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Sulfoaminoglucitols: synthesis of 2-amino-2,3 (and 2,6)-dideoxy-D-glucitol-3 (and 6)-sulfonic acids and X-ray crystal structure of the monohydrate of the 6-sulfo derivative

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Abstract

2-Amino-2,3-dideoxy-D-glucitol-3-sulfonic acid (**3**) and 2-amino-2,6-dideoxy-D-glucitol-6-sulfonic acid (**4**) were prepared by reduction of 2-amino-2,3 (and 2,6)-dideoxy-D-glucopyranose-3 (and 6)-sulfonic acids with sodium borohydride. The crystal structure of **4** monohydrate ($C_6H_{15}NO_7S \cdot H_2O$) is orthorhombic, space group $P2_12_12_1$ with unit cell dimensions $a =$ 8.289(2), $b = 24.548(5)$, and $c = 5.149(2)$ Å. A planar zig-zag conformation is observed in which N-2 and O-4 atoms are aligned 1,3-parallel, stabilized by an intramolecular hydrogen bond (N–H · · · O-4). The sulfo and the amino group form a zwitterion and two conformations are found for the ammonium group.

Keywords: Alditol sulfonic acids; Taurine analogues; Sulfonic acids; X-Ray structures; Hydrogen bonds; Zwitterions

1. Introduction

Sulfonic acids and their derivatives are important constituents of living organisms [1]. Taurine (2-aminoethanesulfonic acid) and related compounds such as homotaurine

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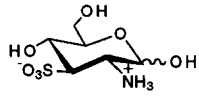
(3-aminopropanesulfonic acid), cysteic acid or guanidotaurine possess physiological properties essential for the well-being of various species [2–4]. Taurine is present in relatively high concentration in the central nervous system and brain [5], acts as neurotransmitter in retine [6], and shows cardioprotective activity [7].

Synthesis of natural (*S*)-2-hydroxymethyl taurine (D-cysteinolic acid), isolated from marine micro-organism [8], has been recently described from serine [9,10]. A 5′-deoxy-5′-(dimethyl-arsinoyl)-D-ribofuranosyl derivative of cysteinolic acid has been isolated from brown alga *Sargassum lacerifolium* and its X-ray molecular structure reported [11].

2. Results and discussion

In this paper, we describe the synthesis of the taurine analogues **3** and **4**, by reduction of 2-amino-2,3 (and 2,6)-dideoxy-D-glucopyranose-3 (and 6)-sulfonic acids (**1** and **2**, respectively) with sodium borohydride, in 98 and 69% yield. 3-Sulfoglucosamine (**1**) was prepared by treatment of 2-acetamido-2-deoxy-D-glucose with a mixture of Dowex-1 X-8(OH^-) and Dowex-1 X-8(SO_3^{2-}) resins, using a modification of the method described by Weber and Winzler [12] that will be published elsewhere. 2-Amino-2,6-dideoxy-D-glucopyranose-6-sulfonic acid (**2**) was prepared [13] by oxidation of 2-acetamido-1,3,4-tri-*O*-acetyl-6-*S*-acetyl-2-deoxy-6-thio-β-D-glucopyranose with 30% hydrogen peroxide in acetic acid.



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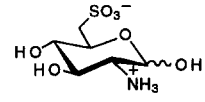

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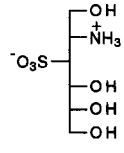

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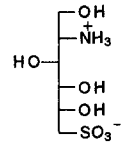


