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Synthesis of non-glycosidic 4,6′-thioether-linked disaccharides as hydrolytically stable glycomimetics

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Abstract—Michael addition of 1,2:3,4-di-*O*-isopropylidene-6-thio-α-D-galactose (**2**) to 2-propyl 6-*O*-acetyl-3,4-dideoxy-α-D-*glycero*-hex-3-enopyranosid-2-ulose (**1**) afforded, as the major diastereoisomer, 2-propyl 6-*O*-acetyl-3-deoxy-4-*S*-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)-4-thio-α-D-*threo*-hexopyranosid-2-ulose (**3**, 91% yield). Reduction of the carbonyl group of **3**, followed by O-deacetylation gave the two epimers **7** (α-D-*lyxo*) and **8** (α-D-*xylo*) in a 1:2 ratio. On removal of the protecting groups of **8** by acid hydrolysis, formation of an 1,6-anhydro bridge was observed in the 3-deoxy-4-thiohexopyranose unit (**10**). The free non-glycosidic thioether-linked disaccharide 3-deoxy-4-*S*-(6-deoxy-α,β-D-galactopyranos-6-yl)-4-thio-α,β-D-*xylo*-hexopyranose (**11**) was obtained by acetolysis of **10** followed by O-deacetylation. A similar sequence starting from the enone **1** and methyl 2,3,4-tri-*O*-benzoyl-6-thio-α-D-glucopyranoside (**12**) led successfully to 2-propyl 3-deoxy-4-*S*-(methyl 6-deoxy-α-D-glucopyranos-6-yl)-4-thio-α-D-*lyxo*-hexopyranoside (**17**) and its α-D-*xylo* analog (**19**, major product). In this synthetic route, orthogonal sets of protecting groups were employed to preserve the configuration of both reducing ends and to avoid the formation of the 1,6-anhydro ring.

Keywords: Thioether-linked disaccharide analogues; Sugar enones; Michael addition; 4,6′-Thioether-linked sugars

1. Introduction

Coyolosa is a strong hypoglycemic substance isolated from the root of the palm *Acrocomia mexicana*.[1] The structure originally suggested for this compound, comprising two hexopyranose units interconnected by a 6,6′-ether linkage, was a matter of controversy.[2–4] After intensive synthetic work, Haines concluded that coyolosa is not a 6,6′-ether-linked disaccharide.[4] Previously, a disaccharide containing a 5→4 ribose to glucose ether linkage has been reported as constituent of the exotoxin from *Bacillus thuringiensis*.[5] Since the synthesis of this unit in 1971,[6] relatively little work on ether-connected disaccharides has been performed. However, the isolation of coyolosa, in 1997,[1] prompted the development of recent synthesis of 6,6′-ether-connected sugars.[2–4] Also, the syntheses of 2,6′- and 3,6′-ether-linked disaccharide analogues have been described recently.[7] These compounds are representatives of a novel class of hydrolytically stable glycomimetics with 'tail-to-tail' linkages, in contrast to the usual head to tail (reducing) or head to head (non-reducing) disaccharides.

In connection with the current work conducted in our and other laboratories on the synthesis and biological activities of thiodisaccharides[8,9] and disaccharides containing three-bond, disulfide, interglycosidic linkages,[8,10,11] we decided to explore the construction of thioether linkages between hexose moieties. In fact, a few reports were found in the literature on non-glycosidic, thioether-bonded disaccharides. During the 1960s and 1970s some preparations of C-2 symmetric sugar thioethers were described.[12–15] More recently, the

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synthesis of an asymmetric disaccharide mimic having a 3,6-thioether linkage,[16] and other symmetric and asymmetric thioether-linked disaccharide analogues[17] have been reported. The sulfur atom of the thioether linkage is expected to act as a weak hydrogen bonding acceptor, facilitating various biomolecular interactions.[8,18,19] Also, as thioethers display greater flexibility than ethers, owing to the increase in the C–S bond length relative to C–O bond length, thioether-linked disaccharides are expected to possess more conformers than their O-linked counterparts. The conformational flexibility should facilitate binding to the catalytic site of enzymes.[18]

For all these reasons, we report here a practical and highly diastereoselective synthesis of non-glycosidic 4,6′-thioether-linked disaccharides.

2. Results and discussion

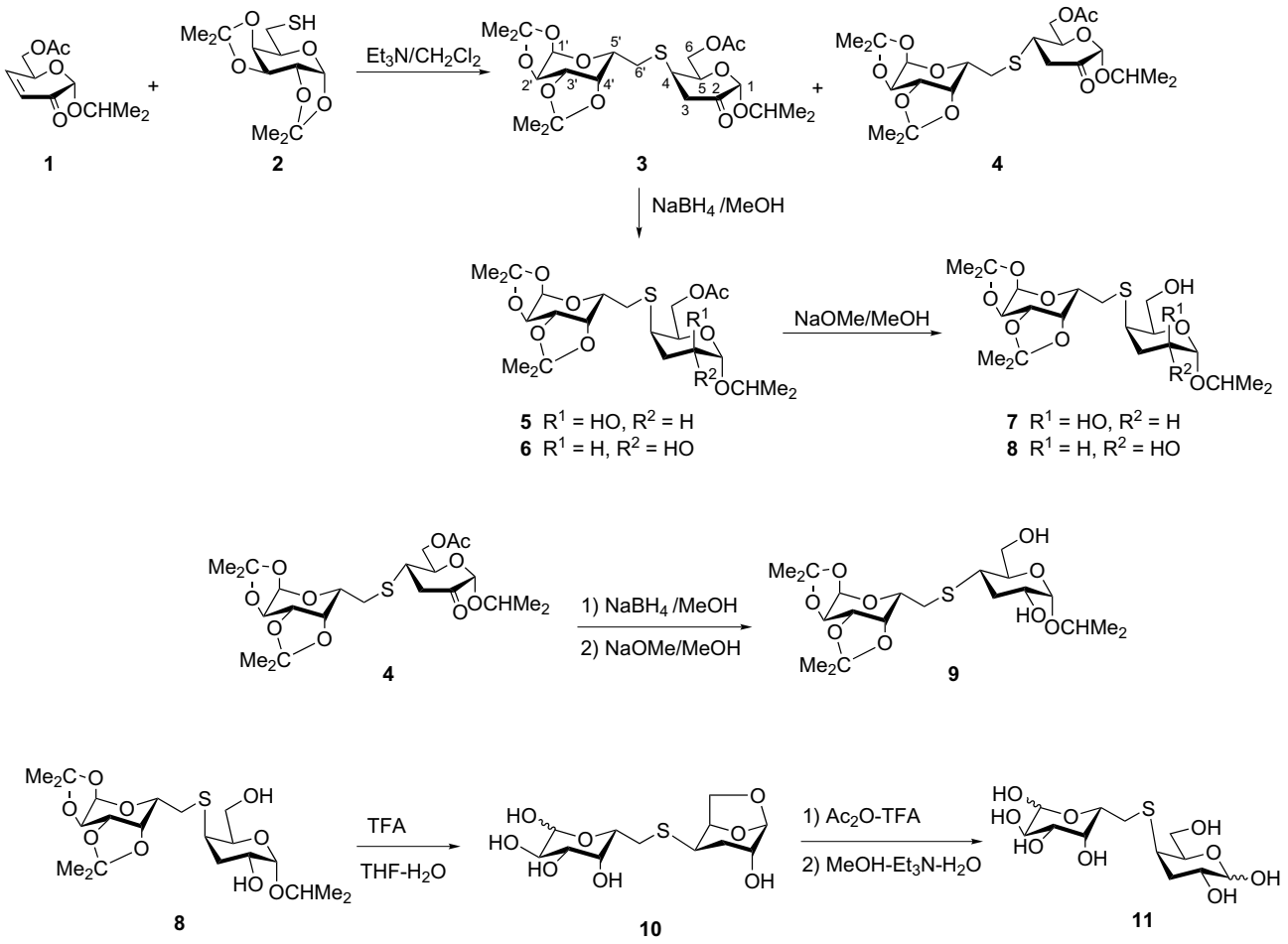
The most common procedure for the construction of ether-[2,4] or thioether-linked hexoses[17] is the direct displacement of a sugar sulfonate (triflate) by a carbohydrate-derived alkoxide or thiolate nucleophile, respectively. As an alternative strategy, we have previously shown that the conjugate addition of 1-thioaldose derivatives to carbohydrate-derived enones (dihydropyranones) constitute a convenient and direct method to form the *S*-linkage of thiodisaccharides.[9] Similarly, Witczak and co-workers[20–23] prepared thiodisaccharides by Michael addition of thiosugars to levoglucosenone, and Thiem[24] described analogous reactions. In this procedure, the use of 1-thioaldose derivatives as nucleophiles establishes a thioglycosidic bond between the constituent sugar moieties. However, carbohydrates bearing thiol groups in non-anomeric positions give rise, to the formation of a thioether linkage. Thus, Chandrasekaran et al.,[16] prepared a non-glycosidic 3,6′-linked thiodisaccharide through Michael addition using an α,β-unsaturated aldonolactone derivative as acceptor. As sulfur is less basic and more nucleophilic than oxygen, thioether based disaccharide analogues are expected to be easier to synthesize than their O-linked counterparts.

