CHIROPTICAL STUDIES ON 1-THIO-D-GLYCOPYRANOSIDES

AND A PROPOSAL OF RING OXYGEN HELICITY RULE

Emiri Ohtaki, Hiroshi Meguro and Katura Tuzimura

Department of Food Chemistry, Faculty of Agriculture, Tohoku

University, Amamiyamachi-Tsutsumidori, Sendai, Japan

Previously[1] we reported ORD and CD of some 1-thio-D-glycofuranosides as model compounds of D-glycofuranosides. There it was revealed that the second band of the ring oxygen (140-170 nm) should be the most important in determining anomeric configurations and that the rotational strengths of the bands were almost proportional to the molecular rotations at 589 nm. Here we report the ORD and CD of 1-thio-D-glycopyranosides in order to compare those of the pyranosides with those of the furanosides.

Six compounds (I)-(VI) in Fig.1 were studied by the same methods as those of the 1-thio-D-glycofuranosides. Thus the CD gave the maximum around 230 nm (Band A) and plain increase or decrease curves around 200 nm suggesting the signs of the nearest CD maximum (Band B). The graphic methods of the one term and the two term Drude equations[2] showed negligible small rotational strengths of Band B in 180-200 nm wavelength region and very large rotational strengths of Band C in 150-180 nm. The wavelengths of the Cotton effects, the signs and the rotational strengths (k or [θ]) of Bands A,B and C are shown in the Table together with the anomeric configurations and conformations. The ratios between the rotational strengths of Band C (kc) and the molecular rotations $[M]_D$ are also shown.

The PMR of these compounds are also studied to determine their conformations in $D_2O$. The chemical shifts of the anomeric protons (δ) were

about 5.4 ppm for α anomers ((I) and (II)), about 4.5 ppm for β anomers ((III)-
(VI)). The coupling constants between 1-H and 2-H were about 5.3 cps for α
anomers, about 9.0 cps for β anomers. The coupling constant between 2-H and 3-H
of (I) was about 10.2 cps. These PMR results, together with the possible
similarities of the conformations with the D-glycopyranosides,[3] suggest the
$^4C_1$ chair conformations for (I)-(VI). It shows that the glycosidic thioalkyl
groups take axial conformations when the anomeric configurations are α and take
equatorial conformations when they are β. It should be added that in the 1-thio
-D-glycofuranosides the anomeric substituents could take quasi-axial, isoclinal
or quasi-equatorial positions although it was difficult to determine by PMR.

The results obtained in the pyranosides were fundamentally the same as
those in the furanosides and summarized as follows.

(1) The signs of Band C were associated with the anomeric configurations. Thus
α configurations gave positive signs and β configurations gave negative signs.

(2) Band C was assumed as the second band of the ring oxygen. The band showed
red shifts from the wavelength region between 140-160 nm in (III)-(VI) which
have equatorial anomeric substituents, to 180 nm in (I) and (II) which have
those of axial conformation.[4]

(3) The rotational strengths of Band C (kc) increased according to the order of
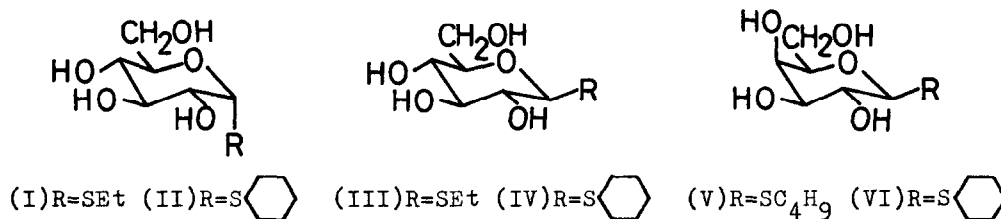equatorial, quasi-equatorial, isoclinal or quasi-axial and axial conformations



(I)R=SEt (II)R=S⟨⟩   (III)R=SEt (IV)R=S⟨⟩   (V)R=SC$_4$H$_9$ (VI)R=S⟨⟩

Fig.1  (I) Ethyl 1-thio-α-D-glucopyranoside[5], (II) Cyclohexyl 1-thio-α-D-
glucopyranoside[5], (III) Ethyl 1-thio-β-D-glucopyranoside[6], (IV) Cyclohexyl
1-thio-β-D-glucopyranoside [6], (V) n-Butyl 1-thio-β-D-galactopyranoside[6] and
(VI) Cyclohexyl 1-thio-β-D-galactopyranoside[6]

