with 30 ml of water and extracted with chloroform. The chloroform extract was washed with saturated aqueous bicarbonate, dried, and evaporated. The oily residue was dissolved in benzene and passed through a short column of silica gel. The benzene eluent was evaporated and the residue was recrystallized from cyclohexane giving 50 mg (27%) of red-brown solid.

Anal. Calcd for $C_{24}H_{26}BrNO_7$: C, 55.4; H, 5.04; N, 2.69. Found: C, 55.9; H, 5.04; N, 2.90.

4,6-Di-*n*-butyloxycarbonyl-8-trifluoroacetoxy-2-trifluoromethyl-9,11-dimethyl-5H-oxazolo[4,5-*b*]phenoxazine (6).—The amino diester **2**, 520 mg, was dissolved in 20 ml of trifluoroacetic anhydride that contained 1 g of dry sodium trifluoroacetate. The mixture was stirred at 45° for 18 hr, then an equal volume of benzene was added, and the mixture was evaporated. The residue was dissolved in chloroform, washed with water, dried, and evaporated. Recrystallization of the residue from ethyl acetate–*n*-hexane gave 599 mg (79%) of brilliant yellow solid, mp 201–202.

Anal. Calcd for $C_{28}H_{26}F_6N_2O_8$: C, 53.2; H, 4.14; F, 18.0; N, 4.43. Found: C, 53.2; H, 4.31; F, 17.7; N, 4.63.

Acknowledgment.—The authors are indebted to Dr. Peter Lim and his group for the ultraviolet spectra and to Mr. O. P. Crews, Jr., for large-scale preparations of **2**.

Molecular Rotations of Poly-*O*-acetyl (or Benzoyl) Carbohydrates in Relation to Their Structures. The Rules Which Even D-Mannose Derivatives Obey

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The molecular rotation of a poly-*O*-acetyl- or -benzoylglycopyranosyl halide is plotted against the atomic refraction of the halogen. It becomes obvious that straight lines can be obtained here and, moreover, if a definite proper value of the abscissa is given to hydrogen, the molecular rotations of the corresponding "hydrides" can exist on the above straight lines. Next, the inclinations of these lines are discussed from the viewpoint of the structural formulas of their corresponding compounds and a new empirical rule is obtained. D-Mannose derivatives show no optical abnormalities throughout the course of this study.

Brauns found[1] that, for the poly-*O*-acetylglycopyranosyl halides of four monosaccharides (glucose, fructose, xylose, and arabinose), the differences in specific rotation (but not the molecular rotation) for Cl − F, Br − Cl, and I − Br are proportional to the corresponding differences in atomic diameters. He proved afterwards however, that this rule is not applicable to the mannose derivatives.[2] Concerning the hepta-*O*-acetylglycopyranosyl halides of disaccharides, Brauns concluded[3] that the derivatives of melibiose and maltose follow the atomic dimension relationship, whereas those of the other three [gentiobiose, cellobiose, and 4-*O*-(β-D-glucopyranosyl)-α-D-mannose] agree with this relationship only when the fluorine derivatives are excluded.

In 1924, Hudson reported[4] that the difference between the molecular rotation of a poly-*O*-acetylglycopyranosyl halide and half the sum of the molecular rotations of anomers of the corresponding acetates is approximately constant for a definite kind of halogen, regardless of the parent sugar. In this case also, a deviation was noticed in the mannose derivatives. Later, Hudson used[5] the value of the molecular rotation of the 1,5-anhydride of the corresponding poly-*O*-acetylalditol, in place of the above-mentioned half of the sum.

Korytnyk recalculated[6] the partial molecular rotation of the (C-1–Cl) moiety in poly-*O*-acetylaldopyranosyl chloride molecules, and he also pointed out that the values in both D-mannose and D-xylose derivatives are different from those in the other sugar derivatives.

In this article, the author has first compared the values of the molecular rotation, $[M]^{20}D$ (in chloroform), not only of the poly-*O*-acetylglycopyranosyl halides but also of the poly-*O*-benzoylglycopyranosyl

TABLE I

$[M]^{20}D$ (IN CHLOROFORM) OF POLY-*O*-ACETYLALDOPYRANOSYL COMPOUNDS (MONOSACCHARIDES)

Derivative of	Compd	$[M]^{20}D$ for X at C-1: H	F	Cl	Br	I
2,3,4-Tri-*O*-acetyl-						
β-L-arabinose	**1**	193.1[a]	384.5[b]	720.2[b]	961.8[c]	1309.4[b]
α-D-xylose	**2**	0.0[d]	187.1[e]	504.5[f]	718.6[f]	*v*
β-D-xylose	**2′**	0.0[d]	*v*	−415.5[g,w]	*v*	*v*
β-D-ribose	**3′**	0.0[h]	*v*	−499.8[i,w]	−709.8[j,w]	*v*
α-D-rhamnose	**4**	−131.9[k]	*v*	392.2[l]	582.7[m]	*v*
2,3,4,6-Tetra-*O*-acetyl-						
α-D-galactose	**5**	163.2[n]	*v*	651.0[g,w]	892.3[o]	*v*
β-D-galactose	**5′**	163.2[n]	*v*	54.6[g]	*v*	*v*
α-D-glucose	**6**	129.3[p]	315.6[f]	615.6[f]	813.4[f]	1087.8[f]
β-D-glucose	**6′**	129.3[p]	70.1[q]	−29.3[g]	*v*	*v*
α-D-mannose	**7**	−140.9[r]	75.3[s]	328.6[g]	541.1[s]	872.9[s]
β-D-mannose	**7′**	−140.9[r]	*v*	−125.1[g,w]	*v*	*v*
α-D-talose	**8**	−53.8[t]	*v*	*v*	681.0[u]	*v*

