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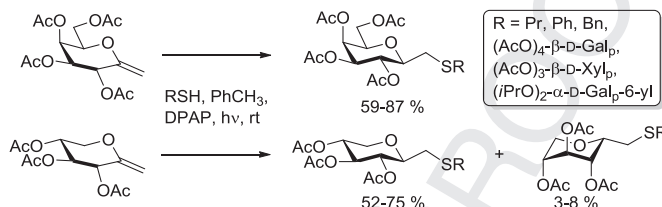
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Graphical Abstract

Photoinitiated hydrothiolation of pyranoid *exo*-glycols: the *D*-galacto and *D*-xylo cases

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János József, László Juhász, Tünde Zita Illyés, Magdolna Csávás, Anikó Borbás, László Somsák*



Highlights

- Photoinitiated thiol-ene reaction of O-acetylated *exo*-glycols.
- Synthesis of β-D-glycopyranosylmethyl-sulfide type glycomimetics.
- Exclusive regio- and stereoselectivity with *exo*-galactal.
- Exclusive regio- and very high stereoselectivity with *exo*-xylal.
- Disaccharide mimicks of Gly-CH₂-S-Gly scaffolds.



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Note

Photoinitiated hydrothiolation of pyranoid *exo*-glycals: the *D*-galacto and *D*-xylo cases

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ARTICLE INFO

Article history:

Received 30 April 2015

Accepted 22 May 2015

Available online xxx

Keywords:

Thiol-ene click reaction

Exo-galactal*Exo*-xylal

Disaccharide mimicks

ABSTRACT

Radical-mediated addition reactions of thiols to *O*-peracetylated *exo*-galactal and *exo*-xylal with 2,2-dimethoxy-2-phenylacetophenone as the photoinitiator resulted in high yielding formation of the corresponding β -*D*-glycopyranosylmethyl-sulfide derivatives (2,6-anhydro-1-deoxy-1-*S*-substituted-1-thioalditols) with exclusive regio- and very high stereoselectivity, including disaccharide mimicks with Gly-CH₂-S-Gly scaffolds.

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Glycomimetic compounds are widely used for deciphering the biological roles of carbohydrate derivatives.¹ Glycomimetics resemble natural carbohydrates in their structure and/or biological function and often serve as lead compounds for drug design.² One of the most important features of such compounds is the hydrolytic stability of the bond(s), which replace the natural *O*-glycosidic linkage(s). A wide range of such replacements were suggested, among others *S*-glycosides and *C*-glycosyl derivatives with a sulfur atom or a methylene group, respectively, in the position of the glycosidic oxygen.¹ In addition, in a number of examples two (or even more) atoms are inserted between the glycon and aglycon³ in the form of e.g., S–S,^{4–8} S–Se,^{8–10} SO₂–N,^{11–13} N–C(=O)–N linking moieties.^{14–17}

Carbohydrate derivatives displaying Gly-CH₂-S-R scaffolds are much less represented among glycomimetics although some synthetic methods, mostly limited to the application of *O*-perbenzylated *exo*-glycals, can be found in the literature. Thus, *exo*-glucal was transformed in several steps into a Glc-CH₂-I derivative,^{18–20} which was reacted under basic conditions with aliphatic and aromatic thiols including sugar derivatives to give the above structures. Ring openings by nucleophiles of an *exo*-glucal-derived spiro-epoxide²¹ as well as a spiro-episulfonium ion²² resulted in ulose derivatives featuring the above structure. Radical-mediated

addition of AcSH to *exo*-glycals furnished *S*-(β -*D*-glycosylmethyl) thioacetates.²³

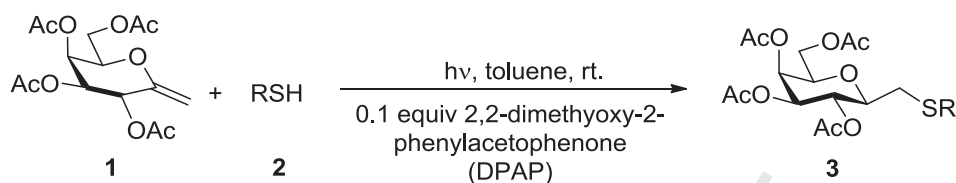
The thiol-ene addition chemistry,^{24,25} either in ionic or radical-mediated versions, has found several applications in carbohydrate chemistry for *S*-glycoconjugation, wherein the sugar derivative generally plays the role of the thiol or is functionalized by *O*- or *C*-appended unsaturated moieties.²⁶ Much less work has been devoted to additions of thiols to sugar 'ene'-s in which the double bond is part of or directly attached to the sugar ring: thus, additions to sugar derived enones²⁷ and some reactions of *endo*-^{28–30} and recently also *exo*-glycals^{30–33} as well as derivatives with an exomethylene group in the 4- and a 5-position of a furanoside and a pyranoside,³⁴ respectively, and a 3-exomethylene-glucofuranose^{31,32} have been reported.

Exo-glycals offer themselves for the construction of Gly-CH₂-S-R type compounds in thiol-ene couplings provided that a sufficient degree of reactivity as well as of regio- and stereoselectivities can be achieved and the reaction conditions are compatible with the protective groups. Base induced anionic additions of thiolates can be expected ineffective with the electron-rich double bond,³³ and acid-catalyzed reactions of thiols yield *S*-glycosides due to the stability of the glycosylium ion.³⁵ Radical-mediated additions must be highly favourable due to the electrophilic nature of thiyl radicals²⁵ and a good regioselectivity may also be foreseen based on the better stabilization of the tertiary glycosyl versus the primary glycosylmethyl radical. Although radical-mediated hydrothiolations

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<http://dx.doi.org/10.1016/j.carres.2015.05.008>

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Table 1
Addition of thiols **2** to *exo*-galactal **1**^a

	R	Ratio of 1 : 2	Yield ^b of 3 (%)
a	Pr	1:10	59
b	Ph	1:10	62
c	Bn	1:10	75
d		1:1.1	72
e		1:1.1	87
f		1:1.1	81

^a Total conversion of **1** was detected after two irradiations of 15 min.

