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Stereochemical analysis of D-glucopyranosyl-sulfoxides via a combined NMR, molecular modeling and X-ray crystallographic approach

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Abstract

(*S*)-α-Methoxyphenylacetic acid (MPAA) was used as an NMR shift reagent in combination with molecular modeling to predict the absolute configuration of a representative epimeric pair of glucopyranosyl sulfoxides. The correctness of this assignment was confirmed by X-ray crystallographic examination of one of the epimers, **3a1**. The crystal structure of ethyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside *S*-oxide monohydrate **3a1** was solved by direct methods and was shown to bear the (*R*)-configuration at the sulfinyl center in accordance with our prediction. Furthermore, the conformation of **3a1** in the solid state was found to be remarkably similar to that predicted by molecular mechanics calculations.

1. Introduction

The stereochemical analysis of chiral sulfoxides remains an important research objective. We have demonstrated that (*S*)-(+)-α-methoxy-phenylacetic acid (MPAA) **1** can be used as a chiral NMR shift reagent to determine the % ee and absolute configuration of a substantial number of acyclic sulfoxides.[1a,b] Others have extended these studies using related chiral aromatic acids.[2a,b] We have also used MPAA in combination with molecular modeling techniques to correctly predict the stereochemistry of some thiosugar sulfoxides.[3] To date, our methodology has enjoyed a 100% success rate. Recently, the Rollin group has prepared a number of epimeric glucopyranosyl sulfoxides, **3a**–**f**, which have important

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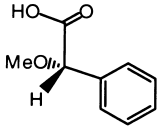
applications as glycosyl donors via the Kahne coupling technique.[4] It has also been shown that these types of molecules undergo interesting diastereoselective cleavage reactions.[5] In this paper, we show how our methods can be used to predict the absolute configuration of **3a1**,**2** — a representative epimeric pair of this family of thiosugar sulfoxides.



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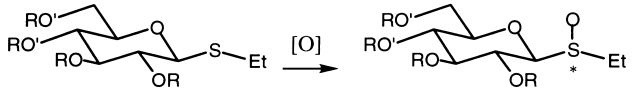
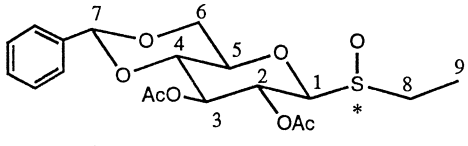


2a-f **3a-f**

a: R = Ac; R' = benzylidene
b: R = R' = Ac
c: R = R' = Bn
d: R = R' = Piv
e: R = R' = Bz
f: R = R' = pNO_2Bz

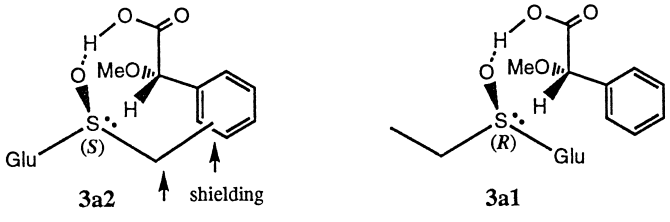
2. Results and discussion

Our initial stereochemical analysis consisted of recording the ^1H (400 MHz) and ^{13}C (100.6 MHz) NMR spectrum of each epimeric sulfoxide **3a1** and **3a2** in $CDCl_3$ and examining the effect of adding (*S*)-(+)-MPAA (3 equiv.) in terms of our two-point, Pirkle-type complexation model[1a] (see Fig. 1); the pendant ethyl group was used to report the relative shielding effects of the aromatic ring for each epimer. As shown in Table 1, the effect of (*S*)-(+)-MPAA addition is to shift the ^1H resonances of the C-8 methylene group of both epimers downfield due to the H-bonding of the basic sulfinyl oxygen with the carboxyl hydrogen but this downfield shift is less for **3a2** due to the counteracting shielding effect of the proximal benzene ring. In addition, ^{13}C resonances assigned to C-8 move upfield for both epimers upon H-bonding as anticipated,[1a] and this shift is augmented by the additional shielding effect of the benzene ring in the case of **3a2**. In addition, both the ^{13}C and ^1H resonances of the methyl groups of **3a2** experience greater shielding than do the corresponding signals of **3a1**. Taken together, these trends can be interpreted using our model (Fig. 1) and on this basis, one would tentatively assign the (*S*)-configuration to the sulfinyl group of **3a2** and the (*R*)-configuration to that of **3a1**.