[a] H. G. Fletcher, Jr., and C. S. Hudson, *J. Am. Chem. Soc.*, **69**, 1672 (1947). [b] D. H. Brauns, *ibid.*, **46**, 1484 (1924). [c] M. Gehrke and F. X. Aichner, *Ber.*, **60**, 918 (1927). [d] H. G. Fletcher, Jr., and C. S. Hudson, *J. Am. Chem. Soc.*, **69**, 921 (1947). [e] D. H. Brauns, *ibid.*, **45**, 833 (1923). [f] D. H. Brauns, *ibid.*, **47**, 1280 (1925). [g] W. Korytnyk and J. A. Mills, *J. Chem. Soc.*, 636 (1959). [h] R. W. Jeanloz, H. G. Fletcher, Jr., and C. S. Hudson, *J. Am. Chem. Soc.*, **70**, 4052 (1948). [i] H. Zinner, *Ber.*, **83**, 153 (1950). [j] P. A. Levene and E. P. Clark, *J. Biol. Chem.*, **46**, 19 (1921). [k] R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, *J. Am. Chem. Soc.*, **72**, 4547 (1950). [l] H. Ohle, W. Marecek, and W. Bourjau, *Ber.*, **62**, 833 (1929). [m] G. Zemplén and A. Gerecs, *ibid.*, **67**, 2049 (1934). [n] H. G. Fletcher, Jr., and C. S. Hudson, *J. Am. Chem. Soc.*, **70**, 310 (1948). [o] W. T. Haskins, R. M. Hann, and C. S. Hudson, *ibid.*, **64**, 1852 (1942). [p] N. K. Richtmyer, C. J. Carr, and C. S. Hudson, *ibid.*, **65**, 1477 (1943). [q] F. Micheel, A. Klemer, M. Nolte, H. Nordiek, L. Tork, and H. Westerann, *Ber.*, **90**, 1612 (1957). [r] H. G. Fletcher, Jr., and H. W. Diehl, *J. Am. Chem. Soc.*, **74**, 3175 (1952). [s] D. H. Brauns, *J. Res. Natl. Bur. Std.*, **7**, 573 (1931). [t] D. A. Rosenfeld, N. K. Richtmyer, and C. S. Hudson, *J. Am. Chem. Soc.*, **70**, 2201 (1948). [u] W. W. Pigman and H. S. Isbell, *J. Res. Natl. Bur. Std.*, **19**, 189 (1937). [v] Unknown. [w] This was assumed from the [M]D, which had been observed in the neighborhood of 20°.

(1) D. H. Brauns, *J. Am. Chem. Soc.*, **45**, 2381 (1923).
(2) D. H. Brauns, *ibid.*, **53**, 2004 (1931).
(3) D. H. Brauns, *ibid.*, **51**, 1820 (1929).
(4) C. S. Hudson, *ibid.*, **46**, 462 (1924).
(5) H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **71**, 3682 (1949).
(6) W. Korytnyk, *J. Chem. Soc.*, 650 (1959).

TABLE II

[M]²⁰D (IN CHLOROFORM) OF POLY-O-ACETYLALDOPYRANOSYL COMPOUNDS (DISACCHARIDES)

Derivative of	Compd	[M]²⁰D for X at C-1 H	F	Cl	Br	I
Hepta-O-acetyl-						
α-melibiose	5(1')-O-(6)6	j	955.9[a]	1260.9[a]	1468.2[a]	j
α-lactose	5'(1')-O-(4)6	j	286.4[b,k]	549.5[c]	760.3[c,k]	1021.9[c,k]
α-maltose	6(1')-O-(4)6	508.9[d]	709.4[a]	1044.7[a]	1259.7[a]	j
β-maltose	6(1')-O-(4)6'	508.9[d]	j	376.0[e,k]	j	j
α-cellobiose	6'(1')-O-(4)6	24.8[f]	195.4[g]	469.6[g]	670.0[g]	938.3[g]
β-cellobiose	6'(1')-O-(4)6'	24.8[f]	−25.5[h]	j	j	j
α-gentiobiose	6'(1')-O-(6)6	80.7[f]	279.7[i]	527.3[i]	707.2[i]	941.3[i]
4-O-(β-D-Glucopyranosyl)-α-D-mannose	6'(1')-O-(4)7	j	86.8[g]	335.4[g]	544.9[g]	832.3[g]