^b Isolated yields after purification by column chromatography.

could be performed with O-benzylated substrates, such protecting groups may be labile under those conditions (cf. a discussion in Ref. 31). On the other hand, O-acyl protection is usually advantageous and stable in radical-mediated reactions,^{36,37} as it was demonstrated recently also by hydrothiolations of O-perbenzoylated *exo*-glucal.^{31,32} In this case both the regio- and stereoselectivities proved excellent as the formation of β -D-glucopyranosylmethyl-sulfides was observed only. As a continuation of these studies, herein we disclose our findings with the photoinitiated thiol-ene reactions of O-peracetylated *exo*-galactal and *exo*-xylal.

The O-peracetylated *exo*-glycals **1** and **4** were synthesized from the corresponding glycosyl cyanides according to our proven procedure.^{38–41} The thiol additions were carried out in toluene at room temperature by irradiation at λ_{max} 365 nm for 15 min in the presence of 2,2-dimethoxy-2-phenylacetophenone (DPAP, 0.1 equiv) as the photoinitiator. The progress of the reaction was controlled by TLC after the first reaction period and irradiation and addition of DPAP were repeated if necessary. The thiols were applied in 10-fold excess for **2a–c** and in slightly more than equimolar amounts for **2d–f**. The results are summarized in Table 1 for *exo*-galactal **1** and in Table 2 for *exo*-xylal **4**.

Each transformation needed two irradiation cycles after, which time total consumption of the *exo*-glycals **1** or **4** was observed. The β -D-galactosylmethyl-sulfides **3** were isolated by column chromatography in good to high yields (59–87%, Table 1). In several reactions of **4** the formation of two products **5** and **6** could be seen. In each of these cases compounds **5** were the major products (52–75%) and **6** could be isolated in very small amounts (<10%, Table 2).

The structure of the products was established by NMR methods. For the D-galactose derivatives **3** the 4C_1 conformation of the pyranoid ring and the equatorial position of the $\text{CH}_2\text{-S-R}$ substituent (corresponding to a β -D C-glycosylic configuration of the C-2 centre) was deduced from the proton spectra. The D-xylose derived **5** existed also in a 4C_1 conformation with a β -D-configured C-2 as revealed by the large three-bond coupling constants of ~ 10 Hz throughout the spectra of these compounds. On the other hand, the proton spectra of **6** exhibited several broad singlet-like signals, which were not well resolved. This was indicative of a pyranoid ring in the 1C_4 conformation (or more probably in a conformational equilibrium involving the 1C_4 chair and boat as well as skew-boat conformations). However, the configuration of the C-2 carbon could not be established on the basis of the proton spectra since both axial and equatorial orientation of substituents of that centre must result in small vicinal couplings in the given conformation. Therefore, the ${}^1J_{\text{C-2,H-2}}$ coupling constants were determined for the pair **5c** and **6c** by ${}^1\text{H}$ decoupled and undecoupled HSQC measurements. ${}^1J_{\text{C,H}}$ coupling constants were obtained by measuring the distance of peaks maxima in F2 (${}^1\text{H}$) dimension from undecoupled HSQC spectra. The practically equal values of these couplings (Table 3, 148.2 Hz for **5c** and 147.4 for **6c**) indicated the axial position of H-2 in both compounds, thereby revealing the α -D configuration for the C-2 atom in **6c**. Variations in the ${}^1J_{\text{C,H}}$ values of the other carbons may also indicate the conformational equilibrium for these derivatives.⁴² For the other xylose derivatives the amounts of the isolated substances did not allow to carry out similar pairwise measurements, therefore, the analogous structure is made probable by the similarities of the ${}^1\text{H}$ NMR spectra

Table 2
Addition of thiols **2** to *exo*-xylal **4**^a

	R	Ratio of 4:2	Yield ^b (%)	
			5	6
a	Pr	1:10	63	4
b	Ph	1:10	52	8
c	Bn	1:10	68	5
d		1:1.1	69	3
e		1:1.1	75	n.d. ^c
f		1:1.1	53	4

^a Total conversion of **4** was detected after two irradiations of 15 min.

^b Isolated yields after purification by column chromatography.

^c The formation of **6** was not detected.

(Table 4). The optical rotations also corroborate these assumptions at least for compounds with non-sugar appendages as derivatives **6a–c** are more dextrorotatory than **5a–c**, respectively. The *S*-glycosyl moieties of the disaccharide like **3d–f**, **5d–f**, and **6d–f** gave the expected signals in the NMR spectra.

In conclusion, the photoinitiated addition of thiols to *O*-peracetylated *exo*-galactal and *exo*-xylal gave the expected *D*-glycosylmethyl-sulfide type compounds in good yields with exclusive regioselectivity. The *D*-galactose derivatives were formed with complete β -stereoselectivity, while in the cases of the *D*-xylose derivatives besides the major β -*C*-glycosylic derivatives the α -counterparts were also isolated in small amounts. This study demonstrated that the thiol-ene reaction of *exo*-glycals with a wide range of thiols can be extended to sugars other than glucose. These reactions of very high regio- and stereoselectivities may be valuable

tools for the construction of new types of glycomimetic compounds.

1. Experimental

1.1. General methods

Melting points were measured in open capillary tubes or on a Kofler hot-stage and are uncorrected. Optical rotations were determined with a Perkin–Elmer 241 polarimeter at room temperature. NMR spectra were recorded with Bruker 360 (360/90 MHz for ¹H/¹³C), Bruker 400 (400/100 MHz for ¹H/¹³C) or Bruker Avance II 500 spectrometer equipped with TXI z-gradient probeheads (500/125.77 MHz for ¹H/¹³C) spectrometer. Chemical shifts are referenced to TMS as the internal reference (¹H), or to the

Table 3
Selected ¹³C NMR data of compounds **5c** and **6c**

	C-2	C-3	C-4	C-5	C-6	C-2	C-3	C-4	C-5	C-6
δ [ppm]	78.7	71.5	73.6	69.1	66.7	74.0	67.3	66.2	66.4	66.1
¹ J _{C,H} [Hz]	148.2	154.0	161.6	162.5		147.4	149.5	164.0	147.4	

Table 4
Selected ¹H NMR data of the D-xylose derived compounds **5** and **6** (δ [ppm], ³J_{H,H} [Hz] or FWHM^a [Hz])

