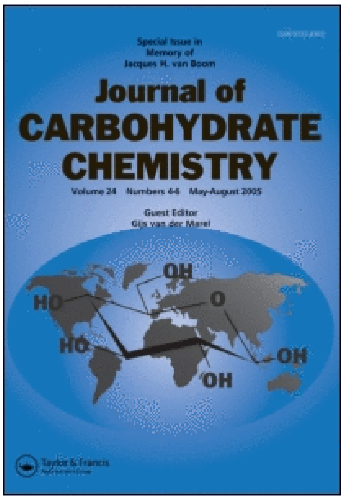

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CALCULATIONS OF COTTON EFFECTS IN THE VACUUM UV REGION IN THE NON-ANOMERIC PART OF PYRANOSES: CORRELATIONS WITH THE ABSOLUTE STEREOCHEMISTRIES

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ABSTRACT

A graphic method of Drude equations was applied to calculate the Cotton effects below 180 nm for a series of 1,5-anhydro-D-alditols I-IX. The calculations, taking the vacuum CD data of Johnson *et al.* into account, gave a Cotton effect at *ca.*140 nm region (Band 2) and a popular band (Band 1) due to the n-σ^* transition at *ca.*180 nm. Band 2, probably due to the σ-electron transition of the C-O or C-C bond, could be correlated with the helical structures of vicinal C-O and C-O bonds (C-O/C-O) and C-O and C-C bonds (C-O/C-C) providing a new additivity rule to calculate intensity (K2) using the vicinal C-O/C-O and C-O/C-C units.

INTRODUCTION

Since C. S. Hudson first proposed his Isorotation Rule,[1] several theoretical and experimental approaches have been reported[2-10] for correlating molecular rotations ($[M]_D$) of carbohydrate molecules with their absolute stereochemistries. However, few studies[11-14] were based on the Cotton effects due to electron transitions which are assumed to be the source of the optical activities. Molecular rotations at a given wavelength, [M](l), can be expressed as the sum of the rotational contributions originating in each of the electronic transitions as follows (Equation 1).

$$[M](\lambda) = \Sigma\ 2[\theta]i\Delta i\lambda i/\sqrt{\pi}(\lambda^2-\lambda i^2) \quad \text{---}\ (1)$$

where $[\theta]i$ is the molecular ellipticity of the CD band at λi nm, Δi is the halfwidth at $1/e$ of the CD peak, and λi is the maximal wavelength. Therefore, for more mechanistic interpretations of the $[M]_D$, it is important to clarify the nature of individual Cotton effects. Although unsubstituted sugars give no CD band in the usually measured region above 200 nm, two alternative methods can be undertaken to estimate the Cotton effect below 200 nm; one is to use a vacuum CD instrument[15-21] which is now accessible near 170 nm in aqueous solution, and the other is to record ORD plain curve in a longer wavelength region.[11-14, 19, 21] In our preceding papers,[11-14] we have applied the latter method to calculate the Cotton effects below 170 nm for a series of 1-thio- and 5-thio-pyranoses. There, we showed that the Cotton effects in the *ca.* 150 nm region associated with a ring oxygen (*-Or-*) governed the $[M]_D$ for both glycopyranosides and glycofuranosides. The result led us to proposing a "Ring Oxygen Helicity Rule"[11-14] as a new interpretation of the rotational contributions at an anomeric position, *i.e.*, A-part in Hudson's Isorotation Rules. In this paper, we applied a similar method for a series of 1-deoxy-D-pyranoses (I-IX, Fig 1) to calculate the Cotton effects below the 200 nm region and correlate them with the absolute stereochemistries in the non-anomeric part of the sugars, *i.e.* B-part in Hudson's Isorotation Rules.

MATERIALS AND METHODS

a) *Model compounds and ORD measurements.*

In order to estimate the rotational contributions from the non-anomeric part of pyranoses we prepared a series of 1- and 1,2-dideoxy-D-pyranoses I-IX and measured their ORD between 300 - 600 nm. They were prepared from the corresponding 1-bromo-per-*O*-acetylated sugars according to the reported methods[18, 22-28] and their physical properties in accord with those reported. ^{13}C and ^{1}H-NMR data (Table 1-4) also supported their structures.