4

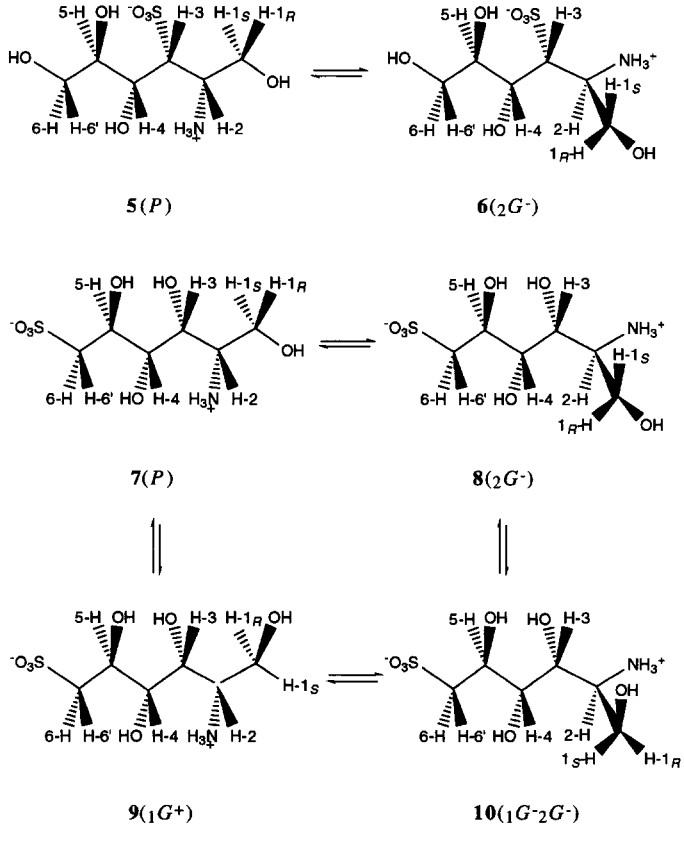
The structures of **3** and **4** were assigned on the basis of analytical, IR, ^1H and ^{13}C NMR, and MS data (see Experimental section). The ^1H NMR data are shown in Table 1. The $^3J_{H,H}$ values $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ are similar for both compounds and indicate [14,15] that, in deuterium oxide, there were an equilibrium between the zig-zag planar conformations *P* (**5** and **7**), which present a 1,3-parallel interaction between the NH_3^+ and OH-4 groups, and the sickle conformations $_2G^-$ (**6** and **8**) free of parallel interactions.

Table 1
^{1}H NMR data for **3** and **4** in D_2O

Compound	H-1	H-1′	H-2	H-3	H-4	H-5	H-6	H-6′	
3 [a]	3.97dd	3.90dd	3.79m	3.56dd	3.85dd	4.13ddd	3.78dd	3.58dd	
4 [b]	3.86dd	3.74dd	3.51td	4.12dd	3.58dd	4.15m	3.37dd	3.02dd	
	$J_{1,2}$	$J_{1',2}$	$J_{1,1'}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
3 [a]	4.0	6.1	12.3	6.4	2.3	9.7	2.6	5.5	11.6
4 [b]	4.3	6.8	12.4	6.8	1.2	8.6	2.1	9.2	14.6

[a] 200 MHz.
[b] 300 MHz.

Conformations associated with chain-end flexibility around C-1–C-2 and C-5–C-6 were also found for **3**. However, **4**, due to the size of the sulfate group, presented only chain-end flexibility around C-1–C-2 associated with ${}_1G^+$ (**9**) and ${}_1G_2^-G^-$ (**10**) conformations.



5(*P*) **6**($_2G^-$)

7(*P*) **8**($_2G^-$)

9($_1G^+$) **10**($_1G^-{}_2G^-$)

Table 2
^{13}C NMR chemical shifts for **3** and **4** in D_2O

Compound	C-1	C-2	C-3	C-4	C-5	C-6
3 [a]	60.49	58.37	54.31	72.28	70.62	63.67
4 [b]	59.67	56.27	66.58	73.65	68.17	54.87

[a] 50.3 MHz.
[b] 75.5 MHz.

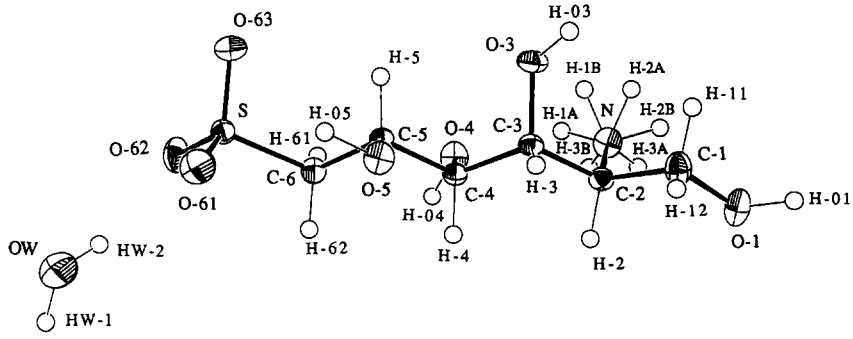


Fig. 1. ORTEP view of **4** showing the atomic numbering. The ellipsoids enclose 50% probability.