3a1,2

Corroborating evidence for these assignments was obtained by noting a striking difference in the effect of MPAA addition on the H-1 resonance of each epimer: for **3a2**, this signal is shifted downfield by ca. 0.1



3a2 **3a1**

Figure 1. Binding model for the interaction of (*S*)-MPAA with the two epimers of **3a**

Table 1
Effect of addition of (*S*)-(+)-MPAA (3 equiv.) on the α-sulfinyl ^{1}H (^{13}C) resonances of **3a1** and **3a2**

	Δδ: **3a2**	Δδ: **3a1**	Δδ: **3a2** - Δδ: **3a1**
C-8H$_A$	0.050	0.052	-0.002
C-8H$_B$	0.002	0.006	-0.004
C-9 (CH$_3$)	-0.023	-0.011	-0.012
C-8	-0.486	-0.326	-0.16
C-9	-0.047	-0.037	-0.01

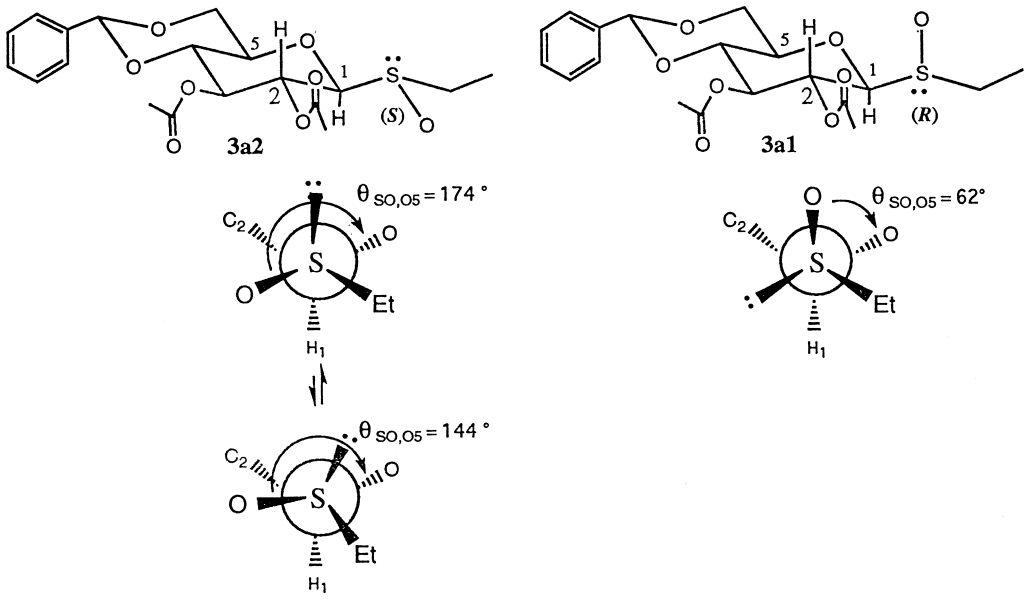


Figure 2. Energy-minimized conformations of **3a1** and **3a2**

ppm (4.582–4.485 ppm) while that of **3a1** is affected to a far lesser extent (Δδ=0.008 ppm; 4.234–4.226 ppm). Such phenomena are strongly reminiscent of previous observations[3,6] where an increase in H-bonding-induced deshielding effects on α-sulfinyl hydrogens could be correlated with a decrease in the inter S*O*–αC*H* distance. Therefore, this latter parameter was probed by determining the conformer populations of the **3a** epimers using semi-empirical (AM1/MOPAC) methods followed by single-point DFT (Spartan 5.0) calculations (see Fig. 2). Two very similar, low energy conformers (ca. 60:40 mixture) featuring an approximately gauche relationship between the sulfinyl oxygen and H-1 were identified for the (*S*)-sulfoxide. A single preferred conformation where the sulfinyl oxygen is *anti* to H-1 was found for the (*R*)-sulfoxide. Thus, H-bonding to the oxygen of the sulfinyl oxygen of the (*S*)-sulfoxide should have a far greater deshielding effect on the H-1 resonance than the corresponding effect for the (*R*)-sulfoxide and on this basis the assignment of the (*S*)-configuration to the sulfinyl group of **3a2** and the (*R*)-configuration to that of **3a1** is strengthened.

