

CHIROPTICAL STUDIES ON 5-THIO-, 1,5-DITHIO-D-GLYCOPYRANOSIDES
AND EXTENSION OF RING OXYGEN HELICITY RULE TO RING SULPHUR

Hiroshi Meguro, Emiri Ohtaki and Katura Tuzimura
Department of Food Chemistry, Faculty of Agriculture,
Tohoku University, Amamiyamachi-Tsutsumidori, Sendai, Japan

N.A. Hughes
School of Chemistry, The University of Newcastle upon Tyne,
Newcastle upon Tyne, NE1 7RU, U.K.

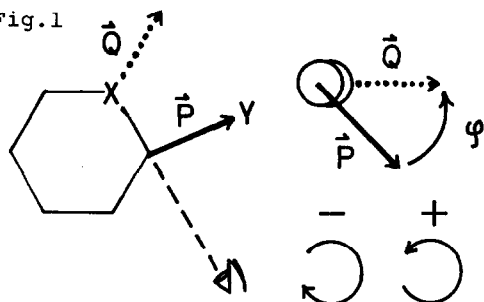
Leslie Hough
Department of Chemistry, Queen Elizabeth College (University of
London), Campden Hill Road, London W8 7AH, U.K.

Previously we reported CD and ORD studies of 1-thio-D-pyranosides¹ and 1-thio-D-furanosides.² These compounds show a strong CD band in the region 140-180 nm, the sign and magnitude of which is associated with the anomeric configurations and conformations of the compounds. The substitution, in these compounds, of sulphur for the glycosidic oxygen enabled the bands due to the glycosidic and ring heteroatoms to be distinguished and above band at 140-180 nm was thus identified as being the second band (Band C) of the ring oxygen atom. The results also led us to propose a ring oxygen helicity rule by which the anomeric configuration and conformation of a 1-thio-D-glycoside can be deduced from the sign and rotational strength of this band¹ (Fig. 1).

These studies have now been extended to include D-pyranosides in which either both glycosidic and ring oxygen atoms have been replaced by sulphur as in the 1,5-dithio-D-pyranosides (I) and (II) or only the ring oxygen atom has been replaced by sulphur as in the 5-thio-D-pyranosides (III)-(VI); the unsubstituted D-pyranosides (VII) and (VIII) were also included for purposes of comparison (Figs. 2 and 3).

The experiments were almost the same as those in the previous reports.^{1,2} The CD bands in the wavelength region 200-300 nm were recorded and the possible

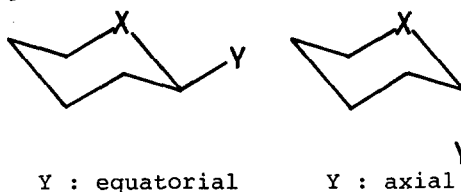
Fig.1



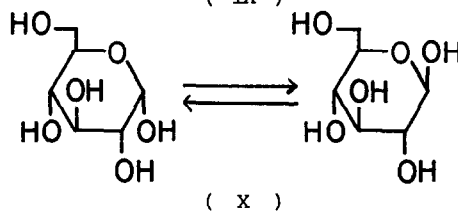
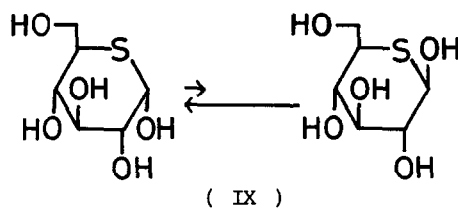
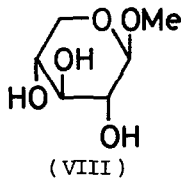
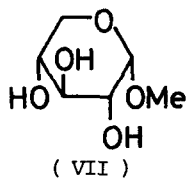
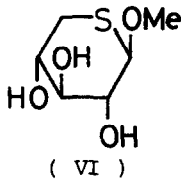
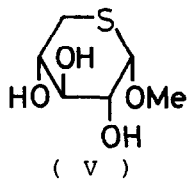
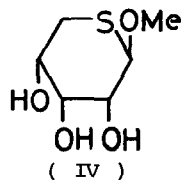
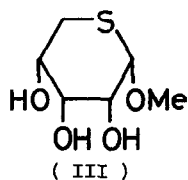
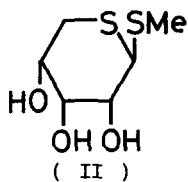
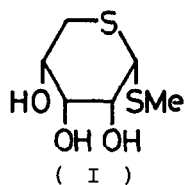
\vec{P} : Direction of glycosidic bond
 \vec{Q} : Direction of permanent dipole moment of the ring heteroatom
 φ : Dihedral angle between \vec{P} and \vec{Q} ⁴⁾

