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Note

X-Ray crystallographic and n.m.r. (^{1}H and ^{13}C) studies of methyl 4,6-*O*-(*R*)-benzylidene-3-*O*-methyl-2-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside and methyl 4,6-*O*-(*R*)-benzylidene-2-*O*-methyl-3-*O*-*p*-tolylsulfonyl-β-D-glucopyranoside

Elizabeth Lee, Patrick McArdle, Noeleen Melody, Desmond Cunningham, and John Gallagher
Chemistry Department, University College, Galway (Ireland)

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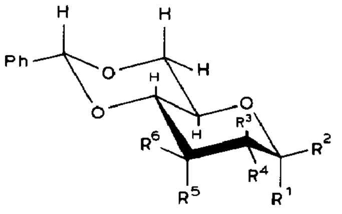
Separate treatment of methyl α- and β-D-glucopyranoside with benzaldehyde–zinc chloride affords the 4,6-*O*-(*R*)-benzylidene derivatives **1** (ref. 1) and **2** (ref. 2), respectively. It has been established[3], by ^{1}H-n.m.r. spectroscopy, that the thermodynamically stable α-D-*gluco* isomer **1** and its derivatives have a *trans*-decalin type ring system with chair conformations and the phenyl group equatorial. In the crystal of the 4,6-*O*-(*S*)-benzylidene derivative of methyl 2,3-di-*O*-methyl-α-D-glucopyranoside, which is formed under conditions of kinetic control, the 1,3-dioxane ring has a chair conformation with the phenyl group axial[4].

We now report ^{1}H- and ^{13}C-n.m.r. data and X-ray crystal structures of the 3-*O*-methyl-2-*O*-*p*-tolylsulfonyl[5] (**3**) derivative of **1** and the 2-*O*-methyl-3-*O*-*p*-tolylsulfonyl[6] (**4**) derivative of **2**, prepared by selective tosylation[7] of the diols followed by Purdie methylation.



	R1	R2	R3	R4	R5	R6
1 *α-gluco*	OMe	H	H	OH	H	OH
3	OMe	H	H	OTs	H	OMe
2 *β-gluco*	H	OMe	H	OH	H	OH
4	H	OMe	H	OMe	H	OTs

0008-6215/90/$03.50

TABLE I

^{13}C Chemical Shift Data[a]

Compound	*Substituents*		*Atom*								
	2	3	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*PhCH*	*CH_3O-1*	*Others*
α-gluco											
1	HO	HO	99.9	72.4	70.5	80.8	62.0	68.5	101.5	54.9	
3	TsO	MeO	99.1	79.6	78.0	82.4	62.6	69.3	101.9	56.2	61.3 (CH_3O-3)
β-gluco											
2	HO	HO	104.2	74.2	72.9	80.3	65.9	68.3	101.5	56.8	
4	MeO	TsO	104.9	82.0	81.4	78.2	65.7	68.5	101.4	57.5	60.8 (CH_3O-2)

[a] In p.p.m. downfield from the signal for internal Me_4Si for solutions in $CDCl_3$.