[a] See ref 3. [b] B. Helferich and R. Gootz, *Ber.*, **62**, 2505 (1929). [c] C. S. Hudson and A. Kunz, *J. Am. Chem. Soc.*, **47**, 2052 (1925). [d] H. G. Fletcher, Jr., L. H. Koehler, and C. S. Hudson, *ibid.*, **71**, 3679 (1949). [e] See footnote *g* in Table I. [f] See footnote *n* in Table I. [g] D. H. Brauns, *ibid.*, **48**, 2776 (1926). [h] F. Micheel, A. Klemer, G. Baum, P. Ristić, and F. Zumbülte, *Ber.*, **88**, 475 (1955). [i] D. H. Brauns, *J. Am. Chem. Soc.*, **49**, 3170 (1927). [j] Unknown. [k] This was assumed from the [M]D, which had been observed in the neighborhood of 20°.

halides[7] (derived from as many sugars as possible), with the polarizability[8] (α), or, for convenience, with the atomic refraction,[10] RD of their halogen atoms, and has obtained some empirical rules. The compounds discussed in this article and their molecular rotations are given in Tables I–IV.

TABLE III

[M]²⁰D (IN CHLOROFORM) OF POLY-O-BENZOYLALDOPYRANOSYL COMPOUNDS

Derivative of	Compd	[M]²⁰D for X at C-1 H	F	Cl	Br	I
2,3,4-Tri-O-benzoyl-						
β-L-arabinose	1B	982.2[a]	k	k	1856.1[b]	k
α-D-xylose	2B	0.0[c]	k	k	623.6[c]	k
α-D-ribose	3B	0.0[d]	k	288.5[e]	409.8[e]	k
β-D-ribose	3'B	0.0[d]	k	−706.9[e]	−1061.2[e]	k
α-D-rhamnose	4B	−1284.7[f]	k	−672.6[g]	−349.5[g]	159.5[g]
2,3,4,6-Tetra-O-benzoyl-						
α-D-glucose	6B	252.0[h]	k	670.4[i]	815.1[i]	985.5[i]
α-D-mannose	7B	−873.2[j,l]	k	−187.6[i]	77.2[i]	316.5[i]

[a] See footnote *a* in Table I. [b] H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **72**, 4173 (1950). [c] See footnote *d* in Table I. [d] See footnote *h* in Table I. [e] R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **73**, 959 (1951). [f] See footnote *k* in Table I. [g] R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **73**, 296 (1951). [h] E. Zissis and N. K. Richtmyer, *ibid.*, **77**, 5154 (1955). [i] R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **72**, 2200 (1950). [j] Y. Asahina, *Arch. Pharm.*, **247**, 157 (1909). [k] Unknown. [l] This was assumed from the [M]D, which had been observed in the neighborhood of 20°.

TABLE IV

[M]²⁰D (IN CHLOROFORM) OF POLY-O-ACETYLKETOPYRANOSYL COMPOUNDS

Derivative of	Compd	[M]²⁰D for X at C-2[g] H	F	Cl	Br	I
1,3,4,5-Tetra-O-acetyl-						
β-D-fructose	1K	−140.9[a]	−316.8[b]	−590.1[c]	−774.3[b]	f
α-L-sorbose	2K	129.3[d]	f	−305.5[e]	f	f

[a] 2,3,4,6-Tetra-O-acetyl-1,5-anhydro-D-mannitol; see footnote *r* in Table I. [b] See ref 1. [c] D. H. Brauns, *J. Am. Chem. Soc.*, **42**, 1846 (1920). [d] 2,3,4,6-Tetra-O-acetyl-1,5-anhydro-D-glucitol; see footnote *p* in Table I. [e] H. H. Schlubach and G. Graefe, *Ann. Chem.*, **532**, 211 (1937). [f] Unknown. [g] The carbon atom, next to the ring oxygen atom, is C-1 in the aldopyranose ring but it is C-2 in the ketopyranose ring.

Now, [M]²⁰D (in chloroform) of poly-O-acetyl- or -benzoylglycopyranosyl halides are plotted against RD of their halogens. They are shown in Figure 1[11,12] (poly-O-acetylaldopyranosyl compounds, monosaccharides), Figure 2 (poly-O-acetyladopyranosyl compounds, disaccharides), Figure 3 (poly-O-benzoylaldopyranosyl compounds), and Figure 4 (poly-O-acetylketopyranosyl compounds), but the data of RD used in this article are as follows:[13] RD of the H atom is 1.028; RD of the F atom is 0.81; RD of the Cl atom is 5.844; RD of the Br atom is 8.741; RD of the I atom is 13.954. On examining the solid lines in these figures, the next empirical rule is found.

