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A nitro sugar derivative route to 2-thioepisophorose and 2-thiosophorose and their remarkable facile epimerization [1]

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Abstract

The addition of 1-thio-D-glucose sodium salt to per-*O*-acetylated 1,2-dideoxy-1-nitro-D-*arabino*-hex-1-enitol, readily available from D-arabinose, afforded the corresponding 2-*S*-glycosylated 1-deoxy-1-nitro-D-mannitol and -D-glucitol peracetates. These, after deacetylation, were transformed by the Nef reaction to 2-thioepisophorose and 2-thiosophorose, respectively. The 2-thiodisaccharides easily epimerize in aqueous sodium bicarbonate at ambient temperature to a 1:4 equilibrium mixture. The predominant 2-thiosophorose was obtained crystalline. A ^{1}H NMR study of the epimerization in deuterium oxide showed that the reaction involves an H-2 proton exchange mechanism.

Keywords: 2-Thio sugars; Disaccharides, 2-thio; 2-Thiosophorose; 2-Thioepisophorose

1. Introduction

Sugar α-nitroalkenes have been shown to be versatile intermediates for great many synthetic purposes [2,3]. These electrophilic species have also been used for benzylthiolation, and the corresponding 2-*S*-benzylthiohexoses have been prepared by a subsequent Nef reaction [4]. The scheme offers a very promising and simple way to synthesize 2-*S*-glycosyl-2-thioglycoses.

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S-Glycosylthioglycoses are of interest since they find multiple uses in carbohydrate enzymology as inhibitors, nonmetabolizable inducers, or model substrates, and they may serve as stable ligands for affinity chromatography [5]. Three 2-*S*-glycosyl-2-thioglycoses, among them 2-thiosophorose [2-*S*-β-D-glucopyranosyl-2-thio-D-glucose, (**8**)] have been synthesized and enzymologically studied.

In 1984 a synthetic strategy involving nucleophilic displacement of a glycose 2-triflate by 1-thioglycose leading to 2-*S*-glycosyl-2-thioglycoses was developed independently [6,7] in two laboratories in order to prepare **8**. It was shown, however, that classical deprotection procedures used to deprotect the anomeric methoxy or acetoxy groups to provide **8** did not yield the expected product [7] in spite of claims to the contrary [6]. Compound **8** was finally prepared by Defaye and co-workers [5,8–10], who introduced a readily cleavable aglycon as protecting group, enabling them to obtain the thiodisaccharide in 39% yield based on starting 1-thio-D-glucose. 2-Thiokojibiose [10] and 2-thioxylobiose [11] were prepared by similar procedures.

The present paper describes an alternative synthesis of **8**, obtained for the first time crystalline, using the aforementioned promising sugar α-nitroalkene route. The procedure also involves an epimerization of 2-thioepisophorose [2-*S*-β-D-glucopyranosyl-2-thio-D-mannose, (**7**)], a major component resulting from the nitro sugar route, in aqueous sodium bicarbonate, a process relative to Berrang–Horton's epimerization of 2-*S*-ethyl-2-thio-D-mannose [12].

Table 1
^{1}H NMR data of compounds prepared

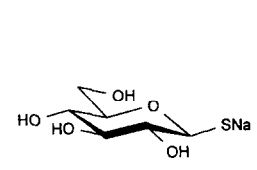
Compound	Chemical shifts [a] (coupling constants [b])							
	H-1a	H-1b	H-2	H-3	H-4	H-5	H-6a	H-6b
3	4.92	4.92	3.96(8.7)	5.47(2.1)	5.74(8.0)	5.18(3.0)	4.36(4.8)	4.23(12.7)
4	4.92	4.92	3.99(5.0)	5.53(3.6)	5.68(7.1)	5.24(3.3)	4.38(5.0)	4.29(12.7)
7α	5.42(1.8)	–	3.51(4.4)	4.16(9.3)	3.47(9.0)	3.82(2.2)	[d](5.6)	3.72(12.5)
7β	5.06(1.8)	–	3.63(4.7)	3.88(9.3)	3.33 [c]	3.34 [c]	[d]	[d]
8α	5.38(3.4)	–	3.10(11.0)	3.81(8.9)	3.45(10.0)	3.89(2.2)	[d](4.7)	3.77(12.1)
8β	4.80(9.0)	–	2.82(10.6)	3.61(8.4)	3.41(10.0)	3.48(2.2)	[d](5.6)	3.73(12.5)
	H-1′	H-2′	H-3′	H-4′	H-5′	H-6′a	H-6′b	
3	4.65(9.8)	3.29(8.5)	3.46	3.46	3.46(1.8)	3.90(5.0)	3.74(12.4)	
4	4.64(9.8)	3.31(8.7)	3.46	3.46	3.46(1.8)	3.88(5.0)	3.70(12.4)	
7α	4.53(9.6)	3.33(8.4)	3.46 [c]	3.40 [c]	3.43 [c]	[d]	[d]	
7β	4.53(9.6)	3.33(8.4)	3.46 [c]	3.40 [c]	3.43 [c]	[d]	[d]	
8α	4.76(9.8)	3.36(8.5)	3.49[c]	3.44[c]	3.45[c](1.8)	3.91(5.0)	3.72(12.4)	
8β	4.79(9.8)	3.32(8.5)	3.49[c]	3.44 [c]	3.45 [c](1.8)	3.91(5.0)	3.72(12.4)	