ORD curves in 300-600 nm were measured on a Jasco J-20 spectrometer and calibrated with a sucrose solution ($[\alpha]_{589}$ = +66.47° (c 1, H_2O)). All

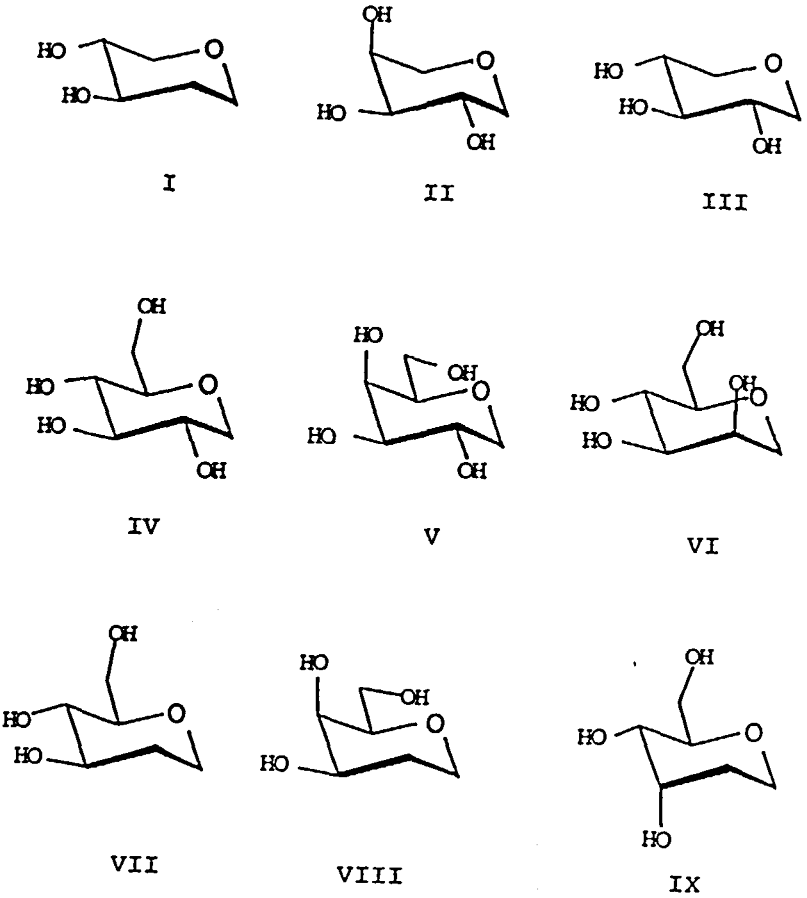


FIG. 1 Structures of Model Compounds I-IX.

measurements were carried out at 21-23 ° C at a concentration of 1 mg/mL. All solvents were purified by distillation before use.

b) *Calculations of Cotton effects below 180 nm.*

A graphic method of Iizuka and Yang[29] was applied to calculate the Cotton effects below 180 nm. The ORD curves in the 300-600 nm region were analyzed first with the Drude one term equation to give a Band C, which was thought to be a *pseudo*-band composed of two bands at *ca.*140 nm and *ca.*180 nm. Therefore, the ORD curves were analyzed next with the Drude two term or three term equation. The calculations were performed in the same manner as previously described[30-32] iteratively using the computerized least-squares minimization. For the compounds IV, VII and VIII, for which vacuum CD data were available in the literature (Bertucci *et al.*[18]), the contributions from the n-σ^* band (Band 1) at ca.180 nm were subtracted from the ORD curve, and the calculation was similarly performed for the modified ORD data.

c) *Conformations of 1,5-anhydro-D-glycitols I-IX in water.*

For the present study, it was crucial to determine the conformational properties of model compounds I-IX in solution. Two factors are important in the conformations; one is the ring conformation and the other is the conformation about the exocylic C5-C6 bond. Both conformational contributions are assumed to have significant effects on the chiroptical property in the non-anomeric part of sugars.

It is presumed that the model compounds I-IX have a stable $^4C_1$ conformation or are in equilibrium with a $^1C_4$ conformation in solution. Empirical free energy calculations by Angyal[33] (Table 1) showed that in all compounds the $^4C_1$ conformation predominated over the $^1C_4$, though compounds I, II, and IX might have a considerable contribution from the $^1C_4$ conformation. The vicinal ^1H-^1H coupling constants data (Table 3) at 400 MHz also showed that all model compounds existed in a stable $^4C_1$ ring conformation in water since they showed large vicinal coupling constants for at least one of H1α/H2β, H2β/H3, H3/H4 and H4/H5α signals.

^{13}C-NMR data (Table 1), particularly the similar chemical shift of C1 among I, VII and VIII, and among II-VI, was consistent with their stable $^4C_1$ ring conformation.

In Table 1, total ^{13}C chemical shifts were compared with the free energy difference (ΔG) between the two ring conformers in the same manner as in the study of Perlin *et al.*[34] These are inherently different parameters but show a parallel change with each other among the stereoisomers I-III, IV-VI and VII-IX; the decrease of the total chemical shifts was accompanied by the decrease of the stability of the $^4C_1$ conformation. This correlation could be explained as follows; shieldings by steric compression in the ^{13}C-NMR and the instability of the ring conformers were both closely related with the unfavorable 1,3-*syn diaxial* interactions between the C-OH

TABLE 1
^{13}C NMR Chemical Shifts (ppm) and Ring Conformations of 1,5-Anhydro-D-Alditols I-IX.