The ^{13}C NMR data are shown in Table 2. The resonance of the carbon bonded to the sulfate group (54.31 and 54.87 ppm) corresponded to the more shielded signal for **3** and **4**, respectively. Assignments of the ^{13}C signals of **4** were based on heteronuclear 2D correlated experiments. The positive-ion FAB mass spectra of **3** and **4** contained intense peaks for $[M + 2\ Na\text{-}H]^+$, $[M + Na]^+$, and $[M + H]^+$. The spectrum of **4** showed also peaks due to dimers $[2\ M + H]^+$ and $[2\ M + Na]^+$, although no larger cluster ions, expected for sulfonic salts [16], were detected.

Crystallography.—The structure of **4**, crystallized as a monohydrate, was confirmed by X-ray analysis [1]. An ORTEP [17] view of the molecule along the *b* axis together with the atomic numbering is shown in Fig. 1. The atom coordinates are listed in Table 3. Bond lengths and angles, and torsional angles are shown in Table 4.

The length of the three S–O bonds are similar [from 1.447(2) to 1.476(2) Å] indicating that the negative charge on the SO_3^- group is delocalized over the three oxygen atoms. The mean S–O distance of 1.460(2) Å observed for this structure is identical to that observed in 2-amino-2,6-dideoxy-α-D-glucopyranose-6-sulfonic acid (**1**) [18] and slightly higher than that found in its methyl α-glycoside [1.449(3) Å] [19]. These values show a remarkable agreement with that obtained (1.458 Å) by ab initio SCF (self-consistent field) 6 − 31 + G^* calculations on methanesulfonate anion [20]. On

[1] Observed and calculated structure factors, and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. The data may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Table 3
Atomic positional parameters and equivalent isotropic thermal parameters for **4** at 293 K [a]

Atom	x/a	y/b	z/c	U_{eq} [b]
C-1	$1366(3)\times10^{-4}$	$4473(1)\times10^{-4}$	$6774(6)\times10^{-4}$	$272(6)\times10^{-4}$
C-2	258(3)	3986(1)	6488(4)	183(4)
C-3	986(3)	3471(1)	7732(4)	166(4)
C-4	124(2)	2955(1)	6834(4)	170(4)
C-5	728(2)	2430(1)	8113(4)	163(4)
C-6	−267(3)	1953(1)	7118(4)	202(5)
O-1	685(3)	4914(1)	5371(5)	397(6)
N	−1354(2)	4120(1)	7661(5)	246(5)
O-3	926(2)	3509(1)	10493(3)	246(4)
O-4	−1575(2)	3006(1)	7362(4)	246(4)
O-5	2410(2)	2374(1)	7515(4)	247(4)
S	223(1)	1314(1)	8551(1)	189(1)
O-61	1742(3)	1127(1)	7445(5)	361(6)
O-62	−1158(3)	967(1)	7817(5)	331(6)
O-63	308(3)	1396(1)	11332(4)	313(5)
O W	1183(5)	119(1)	4144(6)	516(8)
H-11	$162(8)\times10^{-3}$	$456(2)\times10^{-3}$	$850(13)\times10^{-3}$	
H-12	222(7)	436(2)	612(12)	
H-2	1(6)	390(2)	473(11)	
H-3	215(6)	343(2)	728(10)	
H-4	39(6)	292(2)	491(10)	
H-5	53(6)	247(2)	987(11)	
H-61	−129(7)	202(2)	742(10)	
H-62	−6(7)	190(2)	508(10)	
H-01	114(9)	522(3)	638(14)	
H-1A	−208(14)	383(5)	813(24)	
H-2A	−119(15)	431(5)	942(25)	
H-3A	−193(15)	448(5)	706(26)	
H-1B	−160(14)	397(5)	963(24)	
H-2B	−158(15)	438(5)	758(25)	
H-3B	−256(15)	401(5)	694(24)	
H-03	175(7)	370(2)	1096(11)	
H-04	−198(7)	283(2)	608(11)	
H-05	297(7)	208(2)	833(11)	
HW-1	55(10)	3(3)	273(16)	
HW-2	25(10)	−8(3)	513(17)	

[a] Esd values given in parentheses refer to the least significant digit.
[b] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$. U for H atoms equal to non-H atoms to which they are covalently bonded.

the contrary, ab initio calculations on methanesulfonic acid show a 1.59 Å distance for the single S–O bond and 1.428 and 1.420 Å for the double S=O bonds [20]. Recently, in 2-amino-2-deoxy-β-D-glucopyranose-6-sulfate a S–O distance of 1.450(5) Å has been correlated with a S–OH bond type [21]. The bond angles about the sulfonate group in compound **4** are similar to those found in **2** [18], in its methyl α-glycoside [19], and in other sulfonic acids [22,23].

