Carbohydrate Research 344 (2009) 21–28

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Synthesis of regioselectively sulfated xylodextrins and crystal structure of sodium methyl β-D-xylopyranoside 4-*O*-sulfate hemihydrate

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ARTICLE INFO

Article history:
Received 21 August 2008
Received in revised form 9 September 2008
Accepted 10 September 2008
Available online 24 September 2008

Keywords:
Hemicellulose
Sulfation
Regioselectivity
Xylodextrin
Crystal structure

ABSTRACT

Methyl xylobioside and methyl xylotrioside were prepared from the peracetylated anomeric xylosyl trichloroacetimidates by reaction with methanol followed by Zemplén deacetylation. Methyl β-D-xylopyranoside, methyl β-D-xylobioside and methyl β-D-xylotrioside were subjected to treatment with dibutyltin oxide followed by reaction with the trimethylamine/sulfur trioxide complex in tetrahydrofuran. This way, preferential sulfation of the terminal 4-hydroxy group at the nonreducing xylopyranosyl unit was achieved. In addition, partial sulfation at position 2 of the distal xylose unit was observed. The substitution pattern was derived from NMR spectroscopic data and was confirmed by the X-ray structure determination of sodium methyl β-D-xylopyranoside 4-*O*-sulfate. The compound crystallized as a hemihydrate in a triclinic lattice of space group P1 and possesses a pseudomonoclinic 2D supramolecular structure. The sulfation of free pentose oligomers via their intermediate stannylene acetals may thus be exploited to generate biologically active oligosaccharides for biomedical applications.

1. Introduction

Low molecular weight xylans have become available in multigram to kg amounts from process eluents in the dissolving pulp industry and viscose manufacture and may be further converted into xylodextrins.[1] Since renewable materials merit further exploitation for multiple applications, subsequent conversion of these xylans into higher-value products via derivatization should be attempted.[2] Among the approaches for polysaccharide derivatization, sulfation of oligo- and polysaccharides has attracted considerable interest for the development of antithrombotic drugs and as advanced materials for biomedical applications. As examples, regioselectively sulfated cellulose-obtained via protecting group manipulation- has been utilized as inhibitor of adhesion of *Plasmodium falciparum*, while polysulfated β-(1→4)-linked xylans showed inhibitory activity against human immunodeficiency virus-1, respectively.[3,4] Regioselectively sulfated β-(1→3)-linked xylans have been synthesized using the DMF/SO_3 complex and were shown to have antithrombin activity.[5] Sulfated di- and trisaccharides have also been developed as antiasthmatic agents.[6] Common sulfation has mainly been effected using chlorosulfonic acid, DMF/SO_3, N_2O_4/SO_3, and related agents, which often lead to fully or randomly sulfated polysaccharides with concomitant hydrolysis of the saccharide linkages.[7,8] Regioselective derivatization via the intermediate formation of cyclic stannylene acetals has been intensively studied and used as a versatile method for the specific installment of protecting groups—mostly for 1,2-cis oriented diol systems in oligosaccharide synthesis.[9] For xylopyranosides, acylation as well as silylation of stannylene derivatives have been reported to give preferential substitution at O-4 of xylopyranosides.[10–13] While a large body of these studies has been performed in the field of oligosaccharide synthesis, little effort has been invested in comparable reactions on polysaccharides. In a first approach, we describe herein the regioselective introduction of sulfate groups into xylopyranosyl mono-, di- and trisaccharide model compounds complemented by the crystal structure determination of the 4-*O*-monosulfate of methyl β-D-xylopyranoside. Biological data of the sulfated compounds and extension of this approach towards higher xylodextrins will be published in due course.

2. Results and discussion

2.1. Preparation of methyl glycosides of xylooligomers

As defined model compounds of sulfated xylodextrins, methyl glycosides **10** and **12** were synthesized similar to recently published procedures.[14] Thus, a degraded beech wood xylan mixture was subjected to O-acetylation to facilitate chromatographic separation of the oligomers, which furnished mainly per-

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† Member of the European Polysaccharide Network of Excellence (EPNOE).

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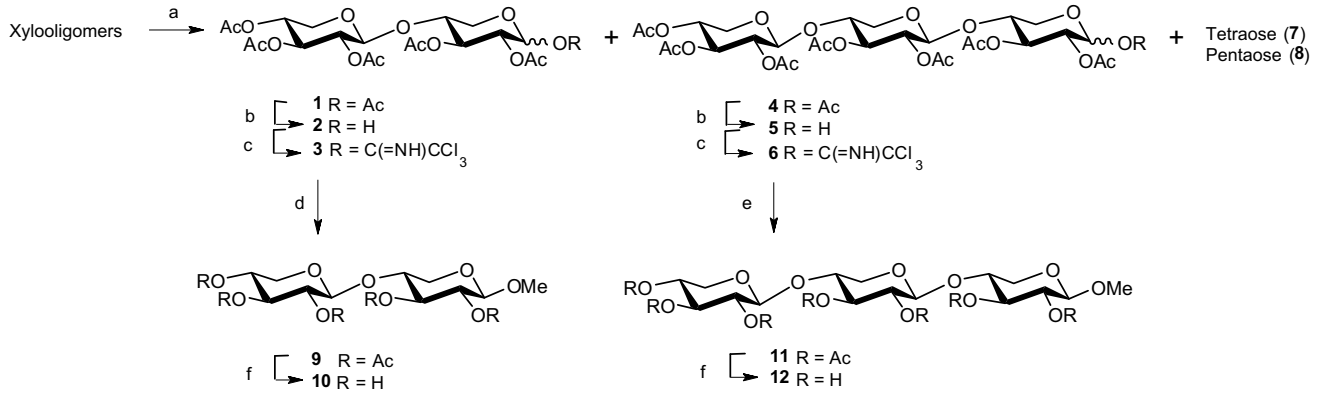
doi:10.1016/j.carres.2008.09.018