We use as a Michael acceptor the enone **1**, which is readily prepared from D-galactose via 2-acetoxy-3,4,6-tri-*O*-acetyl-D-galactal.[25] Conjugate addition of 1,2:3,4-di-*O*-isopropylidene-6-thio-α-D-galactose[26] (**2**) to **1** (Scheme 1) took place in CH_2Cl_2 solution (rt, 18 h) containing a catalytic amount of triethylamine (Et_3N). Column chromatography of the reaction mixture afforded adducts **3** and **4** in about 91% and 6% yield, respectively. These compounds showed diagnostic signals in their ^{13}C NMR spectra (Table 3). Thus, the anomeric carbons of **3** resonate at 97.8 (C-1) and 96.3 ppm (C-1′), the carbonyl carbon at 200.1 ppm, the C-3 methylene carbon at 42.5 ppm and the carbon bonded to sulfur (C-4) at 46.0 ppm. The ^{13}C NMR spectrum of **4** showed similar signals in those regions. The configuration of C-4 in **3** was readily established as *R* on the basis of its ^1H NMR spectrum (Table 1), which showed small coupling constant values between H-4 and H-3a ($J_{3a,4} = 4.6$ Hz), H-3b ($J_{3b,4} = 2.7$ Hz), and H-5 ($J_{4,5} = 1.8$ Hz) indicating equatorial orientation of H-4. C-4 has opposite configuration in **4** as shown by $J_{3b,4}$ (10.9 Hz) and $J_{4,5}$ (10.9 Hz).

The formation of the major diastereoisomer **3** results from the attack of the thiol group of **2** to the face of the enone opposite to the anomeric isopropyl substituent. As observed for related additions to the enone system of dihydropyranones,[9,27,28] the approach of the thiol to the double bond is directed by the axially oriented anomeric substituent.

The carbonyl function of the uloside **3** was reduced with sodium borohydride to afford the partially protected thioether-linked disaccharide analogues **5** and **6**. These two products were isolated by column chromatography in ~91% yield (ratio **5**:**6** ~ 1:2). The 3-deoxy-4-thiopyranose residue of the minor diastereoisomer **5** had the α-D-*lyxo*-hexopyranoside configuration as determined by the small coupling constants $J_{2,3a}$ (3.1 Hz) and $J_{2,3b}$ (3.9 Hz). On the other hand, the large value of one of the $J_{2,3}$ couplings (11.7 Hz) in **6** is indicative of the axial orientation for H-2 and hence, the α-D-*xylo* configuration for the 3-deoxy-4-thiohexopyranoside moiety. The selectivity in the reduction of the carbonyl function of **3** seems to be determined, as for the conjugate addition, by the axial anomeric substituent, vicinal to the carbonyl. However, the sulfur substituent at C-4 of **3** exerts also some steric hindrance on the preferred face of hydride attack. In contrast, the reduction of **4** was highly diastereoselective affording, after O-deacetylation, almost exclusively the non-glycosidic 4,6′-thio-bonded disaccharide **9**. In this case both the thio group and the anomeric substituents hinder the same face of the hexopyranosid-2-ulose moiety in **4**.

Reaction of **5** or **6** with sodium methoxide in methanol afforded the corresponding O-deacetylated products **7** and **8**, respectively. The major product **8** was treated with trifluoroacetic acid (TFA) to remove the anomeric substituent and the isopropylidene protecting groups in one step. However, TLC (*n*-BuOH–EtOH–H_2O, 10:4:4) monitoring of the reaction mixture revealed the presence of one main product (**10**), which was purified by reverse-phase column chromatography (see Section 3). The ^1H NMR spectrum of **10** displayed only three anomeric signals, which agreed with the presence of two equatorial (δ 5.26, $J_{1,2}$ <1 Hz and 5.12, $J_{1',2'} = 3.9$ Hz) and one axial (δ 4.46, $J_{1',2'} = 7.9$ Hz) anomeric protons. In the ^{13}C NMR spectrum of **10** the chemical shifts for the anomeric carbons occurred at 92.30, 96.47, and 100.77 ppm. Comparison of these data with those obtained for **18**, whose structure was rigorously proven



Scheme 1.