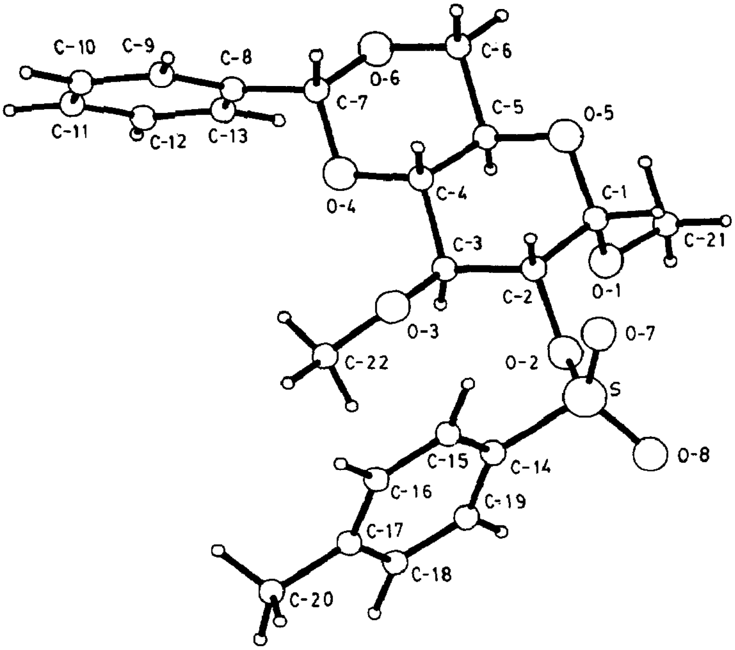


Fig. 1. PLUTO[15] drawing of **3** and the numbering scheme.

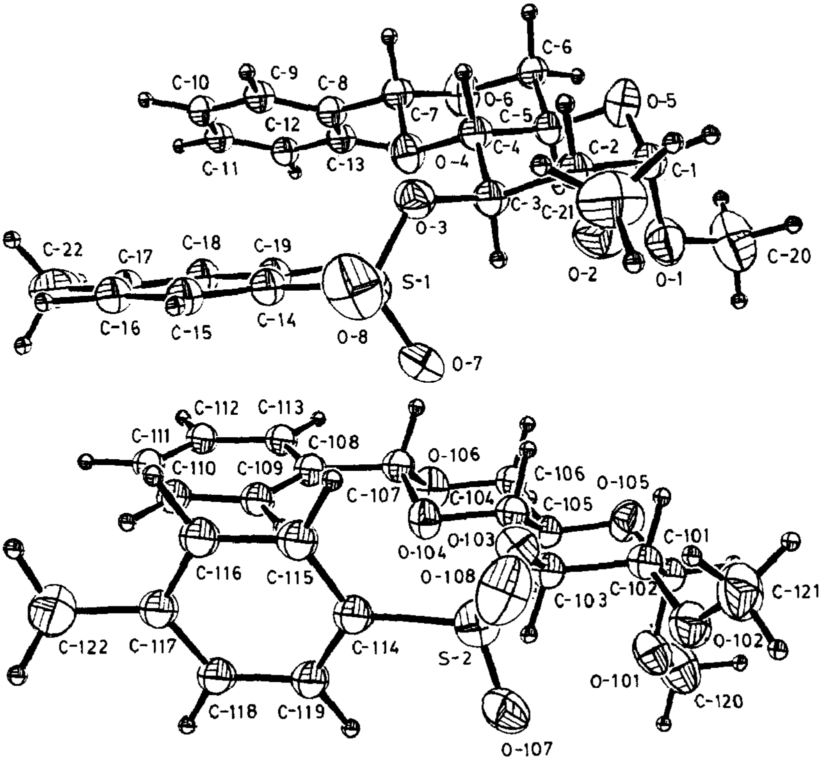


Fig.2. ORTEP[16] drawing of **4** and the numbering scheme.

The ^{13}C-n.m.r. data for **1**–**4** are given in Table I. As expected[8,9], C-2 and C-3 in **3** were deshielded (7.2 p.p.m. and 7.5 p.p.m., respectively) in comparison with **1**, and there were upfield (0.8 p.p.m.) and downfield (1.6 p.p.m.) shifts of the resonances for C-1 and C-4, respectively.