Compounds	C1	C2	C3	C4 (ppm)[a]	C5	C6	Total[d] (ppm)	ΔG ($^4C_1$-$^1C_4$)	Ratio(%)[e] $^4C_1/^1C_4$
(I)	68.4	34.7	73.7[c]	73.1[c]	71.8		321.7	-1.00	84/16
(II)	72.2	69.7[c]	75.3	70.7[c]	71.6		359.5	-1.25	89/11
(III)	72.1	72.0	79.8	72.0	72.1		368.0	-1.70	94/ 6
(IV)	71.4	72.0[c]	80.2	72.4[c]	83.0	63.6	442.6	-4.20	100/ 0
(V)	71.7	69.3[c]	76.7	71.7[c]	82.0	64.0	435.4	-3.50	100/ 0
(VI)	72.5	71.7[c]	76.1	69.9[c]	83.1	63.8	437.1	-3.05	99/ 1
(VII)	68.2	35.8	74.9[c]	74.2[c]	83.0	63.9	400.0	-3.50	100/ 0
(VIII)	68.5	30.7	71.6[c]	70.8[c]	81.9	64.7	388.2	-3.40	100/ 0
(IX)	57.0	34.0	69.2[c]	70.1[c]	78.4	64.0	372.5	-0.90	82 /18

a. Measured at 25 MHz in D_2O solution with internal TPS (3-(trimethylsilyl)-propionic acid d4-sodium salt) standard (0.00 ppm).
b. Assigned by Off-reasonance spectroscopy.
c. Assignments may be reversed.
d. Sum of the chemical shifts (ppm).
e. Calculated with the difference free energy (ΔG) using the following equation
Populations(%)=exp(-G($^4C_1$)/RT)x100/[exp(-G($^4C_1$)/RT)+exp(-G($^1C_4$)/RT)],
where T=298K, R=2.0.

TABLE 2
^1H-NMR Chemical Shifts of 1,5-Anhydrohexitols I-IX in D_2O.

	Chemical Shifts (ppm)[a]									
	H1α	H1β	H2α	H2β	H3	H4	H5α	H5β	H6proR[b]	H6proS[b]
I	3.490	3.920	1.591	2.015	3.644	3.490	3.212	3.941	-	-
II	3.226	3.926	3.841	-	3.651	3.986	3.592	3.826	-	-
III	3.223	3.945	3.581	-	3.389	3.581	3.223	3.945	-	-
IV	3.228	3.985	3.594	-	3.438	3.35	3.35	-	3.682	3.883
V	3.202	4.005	3.833	-	3.58	3.955	3.58	-	3.732	3.701
VI	3.645	3.993	-	3.987	3.662	3.598	3.305	-	3.692	3.902
VII	3.528	3.972	1.633	2.007	3.661	3.27	3.28	-	3.695	3.882
VIII	3.512	4.017	1.722	1.860	3.846	3.830	3.497	-	3.735	3.692
IX	3.77	3.77	1.835	1.928	4.153	3.568	3.69	-	3.69	3.860

a. Measured at 400 MHz using an internal TPS standard (0.000 ppm). Assignments were based on the ^1H-^1H COSY and selective irradiation experiments.
b. Assignments were based on the ^1H-NMR spectra of selectively deuterated analogues for D-glucoses and D-galactoses.[36-39]

TABLE 3

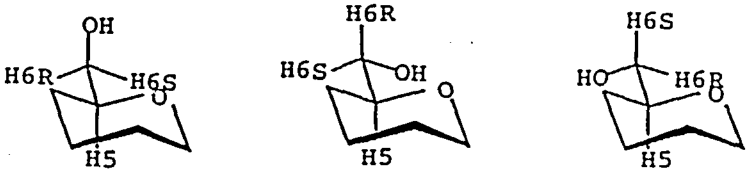
Vicinal ^1H-^1H Coupling Constants of I-IX in D_2O.

	Vicinal Coupling Constants (Hz)[a]								
	$1\alpha,2\beta$	$1\alpha,2\alpha$	$1\beta,2\alpha$	$1\beta,2\beta$	$2\alpha,3$	$2\beta,3$	3,4	$4,5\alpha$	$4,5\beta$
I	b	b	b	3.8	5.0	8.4	11.5	9.6	5.0
II	9.0	-	-	4.8	-	8.9	3.3	1.8	3.9
III	10.1	-	-	5.2	-	9.1	9.0	10.1	5.2
IV	10.9	-	-	5.2	-	9.2	9.2	b	-
V	11.8	-	-	6.4	-	11.6	3.8	>1	-
VI	-	1.5	1.5	-	3.2	-	9.5	9.0	-
VII	12.2	2.2	1.4	4.9	b	11.5	b	b	b
VIII	12.4	2.5	1.6	5.1	b	11.6	3.1	>1	-
IX	b	b	b	b	b	b	2.9	9.3	-

a. Measured at 400 MHz in D_2O solution.
Observed first order couplings, J ± 0.24 (Hz).
b. Not estimated by first-order analyses because of the overlapping of the *mutually coupling signals.*

and C-H bonds. It can be expected that the comparison of the total ^{13}C-chemical shifts provide useful information about the relative potential energies among the stereoisomers. This approach seems to be particularly valuable for carbohydrate molecules with numerous stereoisomers.