Our configurational analysis was further validated by X-ray crystallographic examination of **3a1**. The results of this study showed that **3a1** possesses the (*R*)-configuration at sulfur as shown in the ORTEP

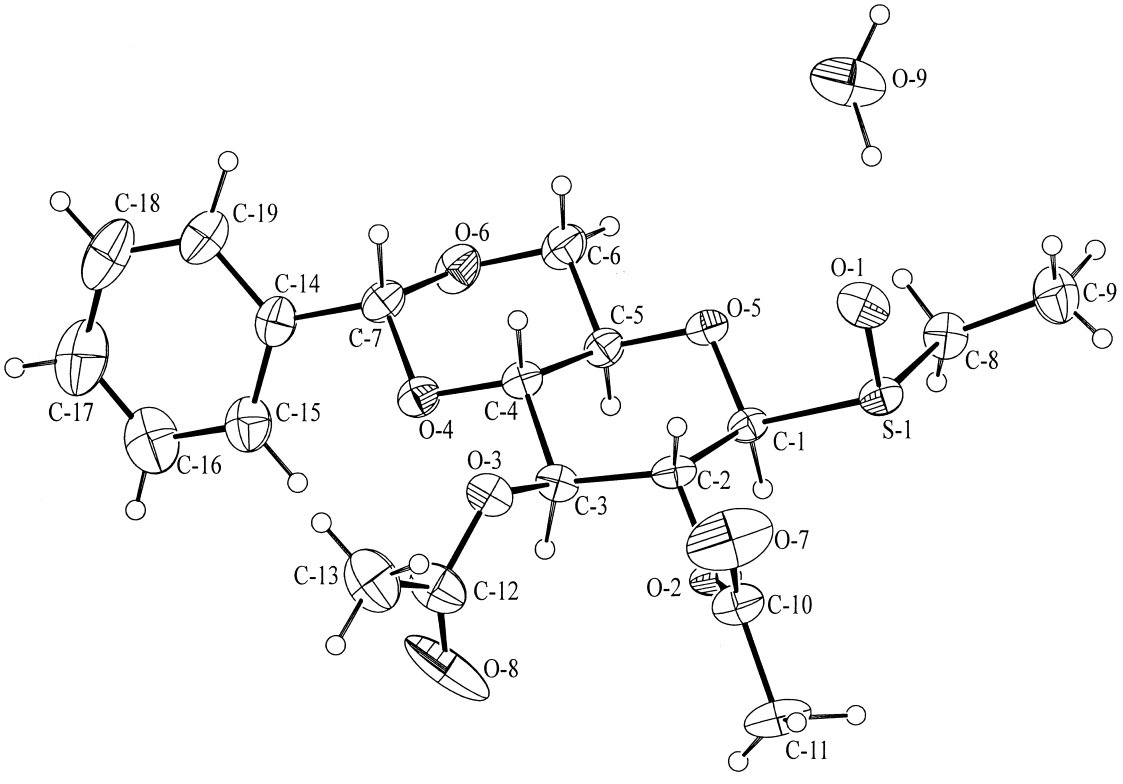


Figure 3. ORTEP view of the (R_S)-2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside *S*-oxide monohydrate molecule **3a1**. Thermal ellipsoids are drawn at the 30% probability level

representation in Fig. 3. The X-ray structure of **3a1** conforms with literature precedent and the results of our molecular modeling experiments. A brief description of the salient features of the X-ray structure is given below.

Crystals of monohydrated **3a1** belong to the space group $P2_1$ with a=10.561(3) Å, b=5.255(1) Å, c=19.200(4) Å and β=93.18(3)°. The positional and isotropic thermal parameters for the non-hydrogen atoms are given in Table 2. The bond lengths and selected bond angles and torsion angles are given in Table 3.

The C–C bond lengths of the glucose ring have a mean value of 1.511 Å which conforms to the mean value of carbohydrate rings.[7] The O_5–C_1 bond (1.403 Å) is significantly shorter than the C_5–O_5 bond (1.427 Å), in agreement with the anomeric effect due to the presence of sulfur at position 1. The glucose ring adopts a $^4C_1$ chair conformation with Cremer–Pople puckering parameters of Q=0.563(3) Å, Θ=10.6(3)° and ϕ=324.1(15)°. The dioxolan ring also assumes a chair conformation (Q=0.568(3) Å, ϕ=2.5(3)° and ϕ=98.6(6)°). The phenyl ring is effectively planar with a maximum deviation less than 0.01 Å from the mean plane. The geometry of the two acetate groups are in good agreement with those generally observed in acetylated carbohydrates[8] with the carbonyl nearly eclipsing the axial hydrogen of the corresponding ring carbon. It is interesting to note that our energy-minimized conformations of **3a1** and **3a2** also feature this particular antiparallel arrangement of acetate groups.