Rule 1.—*Straight lines can be obtained for poly-O-acetyl- or -benzoylglycopyranosyl halides, RX where X is F, Cl, Br, or I by plotting molecular rotation against atomic refraction of X. This fact is indifferent to the configuration at the 1 position.*

Rule 1 suggests that, as is already expected, the atomic refraction (or polarizability[10]) plays a role in determining rotations. [M]²⁰D of some poly-O-acetyl- or -benzoylhexopyranosyl (*i.e.* α-D-glucosyl in Figure 1, α-lactosyl and α-gentiobiosyl in Figure 2, α-D-glucosyl and α-D-mannosyl in Figure 3) iodides, however, usually deviate[12] from rule 1. This indicates a kind of mutual interaction between the bulky iodine atom and CH_2OAc-5 (or CH_2OBz-5) in these molecules.[14] Nevertheless rule 1 would be nothing more than a restatement of the work of Brauns,[1-3] Hudson,[4,5] and Korytnyk[6] if all of these lines were parallel. The fact that they are straight but not parallel resolves some of the anomalies in the earlier work.

Next, an interesting fact is noticed as follows: [M]²⁰D for the "poly-O-acetylglucopyranosyl hydride"[15]

(7) For the poly-O-benzoyl compounds, only those of D-glucopyranosyl bromide and of 2-deoxy-D-*arabino*-hexopyranosyl bromide were studied by Hudson.[4]

(8) From the standpoint of one of the present physical theories of optical rotation,[9] the polarizability of atoms is believed to be one of the most important factors in determining the optical rotatory power of a molecule.

(9) (a) J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937); (b) S. Yamana, *J. Am. Chem. Soc.*, **86**, 1606 (1964); *Tetrahedron*, **21**, 709 (1965).

(10) The polarizability, α, is related to the atomic refraction, RD, by eq 1 where *N* is the Avogadro number.

$$\alpha = (3/4\pi N)\sum_i (R_D)_i \quad (1)$$

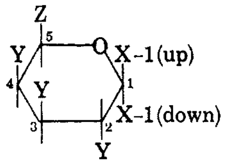
(11) Symbols are as follows: Ar, arabinose derivative; Cel, cellobiose derivative; Fr, fructose derivative; Ga, galactose derivative; Ge, gentiobiose derivative; G, glucose derivative; 4-G-M, 4-O-(β-D-glucopyranosyl)-α-D-mannose derivative; La, lactose derivative; M, mannose derivative; Ma, maltose derivative; Me, melibiose derivative; Rh, rhamnose derivative; Ri, ribose derivative; So, sorbose derivative; Ta, talose derivative; Xy, xylose derivative.

(12) A solid line has more than three points on it. A symbol, ⟶, means, a deviation from the corresponding solid line. Concerning a dashed line, refer to the latter part of this article.

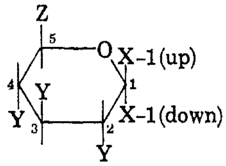
(13) A. I. Vogel, *J. Chem. Soc.*, 1833 (1948).

(14) Ac is CH_3CO; Bz is C_6H_5CO.

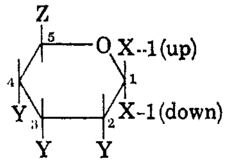
(15) "D-Glucopyranosyl hydride" is 1,5-anhydro-D-glucitol.



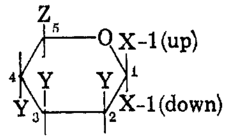
β-L-Ar {1, X-1(up) = Z = H; Y = OAc; 1_B, X-1(up) = Z = H; Y = OBz}
D-Ga {5, X-1(up) = H; Y = OAc; Z = CH_2OAc; 5′, X-1(down) = H; Y = OAc; Z = CH_2OAc}



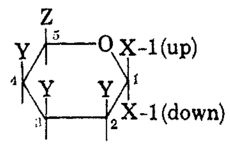
D-Xy {2, X-1(up) = Z = H; Y = OAc; 2′, X-1(down) = Z = H; Y = OAc; 2_B, X-1(up) = Z = H; Y = OBz}
D-G {6, X-1(up) = H; Y = OAc; Z = CH_2OAc; 6′, X-1(down) = H; Y = OAc; Z = CH_2OAc; 6_B, X-1(up) = H; Y = OBz; Z = CH_2OBz}



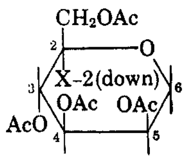
D-Ri {3′, X-1(down) = Z = H; Y = OAc; 3_B, X-1(up) = Z = H; Y = OBz; 3_B′, X-1(down) = Z = H; Y = OBz}



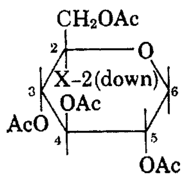
D-Rh {4, X-1(up) = H; Y = OAc; Z = CH_3; 4_B, X-1(up) = H; Y = OBz; Z = CH_3}
D-M {7, X-1(up) = H; Y = OAc; Z = CH_2OAc; 7′, X-1(down) = H; Y = OAc; Z = CH_2OAc; 7_B, X-1(up) = H; Y = OBz; Z = CH_2OBz}