[a] δ in ppm.
[b] Observed first-order splittings in Hz.
[c] Determined from the CH-COSY spectrum.
[d] Not resolved.

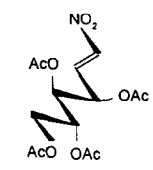
2. Results and discussion

Addition of 1-thio-D-glucose sodium salt (**1**) to 3,4,5,6-tetra-*O*-acetyl-1,2-dideoxy-1-nitro-D-*arabino*-hex-1-enitol [13] (**2**) in methanol, followed by decationization, gave a mixture of 3,4,5,6-tetra-*O*-acetyl-1-deoxy-2-*S*-β-D-glucopyranosyl-1-nitro-D-mannitol (**3**) and -D-glucitol (**4**) in the ratio 2.3:1. The ^{1}H NMR spectra (Table 1) confirmed the structures of **3** and **4**. Coupling constants of vicinal protons H-2–5 (8.7, 2.1, and 8.0 Hz for **3** and 5.0, 3.6, and 7.1 Hz for **4**) were close ($|\Delta| \leq 1.1$ Hz) to those of unsubstituted 1-deoxy-1-nitro-D-mannitol and -D-glucitol [14], respectively. The ^{13}C NMR spectra (Table 2) of both **3** and **4**, with their low-field C-2 signals, further confirmed the proposed structures.

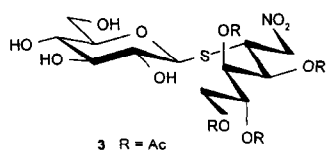
Subsequent deacetylation of **3** and **4** was performed in methanolic HCl to afford **5** and **6**. The former compound was obtained crystalline as a monohydrate. Attempts to isolate the pure isomer **6** failed. During its attempted isolation by chromatography of the mother liquor, it decomposed to products with faster TLC mobilities. The separation afforded only a small additional amount of **5** with an overall yield of 45% based on **1**. The ^{13}C NMR spectrum (Table 2) proved the structure of **5** showing 12 carbon signals including the one at 45.1 ppm belonging to C-2.



1

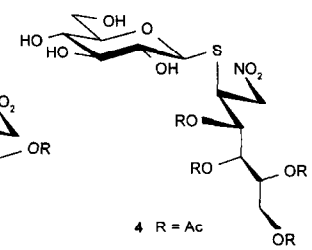


2



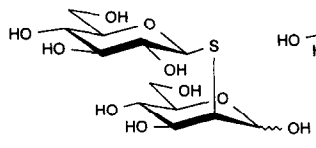
3 R = Ac

5 R = H

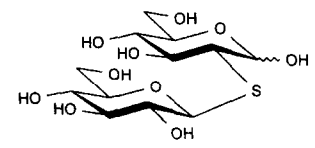


4 R = Ac

6 R = H



7



8

Table 2
^{13}C NMR chemical shifts (δ in ppm) of compounds prepared

Compound	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 [a]	77.6	42.3	72.2	70.1	70.0	61.9	87.4	73.6	78.4	70.4	81.2	63.2
4 [a]	77.8	44.7	71.0	70.8	70.3	63.0	85.6	73.6	78.3	70.3	81.2	63.1
5	78.8	45.1	71.2	70.2	72.0	64.4	86.6	73.5	78.2	70.6	80.9	62.2
6	78.6	48.1	70.6	71.1	72.4	63.7	86.9	73.6	78.2	70.3	80.9	61.8
7α [b]	95.9	52.5	69.8	69.1	73.9	62.9	86.4	73.3	78.1	70.4	81.0	62.9
7β [b]	94.5	55.5	70.9	68.9	73.7	62.9	86.9	73.8	78.1	70.5	81.1	62.9
8α [c]	94.9	51.6	73.9	72.0	73.0	62.0	87.0	73.9	78.4	70.7	81.0	62.9
8β [c]	96.5	54.1	76.2	71.7	76.9	62.0	85.7	74.0	78.3	70.7	81.0	62.9

[a] Additional signals: 21.9–21.1 (CH_3), 174.7–172.2 (C=O).
[b] Anomer ratio: $\alpha:\beta = 4:3$.
[c] Anomer ratio: $\alpha:\beta = 3:1$.