The chain O-1, C-1, C-2, C-3, C-4, C-5, C-6, S and O-62 is nearly planar [maximum deviation from the best plane is 0.171(2) Å]. N, O-3, O-4, and O-63 are on one side, O-5

Table 4
Bond lengths (Å), bond angles, and torsion angles (°) for **4** [a]

Bond lengths			
C-1–C-2	1.515(3)	C-3–O-3	1.425(3)
C-2–C-3	1.540(3)	C-4–O-4	1.440(3)
C-3–C-4	1.524(3)	C-5–O-5	1.435(3)
C-4–C-5	1.532(3)	C-6–S	1.781(2)
C-5–C-6	1.521(3)	S–O-61	1.456(2)
C-1–O-1	1.418(4)	S–O-62	1.476(2)
C-2–N	1.503(3)	S–O-63	1.447(2)
Bond angles			
O-61–S–O-62	112.9(1)	C-2–C-3–O-3	110.2(2)
O-62–S–O-63	111.8(1)	O-3–C-3–C-4	109.9(2)
O-61–S–O-63	112.8(1)	C-3–C-4–C-5	114.5(2)
C-6–S–O-61	108.2(1)	C-3–C-4–O-4	109.2(2)
C-6–S–O-62	103.0(1)	O-4–C-4–C-5	108.1(2)
C-6–S–O-63	107.4(1)	C-4–C-5–C-6	109.0(2)
C-1–C-2–C-3	111.7(2)	C-4–C-5–O-5	107.8(2)
C-1–C-2–N	109.0(2)	O-5–C-5–C-6	112.4(2)
N–C-2–C-3	111.2(2)	C-5–C-6–S	114.5(2)
C-2–C-3–C-4	111.8(2)	C-2–C-1–O-1	108.1(2)
Torsion angles			
O-1–C-1–C-2–C-3	174.4(2)	C-3–C-4–C-5–C-6	178.1(2)
O-1–C-1–C-2–N	−62.2(3)	C-3–C-4–C-5–O-5	−59.6(2)
C-1–C-2–C-3–C-4	−164.5(2)	O-4–C-4–C-5–C-6	56.0(2)
C-1–C-2–C-3–O-3	72.9(2)	O-4–C-4–C-5–O-5	178.3(2)
N–C-2–C-3–C-4	73.4(2)	C-4–C-5–C-6–S	−177.0(1)
N–C-2–C-3–O-3	−49.1(2)	O-5–C-5–C-6–S	63.5(2)
C-2–C-3–C-4–C-5	−176.8(2)	C-5–C-6–S–O-61	−74.9(2)
C-2–C-3–C-4–O-4	−55.4(2)	C-5–C-6–S–O-62	165.3(2)
O-3–C-3–C-4–C-5	−54.0(2)	C-5–C-6–S–O-63	47.2(2)
O-3–C-3–C-4–O-4	67.4(2)		

[a] Esd values given in parentheses refer to the least significant digit.

and O-61 are on the other side of the plane. The torsion angles along the backbone carbons, Table 4, agree with the zig-zag planar **7**(*P*) conformation, one of the conformers found in solution. The deviation from the ideal *P* conformation for the torsion angles around C-1–C-2, C-3–C-4, C-4–C-5, and C-5–C-6 bonds are lower than 6°, although the torsion angles C-1–C-2–C-3–C-4 and C-5–C-6–S–O-62 present a 16° deviation.

This planar conformation occurs in spite of the 1,3-parallel interaction between N and O-4 atoms, designated as N//O. The avoidance of O//O interaction, termed the Hassel–Ottar effect [24,25], has been observed frequently, although recently it was realized [26–29] that O//O interactions in planar zig-zag conformation can be tolerated in alditols and alditols derivatives that contain three contiguous stereogenic centers of altering opposite configuration (DLD or LDL). So, whereas D-glucitol is found in a bent conformation [30], 1-deoxy-1-nitro-L-glucitol exits in the planar conformation [31], and two forms of potassium D-gluconate present straight- and bent-chain conformations [32].