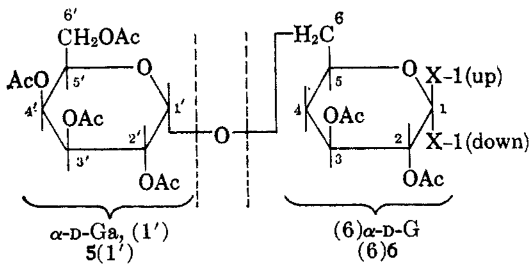
α-D-Ta 8, Y = OAc; Z = CH_2OAc



β-D-Fr, 1_K



α-L-So, 2_K



α-Me, 5(1′)-O-(6)6

lies exactly at the intersection of the line drawn for the poly-*O*-acetyl-α-D-glucopyranosyl halides (α-D-G in Figure 1) and the corresponding lines drawn for β-D-halides (β-D-G in Figure 1). A similar phenomenon may be seen in the α and β series of poly-*O*-benzoyl-D-ribopyranosyl compounds (α-D-Ri and β-D-Ri in Figure 3). Moreover, in spite of the varieties of inclinations of these lines, the abscissa of these two intersecting points (*i.e.*, the points for the "hydrides") are exactly the same. Besides, this abscissal value is applicable to all of the "hydrides," as seen in Figures 1–4. Thus, rules 2 and 3 are obtained.

Rule 2.—*An abscissal value can be found for hydrogen so that the hydrides, RH also fall on the lines, above mentioned in rule 1.*

Rule 3.—*The abscissal value of the point for the "hydride" is −1.8 (by the* RD *scale for halogen) and is not related to the atomic refraction of hydrogen, 1.028.*

It is to be emphasized here that rules 1, 2, and 3 can be seen even for poly-*O*-acetyl- or -benzoyl-α-D-mannopyranosyl compounds. Some interpretations of rules 1, 2, and 3 by using the physical theory will be tried in the other article.

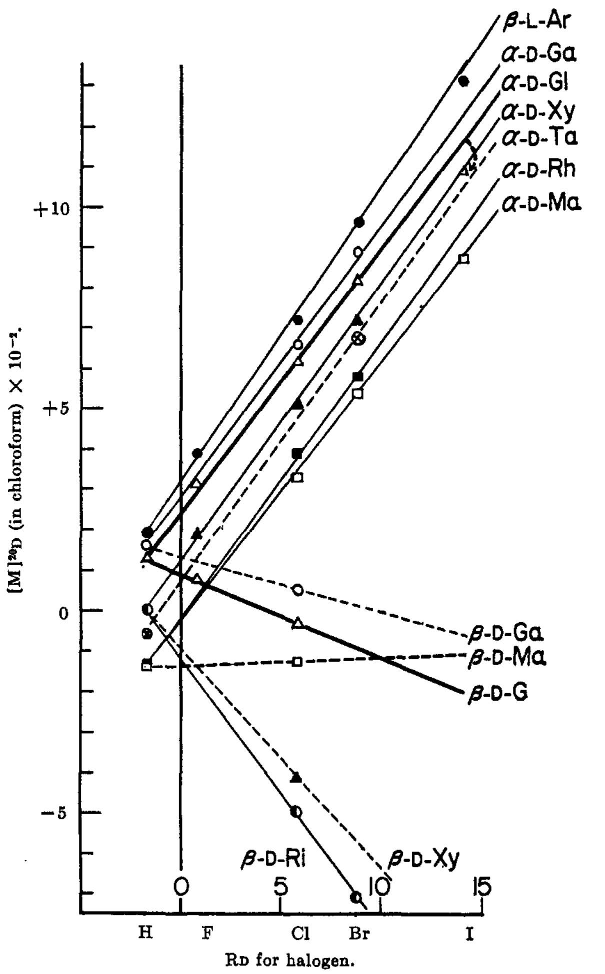


Figure 1.—Molecular rotation of poly-O-acetylaldopyranosyl compound (monosaccharide) as a function of RD of its C¹-attaching halogen atom.[11,12]

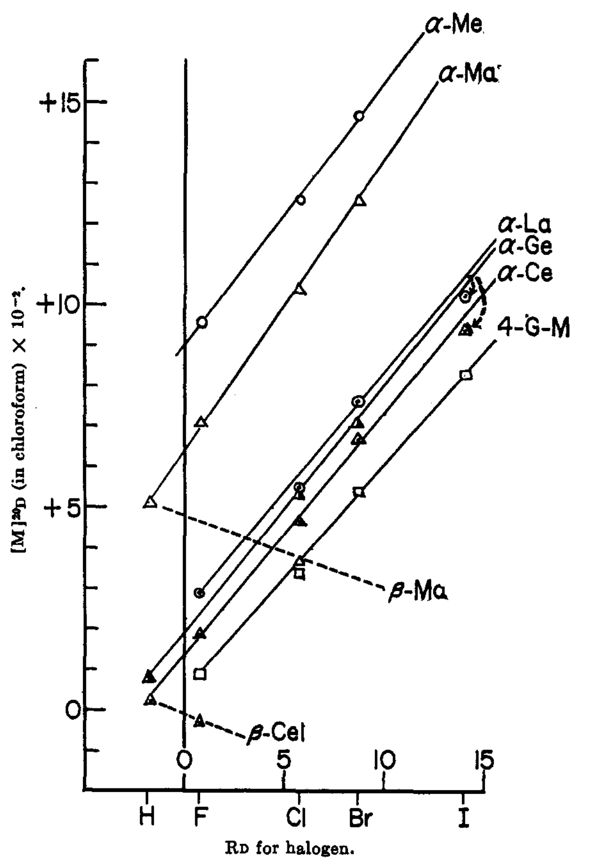


Figure 2.—Molecular rotation of poly-O-acetylaldopyranosyl compound (disaccharide) as a function of RD of its C¹-attaching halogen atom.[11,12]

