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Note

Peracetylated 1,6-dibromo-D-glucitol as efficient precursor of 1,6-diiodo and some mono-, disubstituted and heterocyclic D-glucitol derivatives

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Abstract

2,3,4,5-Tetra-*O*-acetyl-1,6-dibromo-1,6-dideoxy-D-glucitol (**1a**) obtained from D-glucitol was easily transformed into the 1,6-diiodo derivative in excellent yield (97%) by reaction with an excess of sodium iodide in refluxing butanone in 2 h. When the reaction time was prolonged to 24 h and the crude product was acetylated, 1,2,3,4,5-penta-*O*-acetyl-6-deoxy-6-iodo-D-glucitol and D-glucitol hexaacetate were isolated in 50 and 26% yields, respectively. The monodehalogenation then took place regioselectively at C-1. This regioselectivity allowed the synthesis of some mono- and disubstituted derivatives of D-glucitol. Thus, the peracetylated derivatives of D-glucitol, 6-bromo, 6-bromo-1-*S*-butyl, 6-bromo-1-*S*-octyl, 6-*S*-butyl, 6-*S*-butyl-1-*S*-octyl, 1-*S*-butyl, 1,6-di-*S*-octyl and 6-*S*-phenyl were synthesised in good to excellent yields. With $S^{=}$ as binucleophilic reagent, **1a** gave mainly the thiepane derivative (75%) plus the 1-*S*-acetyl-2,6-anhydro-D-glucitol derivative as a by-product (10%).

Keywords: Alditol; D-glucitol; Iodoglucitol; Dehalogenation; Thioalditols; Bromoglucitol; Thiepane

In this report, a short and efficient synthesis of 1,6-dideoxy-1,6-diiodo-D-glucitol is reported. This was carried out by bromine–iodide exchange from 1,6-dibromo-1,6-dideoxy-D-glucitol **1a** to the 1,6-diiodo analogue **4** (Scheme 1). The former was directly synthesised from unprotected D-glucitol **1**.[1,2]

The first synthetic attempt at the target 1,6-dideoxy-1,6-diiodo-D-glucitol derivative was performed with a large excess of sodium iodide (NaI, 10 equiv) in refluxed undistilled butanone during 24 h for complete disappearance of **1a** (Path 1). Two compounds were isolated after acetylation: 1,2,3,4,5-penta-*O*-acetyl-6-deoxy-6-iodo-D-glucitol (**2**) and D-glucitol hexaacetate **3** in yields of 50 and 26%, respectively. No trace of the 1,6-diiodo derivative **4** was detected.

The identification of **2** was fully achieved by correlation with literature. Thus, **2** gave by reaction with the phenylthiolate ion the 6-*S*-phenyl-6-thio-D-glucitol derivative **15** previously obtained in four steps from methyl α-D-glucopyranoside.[3]

Of interest was the formation in excellent yield (97%) of the target 1,6-dideoxy-1,6-diiodo-D-glucitol derivative **4** when the reaction time was reduced to 2 h (Path 2).

Compounds **2** and **3** are probably formed through hydrolysis of an acetoxonium ions intermediate, presumably from a transient diiodide **4** (Scheme 2 Path 1 and 2). Reaction of **1a** unsurprisingly gave mainly **6** (thiepane) with some **5** (2,6-anhydro-D-glucitol) within the presence of a sulfide ion (Scheme 3).[4] Such higher reactivity at C-1 in **1a** was also observed, leading to C-1 substitution with acetate and thiolate ions. Thus, 1,2,3,4,5-penta-*O*-acetyl-6-bromo-6-deoxy-D-glucitol (**7**), 2,3,4,5-tetra-*O*-acetyl-6-bromo-1-*S*-butyl-6-deoxy-1-thio-D-glucitol (**8**) and 2,3,4,5-tetra-*O*-acetyl-6-bromo-6-deoxy-1-*S*-octyl-1-thio-D-glucitol (**10**) were obtained in reasonable yields (50%). Derivatives **7**, **8** and **10** were respectively transformed into 6-*S*-butyl **12** and 6-*S*-phenyl **15** (identical to that obtained from **2** in order to correlate with literature),[3] 1-*S*-butyl **14** and

