1,6-ANHYDRO-1-THIO-β-D-GLUCOPYRANOSE (THIOLEVOGLUCOSAN) AND THE CORRESPONDING SULFOXIDES AND SULFONE

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Starting 1,2,3,4-tetra-*O*-acetyl-6-*O*-tosyl-β-D-glucopyranose (**3**) was converted into 2,3,4-tri-*O*-acetyl-1-thio-6-*O*-tosyl-β-D-glucopyranose (**6**) via intermediate glycosyl bromide **4** and *S*-thiouronium salt **5**. Treatment of compound **6** with sodium methoxide gave 1,6-anhydro-1-thio-β-D-glucopyranose (thiolevoglucosan **2a**). The isomeric sulfoxides **7** and **8** were prepared by selective oxidation of thiolevoglucosan **2a** with hydrogen peroxide or 3-chloroperoxybenzoic acid. The structure of new compounds was confirmed by ^{1}H and ^{13}C NMR spectroscopy or by X-ray analysis; magnetic anisotropy of the sulfinyl and sulfonyl group has been discussed.

Keywords: Thio sugars; Anhydro sugars; Carbohydrates; Sulfoxides; Sulfones; Conformation analysis; Pummerer rearrangement; NMR spectroscopy; Magnetic anisotropy of sulfinyl group; X-ray diffraction.

Chemistry of 1,6-anhydro-β-D-glucopyranose (**1a**) has been studied in detail and its usefulness for synthesis of numerous natural products was demonstrated many times[1]. Less attention has been paid to 1,6-anhydro-1-thio-β-D-glucopyranose (thiolevoglucosan **2a**) which also may be of use in synthesis. Both mentioned compounds, thiolevoglucosan[2] **2a** and levoglucosan[3] **1a** exhibit structural similarity as shown by X-ray analysis, but they differ considerably in reactivity mainly due to high nucleophilicity of the

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sulfur bridge in **2a** and its neighboring-group participation capabilities[4–12]. Previous syntheses of thiolevoglucosan **2a** involve base catalyzed cyclization of precursors containing nucleophilic sulfur group either at carbon C-1 or C-6 and a leaving group such as tosyloxy, mesyloxy, iodine or bromine. Akagi[10] and Skelton[12] used 1,2,3,4-tetra-*O*-acetyl-1-thio-6-*O*-tosyl-β-D-glucopyranose or the corresponding 1-xanthogenate, Lundt[11] used acetylated 6-bromo-6-deoxy-β-D-glucopyranosyl xanthate. Driguez[5] treated 2,3,4-tri-*O*-acetyl-6-*O*-tosyl-α-D-glucopyranosyl bromide with hydrogen sulfide or triethylammonium tetrathiomolybdate to obtain **2a** in high yield. An alternative route[13] leading to substituted **2a** started from ethyl 1-thio-4,6-di-*O*-tosyl-β-D-glucopyranoside and involved the formation of ethyl sulfonium salt as intermediate. On the other hand, Whistler[14] prepared **2a** by cyclization of 6-thio-β-D-glucopyranosyl bromide.

In connection with the recent synthesis[12] of thiolevoglucosan and related anhydro derivatives, we report herein our results regarding the preparation of thiolevoglucosan and its reactivity in oxidation reactions leading to the corresponding sulfoxides and sulfone (see also refs[12,15]). Their structure, conformational behavior in solvents of different polarity, as well as magnetic anisotropy of sulfinyl and sulfonyl group is discussed.

RESULTS AND DISCUSSION

1,2,3,4-Tetra-*O*-acetyl-6-*O*-tosyl-β-D-glucopyranose (**3**) was prepared according to Hardegger's procedure[16a] and it was converted into the glucosyl bromide **4** by treatment with hydrogen bromide in acetic acid[16b]. *S*-Thiouronium salt **5** was prepared by alkylation of thiourea with bromide **4** in boiling acetone and then subjected to reductive cleavage in a two-phase system (water–chloroform) to obtain thioglucose **6**. The crude reaction mixture contained, in addition to major thioglucose **6**, a minor product of intramolecular nucleophilic cyclization, tri-*O*-acetylthiolevoglucosan **2b**. Both compounds **2b** and **6** were converted into the thiolevoglucosan **2a** by treatment with sodium methoxide in methanol.

Sulfoxides **7a** and **8a** were obtained by direct oxidation of unsubstituted thiolevoglucosan **2a**, in contrast to the method of Skelton[12] based on oxidation of thiolevoglucosan triacetate **2b**, followed by Zemplén deacetylation. In our hands, stereoselectivity of the oxidation of thiolevoglucosan **2a** has been changed by modifying the reaction conditions. Thus, using hydrogen peroxide in acetic acid yielded more than 65% of *exo*-sulfoxide **7a**, while 3-chloroperoxybenzoic acid in methanol gave significant amounts of both expected sulfoxides, namely **7a** and **8a**. Surprisingly, oxidation of **2a**

with *tert*-butylhydroperoxide in the presence of (*S*)-BINOL afforded *endo*-sulfoxide **8a** as a single product in almost quantitative yield. The X-ray analysis of **8a** has confirmed the *endo*-orientation of oxygen of the sulfinyl group, the structure of **7a** has been estimated earlier[17]. A stereoselective oxidation of cyclic sulfides with hydrogen peroxide has been already observed and several times discussed in the literature (see, e.g., ref.[18a,b], cf. review[18c]). Treatment of thiolevoglucosan **2a** or its acetate **2b** with an excess of oxidizing agent resulted in the formation of sulfones **9a** and **9b**, respectively. For solid state, the X-ray analysis of **7a**, **8a**, and **9a** evidenced the $^1C_4$ conformation for each of these compounds. However, their conformation in solution may change in dependence on the solvent polarity (see below). Sulfoxide **7a**, when heated with sodium acetate in acetic acid underwent the Pummerer rearrangement to give a mixture containing major compound **10**, as indicated by NMR spectra. Its deacetylation led to an unstable product, which decomposed on standing.

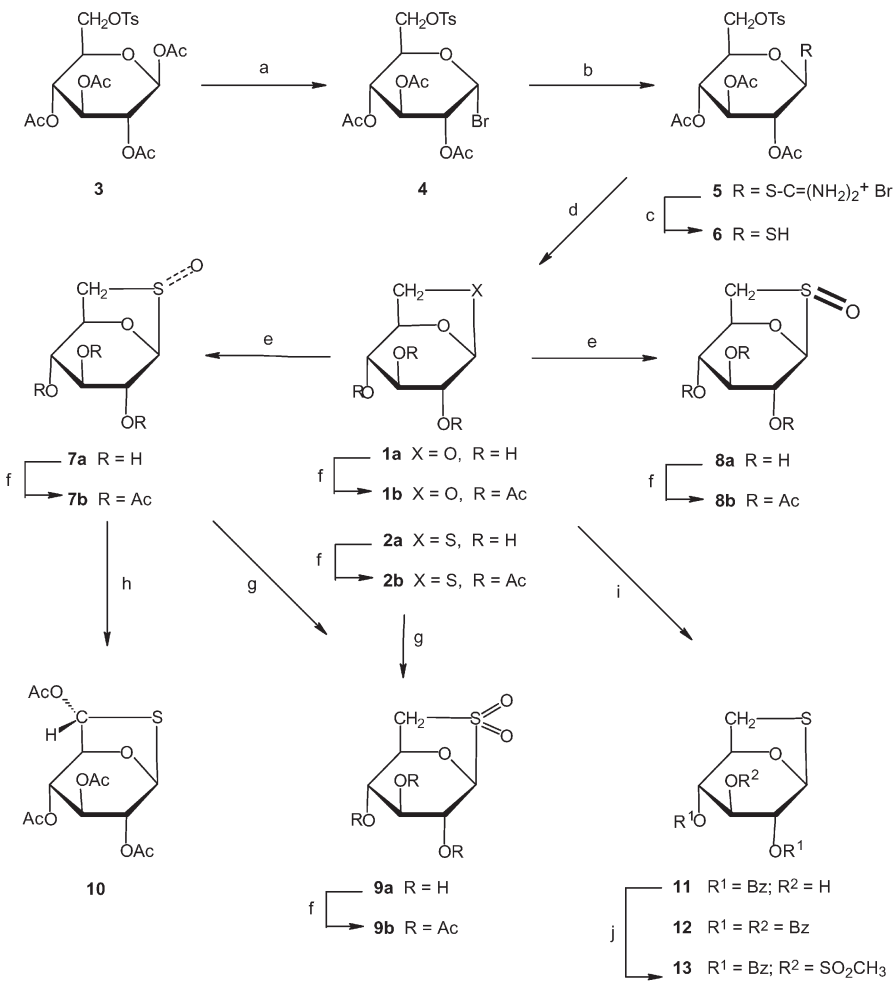
Attempted tosylation of thiolevoglucosan **2a** in pyridine, the reaction frequently used for the transformation of levoglucosan, failed, probably due to the participation of sulfur atom[12,15b] and formation of an unstable sulfonium salt and its subsequent decomposition. On the other hand, partial benzoylation of thiolevoglucosan **2a** yielded a mixture of dibenzoyl and tribenzoyl derivatives **11** and **12**, respectively. Mesylation of **12** led to a stable mesylate **13** (Scheme 1).

NMR Spectra

The structures of all synthesized compounds **1**–**13** were confirmed by ^{1}H and ^{13}C NMR spectra (data are summarized in Tables I–III). Structural assignment of proton signals was obtained using ^{1}H,^{1}H-COSY spectra, characteristic splitting pattern and chemical shifts. Coupling constants were derived from expanded resolution enhanced spectra. Homonuclear decoupling experiments were used to determine the values of some small coupling constants. Carbon signals were assigned from APT and 2D-HMQC spectra.