Besides the ring conformations as studied above, the conformational property about the exocyclic C5-C6 bonds in D-hexopyranoses should play a significant role in determining the rotational property in the non-anomeric part of sugars.[4,6,18,35] It is commonly accepted that the three staggered conformations, namely, *gg*, *gt* and *tg* are in conformational equilibrium in solution by rotation around the C5-C6 axis (Fig.2). A set of vicinal ^1H-^1H coupling constants, the J(H5, H6*proR*) and J(H5, H6*proS*) provide a direct means to determine the rotameric distributions about the C5-C6 bonds in solution. The unambiguous assignments of the two C6 signals, however, are crucial for the success of this method. In our preceding papers,[36-39] we applied our synthetic method of chirally deuterated sugars[40-43] to differentiate them and ascertain the conformational properties about the C5-C6 bond in mono-, di- and oligosaccharides in solution. Here, we assigned the two protons of the model compounds IV-VIII based on the data of the deuterated analogues.[36-39]



gg [(-)-*sc*] *gt* [(+)-*sc*] *tg* [*ap*]

FIG. 2 Three Conformers, *gg*, *gt* and *tg* about C5-C6 Bond.

TABLE 4
Vicinal ^{1}H-^{1}H Coupling Constants of H-6*proR* and H-6*proS* and Rotameric Distributions about C5-C6 Bonds.

Compounds	Configuration of OH-4	Jvic (Hz)[a] H5,H6*proR*	JH5,H6*proS*	Distributions(%)[b] *gg*	*gt*	*tg*
IV	α-equatorial	5.4	1.8	60	40	0
V	β-axial	8.4	3.9	15	70	15
VI	α-equatorial	6.5	2.0	49	53	0
VII	α-equatorial	5.7	2.0	56	44	0
VIII	β-axial	8.0	4.4	16	64	21

a. Observed first order couplings (± 0.2 Hz) for IV, VI and VII, and based on the ABX-analyses for V and VIII.

b. Calculated with following equations for IV, VI and VII (Ref. 37)

$1.7gg + 2.4gt + 11.1tg = J_{H5,H6proS}$ -- (1)
$1.7gg + 10.8gt + 4.1tg = J_{H5,H6proR}$ -- (2)
$gg + gt + tg = 1$ -- (3)

and for V and VIII

$3.6gg + 2.4gt + 11.2tg = J_{H5,H6proS}$ -- (1)
$0.7gg + 10.8gt + 4.9tg = J_{H5,H6proR}$ -- (2)
$gg + gt + tg = 1$ -- (3)

Two modified Karplus type equations[35,36] were used to calculate the time averaged distributions of *gg*, *gt* and *tg* (Table 4). The results indicated two types of conformational properties; one for the compounds with an α-equatorial C4-OH (IV, VI, VII) which were predominated by the two *gauche*-conformations, *gg* and *gt*, and the other for the compounds with a β-axial C4-OH (V and VIII) predominated by the *gt*-conformation. These results are in accord with the conformations of reducing sugars and 1-*O*-methyl derivatives of D-glucopyranoses and galactopyranoses in aqueous solution in our preceding studies.[36-39] The results also indicated that the anomeric OH or OMe group did not play a significant role in determining the conformations at C5-C6.

TABLE 5 Chiroptical Data of 1,5-Anhydroalditols I-IX

Compounds	Solv[b]	Band C[a]				[M]$_D$
		λ(nm)	Sign	[θc][c] x10^{-3}	kc x10^{-8}	
(I)	W	100	-	11.2	0.17	- 47
	M	100	-	11.2	0.17	
	D	100	-	8.5	0.13	
(II)	W	110	+	28.6	0.48	+134
	M	110	+	23.3	0.39	
	D	100	+	26.9	0.41	
(IV)	W	165	+	8.4	0.21	+ 70
	M	170	+	8.1	0.21	
	D	175	+	8.6	0.23	
(V)	W	130	+	20.1	0.41	+127
	M	135	+	17.5	0.36	
	D	105	+	17.5	0.28	
(VI)	W	125	-	15.8	0.30	- 80
	M	145	-	13.1	0.29	
	D	150	-	9.6	0.22	
(VII)	W	170	+	3.9	0.08	+ 24
	M	170	+	2.7	0.07	
	D	140	+	4.7	0.10	
(VIII)	W	150	+	9.6	0.22	+ 70
	M	150	+	7.9	0.18	
	D	150	+	6.6	0.15	
(IX)	W	150	+	14.4	0.33	+102
	M	140	+	15.5	0.33	
	D	150	+	10.5	0.24	

a. Calculated with Drude one-term equation.
b. Solvents : W = water, M = methanol, D = dioxane
c. Calculated with Kronig-Krammer equations assuming halfwidth of Δ = 13.5 nm.