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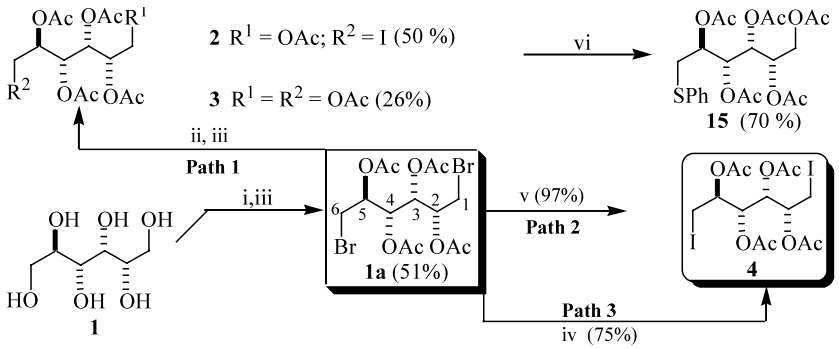


Scheme 1. (i) AcBr, 1,4-dioxane, rt; (ii) NaI (10 equiv), refluxing undistilled butanone, 24 h; (iii) Ac_2O, pyridine; (iv) NaI (10 equiv), refluxing anhyd butanone, 48 h; (v) NaI (10 equiv), refluxing undistilled butanone, 2 h; (vi) PhSH, Me_2SO NaH, rt, 15 min.

6-*S*-butyl-1-*S*-octyl-D-glucitol **13** in excellent yields. This unexpected regioselective transformation then enabled us to synthesise the 1,6-di-*S*-alkyl derivative **13** with two different alkyl chains of different lengths. Note that with an excess of thiolate ion in a Me_2SO–THF mixture, the thioalkylation was reported to occur indiscriminately at the two sites C-1 and C-6 to give the disubstituted compounds **9** and **11** in excellent yields (Scheme 4).[2]

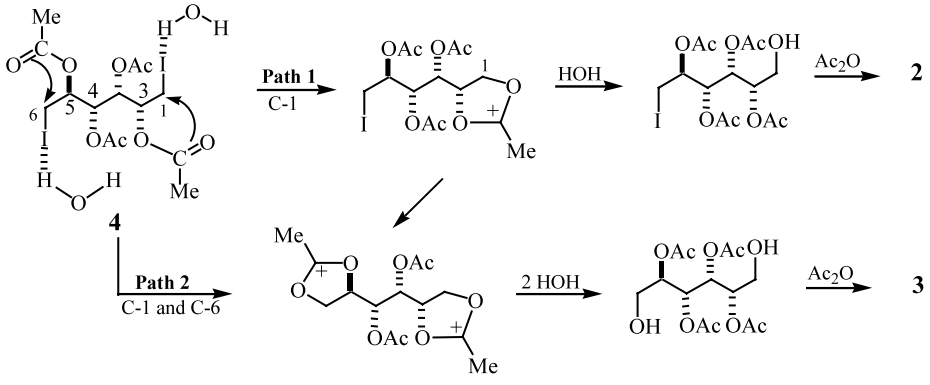
1. Experimental

1.1. General methods

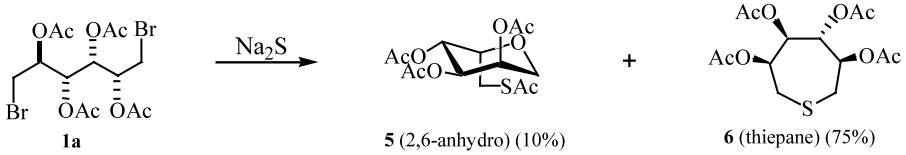
Melting points were determined with a Büchi 535 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra (Tables 1–3) were recorded with a Bruker 300 WB spectrometer; chemical shifts are reported in δ (ppm) relative to Me_4Si. All ^{13}C NMR signals were assigned through C,H-correlated spectra. TLC was performed on Silica Gel 60 F_{254} 230 mesh (E. Merck) and detection by the vanillin–H_2SO_4 reagent. The silica gel used in column chromatography was 35–70 μ (Amicon). Mass spectroscopy analyses were performed by the 'Service d'Analyse de la Faculté de Pharmacie, Université de Reims. Elemental analyses were performed by the 'Service de Microanalyse du CNRS', Université de Reims.