Table 1. ^{1}H NMR chemical shift (δ, ppm) and coupling constant (J, Hz) data for compounds **3**–**9**[a]

Compd	H-1 ($J_{1,2}$)	H-2 ($J_{2,3a}$; $J_{2,3b}$)	H-3a ($J_{3a,4}$)	H-3b ($J_{3b,4}$; $J_{3a,3b}$)	H-4 ($J_{4,5}$)	H-5 ($J_{5,6a}$)	H-6a ($J_{5,6b}$)	H-6b ($J_{6a,6b}$)	H-1′ ($J_{1',2'}$)	H-2′ ($J_{2',3'}$)	H-3′ ($J_{3',4'}$)	H-4′ ($J_{4',5'}$)	H-5′ ($J_{5',6'a}$)	H-6′a ($J_{5',6'b}$)	H-6′b ($J_{6'a,6'b}$)
3	4.73	—	3.12	2.76	3.79	4.74	4.40	4.31	5.47	4.28	4.58	4.19	3.89	2.73	2.60
			(4.6)	(2.7; 15.0)	(1.8)	(3.7)	(8.0)	(11.9)	(5.0)	(2.5)	(7.9)	(1.8)	(8.1)	(4.6)	(14.5)
4	4.77	—	2.85	2.85	3.26	4.32	4.53	4.44	5.51	4.30	4.61	4.21	3.84	2.81	2.71
			(6.8)	(10.9; a)	(10.9)	(1.9)	(5.0)	(12.1)	(5.0)	(2.5)	(7.8)	(1.6)	(8.0)	(5.4)	(13.9)
5	4.89	3.59	2.26[b]	2.18	3.27	4.38	4.28	4.28	5.48	4.28	4.59	4.22	3.90	2.86	2.74
	(<1)	(3.1; 3.9)	(3.1)	(3.9; 15.0)	(2.5)	(7.1)	(4.8)	(a)	(4.9)	(2.4)	(7.9)	(1.9)	(7.9)	(5.1)	(13.8)
6	4.89	4.06	2.18	1.93	3.27	4.23	4.23	4.28	5.49	4.28	4.59	4.25	3.86	2.76	2.67
	(4.0)	(4.8; 11.7)	(3.0)	(3.7; 13.0)	(<1)	(a)	(a)	(a)	(5.0)	(2.4)	(7.9)	(1.8)	(7.4)	(6.0)	(13.9)
7	4.88	3.63	2.28	2.21	3.48	4.24	3.87	3.73	5.50	4.31	4.60	4.17	3.95	2.85	2.71
	(<1)	(2,5; 3.7)	(2.5)	(3.7; 15.0)	(1.9)	(7.6)	(6.7)	(11.6)	(4.8)	(2.3)	(7.8)	(1.1)	(9.3)	(3.2)	(14.6)
8	4.88	4.09	2.19	1.94	3.49	4.10	3.84	3.66	5.51	4.30	4.60	4.18	3.92	2.73	2.68
	(3.9)	(4.3; 12.0)	(3.2)	(3.7; 12.5)	(a)	(7.7)	(5.2)	(11.2)	(5.0)	(2.4)	(7.9)	(1.8)	(9.0)	(3.9)	(14.7)
9	4.89	3.64	2.25	1.76	2.84	3.61	3.87	3.83	5.53	4.31	4.61	4.27	3.83	2.84	2.75
	(3.5)	(4.4; 12.2)	(4.4)	(12.2; 12.2)	(a)	(4.3)	(1.7)	(9.0)	(4.9)	(2.5)	(7.9)	(1.8)	(a)	(6.1)	(13.8)

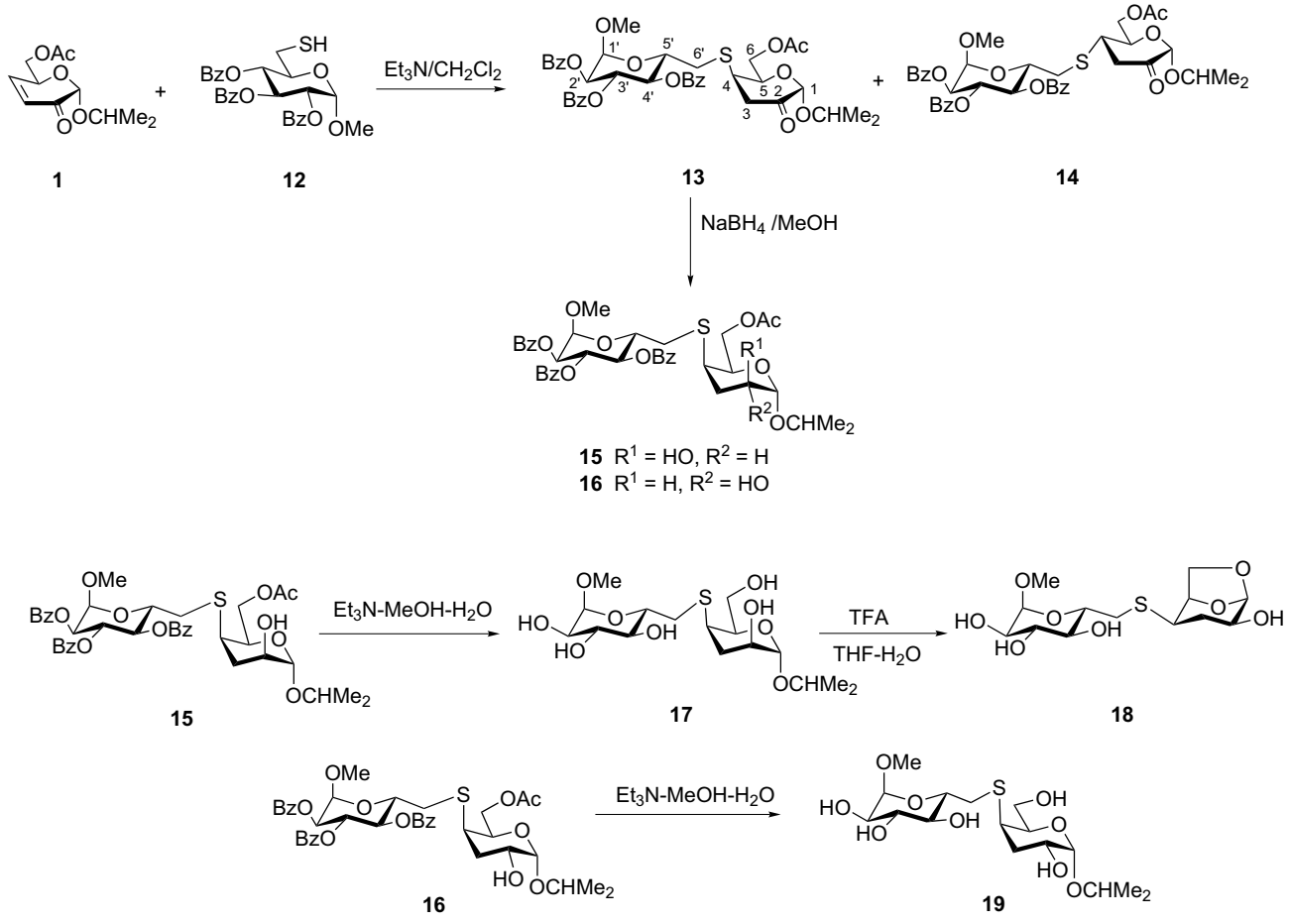
(a) Unavailable because of signal overlap and/or strong coupling.
[a] Determined at 500 MHz for solutions in $CDCl_3$.
[b] Long-range coupling to H-1 ($^{4}J_{1,3b}$ 1.0 Hz).