Replacement of the oxygen atom in 1,6-anhydride bond (levoglucosan **1a**) with sulfur atom (thiolevoglucosan **2a**) leads to prolongation of C(1)–X and C(6)–X bonds which could induce some changes in the conformation of the bicyclic system. The comparison of X-ray data of thiolevoglucosan and levoglucosan as well as the calculation of its energy minimized conformations show that these changes are rather small (see Table IV).

Replacement of oxygen atom with sulfur manifests itself in the NMR spectra by significant upfield shifts of H-6en (~1.0 ppm), H-6ex (~0.6 ppm),



a) HBr, AcOH, 10°C; b) thiourea, acetone, reflux 3 h; c) aq. potassium disulfite, chloroform; reflux 2 h; d)NaOMe,MeOH; e) H_2O_2, AcOH, 0°C; f) Ac_2O, pyridine; g) H_2O_2, AcOH, r.t.; h) NaOAc, Ac_2O, reflux; i) benzoyl chloride, pyridine; j) mesyl chloride, pyridine

SCHEME 1

TABLE I
Proton NMR chemical shifts in compounds **1**–**13**

Compd	Solv.	H-1	H-2	H-3	H-4	H-5	H-6en	H-6ex	Other protons
1a	$CDCl_3$	5.51	3.62	3.80	3.75	4.58	4.22	3.80	OH(2): 2.39; OH(3): 2.41; OH(4): 2.41
	D_2O	5.46	3.53	3.69	3.68	4.63	4.10	3.76	–
1b	$CDCl_3$	5.47	4.61	4.86	4.65	4.63	4.10	3.81	3×OAc: 2.16, 2.13, 2.10
2a	$CDCl_3$	5.55	3.75	3.77	3.72	4.88	3.22	3.21	OH(2): 2.76; OH(3): 3.70; OH(4): 2.44
	CD_3OD	5.31	3.51	3.52	3.42	4.66	3.07	2.99	–
	D_2O	5.47	3.68	3.62	3.60	4.82	3.13	3.10	–
2b	$CDCl_3$	5.46	4.73	4.98	4.64	4.79	3.19	3.08	3×OAc: 2.15, 2.14, 2.10
3	$CDCl_3$	5.65	5.04	5.20	5.04	3.84	4.16	4.10	4×OAc: 2.09, 2.01, 2.00, 1.99; Tos: 7.77(2H), 7.34(2H), 2.45(3H)
4	$CDCl_3$	6.46	4.72	5.49	5.09	4.28	~4.16	~4.16	3×OAc: 2.08, 2.02, 2.00; Tos: 7.79(2H), 7.36(2H), 2.46(3H)
6	$CDCl_3$	4.47	4.87	5.15	4.96	3.74	4.14	4.06	3×OAc: 2.06, 2.00, 1.99; SH:2.22; Tos: 7.79(2H), 7.36(2H), 2.46(3H)
7a	$CDCl_3$[a]	5.20	3.84	3.76	3.44	5.11	4.12	2.65	OH(2): 4.73; OH(3): 5.07; OH(4): 4.65
	CD_3OD	5.18	3.79	3.67	3.41	5.10	4.13	2.65	–
	D_2O	5.37	3.96	3.78	3.58	5.22	4.18	2.81	–
7b	$CDCl_3$	5.38	4.49	4.81	4.86	5.26	3.93	2.91	3×OAc: 2.19, 2.18, 2.14
8a	$CDCl_3$	5.57	4.30	3.94	3.91	4.65	3.27	3.59	OH(2): 2.93; OH(3): 6.00; OH(4): 2.52
	$(CD_3)_2CO$	5.58	4.14	3.72	3.69	4.61	3.00	3.63	OH(2): 4.49; OH(3): 5.66; OH(4): 4.34
	CD_3OD	5.50	4.18	3.65	3.58	4.56	2.83	3.44	–
	D_2O	5.67	4.22	3.71	3.68	4.72	2.93	3.50	–
8b	$CDCl_3$	5.54	5.63	5.47	4.81	4.64	3.23	3.11	3×OAc: 2.13, 2.12, 2.09
9a	$CDCl_3$[a]	4.71	4.09	3.94	3.67	4.87	3.60	3.32	OH(2): 4.84; OH(3): 4.34; OH(4): 4.52
	CD_3OD	4.65	4.03	3.73	3.58	4.82	3.42	3.33	–
	D_2O	4.97	4.12	3.84	3.74	4.98	~3.55	~3.55	–
9b	$CDCl_3$	4.82	5.30	5.11	4.74	4.93	~3.46	~3.46	3×OAc: 2.17, 2.16, 2.14
10	$CDCl_3$	5.56	4.73	5.15	4.64	4.72	6.27	–	4×OAc: 2.14, 2.13, 2.10, 2.08
11	$CDCl_3$	5.77	5.02	4.07	5.06	5.05	3.44	3.25	2×OBz: 8.09(4H), 7.59(2H), 7.40(4H); OH: 3.62
12	$CDCl_3$	5.77	5.16	5.58	5.06	5.07	3.43	3.32	3×OBz: 8.11(6H), 7.60(3H), 7.48(6H)
13	$CDCl_3$	5.63	5.16	5.19	5.05	4.97	3.50	3.18	2×Bz: 8.12(4H), 7.46(4H), 7.62(2H); SO_2CH_3: 3.06

[a] DMSO-d_6 (5 drops) was added to dissolve the sample in $CDCl_3$ (0.6 ml).

TABLE II
^{1}H-^{1}H NMR coupling constants of compounds **1**–**13**

Compd	Solv.	1,2	2,3	3,4	4,5	5,6en	5,6ex	6en,6ex	1,3	2,4	3,5
1a	$CDCl_3$[a]	2.1	1.7	1.9	2.0	0.9	5.4	7.7	1.9	1.7	1.9
	D_2O	1.7	2.3	2.5	1.7	1.2	5.8	7.7	1.5	1.4	1.5
1b	$CDCl_3$	1.7	1.8	2.0	1.8	1.1	5.7	7.8	1.3	0.8	1.5
2a	$CDCl_3$[b]	2.1	1.8	1.9	1.8	[c]	[c]	[c]	1.9	1.8	1.8
	D_2O	1.2	3.3	4.7	2.0	1.6	5.9	10.3	1.1	1.0	
2b	$CDCl_3$	1.1	3.3	4.7	1.9	1.1	6.4	10.0	1.1	0.6	0.9
3	$CDCl_3$	7.9	9.2	9.3	9.9	3.3	4.2	11.1			
4	$CDCl_3$	4.0	9.9	9.8	10.2	~3.3	~3.3	[c]			
6	$CDCl_3$	9.7	9.3	9.3	10.0	3.2	5.0	11.1			
7a	$CDCl_3$[d]	2.3	2.4	2.4	2.3	0.9	8.3	12.5	1.6	1.5	1.6
	D_2O	2.3	~2.0	2.4	~2.0	1.1	8.3	13.6	1.6	0.7	1.6
7b	$CDCl_3$	0.6	2.0	2.0	0.8	1.1	8.6	13.6	1.5	1.8	1.8
8a	$CDCl_3$	1.6	1.8	2.0	2.2	1.4	8.6	13.7	1.7	1.6	1.8
	$(CD_3)_2CO$[e]	1.8	2.9	3.3	2.1	1.3	8.4	13.8	1.1	1.2	1.4
	CD_3OD[f]	1.4	5.9	6.25	2.0	1.25	7.8	13.6	0.5	0.4	0.6
	D_2O	1.3	6.6	7.3	1.9	1.2	7.6	14.0		0.7	
8b	$CDCl_3$	1.0	7.2	8.5	2.2	1.0	7.0	13.5			
9a	$CDCl_3$[d]	1.7	2.9	3.6	2.3	1.5	9.3	12.3	1.3	1.1	1.3
	D_2O	<1	3.6	4.0	2.2	[c]	[c]	[c]			
9b	$CDCl_3$	1.2	3.8	4.7	2.2	[c]	[c]	12.8			
10	$CDCl_3$	0.9	4.3	6.2	2.1	0.4	–	–	0.8		0.6
11	$CDCl_3$[g]	1.6	3.3	2.5	[c]	0.8	6.8	10.2	1.6	0.85	1.3
12	$CDCl_3$	1.3	2.8	3.6	1.8	0.9	6.8	10.1	1.3	0.8	
13	$CDCl_3$	0.8	4.9	6.5	2.1	0.7	6.0	10.0	0.7	0.5	0.4

Additional J(H,H): [a] J(OH,2) = 8.5, J(OH,3) = 7.5, J(OH,4) = 7.2; [b] J(OH,2) = 8.0, J(OH,3) = 9.9, J(OH,4) = 6.8; [c] J-value could not be determined; [d] DMSO-d_6 (5 drops) was added to dissolve the sample in $CDCl_3$ (0.6 ml); [e] J(1,4) = 0.6, J(1,6ex) = 0.6, J(OH,2) = 7.6, J(OH,3) = 7.4, J(OH,4) = 6.3; [f] J(1,4) ≤ 0.3, J(1,6ex) = 0.6; [g] J(OH,3) = 8.1.