1.2. General procedure of iodination

To 2,3,4,5-tetra-*O*-acetyl-1,6-dibromo-1,6-dideoxy-D-glucitol (**1a**, 10 mL)[1,2] in 1 mmol undistilled butanone (10 mL) was added NaI (10 equiv). The mixture was refluxed until complete disappearance of the substrate. The residue obtained after concentration was dissolved



Scheme 2.

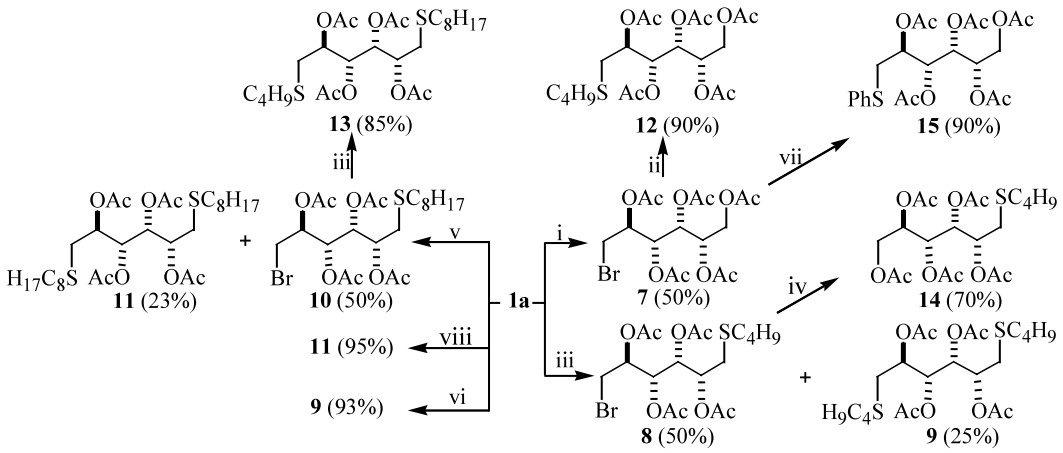


Scheme 3.

Table 1
^{1}H Chemical shifts (δ) for peracetylated D-glucitol derivatives (in $CDCl_3$)