(vide infra), and with literature values (101.3 ppm for 1,6-anhydro-D-Gal*p*[29]) indicated formation of an 1,6-anhydro ring at the 3-deoxy-4-thiopyranose moiety of **10** during acid treatment of **8**. Different reaction conditions, using TFA or HCl, were tested for the removal of the isopropylidene groups of **8**. However, when this

reaction was successfully accomplished, the main product was always the anhydro sugar **10**. Furthermore, the opening of the 1,6-anhydro bridge by acid hydrolysis was ineffective. This transformation could, however, be achieved by acetolysis of **10** with Ac_2O–TFA, followed by treatment with MeOH–Et_3N–H_2O as described for thiodisaccharides derived from levoglucosenone.[21,22] The free thioether-linked disaccharide **11**, obtained by acetolysis–O-deacetylation of **10** was, as expected, a mixture of anomers due to the two free anomeric centers. Thus, its ^{1}H NMR spectrum showed major signals for two α: 5.12 ($J = 3.8$ Hz), 5.06 ($J = 3.5$ Hz), and two β: 4.47 ($J = 7.8$ Hz), 4.46 ($J = 7.9$ Hz) anomeric protons. The ^{13}C NMR spectrum showed the respective resonances at 93.12, 92.49 and 97.24, 99.39 ppm.

The synthesis of non-glycosidic 4,6′-thioether-bonded disaccharide analogues of **7** and **8** having a 6-thio-D-glucopyranose residue, instead of 6-thio-D-galactopyranose, was also carried out. To preserve the configuration of both reducing ends, orthogonal sets of protecting groups were employed for the protection of anomeric and the non-anomeric hydroxyl functions, respectively. Therefore, methyl 2,3,4-tri-*O*-benzoyl-6-thio-D-glucopyranoside[28] (**12**), bearing base-sensitive benzoyl ester groups, was employed as Michael donor. The conjugate addition of **12** to the enone **1** was conducted using the procedure described for the synthesis of **3** and **4**, to afford the Michael adducts **13** and **14** in 82% and 11% yield, respectively (Scheme 2). The structure of the major diastereoisomer **13** was confirmed by NMR analysis (Table 2). In particular, small values of $J_{3a,4}$ (4.7 Hz) and $J_{3b,4}$ (2.3 Hz) indicated equatorial orientation of H-4, that is, same configuration (*R*) as in **3**. The minor diastereoisomer **14** had the opposite configuration at C-4, as confirmed by comparison of its NMR data with those of **4**.

Reduction of the carbonyl group of **13** with sodium borohydride gave the expected epimeric products **15** and **16**. As for the reduction of **3**, the major D-isomer obtained from **13** was the 3-deoxy-4-thio-α-D-*xylo*-hexopyranose derivative **16** (ratio **15**:**16** ~ 1:2), which resulted from the attack of the hydride to the carbonyl from the side opposite to the anomeric substituent. The structure of **15** and **16** was established by comparison of their spectra with those of the respective analogues **5** and **6**.



Scheme 2.

Table 2. ^{1}H NMR chemical shift (δ, ppm) and coupling constant (J, Hz) data for compounds **13**–**19**[a]

Compd	H-1 ($J_{1,2}$)	H-2 ($J_{2,3a}$; $J_{2,3b}$)	H-3a ($J_{3a,4}$)	H-3b ($J_{3b,4}$; $J_{3a,3b}$)	H-4 ($J_{4,5}$)	H-5 ($J_{5,6a}$)	H-6a ($J_{5,6b}$)	H-6b ($J_{6a,6b}$)	H-1′ ($J_{1',2'}$)	H-2′ ($J_{2',3'}$)	H-3′ ($J_{3',4'}$)	H-4′ ($J_{4',5'}$)	H-5′ ($J_{5',6'a}$)	H-6′a ($J_{5',6'b}$)	H-6′b ($J_{6'a,6'b}$)
13	4.73	—	3.15	2.72	3.64	4.75	4.38	4.34	5.21	5.23	6.13	5.43	4.20	2.82	2.74
			(4.7)	(2.3; 15.0)	(a)	(4.7)	(6.9)	(11.7)	(3.5)	(9.8)	(9.8)	(9.8)	(2.7)	(9.0)	(14.2)
14	4.76	—	≈2.80	≈2.80	3.25	4.23	4.57	4.37	5.23	5.25	6.12	5.46	4.19	2.88	2.83
			(a)	(a)	(10.9)	(2.2)	(4.9)	(12.0)	(3.5)	(9.8)	(9.5)	(9.5)	(2.8)	(a)	(14.0)
15	4.89	3.60	≈2.22	≈2.18	3.24	4.39	4.33	4.29	5.20	5.24	6.13	5.45	4.24	2.90	2.84
	(<1)	(<1; <1)	(a)	(a)	(<1)	(≈1)	(4.7)	(11.7)	(3.4)	(10.2)	(9.9)	(9.9)	(2.9)	(8.7)	(14.0)
16	4.89	4.05	2.15	1.97	3.19	4.19	4.26	4.26	5.21	5.24	6.12	5.46	4.23	2.83	2.78
	(3.9)	(3.1; 12.5)	(4.5)	(3.6; 12.8)	(3.5)	(a)	(a)	(a)	(3.6)	(10.2)	(9.7)	(9.7)	(3.3)	(8.4)	(14.0)
17	4.78		2.25	2.11	3.49	4.18	3.80	3.73	4.64	3.39	3.61	3.21	3.66	3.04	2.73
	(2.4)	—	(4.0)	(4.0; 14.4)	(2.6)	(6.8)	(5.9)	(11.4)	(3.7)	(9.7)	(9.1)	(9.5)	(2.3)	(8.2)	(13.9)
18	5.19	3.58	2.17	1.32	3.15	4.57	4.10	3.72	4.65	3.39	3.58	3.20	3.59	3.10	2.62
	(<1)	(1.2; 10.1)	(5.1)	(12.7; 13.0)	(3.3)	(0.7)	(5.2)	(7.7)	(3.8)	(9.7)	(9.0)	(8.9)	(2.2)	(8.4)	(14.2)
19	4.81	3.99	2.12	2.08	3.24	4.10	3.69	3.66	4.64	3.39	3.58	3.23	3.63	3.01	2.70
	(3.1)	(11.5; 4.8)	(3.7)	(3.1; 12.7)	(2.3)	(5.7)	(7.0)	(11.3)	(3.8)	(9.7)	(9.1)	(9.7)	(2.3)	(8.2)	(14.1)

(a) Unavailable because of signal overlap and/or strong coupling.
[a] Determined at 500 MHz for solutions in $CDCl_3$ (**13**–**16**) or in CD_3OD (**17**–**19**).

Removal of the ester protecting groups from **16** with a MeOH–Et_3N–H_2O afforded **19**, having free hydroxyl groups. The same deprotection procedure applied to **15** led to **17**, an epimer of **19**, having the opposite configuration at C-2 of the 3-deoxy-4-thiopyranose moiety. To verify if this unit of **17**, similar to that observed for **8**, undergoes 1,6-dehydration under acidic conditions, compound **17** was treated with a solution of trifluoroacetic acid (TFA). As expected, this reaction led to formation of the 1,6-anhydro derivative **18**, whose structure was unequivocally established by an HMBC experiment (Fig. 1).