Table 5
Geometry of the hydrogen-bonding system and short contacts for **4**. The minor components of the three- and four-center bonds are listed below that of the major hydrogen bond component

Donor–H · · · acceptor	Acceptor symmetry code [a]	D · · · A (Å)	D–H (Å)	H · · · A (Å)	D–H · · · A (°)
Two-center					
O-1 · · · O-62	(i)	2.777(3)	0.99(7)	1.88(7)	149(6)
O-3 · · · O-62	(iv)	2.876(3)	0.84(6)	2.04(6)	171(6)
O-4 · · · O-5	(ii)	2.808(3)	0.85(6)	1.99(6)	162(6)
OW–H-1 · · · O-1	(v)	2.838(4)	0.92(8)	1.92(8)	174(6)
C-2 · · · O-3	(vi)	3.347(3)	0.95(5)	2.50(5)	148(4)
C-6–H-62 · · · O-63	(vi)	3.313(3)	1.07(5)	2.31(5)	155(4)
Three-center					
N–H-2A · · · OW	(i)	2.956(4)	1.03(12)	2.12(12)	137(10)
N–H-2A · · · O-61	(iii)	3.037(4)		2.60(13)	104(8)
N–H-1B · · · O-61	(iii)	3.037(4)	1.10(12)	2.03(13)	149(10)
N–H-1B · · · O-3	(0) [b]	2.819(3)		2.42(12)	99(8)
O-5 · · · O-4	(iv)	2.921(3)	0.95(6)	2.25(6)	125(4)
O-5 · · · O-61	(0) [b]	3.110(3)		2.60(6)	114(4)
Four-center					
N–H-1A · · · O-4	(0) [b]	2.745(3)	0.96(11)	2.11(11)	122(9)
N–H-1A · · · O-63	(iii)	3.087(3)		2.22(12)	146(10)
N–H-1A · · · O-61	(iii)	3.037(3)		2.43(13)	119(9)
N–H-3A · · · OW	(ii)	2.919(4)	1.05(12)	1.95(12)	152(10)
N–H-3A · · · O-1	(0) [b]	2.835(3)		2.56(12)	94(7)
N–H-3A · · · OW	(i)	2.956(4)		2.58(13)	100(8)
N–H-2B · · · OW	(ii)	2.919(4)	0.66(12)	2.40(12)	138(13)
N–H-2B · · · OW	(i)	2.956(4)		2.51(12)	128(13)
N–H-2B · · · O-1	(0) [b]	2.835(3)		2.56(12)	108(11)
N–H-3B · · · O-63	(iii)	3.087(3)	1.10(12)	2.24(13)	130(9)
N–H-3B · · · O-61	(ii)	3.126(4)		2.36(12)	126(9)
N–H-3B · · · OW	(ii)	2.919(4)		2.45(12)	104(8)

[a] Symmetry code: (0) x, y, z; (i) $-x, y+1/2, -z+3/2$; (ii) $x-1/2, -y+1/2, -z+1$; (iii) = (ii + c); (iv) = (ii + a + c); (v) = (i − b − c); (vi) = (0 − c).
[b] Intramolecular hydrogen bonds.

The crystal structure is stabilized by an extensive system of inter- and intra-molecular hydrogen bonds described in Table 5. In accordance with restrictive criteria for hydrogen bond, for D · · · A and H · · · A distances less than 3.00 and 2.40 Å, respectively, a short contact can be assumed to be a hydrogen bond [33]. However, more permissive cutoff limits of 3.2 Å for O · · · O distances [34] and of 2.7 Å for H · · · A in C–H · · · A [35] have been justified.

According to the zwitterion structure of sulfoamino compounds, the nitrogen should carry three hydrogens [19,23]. However six hydrogens were located from difference Fourier syntheses, with occupation factors of 0.5. These hydrogens could be distributed into two different arrangement, conformer *A* and conformer *B*, shown in Fig. 1.