Final transformation of the acyclic precursors **5** and **6** to the thiodisaccharides **7** and **8**, respectively, was accomplished by the Nef reaction. When pure **5** was submitted to the conversion, 85% of **7** was isolated. The thiosugar was essentially pure according to ^1H NMR spectroscopy, i.e., it did not contain more then 5% of impurities.

The structure of **7** was confirmed by NMR spectroscopy. The ^{13}C NMR spectrum showed three characteristic pairs of signals of carbon atoms C-1 (95.9 and 94.5 ppm), C-2 (52.5 and 55.5 ppm), and C-1′ (86.4 and 86.9 ppm), corresponding to α- and β-anomers of **7**, respectively. Integration of the well-resolved doublets of anomeric protons at δ 5.42 and 5.06 revealed that the anomeric ratio at equilibrium was 4:3. Furthermore, the doublet of both H-1′ protons at δ 4.53 with a vicinal coupling constant of 9.6 Hz proved a β-configuration of the *S*-(1 → 2)-thioglycosidic bond of **7**.

The Nef reaction performed with the mixture of **5** and **6** gave, however, besides the corresponding thiodisaccharides **7** and **8**, also a significant amount of degradation products (ca. 15%). This implied that **6** was less stable than **5**, probably due to a 1,3-interaction of its bulky substituents at C-2 and C-4 in a zig-zag conformation changing it into a less stable sickle one. The aforementioned values of the vicinal coupling constants of partially *O*-acetylated precursors **3** and **4** support the explanation.

For transformation of the sodium nitronate of the acyclic precursor **5** into **7**, ozonolysis was also evaluated. Ozonolysis, which has been shown to give the best results for the conversion of 1-deoxy-1-nitroalditols to the corresponding aldoses [15], did not prove very efficient in the case of **5**. It resulted mainly in the formation of degradation products and yielded only about 20% of **7**.

The different behavior of the sodium nitronate of **5** during the Nef reaction and ozonolysis could be easily explained. While the conditions of the former reaction converted the reacting species almost immediately into the free nitronic acids, which were then disproportionated into products, the alkaline conditions of the latter reaction enabled a continuous, simultaneous β-elimination of 1-thio-D-glucose. Moreover, during the ozonolysis also a simultaneous oxidation of the sulfur atom by ozone [16] may have occurred, which could promote a further β-elimination and give rise to additional degradation products.

Therefore, to achieve the highest possible yield of **8**, it was necessary to submit the mixture of **5** and **6** as soon as possible to the Nef reaction. In a most favorable case, a mixture containing 55% of **7** and 30% of **8** was obtained.

Chromatography on a column of a strongly acidic cation-exchange resin in the Ca^{2+} form [17] using water as the mobile phase separated **8** from the mixture of **7** and degradation products, affording sufficiently pure **8** to crystallize spontaneously from methanol, with an overall yield of 34%.

The structure of **8** was confirmed by both ^{1}H and ^{13}C NMR spectra, which were in agreement with published data [10]. The high purity of **8** enabled a more complete assignment of both ^{1}H and ^{13}C NMR spectral data. However, the specific optical rotation of crystalline **8** after anomeric equilibration ($[\alpha]_D = -13.1°$) significantly differed from the literature value of $[\alpha]_D = -27°$ [10]. To ascertain that our value was not influenced by a possible presence of a high content of calcium ions used in isolation procedure and known to form complexes with sugars [17], which could influence their optical rotation, the crystalline sample was subjected to atomic absorption analysis. The analysis revealed a calcium content of 0.06%, i.e., the molar ratio of Ca (as $CaCl_2$):**8** was 1:514. Repeated purification of the crystalline **8** by cation-exchange resin in the H^+ form and recrystallization did not alter its specific rotation.

In attempts to utilize the chromatographic purification procedure also for separation of **7** from its degradation products, the flow rate was slowed down significantly, and no remarkable separation occurred; however, epimerization of **7** to **8** was observed.