*Crystallography**. — Perspective views of **3** and **4** are depicted in Figs. 1 and 2, respectively. The final atomic co-ordinates for **3**, with their standard deviations in parentheses, are listed in Tables II and III, and the corresponding parameters for **4** are given in Tables IV and V. As expected[3], the dioxane and pyranose rings are in chair conformations. The angles between planes 1 and 2 for **3** and **4** were <2° and <3°,

TABLE II

Fractional atomic co-ordinates for **3**

Atom	x	y	z
S-1	−0.0839(1)	−0.0092(3)	−0.3977(1)
O-1	−0.1087(3)	−0.4895(7)	−0.4924(3)
O-2	−0.0981(3)	−0.2067(7)	−0.4074(3)
O-3	−0.2138(3)	−0.2685(8)	−0.2862(3)
O-4	−0.3004(3)	−0.5877(7)	−0.3145(3)
O-5	−0.2435(3)	−0.4567(7)	−0.5177(3)
O-6	−0.3600(4)	−0.7655(8)	−0.4077(4)
O-7	−0.0047(4)	0.0155(9)	−0.4237(4)
O-8	−0.1461(4)	0.0786(8)	−0.4367(4)
C-1	−0.1699(5)	−0.3790(12)	−0.5010(5)
C-2	−0.1753(5)	−0.2746(10)	−0.4232(5)
C-3	−0.2021(5)	−0.3786(11)	−0.3515(4)
C-4	−0.2762(5)	−0.4703(11)	−0.3758(5)
C-5	−0.2630(5)	−0.5727(12)	−0.4537(5)
C-6	−0.3390(7)	−0.6611(14)	−0.4759(6)
C-7	−0.3712(5)	−0.6690(12)	−0.3372(5)
C-20	−0.0975(7)	0.1264(16)	−0.0392(6)
C-21	−0.0928(7)	−0.5889(14)	−0.5620(6)
C-22	−0.1945(7)	−0.3353(16)	−0.2085(5)
C-8	−0.3951(5)	−0.7832(11)	−0.2695(5)
C-9	−0.4516(5)	−0.7307(12)	−0.2170(5)
C-10	−0.4702(6)	−0.8270(14)	−0.1479(6)
C-11	−0.4293(7)	−0.9707(16)	−0.1358(7)
C-12	−0.3737(6)	−1.0297(17)	−0.1899(6)
C-13	−0.3564(6)	−0.9330(14)	−0.2558(6)
C-14	−0.0895(4)	0.0299(10)	−0.2926(4)
C-15	−0.0326(5)	−0.0461(12)	−0.2424(6)
C-16	−0.0365(5)	−0.0177(13)	−0.1610(5)
C-17	−0.0935(6)	0.0919(12)	−0.1283(5)
C-18	−0.1483(6)	0.1634(14)	−0.1801(6)
C-19	−0.1453(5)	0.1335(12)	−0.2625(5)

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* Lists of anisotropic and isotropic thermal parameters, bond lengths, and bond angles have been deposited with, and can be obtained from, Elsevier Science Publishers, B.V., BBA Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/446/*Carbohydr. Res.*, 208 (1990) 221–230.

TABLE III

Fractional atomic co-ordinates for the hydrogen atoms of **3** with attached C atoms in brackets

Atom		x	y	z
H-1		−0.158	−0.301	−0.553
H-2		−0.219	−0.177	−0.431
H-3		−0.159	−0.471	−0.333
H-4		−0.321	−0.375	−0.385
H-5		−0.216	−0.664	−0.445
H-61		−0.331	−0.738	−0.529
H-62		−0.385	−0.570	−0.487
H-7	(C-7)	−0.416	−0.576	−0.349
H-8	(C-9)	−0.482	−0.614	−0.228
H-9	(C-10)	−0.516	−0.787	−0.106
H-10	(C-11)	−0.440	−1.042	−0.082
H-11	(C-12)	−0.345	−1.149	−0.180
H-12	(C-13)	−0.312	−0.975	−0.298
H-13	(C-15)	0.013	−0.125	−0.268
H-14	(C-16)	0.005	−0.080	−0.121
H-15	(C-18)	−0.194	0.244	−0.156
H-16	(C-19)	−0.187	0.193	−0.302
H-17	(C-20)	−0.050	0.060	−0.009
H-18	(C-20)	−0.154	0.084	−0.016
H-19	(C-20)	−0.092	0.260	−0.029
H-20	(C-21)	−0.044	−0.672	−0.550
H-21	(C-21)	−0.078	−0.507	−0.612
H-22	(C-21)	−0.144	−0.663	−0.577
H-23	(C-22)	−0.206	−0.241	−0.163
H-24	(C-22)	−0.133	−0.370	−0.207
H-25	(C-22)	−0.230	−0.445	−0.197