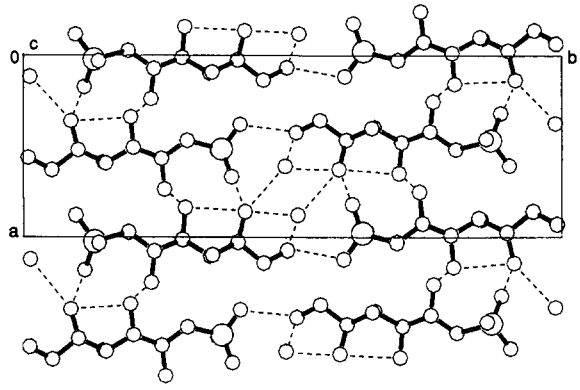


Fig. 2. Projected view of the packing of **4** along the *c* axis. Some of the hydrogen bonds are shown as broken lines.

The six hydrogens of the ammonium group in both conformations participate in three- and four-center hydrogen bonds. The unusual four-center hydrogen bond has been found in ammonium hydrogens of *N*-(1-deoxy-β-D-fructopyranos-1-yl)-glycine [33].

The molecular packing is shown in Fig. 2. The molecules arrange linearly along the *b* axis, forming head-to-tail chains through the strong O-1–H · · · O-62(i) hydrogen bond with the molecule derived from the two-fold screw operation. Each molecular chain is surrounded by another four related between them by pure translational symmetry. Infinite chains of cooperative H-bond along the *c* axis are formed with O-5 · · · O-4 · · · O-5.

The extensive hydrogen-bond network explains the compactness of the crystal structure of **4**, characterized by its high density (D_c 1.67 g cm^{-3}), although lower than the density of its parent compound **2** (1.76 g cm^{-3}) [18], whereas the usual range of density for sugars and alditols is 1.47–1.64 [36]. Crystals of high density as *neo*-inositol (1.69 g cm^{-3}) [37] and galactaric acid (1.83 g cm^{-3}) [38] also present extensive hydrogen bonding.

3. Experimental

General methods.—Melting points are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. FTIR spectra (KBr discs) were recorded with a Bomem MB-120 spectrometer. ^{1}H NMR (200 and 300 MHz) and ^{13}C NMR (50.3 and 75.5 MHz) spectra were recorded with a Varian XL-200 and Bruker AMX-300 for solutions in D_2O (internal DOH 4.75 ppm and internal 1,4-dioxane at 67.4 ppm). Chemical shifts are expressed in δ (ppm) and coupling constants (*J*) in Hz. Heteronuclear 2D correlated spectra were obtained in order to assist in signal assignments. FAB-mass spectra were obtained using a Kratos MS-80 RFA instrument. Ions were produced by a beam of Xe atoms (7 kV), using a matrix consisting of thioglycerol and

NaI as salt. Positive ions were extracted and accelerated over a potential of 10 kV. TLC was performed on Silica Gel HF_{254} (E. Merck) with detection by charring with H_2SO_4.

2-Amino-2,3-dideoxy-D-glucitol-3-sulfonic acid (**3**).—To a solution of 2-amino-2,3-dideoxy-D-glucopyranose-3-sulfonic acid (**1**) (46 mg; 0.35 mmol) in water (1.5 mL) was added sodium borohydride (43 mg; 1.14 mmol) at room temperature, in small portions, during 5 h. The pH was adjusted to 3 with Amberlite IR-120(H^+), and the mixture filtered and coevaporated with MeOH (3 times) affording pure **3** (45 mg, 98%). Recrystallization from water–MeOH gave mp 175 °C (dec), 210 °C (melts); $[\alpha]_D^{24}$ +2°, $[\alpha]_{578}^{24}$ +4°, $[\alpha]_{546}^{24}$ +1°, $[\alpha]_{435}^{24} \cong 0°$ (*c* 0.9, H_2O); R_f 0.42 (3:2:1:1 EtOAc–MeOH–AcOH–H_2O); ν_{max} 3649, 3399 (NH_3^+, OH), 1504 (NH_3^+), 1188 and 1037 cm^{-1} (SO_3^-); FABMS: *m/z* 290 ([M + 2 Na-H]$^+$, 79%), 268 ([M + Na]$^+$, 100), 246 ([M + H]$^+$, 22). For ^1H and ^{13}C NMR spectra, see Tables 1 and 2. Anal. Calcd for $C_6H_{15}NO_7S$: C, 29.38; H, 6.16; N, 5.71; S, 13.07. Found: C, 28.86; H, 5.67; N, 5.50; S, 12.97.