The geometry of the sulfoxide group at C-1 can be compared to three related carbohydrate derivatives[5,9,10] reported in the Cambridge database.[11] The S=O bond length of 1.507(2) Å observed in the present structure is significantly larger than the one observed in DMSO (1.470 Å)[12] but it agrees

Table 2
Final fractional coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms of (R_S)-2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside *S*-oxide monohydrate **3a1**

Atom	x/a	y/b	z/c	U(iso) (Å^2)
S-1	0.62384(6)	1.25	0.43260(3)	0.0387
O-1	0.69204(18)	1.5009(4)	0.42819(10)	0.0510(6)
O-2	0.49948(15)	1.1415(4)	0.28724(10)	0.0420(6)
O-3	0.67459(16)	1.2155(4)	0.17222(8)	0.0430(6)
O-4	0.88105(15)	0.8573(4)	0.19233(9)	0.0426(6)
O-5	0.81244(15)	1.0398(4)	0.36924(9)	0.0401(6)
O-6	1.04177(17)	0.7043(5)	0.26920(9)	0.0559(8)
O-7	0.4652(2)	1.5538(5)	0.27115(18)	0.1057(12)
O-8	0.5365(3)	0.9627(6)	0.11541(15)	0.1319(14)
C-1	0.6797(2)	1.0528(5)	0.36203(13)	0.0340(6)
C-2	0.6344(2)	1.1704(5)	0.29293(14)	0.0352(8)
C-3	0.6912(2)	1.0460(5)	0.23115(13)	0.0366(6)
C-4	0.8317(2)	1.0089(6)	0.24565(13)	0.0374(6)
C-5	0.8586(2)	0.8821(6)	0.31572(13)	0.0399(8)
C-6	0.9994(3)	0.8453(8)	0.32685(15)	0.0567(14)
C-7	1.0128(2)	0.8227(6)	0.20401(14)	0.0449(10)
C-8	0.6984(3)	1.0820(6)	0.50476(15)	0.0462(12)
C-9	0.6768(4)	1.2195(10)	0.57086(17)	0.0718(14)
C-10	0.4246(3)	1.3428(7)	0.27471(15)	0.0510(10)
C-11	0.2897(3)	1.2593(10)	0.2698(2)	0.0745(12)
C-12	0.5988(3)	1.1553(7)	0.11796(16)	0.0639(12)
C-13	0.5988(4)	1.3520(10)	0.06376(19)	0.0823(16)
C-14	1.0621(3)	0.6577(6)	0.14878(14)	0.0491(12)
C-15	0.9874(3)	0.4703(7)	0.11705(16)	0.0630(12)
C-16	1.0363(4)	0.3097(8)	0.06899(19)	0.0846(18)
C-17	1.1564(4)	0.3345(9)	0.0510(2)	0.0977(18)

with the average found in the above-mentioned structures. Similarly, the O_5–C_1–S angle (106.2(1)°) corresponds to the averaged value from the three crystal structures (105.9°). The C_1–S distance (1.829(3) Å) and bond angle C_1–S–C (106.5(1)°) also fall in previously observed ranges. Importantly, the O_5–C_1–S=O torsion angle (55.3°) is similar to that arrived at by energy minimization of **3a1** (61.6°) (see Fig. 2); this conformation results in an *anti* relationship between the S=O and the H-1 bonds as detected by our MPAA complexation experiments.

One structural water molecule appears to be strongly hydrogen bonded to the sulfoxide oxygen, displaying H···O and O···O distances of 1.93(3) and 2.891(3) Å, respectively, and a O–H···O bond of 160(2) Å. This phenomenon further exemplifies the relatively strong basicity of the sulfinyl oxygen — a property which we take advantage of in our NMR experiments using MPAA.

The packing analysis (Fig. 4) reveals the presence of a van der Waals chain along the *b*-axis, resulting in a strong anisotropy of packing. These chains interact with each other through two main types of contact. On one side of the molecule, the phenyl rings of each chain interact, creating hydrophobic contacts. On the other side, the water molecules that are sitting around the 2_1 axis of symmetry are hydrogen bonded into an infinite chain.