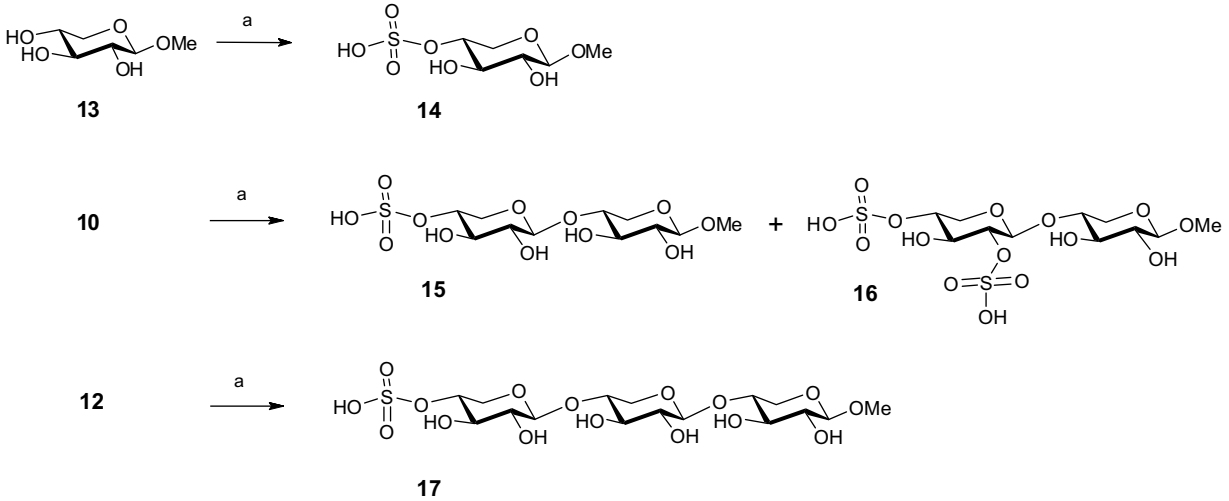
acetylated xylobiose **1** and xylotriose **4** in addition to the tetraose (**7**) and pentaose (**8**) and higher oligomers. The anomeric acetates (α/β ratio ~1:1.3) were then selectively deprotected using Hünig-base/ammonium acetate in DMF, thereby avoiding the formation of the corresponding *N*-benzyl xylosylamines or the use of toxic hydrazinium acetate as reagent.[14,15] This selective anomeric deacetylation under mild conditions has previously also been effective for other mono- and oligosaccharides.[16] This way, the reducing xylobiose **2** and xylotriose **5** were obtained in yields of 92% and 75%, respectively (Scheme 1). Reaction of the reducing xylooligomers with trichloroacetonitrile/DBU afforded the previously reported α-anomeric trichloroacetimidate derivatives **3** and **6**, respectively.[14] Transformation of the donor **3** into the methyl glycoside **9** under promotion with trimethylsilyltrifluoromethane sulfonate at −30 °C was accompanied by hydrolysis and furnished the known methyl xylobioside **9** in 40% isolated yield.[17,18] The use of boron-trifluoride etherate as promotor for glycosidation gave better results and the previously reported methyl trioside **11** was obtained in 50% yield.[19] Deprotection of the acetylated methyl glycosides **9** and **11** by Zemplén deacetylation finally afforded the known methyl glycosides **10** and **12** in high yields, which were then used in the ensuing sulfation reactions.[19]

2.2. Sulfation reactions

Commercially available methyl β-D-xylopyranoside **13**, methyl xylobioside **10** and methyl xylotrioside **12** were converted into the respective intermediate stannylene acetals by reaction with dibutyltin oxide in toluene with continuous separation of water. The stannylene acetal products obtained after removal of the solvent were dissolved in dry THF and reacted at room temperature with an excess of trimethylamine/sulfur trioxide complex for 2–3 days, respectively. The sulfated material was isolated following passage over cation-exchange resin and was finally purified by chromatography on silica gel to give **14** as sodium salt in 74% and **15**, **16** and **17** as potassium salts in 30% and 27% yield, respectively (Scheme 2). The structural assignments of the sulfated products followed from the lowfield-shifted ^{13}C NMR signals seen for the sulfated positions in comparison to the unsulfated educts and xylodextrins, respectively (Table 1).[19,20] All sulfated compounds displayed lowfield–shifted signals of the distal carbon 4 (Fig. 1). The disaccharide product was obtained as a 1:2 mixture of mono- and disulfated derivatives **15** and **16**. In addition to the low-field shifted ^{13}C NMR signal of C-4′ at 76.27 ppm, compound **16** revealed a second low-field shifted carbon signal at 80.11 ppm, which could be correlated via HSQC and HMBC-measurements to the C-2 signal



Scheme 1. Reagents and conditions: (a) Ac_2O, pyr., DMAP, 28 h, rt; (b) DIPEA; NH_4OAc, DMF, 16 h, rt, 92% for **2**, 75% for **5**; (c) Cl_3CCN, DBU, MeCN, CH_2Cl_2, 3 h, −5 °C, 98% for **3**; 50% for **6**; (d) TMSOTf, MeOH, CH_2Cl_2, molecular sieves 4A, 1 h, −30 °C, 40% for **9**; (e) $BF_3{\cdot}Et_2O$, CH_2Cl_2, 0.5 h, −30 °C, 50% for **11**; (f) 1 M NaOMe, MeOH, 8 h, rt, 90% for **10**, 92% for **12**.



Scheme 2. Reagents and conditions: (a) Bu_2SnO, toluene, reflux, 15 h, then $Me_3N{\cdot}SO_3$, THF, 48–72 h, rt, 74% for **14**, 30% for **15** and **16**, 27% for **17**.

Table 1
^{13}C NMR data[a] for sulfated monosaccharide **14,** disaccharides **10**, **15**, and **16**, and trisaccharides **12** and **17**

Residue	Carbon	δ (ppm)					
		14	**10**	**15**	**16**	**12**	**17**
β-Xylp-(1→							
	1		104.00	103.64	101.19	103.98	103.67
	2		74.32	74.27[b]	80.11	74.10	74.08
	3		77.61	75.75[c]	73.73	77.60	75.60[b]
	4		71.05	77.18	76.27	71.03	77.20
	5		67.07	64.40	63.79	67.08	64.89
→4)-β-Xylp-							
	1					103.67	103.61
	2					74.30	74.24
	3					75.80[b]	75.77[b]
	4					78.00	77.91[c]
	5					64.64	64.58
→4)-β-Xylp-OMe							
	1	105.80	105.86	105.83	105.77	105.88	105.85
	2	74.78	74.63	74.59[b]	74.45	74.64	74.61
	3	75.81	75.83	75.66[c]	75.48	75.65[b]	75.64[b]
	4	77.37	78.24	78.17	78.74	78.11	78.13[c]
	5	64.73	64.48	64.90	64.05	64.42	64.40
OCH_3		57.20	57.23	57.19	57.15	57.23	57.20

[a] Spectra (75.47 MHz) were recorded at 297 K in CD_3OD and referenced to 1,4-dioxane (δ 67.40).
[b,c] Assignments within a column may be reversed.

of the non-reducing xylopyranoside unit. The substitution at O-2 also led to high-field shifted signals of the neighboring carbons C-1′ and C-3′ (Table 1.)

2.3. Crystal structure of 14

The sodium salt of **14** was crystallized from ethanol/chloroform with a small amount of water to give thin prisms. Using this material, the crystal structure was determined as described in the experimental section. The compound is the sodium salt hemihydrate of **14**. It crystallizes in the triclinic space group *P*1 and contains two independent Na ions, two independent methyl 4-*O*-sulfo-β-D-xylopyranoside anions and one Na-bonded water molecule in the unit cell, which is simultaneously the asymmetric unit (Fig. 2). The two sulfo-xylopyranoside moieties possess similar bond lengths, bond angles, and conformation (Table 2). All oxygen atoms attached to the pyran rings are in equatorial positions. The sulfate oxygen atoms which are linked to the pyran rings exhibit the longest of all C–O bonds (1.448 Å) and show also the significantly longest S–O bonds (ca. 1.60 Å). The S–O mean bond lengths, 1.480(3) Å, is normal. The two Na ions display modestly distorted octahedral coordination figures with Na–O bond distances in the range 2.315–2.536 Å and a mean value of 2.404(4) Å. The O–Na–O angles are in the range 70–113° and 158–165°. Each Na is coordinated by one pyran-O of one xylopyranoside moiety, by two OH oxygen atoms of another xylopyranoside moiety in a chelating fashion, by two O atoms from two SO_4 groups, and by one H_2O molecule. The two independent Na ions are linked by two SO_4 groups in a bridging fashion and by the water molecule (1w) to form a dimer. As the result, a complex 2D supramolecular sheet structure parallel to (001) is formed, as shown in Figure ure3. The sheets are reinforced by intra-layer hydrogen bonds donated by the four independent OH groups and the water molecule, and accepted by the free sulfate oxygen atoms O(8) and O(8′) and the