TABLE IV

Fractional atomic co-ordinates for **4**

Atom			
S-1	−0.08418(14)	−9.98917	−0.83887(11)
S-2	−0.4393(1)	−0.4491(3)	−0.6611(1)
O-1	−0.1590(4)	0.0095(7)	−1.1269(3)
O-2	0.0012(4)	0.0531(6)	−0.9895(3)
O-3	−0.1152(3)	0.1369(6)	−0.8959(2)
O-4	−0.3281(3)	0.2077(6)	−0.9800(2)
O-5	−0.2115(3)	0.2538(6)	−1.1285(3)
O-6	−0.4487(3)	0.3109(7)	−1.0894(3)
O-7	−0.1073(5)	−0.1317(6)	−0.8831(3)
O-8	0.0175(3)	0.0257(8)	−0.7885(3)
O-101	−0.3482(3)	−0.4977(7)	−0.3711(3)
O-102	−0.5131(4)	−0.4212(7)	−0.4974(3)
O-103	−0.4014(3)	−0.3272(6)	−0.5968(2)
O-104	−0.1836(3)	−0.3002(6)	−0.5186(2)
O-105	−0.2810(4)	−0.2604(6)	−0.3592(3)
O-106	−0.0468(3)	−0.2399(6)	−0.4065(3)

TABLE IV contd.
Fractional atomic Co-ordinates for **4**

Atom			
O-107	−0.4443(4)	−0.5872(6)	−0.6260(3)
O-108	−0.5290(3)	−0.3867(8)	−0.7165(3)
C-20	−0.1906(7)	−0.0113(14)	−1.2076(5)
C-21	0.0977(6)	0.1158(11)	−0.9534(6)
C-22	−0.3772(8)	0.0362(11)	−0.6610(5)
C-120	−0.3091(7)	−0.5350(12)	−0.2916(4)
C-121	−0.6046(6)	−0.3531(11)	−0.5414(5)
C-122	−0.1257(6)	−0.5082(11)	−0.8217(4)
C-1	−0.1273(6)	0.1523(9)	−1.027(4)
C-2	−0.0805(5)	0.1541(9)	−1.0154(4)
C-3	−0.1623(5)	0.1191(8)	−0.9795(3)
C-4	−0.2465(5)	0.2305(8)	−1.0094(4)
C-5	−0.2894(5)	0.2234(9)	−1.0972(4)
C-6	−0.3747(5)	0.3323(9)	−1.1268(4)
C-7	−0.4036(5)	0.3197(9)	−1.0072(4)
C-8	−0.4856(5)	0.3019(8)	−0.9724(3)
C-9	−0.4674(7)	0.3455(11)	−0.8980(5)
C-10	−0.5426(6)	0.3341(12)	−0.8644(6)
C-11	−0.6380(6)	0.2789(9)	−0.9070(5)
C-12	−0.6549(7)	0.2347(11)	−0.9796(5)
C-13	−0.5789(6)	0.2489(10)	−1.0131(5)
C-14	−0.1696(5)	0.0164(9)	−0.7866(4)
C-15	−0.1306(6)	0.0236(9)	−0.7068(4)
C-16	−0.2004(6)	0.0318(10)	−0.6680(5)
C-17	−0.3035(6)	0.0309(11)	−0.7055(5)
C-18	−0.3412(6)	0.0280(10)	−0.7848(4)
C-19	−0.2740(5)	0.0207(9)	−0.8268(4)
C-101	−0.3727(6)	−0.3497(9)	−0.3864(4)
C-102	−0.4249(5)	−0.3284(9)	−0.4719(4)
C-103	−0.3509(5)	−0.3636(8)	−0.5156(3)
C-104	−0.2584(5)	−0.2704(8)	−0.4829(4)
C-105	−0.2111(5)	−0.2993(9)	−0.3963(4)
C-106	−0.1139(5)	−0.2084(9)	−0.3640(4)
C-107	−0.0967(5)	−0.2085(9)	−0.4868(4)
C-108	−0.0205(5)	−0.2341(8)	−0.5272(4)
C-109	−0.0486(6)	−0.3007(10)	−0.5978(4)
C-110	0.0225(6)	−0.3123(10)	−0.6360(5)
C-111	0.1189(7)	−0.2582(10)	−0.6047(5)
C-112	0.1461(7)	−0.1953(12)	−0.5352(5)
C-113	0.0760(6)	−0.1798(11)	−0.4953(5)
C-114	−0.3425(5)	−0.4584(8)	−0.7033(3)
C-115	−0.3347(5)	−0.3519(9)	−0.7538(4)
C-116	−0.2625(5)	−0.3659(9)	−0.7889(4)
C-117	−0.1989(5)	−0.4857(9)	−0.7772(4)
C-118	−0.2070(6)	−0.5909(10)	−0.7257(4)
C-119	−0.2762(5)	−0.5774(9)	−0.6872(4)