At any rate, it is clear that the ordinate value of the intersection of two lines [*i.e.*, $[M]^{20}_D$–RD line and the RD (for halogen) = 0 line] in all figures is the value of the molecular rotation of a hypothetical glycopyranosyl radical (which has no X). The partial molecular rotation, caused by H-1 can, therefore, be obtained by subtracting it from the value of $[M]^{20}_D$ of the corresponding "hydride." This value is not generally zero and must not be neglected.[16]

The Point of "Hydride," RH.—As is already apparent in D-glucopyranosyl compounds in Figure 1 and D-ribopyranosyl compounds in Figure 3, the point of hydride (RH) is given as the intersection of α-D- and β-D-series lines. It is natural, because the hydride RH (strictly speaking, 1,5-anhydro-D-alditol) has two hydrogen atoms at the 1 position and it should accordingly belong to both of α-D- and β-D-series compounds. Thus, the point of RH becomes very useful, generally in drawing each of α-D- and β-D-series lines in figures. Before drawing the other lines, the point of RH should, of course, be settled in advance in figures by the following operations. (a) As in apparent in rule 3, the point of RH should fall on the vertical line in figures which is given by eq 2. (b) Of course, the point of RH is on the horizontal line in figures whose equation is as in eq 3. The intersection of these two lines 2 and 3 is therefore, the point of RH.

$$\text{abscissal value} = -1.8 \qquad (2)$$

$$\text{ordinate value} = [M]^{20}_D \text{ of 1,5-anhydro-D-alditol, RH} \qquad (3)$$

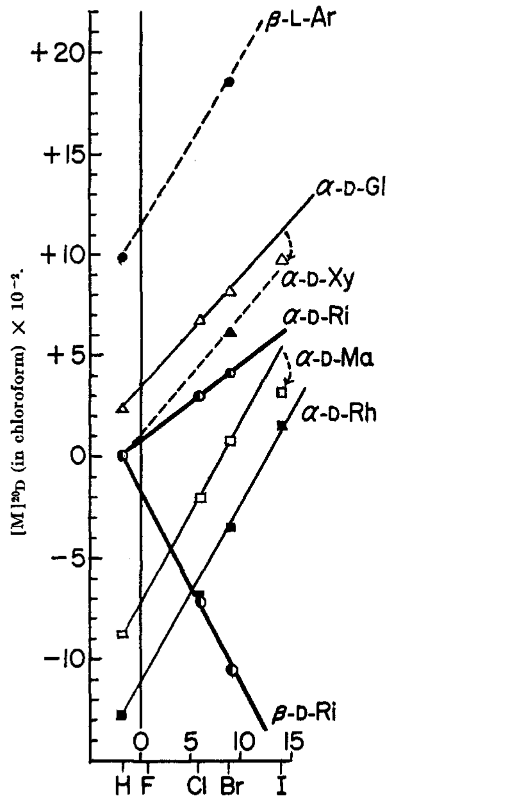
Inclination of $[M]^{20}_D$–RD Line.—The inclination (*i.e.*, angular coefficient) of the $[M]^{20}_D$–RD line of a poly-O-acetyl- or -benzoylglycopyranosyl compound depends upon the parent sugar and also upon the configuration at the 1 position. This fact is especially noticiable in Figure 3 (poly-O-benzoylaldopyranosyl compounds). In order to examine the inclination of $[M]^{20}_D$–RD lines, it is desirable to use as many lines as possible. Therefore, a dotted line is drawn even for a series which has only two known data of $[M]^{20}_D$. (The points of hydrides are used in Figures 1–4.) For simplifying the comparison of their inclinations, the values of angular coefficients (*i.e.*, tan θ, where θ is the angle between a $[M]^{20}_D$–RD line and the axis of the abscissa) of these lines are computed graphically and are given in the third column of Tables V–VII. The fourth column contains the inclination ratio, r,[17] which is defined by eq 4.

$r \equiv$ (angular coefficient of a line)/(angular coefficient of the line of the poly-O-acetyl- or -benzoyl-α-D-xylopyranosyl compound) (4)

Comparing the value of r with the corresponding structural formula, the next two facts become apparent.

(16) Because of the small polarizability of the H atom, the contribution of the H atom to the molecular rotation has often been neglected; see ref 9.

(17) For comparing the inclinations of the lines, r is more suitable than tan θ.



