INTRODUCTION

Absorption peaks in the 730–960 cm⁻¹ region in the infrared spectra of pyranoid sugar derivatives have been correlated with various stereochemical features in the molecule. Axial and equatorial orientations of substituents at the anomeric carbon atom on the pyranose ring have been studied extensively by infrared spectroscopy. Infrared spectroscopic analysis has also been applied to study of the disposition of sulfite ester groups at positions other than C-1 on the aldopyranose ring. Orr reported infrared spectroscopic studies of some sulfated polysaccharides of biological interest. Lloyd and co-workers have reported on various carbohydrate sulfate esters, with particular discussion of the C–O–S vibration. They suggested that the absorption in the 820–850 cm⁻¹ region could be assigned to the C–O–S vibration mode of the C–O–SO₃⁻ group, citing Guthrie and Spedding’s work that sulfonic ester groups on the pyranose ring of monosaccharides do not absorb in the corresponding region. However, this work dealt only with compounds which involved both sulfonic and nitric ester groups in the same molecule. The same observation was reported by Anderson et al. As a matter of fact, the C–O–N vibration seems to show absorption similar to that of the C–O–S vibration in the 800–900 cm⁻¹ region. These absorption peaks are generally weak and are sometimes absent altogether. Derivatives which show a typical difference of infrared absorption peak depending upon the axial or equatorial orientation of a substituent on the pyranose ring would be of interest.

The present paper is concerned with the orientation of the C–O–SO₂⁻R group (R = benzyl or alkyl group) at C-2, C-3, C-4, and C-6 of the pyranose ring of monosaccharides as revealed by study of the 800–900 cm⁻¹ region in the infrared spectra of the sulfonic esters of carbohydrates. The analysis shows a characteristic difference in this spectral region between sulfonyloxy groups oriented axially and those oriented equatorially.

*Part of this work was presented at the International Symposium on the Chemistry of Natural Products held at Kyoto, Japan, from April 12 to 18, 1964.
EXPERIMENTAL

General

Infrared spectra were measured with a Shimadzu AR-6 spectrophotometer (sodium chloride optics). All compounds were examined as pressed discs in potassium bromide. All melting points are uncorrected.

Methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-3-O-(methylsulfonyl)-α-D-allopyranoside (I)

Methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-allopyranoside (I') was prepared by the method of Jeanloz, m.p. 207°, [α]D +65° (c 1.0, chloroform). The derivative (0.3 g) was dissolved in anhydrous pyridine (10 ml) in a 50-ml flask fitted with a calcium chloride tube. The solution was cooled to 0°, and a solution of methanesulfonyl chloride (0.2 ml) in anhydrous pyridine (5 ml) was added at 0°. After standing for 2 days at 0°, the mixture was poured on to cracked ice. The solution was extracted three times with 20-ml portions of chloroform. The chloroform layer was washed with water, saturated sodium hydrogen carbonate solution, water, 3 N hydrochloric acid, and water, dried (anhydrous sodium sulfate), and evaporated under reduced pressure to dryness. The residue was dissolved in the minimum volume of acetone; addition of petroleum ether (b.p. 40-60°) produced crystals; yield 0.3 g, m.p. 176°, [α]D +37° (c 1.0, chloroform).

Anal. Calc. for C17H23NO7S: C, 50.86; H, 5.77; N, 3.49; S, 7.98. Found: C, 51.13; H, 5.64; N, 3.22; S, 7.92.

Methyl 2-acetamido-2-deoxy-3-O-(methylsulfonyl)-α-D-allopyranoside (II)

Compound I (0.2 g) was treated by the procedure described by Jeanloz to give methyl 2-acetamido-2-deoxy-3-O-(methylsulfonyl)-α-D-allopyranoside (II) as an amorphous powder; yield 0.1 g. [α]D +54° (c 0.5, water).


The other sulfonic esters of the hexopyranoses were prepared according to methods given in the references. Details of the spectra of these derivatives are shown in Fig. 1 and Table 1.

RESULTS AND DISCUSSION

C–O–S Vibration

As shown in Fig. 1 and Table 1, the spectra of all the sulfonic esters of hexopyranoses examined exhibited two strong absorptions at 1,170–1,190 cm⁻¹ and at 1,350–1,370 cm⁻¹, due to the symmetrical and asymmetrical stretching vibrations of the –SO₂– group. They also showed a series of absorptions in the 700–900 cm⁻¹ region, where the parent compounds show only slight or no absorption. It seems difficult and unfruitful to analyze the bands at wavenumbers shorter
than 800 cm$^{-1}$, because of the strong contributions from many kinds of vibration modes, including those due to the pyranose ring of monosaccharides, the phenyl group, and other substituents. However, the appearance in all the spectra of a single band in the 840–890 cm$^{-1}$ region is notable.