TABLE III
Carbon-13 NMR chemical shifts of compounds **1–13**

Compd	Solv.	C-1	C-2	C-3	C-4	C-5	C-6	Other carbons
1a	D_2O[a]	104.28	73.03	75.35	73.65	79.11	68.04	–
1b	$CDCl_3$	99.28	69.23	69.71	70.44	73.79	65.38	3×OAC: 170.00, 169.61, 169.02, 20.93, 20.83(2)
2a	$CDCl_3$	83.28	72.43[b]	72.02[b]	71.95[b]	80.96	33.12	–
	D_2O	86.57	77.76	75.33	74.87	84.42	36.75	–
2b	$CDCl_3$	81.70	74.16	69.04	72.07	79.52	34.40	3×OAc: 170.15, 169.88, 169.34, 20.87(3)
4	$CDCl_3$	86.06	71.58[b]	70.36[b]	70.01[b]	67.15[b]	66.25	3×OAc:169.85, 169.63, 169.14, 20.57(2), 20.43; Tos: 145.22, 132.79, 129.87(2), 128.09(2), 21.66
7a	D_2O[a]	104.93	70.03	71.74	71.07	84.10	61.32	–
7b	$CDCl_3$	100.01	67.97	67.12	64.97	78.65	58.99	3×OAc: 169.63, 169.22, 167.61, 20.81, 20.72, 20.68
8a	D_2O[a]	97.26	66.70	75.15	75.76	85.63	56.51	–
8b	$CDCl_3$	92.91	65.20	68.32	73.42	81.57	55.55	3×OAc: 170.66, 170.00, 169.96, 20.85, 20.80, 20.65
9a	D_2O[a]	91.76	70.56	74.18	72.95	81.36	52.45	–
9b	$CDCl_3$	86.69	67.34	68.00	70.49	76.70	50.49	3×OAc: 170.10, 169.25, 169.08, 20.82, 20.70, 20.67
10	$CDCl_3$	83.10	74.54	69.47	69.97	84.73	82.49	4×OAc: 170.25, 170.04, 169.99, 169.42, 20.88, 20.86, 20.85, 20.74
11	$CDCl_3$	81.40	73.94	69.25	74.78	79.35	34.31	2×Bz: 165.73, 165.71, 133.52(2), 133.47(2), 129.95(2), 129.90(2), 129.49, 129.35, 128.43(4)
12	$CDCl_3$	81.72	73.52	68.95	71.71	78.97	33.99	3×Bz: 165.56, 165.37, 164.96, 133.58(2), 133.51, 130.00(4), 129.96(2), 129.30, 129.23, 129.11, 128.57(2), 128.46(2), 128.43(2)
13	$CDCl_3$	82.40	76.95	75.75	73.40	80.90	35.60	SO_2CH_3: 39.00; 2×Bz: 165.83, 165.60, 133.83(2), 130.04(2), 130.00(2), 128.79, 128.75, 128.63(2), 128.61(2)

[a] Spectrum could not be obtained in $CDCl_3$ due to very poor solubility; [b] the assignment of signals may be interchanged.

TABLE IV

Ring torsion angles in crystalline compounds **1a**, **1b**, **2a**, **7a**, **8a**, **9a** from X-ray structure analysis and calculated for energy minimized conformations using MM2+ method.

Torsion angle	**1a**[a]		**1b**[b]		**2a**[c]		**7a**[d]		**8a**[e]		**9a**[e]	
	X-ray	calc.	X-ray	calc.	X-ray	calc.	X-ray	calc.	X-ray	calc.	X-ray	calc.
						Six-membered ring						
O5–C1–C2–C3	–57.3	–54.9	–53.7	–57.4	–53.5	–51.6	–55.3; –57.7	–52.2	–53.4	–49.4	–48.3	–48.1
C1–C2–C3–C4	35.2	34.7	30.3	37.3	37.2	35.0	42.9; 43.1	35.5	37.2	32.3	32.1	32.3
C2–C3–C4–C5	–35.2	–35.5	–32.0	–37.1	–39.5	–37.2	–44.6; –42.8	–37.7	–39.4	–35.9	–36.7	–36.7
C3–C4–C5–O5	55.8	56.1	55.7	56.1	57.4	56.0	59.2; 54.9	56.6	56.1	57.2	56.0	57.7
C4–C5–O5–C1	–75.3	–74.4	–75.4	–74.4	–73.5	–73.5	–71.8; –68.9	–73.9	–70.4	–75.7	–71.5	–75.3
C5–O5–C1–C2	75.9	74.5	75.3	75.9	71.3	71.3	70.1; 70.9	71.7	69.3	71.3	67.7	70.0
						Five-membered ring						
O5–C1–X–C6	18.4	23.3	23.4	20.4	29.4	26.6	28.2; 26.7	28.1	29.8	34.0	35.7	31.5
C1–X–C6–C5	9.9	4.3	4.7	7.2	–1.4	0.3	–0.7; 2.6	–1.2	–0.5	–7.8	–8.0	–5.6
X–C6–C5–O5	–33.7	–30.1	–30.4	–31.9	–26.7	–27.4	–27.6; –30.9	–26.0	–28.4	–20.0	–21.2	–22.0
C6–C5–O5–C1	45.1	45.6	44.6	45.6	50.8	50.2	51.6; 53.7	49.1	53.9	47.6	51.4	48.9
C5–O5–C1–X	–40.6	–44.2	–43.2	–42.5	–50.7	–48.7	–51.2; –51.0	–49.7	–53.3	–53.1	–54.4	–50.2

The X-ray data are taken from: [a] ref.[3]; [b] ref.[19]; [c] ref.[2]; [d] ref.[17] (two independent molecules found in the unit cell); [e] this paper.

C-6 (~30 ppm) and C-1 (~18 ppm). The determination of the configuration of S–O group in isomeric sulfoxides from NMR spectra is not easy task due to the absence of any related coupling constant. The use of some NMR chiral shift reagents 1-(9-anthryl)-2,2,2-trifluoroethanol, methoxy(phenyl)-acetic acid (MPA), methoxy(1-naphthyl)acetic acid (1-NMA) or methoxy-(2-naphthyl)acetic acid (2-NMA), *N*-(2,4-dinitrobenzoyl)-1-phenylethyl-amine was suggested in the literature[20–25] for stereochemical analysis of sulfoxides. We have applied the MPA as chiral shift reagent to sulfoxide triacetates **7b**, **8b** but the induced ^{1}H and ^{13}C chemical shifts could not be interpreted unequivocally in the sense of the configuration of these sulfoxides. The recent method for the determination of the absolute configuration of chiral sulfoxides described by Yabuuchi and Kusumi[26] seems to be more effective but it was not applied.

Magnetic anisotropy of the S–O group has been discussed in literature. The early investigations indicated that the protons in *cis*-arrangement with S–O group were deshielded while in *trans*-arrangement shielded[27,28]. Later studies[29–33] revealed the influence of the lone pair on the shielding or deshielding of neighboring protons. Every group in *anti* position to the lone pair should be shielded, which is in discrepancy with previous observations.

Since in our case the configuration of sulfoxides was unequivocally determined by X-ray measurement, we could analyse the effects observed in their NMR spectra in detail. Changes in proton and carbon-13 chemical shifts induced by oxidation of sulfide to *exo*-sulfoxide, *endo*-sulfoxide and sulfone are summarized in Tables V and VI. The *exo*-sulfoxides **7a**, **7b** show very pronounced chemical shift difference between H-6en and H-6ex ($\Delta\delta$ = 1.02 to 1.47 ppm) since the introduction of S–O group induces an upfield shift of H-6ex *syn*-oriented to S–O (–0.17 to –0.56 ppm) and the opposite downfield shift for H-6en *syn*-oriented to sulfur lone pair (0.74 to 1.05 ppm). On the other hand, in *endo*-sulfoxides **8a**, **8b** there are H-6en and H-6ex much closer ($\Delta\delta$ = 0.12 to 0.63 ppm) as the result of small induced shift to both H-6en *syn*-oriented to S–O (–0.20 to 0.05 ppm) and H-6ex *syn*-oriented to sulfur lone pair (0.03 to 0.40 ppm). The ^{13}C NMR spectra showed most characteristic differences for C-1 with nearly twice larger downfield shift for *exo*-sulfoxides **7a**, **7b** (~18 ppm) than for *endo*-sulfoxides **8a**, **8b** (~11 ppm).

Although the X-ray as well as calculated data show very similar absolute values of torsion angles between oxygen atom and H-6 protons with *syn*- and *anti*-orientation in both sulfoxides (see Table VII), the induced shifts are significantly different. This can be caused by a different chemical envi-

TABLE V
^{1}H NMR chemical shift changes induced by oxidation of sulfur to SO and SO_2

Atom	S ⇒ SO (*exo*)			S ⇒ SO (*endo*)			S ⇒ SO_2		
	7a–2a		**7b–2b**	**8a–2a**		**8b–2b**	**9a–2a**		**9b–2b**
	$CDCl_3$	D_2O	$CDCl_3$	$CDCl_3$	D_2O	$CDCl_3$	$CDCl_3$	D_2O	$CDCl_3$
H-1	–0.35	–0.10	–0.08	0.02	0.20	0.08	–0.84	–0.50	–0.64
H-2	0.09	0.28	–0.24	0.55	0.54	0.90	0.34	0.44	0.57
H-3	–0.01	0.16	–0.17	0.17	0.09	0.49	0.17	0.22	0.13
H-4	–0.28	–0.02	0.22	0.19	0.08	0.17	–0.05	0.14	0.10
H-5	0.23	0.40	0.47	–0.23	–0.10	–0.15	–0.01	0.16	0.14
H-6en	0.90	1.05	0.74	0.05	–0.20	0.04	0.38	0.42	0.27
H-6ex	–0.56	–0.29	–0.17	0.38	0.40	0.03	0.11	0.45	0.38