3. Conclusion

The use of MPAA was originally invented to determine the absolute configuration of quasisymmetrical fatty acid sulfoxides.[1a] However, the methodology can also be used in the analysis of more complex

Table 3
Bond lengths and selected valence and torsion angles for (R_S)-2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside *S*-oxide monohydrate **3a1**

Atoms	distance (Å)	Atoms	distance (Å)
S-1—O-1	1.507(2)	C-1—C-2	1.517(4)
S-1—C-1	1.829(3)	C-2—C-3	1.508(4)
S-1—C-8	1.788(3)	C-3—C-4	1.507(3)
O-2—C-2	1.431(3)	C-4—C-5	1.514(4)
O-2—C-10	1.335(4)	C-5—C-6	1.503(4)
O-3—C-3	1.443(3)	C-7—C-14	1.486(4)
O-3—C-12	1.317(4)	C-8—C-9	1.489(5)
O-4—C-4	1.419(3)	C-10—C-11	1.489(5)
O-4—C-7	1.409(3)	C-12—C-13	1.467(6)
O-5—C-1	1.403(3)	C-14—C-15	1.382(5)
O-5—C-5	1.427(3)	C-14—C-19	1.371(5)
O-6—C-6	1.425(4)	C-15—C-16	1.372(5)
O-6—C-7	1.416(3)	C-16—C-17	1.339(6)
O-7—C-10	1.192(4)	C-17—C-18	1.380(7)
O-8—C-12	1.207(5)	C-18—C-19	1.376(6)
Atoms	**angle (°)**	**Atoms**	**angle (°)**
O-1—S-1—C-1	106.21(12)	S-1—C-1—O-5	108.43(17)
O-1—S-1—C-8	106.51(13)	S-1—C-1—C-2	108.54(17)
C-1—S-1—C-8	98.51(13)	S-1—C-8—C-9	109.8(3)
Atoms	**torsion (°)**	**Atoms**	**torsion(°)**
O-1—S-1—C-1—O-5	55.3(2)	C-8—S-1—C-1—C-2	-176.35(18)
O-1—S-1—C-1—C-2	-66.30(18)	O-1—S-1—C-8—C-9	65.3(3)
C-8—S-1—C-1—O-5	-54.7(2)	C-1—S-1—C-8—C-9	175.1(3)

molecules as we have demonstrated in this paper. The success of the method stems from the stereospecificity of both the aromatic ring-induced shielding effects and the strong carboxyl H-bonding deshielding effects. Since MPAA is commercially available in high enantiomeric purity, we believe our approach is currently the method of choice for the rapid, inexpensive, sensitive and reliable configurational analysis of a wide range of sulfoxides.

4. Experimental

4.1. Materials

(*S*)-(+)-α-Methoxyphenylacetic acid (MPAA) (99% ee) was purchased from Aldrich and used without further purification.

*4.1.1. Synthesis of sulfoxides: **3a1** and **3a2***

meta-Chloroperbenzoic acid (1.1 equiv., 120 mg, 0.694 mmol) was added to a solution of ethyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside[13] (250 mg, 0.631 mmol) in dichloromethane (4 mL) and the mixture was stirred for 2 days at room temperature. The dichloromethane solution

