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Note

N.m.r. studies of some *cis*- and *trans*-fused hexopyranoside *p*-toluenesulfonates

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^{13}C-N.m.r. data for 4,6-*O*-benzylidenehexopyranosides and some derivatives have been reported[1,2], and ^{1}H- and ^{13}C-n.m.r. spectroscopy has been employed to define the conformations of some *cis*- and *trans*-fused benzylidene acetals[3–5]. We now report ^{13}C-n.m.r. data for the 2-*O*- (**2**), 3-*O*- (**3**), 2,3-di-*O*-*p*-tolylsulfonyl[6] (**4**),

TABLE I

^{13}C-N.M.R. CHEMICAL SHIFT DATA[a] FOR METHYL 4,6-*O*-BENZYLIDENE-D-HEXOPYRANOSIDES

Compound	*Substituents*		*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*PhCH*	*CH_3O*
	2	*3*								
α-galacto *series*										
1	HO	HO	100.3	69.5	69.5	76.0	62.8	69.5	101.2	55.6
2	TsO	HO	98.4	76.2	66.5	77.8	62.4	69.0	101.2	55.9
3	HO	TsO	100.3	66.4	78.7	76.3	62.4	69.0	100.7	55.7
4	TsO	TsO	98.4	74.3	74.9	73.4	62.1	68.7	100.4	56.0
5	TsO	AcO	98.2	74.2	74.2	68.9	62.0	68.0	100.7	55.9
β-galacto *series*										
6	HO	HO	103.8	72.8	71.8	75.4	66.7	69.2	101.5	57.3
7	HO	TsO	103.6	68.3	80.5	74.0	66.0	68.8	100.8	57.2
8	TsO	TsO	101.1	77.2	76.4	73.9	65.7	68.4	100.7	57.8
α-gluco *series*										
9	HO	HO	99.9	72.8	71.5	81.0	62.4	68.9	101.9	55.5
10	TsO	HO	98.5	79.7	68.9	81.3	62.2	68.6	102.1	55.7
11	TsO	TsO	98.5	75.8	74.9	79.0	62.4	68.6	101.9	55.9
β-gluco *series*										
12	HO	HO	104.2	74.4	72.9	80.3	65.9	68.3	101.7	56.8
13	TsO	HO	101.8	82.3	71.8	80.2	66.0	68.4	101.7	57.3
14	HO	TsO	104.2	72.9	82.1	77.9	65.9	68.5	101.6	57.7
15	TsO	TsO	102.0	79.3	78.8	78.2	65.7	68.3	101.6	57.3

[a]P.p.m. downfield from Me_4Si.

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and 3-*O*-acetyl-2-*O*-*p*-tolylsulfonyl[7] (**5**) derivatives of methyl 4,6-*O*-benzylidene-α-D-galactopyranoside[6] (**1**), and the 3-*O*- (ref. 6) (**7**) and 2,3-di-*O*-*p*-tolylsulfonyl[8] (**8**) derivatives of methyl 4,6-*O*-benzylidene-β-D-galactopyranoside[6,8] (**6**). Comparative data are reported for the 2-*O*- (ref. 9) (**10**) and 2,3-di-*O*-*p*-tolylsulfonyl[10] (**11**) derivatives of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside[11] (**9**), and for the 2-*O*- (ref. 12) (**13**), 3-*O*- (ref. 12) (**14**), and 2,3-di-*O*-*p*-tolylsulfonyl[13] (**15**) derivatives of the corresponding β-D-glucopyranoside[11] (**12**). N.m.r. line-shifts (^{1}H) induced by $Eu(fod)_3$ were used for some derivatives for complete assignment of signals. Chemical-shift displacements of the ^{13}C resonances of the ring carbons on *p*-tolylsulfonylation of **1** to give **2–4** and on *p*-tolylsulfonylation of **6** to give **7** and **8** are discussed. As expected, comparison of the ^{13}C data (Table I) for the epimeric pairs **1** and **9** and **6** and **12** shows that the greatest difference in their relative chemical shift values occurs for the C-4 resonance, which is markedly shifted up-field in **1** (5 p.p.m.) and **6** (4.9 p.p.m.).

^{13}C-N.m.r. chemical shifts for the *p*-tolylsulfonates **2–5, 7, 8, 10, 11,** and **13–15** are given in Table I, together with data for **1, 6** (both ref. 2), **9,** and **12** (both ref. 1). Selective ^{1}H-spin-decoupling and off-resonance experiments were used for some compounds. For example, the ^{13}C-n.m.r. spectrum of **6** showed four signals at lowest field due to the six aromatic carbons [137.5 (quaternary carbon), 129.3 *(para)*, 128.3 and 126.5 p.p.m. (*ortho* and *meta*)] with little or no change in the positions of these signals throughout the series. Selective irradiation of the H-7 signal confirmed that the signal at 101.5 was due to C-7. The signal at 103.8 was assigned to C-1 following selective irradiation of the H-1 signal. Likewise, the signals at 75.4 and 66.7 were assigned to C-4 and C-5, respectively. Since the resonances due to H-2 and H-3 could not be separated during the lanthanide shift study, the signals at 72.8 and 71.8 p.p.m. could not be assigned unambiguously. However, by comparison with related compounds, the peak at lower field was assigned to C-2. Finally, examination of the off-resonance spectrum showed that the signal at 57.3 p.p.m. was due to the methoxyl carbon, and the signal at 69.2 p.p.m. was assigned to C-6.