Compd	H-1	H-1′	H-2	H-3	H-4	H-5	H-6	H-6′	CH_3(Ac)	CH_3(SAc)	H-(SR)
1a	3.70(d)	3.70(d)	5.08(m)	4.45(dd)	5.48(dd)	5.22(m)	3.39(dd)	3.62(dd)	2.11(s, 3H); 2.09(s, 3H); 2.07(s, 3H)		
2	3.75(dd)	4.28(dd)	5.09(m)	5.31(dd)	5.22(dd)	4.78(m)	3.12(dd)	3.30(dd)	2.09(s, 3H); 2.04 (s, 3H); 2.02(s, 6H); 1.98(s, 3H)		
3	4.01(dd)	4.34(dd)	5.22(m)	5.40(m)	5.40(m)	5.03(m)	4.11(dd)	4.23(dd)	2.12 (s, 3H); 2.07 (s, 3H); 2.06 (s, 3H); 2.05 (s, 3H); 2.04 (s, 3H); 2.03 (s, 3H)		
4	3.35(m)	3.35(m)	4.82(m)	5.43(dd)	5.24(dd)	4.82(m)	2.74(dd)	3.35(m)	2.17(s, 3H); 2.10 (s, 6H); 2.06(s, 3H)		
5	3.00(dd)	3.52(dd)	5.13(ddd)	4.06(dd)	5.38(dd)	5.01(ddd)	3.76(dd)	4.22(dd)	2.04 (s, 3H); 2.01(s, 3H); 1.93 (s, 3H)	2.29 (s, 3H)	
6	2.69(dd)	2.84(dd)	5.33(ddd)	5.15(dd)	5.49(dd)	5.04(ddd)	2.74(dd)	2.88(dd)	2.02 (s, 3H); 1.99 (s, 3H); 1.98 (s, 3H); 1.95 (s, 3H)		
7	3.97(dd)	4.29(dd)	5.12(m)	5.33(m)	5.31(m)	5.02(m)	3.34(dd)	3.48(dd)	2.10 (s, 3H); 2.07(s, 3H); 2.04 (s, 3H); 2.02(s) (3H)		
8	2.57(dd)	2.71(dd)	4.98(m)	5.39(dd)	5.32(dd)	5.01(m)	3.36(dd)	3.48(dd)	2.07 (s, 3H); 2.02 (s, 3H); 1.98 (s, 3H)		2.47(t, 2H); 1.48, 1.33(m, 4H); 0.82(t, 3H)
9	2.70(dd)	2.59(dd)	5.07(m)	5.44(dd)	5.38(dd)	4.94(m)	2.64(dd)	2.53(dd)	2.05 (s, 3H); 2.04 (s, 3H); 2.00 (s, 3H); 1.98 (s, 3H)		2.48(t, 4H); 1.44, 1.19(m, 8H); 0.90(t, 6H)
10	2.57(dd)	2.71(dd)	5.04(m)	5.42(dd)	5.33(dd)	5.06(m)	3.36(dd)	3.48(dd)	2.07(s) (3H); 2.00(s) (6H); 1.98(s) (3H)		2.45(t) (2H); 1.53, 1.20(m) (12H); 0.80(t) (3H)
11	2.67(dd)	2.58(dd)	5.02(m)	5.40(dd)	5.30(t)	4.93(dd)	2.65(dd)	2.51(dd)	1.99 (s, 3H); 1.97 (s, 3H); 1.95 (s, 3H); 1.92 (s, 3H)		2.42(t, 4H); 1.44, 1.15(m, 24H); 0.76(t, 6H)
12	3.93(dd)	4.28(dd)	5.18(m)	5.38(m)	5.36(m)	4.97(m)	2.55(dd)	2.69(dd)	2.02 (s, 3H); 1.99 (s, 3H), 1.97 (s, 3H); 1.94 (s, 3H); 1.93 (s, 3H)		2.41(t, 2H); 1.46, 1.33(m, 4H); 0.82(t, 3H)
13	2.70(m)	2.70(m)	5.08 or 4.98	5.47 or 5.37	5.47 or 5.37	5.08 or 4.98	2.70(m)	2.70(m)	2.08 (s, 3H); 2.07 (s, 3H); 1.98 (s, 3H); 1.95 (s, 3H)		2.46–1.30(m) (20H); 0.85(m) (6H)
14	2.57(dd)	2.68(dd)	5.07(m)	5.47(dd)	5.35(dd)	4.93(m)	2.55(dd)	2.69(dd)	2.00 (s, 3H); 2.03 (s, 3H); 2.08 (s, 3H)		2.47–1.49(m, 6H); 0.84(m, 3H)
15	3.98(dd)	4.33(dd)	5.14(dt)	5.39(dd)	5.42(dd)	5.07(ddd)	3.05(dd)	3.15(dd)	2.11(s, 3H); 2.05 (s, 9H); 1.83 (s, 3H)		7.28 (m, 5H, Ph)
15 [i]	3.98(dd)	4.33(dd)	5.14(dt)	5.39(dd)	5.43(dd)	5.07(ddd)	3.05(dd)	3.15(dd)	2.11; 2.05; 2.04; 2.03; 1.84 (5s, 3H each, 5 O–Ac)		7.25 (m, 5H, Ph)

[i] From ref. [3].



Scheme 4. (i) AcONa (3 equiv), 60 °C, 5 h, Me_2SO; (ii) C_4H_9SH (1.2 equiv), NaH (1.1 equiv) Me_2SO, rt, 15 min; (iii) C_4H_9SH (1.2 equiv), NaH (1.1 equiv), Me_2SO-THF (1:1), rt, 15 min; (iv) AcONa (3 equiv), 60 °C, 24 h, Me_2SO; (v) $C_8H_{17}SH$ (1.2 equiv), NaH (1.1 equiv), Me_2SO, rt, 15 min; (vi) C_4H_9SH (2.2 equiv), NaH (2.4 equiv), Me_2SO-THF (1:1), rt, 15 min; (vii) PhSH (1.2 equiv), NaH (1.2 equiv), Me_2SO-THF (1:1), rt, 15 min; (viii) $C_8H_{17}SH$ (2.2 equiv), NaH (2.4 equiv), Me_2SO-THF, rt, 15 min.