In summary, a convenient procedure for the synthesis of non-glycosidic 4,6′-thioether-linked disaccharides has been developed. The key step is the formation of the thioether bond by a highly diastereoselective Michael addition of a 6-thiohexopyranoside derivative to a sugar enone. The carbonyl group of the 3-deoxy-4-thio-hexopyranosid-2-ulose moiety of the resulting product was reduced to afford the two epimers bearing the D-*xylo* (major product) and D-*lyxo* configurations. The use of orthogonal sets of protecting groups allowed the preparation of thioether-linked disaccharide analogues having defined configurations at the anomeric centers. Conformational studies are being conducted in solution, in order to determine the relative orientation of both pyranose rings connected by a thioether linkage. The synthetic products will be tested as inhibitors of glycosylhydrolases.

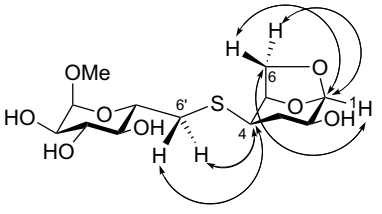


Figure 1. HMBC correlations for **18**.

3. Experimental

3.1. General methods

Melting points were determined in a Fisher–Johns apparatus and are uncorrected. Optical rotations are measured at 20–25 °C with a Perkin–Elmer 341 or 343 polarimeter. ^{1}H and ^{13}C NMR spectra were recorded using Bruker AC 200, Bruker AMX 500 and Avance DRX 500 spectrometers. Chemical shifts are referenced to internal tetramethylsilane (for ^{1}H) or to the residual solvent signals (for ^{13}C: $\delta = 77.00$ ppm for $CDCl_3$ and 49.15 ppm for CD_3OD). Mass spectra were obtained on a Bruker microTOF-Q instrument operating in the ESI mode. Flash-column chromatography was performed on Silica gel (E. Merck, 40–63 μm). Analytical thin layer chromatography (TLC) was performed on Silica Gel 60 F254 (Merck) aluminum supported plates (layer thickness 0.2 mm) with solvent systems given in the text. Visualization of the spots was effected by exposure to UV light and charring with a solution of 5% (v/v) sulfuric acid in EtOH, containing 0.5% *p*-anisaldehyde.

3.2. 2-Propyl 6-*O*-acetyl-3-deoxy-4-*S*-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)-4-thio-α-D-*threo*- (3) and α-D-*erythro*-hexopyranosid-2-ulose (4)

A solution of the enone **1**[25] (0.26 g, 1.14 mmol) and the thiosugar **2**[26] (0.35 g, 1.27 mmol) in dry CH_2Cl_2 (1.4 mL) was flashed with a stream of dry Ar, and a 10% solution of Et_3N (0.1 mL) was added. The mixture

Table 3. ^{13}C NMR chemical shift (δ) for compounds **3**–**9** and **13**–**19**[a]

Compd	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
3	97.84	200.07	42.54	46.00	68.95	65.32	96.26	70.30	70.66	72.00	70.47	29.96
4	97.71	199.91	42.59	43.09	70.31[b]	63.85	96.38	70.40[b]	70.77	71.83	63.85	30.86
5	98.63	67.37	28.35	39.72	67.66	65.50	95.97	69.90	70.35	71.58	69.03	29.50
6	96.47	63.80	33.23	44.04	67.84	65.35	96.06	70.00	70.35	71.42	68.97	30.77
7	98.73	68.17	28.87	40.48	69.56	62.90	96.25	70.34	70.71	72.35	71.04	29.74
8	96.44	69.95	33.50	44.55	64.41	62.67	96.27	70.37	70.67	72.34	71.28	30.97
9	95.79	72.16	35.21	39.73	67.57	62.74	96.41	70.20	70.73	71.67	67.91	30.43
13	97.92	199.23	42.59	47.70	68.84	64.93	96.98	72.08	70.77	72.33	70.04	32.21
14	97.72	199.28	42.73	44.35	70.49	63.68	97.14	72.08	70.24	72.11	70.09	32.73
15	99.13	67.80	29.18	41.90	68.17	65.58	96.96	72.06	70.05	72.31	70.77	32.06
16	96.79	64.05	33.61	46.05	68.15	65.43	96.86	72.09	70.14	72.26	70.49	33.93
17	99.52	69.19	32.26	43.02	73.04[b]	63.52	101.23	73.76[b]	74.90[b]	74.63[b]	73.57[b]	34.84
18	103.66	70.34	33.62	43.82	76.58	66.40	101.33	73.72	75.11	74.56	73.24	34.20
19	98.14	66.04	34.60	47.57	72.10	64.44	101.38	73.77	75.08	74.74	74.06	35.46

[a] Determined at 500 MHz for solutions in $CDCl_3$ (**3**–**9**, **13**–**16**) or in CD_3OD (**17**–**19**).
[b] Assignments can be mutually interchanged.

was stirred at rt for 18 h, when TLC (toluene–EtOAc, 9:1) showed complete consumption of **1**, and formation of two new products having $R_f = 0.52$ and 0.39. The reaction mixture was concentrated and the resulting residue was subjected to column chromatography (hexane–EtOAc, 6:1). The less polar compound ($R_f = 0.52$) was isolated as a syrup and identified as **3** (524 mg, 91.2%); $[\alpha]_D$ −28.0 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) carbohydrate resonances see Table 1, δ: 4.00 [m, 1H, $J = 6.0$ Hz, $(CH_3)_2CHO$], 2.07 (s, 3H, CH_3CO), 1.55, 1.43, 1.32, 1.31, [4s, 12H, $2\times(CH_3)_2C$], 1.26, 1.16 [2d, 6H, $(CH_3)_2CHO$]; ^{13}C NMR (125.7 MHz, $CDCl_3$) carbohydrate resonances see Table 3; δ: 170.72 (CH_3CO), 109.29, 108.86 [$2\times(CH_3)_2C$], 70.39 [$(CH_3)_2CHO$], 26.03, 25.90, 24.92, 24.24 [$2\times(CH_3)_2C$], 23.29, 21.83 [$(CH_3)_2CHO$], 20.89 (CH_3CO); Anal. Calcd for $C_{23}H_{36}O_{10}S$: C, 54.75; H, 7.19; S, 6.35. Found: C, 54.47; H, 7.11; S, 6.31.

The minor product was obtained next ($R_f = 0.39$) and characterized as **4** (32 mg, 5.6%); $[\alpha]_D$ +22.2 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) carbohydrate resonances see Table 1, δ: 3.99 [m, 1H, $J = 6.1$ Hz, $(CH_3)_2CHO$], 2.10 (s, 3H, CH_3CO), 1.53, 1.44, 1.34, 1.33, [4s, 12H, $2\times(CH_3)_2C$], 1.27, 1.18 [2d, 6H, $(CH_3)_2CHO$]; ^{13}C NMR (125.7 MHz, $CDCl_3$) carbohydrate resonances see Table 3, δ: 170.76 (CH_3CO), 109.37, 108.74 [$2\times(CH_3)_2C$], 71.49 [$(CH_3)_2CHO$], 26.04, 25.91, 24.87, 24.32 [$2\times(CH_3)_2C$], 23.21, 21.73 [$(CH_3)_2CHO$], 20.86 (CH_3CO); Anal. Calcd for $C_{23}H_{36}O_{10}S$: C, 54.75; H, 7.19; S, 6.35. Found: C, 54.39; H, 7.20; S, 6.42.