![Infrared spectra of the methanesulfonates of methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-allopyranoside and -glucopyranoside in the 600–1,600 cm$^{-1}$ region. I, Methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-3-O-(methylsulfonyl)-α-D-allopyranoside (see Experimental); I', methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-allopyranoside (see Experimental); III, methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-3-O-(methylsulfonyl)-α-D-glucopyranoside$^6$, m.p. 208$^\circ$; III', methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside$^6$, m.p. 255$^\circ$. Details of the absorption frequencies of the C–O–S vibration are described in the text.

The assignment of this absorption is considered to be the C–O–SO$_2$–R group; this is further divided into C–O–S, C–S, C–R, and S=O vibration modes, since the parent compounds show no absorption in the region mentioned above. A study of the published spectra of other organic compounds reveals that the C–S stretching vibration is mainly assigned to absorption at wavenumbers shorter than 800 cm$^{-1}$ and that the C–H out-of-plane vibrations of monosubstituted and 1,4-disubstituted benzene rings are near 720–780 cm$^{-1}$ and 820 cm$^{-1}$, respectively. The absorption frequency of the band in the 840–890 cm$^{-1}$ region was unchanged with variations in the kind of hexopyranos- in the kind and position of the sulfon- yloxy group on the pyranose ring, and in the kind of phase used for measurement of the spectra.

These facts exclude the possibility of assigning both the C–H vibration of the pyranose ring and the C–S and CH$_3$ vibrations of the substituents on the benzene ring to this absorption, but permit assignment of the absorption to the C–O–S vibration. The assignment is supported by the infrared spectroscopic observations.
### INFRARED SPECTRA OF SULFONIC ESTERS

**TABLE I**

ABSORPTION FREQUENCIES OF THE SULFONIC ESTERS OF SOME HEXOPYRANOSE DERIVATIVES IN THE 800–900 cm⁻¹ REGION

<table>
<thead>
<tr>
<th>Compounda</th>
<th>Absorption peaksb (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>835 w 855 w 890 vs</td>
</tr>
<tr>
<td>IV</td>
<td>860 vs 890e vw</td>
</tr>
<tr>
<td>V</td>
<td>850 vs 880 w</td>
</tr>
<tr>
<td>VI</td>
<td>840c m 860 s 890 vw</td>
</tr>
<tr>
<td>VII</td>
<td></td>
</tr>
<tr>
<td>VIII</td>
<td>820 m 850e s 860 vs 880 w</td>
</tr>
<tr>
<td>IX</td>
<td>820 s 855 vs 880 vw</td>
</tr>
<tr>
<td>X</td>
<td>840 s 850 vs 880 vw 890e w</td>
</tr>
<tr>
<td>XI</td>
<td>813 w 840 vs 855 w 880 w</td>
</tr>
<tr>
<td>XII</td>
<td></td>
</tr>
<tr>
<td>XIII</td>
<td>820 s 840 s 865 w 880 w  895 vw</td>
</tr>
<tr>
<td>XIV</td>
<td>840 s 865 w 880 w 895 vw</td>
</tr>
<tr>
<td>XV</td>
<td></td>
</tr>
<tr>
<td>XVI</td>
<td>820 m 840 s 880 w</td>
</tr>
<tr>
<td>XVII</td>
<td>840 vs 880 w</td>
</tr>
</tbody>
</table>

aII, see Experimental; IV, m.p. 186°, prepared by removal of the benzylidene group from III; V, m.p. 80–84°; VII, m.p. 96–98°; VIII, m.p. 192°; IX, m.p. 135°; X, m.p. 91°; XI, m.p. 124°; XII, m.p. 195°; XIII, m.p. 200°; XIV, m.p. 186°; XV, m.p. 143–146°, prepared by the p-toluenesulfonation and acetylation of 2-benzamido-2-deoxy-D-glucopyranose, m.p. 166–199° according to the usual procedure; XV, m.p. 90°, prepared by the benzylsulfonation of 2-acetamido-4,6-O-benzylidene-2-deoxy-D-glucopyranose m.p. 230°; XVI, m.p. 120°, prepared by the p-toluenesulfonation of 2-acetamido-1,3-di-O-acetyl-2-deoxy-D-glucopyranose; XVII, m.p. 171°, prepared by the methanesulfonation of 2-acetamido-1,3-di-O-acetyl-2-deoxy-6-O-trityl-D-glucopyranose, m.p. 105–107°, which was prepared by the tritylation of 2-acetamido-1,3-di-O-acetyl-2-deoxy-D-glucopyranose; XVII, m.p. 171°, prepared by the methanesulfonation of 2-acetamido-1,3-di-O-acetyl-2-deoxy-6-O-trityl-D-glucopyranose.
bm = moderate; s = strong; v = very; w = weak.
cshoulder.