respectively. The $^{4}C_{1}$ conformation of the pyranose rings in **3** and **4** is reflected by the approximately equal displacement of C-1 and C-4 from the plane formed by C-2, C-3, C-5, and O-5, and of C-101 and C-104 from the plane formed by C-102, C-103, C-105, and O-105 in **4**.

TABLE V

Fractional atomic co-ordinates for the hydrogen atoms of **4** with attached carbon atoms in brackets

Atom		x	y	z
H-1		−0.071	0.186	−1.128
H-2		−0.050	0.263	−0.998
H-3		−0.192	0.009	−0.993
H-4		−0.213	0.337	−0.990
H-5		−0.319	0.114	−1.115
H-6	(C-6)	−0.412	0.318	−1.188
H-7	(C-6)	−0.344	0.442	−1.115
H-8	(C-7)	−0.367	0.425	−0.991
H-9	(C-9)	−0.393	0.390	−0.865
H-10	(C-10)	−0.527	0.368	−0.805
H-11	(C-11)	−0.698	0.271	−0.882
H-12	(C-12)	−0.728	0.187	−1.013
H-13	(C-13)	−0.595	0.217	−1.073
H-14	(C-15)	−0.049	0.023	−0.676
H-15	(C-16)	−0.172	0.039	−0.606
H-16	(C-18)	−0.423	0.031	−0.815
H-17	(C-19)	−0.303	0.019	−0.889
H-18	(C-20)	−0.214	−0.124	−1.221
H-19	(C-20)	−0.127	0.014	−1.227
H-20	(C-20)	−0.255	0.060	−1.236
H-21	(C-21)	0.155	0.030	−0.936
H-22	(C-21)	0.097	0.177	−0.903
H-23	(C-21)	0.116	0.189	−0.993
H-24	(C-22)	−0.455	0.035	−0.701
H-25	(C-22)	−0.364	0.136	−0.627
H-26	(C-22)	−0.364	−0.058	−0.623
H-101		−0.424	−0.317	−0.356
H-102		−0.448	−0.215	−0.484
H-103		−0.330	−0.478	−0.510
H-104		−0.281	−0.157	−0.494
H-105		−0.193	−0.414	−0.386
H-106	(C-106)	−0.076	−0.235	−0.304
H-107	(C-106)	−0.133	−0.093	−0.369
H-108	(C-107)	−0.123	−0.096	−0.494
H-109	(C-109)	−0.125	−0.344	−0.624
H-110	(C-110)	0.000	−0.366	−0.692
H-111	(C-111)	0.173	−0.266	−0.635
H-112	(C-112)	0.224	−0.155	−0.509
H-113	(C-113)	0.099	−0.125	−0.440
H-114	(C-115)	−0.385	−0.258	−0.766
H-115	(C-116)	−0.255	−0.280	−0.827
H-116	(C-118)	−0.158	−0.686	−0.715
H-117	(C-119)	−0.279	−0.658	−0.645
H-118	(C-120)	−0.293	−0.651	−0.286
H-119	(C-120)	−0.366	−0.509	−0.265
H-120	(C-120)	−0.239	−0.474	−0.263
H-121	(C-121)	−0.666	−0.433	−0.558
H-122	(C-121)	−0.596	−0.307	−0.593
H-123	(C-121)	−0.623	−0.267	−0.508
H-124	(C-122)	−0.130	−0.415	−0.859
H-125	(C-122)	−0.147	−0.606	−0.856
H-126	(C-122)	−0.048	−0.519	−0.782