Consequently, we determined the preferred conformations of model compounds I-IX. The chiroptical properties in non-anomeric parts of sugars will be discussed on the bases of these conformational properties.

Results and Discussions

1) *Band C of Compounds I-IX* (See Table 5).

The one term Drude equation was applied to calculate the Cotton effects below 200 nm. The ORD curves in the 300-600 nm region fit with the equation (Fig. 3) for all compounds in three solvents;

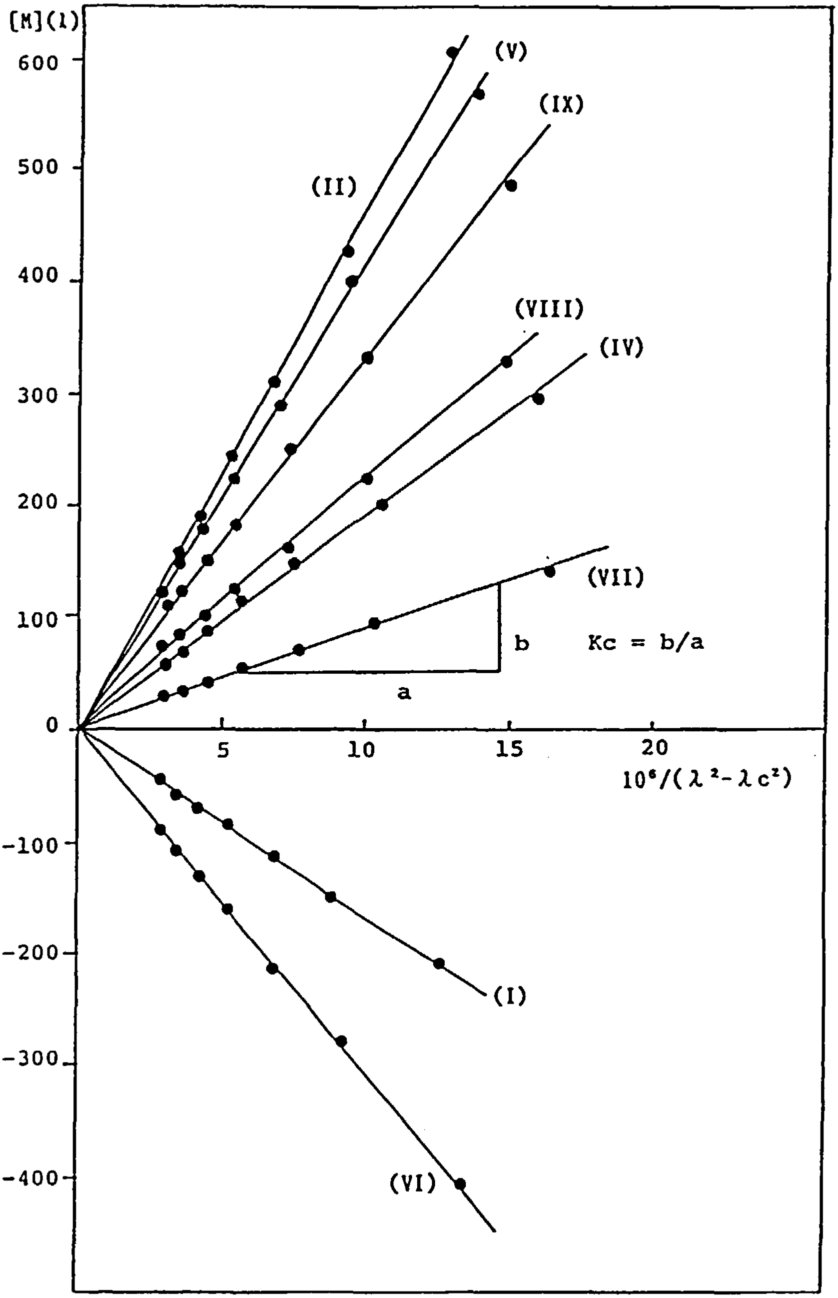


FIG. 3 Graphic Method with Drude's One Term Equation for Calculating Band C.

water, methanol and dioxane to give a single band (Band C). This result showed that optical rotations $[M](\lambda)$ including $[M]_D$ of I-IX in the 300 - 600 nm region can be approximated by the contribution of Band C according to the following equation,

$$[M](\lambda) = Kc/(\lambda^2 - \lambda c^2).$$

The Band C gave the maximal wavelength (λc nm) between 100-170 nm where the n-σ^* transition of *-O-* (160-180 nm) or σ-σ^* transition of C-O or C-C bonds (130-150 nm) are involved. The strength (Kc) of Band C ($-0.3 \times 10^8 \sim +0.5 \times 10^8$) was larger than the band associated with the $n-\sigma^*$ transition of *-O-* (Johnson *et al.*[15-18]) suggesting that this band is mainly due to the σ-σ^* transitions. On the other hand, a strong solvent effect on the Kc value was observed particularly for the compounds II, V, VI and VIII with axially oriented C-OH groups; the change of the polarity of solvents from water to dioxane decreased the Kc suggesting that the band might also be associated with n-electron transitions.