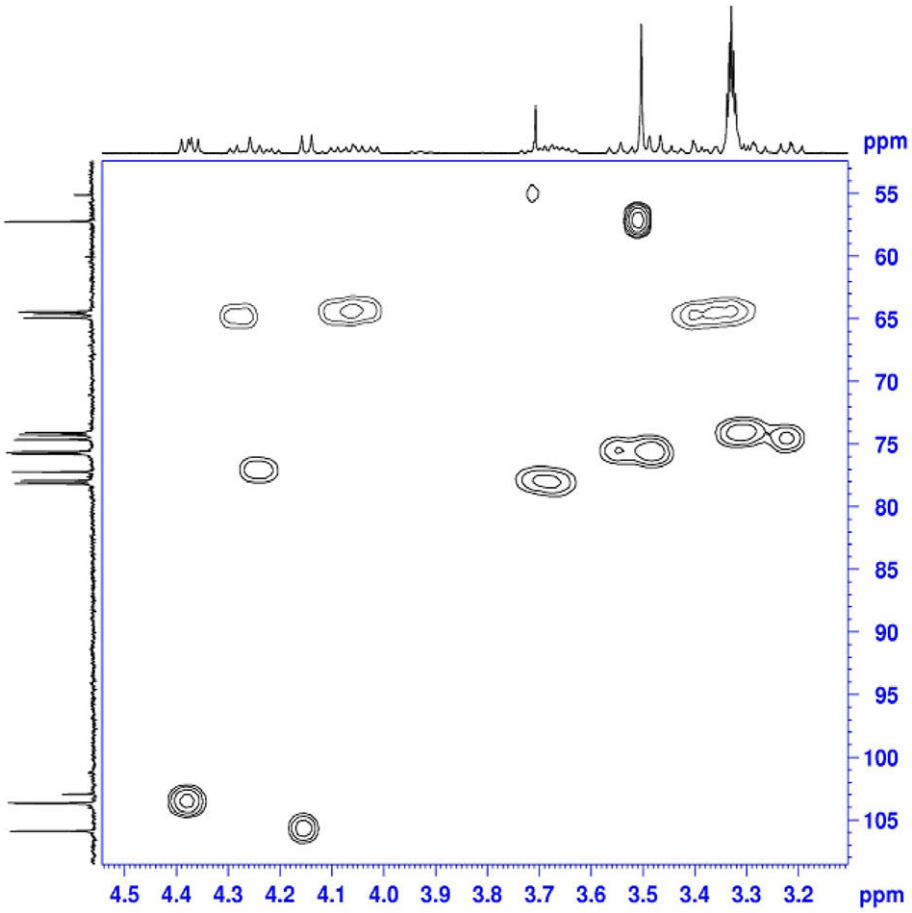


Figure 1. Expansion plot of the HSQC-spectrum of the 4″-O-sulfated methyl β-xylotrioside (**17**).

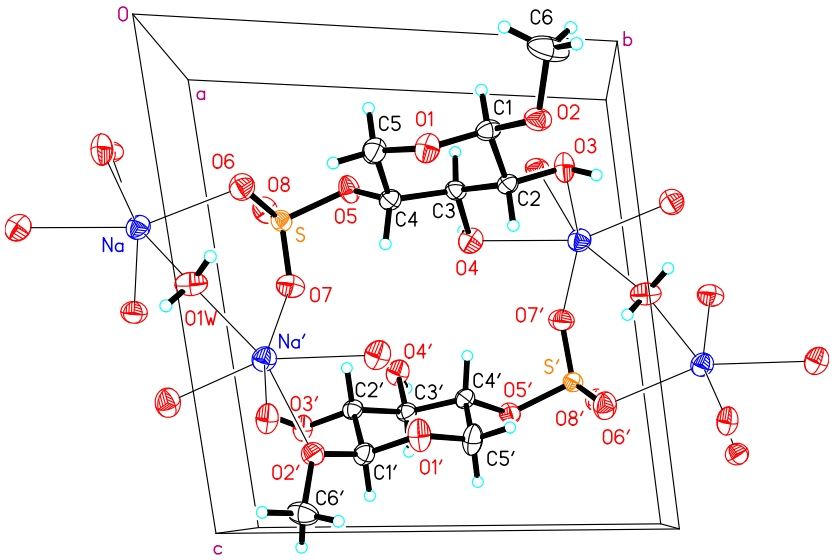


Figure 2. Perspective view of the asymmetric unit (labelled atoms) of the sodium salt hemihydrate of **14** showing 40% ellipsoids.

Table 2
Selected bond lengths and angles for the sodium salt hemihydrate of **14**

	Molecule 1	Molecule 2
Bond lengths (Å)		
Na–O(2)	2.494(4)	2.536(4)
Na–O(3)	2.419(4)	2.428(3)
Na–O(4)	2.436(3)	2.464(3)
Na–O(6)	2.338(4)	2.343(4)
Na–O(7′), Na′–O(7)	2.315(4)	2.328(4)
Na–O(1w), Na′–O(1w)	2.366(4)	2.382(4)
S–O(5)	1.604(3)	1.597(3)
S–O(6)	1.440(3)	1.441(3)
S–O(7)	1.448(4)	1.430(4)
S–O(8)	1.440(3)	1.438(3)
C(1)–C(2)	1.499(5)	1.523(5)
C(2)–C(3)	1.517(5)	1.509(5)
C(3)–C(4)	1.522(5)	1.521(5)
C(4)–C(5)	1.527(6)	1.528(6)
C(1)–O(1)	1.436(5)	1.437(5)
C(1)–O(2)	1.385(4)	1.376(5)
C(2)–O(3)	1.418(4)	1.412(4)
C(3)–O(4)	1.423(5)	1.426(5)
C(4)–O(5)	1.448(4)	1.448(4)
C(5)–O(1)	1.426(5)	1.414(5)
C(6)–O(2)	1.423(6)	1.435(5)
Bond angles (°)		
C(5)–O(1)–C(1)	111.4(3)	111.8(3)
O(1)–C(1)–C(2)	109.3(3)	109.5(3)
C(1)–C(2)–C(3)	107.9(3)	107.7(3)
C(2)–C(3)–C(4)	110.9(3)	111.3(3)
C(3)–C(4)–C(5)	112.6(3)	110.4(3)
C(4)–C(5)–O(1)	110.0(3)	110.8(3)
C(4)–O(5)–S	118.8(2)	118.6(2)
Hydrogen bonds (Å)		
O(3)→O(8)	2.876(4)	2.830(4)
O(4)→O(1)	2.842(4)	2.934(5)
O(1w)→O(8), O(1w)→O(8′)	2.852(5)	2.823(5)

Dimensions of molecule 2 refer to atoms with corresponding atom labels primed, except where given by a second set of atom labels.

pyranose oxygen atoms O(1) and O(1′) (see Table 2 for hydrogen bond lengths). The sheets described are stacked one above the other along the c-axis and are held together only by van-der-Waals forces, as is evident from Figure 3. This figure reveals also clearly the monoclinic pseudo-symmetry, pseudo-space group *C*2, of the structure, which is described in Section 3. The twofold pseudo-axes pass for instance parallel to the view direction through the water molecules and relate the Na ions and sulfo-xylopyranoside moieties with unprimed atom labels to those having primed atom labels (for atom labels see Fig. 2).

3. Conclusions

Regioselective sulfation of unprotected methyl xylooligosaccharides may be achieved in fair yields at the distal 4-hydroxy-group via intermediate dibutylstannylene acetal formation followed by treatment with the trimethylamine/sulfur trioxide complex. A high-resolution crystal structure of sodium methyl β-D-xylopyranoside 4-*O*-sulfate hemihydrate was obtained.