Careful evaluation of the epimerization [18], previously and erroneously described as catalyzed by calcium ions [1], showed that it is a process analogous to epimerization of 2-*S*-ethyl-2-thio-D-mannose [12]. Thus, **7** on 24 h standing in M $NaHCO_3$ in D_2O at ambient temperature afforded an equilibrium mixture of **7** and **8**. Similarly, the same mixture was obtained from starting **8**. Integration of the ^{1}H NMR signals of anomeric protons of both sugars revealed that the epimerization equilibrium of **7** and **8** was 1:4. Application of the epimerization procedure to the mixture of **7** and **8** obtained after the Nef transformation of **5** and **6** gave crystalline **8** with an overall yield of 56% based on starting **1**. Due to the remarkably easy epimerization it was necessary to store syrupy **7** in a quartz vessel; otherwise **7** slowly epimerized and **8** crystallized from the syrup.

When the epimerization was done in D_2O, it was accompanied by the proton exchange at C-2, as seen in the ^{1}H NMR spectra of **7** and **8**. The original doublets of the H-1 protons of both α- and β-anomers of **7**, as well as that of the α-anomer of **8**, were changed into singlets. Observation of the phenomenon for the signal of the H-1β proton of **8** was ambiguous because of its overlapping with the H-1′ proton. Similarly, for example, the well-resolved quartet of the H-3α proton of **7** was changed into a doublet. This, together with the results of the investigation of mutual interconversion of 2-*S*-ethyl-2-thio-D-glucose and -D-mannose in aqueous $NaHCO_3$ [19], suggests that it proceeds via the acyclic aldehydo forms of the sugars.

The synthesis developed avoids the difficulties connected with deprotection of the anomeric hydroxyl group of **8** that occurred in previous procedures which yielded a less well-characterized product. Moreover, in view of the many precedents of simple transformations of nitroalditols into reducing sugars (e.g., refs. [15,20]), it encourages other applications of these acyclic species in oligosaccharide synthesis.

3. Experimental

General methods and materials.—Melting points were measured on a Kofler stage. Microanalyses were obtained using a Perkin–Elmer 240 instrument, and optical rotations at 20 °C using a Perkin–Elmer 141 polarimeter. Calcium content was determined using a Carl–Zeiss–Jena AAS 30 spectrometer at 422.7 nm. ^{13}C NMR (75.46 MHz, internal methanol, δ 50.15) and ^{1}H NMR spectra [300.13 MHz, internal sodium 3-(trimethylsilyl)propionate, δ 0.00] were obtained at 20 °C using a Bruker AM-300 spectrometer. Chromatography was performed on columns C_1 (3 × 60 cm) of Lachema Silica Gel L (40–100 μm) by elution with A, 2:2:1 EtOAc–hexane–MeOH and TLC monitoring on Lachema Silufol plates detected with alkaline silver nitrate, and C_2 (1.2 × 95 cm) of Dowex 50W-X8 (Ca^{2+}) resin (200–400 mesh) by elution with water and monitoring with a Knauer 5100 differential refractometer and by descending PC using B, 5:1:4 BuOH–EtOH–water and detection with alkaline silver nitrate. A Fischer 502 ozone generator was used for the preparation of ozone from gaseous oxygen. 1-Thio-D-glucose sodium salt was purchased from Aldrich. Solvents were evaporated under diminished pressure at < 40 °C.

1-Deoxy-2-S-β-D-glucopyranosyl-1-nitro-2-thio-D-mannitol (**5**) *and -D-glucitol* (**6**).—1-Thio-D-glucose sodium salt (**1**, 1.0 g, 4.6 mmol) was added to a solution of 3,4,5,6-tetra-*O*-acetyl-1,2-dideoxy-D-*arabino*-hex-1-enitol [13] (**2**, 2.8 g, 7.8 mmol) in MeOH (50 mL), and the mixture was stirred at ambient temperature for 20 min. Then Dowex 50W (H^+) resin (10 mL, prewashed with MeOH) was added to the resulting yellowish solution. The neutral solution was filtered, the resin washed with MeOH (5 × 5 mL), and the collected filtrates were concentrated to a syrupy mixture, which was purified by chromatography on column C_1. Obtained was a mixture of 3,4,5,6-tetra-*O*-acetyl-1-deoxy-2-*S*-β-D-glucopyranosyl-1-nitro-2-thio-D-mannitol (**3**) and -D-glucitol (**4**) (1.48 g, 71%) in the ratio 2.3:1 (by ^{13}C NMR), TLC (solvent A), R_f 0.67.