Here it should be noticed that the ratio of the $[M]_D/Kc$ was constant within 3.04-3.78 (in water). This means that the empirical $[M]_D$ rules[2-10] are applicable to explain the Band C. For example, the sugars with right handed helical vicinal C-OH/C-OH bonds (II, V, VIII, IX) showed a positive Kc, while the sugars with left handed helical C-OH/C-OH bonds (I, VI, VII) showed a negative Kc. The contributions from each vicinal OH/OH interaction in a molecule were additive as discussed in the following section.

2) *Band 1 at 180 nm and Band 2 at ca. 140 nm calculated with two or three term Drude equations* (See Table 6).

The high intensity of Kc, the extensive shift of the λc (100-170 nm) among compounds I-IX, and the strong solvent effect as described above strongly suggested the association of at least two types of electron transitions; one is the n-electron transition and the other one is the σ-electron transition. It is possible[29] that when there exist two bands (Band 1 and Band 2) with the same sign and the relative maximal wavelength is $300 >> \lambda 1 > \lambda 2$ (nm), the ORD curves in 300-600 nm fit with the one term Drude equation to give Band C with a

TABLE 6
Cotton Effects Below 180 nm Calculated With Drude Two or Three Term Equations.

Compounds	λ (nm)	Sign	$[\theta]^{a}$ x10^{-3}	k x10^{-8}	$[MA]_{589}^{b}$	$[M]_{D}$
(I)	178	+	3.0	0.08	+25	- 47
	140	-	11.3	0.24	-73	
(II)	178	-	3.0	0.08	-25	+134
	140	+	24.9	0.53	+162	
(IV)	178	+	1.7	0.03	+10	+70
	146	+	7.6	0.17	+52	
(V)	178	-	3.0	0.08	-25	+127
	140	+	23.4	0.50	+153	
(VI)	178	+	3.0	0.08	+25	- 80
	140	-	17.8	0.38	-116	
(VII)	179	+	5.3	0.13	+41	+ 24
	145	-	9.1	0.20	-61	
	140	+	6.6	0.14	+43	
(VIII)	178	+	0.7	0.02	+ 6	+ 70
	172	-	3.1	0.08	-25	
	162	+	10.9	0.27	+84	
(IX)	178	+	3.0	0.08	+25	+102
	130	+	12.6	0.25	+76	

a. Calculated with Kronig-Krammer equation assuming halfwidth of Δ = 13.5 nm.
b. Rotational contributions of each Band on the molecular rotations at 589 nm.

maximal wavelength (λc) in the relation λ1>λc>λ2 (nm). On the other hand, when there exist two bands with the opposite sign and the relative strength is K2>K1, the ORD curve fits with the one term equation to give a Band C with the maximal wavelength as λc<λ2<λ1<<300. In both cases the Kc values of Band C can be approximated with the sum of K1 (Band 1) and K2 (Band 2) (Equation 2).

$$Kc = K1 + K2 \quad ----- \quad (2)$$

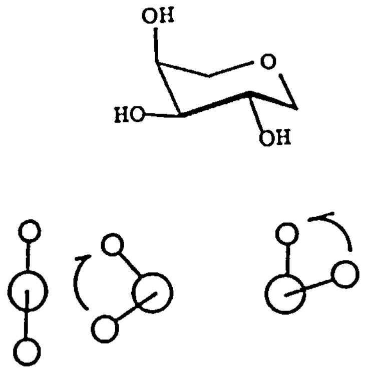
Recently, Bertucci *et al.*[18] studied the vacuum CD for IV, VII, and VIII in aqueous solution and showed that a positive band (Band 1) was observed at *ca.* 180 nm for D-glucose type sugars (IV and VII) with an equatorial C4-OH, and a negative Band 1 due to the n-σ^* band for D-galactose type sugars (VIII) with an axial C4-OH. The results were correlated with the stereochemistries at C4 as well as the conformational properties about the C5-C6 bonds. The conformational properties reported[18] were based on the ambiguous assignments of the H6*proR* and H6*proS* signals in the NMR analyses, in contradiction with our results, and should be corrected as those described previously.[36-39] Taking the vacuum CD data of Bertucci *et al.*[18] into account, we calculated the second band (Band 2) due to the σ-electron transition using the following two term Drude equation (3),

$$[M](\lambda) = K1/(\lambda^2-\lambda 1^2) + K2/(\lambda^2-\lambda 2^2) \quad ---- \; (3)$$
$$= [M1](\lambda) + [M2](\lambda)$$
$$\text{where} \quad K1 = 2[\theta 1]\Delta 1 \lambda 1/\sqrt{\pi}$$