4. Experimental

4.1. General

Concentration of solutions was performed under diminished pressure at temperatures <40 °C. Methyl xylopyranoside was purchased from Fluka. A hydrolytically degraded sample of xylan was obtained from Lenzing AG. Dichloromethane and dry pyridine were dried by refluxing with CaH_2 (5 g per L) for 16 h, then distilled and stored under argon over molecular sieves 0.4 nm. DMF was stirred with CaH_2 (5 g per L) for 16 h at 20 °C, distilled under reduced pressure and stored over activated molecular sieves 0.3 nm. Column chromatography was performed on Silica Gel 60 (230–400 mesh, Merck). Analytical TLC was performed using Silica Gel 60 F_{254} HPTLC plates with 2.5 cm concentration zone (Merck). Spots were detected by treatment with anisaldehyde—H_2SO_4. Size—exclusion chromatography was performed on Bio-Gel® P-2 Gel, Extra fine <45 μm (wet) from Bio-Rad Laboratories. Ion exchange chromatography was performed on a Dowex 50 W × 8 resin, H+ form, 50–100 mesh and/or on a Chelex® 100, Na^+-form, 200–400 mesh resin from Fluka which was transformed into the K^+-form by treatment with HCl (1 M) and KOH (1 M). Melting points were determined on a Kofler hot stage microscope and are uncorrected. Optical rotations were measured with a Perkin–Elmer 243 B polarimeter. NMR spectra were recorded at 297 K in D_2O and $CDCl_3$ with a Bruker DPX 300 or Avance 400 spectrometer (^1H at 300.13 MHz, ^{13}C at 75.47 MHz or ^1H at 400.13 MHz, ^{13}C at

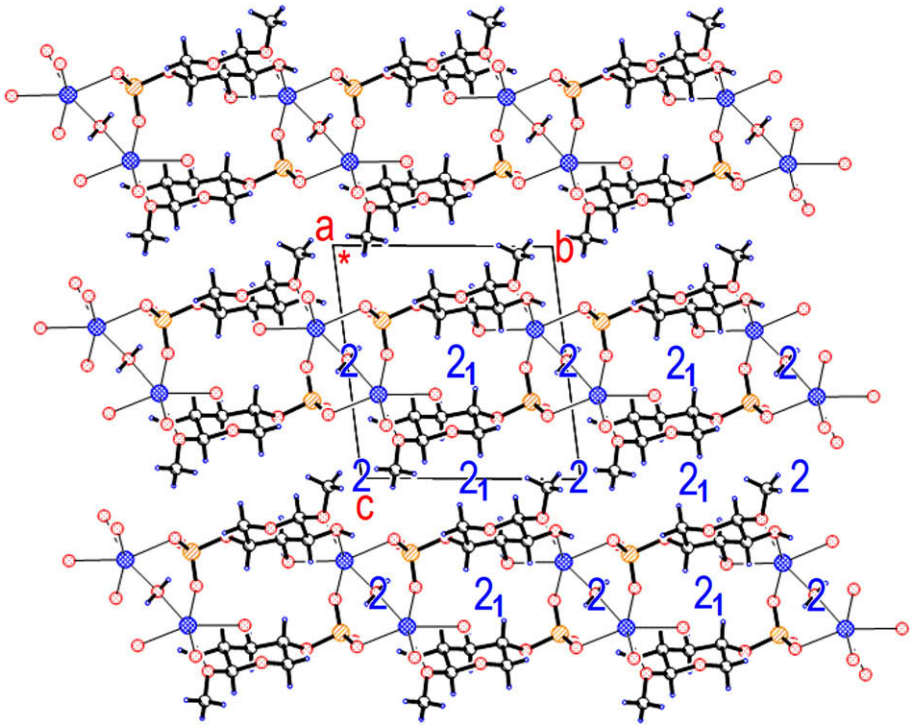


Figure 3. Packing diagram of the sodium salt hemihydrate of **14** in a view down the *a*-axis of the triclinic unit cell. This view direction shows clearly the pseudo-symmetry of the structure with twofold pseudoaxes and pseudo-screw axes indicated by the symbols "2" and "2_1" in the lower right part of the figure (all axes along view direction). The four outermost symbols "2" represent the corners of the monoclinic *C*2 pseudocell. Moreover, the layer-like architecture of the structure parallel to (0 0 1) can be recognized.

100.61 MHz, respectively) using standard Bruker NMR software. ^{1}H NMR spectra were referenced to tetramethylsilane or 2,2-dimethyl-2-silapentane-5-sulfonic acid. ^{13}C NMR spectra were referenced to chloroform for solutions in $CDCl_3$ (δ 77.00) or dioxane (δ 67.40) for solutions in D_2O). For mass spectrometry analyses, samples were dissolved in the appropriate amount of water to give a solution of approx. 1 nmol/μL. Just before analysis an aliquot of the respective sample was diluted in 50% aq acetonitrile containing 0.1% formic acid to give a final concentration of ~10 pmol/μL. This solution was subjected to offline ESI-TOFMS on a Waters Micromass Q-TOF Ultima Global. Capillary voltage was adjusted to obtain approx. 200 counts/s. The MS had been previously tuned with [Glu1]-fibrinopeptide B to give highest possible sensitivity and a resolution of ca. 10.000 (FWHM). Mass tuning of the TOF analyzer was done in the tandem MS mode using again [Glu1]-fibrinopeptide B. Elemental analyses were provided by Dr. J. Theiner, Mikroanalytisches Laboratorium, Institut für Physikalische Chemie, Universität Wien.

4.2. X-ray crystallographic study

The sodium salt of **14** was crystallized from ethanol/chloroform in the presence of a small amount of water to give thin prisms of modest quality. X-ray data were collected with a prism of 0.60 × 0.10 × 0.08 mm on a Bruker Smart APEX CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and ω-scan frames covering a complete sphere of the reciprocal space. After data integration with program SAINT,[21] the structure was solved by direct methods and refined on F^2 with the program package SHELX97.[22] All non-hydrogen atoms were refined anisotropically using DELU 0.03 0.03 restraints for all U_{ij} and SAME restraints for the 1–2 and 1–3 distances of the two independent sulfoxylopyranoside anions. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. Crystal data are **2** ($C_6H_{11}O_5SO_3Na)\cdot H_2O$ = $C_{12}H_{24}Na_2O_{17}S_2$, M_r = 550.41, triclinic, space group *P*1 (no. 1), T = 297 K, a = 6.149(2) Å, b = 9.638(4) Å, c = 10.117(6) Å, α = 79.002(8)°, β = 76.291(7)°, γ = 71.942(7)°, V = 549.3(4) Å^3, Z = 1, ρ_{calc} = 1.664 g/cm^3, μ = 0.364 mm^{-1}. Of 7255 reflections collected up to θ_{max} = 27.5°, 5305 were independent, R_{int} = 0.143, and 4406 were observed ($I > 2\sigma(I)$); final R indices: $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.072$ (all data), $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2} = 0.152$ (all data). Atomic parameters and further details of the structure determination have been deposited. CCDC 698892 contains the supplementary crystallographic data for this paper. Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk). Views of the structure are shown in Figures 2 and 3. Selected bond lengths and angles are given in Table 2. The structure displays a distinct monoclinic pseudosymmetry with pseudo space group *C*2, in which twofold pseudo-axes passing through the water molecules relate pairs of Na cations and pairs of methyl 4-*O*-sulfo-β-D-xylopyranoside anions. The matrix −1 2 0/−1 0 0/0 −1 1 transforms the primitive unit cell into this pseudomonoclinic *C*-centred cell of the dimensions a' = 18.327, b' = 6.149, c' = 12.571 Å, α' = 87.31°, β' = 128.99°, γ' = 89.46°, and V' = 1099 Å^3. The deviations of α' and γ' from 90° and a trial structure refinement in space group *C*2 that resulted in distinctly larger R-indices than given above (R_1 = 0.153, wR_2 = 0.274) proved that the real structure of the compound is triclinic *P*1. For crystal structure determinations of three sodium carbohydrate sulfonates see Ref. 23.