For **3**, C-5 lies 0.73 Å below, and C-7 lies 0.67 Å above, plane 1 (C-6, O-6, C-4, and O-4) and C-4 lies 0.72 Å above, and C-1 lies 0.71 Å below, plane 2 (C-2, C-3, C-5, and O-5 of the pyranose ring). The angle between plane 1 and the aromatic ring C-8/13 is 107.7°. Plane 2 makes an angle of 81.9° with the aromatic ring C-14/19.

The asymmetric unit of the crystal of **4** contained two distinct molecules (*A* and *B*) that differ only in the orientation of the aromatic rings. The angles between plane 1 and the aromatic ring in *A* and *B* were 134.10° and 15.53°, respectively. The angles between plane 2 and the aromatic ring in *A* and *B* were 152.25° and 103.43°, respectively. The aromatic rings were orientated at angles of 22.67° and 91.61° in *A* and *B*, respectively. Planes 1 and 2 were almost parallel, with angles of <3° in both *A* and *B*.

TABLE VI

Crystal data

	3	**4**
Formula	$C_{22}H_{26}O_8S$	$C_{22}H_{26}O_8S$
M (a.m.u.)	450.503	450.503
	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
a (Å)	16.961(6)	13.821(3)
b (Å)	7.938(3)	9.118(2)
c (Å)	16.580(7)	18.411(3)
U (Å^3)	2232.27	2179.98
Z	4	4
D_c (g.cm^{-3})	1.34	1.37
μ (cm^{-1})	1.47	1.50
F (000)	952	952
Radiation Mo-K_α		
Graphite monochromator	λ = 0.7093 Å	λ = 0.7093 Å
Diffractometer	Hilger Y290	Enraf–Nonius CAD4F
Orienting reflections		
Range	25, $13<\theta<20°$	25, $13<\theta<20°$
Temperature (°)	22	22
Scan method	ω–2θ	ω–2θ
Data collection range	$2<2\theta<48°$	$2<2\theta<48°$
No. of unique data	1508	3655
Total $I<3\sigma I$	1227	2731
No of parameters fitted	220	368
R^a	5.7%	5.6%
$R_w{}^b$	6.74%	5.9%
Quality-of-fit indicator[c]	0.829	1.82
Largest shift/e.s.d., final cycle	<0.001	<0.002
Largest positive peak (e/Å^3)	0.15	0.21
Largest negative peak (e/Å^3)	−0.12	−0.12

[a] $R = [\Sigma| |F_0| - |F_c| |] / \Sigma |F_o|$. [b] $Rw = \{[\Sigma w(|F_o - F_c|^2]/[\Sigma w(|F_0|)^2]\}^{1/2}$; $w = 1/[(\sigma F_o)^2 - 0.00105 {*} F_o{}^2]$.
[c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

EXPERIMENTAL

The 4,6-*O*-benzylidene derivatives **3** and **4** were prepared as described[5-7]. N.m.r. spectra were recorded with a Jeol GX-270(^{1}H, ^{13}C) spectrometer for solutions in $CDCl_3$ (internal Me_4Si). N.m.r. line-shifts (^{1}H) induced by $Eu(fod)_3$ were used for some assignments.