Table 2
Coupling constants (Hz) for peracetylated D-glucitol derivatives (in $CDCl_3$)

Compd	$J_{1,1'}$	$J_{1,2}$	$J_{1',2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6'}$	$J_{5,6}$	$J_{6,6'}$
1a	–	4.6	4.6	7.8	3.5	7.3	3.7	4.8	11.6
2	12.2	5.9	3.8	6.8	3.8	6.3	3.9	5.9	11.3
3	12.1	6.1	4.0	6.3	4.1	6.7	3.7	5.3	12.4
4	–	–	–	7.0	3.4	7.0	–	6.5	11.3
5	14.5	6.2	3.3	3.5	11.0	0	4.7	1.8	10.7
6	14.6	7.2	3.9	1.4	8.1	6.0	4.6	7.4	15.4
7	12.2	5.8	3.8	–	–	–	3.8	6.3	11.5
8	14.2	6.9	5.2	6.1	4.1	6.7	3.6	6.2	11.6
9	16.0	5.5	4.8	6.2	5.2	6.9	6.9	7.2	14.0
10	14.2	6.9	5.2	6.1	4.1	6.7	3.6	6.2	11.6
11	14.2	4.9	4.7	6.1	5.2	6.4	6.9	7.1	14.3
12	12.0	6.1	3.9	–	–	–	5.1	7.5	14.3
13	–	–	–	5.2	5.2	5.2	–	–	–
14	14.2	6.9	5.4	5.7	4.4	6.8	3.3	5.4	12.4
15	12.1	6	4	6.3	4.1	5.9	4.5	7.3	14.4
15 [i]	12	6	4	6.4	4.0	6	4.5	7.2	14.4

[i] From ref. [3]

in CH_2Cl_2 and the solution was washed with saturated aq $Na_2S_2O_3$. The crude product was chromatographed on silica gel with 3:1 hexane–AcOEt as eluent.

1.2.1. 1,2,3,4,5-Penta-*O*-acetyl-6-deoxy-6-iodo-D-glucitol (2) and 1,2,3,4,5,6-hexa-*O*-acetyl-D-glucitol (3). Following the general procedure, **1a** (600 mg) was allowed to react with NaI during 24 h. The following products were isolated after acetylation: **2**, Yield 318 mg (50%); Syrup; R_f 0.46 in 5:3 hexane–EtOAc. Anal. Calcd for $C_{16}H_{23}O_{10}I$: C, 38.25; H, 4.58; O, 31.87; I, 25.30. Found: C, 38.31; H, 4.60. **3**, Yield 142 mg (26%%); Mp 97.9–98.7; R_f 0.31 in 5:3 hexane–EtOAc. Anal. Calcd for $C_{18}H_{26}O_{12}$: C, 49.77; H, 6.03; O, 44.20. Found: C, 49.74; H, 6.20.

1.2.2. 2,3,4,5-Tetra-*O*-acetyl-1,6-dideoxy-1,6-diiodo-D-glucitol (4). Obtained from **1a** (450 mg) following the general procedure after stirring during only 2 h. Yield 525 mg (97%); Syrup; R_f 0.58 in 5:3 hexane–EtOAc. Anal. Calcd for $C_{14}H_{20}O_8I_2$: C, 29.49; H, 3.54; I, 44.52. Found: C, 29.40; H, 3.55.

1.2.3. 3,4,5-Tri-*O*-acetyl-1-*S*-acetyl-2,6-anhydro-1-thio-D-glucitol (5) and 2,3,4,5-Tetra-*O*-acetyl-1,6-thioanhydro-D-glucitol (6). To 1 mmol of **1a** (476 mg) in 30 mL of 15:1 acetone–water, was added $Na_2S{\cdot}9H_2O$ (5 equiv). The mixture was vigourously stirred for 1 night at rt. After concentration and subsequent acetylation, the crude product was chromatographed on silica gel

Table 3
^{13}C Chemical shifts (δ) for peracetylated D-glucitol derivatives (in $CDCl_3$)