The K1 values of Band 1 ($n-\sigma^*$) were estimated from the reported $[\theta 1]$, $\lambda 1$ and $\Delta 1$ values with the Kronig-Krammer equation (1). Drude one term or two term equations were applied for the calculated ORD curve $[M2](\lambda)$ in the 300 - 600 nm region to give the second band at *ca.*140 nm. For the compounds (I, II, V, VI and IX) for which vacuum CD data were missing in the literature, we assumed the maximal wavelength and the intensity of Band 1 to be at 178 nm and $+0.08 \times 10^8$ respectively for D-glucose type sugars and $K1 = -0.08 \times 10^8$ for D-galactose type sugars. These values were taken as the mean values of the data of Bertucci *et al.*[18] and calculations using these values fit well with the ORD curves in 300 - 600 nm region. The calculation was performed on the ORD data from measurements in water. The results summarized in Table 6 showed that the compounds I-IX gave a second band (Band 2) at *ca.* 140 nm in addition to the Band 1 ($n-\sigma^*$ band of a ring oxygen). The Band 2 at *ca.*140 nm was ascribed to the σ-electron transition bands of the C-O or C-C bonds. Here it should be noticed that the wavelength shifts of Kc were in accord with the prediction as already described, and the sum of K1 and K2 was equal to Kc, satisfying the equation (2).

d) *Correlations of the Band 2 with the stereochemistries in non-anomeric part of pyranoses.*

The $n-\sigma^*$ band was in all compounds smaller than the Band 2 (Table 6), and the optical rotation ($[M]_D$) was primarily governed by



K2(O/O)	0	+0.20	-0.20
K2(O/C)	0	+0.10	-0.10

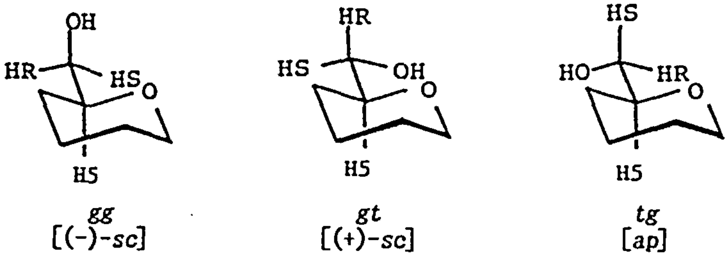
FIG. 4 The Strength (K2) of Vicinal C-O/C-O and C-O/C-C Interactions.

the Band 2, probably due to the σ-electron transition of the C-O bonds and the C-C bonds polarized by substitution of OH or *-O-*. Here, we attempted to correlate the strength (K2) of Band 2 at *ca.* 140 nm with the absolute stereochemistries of I-IX.

The electronic origin of Band 2 is difficult to specify, however, the λ2 values (*ca.* 140 nm) and the strong K2 values strongly suggested that the Band 2 was associated with the σ-electron transition of C-O or C-C bonds. On this basis we took a working hypothesis similar to the pairwise interaction rule[2,5,6,7] and exciton chirality theory[44,45] that the Band 2 was associated with the interactions between vicinal C-O/C-O bonds and C-O/C-C bonds (C-C bond polarized by a substitution of an oxygen atom). The K2 values of compounds I-IX were assumed to be the sum of the K2(O/O) and K2(O/C) values (Fig. 4) which are rotational contributions from the C-O/C-O and C-O/C-C interactions, respectively (equation 4).

$$K2 = \Sigma K2(O/O) + \Sigma K2(O/C) \qquad \text{----} \; (4)$$

Under these assumptions, the K2 data of I-IX could be expressed as the sum of the K2(O/O) and K2(O/C) values; the compounds (II and V) rich in clockwise C-O/C-O or C-O/C-C units gave large positive K2 values, while the compounds (I, VI), rich in anti-clockwise C-O/C-O



	gg	*gt*	*tg*
K2(O/O)	−0.20	+0.20	−
K2(O/C)	+0.10	−	−0.10
Total	−0.10	+0.20	−0.10

FIG. 5 The Strength of the Band 2 (K2) Arising from Each Three Rotamers about the C5-C6 Bond.

TABLE 7

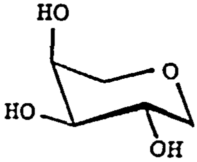
Calculations of the strength (K2) of the second band based on pairwise C-O/C-O and C-O/C-C interactions.