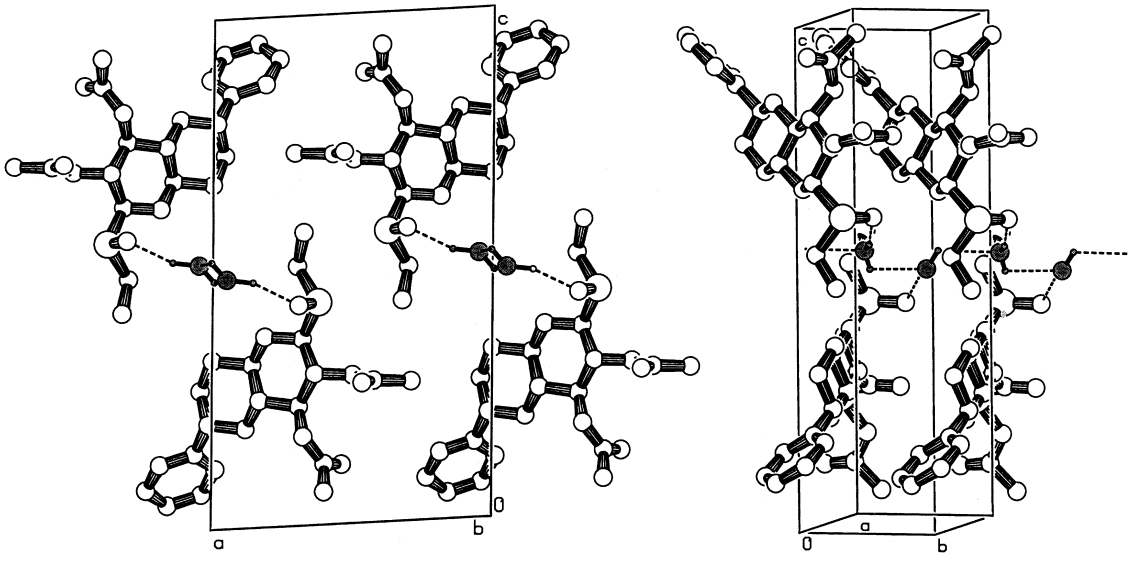


Figure 4. Two different views of the packing arrangement of (R_S)-2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside *S*-oxide **3a1**. The water molecule has been colored in gray. Except for the water molecules, hydrogen atoms have been omitted for clarity. Hydrogen bonds are represented as dotted lines

was then washed successively with a saturated aqueous solution of sodium bicarbonate and water. The organic phase was dried over magnesium sulfate and filtered, and the filtrate was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using a (1:1 v/v) petroleum ether:ethyl acetate mixture as eluant. Both epimers were isolated separately as colorless solids in 56 and 43% yield, respectively.

*4.1.2. (*R$_S$*)-Ethyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-*D*-glucopyranoside* S*-oxide* ***3a1***

R_f 0.11 (silica gel, 6:4 (v/v) EtOAc:pet. ether); mp 210–212°C (cyclohexane:ethyl acetate); $[\alpha]_D$=−135 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.47–7.34 (m, 5H, H-Ar), 5.52 (s, 1H, H-7), 5.51 (overlapping dd, 1H, $J_{3,4}$=$J_{2,3}$=9.3 Hz, H-3), 5.46 (overlapping dd, 1H, $J_{2,3}$=$J_{1,2}$=9.3 Hz, H-2), 4.39 (dd, 1H, $J_{5,6a}$=4.8 Hz, $J_{6a,6b}$=10.3 Hz, H-6a), 4.23 (d, 1H, $J_{1,2}$=9.5 Hz, H-1), 3.91 (overlapping dd, 1H, $J_{5,6b}$=$J_{6a,6b}$=10.3 Hz, H-6b), 3.81 (overlapping dd, 1H, $J_{4,5}$=$J_{3,4}$=9.3 Hz, H-4), 3.69 (ddd, 1H, H-5), 3.15 (dq, 1H, J_{AB}=12.8 Hz, -SO-C*H*$_2$-CH$_3$), 2.78 (dq, 1H, J_{AB}=12.8 Hz, -SO-C*H*$_2$-CH$_3$), 2.09 and 2.08 (s, 2×3H, C*H*$_3$-CO-), 1.36 (t, 3H, *J*=7.6 Hz, -SO-C*H*$_2$-CH$_3$); ^{13}C NMR ($CDCl_3$, 62.89 MHz) δ 170.4 and 169.0 (2 *C*O-CH$_3$), 136.5 (1 quaternary aromatic C), 129.3 (1 *para* aromatic C), 128.3 and 126.1 (each 2 *ortho* and 2 *meta* aromatic Cs), 101.6 (C-7), 87.3 (C-1), 77.6 (C-4), 72.8 (C-3), 71.3 (C-5), 68.0 (C-6), 67.4 (C-2), 41.3 (-SO-*C*H$_2$-CH$_3$), 20.8 and 20.6 (2 *C*H$_3$-CO-), 7.5 (-SO-CH$_2$-*C*H$_3$). MS (ionspray, MeOH); *m/z* 275 ((M−SOEt, AcOH)$^+$); 335((M−SOEt)$^+$); 413 (M+H)$^+$; 435 (M+Na)$^+$; 825.0 (dimer+H)$^+$. HRMS calcd for $C_{19}H_{24}O_8S$: 412.1192; found: 412.1184.