Table 6
Experimental conditions for the crystal structure determination of **4**

molecular formula	$C_6H_{15}NO_7S \cdot H_2O$
molecular weight	263.28
crystal system	orthorhombic
space group	$P2_12_12_1$
unit-cell dimensions	$a = 8.289(2)$, $b = 24.548(5)$, $c = 5.149(2)$ Å
unit-cell volume, *V*	1047.7(5) Å^3
formula units per unit cell, *Z*	4
calculated density, D_c	1.67 g cm^{-3}
radiation	Mo K_α
wavelength	0.71069 Å
F(000) value	572
absorption coefficient, μ	0.32 mm^{-1}
temperature, *T*	293 K
crystal shape	prismatic
crystal size	0.20×0.32×0.40 mm
diffractometer	Enraf–Nonius CAD-4
determination of unit cell	least squares
number of reflections used	25
θ-range	2–15°
intensity data collection	$w/2\theta$ scan mode
maximum θ	30°
range of *h*, *k*, and *l*	0–11, 0–34, and 0–7
standard reflections	(2 1 1), (−1 7 0), and (3 9 1)
internal agreement	R_{int} 0.053
number of measured reflections	1800
number of significant reflections	1635
criterion for significance	$I > 2\sigma(I)$
number of refined parameters	205
final *R*	0.039
final ωR	0.050
goodness-of-fit *S*	1.11
final max. and aver. shift/esd	0.012 and 0.003
final max. and min. in $\Delta\rho$	0.20 and −0.30 e Å^{-3}

2-Amino-2,6-dideoxy-D-glucitol-6-sulfonic acid (**4**).—To a solution of 2-amino-2,6-dideoxy-D-glucopyranose-6-sulfonic acid (**2**) [13] (250 mg; 1.0 mmol) in water (4 mL) was added sodium borohydride (230 mg; 6.1 mmol) as described above. The pH was adjusted to 3 with Amberlite IR-120(H^+), and the mixture filtered and coevaporated with MeOH gave a residue that purified by column chromatography on Biogel P2 (1:1 MeOH–H_2O) yielded **4**, 173 mg (69%). Recrystallized from water–isopropanol gave mp 200–202 °C (dec); $[\alpha]_D^{22}$ +2°, $[\alpha]_{578}^{22}$ +3°, $[\alpha]_{546}^{22}$ +5°, $[\alpha]_{435}^{22}$ +12° (*c* 1.0, H_2O); R_f 0.3 (3:2:1:1 EtOAc–MeOH–AcOH–H_2O); ν_{max} 3567, 3213 (NH_3^+ , OH), 1587, 1504 (NH_3^+), 1215 and 1063 cm^{-1} (SO_3^-); FABMS: *m/z* 513 ([2 M + Na]$^+$, 8%), 491 ([2 M + H]$^+$, 11), 290 ([M + 2 Na–H]$^+$, 9), 268 ([M + Na]$^+$, 44), 246 ([M + H]$^+$, 100). For ^1H and ^{13}C NMR spectra, see Tables 1 and 2. Anal. Calcd for $C_6H_{15}NO_7S \cdot 1.5\ H_2O$: C, 26.47; H, 6.66; N, 5.14. Found: C, 26.75; H, 6.99; N, 4.76.

Crystal analysis.—A summary of the crystal data, data-collection and structure refinement parameters for **4** is given in Table 6. Data were corrected for Lorentz and polarization factors, extinctions were ignored, and an empirical absorption correction following the DIFABS procedure [39] was applied to the isotropically refined data. Maximum and minimum absorption correction factors were 1.578 and 0.743 respectively.

The S atom was located through Patterson methods and was used to reveal the other atoms by SHELXS86 [40]. An unexpected water molecule was found and the initial residual value calculated for these atomic positions was 0.110. The structure was refined isotropically ($R = 0.083$, unit weights) and then anisotropically, minimising the function $\Sigma\omega(|F_o| - |F_c|)^2$, where $\omega = 1/\sigma^2(F_o)$. A difference Fourier synthesis revealed the position of all the hydrogen atoms, that were included in the final refinement calculations with fixed U_{iso} values equal to the U_{eq} of the carrier atoms. Atomic scattering factors were taken from the International Tables for the X-Ray Crystallography [41], and all calculations were performed with the X-Ray System package [42]. The bond lengths (Å) and angles (°), and torsional angles (°) in Table 4 were calculated by the program PARST, written by Nardelli [43].

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