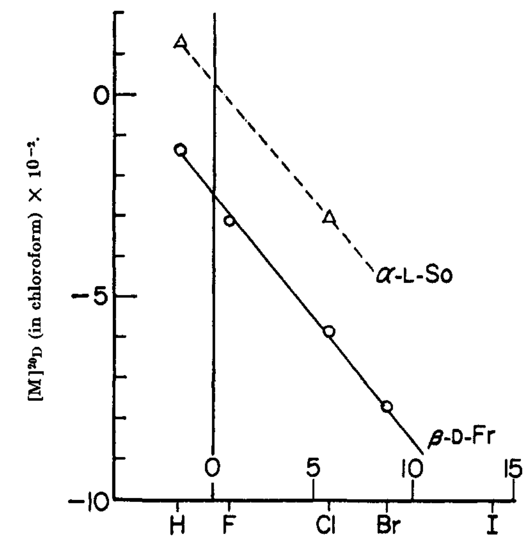
RD for halogen.

Figure 3.—Molecular rotation of poly-*O*-benzoylaldopyranosyl compound as a function of RD of its C^1-attaching halogen atom.[11,12]

Table V
Inclination Ratio of [M]^{20}D–RD Line of Poly-*O*-acetylaldopyranosyl Compounds

Derivative of	Compd	Angular coeff (tan θ)	Inclination ratio, *r*
Monosaccharides			
β-L-Arabinose	1	1.4500	1.0450
α-D-Xylose	2	1.3875	1.0000
α-D-Rhamnose	4	1.3750	0.9910
α-D-Galactose	5	1.3625	0.9820
α-D-Glucose	6	1.3000	0.9369
α-D-Mannose	7	1.2875	0.9279
α-D-Talose	8	1.3875	1.0000
β-D-Xylose	2′	−1.0857	−0.7825
β-D-Ribose	3′	−1.3167	−0.9490
β-D-Galactose	5′	−0.2750	−0.1982
β-D-Glucose	6′	−0.4250	−0.3063
β-D-Mannose	7′	0.0375	0.0270
Dissaccharides			
α-Melibiose	5(1′)-O-(6)6	1.2800	0.9225
α-Lactose	5′(1′)-O-(4)6	1.2000	0.8649
α-Maltose	6(1′)-O-(4)6	1.4625	1.0541
α-Cellobiose	6′(1′)-O-(4)6	1.2000	0.8649
α-Gentiobiose	6′(1′)-O-(6)6	1.2375	0.8919
4-*O*-(β-D-Glucopyranosyl)-α-D-mannose	6′(1′)-O-(4)7	1.1286	0.8134
β-Maltose	6(1′)-O-(4)6′	−0.3500	−0.2522
β-Cellobiose	6′(1′)-O-(4)6′	−0.3875	−0.2793

Fact 1.—*For poly-O-acetylaldopyranosyl compounds, (Table V), r of the* α-D *(or* β-L*) series (which has axial X-1 below the plane of the ring) is positive in sign and is roughly constant. That of the* β-D *(or* α-L*) series (which has equatorial X-1 above the plane of the ring), is however greatly influenced by the parent sugar, and its sign is usually negative, except for* β-D*-mannose derivatives.*



RD for halogen.

Figure 4.—Molecular rotation of poly-*O*-acetylketopyranosyl compound as a function of RD of its C^2-attaching halogen atom.[11,12]

Table VI
Inclination Ratio of [M]^{20}D–RD Line of Poly-*O*-benzoylaldopyranosyl Compounds

Derivative of	Compd	Angular coeff (tan θ)	Inclination ratio, *r*
β-L-Arabinose	1_B	1.6750	1.3958
α-D-Xylose	2_B	1.2000	1.0000
α-D-Ribose	3_B	0.7875	0.6563
α-D-Rhamnose	4_B	1.7875	1.4896
α-D-Glucose	6_B	1.1000	0.9167
α-D-Mannose	7_B	1.7750	1.4792
β-D-Ribose	$3_B{}'$	−1.9125	−1.5938

Table VII
Inclination Ratio of [M]^{20}D–RD Line of Poly-*O*-acetylketopyranosyl Compounds

Derivative of	Compd	Angular coeff (tan θ)	Inclination ratio, *r*
β-D-Fructose	1_K	−1.2200	−0.8793
α-L-Sorbose	2_K	−1.1200	−0.8072

Fact 2.—*For poly-O-benzoylaldopyranosyl compounds (Table VI), r of the* α-D *(or* β-L*) series is positive in sign and is somewhat influenced by the parent sugar, but is almost indifferent to the group attached at C-5.*

It is now apparent in Figures 1–3 that half the sum of the values of [M]^{20}D of the anomer can be equal to [M]^{20}D of the corresponding "hydride," only when the [M]^{20}D–RD line of the β series is the mirror image of that of the α series, with regard to the axis of the abscissa. In that case only, Hudson's method[5] is correct.

In fact 1, β-D-mannose derivatives seem to show yet an optically abnormal character which will be taken away, as follows.