*4.1.3. (*S$_S$*)-Ethyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-*D*-glucopyranoside* S*-oxide* ***3a2***

R_f 0.20 (silica gel, 6:4 (v/v) EtOAc:pet. ether); mp 204–206°C (cyclohexane:ethyl acetate); $[\alpha]_D$=−86 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.46–7.34 (m, 5H, H-Ar), 5.52 (s, 1H, H-7), 5.44 (overlapping dd, 1H, $J_{3,4}$=$J_{2,3}$=9.8 Hz, H-3), 5.27 (overlapping dd=t, 1H, $J_{2,3}$=$J_{1,2}$=9.8 Hz, H-2), 4.49 (d, 1H, $J_{1,2}$=9.8 Hz, H-1), 4.44 (dd, 1H, $J_{5,6a}$=4.1 Hz, $J_{6a,6b}$=10.0 Hz, H-6a), 3.78 (overlapping dd, 1H, $J_{4,5}$=$J_{3,4}$=9.8 Hz, H-4), 3.74–3.64 (m, 2H, H-5 and H-6b), 2.95 and 2.86 (AB q of q, 2H, J_{AB}=13.0

Hz, -SO-C*H*$_2$-CH$_3$), 2.09 and 2.08 (s, 2×3H, 2 C*H*$_3$-CO-), 1.40 (t, 3 H, J=7.5 Hz, -SO-CH$_2$-C*H*$_3$); ^{13}C NMR ($CDCl_3$, 62.89 MHz) δ 170.3 and 170.2 (2 *C*O-CH$_3$), 136.8 (1 quaternary aromatic C), 129.7 (1 *para* aromatic C) 128.7 and 126.5 (each 2 *ortho* and 2 *meta* aromatic Cs), 102.0 (C-7), 90.6 (C-1), 78.4 (C-4), 72.7 (C-3), 71.7 (C-5), 69.2 (C-2), 68.5 (C-6), 41.7 (-SO-*C*H$_2$-CH$_3$), 21.1 and 21.0 (1 C each, 2 *C*H$_3$CO-), 7.2 (1 C, -SO-CH$_2$-*C*H$_3$). MS (ionspray, MeOH); m/z 275.0 ((M−S(O)Et, AcOH)$^+$), 335.0 ((M−S(O)Et)$^+$), 435.0 ((M+Na)$^+$), 825.0 ((dimer+H)$^+$). HRMS calcd for $C_{19}H_{24}O_8S$: 412.1192; found: 412.1181.

4.2. NMR measurements

^{1}H NMR spectra were recorded at 300 K on a Bruker AMX-400 MHz spectrometer using a 5 mm inverse probehead, with an Aspect X-32 computer and Aspect 3000 processing controller. Standard microprograms from Bruker software were employed. All spectra were run using 32K data points over the entire spectral width. The spectral window was set at 15 ppm which gave an FID resolution of 0.18 Hz. The line broadening used in spectral presentation was set to 0.18 Hz. The spectra were acquired using a pulse width of 7.0 μs and a delay time of 0.5 s. Sulfoxide samples (3–5 mg) were dissolved in 0.5 mL $CDCl_3$ which had been previously filtered through basic alumina and dried over $MgSO_4$. The complexation experiments were carried out by adding 3 equiv. of (*S*)-MPAA to the $CDCl_3$ solution. (This is an arbitrary amount of reagent and is not meant to imply that the stoichiometry of the sulfoxide:shift reagent complex is 1:3.) All chemical shifts are referenced to an internal TMS standard and are reported with a precision of ±0.001 ppm.