Comparison of the ^{13}C-n.m.r. data for **1** and the *p*-tolylsulfonyl derivatives **2–4** showed that sulfonylation caused an up-field shift of 1.9–3.1 p.p.m. in the resonances of the β-carbons (C-1 in **2** and **4** compared to **1**, and C-2 in **3** compared to **1**) and strong deshielding of the α-carbons [shifts ranging from 4.8 p.p.m. (for C-2 in **4** compared to **1**) to 9.2 p.p.m. (for C-3 in **3** compared to **1**)]. A similar trend was observed on sulfonylation of HO-3 and HO-2 in **2** and **3**, respectively (β-carbons: 1.9 p.p.m. for C-1 in **3** compared to **4**, and 4.4 p.p.m. for C-4 in **2** compared to **4**; α-carbons: 7.9 p.p.m. for C-2 of **3** relative to **4**, and 8.4 p.p.m. for C-3 of **2** relative to **4**).

Comparison of the data for the β-D-*galacto* derivative **6** and the *p*-tolylsulfonates **7** and **8** shows that sulfonylation caused up-field shifts in the resonances of the β-carbons (2.7 p.p.m. for C-1 in **8** compared to **6**, and 4.5 p.p.m. for C-2 in **7** compared to **6**) and strong deshielding of the α-carbons (shifts of 4.4 p.p.m. for

TABLE II

OBSERVED, RELATIVE SHIFT-GRADIENTS[a,b] (^{1}H) FOR COMPOUNDS **1–3, 6, 7,** AND **12–14**

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6a*	*H-6e*	*H-7*	*OH*	*OMe*
1	4.5	10	10	3.9	2.8	1.3	1.5	1.6		2.1
2[c]	3.3	10	9.2	3.5	1.4	0.8	1.0	1.1		0.7
3	6.6	6.9	10	3.3	3.6	1.7	1.7	1.6	28.1	2.1
6	5.0	10	10	3.4	2.1	1.3	1.3	1.4		1.8
7	9.1	10	6.2	2.3	2.7	1.3	1.7	1.4	17.7	4.14
12	4.8	9.4	10	4.2	2.8	1.6	1.3	1.4		1.5
13	3.8	10	5.6	0.9	2.2	0.01	0.5	−0.2	19.0	1.3
14	7.0	10	8.9	4.4	2.4	1.5	1.7	1.8	22.6	1.8

[a]P.p.m. per mol of Eu(fod)$_3$ per mol of substrate. [b]All shifts for a given compound are normalised to the hydrogen(s) which exhibit the greatest induced shift. [c]Accurate shift data could not be obtained for the hydroxyl proton since its signal broadened almost to the baseline with increasing Eu(fod)$_3$/substrate ratio.

C-2 in **8** compared to **6**, and 7 p.p.m. for C-3 in **7** compared to **6**). Sulfonylation of HO-2 in **7** caused an up-field shift in the resonance of the β-carbon (2.5 p.p.m. for C-1 in **7** compared to **8**) and a down-field shift in the resonance of the α-carbon (8.9 p.p.m. for C-2 in **7** compared to **8**). Similar changes in the direction and relative magnitudes of shifts were observed for the D-glucopyranoside sulfonates, **10, 11,** and **13–15**.

The characteristic chemical-shift data provided in this report should contribute to future ^{13}C-n.m.r. assignments for more complex carbohydrate structures having selectively *O*-sulfonylated D-gluco- and D-galactopyranose units.

Eu(fod)$_3$-induced shifts. — Table II shows the relative shift gradients for **1–3, 6, 7,** and **12–14** derived from the experimental plots of induced shift *vs.* molar ratio of shift reagent to substrate. The large shift values for the resonances of H-2 and H-3 in **12** and the correspondingly large shift value for H-2 and H-3 in **1** and **6**, which were not individually resolved throughout the entire study, together with the relatively small value for the methoxyl group in each compound, indicate exclusive binding with the shift reagent by the hydroxyl groups. The results indicate that the shift reagent may occupy a position equally close to H-2 and H-3 and slightly nearer to H-1 than to H-4. The large shift value for the hydroxyl signal for **3, 7, 13,** and **14** indicates strong association of the shift reagent with the hydroxyl oxygen in each of these compounds. However, the shift-gradients for the resonances of the methoxyl protons in **3** and **7** (relative to the methoxyl signals for **2, 6, 12, 13,** and **14**), together with the not insignificant shift-gradients derived from a preliminary Eu(fod)$_3$-induced shift study of ethyl *p*-tolylsulfonate, indicate a degree of competitive binding with the shift reagent between the dominant hydroxyl and the methoxyl and *p*-tolylsulfonyl[14] groups.

EXPERIMENTAL

^{1}H-N.m.r. spectra were recorded with JEOL MH-100 and GX-270 spectrometers. ^{13}C-N.m.r. spectra were recorded with the JEOL GX-270 spectrometer. Spectra were obtained for solutions in $CDCl_3$ (internal Me_4Si).

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