^{1}H-N.m.r. data. — (*a*) *Methyl 4,6-*O*-benzylidene-3-O-methyl-2-*O*-p-tolylsulfonyl-α-*D*-glucopyranoside* (**3**): δ 7.77 and 7.36–7.18 (d, 2 H, and m, 7 H, Ph and MeC_6H_4), 5.41 (s, 1 H, PhC*H*), 4.81 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.27 (dd, 1 H, $J_{1,2}$ 3.9, $J_{2,3}$ 9.3 Hz, H-2), 4.19 (dd, 1 H, $J_{6a,6e}$ 9.7, $J_{5,6e}$ 4.4 Hz, H-6*e*), 3.73 (sextet, 1 H, $J_{5,6e}$ 4.4, $J_{5,6a} = J_{4,5} = 9.3$ Hz, H-5), 3.35 (t, 1 H, $J_{3,4} = J_{4,5} = 9.3$ Hz, H-4), 3.25 (s, 3 H, MeO-1), 3.19 (s, 3 H, MeO-3), 2.36 (s, 3 H, Ts*Me*), 3.66–3.56 (H-3,6*a*). During the shift study, H-3,6*a* gave triplets. These assignments were made by spin-decoupling of the normal and shifted spectra.

(*b*) *Methyl 4,6-*O*-benzylidene-2-*O*-methyl-3-*O*-p-tolylsulfonyl-β-*D*-glucopyranoside* (**4**): δ 7.73 (d, 2 H, J_{AA} 8.4 Hz, Ts 2 H-A), 7.36–7.25 (m, 5 H, Ph), 7.03 (d, 2 H, J_{BB} 8.6 Hz, Ts 2 H-B), 5.37 (s, 1 H, PhC*H*), 4.81 (t, $J_{2,3}$ 9.0, $J_{3,4}$ 9.2 Hz, H-3), 4.37 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 4.35 (q, $J_{5,6e}$ 4.8, $J_{6a,e}$ 10.7 Hz, H-6*e*), 3.72 (t, 1 H, $J_{6a,e} = J_{5,6a} = 10.7$ Hz, H-6*a*), 3.60 (t, 1 H, $J_{3,4} = J_{4,5} = 9.2$ Hz, H-4), 3.56 (s, 3 H, MeO-1), 3.43 (m, 1 H, $J_{4,5}$ 9.2, $J_{5,6e}$ 4.8, $J_{5,6a}$ 10.7 Hz, H-5), 3.41 (s, 1 H, MeO-2), 3.12 (t, 1 H, $J_{1,2}$ 7.3, $J_{2,3}$ 9.0 Hz, H-2), 2.31 (s, 3 H, Ts*Me*).

Crystallographic data are given in Table VI. The structures of **3** and **4** were solved by direct methods, SHELX 86[10], and refined by full-matrix least squares using SHELX 76[11]. Data were corrected for Lorentz and polarisation effects, but not for absorption. Hydrogen atoms were included in the calculated positions with fixed thermal parameters. For **3**, S, O, C-1/8, and the C of the methyl groups were refined anisotropically. For **4**, S, O, and the C of the methyl groups were treated as having anisotropic thermal parameters. The thermal parameters were terms U_{ij} of

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{33}klb^*c^*)].$$

The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature[12-14]. For all planes calculations, the maximum deviation from the plane for the points in the plane was 0.01 Å. All calculations were performed on a VAX 8700 computer.

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