4.3. Crystal structure determination

Single crystals suitable for X-ray work were grown by slow evaporation from a chloroform:methanol:water (1:2:0.3 v/v) mixture. The diffraction patterns were obtained from a single crystal of approximately 0.1×0.2×1 mm mounted on a glass fiber using a Nonius CAD4 diffractometer. Accurate unit–cell dimensions were determined by a least-squares fit of the setting angles at high 2Θ values. The intensities of 3418 independent reflections were measured inside the sphere limited by 2Θ<600 at the Mo wavelength and 2810 were considered as observed, such as $I/\sigma(I)>2\sigma$. All the intensities were corrected for background noise. Lorentz and polarization corrections were applied, but no correction was made for absorption, given the crystal dimensions and the small value of the absorption coefficient at the wavelength used. Scattering factors were taken from the *International Tables of Crystallography* (1974).[14] Crystal data are given in Table 4. The structure was solved by direct methods, using the TeXsan software,[15] allowing the location of all C-, O- and S-atoms. The H-atoms were located by successive difference Fourier maps, and isotropic refinement. The last cycles were performed using an anisotropic thermal temperature factor for non-hydrogen atoms, whereas the hydrogen atoms were assigned an isotropic temperature factor. The final *R*-value was 0.050. During the refinement, each reflection was assigned a weight $\omega=1/\sigma(F_o)^2$ derived from $\sigma(I)$ and the function minimized was $\sum\omega(F_o-F_c)^2$. A final electron density map showed no significant residual density. Geometrical calculations and ORTEP representations were obtained with PLATON.[16] Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Table 4
Crystal data of (R_S)-2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside *S*-oxide monohydrate **3a1**

Formula	$C_{19}H_{24}O_8S, H_2O$
Molecular weight	430.47
Crystal system	Monoclinic
Space group	$P2_1$
a(Å)	10.561(3)
b(Å)	5.255(1)
c(Å)	19.200(4)
β(°)	93.18(3)
V(Å^3)	1063.9(4)
D_{calc}(g.cm^{-3})	1.344
Z	2
F(000)	456
μ(cm^{-1})	1.99
Crystal size (mm)	0.1 x 0.2 x 1
T(K)	292
$2\Theta_{max}$ (°)	60.9
Wavelength (Mo Ka) (Å)	0.71069
No. unique reflections	3418
No observed [I>-2σ(I)] reflections	2810
No. refined parameters	365
Final R	0.050
Final ωR	0.047

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References

1. (a) Buist, P. H.; Marecak, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 5073. (b) Buist, P. H.; Marcecak, D. M.; Holland, H. L.; Brown, F. M. *Tetrahedron: Asymmetry* **1995**, *6*, 7.
2. (a) Borde, X.; Nugier-Chavin, C.; Noiret, N.; Patin, H. *Tetrahedron: Asymmetry* **1998**, *9*, 1087. (b) Fauconnot, L.; Nugier-Chavin, C.; Noiret, N.; Patin, H. *Tetrahedron Lett.* **1997**, *38*, 7875.
3. Buist, P. H.; Behrouzian, B.; Cassel, S.; Lorin, C.; Rollin, P.; Imberty, A.; Perez, S. *Tetrahedron: Asymmetry* **1997**, *8*, 1959.
4. Yan, L.; Taylor, C. M.; Goodnow Jr., R.; Kahne, D. *J. Am. Chem. Soc.* **1994**, *116*, 6953.
5. Khiar, N.; Alonso, I.; Rodriguez, N.; Fernandez-Mayoralas, A.; Jimenez-Barbero, J.; Nieto, O.; Cano, F.; Foces-Foces, C.; Martin-Lomas, M. *Tetrahedron Lett*. **1997**, *38*, 8267.
6. Fraser, R. R.; Durst, T.; McClory, M. R.; Viau, R.; Wigfield, Y. Y. *Int. J. Sulfur Chem., A* **1971**, *1*, 133.
7. Jeffrey, G. A.; Taylor, R. *J. Comput. Chem*. **1980**, *1*, 99.
8. Pérez, S.; Saint-Pierre, J.; Marchessault, R. H. *Can. J. Chem.* **1978**, *56*, 2866.
9. Novotny, J.; Podlaha, J.; Cerny, M. *Collect. Czech. Chem. Commun.* **1991**, *56*, 2169.
10. Showalter, H. D. H.; Winters, R. T.; Sercel, A. D.; Michel, A. *Tetrahedron Lett*. **1991**, *32*, 2849.
11. Allen, F. H.; Kennard, O. *Chemical Design Automation News* **1993**, *8*, 31.
12. Bastiansen, O.; Viervoll, H. *Acta Chem. Scand.* **1948**, *2*, 702.
13. Shou-Fu, L.; QinQin, O.; Zhong-Wu, G.; Biao, Y.; Yong-Zheng, H. *J. Org. Chem*. **1997**, *62*, 8400.
14. *International Tables for X-Ray Crystallography*; Kynoch Press: UK, 1974; Vol. IV, pp. 282–288.
15. TeXsan, Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX 77381.
16. Spek, A. L. *J. Appl. Crystallogr*. **1988**, *21*, 578.