Atom	S ⇒ SO (*exo*)			S ⇒ SO (*endo*)			S ⇒ SO_2		
	16a–15a		**16b–15b**	**17a–15a**		**17b–15b**	**18a–15a**		**18b–15b**
	$CDCl_3$	D_2O	$CDCl_3$	$CDCl_3$	D_2O	$CDCl_3$	$CDCl_3$	D_2O	$CDCl_3$
H-1	–0.29	–0.13	–0.10	0.09	0.22	–0.12	–	–0.53	–0.68
H-2	0.05	0.21	0.18	0.55	0.48	0.70	–	0.35	0.44
H-3	–0.05	0.02	–0.01	0.12	0.09	0.08	–	0.25	0.11
H-4	0.02	0.03	0.00	0.25	0.29	0.26	–	0.24	0.19
H-5	0.14	0.23	0.38	–0.25	–0.11	–0.15	–	0.17	0.18
H-6en	0.95	1.03	0.79	–0.10	–0.04	–0.07	–	0.44	0.27
H-6ex	–0.56	–0.40	–0.30	0.37	0.61	0.33	–	0.39	0.29

TABLE VI
^{13}C NMR chemical shift changes induced by oxidation of sulfur to SO and SO_2

Atom	S ⇒ SO (*exo*)			S ⇒ SO (*endo*)			S ⇒ SO_2	
	7a–2a		**7b–2b**	**8a–2a**		**8b–2b**	**9a–2a**	**9b–2b**
	$CDCl_3$	D_2O	$CDCl_3$	$CDCl_3$	D_2O	$CDCl_3$	D_2O	$CDCl_3$
C-1	–	18.36	18.31	–	10.69	11.21	5.19	4.99
C-2	–	–7.73	–6.19	–	–11.06	–8.96	–7.20	–6.82
C-3	–	–3.59	–1.92	–	–0.18	–0.72	–1.15	–1.04
C-4	–	–3.80	–7.10	–	0.89	1.35	–1.92	–1.58
C-5	–	–0.32	–0.87	–	1.21	2.05	–3.06	–2.82
C-6	–	24.57	24.59	–	19.76	21.15	15.70	16.09

Atom	S ⇒ SO (*exo*)			S ⇒ SO (*endo*)			S ⇒ SO_2	
	16a–15a		**16b–15b**	**17a–15a**		**17b–15b**	**18a–15a**	**18b–15b**
	$CDCl_3$	D_2O	$CDCl_3$	$CDCl_3$	D_2O	$CDCl_3$	D_2O	$CDCl_3$
C-1	20.37	19.38	19.14	9.31	8.71	6.69	4.99	3.71
C-2	–5.03	–5.85	–6.68	–4.34	–6.19	–6.81	–5.76	–6.45
C-3	–0.88	–0.88	–0.40	–2.61	–1.02	0.16	–1.02	–0.29
C-4	–0.90	–1.62	–1.46	–0.07	–0.18	–0.14	–1.77	–1.66
C-5	–0.27	1.26	1.30	–2.89	–1.54	–1.49	–2.73	–2.85
C-6	27.96	27.72	27.38	18.70	18.52	17.77	17.83	17.06

ronment of the *endo*- and *exo*-oriented sulfoxide group in **7a** and **8a**, together with certain differences in the conformation of pyranose ring.

The conformation of pyranose ring can be monitored by vicinal proton couplings *J*(2,3) and *J*(3,4) which are known to be very sensitive to the population of the chair and boat form in solution[34,35]. Table VIII shows the calculated chair-boat populations in levoglucosan **1a**, thiolevo-glucosan **2a**, sulfoxides **7a**, **8a**, sulfone **9a** and their acetates **1b**, **2b**, **7b**, **8b** and **9b**. It can be seen that population of the chair conformation $^1C_4$ depends to a smaller or larger extent not only on the structure but also on the type of solvent. The content of the boat conformation $B_{3,O}$ is higher for acetates than for hydroxy compounds and it increases also when going from $CDCl_3$ to water as the solvent. For *endo*-sulfoxide **8a** we could observe a dramatic decrease in the chair form content in the series of solvent with increasing permittivity – $CDCl_3$ (94%), CD_3COCD_3 (74%), CD_3OD (25%), D_2O (11%). It seems that in compounds with *endo*-S–O group the chair form can be stabilized by hydrogen bond between C(3)–OH and S–O, the existence of which is less favored in polar solvents and it is excluded in acetates (~100% boat form calculated for *endo*-sulfoxide triacetate **8b**).

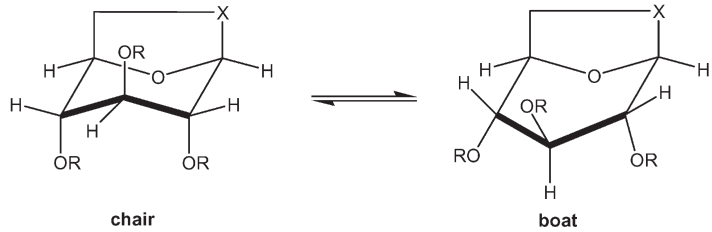
To check whether the above discussed different induced shifts of H-6en and H-ex are usable for determination of the configuration of sulfoxide group in other 1,6-anhydro-1-thio-β-D-hexopyranose derivatives we have measured and analyzed NMR data of a recently prepared series of compounds **15**–**18** (Scheme 2) derived from 1,6-anhydro-1-thio-β-D-galactose[36] (synthesis of these compounds will be described in a separate paper). The NMR data of these compounds together with data of 1,6-anhydro-β-D-galactopyranose (**14**) for comparison are shown in Tables IX–XI.

TABLE VII
The X-ray determined and calculated torsion angles between oxygen atoms of sulfoxides **7a**, **8a** and hydrogen atoms H-6en and H-6ex

Torsion angle	*exo*-Sulfoxide **7a**		*endo*-Sulfoxide **8a**	
	X-ray	calc.	X-ray	calc.
H6en–C6–S–Oen	–	–	11.8	5.9
H6ex–C6–S–Oen	–	–	128.9	124.0
H6en–C6–S–Oex	–136.0	–131.3	–	–
H6ex–C6–S–Oex	–15.4	–13.0	–	–

TABLE VIII

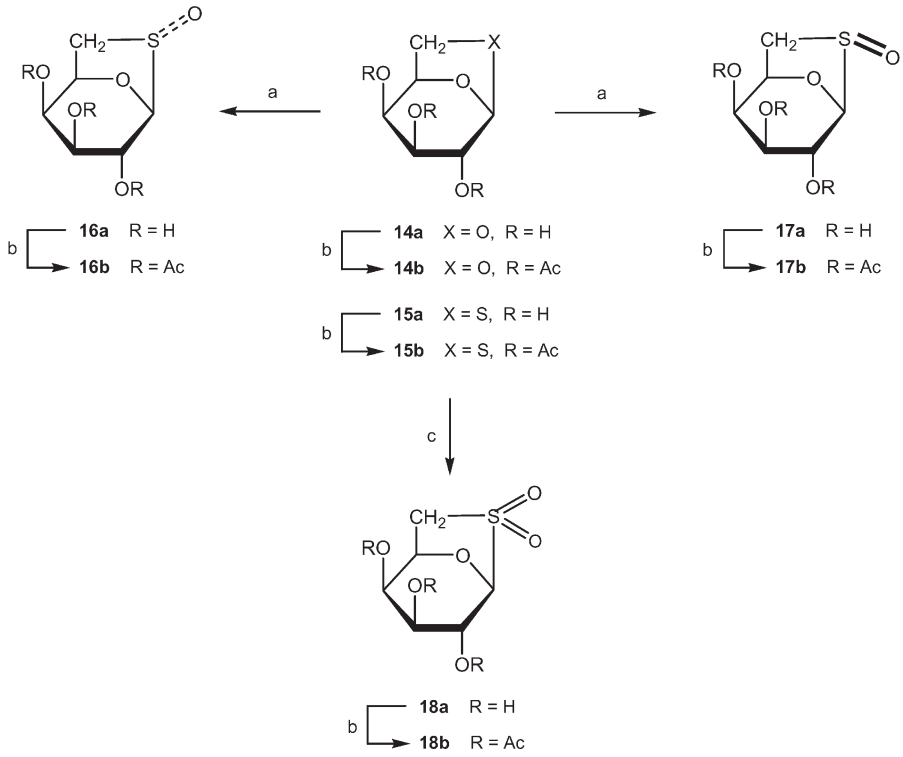
Chair–boat equilibrium calculated from ^{1}H-^{1}H NMR coupling constants J(2,3) and J(3,4) in compounds:



Compd.	X	R	Solvent	Chair, %[a]
1a	O	H	$CDCl_3$	95
			D_2O	86
1b	O	Ac	$CDCl_3$	94
2a	S	H	$CDCl_3$	95
			D_2O	60
2b	S	Ac	$CDCl_3$	60
7a	SO (*exo*)	H	$CDCl_3$[b]	85
			D_2O	88
7b	SO (*exo*)	Ac	$CDCl_3$	92
8a	SO (*endo*)	H	$CDCl_3$	94
			CD_3COCD_3	74
			CD_3OD	25
			D_2O	11
8b	SO (*endo*)	Ac	$CDCl_3$	0
9a	SO_2	H	$CDCl_3$[b]	72
			D_2O	63
9b	SO_2	Ac	$CDCl_3$	55

[a] The average values of the chair population calculated from J(2,3) and J(3,4) are given; [b] DMSO-d_6 (5 drops) was added to dissolve the sample in $CDCl_3$ (0.6 ml).