3.3. 2-Propyl 6-*O*-acetyl-3-deoxy-4-*S*-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)-4-thio-α-D-*lyxo*- (5) and α-D-*xylo*-hexopyranosides (6)

To a solution of compound **3** (0.21 g, 0.417 mmol) in MeOH (6 mL) was added sodium borohydride (16 mg, 0.42 mmol). The mixture was stirred at 0 °C for 0.5 h, and then treated in batch with Dowex 50W (H^+) resin, filtered, and concentrated. The residue showed by TLC (hexane–EtOAc, 1:5) two spots having $R_f = 0.40$ and 0.28. The mixture was separated by column chromatography with 3:1 hexane–EtOAc. From the first fractions was isolated the product of $R_f = 0.40$, which was identified as **5** (63 mg, 29.8%); $[\alpha]_D$ −33.6 (*c* 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) carbohydrate resonances see Table 1, δ: 3.94 [m, 1H, $J = 6.2$ Hz, $(CH_3)_2CHO$], 2.05 (s, 3H, CH_3CO), 1.53, 1.43, 1.32, 1.30, [4s, 12H, $2\times(CH_3)_2C$], 1.19, 1.13 [2d, 6H, $(CH_3)_2CHO$]; ^{13}C NMR (125.7 MHz, $CDCl_3$) carbohydrate resonances see Table 3, δ: 170.45 (CH_3CO), 109.16, 108.54 [$2\times(CH_3)_2C$], 68.70 [$(CH_3)_2CHO$], 25.70, 25.56, 24.56, 24.00 [$2\times(CH_3)_2C$], 22.81, 21.08 [$(CH_3)_2CHO$], 20.55 (CH_3CO); ESIMS: *m*/*z* calcd for $[C_{23}H_{38}O_{10}S+Na]^+$: 529.208, found: 529.212; *m*/*z* calcd for $[C_{23}H_{38}O_{10}S+K]^+$: 545.182, found: 545.183.

Further fractions from the column ($R_f = 0.28$) afforded syrupy **6** (128 mg, 60.7%); $[\alpha]_D$ +22.1 (*c* 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) carbohydrate resonances see Table 1, δ: 3.93 [m, 1H, $J = 6.3$ Hz, $(CH_3)_2CHO$], 2.04 (s, 3H, CH_3CO), 1.54, 1.43, 1.33, 1.31 [4s, 12H, $2\times(CH_3)_2C$], 1.23, 1.16 [2d, 6H, $(CH_3)_2CHO$]; ^{13}C NMR (125.7 MHz, $CDCl_3$) carbohydrate resonances see Table 3, δ: 170.55 (CH_3CO), 109.29, 108.73 [$2\times(CH_3)_2C$], 70.34 [$(CH_3)_2CHO$], 25.71, 25.58, 24.59, 23.98 [$2\times(CH_3)_2C$], 22.88, 21.71 [$(CH_3)_2CHO$], 20.59 (CH_3CO); ESIMS: *m*/*z* calcd for $[C_{23}H_{38}O_{10}S+Na]^+$: 529.208, found: 529.211; *m*/*z* calcd for $[C_{23}H_{38}O_{10}S+K]^+$: 545.182, found: 545.187.

3.4. 2-Propyl 3-deoxy-4-*S*-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)-4-thio-α-D-*lyxo*-hexopyranoside (7)

To a solution of **5** (50 mg, 0.10 mmol) in MeOH (1 mL) was added 0.1 M NaMeO in MeOH (1 mL). The solution was stirred at rt for 1 h and treated with Dowex

50W (H^+) resin, filtered, and concentrated. Flash chromatography with 2:1 hexane–EtOAc afforded syrupy **7** (43 mg, 93.8%); $[\alpha]_D$ −31.3 (*c* 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) carbohydrate resonances see Table 1, δ: 3.94 [m, 1H, $J = 6.5$ Hz, $(CH_3)_2CHO$], 1.56, 1.45, 1.34, 1.33, [4s, 12H, $2\times(CH_3)_2C$], 1.21, 1.15 [2d, 6H, $(CH_3)_2CHO$]; ^{13}C NMR (125.7.3 MHz, $CDCl_3$) carbohydrate resonances see Table 3, δ: 109.54, 108.99 [$2\times(CH_3)_2C$], 68.63 [$(CH_3)_2CHO$], 25.90 (×2), 24.85, 24.29 [$2\times(CH_3)_2C$], 23.29, 21.23 [$(CH_3)_2CHO$]; ESIMS: *m*/*z* calcd for $[C_{21}H_{36}O_9S+Na]^+$: 487.197, found: 487.200; *m*/*z* calcd for $[C_{21}H_{36}O_9S+K]^+$: 503.171, found: 503.181.

3.5. 2-Propyl 3-deoxy-4-*S*-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)-4-thio-α-D-*xylo*-hexopyranoside (8)

Deacetylation of **6** (102 mg, 0.20 mmol) was conducted as described for the analogous **5** (Section 3.4) affording syrupy **8** (88 mg, 94.1%); $[\alpha]_D$ −47.2 (*c* 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) carbohydrate resonances see Table 1, δ: 3.93 [m, 1H, $J = 6.3$ Hz, $(CH_3)_2CHO$], 2.79 (OH-6), 1.88 (OH-2), 1.57, 1.45, 1.34 (×2) [4s, 12H, $2\times(CH_3)_2C$], 1.25, 1.17 [2d, 6H, $(CH_3)_2CHO$]; ^{13}C NMR (125.7 MHz, $CDCl_3$) carbohydrate resonances see Table 3, δ: 109.42, 108.96 [$2\times(CH_3)_2C$], 69.81 [$(CH_3)_2CHO$], 25.94, 25.90, 24.88, 24.28 [$2\times(CH_3)_2C$], 23.37, 21.73 [$(CH_3)_2CHO$]; ESIMS: *m*/*z* calcd for $[C_{21}H_{36}O_9S+Na]^+$: 487.197, found: 487.200; *m*/*z* calcd for $[C_{21}H_{36}O_9S+K]^+$: 503.171, found: 503.175.

3.6. 2-Propyl 3-deoxy-4-*S*-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)-4-thio-α-D-*erythro*-hexopyranoside (9)

To a solution of **4** (50 mg, 0.10 mmol) in MeOH (1 mL) was added sodium borohydride (5 mg, 0.13 mmol) and the mixture was stirred at 0 °C for 0.5 h. Then, a 0.1 M solution of NaMeO in MeOH (0.3 mL) was added, and the stirring was continued at rt for an additional 0.5 h. The mixture was treated in batch with Dowex 50W (H^+) resin, filtered and concentrated. Flash chromatography with 2:1 hexane–EtOAc led to syrupy **9** (38 mg, 82.6%); $[\alpha]_D$ +41.6 (*c* 0.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) carbohydrate resonances see Table 1, δ: 3.93 [m, 1H, $J = 6.5$ Hz, $(CH_3)_2CHO$], ≈1.95 (br s, 2H, OH-2, OH-6), 1.53, 1.44, 1.34, 1.32 [4s, 12H, $2\times(CH_3)_2C$], 1.23, 1.17 [2d, 6H, $(CH_3)_2CHO$]; ^{13}C NMR (125.7 MHz, $CDCl_3$) carbohydrate resonances see Table 3, δ: 109.27, 108.26 [$2\times(CH_3)_2C$], 69.92 [$(CH_3)_2CHO$], 25.90, 25.83, 24.74, 24.31 [$2\times(CH_3)_2C$], 23.25, 21.64 [$(CH_3)_2CHO$]; ESIMS: *m*/*z* calcd for $[C_{21}H_{36}O_9S+Na]^+$: 487.197, found: 487.201; *m*/*z* calcd for $[C_{21}H_{36}O_9S+K]^+$: 503.171, found: 503.181.