Compound	R	H-1 _A	H-1 _B	H-2	H-3	H-4	H-5	H-6 _{eq}	H-6 _{ax}
5a	Pr	2.67	2.58	3.55	4.95	5.18	4.99	4.14	3.29
		3.0, 14.1	7.6, 14.1	3.0, 7.6, 9.4	9.4	9.4	5.7, 9.4, 10.7	5.7, 11.2	10.7, 11.2
6a		2.78	2.60	3.84	4.89	5.07	4.70	4.03	3.86
		7.5, 13.6	6.3, 13.6	— ^b	7.0 ^d	8.2 ^d	7.5 ^d	1.7, 13.2	2.2, 13.2
5b	Ph	3.11	2.98	3.56	4.97	5.17	5.01	4.14	3.27
		3.0, 13.9	8.0, 13.9	3.0, 8.0, 9.4	9.4	9.4	5.6, 9.4, 11.1	5.6, 11.1	11.1
6b		3.20	3.02	3.85	4.93	5.08	4.68	4.02	3.83
		7.7, 13.7	7.0, 13.7	— ^b	6.7 ^a	7.9 ^d	7.2 ^d	1.0, 13.3	2.1, 13.3
5c	Bn	2.53	2.44	3.49	4.91	5.14	4.98	4.14	3.26
		3.0, 14.3	7.7, 14.3	3.0, 7.7, 9.4	9.4	9.4	5.5, 9.4, 10.5	5.5, 11.2	10.5, 11.2
6c		2.72	2.52	3.66	4.79	5.02	4.65	3.98	3.75
		7.7, 13.7	6.1, 13.7	1.9, 6.1, 7.7	6.9 ^d	8.0 ^d	6.7 ^d	13.6	2.3, 13.6
5d	(AcO) ₄ -β-D-Galp	2.99	2.63	3.65	4.88	5.12	4.93	4.12	3.23
		2.7, 14.1	7.5, 14.1	2.7, 7.5, 9.5	9.5	9.5	5.7, 9.5, 10.5	5.7, 11.2	10.5, 11.2
6d		3.02	2.73	3.95	4.87	5.04	4.70	4.03	3.95
		8.1, 13.5	5.5, 13.5	— ^b	7.2 ^d	— ^b	6.6 ^d	1.8, 13.3	2.2, 13.3
5f	(iPrO) ₂ -α-D-Galp-6-yl	2.75	2.53	3.52	4.86	5.13	4.92	4.09	3.24
		— ^b	8.2, 14.3	2.7, 8.2, 9.5	9.5	9.5	5.5, 9.5, 10.5	5.5, 11.2	10.5, 11.2
6f		2.85	2.66	3.93	4.86	5.06	4.70	4.02	3.87
		8.2, 13.8	5.4, 13.8	— ^b	6.7 ^d	7.6 ^d	6.6 ^d	1.6, 14.8	—

^a FWHM: full width at half-maximum for the signals.^b Overlapping multiplets from which the coupling constants could not be extracted.

residual solvent signals (¹³C). ¹J_{C,H} coupling constants were determined by measuring the distance of peak maximums in F2 (¹H) dimension from uncoupled HSQC spectra. The assignments of the ¹H NMR signals of compounds **3d**, **3f**, **5e** and **5f** were performed by their COSY spectra. Mass spectra were recorded with a Thermo LTQ XL mass spectrometer (Thermo Electron Corp., San Jose, CA, USA) operated in a full scan positive ion ESI mode. TLC was performed on DC-Alurolle Kieselgel 60 F₂₅₄ (Merck). TLC plates were visualized under UV light, and by gentle heating. For column chromatography Kieselgel 60 (Merck, particle size (0.063–0.200 mm) was applied. Thiols **2a–c** were purchased from Sigma–Aldrich or prepared according to literature procedures (**2d**, **2e**, **2f**)⁴⁵.

1.2. General procedure for the photoinitiated reaction of exo-glycals with thiols

To a solution of the starting glycal (**1** or **4**, 50–100 mg) in dry toluene (4 mL/100 mg), a thiol **2** (10 equiv of **2a–c**, 1.1 equiv of **2d–f**) and 2,2-dimethoxy-2-phenylacetophenone (DPAP, 0.1 equiv) were added. The solution was irradiated by a mercury vapor lamp (λ_{max}=365 nm) at rt for 15 min. After addition of another 0.1 equiv of DPAP irradiation was continued and, when the starting material disappeared (TLC, eluent 5:1 hexane–acetone), the solvent was removed under diminished pressure, then the residue was purified using column chromatography (eluent A 5:1 hexane–acetone; eluent B 6:1 hexane–acetone; eluent C 2:1 hexane: acetone).

1.2.1. 3,4,5,7-Tetra-O-acetyl-2,6-anhydro-1-deoxy-1-S-propyl-1-thio-D-glycero-L-manno-heptitol (**3a**)

By the general procedure, starting from **1** (100 mg, 0.29 mmol) to give **3a** (eluent A) as a colorless oil (72 mg; 59%). *R*_f=0.42, (eluent C), [α]_D+5.0 (c=0.52, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ: 5.41 (dd, 1H, *J*=1.1, 3.5 Hz, H-5), 5.17 (pt, 1H, *J*=9.8 Hz, H-3), 5.02 (dd, 1H,

J=3.5, 9.8 Hz, H-4), 4.13 (dd, 1H, *J*=6.5, 11.3 Hz, H-7_A), 4.07 (dd, 1H, *J*=6.5, 11.3 Hz, H-7_B), 3.90 (ddd, 1H, *J*=1.1, 6.5, 6.5 Hz, H-6), 3.60 (ddd, 1H, *J*=3.7, 7.2, 9.8 Hz, H-2), 2.69 (dd, 1H, *J*=7.2, 14.2 Hz, H-1_A), 2.65 (dd, 1H, *J*=3.7, 14.2 Hz, H-1_B), 2.53–2.62 (m, 2H, S–CH₂), 2.15, 2.05, 2.04, 1.97 (4×s, 4×3H, OAc), 1.66–1.53 (m, 2H, CH₂), 0.97 (t, 3H, *J*=7.3 Hz, CH₃). ¹³C NMR (101 MHz, CDCl₃) δ: 170.41 (CO), 79.95, 74.34, 72.15, 69.16, 67.76 (C-2–C-6), 61.74 (C-7), 35.54, 33.58 (C-1, CH₂S), 22.97, 20.98, 20.84, 20.76, 13.56 (CH₃). C₁₈H₂₈O₉S (M_r: 420.47 g/mol); MS: [M+H]⁺=421.58; [M+K]⁺=459.50.