The values of coupling constant *J*(2,3) for compounds **15**–**18** show a very small population of the boat form of hexapyranose ring in the whole series. Changes in proton and carbon-13 chemical shifts induced by oxidation of sulfides **15a**, **15b** to sulfoxides **16a**, **16b**, **17a**, **17b** and sulfones **18a**, **18b** are summarized in Tables V and VI. One of the sulfoxides shows again a large non-equivalence of the chemical shifts of H-6en and H-6ex which indicates, in analogy to the above discussed *gluco* derivatives, the *exo*-configuration of the S–O group (sulfoxide **16a**). The second sulfoxide has much closer H-6en and H-6ex signals and could be assigned (per analogy) to *endo*-sulfoxide **16b**. Perhaps the most straightforward and easy interpretable NMR parameter for distinguishing the *exo*- and *endo*-sulfoxide in both *gluco* and *galacto* derivatives is the chemical shift of H-2. Proton H-2 shows dramatic downfield shift (0.55–0.70 ppm) in case of *endo*-sulfoxide, obviously due to the van der Waals deshielding effect of the S–O group which is in



a) 3-chloroperoxybenzoic acid, MeOH; b) Ac_2O, pyridine; c) H_2O_2, AcOH

SCHEME 2

1,3-*syn*-axial relation to H-2 (distance H(2)···O ≅ 2.75 Å). The downfield shift is still pronounced (0.90 ppm) in *endo*-sulfoxide triacetate **8b** with ~100% of the boat form, which brings H-2 still more close to the S–O oxygen (distance H(2)···O ≅ 2.45 Å). The proton chemical shifts induced by the oxidation of sulfides to sulfoxides and sulfones are graphically shown in Figs 1 and 2.

*X-ray Structure Analysis of **8a** and **9a***

A perspective view of the *endo*-sulfoxide **8a** with atom numbering is depicted in Fig. 3. The distances and angles of non-hydrogen atoms in both rings of *endo*-sulfoxide are unexceptionally close to those in *exo*-sulfoxide **7a** (ref.[17]). Also the conformations of the rings remain the distorted chair as follow from the ring puckering parameters[38] for the pyranose ring (θ = 159.7(2)°, φ = 173.4(6)°; O5 as pivot atom) and envelope (φ = 247.0(2)°, S1 as pivot atom) for the 1,3-oxathiolane ring.

TABLE IX
Proton NMR chemical shifts in *galacto* derivatives **14**–**18**

Compd	Solv.	H-1	H-2	H-3	H-4	H-5	H-6en	H-6ex	Other protons
14a	$CDCl_3$	5.44	3.87	3.95	4.01	4.47	4.22	3.69	2-OH: 2.00; 3-OH: 2.51; 4-OH: 2.99
	D_2O	5.40	3.79	3.93	4.04	4.49	4.31	3.65	–
14b	$CDCl_3$	5.41	4.74	5.23	5.23	4.47	4.33	3.72	3×OAc: 2.13(2), 2.02
15a	$CDCl_3$	5.46	4.00	3.87	3.95	4.84	3.33	3.03	2-OH: 2.30; 3-OH: 3.68; 4-OH: 3.16
	D_2O	5.44	3.94	3.87	3.97	4.77	3.36	3.00	–
15b	$CDCl_3$	5.48	4.86	5.15	5.20	4.79	3.38	3.08	3×OAc: 2.14, 2.13, 2.07
16a	$CDCl_3$[a]	5.17	4.05	3.82	3.97	4.98	4.28	2.47	2-OH: 5.07; 3-OH: 4.40; 4-OH: 4.37
	D_2O	5.31	4.15	3.89	4.00	5.10	4.39	2.60	–
16b	$CDCl_3$	5.38	5.04	5.14	5.20	5.17	4.17	2.78	3×OAc: 2.18, 2.15, 2.05
17a	$CDCl_3$	5.55	4.55	3.99	4.20	4.59	3.23	3.40	2-OH: 2.38; 3-OH: 6.24; 4-OH: 3.53
	D_2O	5.66	4.42	3.96	4.26	4.66	3.32	3.61	–
17b	$CDCl_3$	5.36	5.56	5.23	5.46	4.64	3.31	3.41	3×OAc: 2.17, 2.13, 2.12
18a	D_2O	4.91	4.29	4.12	4.21	4.94	3.80	3.39	–
18b	$CDCl_3$	4.80	5.30	5.26	5.39	4.97	3.65	3.37	3×OAc: 2.18(2), 2.10

[a] DMSO-d_6 (5 drops) was added to dissolve the sample in $CDCl_3$ (0.6 ml).

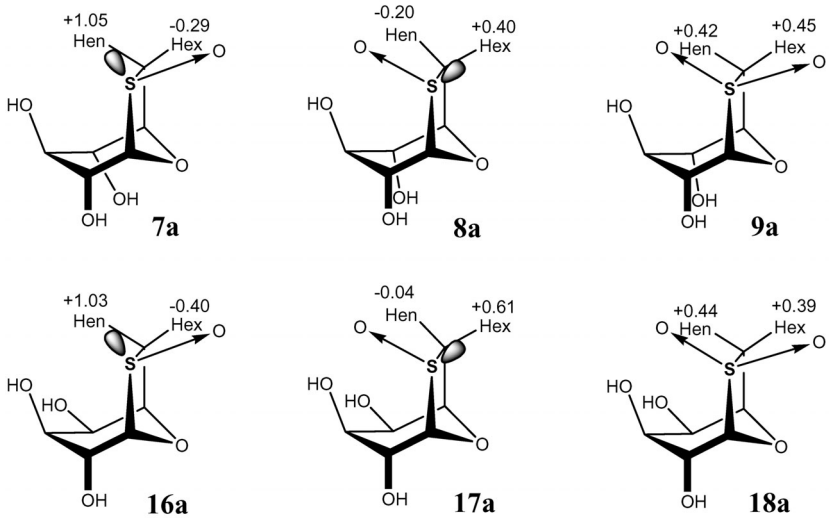


FIG. 1
^{1}H NMR chemical shift changes of H-6en and H-6ex induced by oxidation of thiols **2a**, **15a** to *exo*-sulfoxides **7a**, **16a**, *endo*-sulfoxides **8a**, **17a** and sulfones **9a**, **18a** in D_2O

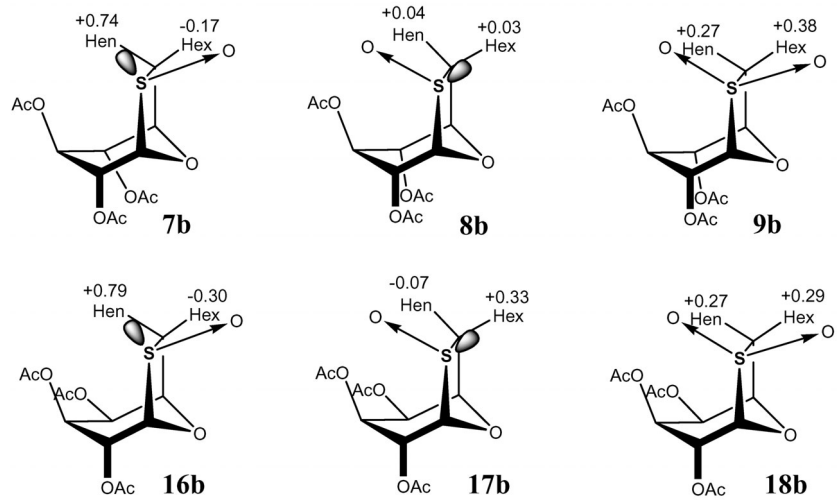


FIG. 2
^{1}H NMR chemical shift changes of H-6en and H-6ex induced by oxidation of thiols **2b**, **15b** to *exo*-sulfoxides **7b**, **16b**, *endo*-sulfoxides **8b**, **17b** and sulfones **9b**, **18b** in $CDCl_3$

Major changes appear in the hydrogen-bond network (Table XII). Contrary to *exo*-sulfoxide **7a** where the sulfoxide oxygen was involved in a short intermolecular hydrogen bond (average O3–O1 2.673 Å), in the *endo*-sulfoxide **8a** the orientation of sulfoxide oxygen enables the formation of intramolecular hydrogen bond O3···O1, which by its lengths 2.622(2) Å is the tenth shortest from 89 intramolecular contacts between the $(C)_2$–S–O moiety and hydroxyl group found in the Cambridge Structural Database. At the same time O3 is acceptor of hydrogen from intermolecular bond with O4, which together with O2···O5 interaction is building the three dimensional net in the crystal.

TABLE X
^{1}H-^{1}H NMR coupling constants in *galacto* derivatives **14**–**18**

Compd	Solv.	1,2	2,3	3,4	4,5	5,6en	5,6ex	6en,6ex	1,3	2,4	3,5	4,6ex
14a	$CDCl_3$[a]	2.1	1.8	5.1	4.5	0.65	4.8	8.0	1.6	–	1.3	1.15
	D_2O[b]	2.0	1.6	5.1	4.1	0.8	5.2	7.6	1.4	0.6	1.4	1.2
14b	$CDCl_3$	1.4	1.4	5.3	4.4	0.7	5.3	7.7	1.3	–	1.3	0.8
15a	$CDCl_3$[c]	1.9	2.0	5.25	5.2	0.7	6.8	10.65	1.8	0.5	1.1	0.8
	D_2O[d]	1.8	1.8	5.1	4.8	0.9	7.3	10.4	1.5	0.5	1.2	0.9
15b	$CDCl_3$[e]	1.7	1.8	5.3	4.6	0.9	7.2	10.0	1.4	0.6	1.2	0.8
16a	$CDCl_3$[f]	2.0	2.5	4.1	4.6	0.7	7.6	12.8	1.5	≤0.5	1.2	0.8
	D_2O[g]	2.0	2.7	3.8	4.6	0.8	7.6	13.3	1.4	0.6	1.1	0.9
16b	$CDCl_3$[h]	1.7	2.35	4.3	4.6	0.8	7.45	13.2	1.6	0.5	1.3	1.1
17a	$CDCl_3$[i]	1.6	1.7	5.1	5.1	1.05	7.95	14.1	1.3	0.9	1.1	1.05
	D_2O[j]	1.6	2.55	5.0	5.0	1.2	8.0	14.0	1.1	0.5	1.0	0.9
17b	$CDCl_3$[k]	1.3	2.9	5.0	5.0	1.5	7.8	13.2	1.0	0.45	1.0	0.7
18a	D_2O[l]	1.5	2.2	4.6	4.6	1.4	9.0	13.0	1.4	–	1.4	–
18b	$CDCl_3$[m]	1.4	2.0	4.9	4.6	1.4	8.9	12.8	1.4	0.6	1.3	0.6

