hydrogenolyzed for another 16 h at 100 psi and then filtered through Celite. The filter was washed with $CH_2Cl_2$ (50 ml) after which the filtrate was concentrated to 10 ml, diluted with EtOAc (30 ml), washed successively with water and saturated aq. $NaHCO_3$, dried and concentrated to give the crude 2″,3″-diol (218 mg, 87%); $\delta_C(CDCl_3)$ 17.3 and 17.5 (BDA), 38.5 (OMs), 47.8 and 47.9 (BDA), 52.4 (6″-OMe), 55.5 (PMP-OMe), 60.8, 63.6, 65.5, 68.8, 69.6, 70.4, 70.7, 71.3, 71.8, 73.8, 75.0 and 79.1, (C-2–5, -2′–5′, -2″–5″), 97.4, 99.0, 99.4, 99.9 and 103.2 (C-1, -1′, -1″, BDA), 114.6–155.4 (Ph), 164.9 and 165.1 (Ph*C*O), 168.4 (C-6″).

DBU (54 µl, 0.36 mmol) was added under nitrogen to the crude diol (218 mg, 0.22 mmol) in dry $CH_2Cl_2$ (5 ml) and the mixture was stirred at room temperature for 16 h. Additional DBU (27 µl, 0.18 mmol) was then added and the mixture was stirred for another 24 h, whereafter $NH_4Cl$ (saturated aq., 5 ml) was added. The phases were separated and the water phase was extracted twice with $CH_2Cl_2$ (10 ml). The combined organic extracts were washed with water, dried and concentrated. Purification on a silica gel column (toluene–EtOAc 1 : 2) gave *p*-methoxyphenyl (methyl 4-deoxy-β-L-*threo*-hex-4-enopyranosyluronate)-(1→2)-[3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-β-D-xylopyranosyl]-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside **19** (141 mg, 72%); $\delta_C(CDCl_3)$ 16.8 and 17.2 (BDA), 47.1 and 47.3 (BDA), 51.8 (6″-OMe), 55.2 (PMP-OMe), 60.8, 63.3, 65.1, 66.8, 69.4, 70.3, 70.9, 73.7 and 75.4 (C-2–5, -2′–5′, -2″, 3″), 98.6, 98.9, 99.0, 99.1 and 102.8 (C-1, -1′, -1″, BDA), 111.5 (C-4″), 114.2–154.9 (Ph), 140.3 (C-5″), 162.0 (C-6″), 164.7 and 164.8 (Ph*C*O).

Aq. $CF_3COOH$ (95%; 2 ml) was added to an ice-cooled solution of **19** (93 mg, 0.10 mmol) in $CH_3CN$ (1 ml) and the mixture was stirred for 2 h, then diluted with toluene and evaporated. Co-evaporation of the residue twice from toluene followed by silica gel chromatography ($CHCl_3$–MeOH 9 : 1) yielded the 3′,4′-diol (79 mg, 96%); $\delta_C(CDCl_3)$ 52.7 (6″-OMe), 55.5 (PMP-OMe), 61.8, 65.0, 66.1, 69.3, 70.2, 70.4, 71.4, 74.7, 74.9 and 79.8 (C-2–5, -2′–5′, -2″, -3″), 98.8, 99.3 and 102.3 (C-1, -1′, -1″), 112.0 (C-4″), 114.4–155.2 (Ph), 140.5 (C-5″), 162.8 (C-6″), 165.1 and 165.3 (Ph*C*O).

The diol (127 mg, 0.16 mmol) was stirred in acetic anhydride–pyridine (1 : 1; 5 ml) at room temperature for 1 h, when the mixture was diluted with toluene and concentrated. Co-evaporation of the residue twice from toluene followed by silica gel chromatography (toluene–EtOAc 3 : 1) yielded **20** (108 mg, 75%); $[\alpha]_D$ +49 (*c* 1 in $CHCl_3$) (Found: C, 58.98; H, 5.28. Calc. For $C_{46}H_{48}O_{21}$: C, 58.97; H, 5.16%); $\delta_C(CDCl_3)$ 20.4, 20.6, 20.6 and 20.8 (*Me*CO), 52.3 (6″-OMe), 55.5 (PMP-OMe), 60.1, 62.5, 66.2, 67.8, 68.7, 69.0, 69.5, 71.4, 73.5, and 75.2 (C-2–5, -2′–5′, -2″, -3″), 95.9, 97.9 and 102.2 (C-1, -1′, -1″), 107.8 (C-4″), 114.4–155.0 (Ph), 141.9 (C-5″), 161.3 (C-6″), 164.7 and 164.9 (Ph*C*O), 169.4 and 169.5 (Me*C*O).

### (4-Deoxy-β-L-*threo*-hex-4-enopyranosyluronic acid)-(1→2)-β-D-xylopyranosyl-(1→4)-D-xylopyranose 21

CAN (70 mg, 0.13 mmol) was added to a cooled (0 °C) solution of **20** (25 mg, 0.027 mmol) in $CH_3CN$–water (2 : 1; 3 ml). The reaction mixture was stirred for 30 min, then diluted with EtOAc (20 ml) and washed successively with water and brine. The organic phase was dried ($MgSO_4$), filtered and concentrated to give the crude hemiacetal, which was directly dissolved in acetic anhydride–pyridine (1 : 1; 2 ml) and the solution was stirred overnight at room temperature. Dilution of the solution with toluene followed by concentration and silica gel chromatography (toluene–EtOAc 3 : 1) afforded the anomeric acetate (23 mg, 99%); $\delta_C(CDCl_3)$ 20.5, 20.6 and 20.8 (*Me*CO), 52.4 (6″-OMe), 61.5, 62.5, 66.0, 67.8, 68.5, 68.7, 69.8, 71.3, 73.5 and 75.8 (C-2–5, -2′–5′, -2″, -3″), 91.3, 96.1 and 102.1 (C-1, -1′, -1″), 107.4 (C-4″), 128.0–133.2 (Ph), 142.3 (C-5″), 161.4 (C-6″), 164.7 and 164.9 (Ph*C*O), 168.4, 169.5 and 169.6 and 169.7 (Me*C*O).

1 M NaOMe (5 drops) was added to a solution of the hemiacetal (23 mg, 0.028 mmol) in MeOH (2 ml). After 30 min, water (1 ml) was added to hydrolyze the methyl ester and the mixture was stirred for an additional 30 min. Dowex 50 ($H^+$) ion-exchange resin was added to neutralise the solution. Filtration and concentration gave a crude product, which was dissolved in water, washed with diethyl ether, and purified on a Bio-Gel P-2 column to give **21** (8 mg, 64%) after freeze-drying; $[\alpha]_D$ +57 (*c* 0.3 in $H_2O$); $\delta_C(D_2O)$ 59.4, 63.7, 65.8, 66.6, 69.8, 70.7, 71.7, 72.0, 74.6, 74.7, 74.9, 77.1, 77.3 and 78.6 (C-2–5, -2′–5′, -2″, -3″), 92.6, 97.2, 98.8 and 102.2 (C-1, -1′, -1″), 107.7 (C-4″), 146.7 (C-5″), 169.6 (C-6″); *m*/*z* 464.2 $[M + Na]^+$.

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