	Sum of C-O/C-O and C-O/C-C values					K2 x 10^{-8}	
Compounds	C1/C2	C2/C3	C3/C4	C4/C5	C5/C6	Total	Experi.
I	0	0	−0.2	0	0	−0.20	−0.24
II	0	+0.2	+0.1	+0.2	0	+0.50	+0.53
III	0	+0.2	−0.2	0	0	0	0
IV	0	+0.2	−0.2	+0.1	+0.02	+0.12	+0.17
V	0	+0.2	+0.1	+0.1	+0.11	+0.51	+0.50
VI	−0.2	−0.1	−0.2	+0.1	+0.06	−0.34	−0.38
VII	0	0	−0.2	+0.1	+0.03	−0.07	-0.06^{b}
VIII	0	0	+0.1	+0.1	+0.09	+0.29	$+0.27^{c}$
IX	0	+0.1	+0.1	+0.1	$+0.03^{a}$	+0.33	+0.25

a. The conformations about the C5-C6 bonds were assumed to be the same as those of compound VII.

b. Sum of the K2 values of the two bands at 145 nm and 140 nm.

c. K2 values of the Band 2 at 162 nm.



	C1/C2	C2/C3	C3/C4	C4/C5
K2(O/O)	-	+0.20	+0.20	+0.20
K2(O/C)	-	-	-0.10	-
Total		+ 0.50 (Observed 0.53)		

FIG. 6 Calculation of the Intensity (K2) of the Band 2 Based on the Vicinal C-O/C-O and C-O/C-C Interactions.

TABLE 8
ORD Data of 1,5-Anhydro-D-Alditols I-IX

Compounds	Solvents	Molecular Rotations [M](l) 600	550	500	450	400	350	300 nm
D-threo-pentitol (I)	W	-47	-57	-70	-89	-113	-149	-209
	M	-41	-49	-62	-80	-101	-139	-199
	D	-33	-35	-46	-59	- 77	-108	-153
L-arabini(II)	W	120	153	190	242	310	422	603
	M	99	122	147	189	247	342	488
	D	85	104	130	169	214	299	425
D-gluci (IV)	W	59	72	88	111	145	200	297
	M	58	70	87	111	145	205	306
	D	57	68	84	105	140	196	294
D-galacti(V)	W	121	146	177	223	288	399	569
	M	94	115	145	182	237	331	479
	D	77	91	114	141	186	251	353
D-manni (VI)	W	-90	-108	-130	-160	-212	-286	-407
	M	-87	-104	-126	-160	-210	-290	-420
	D	-78	- 91	-108	-137	-174	-238	-342
D-arabino-hexitol (VII)	W	31	32	41	53	68	92	138
	M	30	39	45	54	66	89	131
	D	28	35	41	53	71	100	143
D-lyxo-hexitol (VIII)	W	73	82	100	122	161	225	329
	M	54	68	80	98	131	180	265
	D	28	35	41	53	71	100	143
D-ribo-hexitol (IX)	W	111	122	150	182	250	332	484
	M	86	110	142	179	238	320	461
	D	90	99	123	153	193	259	384

a. Solvents: W = water, M = methanol, D = dioxane or C-O/C-C, gave negative K2 values. Therefore, it is apparent that the right-helix C-O/C-O and C-O/C-C gave a positive K2 and the left-helix gave a negative K2. When the two bonds are coplanar, the K2 is assumed to be zero. Moreover, the data from the compounds of V and VI were used to estimate the contributions of K2(O/O) and K2(O/C) as *ca.* ± 0.2×10^{8} and *ca.* ± 0.1×10^{8} (equation 5), respectively (Fig. 4). The result that the K2(O/O) was twice as strong as the K2(O/C) seemed to be reasonable since the dipole-moment or the polarity of the C-O is larger than that of the C-C bond.

The K2 values recalculated using these values for I-IX are summarized in Table 7. Here for the compounds with exocyclic C5-C6 bonds, the rotameric distributions of the three possible conformations, *gg*, *gt* and *tg*, determined by ^{1}H-NMR spectroscopy (Table 4) were used to estimate the contributions from the C5-C6 bonds; K2 values along the C5-C6 bond were estimated as the weight averaged values for the three conformers (Fig. 5). The K2 values thus calculated were in good agreement with the experimental values. This strongly suggests that the chiroptical behaviors in the non-anomeric part of carbohydrate molecules can be approximated from two bands, Band 1 due to the $n-\sigma^{*}$ transition of ring oxygen and a Band 2 due to the σ-electron transition of the C-O and C-C bonds.

In conclusion we have explained the optical rotational behavior in the non-anomeric part of pyranoses using Band 1 and Band 2 calculated using Drude equations and vacuum CD data. We had already explained the rotational behaviors at the anomeric positions by "Ring Oxygen Helicity Rule".[11-14] The optical rotations of carbohydrate molecules are interpreted as the sum of the rotational contributions from these two parts. Present results agree in this respect with Hudson's Isorotation Rules postulated in 1909.[1]

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