Additional J(H,H): [a] J(1,6ex) = 0.5, J(1,6en) = 0.35, J(OH,2) = 9.9, J(OH,3) = 8.1, J(OH,4) = 8.7; [b] J(1,5) < 0.3, J(1,6en) < 0.3, J(1,6ex) = 0.5, J(2,5) = 0.6; [c] J(OH,2) = 8.8, J(OH,3) = 10.7, J(OH,4) = 8.7, J(1,6ex) ≤ 0.5, J(2,5) = 0.55; [d] J(2,5) = 0.6; [e] J(2,5) = 0.5, J(1,6ex) ≤ 0.3; [f] J(1,6ex) = 1.3, J(OH,2) = 5.8, J(OH,3) = 2.3, J(OH,4) = 7.0; [g] J(1,6ex) = 1.25, J(2,5) = 0.6, J(1,5) = 0.6, J(1,6en) = 0.7; [h] J(1,6en) = 0.7, J(1,6ex) = 1.25, J(1,5) < 0.5, J(2,5) = 0.5; [i] J(OH,2) = 8.2, J(OH,3) = 8.8, J(OH,4) = 8.8, J(1,6en) = 0.65; [j] J(1,6en) = 0.65; [k] J(1,6en) = 0.5; [l] J(1,6ex) = 1.5; [m] J(1,6ex) = 1.3, J(1,5) ≤ 0.5, J(2,5) = 0.4.

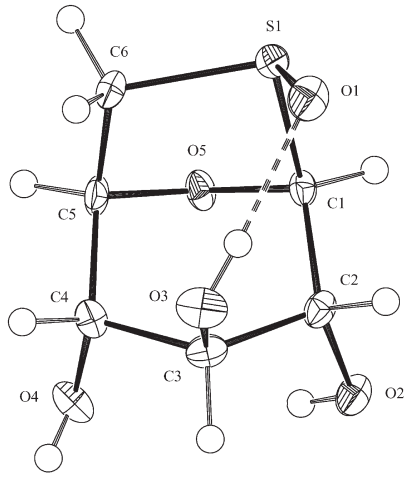


FIG. 3
Molecular structure of **8a**, displacement ellipsoids are drawn[37] on 50% probability level. Selected bond distances (in Å) and angles (in °): S(1)–O(1) 1.5182(14), S(1)–C(1) 1.8601(19), S(1)–C(6) 1.8295(18); O(1)–S(1)–C(6) 107.23(8), O(1)–S(1)–C(1) 108.85(9), C(6)–S(1)–C(1) 89.42(9)

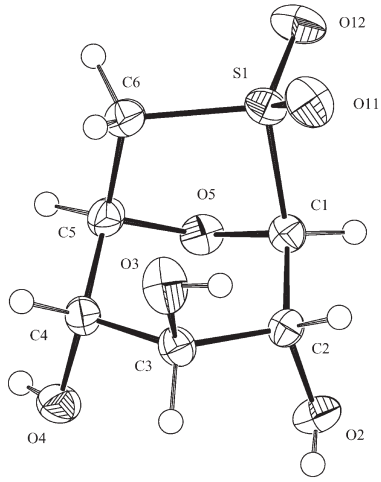


FIG. 4
Molecular structure of **9a**, displacement ellipsoids are drawn[37] on 50% probability level. Selected bond distances (in Å) and angles (in °): S(1)–O(11) 1.4367(11), S(1)–O(12) 1.4468(11), S(1)–C(1) 1.8190(15), S(1)–C(6) 1.7858(15); O(11)–S(1)-O(12) 116.57(7), O(11)–S(1)–C(6) 114.77(8), O(12)–S(1)–C(6) 108.60(8), O(11)–S(1)–C(1) 112.86(7), O(12)–S(1)–C(1) 108.11(7), C(6)–S(1)–C(1) 93.41(7)

TABLE XI
^{13}C NMR chemical shifts in *galacto* derivatives **14**–**18**

Compd	Solv.	C-1	C-2	C-3	C-4	C-5	C-6	Other carbons
14a	D_2O	103.38	73.97	72.86	66.97	77.01	66.25	–
14b	$CDCl_3$	98.84	70.96	67.36	64.72	72.02	64.37	3×OAC: 169.42, 169.23, 169.07, 20.64, 20.57, 20.40
15a	$CDCl_3$	82.39	73.40	70.96	64.44	79.86	29.88	–
	D_2O	85.02	76.82	73.03	67.75	81.11	31.94	–
15b	$CDCl_3$	80.99	73.59	67.37	65.62	76.04	30.75	3×OAc: 169.68, 169.42, 169.30, 20.91, 20.90, 20.65
16a	$CDCl_3$	102.76	68.37	70.08	63.54	79.59	57.84	–
	D_2O	104.40	70.97	72.15	66.13	82.37	59.66	–
16b	$CDCl_3$	100.13	66.91	66.97	64.16	77.34	58.13	3×OAc: 169.06, 168.92, 168.09, 20.68, 20.53, 20.50
17a	$CDCl_3$	91.70	69.06	68.35	64.37	76.97	48.58	–
	D_2O	93.73	70.63	72.01	67.57	79.57	50.46	–
17b	$CDCl_3$	87.68	66.78	67.53	65.48	74.55	48.52	3×OAc: 169.86, 169.48, 168.98, 20.83(2), 20.67
18a	D_2O	90.01	71.06	72.54	65.98	78.38	49.77	–
18b	$CDCl_3$	84.70	67.14	67.08	63.96	73.15	47.81	3×OAc: 169.40, 169.16, 168.93, 20.86, 20.66, 20.51

TABLE XII
Parameters of hydrogen bonds in the investigated crystals of compounds **8a** and **9a**

Compd	Specification D–H···A	Distances, Å			Bond angle, ° D H A
		D–H	H···A	D···A	
8a	O2–H2···O5[a]	0.77(3)	2.20(3)	2.842(2)	142(2)
	O4–H14···O3[b]	0.76(3)	1.97(3)	2.718(2)	172(3)
	O3–H13···O1	0.83(3)	1.81(3)	2.622(2)	165(3)
9a	O2–H12···O12[c]	0.75(3)	2.07(3)	2.8097(17)	172(2)
	O3–H13···O4[d]	0.85(3)	2.14(2)	2.8992(16)	148(2)
	O4–H14···O2[e]	0.78(3)	2.03(2)	2.8033(17)	172(2)

Symmetry transformations used to generate equivalent atoms: [a] $2 - x, y - 0.5, 1.5 - z$; [b] $0.5 + x, -0.5 - y, 1 - z$; [c] $0.5 - x, -y, z - 0.5$; [d] $1 - x, 0.5 + y, 0.5 - z$; [e] $0.5 + x, -0.5 - y, 1 - z$.

The view of molecular structure of sulfone **9a** is represented in Fig. 4. The major change in the conformation of **9a** can be observed in puckering of 5-membered ring which is close to half-chair (φ = 237.3(2)°, S1 as pivot atom), whereas the pyranose ring (θ = 155.7(1)°, φ = 165.0(4)°; O5 as pivot atom) preserves distorted chair geometry.

It is of interest that the increase in C–S–O angles in the sulfone moiety brings its oxygen atom far from OH group and would enable only a weak intramolecular hydrogen bond: therefore, all hydroxyls are involved in stronger intermolecular hydrogen bond network (Table XII).

EXPERIMENTAL

Melting points were determined using a Boëtius micro melting-point apparatus and are uncorrected. The optical rotation was measured on a Bendix–Ericsson ETL-143A polarimeter at 22 °C, $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. NMR spectra (δ, ppm; *J*, Hz) were measured on a Varian UNITY-500 instrument (^{1}H at 500 MHz; ^{13}C at 125.7 MHz) in $CDCl_3$ and/or D_2O. X-ray measurement was performed on a Nonius KappaCCD diffractometer (λ = 0.71069 Å, 150(2) K). Mass spectra were recorded on a Finnigan MAT INCOS 50 spectrometer using EI ionization (70 eV). Column chromatography was carried out on Kieselgel 60 (Merck, 0.063–0.200 mm). Thin layer chromatography (TLC) was performed with Alufolien plates (Merck 5554) and compounds were visualized using a 50% sulfuric acid spray followed by charring. Solutions were dried with anhydrous magnesium sulfate (unless otherwise stated) and evaporated at a reduced pressure at temperatures below 40 °C. Analytical samples were dried over phosphorous pentoxide at 0.1 Pa.

1,6-Anhydro-1-thio-β-D-glucopyranose (**2a**)

Triacetate **2b** (5 g, 16.4 mmol) in absolute methanol (10 ml) was treated with a 2 M solution of sodium methoxide (2 ml). After 12 h at 0 °C, the solution was neutralized with acetic acid and evaporated to dryness. The residue was purified by column chromatography (150 g silica gel, 5% methanol in ethyl acetate) to give **2a** (2.9 g, 99%) which crystallized on standing. Crystallization from ethanol gave **2a**, m.p. 165–180 °C (decomp.), $[\alpha]_D$ –52 (*c* 0.75, water), R_F 0.47 (ethyl acetate–methanol 9:1); ref.[10] gives m.p. 180 °C (decomp.), $[\alpha]_D$ –5.1 (*c* 0.8, water); the latter $[\alpha]_D$ value is obviously a typing error; ref.[14] gives $[\alpha]_D$ –54 (*c* 1.0, water).