As shown in Table V, the *r* value (1.0450) of poly-*O*-acetyl-β-L-arabinose derivatives (1) is larger (*i.e.*, more positive) than that (1.0000) of poly-*O*-acetyl-α-D-xylose derivatives (2). Therefore

$$(r \text{ of } 1) > (r \text{ of } 2) \quad (5)$$

$$(r \text{ of } 1) - (r \text{ of } 2) > 0 \quad (5')$$

On the other hand, the structural formula of **1** and that of **2** are different from each other only in the orientation of OAc-4 (the configuration of C-4 is (up) in **1** and (down) in **2**).[18] This structural difference should be the reason for their difference in r value. Of course, the configuration of X-1 is (down) in **1** and **2**. It can be said, therefore, that the part of the inclination ratio[19] which is due to the X-1 change below the plane of the ring under the influence of OAc-4 (up) is larger (or more positive) than that under the influence of OAc-4 (down). Using a new symbol ($\forall$) the inequality 5′ is rewritten as follows.

$$\text{X-1(down)} \forall \text{OAc-4(up)} - \text{X-1(down)} \forall \text{OAc-4(down)} > 0$$

or

$$\text{X-1(down)} \forall [\text{OAc-4(up)} - \text{OAc-4(down)}] > 0$$

$$\text{X-1(down)} \forall [\text{OAc-4}\{\text{(up)} - \text{(down)}\}] > 0 \quad (8)$$

Equation 8 can also be obtained by comparing poly-*O*-acetyl-α-D-galactose derivatives (**5**) with poly-*O*-acetyl-α-D-glucose derivatives (**6**) or poly-*O*-acetyl-α-D-mannose derivatives (**7**) with poly-*O*-acetyl-α-D-talose derivatives (**8**). As many comparisons of r_{XK}'s as possible in monosaccharides are given in Table VIII.

Table VIII shows that the term which has the factor {[up–down]} is almost always positive in sign, and this is right even for α-D- and β-D-mannose derivatives (7_B and 7′). This phenomenon is paraphrased as in rule 4.

Rule 4.—*A configuration change from (down) to (up), at any position of the aldopyranose ring, makes the inclination ratio of the* $[M]^{20}D$–R_D *line change toward the plus direction.*[20]

TABLE VIII

COMPARISON BETWEEN TWO PARTIAL INCLINATION RATIOS, r_{XK}'S IN MONOSACCHARIDES

Position of the structural diff	Comparison of r	Inequality
Poly-*O*-acetylaldopyranosyl Compounds[a]		
2	$5 \doteq 8$, $6 \doteq 7$	X-1(down) $\forall$ [OAc-2{(up) − (down)}] $\doteq 0$
	$6' < 7'$	X-1(up) $\forall$ [OAc-2{(up) − (down)}] > 0
3	$2' > 3'$	X-1(up) $\forall$ [OAc-3{(up) − (down)}] > 0
4	$1 > 2$, $5 > 6$, $7 < 8$	X-1(down) $\forall$ [OAc-4{(up) − (down)}] > 0
	$5' > 6'$	X-1(up) $\forall$ [OAc-4{(up) − (down)}] > 0
5	$1 > 5$, $2 > 6$	X-1(down) $\forall$ [H-5(up) − CH_2OAc-5(up)] > 0
	$4 > 7$	X-1(down) $\forall$ [CH_3-5(up) − CH_2OAc-5(up)] > 0
	$2' < 6'$	X-1(up) $\forall$ [H-5(up) − CH_2OAc-5(up)] < 0
Poly-*O*-benzoylaldopyranosyl Compounds[b]		
2	$6_B < 7_B$	X-1(down) $\forall$ [OBz-2{(up) − (down)}] > 0
3	$2_B > 3_B$	X-1(down) $\forall$ [OBz-3{(up) − (down)}] > 0
4	$1_B > 2_B$	X-1(down) $\forall$ [OBz-4{(up) − (down)}] > 0
5	$2_B > 6_B$	X-1(down) $\forall$ [H-5(up) − CH_2OBz-5(up)] > 0
	$4_B \doteq 7_B$	X-1(down) $\forall$ [CH_3-5(up) − CH_2OBz-5(up)] $\doteq 0$

[a] *Cf.* Figure 1 and Table V. [b] *Cf.* Figure 3 and Table VI.

After all, four empirical rules can be obtained concerning the molecular rotations (rules 1–4) in this article which even D-mannose derivatives are not exceptions. These rules may be useful in construction of a new theory of optical rotation.

Acknowledgment.—The author wishes to express his many thanks to Mr. Masahiro Ohshita for his assistance in calculating the molecular rotations.

(18) In order to indicate the configurations, the designations (up) and (down) are used. *For example,* OAc-4(up) *refers to the* OAc *group which* attaches to C-4 above the plane of the ring, and so on, but here the D-aldopyranose ring is located so that the ring oxygen atom is on the back and the 1 position is on the right (see the structural formulas).

(19) It is not unreasonable here to assume that, generally speaking, the inclination ratio (r) is composed of all the possible partial inclination ratios, r_{XK}'s, in the molecule. Therefore

$$r = \sum_K r_{XK} \quad (6)$$

and

$$r_{XK} = (X) \forall (K) \quad (7)$$

but here K refers to a unit group and r_{XK} is the partial inclination ratio, due *to the* X *change under the influence of* K. $\forall$ *is* the inverted A and is pronounced "inverted A." This notation $\forall$ can be treated in the same way as the multiplication symbol, ×, of the algebra.

(20) The interpretation of rule 4 by using the physical theory is left for the future.