4.3. Preparation of acetylated xylooligosaccharides

The oligosaccharide mixture from Lenzing AG (4 g) containing xylobiose and xylotriose was dried under vacuum and dissolved in dry pyridine (10 mL). The solution was cooled to 5 °C, and 4-*N*,*N*-dimethylaminopyridine (20 mg, 0.16 mmol) and acetic anhydride (60 mL) were added. After 28 h, the mixture was cooled to 0 °C, MeOH (100 mL) was added, and the solution was stirred for

30 min. The mixture was co-evaporated three times with toluene (50 mL). The resulting syrupy product (10 g) was purified by column chromatography (*n*-hexane–EtOAc). The polarity of the system was increased from 2:1→2:1.5→1:1 *n*-hexane–EtOAc to yield first 2.3 g of hexa-*O*-acetyl-xylobiose (**1**) as a colorless syrup followed by 1.6 g of octa-*O*-acetyl-xylotriose (**4**) as well as fractions containing a mixture of **1** and **4**. Further elution of the column afforded 40 mg of deca-*O*-acetylxylotetraose (**7**) as a colorless syrup; R_f = 0.5 (2:3 *n*-hexane–EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) of **7** showed a mixture of α:β anomers in a ratio of 1:1.25, respectively; data for β isomer: δ 5.64 (d, 1H, $J_{1,2}$ 7.2 Hz, H-1), 5.13 (t, 1H, $J_{3,2} = J_{3,4}$ 8.4 Hz, H-3), 5.09 (t, 1H, $J_{3''',2'''} = J_{3''',4'''}$ 7.8 Hz, H-3‴), 5.06 (t, 1H, $J_{3',2'} = J_{3',4'}$ 8.4 Hz, H-3′), 5.05 (t, 1H, $J_{4'',3''} = J_{3'',2''}$ 8.2 Hz, H-3″), 4.96 (dd, 1H, H-2), 4.87 (dd, 1H, $J_{4''',5a'''}$ 4.7 Hz, H-4‴), 4.79 (dd, 1H, $J_{1''',2'''}$ 6.0 Hz, H-2‴), 4.74 (dd, 2H, H-2′, H-2″), 4.55 (d, 1H, H-1‴), 4.47 (d, 1H, $J_{1'',2''}$ 6.6 Hz, H-1″), 4.47 (d, 1H, $J_{1',2'}$ 6.6 Hz, H-1′), 4.09 (dd, 1H, $J_{5a''',4'''}$ 4.7, $J_{5a''',5b'''}$ 12.0 Hz, H-5a‴), 3.995 (dd, 1H, $J_{5a,4}$ 5.1, $J_{5a,5b}$ 12.0 Hz, H-5a), 3.95 and 3.94 (m, 2H, H-5″a, H-5a′), 3.85–3.75 (m, 3H, H-4, H-4′, H-4″), 3.46 (dd, 1H, $J_{5a,4}$ 8.9 Hz, H-5b), 3.39 (dd, 1H, $J_{4''',5b'''}$ 7.6 Hz, H-5‴b), 3.31 (m, 2H, H-5b′, H-5b″), 2.06 – 2.00 (6s, 30H, 10 × CH_3); data for α isomer: δ 6.20 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.36 (dd, 1H, $J_{3,2}$ 9.0, $J_{3,4}$ 10.1 Hz, H-3), 4.94 (dd, 1H, H-2); remaining signals are similar to the β isomer. Finally dodeca-*O*-acetyl-xylopentaose peracetate (**8**) was isolated as a syrup (20 mg); R_f = 0.3 (2:3 *n*-hexane–EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) for β isomer: δ 5.64 (d, 1H, $J_{1,2}$ 7.2 Hz, H-1), 5.16–5.01 (m, 4H, H-3, H-3′, H-3″, H-3‴), 4.81 – 4.70 (m, 6H, H-2, H-2′, H-2″, H-2‴, H-2⁗, H-4⁗), 4.56 (d, 1H, $J_{1'''',2''''}$ 5.9 Hz, H-1⁗), 4.47 (d, 3H, *J* 6.6 Hz, H-1′, H-1″, H-1‴), 4.02–3.87 (m, 5H, H-5a, H-5a′, H-5a″, H-5a‴, H-5a⁗), 3.83 – 3.76 (m, 4H, H-4, H-4′, H-4″, H-4‴), 3.49–3.27 (m, 5H, H-5b, H-5b′, H-5b″, H-5b‴, H-5b⁗) 2.09–2.02 (m, 36H, 12 × CH_3).

4.4. 2,3,2′,3′,4′-Penta-*O*-acetyl-xylobiose (2)

A solution of compound **1** (2.5 g, 4.6 mmol) in a mixture of dry DMF (10 mL) and DIPEA (8 mL, 46.8 mmol, 10 equiv) was stirred with ammonium acetate (4.3 g, 56.1 mmol; crystals were prewashed with 2 × 50 mL portions of diethylether and were dried for 15 min under diminished pressure) for 16 h at rt. The reaction mixture was decanted from the undissolved crystals of ammonium acetate, diluted with CH_2Cl_2 (300 mL) and washed with 1 M aq $NaHCO_3$ (2 × 20 mL), water (20 mL), dried over $MgSO_4$, and concentrated under diminished pressure. The resulting colorless syrup was submitted to silica gel chromatography (3:2 EtOAc–*n*-hexane) to yield 2.1 g (92%) of **2** as colorless crystals; mp 158–163 °C, lit[14] mp 171 °C; R_f = 0.4 (3:2 EtOAc–*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) for α isomer: δ 5.43 (t, 1H, $J_{3,2} = J_{3,4}$ 9.4 Hz, H-3), 5.33 (t, 1H, $J_{1,2}$ 4.0, $J_{1,OH}$ 3.4 Hz, H-1), 5.09 (t, 1H, $J_{3',2'}$ 7.5, $J_{3',4'}$ 8.0 Hz, H-3′), 4.88 (ddd, 1H, $J_{4',5'a}$ 4.3, $J_{4',5'b}$ 7.5 Hz, H-4′), 4.80 (dd, 1H, H-2′), 4.79 (dd, 1H, H-2), 4.57 (d, 1H, $J_{1',2'}$ 5.7 Hz, H-1′), 4.11 (dd, 1H, $J_{5'a,5'b}$ 12.5 Hz, H-5′a), 3.85–3.70 (m, 3H, H-5a, H-4, H-5b), 3.40 (dd, 1H, $J_{5'b,4'}$ 7.5 Hz, H-5′b), 2.79 (d, 1H, OH), 2.08, 2.06, 2.05, 2.04 (4s, 15H, 5 × CH_3). The ^{1}H NMR spectrum also indicated the presence of the β isomer in approx 30%.