Ring Heteroatom Helicity Rule

Fig.2



X=S Y=S 1,5-Dithio-D-pyranosides
 X=S Y=O 5-Thio-D-pyranosides
 X=O Y=S 1-Thio-D-pyranosides
 X=O Y=O D-Pyranosides



- (I) Methyl 1,5-dithio- α -D-ribofuranoside⁶⁾
 (II) Methyl 1,5-dithio- β -D-ribofuranoside⁶⁾
 (III) Methyl 5-thio- α -D-ribofuranoside⁷⁾
 (IV) Methyl 5-thio- β -D-ribofuranoside⁷⁾
 (V) Methyl 5-thio- α -D-xylofuranoside⁸⁾
 (VI) Methyl 5-thio- β -D-xylofuranoside⁸⁾
 (VII) Methyl α -D-xylofuranoside
 (VIII) Methyl β -D-xylofuranoside
 (IX) 5-Thio-D-glucose
 (X) D-Glucose

Fig.3 Structures of Compounds

Table Chiroptical data for aqueous solutions of some D-glycopyranosides and related 5-thio- and 1,5-dithio-analogues.

Comp.	Anom. Config.	Ring Heteroatom	Glycosidic Heteroatom	Band C ^a			[M] _D	kc/[M] _D x10 ⁻⁵
				λ _c (nm)	Sign	kc x10 ⁻⁸		
I	α	S	S	180	+	1.22	+411	2.97
II	β	S	S	170	-	0.49	-156	3.14
III	α	S	O	190	+	1.75	+575	3.04
IV	β	S	O	180	-	1.03	-359	2.87
V	α	S	O	190	+	1.90	+620	3.06
VI	β	S	O	180	-	0.40 ^b	-126	3.17
VII	α	O	O	150	+	0.72	+257	2.81
VIII	β	O	O	150	-	0.30	-105	2.83
IX	α↔β	S	O	190	+	1.16	+383	3.03
X	α⇌β	O	O	150	+	0.28	+ 93	3.01

a : Calculated by the one-term Drude equation. b : Calculated by the two-term Drude equation. ORD measurements : On a Jasco ORD/UV-5, 1 cm cell, about 1-5 mg/ml in comp.(I)-(IX) and about 40 mg/ml in comp.(X). [M]_D measurements : On a Jasco ORD/UV-5, 1 cm cell, about 10-40 mg/ml.

bands below 200 nm were calculated by the one-term or two-term Drude equations using the ORD data from the 300-600 nm region.² Weak CD maxima due to the first thioether band were found around 210-250 nm (Band A).³ The above calculations using the Drude equations indicate the presence of strong bands in the region 170-190 nm for the ring sulphur compounds (I)-(VI) and around 150 nm for the ring oxygen compounds (VII) and (VIII). These wavelengths are consistent with these maxima being the second band (Band C) associated with the ring heteroatom. The significant points can be summarised as follows (see also Table).

1) The sign of Band C is determined by the anomeric configuration: positive for α-anomers and negative for β-anomers.

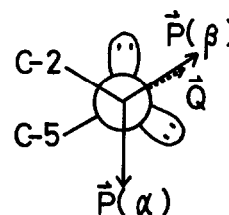
2) The magnitude of Band C is related to the anomeric conformation: assuming that compounds (I)-(VIII) adopt the ⁴C₁ conformation then axial glycosidic substituents give strong bands and equatorial glycosidic substituents give weak bands.

3) The rotational strength or magnitude of Band C is also proportional to the magnitude of $[M]_D$; the ratios of $kc/[M]_D$ are in the region $2.81-3.17 \times 10^5$.

These findings are consistent with the earlier results¹ from 1-thio- \underline{D} -pyranosides. They support our previous hypothesis that Band C is the second CD band of the ring heteroatom and is not associated with those of the glycosidic heteroatom. The bands are located at 20-40 nm higher wavelengths (170-190 nm) when the ring heteroatom is sulphur than when it is oxygen (150 nm). It also appears that the ring oxygen helicity rule can be extended to include ring sulphur compounds and may well be general for any ring heteroatom. Consideration of the signs, the ratios of $kc/[M]_D$, and the calculated wavelengths of Band C in the free sugars (IX) and (X) also suggest that the rule can be extended to free sugars as well as glycosides.

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3. The signs of Band A are not directly associated with the anomeric configurations and will be discussed elsewhere.
4. In β -pyranosides φ is about 0° according to the ideal tetrahedral Dreiding models, however the deformation of the ring by 1,3 diaxial repulsion⁵ suggest that φ should be small negative (-5° under assumption from the calculation using cyclohexane).
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