The syrupy mixture of **3** and **4** (1.1 g, 2.4 mmol) was dissolved in methanolic M HCl (37 mL) and left to stand at ambient temperature for 36 h. Water (40 mL) and Dowex 1 (HCO_3^-, 100 mL) were added, the suspension was stirred for 2 min, and the neutral solution was filtered and the resin was washed with water (5 × 30 mL). The combined filtrates were concentrated to a syrup (0.91 g, 97%) containing **5** and **6** in the ratio 2.5:1 [TLC (solvent A), R_f 0.16]. Crystallization from MeOH afforded **5** monohydrate (0.3 g, 32%), mp 148–150 °C, $[\alpha]_D$ −27.3° (*c* 0.5, H_2O). Anal. Calcd for $C_{12}H_{23}NO_{11}S \cdot H_2O$: C, 35.38; H, 6.19; N, 3.44. Found: C, 35.04; H, 5.93; N, 3.19.

Purification of the mother liquor by column chromatography on C_1 (solvent A) and crystallization afforded second crop of **5** monohydrate (0.12 g, 13%) and a residual 1:1 mixture of **5** and **6** (0.2 g, 21%).

2-S-β-D-Glucopyranosyl-2-thio-D-mannose (2-thioepisophorose, **7**).—4.5 M H_2SO_4 (3.5 mL) was added to a stirred solution of **5** (0.4 g, 1.03 mmol) in M NaOH (3.5 mL). After 20 min at ambient temperature, water (100 mL) and powdery barium carbonate (5 g) were added, and the suspension was stirred for 2 h. The neutral mixture was filtered and washed with water (3 × 50 mL). The filtrates were treated with Dowex 50W (H^+) and Dowex 1 (HCO_3^-) resins, and the final, neutral solution was concentrated to yield

syrupy **7** (0.32 g, 85%), $[\alpha]_D$ −30.2° (*c* 0.6, H_2O). Anal. Calcd for $C_{12}H_{22}O_{10}S$: C, 40.22; H, 6.19. Found: C, 39.88; H, 6.32.

2-S-β-D-Glucopyranosyl-2-thio-D-glucose (2-thiosophorose, **8**).—(a) Starting from **1** (0.42 g, 1.9 mmol) and **2** (0.84 g, 2.3 mmol), and following the procedure described above for the preparation of **5** and **6**, but without any column chromatographic purification or crystallization, a crude mixture of **5** and **6** (0.7 g) was obtained. This was dissolved in M NaOH (10 mL), 4.5 M H_2SO_4 (10 mL) was added immediately, and after 20 min the solution was neutralized and deionized as above. The procedure afforded a syrup (0.65 g) that was fractionated on column C_2 (flow rate 8 mL/h) to give a first portion of **8** (0.14 g, 20%), mp (MeOH) 178–180 °C, $[\alpha]_D$ −8.0° (3 min) → −13.1° (equil) (*c* 0.5, H_2O); lit. [10] $[\alpha]_D$ −27° (equil) (*c* 0.3, H_2O). Anal. Calcd for $C_{12}H_{22}O_{10}S$: C, 40.22; H, 6.19. Found: C, 39.98; H, 6.19. Atomic absorption analysis: Ca, 0.06%.

Repeated fractionation of the second fraction, which contained both **7** and **8**, and degradation products, gave a second portion of **8** (0.10 g, 14%) and a residual mixture of **7**, **8**, and degradation products (0.3 g).

(b) A solution of **7** (0.1 g) in M $NaHCO_3$ (5 mL) was left to stand at ambient temperature for 24 h. Then Dowex 50W (H^+) resin (10 mL) was added, and the suspension was stirred for 10 min. The neutral solution was concentrated to a syrup (95 mg), which crystallized from MeOH affording **8** (55 mg).

(c) In a repeated procedure (a) for the preparation of **8**, the syrup (0.65 g) to be separated on the column was dissolved in M $NaHCO_3$ (20 mL) and left to stand at ambient temperature for 24 h. Further work up according to (b) afforded a syrup, which was separated on column C_2 affording **8** (0.39 g, 56%) and a mixture of **7**, **8**, and degradation products (0.20 g).

Epimerization of **7** *and* **8** *in* D_2O.—A solution of **7** (20 mg) and $NaHCO_3$ (42 mg) in D_2O (0.5 mL) in a 5 mm NMR test tube was kept at ambient temperature, and every 4–12 h subjected to ^1H NMR measurement. After 24 h, no further changes in the NMR spectra were observed. The same procedure carried out with **8** resulted in the same equilibrium mixture of **7** and **8**.

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