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Note

Infrared spectra of sulfonic esters of carbohydrates*

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In an infrared (i.r.) study of esters of *p*-toluenesulfonic acid, Tipson[1] assigned frequencies in the regions 1610–1600, 1375–1350, 1195–1165, and 830–815 cm^{-1} to the *p*-tolylsulfonyloxy group. Other studies, by Honeyman and coworkers[2–4] and Guthrie and Spedding[5], of 4,6-acetals of methyl D-glycosides containing nitrate and sulfonate groups extended i.r. frequency assignments to include methylsulfonyl groups and the 670 cm^{-1} region. Onodera *et al.*[6] examined the 900–800 cm^{-1} region in the i.r. spectra of a number of sulfonic esters of monosaccharides, and reported a characteristic difference in this region between axial and equatorial sulfonyloxy groups; an axial sulfonyloxy group showed a strong absorption band at 890–880 cm^{-1}, whereas equatorial sulfonyloxy groups absorbed at 850–840 cm^{-1}. Precedents for the finding[6] that configurational differences may be correlated with i.r. absorption bands can be cited[7,8]; in sugars in the pyranoid form, i.r. bands in the regions 845–810 and 900–890 cm^{-1} were respectively assigned[7] to equatorial and axial C-1–H group vibrations. From an examination of a number of sulfated polysaccharides, Orr[8] assigned bands at 825 and 855 cm^{-1} to C–O–S stretching in sulfate groups attached equatorially and axially, respectively. This assignment[8] found support in studies of carrageenan[9,10], of isomeric chondroitin sulfates[11], and of monosaccharide sulfates[12]. However, later work on sulfuric esters of carrageenan[13] and monosaccharides[14,15] showed that Orr's assignments[8] of i.r. bands in the 900–800 cm^{-1} region on the basis of axial or equatorial disposition were invalid. We have concluded[16], based on the following evidence, that the premise of Onodera *et al.*[6] is also not valid.

The frequencies due to sulfonate groups in compounds that we prepared are shown in Table I. These compounds have the D-*gluco*, D-*manno*, D-*galacto*, and D-*xylo* configurations. All of these compounds gave n.m.r. spectra consistent with the $^4C_1$(D) conformation, so that the axial or equatorial disposition of substituents can be stated

*Dedicated to Professor Dexter French on the occasion of his 60th birthday.
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TABLE I

ABSORPTION FREQUENCIES OF THE SULFONIC ESTERS OF SOME ALDOSE DERIVATIVES IN THE 900–800 cm^{-1} REGION

Compound No.	*Name*	*Absorption bands*[a] *(cm^{-1})*			
1	Methyl 3,4-di-*O*-methyl-2,6-di-*O*-(methylsulfonyl)-α-D-glucopyranoside		815s	847s	873m
2	Methyl 3,4,6-tri-*O*-methyl-2-*O*-(methylsulfonyl)-α-D-glucopyranoside			850s	863s
3	Methyl 2,4-di-*O*-(methylsulfonyl)-α-D-xylopyranoside			841s	
4	Methyl 2,3-di-*O*-(methylsulfonyl)-α-D-mannopyranoside		820m	834s	867s
5	Methyl 4,6-di-*O*-methyl-2,3-di-*O*-(methylsulfonyl)-α-D-mannopyranoside			849s	867s
6	Methyl 4-*O*-methyl-2,3,6-tri-*O*-(methylsulfonyl)-α-D-mannopyranoside		825m	849s	867s
7	Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(methylsulfonyl)-α-D-galactopyranoside			849w	
8	Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-(methylsulfonyl)-α-D-glucopyranoside	818m	832m	845w	885w
9	Methyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-(methylsulfonyl)-α-D-galactopyranoside		811m	831vw	850m
10	Methyl 3,4-di-*O*-methyl-2,6-di-*O*-(methylsulfonyl)-α-D-galactopyranoside		830s	852s	864s
11	Methyl 4,6-dichloro-4,6-dideoxy-2,3-di-*O*-*p*-tolylsulfonyl-α-D-galactopyranoside		815m	848s	872m
12	Methyl 2,3-di-*O*-benzyl-6-*O*-(methylsulfonyl)-α-D-galactopyranoside		825s		883m
13	Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-(methylsulfonyl)-α-D-galactopyranoside			833s	
14	Methyl 6-deoxy-2-*O*-(methylsulfonyl)-α-D-glucopyranoside			833m	869s
15	Methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside		813m	840w	862s

[a]Key: m = moderate, s = strong, v = very, and w = weak.

positively. Compounds **1–3** and **11** showed strong i.r. absorption bands in the 850–840 cm^{-1} region, as expected[6] for equatorial sulfonyloxy groups, but the weak absorption[6] at 890–880 cm^{-1} was absent. These compounds have a methanesulfonate group at C-2, but other compounds (such as **10**, **14**, and **15**) that have the same equatorial substituent at C-2 do not absorb in the 850–840 cm^{-1} region. In fact, other than compounds **1–3** and **11**, none of the compounds we have examined show i.r. bands in accord with the findings of Onodera *et al.*[6]. Indeed, compounds **4** and **13** show no bands whatsoever in the regions 850–840 and 890–880 cm^{-1}.