1.2.2. 3,4,5,7-Tetra-O-acetyl-2,6-anhydro-1-deoxy-1-S-phenyl-1-thio-D-glycero-L-manno-heptitol (**3b**)

By the general procedure, starting from **1** (100 mg, 0.29 mmol) to give **3b** (eluent A) as a yellow oil (82 mg; 62%). *R*_f=0.37 (eluent C), [α]_D–15.0 (c=0.53, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ: 7.39–7.33 (m, 2H, aromatic), 7.32–7.25 (m, 2H, aromatic), 7.23–7.17 (m, 1H, aromatic), 5.40 (dd, 1H, *J*=1.3, 3.5 Hz, H-5), 5.22 (pseudo t, 1H, *J*=10.0 Hz, H-3), 5.02 (dd, 1H, *J*=3.5, 10.0 Hz, H-4), 4.10 (dd, 1H, *J*=6.8, 11.3 Hz, H-7_A), 4.04 (dd, 1H, *J*=6.8, 11.3 Hz, H-7_B), 3.87 (ddd, 1H, *J*=1.3, 6.8, 6.8 Hz, H-6), 3.62 (ddd, 1H, *J*=4.4, 6.7, 10.0 Hz, H-2), 3.08 (dd, 1H, *J*=4.4, 13.6 Hz, H-1_A), 3.12 (dd, *J*=6.7, 13.6 Hz, 1H, H-1_B), 2.16, 2.05, 2.04, 1.98 (4×s, 4×3H, OAc). ¹³C NMR (101 MHz, CDCl₃) δ: 170.55, 170.37, 170.28, 170.01 (4×CO), 130.01, 129.05, 126.63 (aromatic), 77.98, 74.37, 72.08, 69.25, 67.69 (C-2–C-6), 61.53 (C-7), 36.33 (C-1), 20.97, 20.84, 20.74 (CH₃). C₂₁H₂₆O₉S, M_r: 454.49 g/mol; MS: [M+H]⁺=455.58; [M+K]⁺=493.50.

1.2.3. 3,4,5,7-Tetra-O-acetyl-2,6-anhydro-1-deoxy-1-S-benzyl-1-thio-D-glycero-L-manno-heptitol (**3c**)

By the general procedure, starting from **1** (100 mg, 0.29 mmol) to give **3c** (eluent A) as a colorless oil (102 mg; 75%). *R*_f=0.37 (eluent C), [α]_D–10.0 (c=0.56, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ: 7.40–7.16 (m, 5H, aromatic), 5.41 (dd, 1H, *J*=1.2, 3.4 Hz, H-5), 5.16 (pseudo t, 1H, *J*=10.1 Hz, H-3), 5.00 (dd, 1H, *J*=3.4, 10.1 Hz, H-4), 4.16

(dd, 1H, $J=6.7, 11.3$ Hz, H-7_A), 4.10 (dd, 1H, $J=6.7, 11.3$ Hz, H-7_B), 3.89 (ddd, 1H, $J=1.2, 6.7, 6.7$ Hz, H-6), 3.80 (s, 2H, SCH₂), 3.57 (ddd, 1H, $J=3.6, 7.2, 10.1$ Hz, H-2), 2.56, (dd, 1H, $J=7.2, 14.4$ Hz, H-1_A), 2.52 (dd, 1H, $J=3.6, 14.4$ Hz, H-1_B), 2.16, 2.05, 1.98, 1.97 (4×s, 4×3H, OAc). ¹³C NMR (101 MHz, CDCl₃) δ: 170.56, 170.37, 170.29, 169.82 (CO), 138.18, 129.18, 128.58, 127.19 (aromatic), 79.64, 74.35, 72.10, 68.98, 67.73 (C-2–C-6), 61.81 (C-7), 37.14, 32.27 (C-1, SCH₂), 20.87, 20.83, 20.73 (CH₃). C₂₂H₂₈O₉S, M_r: 468.52 g/mol; MS: [M+H]⁺=469.67; [M+K]⁺=507.58.

1.2.4. 3,4,5,7-Tetra-O-acetyl-2,6-anhydro-1-deoxy-1-S-(2,3,4,5-tetra-O-acetyl-β-D-galactopyranosyl)-1-thio-D-glycero-L-manno-heptitol (3d)

By the general procedure, starting from **1** (50 mg, 0.145 mmol) to give **3d** (eluent B) as a yellow oil (74 mg; 72%). $R_f=0.13$ (eluent C), [α]_D –27.1 (c=0.55, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ: 5.40 (dd, 1H, $J=1.1, 3.4$ Hz, H-5), 5.38 (dd, 1H, $J=1.1, 3.4$ Hz, H-4'), 5.19 (pseudo t, 1H, $J=9.9$ Hz, H-2'), 5.18 (t, 1H, $J=10.0$ Hz, H-3), 5.02 (dd, 1H, $J=3.4, 10.0$ Hz, H-4), 5.0 (dd, 1H, $J=3.4, 9.9$ Hz, H-3'), 4.56 (d, 1H, $J=9.9$ Hz, H-1'), 4.14 (m, 2H, H-7_{AB}), 4.05 (dd, 1H, $J=11.3, 6.8$ Hz, H-6'_A), 4.03 (dd, 1H, $J=11.3, 6.8$ Hz, H-6'_B), 3.90 (dd, 1H, $J=1.1, 6.5$ Hz, H-6), 3.86 (ddd, 1H, $J=1.1, 6.8, 6.8$ Hz, H-5'), 3.70 (ddd, $J=1H, 2.9, 7.4, 10.0$ Hz, H-2), 2.98 (dd, 1H, $J=2.9, 14.0$ Hz, H-1_A), 2.74 (dd, $J=7.4, 14.0$ Hz, H-1_B), 2.13, 2.12, 2.06, 2.04, 2.01, 2.01, 1.95, 1.94 (8×s, 8×3H, OAc). ¹³C NMR (101 MHz, CDCl₃) δ: 170.41, 170.37, 170.25, 170.18, 170.04, 169.64 (CO), 83.27, 78.22, 74.53, 74.37, 72.13, 71.92, 68.74, 67.62, 67.32, 67.15 (C-2–C-6 and C-1'–C-5'), 61.34 (C-7), 61.31 (C-6'), 30.58 (C-1), 20.85, 20.83, 20.73, 20.69, 20.66, 20.62 (CH₃). C₂₉H₄₀O₁₈S, M_r: 708.68 g/mol; MS: [M+Na]⁺=731.83.