4.5. 2,3,2′,3′,4′-Penta-*O*-acetyl-α-D-xylobiosyl trichloroacetimidate (3)

Trichloroacetonitrile (2.4 mL, 24.4 mmol) and DBU (150 μL, 0.6 mmol) were added successively to a solution of reducing pentaacetate **2** (1.0 g, 2.0 mmol) in dry CH_2Cl_2 (12 mL) at −5 °C. After 3 h the reaction mixture was concentrated and the residue was purified by silica gel column chromatography (1:1→2:1 EtOAc–*n*-hexane) to yield 1.2 g (98%) of **3** as colorless foam; R_f = 0.6 (2:1 EtOAc–*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 (s, 1H, NH), 6.42 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 5. 50 (t, 1H, $J_{3,2} = J_{3,4}$ 10.1 Hz, H-3), 5.095 (t, 1H, $J_{3',2'} = J_{3',4'}$ 7.6 Hz, H-3′), 5.00 (dd, 1H, $J_{2,3}$ 10.1 Hz, H-2), 4.88 (ddd, 1H, $J_{4',3'} = J_{4',5b'}$ 7.6, $J_{4',5a'}$ 4.6 Hz, H-4′), 4.80 (dd, 1H, $J_{2',1'}$ 5.8 Hz, H-2′), 4.58 (d, 1H, H-1′), 4.12 (dd, 1H, $J_{5a',5b'}$ 12.0, H-5a′), 3.90–3.77 (m, 3H, H-4, H-5a, H-5b), 3.41 (dd, 1H, H-5′b), 2.06 (s, 6H), 2.04 (s, 6H), and 2.01 (s, 3H, 5 × CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.11, 170.03, 169.86, 169.55, 169.14 (5 × CO), 161.11 (C=NH), 99.70 (C-1′), 93.17 (C-1), 90.73 (CCl_3), 74.90 (C-4), 70.31, 70.24, 70.03, 69.78 (C-2, C-3, C-2′, C-3′), 68.21 (C-4′), 61.46 (C-5, C-5′), 20.90, 20.77 (double intensity), 20.65, 20.49 (5 × CH_3).

4.6. 2,3,2′,3′,2″,3″,4″-Hepta-*O*-acetyl-xylotriose (5)

Xylotriose peracetate **4** (2.21 g, 3.06 mmol) was treated with DIPEA (5.24 mL, 30.6 mmol, 10 equiv) in dry DMF (60 mL) using NH_4OAc crystals (2.83 g, 36.7 mmol) following the same procedure as described for **2**. Column chromatography using 2:1→1:2 *n*-hexane–EtOAc gave 1.82 g (75%) of **5** as an amorphous material; R_f = 0.5 (1:2 *n*-hexane–EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) for α-isomer: δ 5.42 (dd, 1H, $J_{3,2}$ 8.2, $J_{3,4}$ 9.8 Hz, H-3), 5.32 (t, 1H, $J_{1,2} = J_{1,OH}$ 3.7 Hz, H-1), 5.09 (t, 1H, $J_{3'',2''}$ 7.7 Hz, H-3″), 5.06 (t, 1H, $J_{3',2'} = J_{3',4'}$ 8.5 Hz, H-3′), 4.87 (ddd, 1H, $J_{4'',5''a}$ 4.6, $J_{4'',3''} = J_{4'',5''b}$ 7.7 Hz, H-4″), 4.79 (dd, 1H, $J_{2'',1''}$ 5.9 Hz, H-2″), 4.74 (dd, 1H, $J_{2',1'}$ 6.7 Hz, H-2′), 4.73 (dd, 1H, H-2), 4.56 (d, 1H, H-1″), 4.49 (d, 1H, Hz, H-1′), 4.09 (dd, 1H, $J_{5a'',5b''}$ 11.9 Hz, H-5a″), 4.01–3.91 (m, 2H, H-5a, H-5a′), 3.87–3.72 (m, 2H, H-4, H-4′), 3.67 (dd, 1H, $J_{5b',4'}$ 4.2, $J_{5b',5a'}$ 9.2 Hz, H-5b′), 3.39 (dd, 1H, $J_{5b'',5a''}$ 12.0 Hz, H-5b″), 3.36–3.28 (m, 1H, H-5b), 2.08–2.02 (21H, 7 × CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.98, 169.89, 169.84, 169.72, 169.42, 169.39, 169.18 (CO), 100.46 (C1′), 99.38 (C1″), 95.86 (C1β), 90.24 (C1α), (74.73 (C4′), 74.16 (C4), 71.92 (C3), 70.95 (C2′), 70.27 (C2″), 70.28 (C3″), 69.97 (C3′), 69.74 (C2), 68.25 (C4″), 63.37 (C5), 62.60 (C5′), 61.48 (C5″), 21.03, 20.89, 20.81, 20.75, and 20.62 (CH_3).

4.7. Methyl 2,3,2′,3′,4′-penta-*O*-acetyl-β-D-xylobioside (9) and methyl β-D-xylobioside (10)

Dry MeOH (31.8 μL, 0.78 mmol) was placed in a flask containing molecular sieves (3 Å) in dry CH_2Cl_2 (5.0 mL) and cooled to −30 °C under Ar for 30 min. α-Trichloroacetimidate derivative **3** (0.5 g, 0.78 mmol) was dissolved in dry CH_2Cl_2 (5 mL) and cooled to −30 °C in a separate flask. TMSOTf (36.1 μL, 0.2 mmol) was added to the flask containing MeOH in CH_2Cl_2 and the trichloroacetimidate solution was added subsequently. The reaction mixture was stirred for 1 h, then diluted with CH_2Cl_2 (50 mL) and neutralized by adding triethylamine (0.2 mL) with a syringe. Molecular sieves were filtered off and the filtrate was concentrated under diminished pressure. Purification of the residue by silica gel column chromatography (1:2→2:3 EtOAc–*n*-hexane) gave 160 mg of **9** (40%) as colorless crystals, mp 138–141 °C, lit.[17,18] mp 145–146 °C; R_f = 0.5 (2:1 EtOAc–*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.12 (t, 1H, $J_{3,2}$ 8.5 Hz, H-3), 5.09 (t, 1H, $J_{3',2'}$ 8.0 Hz, H-3′), 4.87 (ddd, 1H, $J_{5a',4'}$ 4.3, $J_{4',3'}$ 8.0 Hz, H-4′), 4.84 (dd, 1H, H-2), 4.80 (dd, 1H, $J_{1',2'}$ 5.9 Hz, H-2′), 4.56 (d, 1H, H-1′), 4.34 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1), 4.10 (dd, 1H, $J_{5a',4'}$ 4.3, $J_{5a',5b'}$ 11.9 Hz, H-5a′), 4.00 (dd, 1H, $J_{5a,5b}$ 11.6, $J_{5a,4}$ 5.2 Hz, H-5a), 3.84 (ddd, 1H, $J_{4,5b}$ 9.0 Hz, H-4), 3.46 (s, 3H, Me), 3.40 (dd, 1H, $J_{5b',4'}$ 7.7 Hz, H-5b′), 2.05 (s, 6H), 2.04 (s, 6H) and 2.03 (s, 3H, 5 × Ac). ^{13}C NMR (75 MHz, $CDCl_3$): δ 101.92 (C-1), 99.57 (C-1′), 74.93 (C-4), 72.49 (C-3), 71.20 (C-3′), 70.38 and 70.29 (C-2,2′), 68.25 (C-4′), 62.81 (C-5), 61.43 (C-5′), 56.79 (OMe), 20.96, 20.75, 20.67, 20.59, 20.57 (5 × CH_3).