Compd	C-1	C-2	C-3	C-4	C-5	C-6	CO(Ac)	Me(Ac)	CO(SAc)	Me(SAc)	C-(SR)
1a	31.7	70.9	50.1	70.2	70.4	29.4	167.9; 168.4; 168.6	19.7			
2	62.1	69.6	68.5	71.1	70.2	2.6	170.7; 170.2; 170.0; 169.8	21.0; 20.8			
3	62.14	69.64	68.69	69.01	68.88	61.75	170.84; 170.74; 170.38; 170.18; 170.13	21.08; 21.04; 20.85			
4	2.9	71.2; 70.9; 70.6; 69.8	2.5	170.1; 170.0; 169.9	21.2; 20.9						
5	72.3	67.8	79.4	74.5	77.3	30.8	169.6; 169.3	20.7	194.5	30.4	
6	33.1	71.3	70.8	70.6	75.2	33.1	169.8; 169.5; 169.1; 169.0	20.8; 20.6			
7	61.6	69.1	67.9	69.6	69.4	29.8	170.1; 169.6; 169.5; 169.4	20.5; 20.3			
8	32.0	69.9	68.8	71.0	69.6	29.7	169.8; 169.4	21.6; 20.5; 20.3			32.0; 31.3; 13.4
9	30.9	69.4	68.9	70.2	68.9	30.5	169.1; 168.6	19.8; 19.6			31.4; 28.7; 20.9; 12.6
10	32.4	69.9	70.0	70.3	69.6	28.6	169.8; 169.5	21.6; 20.5; 20.3			32.1; 31.6; 29.7; 29.3; 28.9; 13.4
11	31.7	70.3	69.7	71.1	69.7	32.2	169.6	20.4; 20.6			32.5; 31.6; 29.3; 29.2; 29.0; 28.6; 22.4; 13.8
12	62.2	69.9	68.8	71.0	69.6	32.1	170.1; 169.8; 169.7; 169.6; 169.5	20.6; 20.4			32.2; 32.2; 31.7; 13.9
13	32.9 or 32.6	70.2 or 70.7	71.6 or 70.3	70.2 or 70.7	32.9 or 32.6	170.6; 170.3; 170.1	23.0; 22.2; 21.2; 21.0			32.6–29.2; 14.0; 14.4	
14	32.1	69.6	68.5	70.3	68.9	61.2	170.3; 170.0; 169.6	21.7; 20.6; 20.5; 20.3			32.1–29.5; 13.4
15	62.2	69.7	68.7	70.7	70.3	35.1	170.2; 169.7; 169.6	21.1; 21.0; 20.9			134.9; 130.5; 128.9; 126.8
15 [3]	61.8	70.4–68.4	34.9	170–169.5	20.9–20.6			135; 130.6; 129; 126.9			

with 4:1 hexane–EtOAc as eluent. The following products were isolated: **5**, Yield 35 mg (10%); Syrup; R_f 0.38 in 5:3 hexane–EtOAc. Anal. Calcd for $C_{14}H_{20}O_8S$: C, 48.26; H, 5.79; S, 9.20. Found: C, 48.72; H, 5.93. **6**, Yield 262 mg (75%); Mp 76–78 °C; R_f 0.26 in 5:3 hexane–EtOAc. Anal. Calcd for $C_{14}H_{20}O_8S$: C, 48.26; H, 5.79; O, 36.78; S, 9.20. Found: C, 48.33; H, 5.79.

1.2.4. 1,2,3,4,5-Penta-*O*-acetyl-6-bromo-6-deoxy-D-glucitol (7). To 400 mg (0.84 mmol) of **1a** in 5 mL anhyd Me_2SO was added AcONa (210 mg 3 equiv; 2.52 mmol). The mixture was stirred for 3 h at 60 °C under argon atmosphere. The crude product obtained after concentration was treated with brine (10 mL) and extracted with 10 mL Et_2O. The aq layer was washed twice with 10 mL Et_2O and the organic layers were combined together and dried (Na_2SO_4). The crude product obtained after concentration was chromatographed on silica gel with 7:3 hexane–EtOAc. Syrup; Yield 192 mg (50%); $[\alpha]_D^{25}$ +12.5 (*c* 3.6, $CHCl_3$); R_f 0.55 in 1:1 hexane–EtOAc. Anal. Calcd for $C_{16}H_{23}O_{10}Br$: C, 42.20; H, 5.09; Br, 17.55. Found: C, 42.44; H, 5.25.

1.3. General procedure for thioetherification

To a solution of **1a** (1 mmol 476 mg) in Me_2SO (5 mL), was added alkanethiol (n-$C_nH_{2n+1}SH$) or phenylthiol (1.2×10^{-3} mol, 1.2 equiv) and sodium hydride (46 mg; 1.1 equiv 1.1 mmol). The mixture was stirred 15 min at rt under argon atmosphere and extracted with 10 mL of brine and 10 mL Et_2O. The aq layer was washed twice with 10 mL Et_2O. The organic layers were collected and dried on Na_2SO_4. After filtration and concentration, the crude product was chromatographed on silica gel with 7:1 hexane–EtOAc.