1.2.5. 3,4,5,7-Tetra-O-acetyl-2,6-anhydro-1-deoxy-1-S-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-1-thio-D-glycero-L-manno-heptitol (3e)

By the general procedure, starting from **1** (50 mg, 0.145 mmol) to give **3e** (eluent B) as a colorless oil (80 mg; 87%). $R_f=0.16$ (eluent C), [α]_D –62.0 (c=0.59, CHCl₃). ¹H NMR (360 MHz, CDCl₃) δ: 5.39 (dd, 1H, $J=1.1, 3.4$ Hz, H-5), 5.21 (pseudo t, 1H, $J=10.0$ Hz, H-3), 5.11 (pseudo t, 1H, $J=8.0$ Hz, H-3'), 5.00 (dd, 1H, $J=3.4, 10.0$ Hz, H-4), 4.92 (pseudo t, 1H, $J=8.0$ Hz, H-2'), 4.94–4.82 (m, 1H, H-4'), 4.67 (d, 1H, $J=8.1$ Hz, H-1'), 4.21 (dd, 1H, $J=4.8, 11.8$ Hz, H-5'_{eq}), 4.11 (dd, 1H, $J=6.5, 11.2$ Hz, H-7_A), 4.03 (dd, 1H, $J=6.8, 11.2$ Hz, H-7_B), 3.86 (ddd, $J=1H, 1.1, 6.5, 6.8$ Hz, H-6), 3.65 (ddd, 1H, $J=2.9, 6.9, 10.0$ Hz, H-2), 3.36 (dd, 1H, $J=8.5, 11.8$ Hz, H-5'_{ax}), 2.91 (dd, 1H, $J=2.9, 14.2$ Hz, H-1_A), 2.70 (dd, 1H, $J=6.9, 14.2$ Hz, H-1_B), 2.14, 2.06, 2.04, 2.03, 2.02, 2.02, 1.95 (7×s, 7×3H, OAc). ¹³C NMR (91 MHz, CDCl₃) δ: 170.46, 170.38, 170.25, 169.88, 169.73, 169.51 (CO), 83.25, 78.35, 74.34, 72.17, 71.67, 69.78, 68.52, 67.60 (C-2–C-6 and C-1'–C-4'), 65.06 (C-7), 61.45 (C-5'), 31.13 (C-1), 20.91, 20.80, 20.70 (CH₃). C₂₆H₃₆O₁₆S, M_r: 636.62 g/mol; MS: [M+Na]⁺=659.92.

1.2.6. 3,4,5,7-Tetra-O-acetyl-2,6-anhydro-1-deoxy-1-S-(1,2:3,4-di-O-isopropylidene-β-D-galactopyranose-6-yl)-1-thio-D-glycero-L-manno-heptitol (3f)

By the general procedure, starting from **1** (100 mg, 0.29 mmol) to give **3f** (eluent B) as a colorless oil (145 mg; 81%). $R_f=0.30$ (eluent C), [α]_D –27.0 (c=0.51, CHCl₃). ¹H NMR (360 MHz, CDCl₃) δ: 5.48 (d, 1H, $J=5.1$ Hz, H-1'), 5.36 (dd, 1H, $J=1.2, 3.4$ Hz, H-5), 5.07 (pseudo t, 1H, $J=10.0$ Hz, H-3), 4.96 (dd, 1H, $J=3.4, 10.1$ Hz, H-4), 4.57 (dd, 1H, $J=2.4, 7.9$ Hz, H-3'), 4.26 (dd, 1H, $J=2.4, 5.1$ Hz, H-2'), 4.20 (dd, 1H, $J=1.9, 7.9$ Hz, H-4'), 4.1–3.98 (m, 2H, H-7), 3.90–3.85 (m, 1H, H-6), 3.85–3.80 (m, 1H, H-5'), 3.60 (ddd, 1H, $J=3.1, 8.1, 10.0$ Hz, H-2), 2.83 (dd, 1H, $J=6.2, 13.6$ Hz, H-6'_A), 2.75 (dd, 1H, $J=7.6, 13.6$ Hz, H-6'_B), 2.70 (dd, 1H, $J=8.1, 14.4$ Hz, H-1_A), 2.63 (dd, 1H, $J=3.1, 14.4$ Hz, H-1_B), 2.12, 2.09, 2.00, 1.92 (4×s, 4×3H, OAc), 1.51, 1.39, 1.29, 1.28 (4×s, 4×3H, CH₃). ¹³C NMR (91 MHz, CDCl₃) δ: 170.51, 170.22, 170.15,

169.84 (CO), 109.26, 108.56 (C), 96.71, 80.02, 74.25, 71.97, 71.80, 70.99, 70.48, 68.98, 67.69, 67.07 (C-2–C-6 and C-1'–C-5'), 61.72 (C-7), 32.96 (C-6'), 32.40 (C-1), 26.08, 26.01, 24.93, 24.49 (CH₃), 20.83, 20.72, 20.63 (CH₃CO). C₂₇H₄₀O₁₄S, M_r: 620.66 g/mol; MS: [M+H₂O]⁺=638.25.