All of the compounds that we examined showed weak bands near 670 and 1600 cm^{-1}, and strong bands in the regions 1380–1330 and 1197–1163 cm^{-1}. The phase used (Nujol, chloroform, or potassium bromide) for measurement of our i.r. spectra did not affect the absorption bands in the 900–800 cm^{-1} region, in agreement with the observations of Onodera *et al.*[6].

Our measurements of i.r. bands in the 900–800 cm^{-1} region for sulfonic esters show variability due to factors other than configurational difference. The variability of the absorption frequency in this region for small differences in structure has been noted previously in authoritative reviews[17,18], and is advantageous for identification of compounds. Reliable evidence for the disposition of sulfonyloxy groups must depend on conformational analysis[19] of these carbohydrate esters by methods other than that of i.r.-spectral examination of the 900–800 cm^{-1} region.

EXPERIMENTAL

Infrared spectra were recorded with a Beckman* IR9 instrument; this is an automatic recording, double-beam, infrared spectrophotometer equipped with a grating. The i.r. spectra of the sulfonic esters were measured for chloroform solutions, potassium bromide pellets, and Nujol mulls, and frequencies were measured to an accuracy of within ± 2 cm^{-1}. The instrument was calibrated by use of the infrared spectrum of polystyrene.

Proton magnetic resonance spectra were recorded at 100 MHz with a Varian HA-100 spectrometer operating in the frequency-sweep mode, with tetramethylsilane as the internal reference.

The following known compounds were examined: methyl 3,4-di-*O*-methyl-2,6-di-*O*-(methylsulfonyl)-α-D-glucopyranoside[20] (**1**), methyl 3,4,6-tri-*O*-methyl-2-*O*-(methylsulfonyl)-α-D-glucopyranoside[20] (**2**), methyl 2,4-di-*O*-(methylsulfonyl)-α-D-xylopyranoside[21] (**3**), methyl 2,3-di-*O*-(methylsulfonyl)-α-D-mannopyranoside[22] (**4**), methyl 4,6-di-*O*-methyl-2,3-di-*O*-(methylsulfonyl)-α-D-mannopyranoside[23] (**5**), methyl 4-*O*-methyl-2,3,6-tri-*O*-(methylsulfonyl)-α-D-mannopyranoside[23] (**6**), methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(methylsulfonyl)-α-D-galactopyranoside[24] (**7**), methyl 2,3-di-*O*-benzyl-4,6-di-*O*-(methylsulfonyl)-α-D-glucopyranoside[25] (**8**), methyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-(methylsulfonyl)-α-D-galactopyranoside[26] (**9**), methyl 3,4-di-*O*-methyl-2,6-di-*O*-(methylsulfonyl)-α-D-galactopyranoside[23] (**10**), and methyl 4,6-dichloro-4,6-dideoxy-2,3-di-*O*-*p*-tolylsulfonyl-α-D-galactopyranoside[27] (**11**), as well as methyl 2,3-di-*O*-benzyl-6-*O*-(methylsulfonyl)-α-D-galactopyranoside (**12**), m.p. 100–102°, $[\alpha]_D^{29}$ +46.1° (*c* 1, chloroform), and methyl 2,3-di-*O*-benzyl-4,6-di-*O*-(methylsulfonyl)-α-D-galactopyranoside (**13**), a syrup, $[\alpha]_D^{29}$ +59.0° (*c* 1.9, chloroform), which were prepared by methanesulfonylation of methyl 2,3-di-*O*-benzyl-α-D-galactopyranoside[28] by using conventional procedures[23]. Similarly, methyl 6-deoxy-2-*O*-

*Reference to a brand or firm name does not constitute endorsement by the U.S. Department of the Army over others of a similar nature not mentioned.

(methylsulfonyl)-α-D-glucopyranoside (**14**), m.p. 155°, $[\alpha]_D^{28}$ +109° (*c* 2.4, ethanol) was prepared by methanesulfonylation[23] of methyl 6-deoxy-α-D-glucopyranoside[29]. Methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside (**15**), m.p. 219–221°, $[\alpha]_D^{24}$ +51° (*c* 2.3, chloroform) was obtained by benzoylation of methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside[30].

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