2,3,4-Tri-*O*-acetyl-1,6-anhydro-1-thio-β-D-glucopyranose (**2b**)

To a solution of sodium methoxide in methanol (5 g of Na in 420 ml methanol), thioglucose **6** (35 g, 0.073 mol) was added and the reaction mixture was kept at 4 °C for 12 h. After neutralization with acetic acid the solvents were evaporated and the residue (89 g) containing product **2a** and salts was refluxed in acetic anhydride (150 ml) in the presence of anhydrous sodium acetate (35 g) for 5 h. The reaction mixture was then poured into ice water and extracted with chloroform. The organic layer was washed with aqueous $NaHCO_3$, water, dried over anhydrous $CaCl_2$ and evaporated to give **2b** (12 g, 55%), m.p. 92–94 °C (ethanol), $[\alpha]_D$ –50 (*c* 0.95, $CHCl_3$); R_F 0.74 (ethyl acetate–methanol 9:1); ref.[11] gives m.p.

86–88 °C; ref.[10] m.p. 93–94 °C, $[\alpha]_D$ –25.2 (*c* 1.1, $CHCl_3$); ref.[14] m.p. 79–81 °C, $[\alpha]_D$ –55 (*c* 0.3, $CHCl_3$); ref.[5] gives m.p. 79–81 °C, $[\alpha]_D$ –51.6 (*c* 1.0, $CHCl_3$).

1,2,3,4-Tetra-*O*-acetyl-6-*O*-tosyl-β-D-glucopyranose (**3**)

To a cooled (<5 °C), stirred solution of anhydrous D-glucose (200 g, 1.1 mol) in dry pyridine (1 l), tosyl chloride (220 g, 1.15 mol) was added in portions over a period of 30 min. The reaction mixture was allowed to warm to room temperature and stirring continued for 12 h. Acetic anhydride (800 ml, 7.8 mol) was then added to it dropwise during 2 h under stirring and cooling while the temperature was maintained below 50 °C. The reaction mixture was allowed to stand at room temperature overnight. The precipitated product was filtered off and crystallized from chloroform–ethanol to give **3** (196 g, 35%); R_F 0.34 (benzene–acetone 10:1), m.p. 207–209 °C, $[\alpha]_D$ +24 (*c* 0.8, $CHCl_3$), in agreement with refs[16a–16c]. Mother liquors were worked up in usual way to give syrupy residue (320 g) which contained in addition to compound **3**, the corresponding α-anomer and 1,3,4-tri-*O*-acetyl-2,6-di-*O*-tosyl-α-D-glucopyranose[16d,16e].

2,3,4-Tri-*O*-acetyl-6-*O*-tosyl-α-D-glucopyranosyl Bromide (**4**)

To a cooled solution (<10 °C) of hydrogen bromide in acetic acid (36%, 380 g) compound **3** (190 g, 0.38 mol) was added in portions. After 3 h, chloroform (700 ml) was added and the reaction mixture was poured into ice water. The organic layer was washed with water, neutralized with saturated solution of $NaHCO_3$, purified with the charcoal and dried with anhydrous $CaCl_2$. The crude product was crystallized from the mixture diethyl ether–light petroleum to give bromide **4** (142 g, 72%), R_F 0.42, R_F (**3**) 0.34 (benzene–acetone 10:1), m.p. 110 °C, $[\alpha]_D$ +166 (*c* 0.48, $CHCl_3$); ref.[16b] gives m.p. 88–89 °C, $[\alpha]_D$ +166.1 (*c* 3.75, $CHCl_3$).

S-(2,3,4-Tri-*O*-acetyl-6-*O*-tosyl-β-D-glucopyranosyl)thiouronium Bromide (**5**)

Bromide **4** (120 g, 0.23 mol) was dissolved in dry acetone (700 ml), thiourea (35 g, 0.46 mol) was added and the reaction mixture was refluxed for 3 h (*c*f. ref.[39]). After cooling, precipitated crystals of crude thiouronium salt **5** (95.5 g, 70%), were filtered off and dried over P_2O_5; after crystallization of **5** from acetone–diethyl ether–light petroleum, m.p. 169–170 °C, $[\alpha]_D$ +13 (*c* 0.28, water). The crude **5**, containing a small amount of thiol **6**, was used without further purification.

2,3,4-Tri-*O*-acetyl-1-thio-6-*O*-tosyl-β-D-glucopyranose (**6**)

A modified procedure[40] was used for the preparation of compound **6**. To a suspension of the *S*-thiuronium bromide **5** (70 g, 0.12 mol) in water (500 ml), chloroform (250 ml) and potassium disulfite (70 g) were added. The reaction mixture was refluxed for 2 h, then allowed to warm to room temperature. The chloroform layer was filtered, crystals of the starting material **5** (3.5 g) were separated, the chloroform solution was dried and evaporated. The crude thiol was purified by crystallization from diethyl ether–light petroleum to give **6** (35 g, 65%), m.p. 168–170 °C, $[\alpha]_D$ +29 (*c* 1.0, $CHCl_3$), R_F 0.3 (benzene–acetone 10:1). For $C_{19}H_{24}O_{10}S_2$ (476.6) calculated: 47.90% C, 5.07% H, 13.46% S; found: 48.26% C, 5.34% H, 13.50% S. Mother liquors contained small amount of thiolevoglucosan triacetate **2b**.

1,6-Anhydro-1-thio-β-D-glucopyranose (*S*)-*S*-Oxide (**7a**) and
1,6-Anhydro-1-thio-β-D-glucopyranose (*R*)-*S*-Oxide (**8a**)

A) Thiolevoglucosan **2a** (0.1 g, 0.56 mmol) was dissolved in acetic acid (2 ml), and aqueous solution of 10% hydrogen peroxide (0.19 g, 0.56 mmol) was added to it dropwise at room temperature. Then the reaction mixture was kept at 0 °C for 3 h. The precipitated crystalline product was filtered off and recrystallized from ethanol to obtain **7a** (0.07 g, 65%), m.p. 206–208 °C (decomp.), $[\alpha]_D$ –121 (*c* 0.78, water), R_F 0.09, R_F (**2a**) 0.47 (ethyl acetate–methanol 9:1); ref.[12] gives m.p. 231 °C (methanol), $[\alpha]_D$ –117 (water). For $C_6H_{10}O_5S$ (194.2) calculated: 37.11% C, 5.19% H, 16.51% S; found: 37.05% C, 5.16% H, 16.54% S.

B) To a cooled (–5 °C) solution of thiolevoglucosan **2a** (0.5 g, 2.8 mmol) in methanol (15 ml) a solution of 0.6 g (3.48 mmol) of 3-chloroperoxybenzoic acid (75–80%) in methanol (5 ml) was added dropwise under stirring and cooling within 5 min. Then the reaction mixture was stirred at room temperature for 30 min. Separated crystals of **7a** (0.25 g, 46%) were recrystallized from methanol–ethyl acetate to give 0.2 g (36.7%) of pure **7a**. Combined mother liquors were concentrated to 1 ml volume. TLC (ethyl acetate–methanol 9:1) revealed the presence of **7a** (R_F 0.09) and **8a** (R_F 0.26). Chromatographic separation on silica gel (25 g, ethyl acetate–methanol 97:3) gave 0.13 g (24%) of *endo*-sulfoxide **8a**, which was crystallized from methanol–ethyl acetate, m.p. 135–137 °C, $[\alpha]_D$ –94 (*c* 0.77, water). For $C_6H_{10}O_5S$ (194.2) calculated: 37.11% C, 5.19% H, 16.51% S; found: 36.96% C, 5.28% H, 16.31% S.

C) To 3 ml of anhydrous tetrachloromethane was added (*S*)-BINOL (7 mg, 0.0125 mmol), $Ti(O\text{-}1\text{-}iPr)_4$ (0.0036 ml, 0.0125 mmol) and water (0.0045 ml, 0.25 mmol). The mixture was stirred at room temperature for 1 h, subsequently cooled to 0 °C and thiolevoglucosan **2a** (100 mg, 0.5 mmol) was added. After 30 min, *tert*-butylhydroperoxide (0.15 ml of 70% water solution, 1 mmol) was added dropwise and the reaction mixture was stirred at 0 °C for 27 h. Tetrachloromethane was evaporated and the residue was separated by chromatography in ethyl acetate–methanol 1:1. *endo*-Sulfoxide **8a** (105 mg, 97%) contained only traces of **7a**.

Crystal structure analysis of compound **8a**. A colorless crystal of dimensions 0.4 × 0.35 × 0.3 mm is orthorhombic, space group $P2_12_12_1$, $C_6H_{10}O_5S$, M = 194.20, a = 6.3327(8) Å, b = 7.2541(9) Å, c = 16.478(3) Å, V = 756.97(19) Å^3, Z = 4, D_x = 1.704 Mg m^{-3}. All data were collected on a Nonius MACHIII diffractometer using monochromatized MoKα radiation (λ = 0.71069 Å) at 150(2) K. Absorption correction was neglected (μ = 0.407 mm^{-1}). A total of 1558 measured reflections in the range h = 0 to 7, k = 0 to 8, l = –19 to 19 (θ_{max} = 25°) out of which 1336 were unique (R_{int} = 0.0127) and 1280 observed according to the $I > 2\sigma(I)$ criterion. The structure was solved by direct methods (SIR92 [41]) and refined by full-matrix least squares on F^2 (SHELXL97 [42]). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbons were calculated into idealized positions and constrained during refinement (riding model) with assigned displacement parameter $H_{iso}(H) = 1.2U_{eq}$(pivot atom). The hydrogen atoms of hydroxyls were found on difference map and refined isotropically. The refinement converged (Δ/σ_{max} = 0.001) to R = 0.024 for observed reflections and wR = 0.064, GOF = 1.098 for 121 parameters and all 1336 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.242, $\Delta\rho_{min}$ = –0.293. The absolute configuration was established by the anomalous dispersion effect, chirality parameter 0.02(9). CCDC 284672 (for **8a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from

the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

2,3,4-Tri-*O*-acetyl-1,6-anhydro-1-thio-β-D-glucopyranose (*S*)-*S*-Oxide (**7b**)

Sulfoxide **7a** (0.3 g, 1.6 mmol) was dissolved in dry pyridine (30 ml) and acetic anhydride (1.5 ml) was added. After 12 h the crystalline product was filtered off to obtain **7b** (0.2 g, 40%); the second crop of **7b** (0.275 g, 55%) was obtained from the mother liquors. After crystallization from ethanol–diethyl ether–petroleum ether, compound **7b** had m.p. 117–119 °C (decomp.), $[\alpha]_D$ –61 (*c* 0.55, $CHCl_3$); ref.[12] gives m.p. 122–123.5 °C, $[\alpha]_D$ –75 ($CHCl_3$). For $C_{12}H_{16}O_8S$ (320.3) calculated: 44.99% C, 5.03% H, 10.01% S; found: 45.22% C, 5.07% H, 9.79% S.