1.2.7. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-propyl-1-thio-D-gulo-hexitol (5a)

By the general procedure, starting from **4** (100 mg, 0.37 mmol) to give **5a** (eluent B) as a colorless oil (80 mg; 63%). $R_f=0.47$ (eluent C), [α]_D –50° (c=0.59, CHCl₃). ¹H NMR (360 MHz, CDCl₃) δ: 5.18 (t, 1H, $J=9.4$ Hz, H-4), 4.99 (ddd, 1H, $J=5.7, 9.4, 10.7$ Hz, H-5), 4.95 (pseudo t, 1H, $J=9.4$ Hz, H-3), 4.14 (dd, 1H, $J=5.7, 11.2$ Hz, H-6_{eq}), 3.55 (ddd, 1H, $J=3.1, 7.6, 9.4$ Hz, H-2), 3.29 (dd, 1H, $J=10.7, 11.2$ Hz, H-6_{ax}), 2.67 (dd, 1H, $J=3.1, 14.1$ Hz, H-1_A), 2.58 (dd, 1H, $J=7.6, 14.1$ Hz, H-1_B), 2.45–2.55 (m, 2H, SCH₂), 2.05, 2.03, 2.03 (3×s, 3×3H, OAc), 1.66–1.51 (m, 2H, CH₂), 0.98 (t, $J=7.3$ Hz, 3H, CH₃). ¹³C NMR (91 MHz, CDCl₃) δ: 170.41, 169.85, 169.72 (CO), 79.00, 73.74, 71.73, 69.21 (C-2–C-5), 66.79 (C-6), 35.41, 33.57 (C-1, SCH₂), 22.86 (CH₃CO), 20.76 (CH₂), 13.45 (CH₃). C₁₅H₂₄O₇S, M_r: 348.41 g/mol; MS: [M+H]⁺=349.58; [M+K]⁺=387.58.

1.2.8. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-phenyl-1-thio-D-gulo-hexitol (5b)

By the general procedure, starting from **4** (100 mg, 0.37 mmol) to give **5b** (eluent B) as a colorless oil (73 mg; 52%). $R_f=0.42$ (eluent C), [α]_D –49.0 (c=0.53, CHCl₃). ¹H NMR (360 MHz, CDCl₃) δ: 7.41–7.16 (m, 5H, aromatic), 5.17 (pseudo t, 1H, $J=9.4$ Hz, H-4), 5.01 (ddd, 1H, $J=5.6, 9.4, 11.1$ Hz, H-5), 4.97 (t, 1H, $J=9.4$ Hz, H-3), 4.14 (dd, 1H, $J=5.6, 11.1$ Hz, H-6_{eq}), 3.56 (ddd, 1H, $J=3.0, 8.0, 9.4$ Hz, H-2), 3.27 (pt, 1H, $J=11.1$ Hz, H-6_{ax}), 3.11 (dd, 1H, $J=3.0, 13.9$ Hz, H-1_A), 2.98 (dd, 1H, $J=8.0, 13.9$ Hz, H-1_B), 2.03, 2.02, 2.02 (3×s, 3×3H, OAc). ¹³C NMR (91 MHz, CDCl₃) δ: 170.32, 169.75, 169.67 (CO), 135.91, 129.63, 128.97, 126.46 (aromatic), 77.47, 73.58, 71.74, 69.05 (C-2–C-5), 66.76 (C-6), 36.11 (C-1), 20.68 (CH₃). C₁₈H₂₂O₇S, M_r: 382.43 g/mol; MS: [M+H]⁺=383.58; [M+K]⁺=421.58.

1.2.9. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-benzyl-1-thio-D-gulo-hexitol (5c)

By the general procedure, starting from **4** (100 mg, 0.37 mmol) to give **5c** (eluent B) as a colorless oil (99 mg; 68%). $R_f=0.38$ (eluent C), [α]_D –58.0 (c=0.52, CHCl₃). ¹H NMR (360 MHz, CDCl₃) δ: 7.35–7.19 (m, 5H, aromatic), 5.14 (t, 1H, $J=9.4$ Hz, H-4), 5.01 (ddd, 1H, $J=5.5, 9.4, 10.5$ Hz, H-5), 4.91 (t, 1H, $J=9.5$ Hz, H-3), 4.14 (dd, 1H, $J=5.5, 11.2$ Hz, H-6_{eq}), 3.74 (d, 1H, $J=13.5$ Hz, CH_{2A}), 3.71 (d, 1H, $J=13.5$ Hz, CH_{2B}), 3.49 (ddd, 1H, $J=3.0, 7.7, 9.4$ Hz, H-2), 3.26 (dd, 1H, $J=10.5, 11.3$ Hz, H-6_{ax}), 2.53 (dd, 1H, $J=3.0, 14.3$ Hz, H-1_A), 2.44 (dd, 1H, $J=7.7, 14.3$ Hz, H-1_B), 2.03, 2.01, 1.95 (3×s, 3×3H, OAc). ¹³C NMR (91 MHz, CDCl₃) δ: 170.41, 169.85, 169.62 (CO), 138.03, 129.11, 128.51, 127.11 (aromatic), 78.84, 73.70, 71.59, 69.19 (C-2–C-5), 66.79 (C-6), 36.94 (C-1), 32.10 (SCH₂), 20.76 (CH₃). C₁₉H₂₄O₇S, M_r: 396.45 g/mol; MS: [M+H]⁺=397.58; [M+K]⁺=435.58.

1.2.10. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-(2,3,4,5-tetra-O-acetyl-β-D-galactopyranosyl)-1-thio-D-gulo-hexitol (5d)

By the general procedure, starting from **4** (50 mg, 0.185 mmol) to give **5d** (eluent B) as a colorless oil (81 mg; 69%). $R_f=0.16$ (eluent C), [α]_D –47.0 (c=0.58, CHCl₃). ¹H NMR (360 MHz, CDCl₃) δ: 5.39 (dd, 1H, $J=1.1, 3.3$ Hz, H-4'), 5.19 (t, 1H, $J=10.0$ Hz, H-2'), 5.12 (t, 1H, $J=9.5$ Hz, H-4), 5.00 (dd, 1H, $J=3.3, 10.0$ Hz, H-3'), 4.93 (ddd, 1H, $J=5.7, 9.5, 10.5$ Hz, H-5), 4.88 (t, 1H, $J=9.5$ Hz, H-3), 4.51 (d, 1H, $J=10.0$ Hz, H-1'), 4.12 (dd, 1H, $J=6.6, 11.2$ Hz, H-6'_A), 4.10 (dd, 1H, $J=5.7, 11.2$ Hz, H-6'_B), 4.05 (dd, 1H, $J=6.8, 11.4$ Hz, H-6'_B), 3.89 (ddd, 1H, $J=1.1, 6.6, 6.8$ Hz, H-5'), 3.65 (ddd, 1H, $J=2.7, 7.5, 10.0$ Hz, H-2), 3.23 (dd, 1H, $J=10.5, 11.2$ Hz, H-6_{ax}), 2.99 (dd, 1H, $J=2.7, 14.1$ Hz, H-