*Carbohydrate Res.*, 1 (1965) 208–213
on sulfates of monosaccharides$^8$, alkylsulfuric esters$^5$, and some sulfonic esters of cyclohexanol$^{14}$.

From these data, the characteristic absorption band in the 840–890 cm$^{-1}$ region is tentatively assigned to the C–O–S vibration mode of the C–O–SO$_2$–R group in the pyranose ring, but it is open to confirmation by study of types of sulfonic esters other than those of the pyranoses.

**On the shift in the absorption frequency of the C–O–S vibration**

According to Mills$^{12}$, the stable conformation of 4,6-O-benzylidene-D-glucopyranose is a rigid, fused-ring structure of the trans-decalin type. Therefore, it is believed that compound I, methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-3-O-(methylsulfonyl)-a-D-glucopyranoside (III), and their unbzylidenated parents (II and IV) have similar stable conformations. The orientation of the sulfonyloxy group of compound I is axial on the pyranose ring, whereas that of compound III is equatorial. There is no gross difference between the n.m.r. spectra of compounds I and III. Especially, no difference was observed in the chemical shift of the proton signal of the S–CH$_3$ group of the two compounds. This indicates that the n.m.r. spectra are not useful for determining the spatial orientation of methylsulfonyloxy groups on the pyranose ring of monosaccharides. On the other hand, a marked difference was observed in the absorption frequencies of the C–O–S vibration in the infrared spectra of the two compounds, as shown in Fig. 1. Compound I, having an axial sulfonyloxy group, shows a strong absorption band at 880 cm$^{-1}$ and a very weak one at 850 cm$^{-1}$, whereas compound III, having an equatorial sulfonyloxy group, shows a strong absorption at 850 cm$^{-1}$ and a very weak one at 880 cm$^{-1}$. This difference remained unchanged with variation in the phase used for the measurement (potassium bromide, chloroform, and Nujol). The same difference in the infrared spectra was observed to exist between the 3-methanesulfonates (II and IV) of methyl 2-acetamido-2-deoxy-a-propylpyranoside and -glucopyranoside. All other sulfonic esters disposed equatorially on the pyranose ring of monosaccharides showed the characteristic absorption band of the C–O–S vibration at 845 ± 5 cm$^{-1}$, as shown in Table I. These results suggest that the observed shift in frequency is associated only with the difference in the spatial orientation of the sulfonyloxy group on the pyranose ring, as suggested earlier for the sulfates of carbohydrates$^2$. For confirmation, the axial sulfonyloxy group at C-2 and C-4 of the pyranose ring should be studied.

From these results, it is concluded that axial sulfonyloxy groups on pyranose rings show a strong absorption band at 880–890 cm$^{-1}$ and a weak absorption band at 840–850 cm$^{-1}$, and that equatorial sulfonyloxy groups on the pyranose ring show a strong absorption band at 840–850 cm$^{-1}$ and a weak one at 880–890 cm$^{-1}$. When the characteristic absorption bands of the sulfates are compared with those of the sulfonic esters in the 800–900 cm$^{-1}$ region, it is observed that the bands of the former lie at lower wavenumbers (by about 10–40 cm$^{-1}$).

Infrared spectroscopic analysis of sulfonyloxy groups might be especially...
useful for the conformational determination of oligo- and poly-saccharides of biological interest.

ACKNOWLEDGMENT

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SUMMARY

The orientation of sulfonloxy groups at different carbon atoms of the pyranose ring of monosaccharides has been examined by analysis of infrared spectra in the 800–900 cm⁻¹ region, with particular reference to axial and equatorial orientations of the sulfonloxy groups. Axial sulfonloxy groups show a strong absorption band at 880–890 cm⁻¹, whereas equatorial ones absorb at 840–850 cm⁻¹. The absorption frequency is not affected by variations in the kind of hexopyranose, by the kind and position of the sulfonloxy groups on the pyranose ring, or by the kind of phase used for the measurement.

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