3.7. 1,6-Anhydro-3-deoxy-4-*S*-(6-deoxy-α,β-D-galactopyranos-6-yl)-4-thio-β-D-*xylo*-hexopyranose (10)

To a solution of **8** (100 mg, 0.215 mmol) in 4:1 THF–H_2O (2 mL) was added 0.5 mL of TFA and stirred at 60 °C. After 4 h no starting **8** was detected by TLC (toluene–EtOAc, 8:2). The reaction mixture was concentrated, dissolved in water (1 mL), and monitored by TLC (*n*-BuOH–EtOH–H_2O, 10:4:4) showing a major component ($R_f = 0.56$). Purification was achieved by filtering the solution through an octadecyl C-18 minicolumn (Amprep, Amersham Biosciences), which was then eluted with water. The syrupy product isolated was characterized as **10** (51 mg, 73%); $[\alpha]_D$ +31.4 (*c* 0.6, MeOH); ^1H NMR (500 MHz, D_2O) anomeric region δ: 5.26 ($J_{1,2}$ <1 Hz, H-1), 5.12 ($J_{1',2'} = 3.9$ Hz, H-1′), 4.46 ($J_{1',2'} = 7.9$ Hz, H-1′); ^{13}C NMR (125.7 MHz, D_2O) anomeric region δ: 100.77 (C-1), 96.47, 92.30 (C-1′); Anal. Calcd for $C_{12}H_{20}O_8S\cdot H_2O$: C, 42.10; H, 6.48. Found: C, 42.44; H, 6.37.

3.8. 3-Deoxy-4-*S*-(6-deoxy-α,β-D-galactopyranos-6-yl)-4-thio-α,β-D-*xylo*-hexopyranose (11)

To a solution of compound **10** (42 mg, 0.124 mmol) in acetic anhydride (2.8 mL), cooled to 0 °C was added CF_3COOH (1 mL) and the mixture was stirred at room temperature during 8 h. The solvent was evaporated to afford a residue that showed by TLC (hexane–EtOAc, 2:3) a main product having $R_f = 0.30$. Purification by column chromatography (hexane–EtOAc, 1:1) afforded the per-*O*-acetyl derivative of **11**, as a mixture of anomers. ^1H NMR (500 MHz, $CDCl_3$) anomeric region δ: 6.34 ($J = 3.4$ Hz), 6.22 ($J = 3.4$ Hz), 5.70 ($J = 7.3$ Hz), and 5.66 ($J = 8.3$ Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) anomeric region δ: 93.10, 92.21, 89.53, and 89.31.

Further O-deacetylation with MeOH–Et_3N–H_2O (4:1:2, 5 mL) at room temperature for 3 h, led to the free non-glycosidic 4,6′-thioether-linked disaccharide **11** (26 mg, 61% overall); $[\alpha]_D$ −2.0 (*c* 0.6, MeOH); ^1H NMR (500 MHz, CD_3OD) anomeric region δ: 5.12 ($J = 3.8$ Hz), 5.06 ($J = 3.5$ Hz), 4.47 ($J = 7.8$ Hz), and 4.46 ($J = 7.9$ Hz); ^{13}C NMR (125.7 MHz, CD_3OD) anomeric region δ: 99.39, 97.24, 93.12, 92.49.

3.9. 2-Propyl 6-*O*-acetyl-3-deoxy-4-*S*-(methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-α-D-glucopyranos-6-yl)-4-thio-α-D-*threo*- (13) and α-D-*erythro*-hexopyranosid-2-ulose (14)

The reaction of the dihydropyranone **1** (104 mg, 0.456 mmol) and the thiosugar **12**[30] (0.24 g, 0.460 mmol) was conducted under the conditions described above (Section 3.2). The reaction mixture, which showed by TLC (toluene–EtOAc, %:1) two spots having $R_f = 0.59$ and 0.38, was subjected to column chromatography (toluene–EtOAc, 14:1). Concentration of the fractions that

contained the product of $R_f = 0.59$ led to foamy compound **13** (280 mg, 81.9%); $[\alpha]_D$ +62.2 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) carbohydrate resonances see Table 2, δ: 8.00–7.25 (m, 15H, H-aromatic), 4.01 [m, 1H, $J = 6.3$ Hz, $(CH_3)_2CHO$], 3.53 (s, 3H, CH_3O), 2.07 (s, 3H, CH_3CO), 1.28, 1.18 [2d, 6H, $(CH_3)_2CHO$]; ^{13}C NMR (125.7 MHz, $CDCl_3$) carbohydrate resonances see Table 3, δ: 170.52 (CH_3CO), 165.81, 165.68, 165.53 (ArCO), 129.15, 129.00, 128.71 (C-aromatic), 133.54, 133.36, 133.07, 129.91, 129.86, 129.62, 128.47, 128.39, 128.24 (CH-aromatic), 71.65 [$(CH_3)_2CHO$], 55.79 (CH_3O), 23.24, 21.77 [$(CH_3)_2CHO$], 20.71 (CH_3CO); Anal. Calcd for $C_{39}H_{42}O_{13}S$: C, 62.39; H, 5.64. Found: C, 62.31; H, 5.37.

The more polar product ($R_f = 0.38$) was identified as **14** (40 mg, 11.2%); $[\alpha]_D$ +114.4 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) carbohydrate resonances see Table 2, δ: 8.05–7.20 (m, 15H, H-aromatic), 3.97 [m, 1H, $J = 6.3$ Hz, $(CH_3)_2CHO$], 3.52 (s, 3H, CH_3O), 2.06 (s, 3H, CH_3CO), 1.24, 1.16 [2d, 6H, $(CH_3)_2CHO$]; ^{13}C NMR (125.7 MHz, $CDCl_3$) carbohydrate resonances see Table 3, δ: 170.49 (CH_3CO), 165.79, 165.75, 165.49 (ArCO), 133.55, 133.35, 133.07, 129.96, 129.90, 129.83, 129.66, 128.51, 128.41, 128.26 (CH-aromatic), 129.26, 129.11, 128.81 (C-aromatic), 71.62 [$(CH_3)_2CHO$], 55.92 (CH_3O), 23.18, 21.73 [$(CH_3)_2CHO$], 20.71 (CH_3CO); Anal. Calcd for $C_{39}H_{42}O_{13}S$: C, 62.39; H, 5.64. Found: C, 62.09; H, 5.57.