Methyl xylobioside **10** was obtained by Zemplén reaction of **9** (0.77 g, 1.53 mmol) using 1 M NaOMe (240 μL, 7.6 mmol) in dry MeOH (10 mL) at rt for 2 h. The solution was made neutral by addition of DOWEX cation-exchange resin (H^+) and the suspension was filtered. The filtrate was concentrated and the residue was purified

by silica gel column chromatography (10:20:1→20:20:1 EtOH–$CHCl_3$–H_2O) to yield **10** as a white solid. Yield: 0.40 g, (90%); ^{1}H NMR (300 MHz, MeOD): δ 4.32 (d, 1H, $J_{1',2'}$ 7.4 Hz, H-1′), 4.13 (d, 1H, $J_{1,2}$ 7.4 Hz, H-1), 4.00 (dd, 1H, $J_{5a,4}$ 5.2, $J_{5a,5b}$ 11.6 Hz, H-5a), 3.89 (dd, 1H, $J_{5a',4'}$ 5.2, $J_{5a',5b'}$ 11.3 Hz, H-5a′), 3.67–3.56 (m, 1H, H-4), 3.53–3.41 (m, 1H, H-4′), 3.51 (t, 1H, $J_{3,2} = J_{3,4}$ 9.0 Hz, H-3), 3.34 (s, 3H, OMe), 3.33–3.26 (m, 3H, H-3′, H-5b, H-5b′), 3.23–3.16 (m, 2H, H-2, H-2′); ^{13}C NMR data see Table 1.

4.8. Methyl 2,3,2′,3′,2″,3″4″-hepta-*O*-acetyl-β-D-xylotrioside (11) and methyl β-D-xylotrioside (12)

Xylotriose **5** (1.4 g, 1.97 mmol) was treated with Cl_3CCN (2.48 mL, 24 mmol) and DBU (86 μL, 0.57 mmol) in dry CH_2Cl_2 (30 mL) at −5 °C following the same procedure as described before for the synthesis of compound **3**. After 3 h the solution was concentrated and the residue was purified by silica gel column chromatography (1:1 *n*-hexane–EtOAc) to yield **6** as a white solid (0.81 g, 50%) which was immediately subjected to the subsequent reaction. Dry MeOH (50 μL, 1.23 mmol) and molecular sieves (3 Å) were cooled to −30 °C under Ar. The α-trichloroacetimidate donor **6** (0.64 g, 0.75 mmol) was dissolved in CH_2Cl_2 (5 mL) and cooled under Ar to −30 °C. A solution of $BF_3{\cdot}Et_2O$ (24 μL, 0.18 mmol) in CH_2Cl_2 (3 mL) was added with a syringe into the flask containing MeOH and subsequently the solution of **6** was added slowly at −30 °C. After 0.5 h, the reaction was stopped by adding Et_3N (0.2 mL) with a syringe. The solution was filtered and the filtrate was concentrated in vacuo. The product was purified by silica gel column chromatography (2:1→3:2 *n*-hexane–EtOAc) to yield **11** (0.27 g, 50%) as colorless prisms; mp 93–95 °C and 140–142 °C (dimorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.10 (t, 1H, $J_{3,2} = J_{3,4}$ 9.0 Hz, H-3), 5.09 (t, 1H, $J_{3'',4''} = J_{3'',2''}$ 8.0 Hz, H-3″), 5.065 (t, 1H, $J_{3',4'} = J_{3',2'}$ 8.8 Hz, H-3′), 4.88 (ddd, 1H, $J_{5a'',4''}$ 4.8 Hz, H-4"), 4.83 (dd, 1H, $J_{1,2}$ 7.6 Hz, H-2), 4.80 (dd, 1H, $J_{1'',2''}$ 6.0 Hz, H-2″), 4.75 (dd, 1H, $J_{1',2'}$ 6.5 Hz, H-2′), 4.54 (d, 1H, H-1″), 4.48 (d, 1H, H-1′), 4.34 (d, 1H, H-1), 4.09 (dd, 1H, $J_{5a'',5b''}$ 12.4 Hz, H-5a″), 3.97 (dd, 1H, $J_{5a,4}$ 5.6, $J_{5a,5b}$ 12.4 Hz, H-5a), 3.94 (dd, 1H, $J_{5a',4'}$ 4.8, $J_{5a',5b'}$ 12.0 Hz, H-5a′), 3.83–3.77 (m, 2H, H-4, H-4′), 3.46 (s, 3H, OMe), 3.39 (dd, 1H, $J_{5b'',4''}$ 7.6 Hz, H-5b″), 3.32 (dd, 1H, $J_{5'b,4'}$ 7.6 Hz, H-5b′), 3.30 (dd, 1H, *J* 9.5 Hz, H-5b) and 2.06-2.03 (21H, 7 × CH_3).

Methyl xylotrioside heptaacetate **11** (180 mg, 0.249 mmol) was dissolved in dry MeOH (5 mL) and a solution of 1 M methanolic NaOMe (80 μL, 2.49 mmol) was added. The solution was stirred at rt for 8 h. Dowex ion-exchange resin (H^+-form) was added until the pH of the suspension was neutral and the resin was filtered off and washed with MeOH (3 × 5 mL). The filtrate was concentrated under diminished pressure and the residue was finally purified by silica gel column chromatography (15:20:1 $CHCl_3$–EtOH–H_2O) yielding **12** as a colorless amorphous solid (99 mg, 92%). ^{1}H NMR (300 MHz, MeOD): δ 4.34 (d, 1H, $J_{1',2'}$ 7.5 Hz, H-1′), 4.32 (d, 1H, $J_{1'',2''}$ 7.4 Hz, H-1″), 4.12 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.04 (dd, 1H, $J_{5a',5b'}$ 11.4, $J_{5a',4'}$ 5.2 Hz, H-5a′), 4.01 (dd, 1H, $J_{5a,5b}$ 11.4, $J_{5a,4}$ 5.2 Hz, H-5a), 3.88 (dd, 1H, $J_{5a'',5b''}$ 11.3, $J_{5a'',4''}$ 5.3 Hz, H-5a″), 3.66 and 3.65 (m, 2H, H-4′, H-4), 3.49 (m, 1H, H-4″), 3.49 (s, 3H, OMe), 3.45 and 3.44 (2t, 2H, $J_{3,2} = J_{3,4} = J_{3',2'} = J_{3',4'}$ 8.8 Hz, H-3′, H-3), 3.36 (m, 1H, H-5b), 3.34 (t, 1H, H-3″), 3.34 (m, 1H, H-5b′), 3.26 (dd, 1H, H-2′), 3.23 (dd, 1H, H-5b″), 3.21 (dd, 1H, H-2″) and 3.185 (dd, 1H, H-2). ^{13}C NMR data see Table 1.