1A), 2.63 (dd, 1H, $J=7.5$, 14.1 Hz, H-1_B), 2.12, 2.04, 2.03, 2.00, 1.99, 1.97, 1.93 (7×s, 7×3H, OAc). ¹³C NMR (91 MHz, CDCl₃) δ: 170.27, 170.10, 169.90, 169.71, 169.55 (CO), 83.34, 77.93, 74.43, 73.65, 71.85, 71.35, 68.98, 67.20, 66.66, (C-2–C5 and C-1'–C-5') 66.73 (C-6), 61.26 (C-6'), 30.54 (C-1), 20.68, 20.63, 20.51 (CH₃). C₂₆H₃₆O₁₆S, M_r: 636.62 g/mol; MS: [M+Na]⁺=659.92.

1.2.11. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-1-thio-D-gulo-hexitol (5e)

By the general procedure, starting from **4** (50 mg, 0.185 mmol) to give **5e** (eluent B) as a colorless oil (78 mg; 75%). $R_f=0.20$ (eluent C), [α]_D –96 (c=0.52, CHCl₃). ¹H NMR (360 MHz, CDCl₃) δ: 5.14 (t, 1H, $J=9.4$ Hz, H-4), 5.12 (t, 1H, $J=8.4$ Hz, H-3'), 4.99–4.82 (m, 4H, H-3, H-5, H-2', H-4'), 4.58 (d, 1H, $J=8.4$ Hz, H-1'), 4.19 (dd, 1H, $J=5.0$, 11.7 Hz, H-5'eq), 4.09 (dd, 1H, $J=5.6$, 11.2 Hz, H-6eq), 3.58 (ddd, 1H, $J=2.9$, 7.0, 9.8 Hz, H-2), 3.34 (dd, 1H, $J=8.8$, 11.7 Hz, H-5'ax), 3.24 (t, 1H, $J=11.2$ Hz, H-6ax), 2.90 (dd, 1H, $J=2.9$, 14.0 Hz, H-1A), 2.63 (dd, 1H, $J=7.0$, 14.0 Hz, H-1B), 2.05, 2.02, 2.01, 2.01, 1.99, 1.98 (6×s, 6×3H, OAc). ¹³C NMR (91 MHz, CDCl₃) δ: 170.43, 169.89, 169.85, 169.70, 169.53 (CO), 83.17, 78.04, 73.79, 71.93, 71.27, 69.64, 69.12, 68.62 (C-2–C-5 and C-1'–C-4'), 66.83 (C-6), 65.35 (C-5'), 30.85, 20.79 (CH₃). C₂₃H₃₂O₁₄S, M_r: 564.56 g/mol; MS: [M+Na]⁺=588.08.

1.2.12. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-(1,2:3,4-di-O-isopropylidene-β-D-galactopyranose-6-yl)-1-thio-D-gulo-hexitol (5f)

By the general procedure, starting from **4** (100 mg, 0.38 mmol) to give **5f** (eluent B) as a colorless oil (108 mg; 53%). $R_f=0.36$ (eluent C), [α]_D –71 (c=0.58, CHCl₃). ¹H NMR (360 MHz, CDCl₃) δ: 5.47 (d, 1H, $J=5.0$ Hz, H-1'), 5.13 (pseudo t, 1H, $J=9.5$ Hz, H-4), 4.92 (ddd, 1H, $J=5.5$, 9.5, 10.5 Hz, H-5), 4.86 (pseudo t, 1H, $J=9.5$ Hz, H-3), 1H, 4.57 (dd, $J=2.4$, 7.9 Hz, H-4'), 4.27 (dd, 1H, $J=2.2$, 5.1 Hz, H-2'), 4.25 (pseudo t, 1H, $J=2.2$ Hz, H-3') 4.09 (dd, 1H, $J=5.5$, 11.2 Hz, H-6eq), 3.85 (m, 1H, H-5'), 3.52 (ddd, 1H, $J=2.7$, 8.2, 9.5 Hz, H-2), 3.24 (dd, 1H, $J=10.5$, 11.2 Hz, H-6ax), 2.80–2.69 (m, 3H, H-1A and 2×H-6'), 2.57 (dd, 1H, $J=8.2$, 14.3 Hz, H-1B), 2.00, 1.99, 1.98 (3×s, 3×3H, OAc), 1.50, 1.40, 1.31, 1.28 (4×s, 4×3H, CH₃). ¹³C NMR (91 MHz, CDCl₃) δ: 170.38, 169.86, 169.73 (CO), 109.29, 108.65 (C), 96.68, 78.97, 73.74, 71.74, 71.65, 70.95, 70.55, 69.23, 67.72 (C-2–C-5 and C-1'–C-5'), 66.75 (C-6), 33.96 (C-1), 32.78 (C-6'), 26.10, 26.05, 24.96, 24.51, 20.76 (CH₃). C₂₄H₃₆O₁₂S, M_r: 548.60 g/mol; MS: [M+H₂O]⁺=566.42.

1.2.13. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-propyl-1-thio-D-ido-hexitol (6a)

By the general procedure, starting from **4** (100 mg, 0.37 mmol) to give **6a** (eluent B) as a colorless oil (5 mg; 4%). $R_f=0.42$ (eluent C), [α]_D –37 (c=0.25, CHCl₃). ¹H NMR (360 MHz, CDCl₃) δ: 5.08 (td, 1H, $J=1.4$, 3.3 Hz, H-4), 4.89 (broad signal, H-3), 4.70 (broad signal, H-5), 4.03 (dd, 1H, $J=1.7$, 13.2 Hz, H-6eq), 3.86 (dd, 1H, $J=2.2$, 13.2 Hz, H-6ax), 3.82–3.86 (m, 1H, H-2), 2.78 (dd, 1H, $J=7.5$, 13.6 Hz, H-1A), 2.60 (dd, 1H, $J=6.3$, 13.6 Hz, H-1B), 2.56–2.48 (m, 2H, SCH₂), 2.14, 2.13, 2.11 (3×s, 3×3H, OAc), 1.63–1.54 (m, 2H), 0.98 (t, $J=7.3$ Hz, 3H).