3.10. 2-Propyl 6-*O*-acetyl-3-deoxy-4-*S*-(methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-α-D-glucopyranos-6-yl)-4-thio-α-D-*lyxo*- (15) and α-D-*xylo*-hexopyranosides (16)

A solution of compound **13** (248 mg, 0.33 mmol) in MeOH (2.0 mL) was cooled to 0 °C and sodium borohydride (16 mg, 0.42 mmol) was added. The mixture was stirred at 0 °C for 0.5 h, and processed as described above (Section 3.3) to give a syrup, which showed by TLC (hexane–EtOAc, 1.5:1) two spots of $R_f = 0.32$ and 0.23. Separation by column chromatography with 3:1 hexane–EtOAc afforded **15** (85 mg, 34.1%) as a foam; $[\alpha]_D$ +65.5 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): carbohydrate resonances see Table 2, δ: 8.07–7.18 (m, 15H, H-aromatic), 4.95 [m, 1H, $J = 6.4$ Hz, $(CH_3)_2CHO$], 4.12 (br s, 1H, OH), 3.52 (s, 3H, CH_3O), 2.05 (s, 3H, CH_3CO), 1.22, 1.16 [2d, 6H, $(CH_3)_2CHO$]; ^{13}C NMR (125.7 MHz, $CDCl_3$) carbohydrate resonances see Table 3, δ: 170.64 (CH_3CO), 165.82, 165.71, 165.55 (ArCO), 133.58, 133.38, 133.09, 129.93, 129.89, 128.51, 128.41, 128.26 (CH-aromatic), 129.17, 129.01, 128.71 (C-aromatic), 69.36 [$(CH_3)_2CHO$], 55.82 (CH_3O), 23.14, 21.50 [$(CH_3)_2CHO$], 20.77 (CH_3CO); ESIMS: *m*/*z* calcd for $[C_{39}H_{44}O_{13}S+Na]^+$: 775.239, found: 775.232.

From further fractions of the column ($R_f = 0.23$) was obtained **16** (151 mg, 60.7%) as an amorphous solid; $[\alpha]_D$ +84.7 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) carbohydrate protons see Table 2, δ: 8.05–7.15 (m, 15H, H-aromatic), 3.94 [m, 1H, $J = 6.5$ Hz, $(CH_3)_2CHO$], 3.53 (s, 3H, CH_3O), 2.01 (s, 3H, CH_3CO), 1.82 (br s, 1H, OH), 1.25, 1.18 [2d, 6H, $(CH_3)_2CHO$]; ^{13}C NMR (125.7 MHz, $CDCl_3$) carbohydrate resonances see Table 3, δ: 170.56 (CH_3CO), 165.77, 165.69, 165.46 (ArCO), 129.88, 129.83, 129.60, 128.43, 128.35, 128.20 (CH-aromatic), 129.16, 129.00, 128.77 (C-aromatic), 70.69 [$(CH_3)_2CHO$], 55.74 (CH_3O), 23.17, 21.92 [$(CH_3)_2CHO$], 20.67 (CH_3CO); ESIMS: *m*/*z* calcd for $[C_{39}H_{44}O_{13}S+Na]^+$: 775.239, found: 775.236.

3.11. 2-Propyl 3-deoxy-4-*S*-(methyl 6-deoxy-α-D-glucopyranos-6-yl)-4-thio-α-D-*lyxo*-hexopyranoside (17) and 1,6-anhydro-3-deoxy-4-*S*-(methyl 6-deoxy-α-D-glucopyranos-6-yl)-4-thio-β-D-*lyxo*-hexopyranose (18)

A suspension of compound **15** (60 mg, 0.08 mmol) and MeOH–Et_3N–H_2O (4:1:2, 7 mL) was vigorously stirred at rt. The solid was dissolving gradually and, after 6 h, TLC showed a spot of $R_f = 0.0$ (UV inactive) and no starting **15** remaining. The solvent was evaporated and the residue, dissolved in 1:1 MeOH–H_2O (1 mL), was applied to a column of Dowex MR-3C, mixed-bed ion-exchange resin, and eluted with 1:1 MeOH–H_2O. The eluent was concentrated and the deionized product was purified by dissolution in 2:1 MeOH–H_2O (0.5 mL) and filtration through an octadecyl C-18 minicolumn (Amprep, Amersham Biosciences). Concentration of the filtrate afforded syrupy **17** (25 mg, 79%); $[\alpha]_D$ +138.7 (*c* 1.2, MeOH); ^1H NMR (500 MHz, CD_3COD) carbohydrate resonances see Table 2, δ: 4.02 [m, 1H, $J = 6.2$ Hz, $(CH_3)_2CHO$], 3.42 (s, 3H, CH_3O), 1.23, 1.16 [2d, 6H, $(CH_3)_2CHO$]; ^{13}C NMR (125.7 MHz, CD_3COD) carbohydrate resonances see Table 3, δ: 70.13 [$(CH_3)_2CHO$], 55.75 (CH_3O), 23.70, 21.64 [(CH_3CHO)]; Anal. Calcd for $C_{16}H_{30}O_9S{\cdot}H_2O$: C, 46.14; H, 7.74; S, 7.70. Found: C, 46.32; H, 7.80; S, 7.85.

Treatment of **17** (25 mg, 0.063 mmol) with 2 M TFA in a mixture of THF–H_2O (4:1) at 70 °C afforded, after evaporation, compound **18** (20 mg, 94%). $[\alpha]_D$ +85.6 (*c* 0.25, MeOH); ^1H NMR (500 MHz, CD_3OD) carbohydrate resonances see Table 2; δ 3.44 (s, 3H, CH_3O); ^{13}C NMR (125.7 MHz, CD_3OD) carbohydrate resonances see Table 3, δ: 55.75 (CH_3O); ESIMS: *m*/*z* calcd for $[C_{13}H_{22}O_8S+Na]^+$: 361.093, found: 361.088.

3.12. 2-Propyl 3-deoxy-4-*S*-(methyl 6-deoxy-α-D-glucopyranos-6-yl)-4-thio-α-D-*xylo*-hexopyranoside (19)

Compound **16** (95 mg, 0.126 mmol) was deacetylated as described for **15** (Section 3.11), to afford the free non-glycosidic 4,6′-thioether-linked disaccharide **19** (40 mg, 80%); $[\alpha]_D$ +136.7 (*c* 1.0, MeOH); ^1H NMR (500 MHz, CD_3OD) carbohydrate resonances see Table

2, δ: 3.97 [m, 1H, $J = 6.2$ Hz, $(CH_3)_2CHO$], 3.44 (s, 3H, CH_3O), 1.26, 1.18 [2d, 6H, $(CH_3)_2CHO$]; ^{13}C NMR (125.7 MHz, CD_3OD) carbohydrate resonances see Table 3, δ: 70.82 [$(CH_3)_2CHO$], 55.86 (CH_3O), 23.87, 21.88 [$(CH_3)_2CHO$]; ESIMS: m/z calcd for $[C_{16}H_{30}O_9S+Na]^+$: 421.150, found: 421.146.

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