4.9. Methyl 4-*O*-sulfo-β-D-xylopyranoside sodium salt (14)

Methyl β-D-xylopyranoside **13** (0.5 g, 3.045 mmol) and dibutyltin oxide (0.818 g, 3.29 mmol, 1.08 equiv) were heated at reflux in toluene (100 mL) for 15 h with continuous separation of water. The solution was concentrated under reduced pressure. The residue was taken up in dry THF (15 mL) and $SO_3{\cdot}Me_3N$ (0.472 g, 3.39 mmol) was added. After being stirred for 48 h at rt, Na^+ chelex ion exchange resin (5 g) was added to remove salts. The reaction mixture was filtered, and the solvent was evaporated under diminished pressure. The residue was diluted with CH_3OH (5 mL), then loaded onto a cation exchange resin column (Chelex 100, Na^+-form; 200–400 mesh, 1.5 × 7 cm). The column was eluted with MeOH. One molar of NaOH was added until pH was between 7 and 8. The eluent was concentrated to a residue that was purified by chromatography on silica gel using 1:3 EtOH–$CHCl_3$ as eluent to give the sulfated product **14** (0.7 g, 74%), which crystallized from the same eluent EtOH–$CHCl_3$ as colorless needles; mp 189–191 °C; $[\alpha]_D^{23}$ −25 (*c* 0.9, CH_3OH); ^{1}H NMR (300 MHz, MeOD): δ 4.24–4.15 (m, 2H, H-4, H-5a), 4.13 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 3.51 (t, 1H, $J_{3,2} = J_{3,4}$ 9.0 Hz, H-3), 3.48 (s, 3H, OMe), 3.35 (m, 1H, H-5b), 3.23 (dd, 1H, H-2). ^{13}C NMR see Table 1. Anal. Calcd for $C_6H_{11}O_8SNa{\cdot}0.5H_2O$: C, 26.19, H, 4.395, S, 11.65. Found: C, 26.13, H, 4.45, S, 11.38.

4.10. Methyl 4-*O*-sulfo-β-D-xylopyranosyl-(1→4)-β-D-xylopyranoside potassium salt (15) and methyl 2,4-di-*O*-sulfo-β-D-xylopyranosyl-(1→4)-β-D-xylopyranoside dipotassium salt (16)

Methyl xylobioside **10** (210 mg, 0.7 mmol) was converted into the corresponding stannylene derivative following the same procedure as described for the synthesis of **14** using dibutyltin oxide (381 mg, 1.53 mmol) in dry toluene (150 mL) for 48 h. The solvent was removed under diminished pressure and the residue was dissolved in dry THF (15 mL). $SO_3{\cdot}Me_3N$ (140 mg, 1.00 mmol) was added to the solution and the reaction mixture was stirred for 72 h at rt. K^+ chelex ion exchange resin was added, the mixture was filtered, and the solvent was removed under reduced pressure. The residue was dissolved in MeOH (2 mL), loaded onto a cation exchange resin column (Chelex 100, K^+-form; 200–400 mesh, 1.5 × 7 cm). After elution with MeOH, 1 M KOH was added to adjust the pH to 8.0. MeOH was removed under diminished pressure and the product was purified by silica gel column chromatography (1:3 EtOH-$CHCl_3$,) yielding a mixture of mono-sulfated (**15**) and disulfated (**16**) derivative in a ratio of 1:2, respectively, as colorless syrup. Yield: 46 mg, (30%); ^{1}H NMR (300 MHz, MeOD) for **15**: δ 4.36 (d, 1H, $J_{1',2'}$ 7.6 Hz, H-1′), 4.25 (m, 1H, H-4′), 4.20 (m, 1H, H-5a′), 4.14 (d, 1H, $J_{1,2}$ 7.4 Hz, H-1), 4.02 (dd, 1H, $J_{5a,4}$ 5.1, $J_{5a,5b}$ 11.6 Hz, H-5a), 3.66–3.57 (m, 1H, H-4), 3.48 (s, 3H, OMe), 3.49 (m, 2H, H-3, 3′), 3.31 (m, 2H, H-5b, 5b′), 3.30 (m, 1H, H-2′), 3.21 (dd, 1H, H-2); ^{1}H NMR (300 MHz, MeOD) for **16**: δ 4.66 (d, 1H, $J_{1',2'}$ 6.4 Hz, H-1′), 4.30 (m, 1H, H-5a′), 4.28 (m, 1H, H-4′), 4.15 (d, 1H, $J_{1,2}$ 7.4 Hz, H-1), 4.11 (dd, 1H, $J_{2',3'}$ 8.0 Hz, H-2′), 4.08 (dd, 1H, $J_{5a,4}$ 4.9, $J_{5a,5b}$ 12.0 Hz, H-5a), 3.81 (t, 1H, $J_{3',4'}$ 7.8 Hz, H-3′), 3.62 (m, 1H, H-4), 3.51 (t, 1H, $J_{3,4}$ 8.7 Hz, H-3), 3.49 (dd, 1H, H-5b′), 3.48 (s, 3H, OMe), 3.36 (dd, 1H, $J_{5b,4}$ 9.5 Hz, H-5b), 3.20 (dd, 1H, $J_{2,3}$ 8.7 Hz, H-2); ^{13}C NMR data see Table 1. ESI-TOFMS: *m*/*z* = 523.03 [M+3Na] calcd 523.22.

4.11. Methyl 4-*O*-sulfo-β-D-xylopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-β-D-xylopyranoside potassium salt (17)

Methyl xylotrioside **12** (62 mg, 0.14 mmol) was transformed into the stannylene derivative and subsequently into the regioselectively sulfated trisaccharide **17** following the same procedure as described above by treatment with Bu_2SnO (140 mg, 0.56 mmol) in dry toluene (100 mL) at 120 °C. After workup and treatment with $Me_3N{\cdot}SO_3$ (62 mg, 0.45 mmol) in dry THF (5 mL) for 72 h at rt, K^+ chelex ion exchange resin was added, the suspension was filtered and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (3:1 EtOH–$CHCl_3$) and then on a G-25 Sephadex PD-10 column (water) which gave **17**

as syrup. Yield: 21 mg (27%); $[\alpha]_D^{20}$ −50 (*c* 0.3, H_2O); ^1H NMR (400 MHz, MeOD): δ 4.38 (d, 1H, $J_{1'',2''}$ 8.0 Hz, H-1″), 4.36 (d, 1H, $J_{1',2'}$ 7.2 Hz, H-1′), 4.28 (dd, 1H, $J_{5a'',4''}$ 5.6, $J_{5a'',5b''}$ 10.8 Hz, H-5b″), 4.24 (ddd, 1H, $J_{3'',2''} = J_{3'',4''}$ 8.8 Hz, H-4″), 4.14 (d, 1H, $J_{1,2}$ 7.2 Hz, H-1), 4.08 (dd, 1H, $J_{5a',4'}$ 5.2, $J_{5a',5b'}$ 11.6 Hz, H-5a′), 4.03 (dd, 1H, $J_{5a,4}$ 5.2, $J_{5a,5b}$ 11.6 Hz, H-5a), 3.69 and 3.67 (m, 2H, H-4, H-4′), 3.54 (t, 1H, $J_{3'',2''} = J_{3'',4''}$ 8.8 Hz, H-3″), 3.50 (s, 3H, OMe), 3.46 (t, 2H, H-3, H-3′), 3.40 (dd, 1H, $J_{5b'',4''}$ 9.0 Hz, H-5b″), 3.39 and 3.36 (m, 2H, H-5b, H-5b′), 3.32 and 3.28 (dd, 2H, H-2′, H-2″), 3.21 (dd, 1H, $J_{2,3}$ 8.8 Hz, H-2); ^{13}C NMR (100 MHz, MeOD) see Table 1. ESI-TOFMS: *m/z* = 547.09 [M+K] calcd. 547.07.

Acknowledgments

Authors are grateful to Daniel Kolarich and Martin Pabst for providing the MS data. Financial support by the Austrian Christian-Doppler-Research Society in the framework of the CD-Laboratory 'Pulp Reactivity' and the competence centre WOOD Kplus is gratefully acknowledged.

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