1.2.14. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-phenyl-1-thio-D-ido-hexitol (6b)

By the general procedure, starting from **4** (100 mg, 0.37 mmol) to give **6b** (eluent B) as a colorless oil (11 mg; 8%). $R_f=0.38$ (eluent C), [α]_D –47 (c=0.53, CHCl₃). ¹H NMR (360 MHz, CDCl₃) δ: 7.46–7.06 (m, 5H, aromatic), 5.08 (td, 1H, $J=1.3$, 3.1 Hz, H-4), 4.93 (broad signal, 1H, H-3), 4.97 (ddd, 1H, $J=1.0$, 2.1, 3.3 Hz, H-5), 4.04 (dd, 1H, $J=1.0$, 13.3 Hz, H-6eq), 3.83 (dd, 1H, $J=2.1$, 13.3 Hz, H-6ax), 3.82–3.88 (m, 1H, H-2), 3.20 (dd, 1H, $J=7.7$, 13.7 Hz, H-1A), 3.02 (dd, 1H, $J=7.0$, 13.7 Hz, H-1B), 2.11, 2.09, 2.08 (3×s, 3×3H, OAc).

1.2.15. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-benzyl-1-thio-D-ido-hexitol (6c)

By the general procedure, starting from **4** (100 mg, 0.37 mmol) to give **6c** (eluent B) as a colorless oil (8 mg; 5%). $R_f=0.35$ (eluent C), [α]_D –50 (c=0.40, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ: 7.34–7.22 (m, 5H, aromatic), 5.02 (broad signal, 1H, H-4), 4.79 (broad signal, 1H, H-3), 4.65 (broad signal, 1H, H-5), 4.97 (d, 1H, $J=13.6$, 11.2 Hz, H-6eq), 3.75 (dd, 1H, $J=2.3$, 13.6 Hz, H-6ax), 3.74 (s, 2H, CH₂), 3.66 (ddd, 1H, $J=1.9$, 6.1, 7.7 Hz, H-2), 2.71 (dd, 1H, $J=7.7$, 13.7 Hz, H-1A), 2.52 (dd, 1H, $J=6.1$, 13.7 Hz, H-1B), 2.11, 2.09, 2.07 (3×s, 3×3H, OAc). ¹³C NMR (125.77 MHz, CDCl₃) δ: 169.87, 168.59 (CO), 138.34, 129.04, 128.71, 127.31 (aromatic), 74.17, 67.44, 66.67, 66.72 (C-2–C-5), 66.28 (C-6), 37.35 (C-1), 31.73 (SCH₂), 21.16, 21.0, 20.86 (CH₃).

1.2.16. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-(2,3,4,5-tetra-O-acetyl-β-D-galactopyranosyl)-1-thio-D-ido-hexitol (6d)

By the general procedure, starting from **4** (100 mg, 0.37 mmol) to give **6d** (eluent B) as a colorless oil (3.5 mg; 3%). $R_f=0.15$ (eluent C), [α]_D –45 (c=0.175, CHCl₃). ¹H NMR (360 MHz, CDCl₃) δ: 5.44 (dd, 1H, $J=1.0$, 3.3 Hz, H-4'), 5.22 (t, 1H, $J=10.0$ Hz, H-2'), 5.04 (broad signal, 1H, H-4), 5.04 (dd, 1H, $J=3.3$, 10.0 Hz, H-3'), 4.87 (broad signal, 1H, H-3), 4.70 (broad signal, 1H, H-5), 4.55 (d, 1H, $J=9.9$ Hz, H-1'), 4.09–4.16 (m, 2H, H-6'AB), 4.03 (dd, 1H, $J=1.8$, 13.3 Hz, H-6eq), 3.95 (td, 1H, $J=1.1$, 6.6 Hz, H-5'), 3.91–3.97 (m, 1H, H-2), 3.86 (dd, 1H, $J=2.2$, 13.3 Hz, H-6ax), 3.01 (dd, 1H, $J=8.1$, 13.5 Hz, H-1A), 2.72 (dd, 1H, $J=5.5$, 13.5 Hz, H-1B), 2.17, 2.16, 2.15, 2.14, 2.12, 2.06, 2.05 (7×s, 7×3H, OAc).

1.2.17. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-(1,2:3,4-di-O-isopropylidene-β-D-galactopyranose-6-yl)-1-thio-D-ido-hexitol (6f)

By the general procedure, starting from **4** (100 mg, 0.37 mmol) to give **6f** (eluent B) as a colorless oil (7 mg; 3.5%). $R_f=0.33$ (eluent C), [α]_D –40 (c=0.35, CHCl₃). ¹H NMR (360 MHz, CDCl₃) δ: 5.52 (d, 1H, $J=5.0$ Hz, H-1'), 5.06 (broad signal, 1H, H-4), 4.86 (broad signal, 1H, H-3), 4.70 (broad signal, 1H, H-5), 4.61 (dd, $J=2.3$, 7.9 Hz, H-4'), 4.33–4.27 (m, 2H, H-3', H-2'), 4.02 (dd, 1H, $J=1.6$, 14.8 Hz, H-6eq), 3.86–3.95 (m, 1H, H-2), 3.90–3.84 (m, 2H, H-5', H-6ax), 2.85 (dd, 1H, $J=8.2$, 13.8 Hz, H-1A), 2.82–2.69 (m, 2H, H-6'), 2.66 (dd, 1H, $J=5.4$, 13.8 Hz, H-1B), 2.13, 2.12, 2.11 (3×s, 3×3H, OAc), 1.54, 1.44, 1.34, 1.33 (4×s, 4×3H, CH₃).

Acknowledgments

This work was supported by the Hungarian Scientific Research Fund (Grants: OTKA 109208 and 109450) and the BAROSS REG_EA_09-1-2009-0028 (LCMS_TAN) project. Dr. A. Kiss-Szikszai is thanked for recording the mass spectra.

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