2,3,4-Tri-*O*-acetyl-1,6-anhydro-1-thio-β-D-glucopyranose (*R*)-*S*-Oxide (**8b**)

Sulfoxide **8a** (0.09 g) in pyridine (5 ml) was treated dropwise with acetic anhydride (1.5 ml) and the reaction mixture was left standing at 0 °C overnight. Then ice water was added and the reaction mixture was extracted with dichloromethane, the organic layer was washed with dilute hydrochloric acid, sodium hydrogencarbonate and water, and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the solid residue was crystallized from ethyl acetate–petroleum ether to give **8b** (80 mg, 54%), m.p. 114–116 °C, $[\alpha]_D$ –133 (*c* 0.74, $CHCl_3$); ref.[12] gives m.p. 119–120 °C, $[\alpha]_D$ –149 ($CHCl_3$). FAB MS, *m/z*: 321 [M + H^+].

1,6-Anhydro-1-thio-β-D-glucopyranose *S*-Dioxide (**9a**)

A solution of thiolevoglucosan (**2a**; 0.1 g, 0.56 mmol) in acetic acid (0.2 ml) was treated with 30% H_2O_2 (0.31 g, 2.74 mmol) and the reaction was monitored by TLC. After 5 days, the second portion of 30% H_2O_2 (0.31 g) was added and the reaction time was prolonged for another 5 days. During the course of oxidation the product **9a** continuously precipitated from the reaction mixture. Crystals were filtered off, washed with ethanol and dried to give **9a** (0.023 g, 20%), m.p. ~ 200 °C (decomp.), $[\alpha]_D$ –32 (*c* 0.8, water), R_F 0.46, R_F (**7a**) 0.12 (ethyl acetate–methanol 9:1); ref.[12] gives m.p. 208–209 °C, $[\alpha]_D$ –40.6 (water). For $C_6H_{10}O_6S$ (210.2) calculated: 34.28% C, 4.79% H, 15.25% S; found: 34.34% C, 4.82% H, 14.65% S.

Crystal structure analysis of compound **9a**. A colorless crystal of dimensions 0.45 × 0.45 × 0.2 mm is orthorhombic, space group $P2_12_12_1$, $C_6H_{10}O_6S$, M = 210.20, a = 6.9660(2) Å, b = 10.4660(2) Å, c = 10.8700(3) Å, V = 792.49(4) $Å^3$, Z = 4, D_x = 1.762 Mg m^{-3}. Diffraction experiment was carried on a Nonius KappaCCD diffractometer using monochromatized MoKα radiation (λ = 0.71069 Å) at room temperature. Absorption correction was neglected (μ = 0.405 mm^{-1}). A total of 12390 measured reflections in the range h = –9 to 8, k = –13 to 13, l = –14 to 14 (θ_{max} = 27.5°) out of which 1813 were unique (R_{int} = 0.024) and 1758 observed according to the $I > 2\sigma(I)$ criterion. The structure was solved by direct methods (SIR92 [41]) and refined by full-matrix least squares on F^2 (SHELXL97 [42]). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbons were calculated into idealized positions and constrained during refinement (riding model) with assigned displacement parameter $H_{iso}(H) = 1.2U_{eq}$(pivot atom). The hydrogen atoms of hydroxyls were found on difference map and refined isotropically. The refinement converged (Δ/σ_{max} = 0.000) to R = 0.024 for observed reflections; wR = 0.064, GOF = 1.080 for 131 parameters and all 1813 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.183, $\Delta\rho_{min}$ =

–0.298. The absolute configuration was established by the anomalous dispersion effect, chirality parameter 0.00(9). CCDC 284673 (for **9a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

2,3,4-Tri-*O*-acetyl-1,6-anhydro-1-thio-β-D-glucopyranose *S*-Dioxide (**9b**)

To a solution of thiolevoglucosan triacetate **2b** (0.5 g, 1.6 mmol) in acetic acid (1 ml), 30% H_2O_2 (1.2 g, 10.6 mmol) was added dropwise at 0 °C. The reaction mixture was kept at room temperature for 4 days. Then acetic acid was evaporated and the residue was crystallized from ethanol to give *S*-dioxide **9b** (0.375 g, 70%), m.p. 167–169 °C, $[\alpha]_D$ –11 (*c* 0.88, CH_2Cl_2); ref.[12] gives m.p. 181–182 °C, $[\alpha]_D$ –21.7 ($CHCl_3$). For $C_{12}H_{16}O_9S$ (336.3) calculated: 42.86% C, 4.76% H, 9.53% S; found: 42.96% C, 4.80% H, 9.58% S.

(6*R*)-6-*C*-Acetoxy-2,3,4-tri-*O*-acetyl-1,6-anhydro-1-thio-β-D-glucopyranose (**10**)

Sulfoxide **7a** (0.1 g, 0.52 mmol) and fused sodium acetate (0.05 g) were refluxed in acetic anhydride (5 ml) for 3 h. The reaction mixture was poured into ice water (20 ml), the solution was neutralized with sodium hydrogencarbonate and was extracted with chloroform (3 × 10 ml). The organic layer was separated, dried and filtered through a short column of silica gel. Then the solvent was evaporated under reduced pressure (oil pump) to obtain a colorless syrupy compound **10** (0.17 g, 61%) which was pure according to TLC (R_F 0.84, R_F (**7a**) 0.07) in acetone–benzene–ethyl acetate –water 4:1:2:2, $[\alpha]_D$ –156 (*c* 1.0, $CHCl_3$); ref.[12] gives $[\alpha]_D$ –218 ($CHCl_3$). For $C_{14}H_{18}O_9S$ (362.4) calculated: 46.41% C, 5.61% H, 8.85% S; found: 46.49% C, 5.18% H, 9.07% S.

2,4-Di-*O*-benzoyl-1,6-anhydro-1-thio-β-D-glucopyranose (**11**) and
2,3,4-Tri-*O*-benzoyl-1,6-anhydro-1-thio-β-D-glucopyranose (**12**)

To a stirred and cooled (–5 °C) solution of thiolevoglucosan **2a** (1 g, 5.6 mmol) in pyridine (15 ml) benzoyl chloride (1.6 g, 10 mmol) in acetone (2 ml) was added dropwise. Then the temperature was allowed to warm to room temperature. After 12 h TLC (benzene–acetone 10:1) revealed product **11** and a small amount of starting compound. Another portion of benzoyl chloride (0.8 g, 5 mmol) in acetone (1 ml) was added and the reaction mixture was left standing at room temperature for another 5 h. The reaction mixture was then poured into a cold aqueous solution of $NaHCO_3$, extracted with chloroform, and the organic layer was evaporated to obtain a syrup. After adding ether to it, a solid precipitated and was crystallized from chloroform–diethyl ether to give **12** (1.22 g, 44%), m.p. 169–172 °C, $[\alpha]_D$ –22 (*c* 0.85, $CHCl_3$); ref.[10] gives m.p. 168–170 °C, $[\alpha]_D$ –31.5 (*c* 0.54, $CHCl_3$). For $C_{27}H_{22}O_7S$ (490.5) calculated: 66.11% C, 4.52% H, 6.54% S; found: 65.80% C, 4.52% H, 6.64% S. Mother liquors were evaporated and the syrupy residue was separated on a silica gel column (benzene–acetone 10:1) to obtain a second portion of the tribenzoate **12** (1.27 g, 46%) and 2,4-di-*O*-benzoyl derivative **11** (0.085 g, 4%), m.p. 123–124 °C, $[\alpha]_D$ –16 (*c* 1.9, $CHCl_3$); ref.[10] gives m.p. 124–126 °C, $[\alpha]_D$ –24.6 (*c* 0.32, $CHCl_3$). For $C_{20}H_{18}O_6S$ (386.4) calculated: 62.16% C, 4.69% H, 8.30% S; found: 61.95% C, 4.76% H, 8.52% S.

2,4-Di-*O*-benzoyl-3-*O*-mesyl-1,6-anhydro-1-thio-β-D-glucopyranose (**13**)

To a cool solution (<0 °C) of 2,4-di-*O*-benzoyl derivative **11** (0.056 g, 0.14 mmol) in dry pyridine (1 ml), mesyl chloride (0.017 g, 0.15 mmol) in pyridine (0.5 ml) was added. After 12 h, the mixture was poured into ice water. After 1 h, the crystalline product was filtered off and recrystallized from aqueous ethanol to obtain **13** (0.04 g, 87%), m.p. 164–166 °C, $[\alpha]_D$ –33 (*c* 0.55, $CHCl_3$). MS, *m/z*: 464.2 [M^+].

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