1.3.1. 2,3,4,5-Tetra-*O*-acetyl-6-bromo-1-*S*-butyl-6-deoxy-1-thio-D-glucitol (8). Syrup; Yield 243 mg (50%); $[\alpha]_D^{26}$ +12.5 (*c* +3, 1.5 $CHCl_3$); R_f 0.48 in 7:3 hexane–EtOAc. Anal. Calcd for $C_{18}H_{29}O_8BrS$: C, 44.54; H, 6.02; Br, 16.46; S, 6.61. Found: C, 44.79; H, 6.11.

1.3.2. 2,3,4,5-Tetra-*O*-acetyl-6-bromo-6-deoxy-1-*S*-octyl-1-thio-D-glucitol (10). Syrup; Yield 271 mg (50%); $[\alpha]_D^{21}$ +2.7 (*c* 2, $CHCl_3$); R_f 0.47 in 7:3 hexane–EtOAc. Anal. Calcd for $C_{22}H_{37}O_8BrS$: C, 48.79; H, 6.89; Br, 14.76; S, 5.92. Found: C, 48.96; H, 6.91.

1.3.3. 1,2,3,4,5-Penta-*O*-acetyl-6-*S*-butyl-6-thio-D-glucitol (12). Obtained from **7** (340 mg) and 1.2 equiv of C_4H_9SH, 1.1 equiv of NaH, 7 mL Me_2SO, rt, 15 min. Syrup; Yield 313 mg (90%); $[\alpha]_D^{22}$ +2.6 (*c* 1.4, $CHCl_3$); R_f 0.60 in 5:3 hexane–EtOAc. Anal. Calcd for $C_{20}H_{32}O_{10}S$: C, 51.71; H, 6.94; S, 6.90. Found: C, 51.87; H, 7.08.

1.3.4. 2,3,4,5-Tetra-*O*-acetyl-6-*S*-butyl-1-*S*-octyl-1,6-dithio-D-glucitol (13). Obtained from **10** (220 mg, 0.41 mmol), n-C_4H_9SH (0.05 mL, 1.2 equiv, 0.41 mmol), 5 mL of Me_2SO and NaH (18 mg, 0.45 mmol, 1.1 equiv). Chromatography used 7:1 hexane–EtOAc as eluent. Syrup; Yield 190 mg (85%); R_f 0.62 in 7:3 hexane–EtOAc. Anal. Calcd for $C_{26}H_{46}O_8S_2$: C, 56.70; H, 8.42; S, 11.64. Found: C, 56.97; H, 8.70.

1.3.5. 2,3,4,5,6-Penta-*O*-acetyl-1-*S*-butyl-1-thio-D-glucitol (14). To a solution of 0.24 g (0.49 mmol) of **8** in 2.5 mL of Me_2SO, was added 3 equiv (120 mg; 1.47 mmol) of AcONa. The mixture was stirred during 24 h at 60 °C. The solution was subsequently extracted by 10 mL of diethylether and 10 mL of brine. The aq layer was washed twice with 10 mL of diethylether. The organic layers were collected and dried on Na_2SO_4. After filtration and concentration, the crude product was chromatographed with 4:1 hexane–EtOAc. Syrup; Yield 161 mg (70%); R_f 0.60 in 3:2 hexane–EtOAc. Anal. Calcd for $C_{20}H_{32}O_{10}S$: C, 51.71; H, 6.94; S, 6.90. Found: C, 51.93; H, 7.10.

1.3.6. 1,2,3,4,5-Penta-*O*-acetyl-6-*S*-phenyl-6-thio-D-glucitol (15). Obtained following the thioetherification general procedure from **7** (and from **2a**, 400 mg) and PhSH (2.2 equiv), NaH (2.4 equiv), 10 mL of 1:1 Me_2SO–THF, rt, 15 min. Syrup; Yield 384 mg (90%); R_f 0.27 in 7:3 hexane–EtOAc. Anal. Calcd for $C_{22}H_{28}O_{10}S$: C, 54.54; H, 5.82; S, 6.62. Found: C, 54.75; H, 5.88.

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