Table   Chiroptical data of 1-thio-$\underline{D}$-glycopyranosides

| Comp. | Anomeric Config.& Conform. | Solv. | Band A | | | Band B | | Band C | | | | $[M]_D$ | $kc/[M]_D$ $\times 10^{-5}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $\lambda_{max}$ (nm) | Sign | $[\theta]$ $\times 10^{-3}$ | $\lambda_{max}$ (nm) | Sign | $\lambda_{max}$ (nm) | Sign | kc $\times 10^{-8}$ | $[\theta c]$ $\times 10^{-3}$ | | |
| I | $\alpha$ (ax) | W | 218 | + | 4 | 200 | − | 180 | + | 2.03 | 66 | +610 | 3.32 |
| | | M | 224 | + | 4 | 200 | − | 180 | + | 2.18 | 71 | | |
| II | $\alpha$ (ax) | W | 219 | + | 6 | 196 | − | 180 | + | 1.92 | 63 | +626 | 3.06 |
| III | $\beta$ (eq) | W | 217 | + | 2 | 200 | + | 140 | − | 0.44 | 18 | −134 | 3.28 |
| | | M | 224 | + | 2 | 200 | + | 150 | − | 0.44 | 17 | | |
| IV | $\beta$ (eq) | W | 219 | + | 3 | 200 | + | 160 | − | 0.52 | 19 | −175 | 2.97 |
| V | $\beta$ (eq) | W | 220 | + | 2 | 200 | + | 140 | − | 0.25 | 10 | − 70 | 3.57 |
| VI | $\beta$ (eq) | W | 219 | + | 3 | 200 | + | 150 | − | 0.40 | 15 | −109 | 3.66 |

Solvent(W:Water,M:Methanol). CD,$[M]_D$ and ORD measurements, kc and $[\theta c]$: These
details are the same as in previous work[1].

which relatively corresponded to the order of $\beta$-pyranosides (0.25-0.44), $\beta$ or
$\alpha$-furanosides (0.41-1.25) and $\alpha$-pyranosides (1.92-2.18).
(4) The kc were proportional to the corresponding $[M]_D$ and the ratio between
the two $kc/[M]_D$ were about 2.9-3.6 X $10^5$ which were almost the same as those
in 1-thio-$\underline{D}$-glycofuranosides (3.0-3.8 X $10^5$)[1]. It strongly suggests that the
rotational contribution of the anomeric part of the molecule in Hudson's iso-
rotation rule might be interpreted as the contributions from Band C.
(5) Band A gave the same positive signs for (I)-(VI) suggesting the signs
should be independent of the anomeric configurations. Band B seemed to be
associated with the anomeric configurations but the signs were opposite to
those of Band C. These two bands will be discussed elsewhere.

In conclusion we propose a ring oxygen helicity rule in order to express
the relation between Band C and the anomeric configurations and conformations
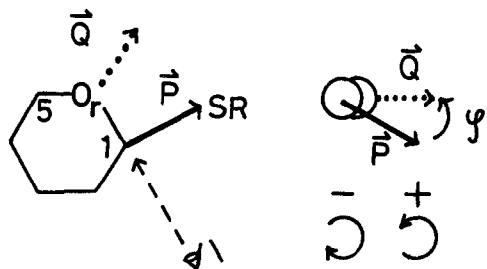using a helical projection of the two vectors $\vec{P}$ and $\vec{Q}$ (Fig.2).

Fig. 2

Here $\vec{P}$ is a vector which has the direction from C-1 to S along the glycosidic bond and $\vec{Q}$ is a vector which has the same direction as that of the permanent dipole of the ring oxygen. The projection is made from the C-1 to the ring oxygen along the C-O bond. When $\vec{P}$ and $\vec{Q}$ are clockwise, the configuration is β and the sign is negative. When $\vec{P}$ and $\vec{Q}$ are anticlockwise, the configuration is α and the sign is positive. The rotational strength increases with the increase of the dihedral angle $\varphi$ between $\vec{P}$ and $\vec{Q}$ from $0°$ to $120°$ or from equatorial to axial. It might be used for the anomeric configuration and conformation analysis of these compounds.

We thank Prof. L.Hough and Dr. A.C.Richardson for reading and correcting the manuscript.

<div align="center">References</div>

1) Preceding paper

2) E.Iizuka and J.T.Yang, Biochem.,$\underline{3}$,1519 (1964)

3) R.J.Yu and C.T.Bishop, Can.J.Chem.,$\underline{45}$,2195 (1967)

4) In (I) and (II) Band C at 180 nm were assumed as the red shift of the second band of C-O which is usually found at 160 nm based on the disappearence of the corresponding band at 160 nm and the opposite signs of Bands B.

5) E.Pacsu and E.J.Wilson,Jr., J.Am.Chem.Soc.,$\underline{61}$,1450 (1939)

6) B.Helferich and D.Türk, Chem.Ber.,$\underline{89}$,2215 (1959)