Molecular Rotations of Poly-*O*-acetyl Carbohydrates in Relation to Their Structures. II.[1] Glycopyranoside

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The abscissal value of the figures in the previous paper[1] is assumed to correspond to a new optical property, *S* (and not generally, atomic refraction, R_D itself), and *S* values of some radicals are estimated. Next, by plotting the molecular rotation, M^{20}_D, of a glycopyranoside (whether acetylated or unacetylated) against the *S* value of its aglycon moiety, various slopes are obtained and they are interpreted qualitatively by using the estimation methods of optical rotation.

Recently, some empirical rules were obtained concerning the molecular rotations of fully acetylated or benzoylated glycopyranosyl compounds, and these are understood visually in Figures 1–4 of the previous paper.[1–3,5]

Concerning the compound whose aglycon moiety is a radical (and not an atom), however, only the tetra-*O*-acetyl-D-glucopyranosyl series has been examined.[5] Arndt insisted that, in the tetra-*O*-acetyl-D-glycopyranosyl series, some radicals such as (OAc), $OC(CH_3)_3$, SCH_3, and OC_6H_5, etc., at C-1 have their own abscissal values (*i.e.*, atomic refraction) in Figure 1 and their corresponding molecular rotations, $[M]_D$, fall just on their standard lines,[3,5] but his examination was limited only to the tetra-*O*-acetyl-D-glucopyranosyl series and therefore is incomplete. In this article, as many kinds of sugars as possible are examined.[6]

Molecular rotations under discussion are given in Tables I–IV.

Now, the author tries to see on which abscissal value the molecular rotation M_D of a compound whose aglycon moiety is a radical falls,[3] as follows. First, a horizontal line which is expressed by eq 1 is called

$$\text{ordinate value} = M^{20}_D \text{ value of a compound} \qquad (1)$$

"line 1." The intersection of line 1 and its corresponding standard line is marked in Figure 1. Concretely speaking, M^{20}_D of methyl 2,3,4-tri-*O*-acetyl α-D-xylopyranoside is given by the intersection of the α-D-Xy line and the horizontal line expressed by its eq 1 (ordinate value = 347.2, M^{20}_D of methyl 2,3,4-tri-*O*-acetyl α-D-xylopyranoside) in Figure 1. In like manner, the points of M^{20}_D of various methyl acetylated glycopyranosides are fixed and shown by the black squares.

It is clear that the abscissal values of these marks, in only α-D- (or β-L-) aldopyranosyl and β-D- (or α-L-) keto-

TABLE I

M^{20}_D (IN CHLOROFORM) OF POLY-*O*-ACETYLALDOPYRANOSYL COMPOUNDS

Derivatives of 2,3,4-tri-*O*-acetyl-	M^{20}_D for X at C-1 OH	OCH$_3$	OC$_6$H$_5$	OAc
β-L-Arabinose	*u*	528.3[a,v]	*u*	468.5[a,v]
α-D-Xylose	194.6[b,v]	347.2[b]	475.7[c]	284.2[d]
β-D-Xylose	*u*	−176.8[b,v]	−177.9[c]	−77.7[b,v]
β-D-Ribose	*u*	−50.5[e,v]	*u*	−165.5[e,v]
β-D-Rhamnose	−81.6[f,w]	*u*	*u*	
Derivatives of 2,3,4,6-Tetra-*O*-acetyl-				
α-D-Galactose	503.0[g,v]	481.9[h]	744.8[i]	416.5[j]
β-D-Galactose	81.2[k]	−50.7[h]	−3.0[l]	97.6[j]
α-D-Glucose	487.6[m]	472.8[n]	716.0[c]	396.6[n]
β-D-Glucose	7.6[o,v,w]	−65.9[n]	−95.5[c]	14.8[n]
α-D-Mannose	80.5[p,v]	177.2[q]	313.6[r]	221.3[p,v]
β-D-Mannose	−47.4[p]	−170.3[q]	−266.3[r,v]	−111.6[s]
α-D-Talose	149.1[t]	*u*	*u*	274.0[t]

[a] C. S. Hudson and J. K. Dale, *J. Am. Chem. Soc.*, **40**, 992 (1918). [b] C. S. Hudson and J. K. Dale, *ibid.*, **40**, 997 (1918). [c] E. M. Montgomery, N. K. Richtmyer, and C. S. Hudson, *ibid.*, **64**, 690 (1942). [d] C. S. Hudson and J. M. Johnson, *ibid.*, **37**, 2748 (1915). [e] P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, **92**, 109 (1931). [f] E. Fischer, M. Bergmann, and A. Rabe, *Ber.*, **53**, 2362 (1920). [g] H. H. Schlubach and R. Gilbert, *ibid.*, **63**, 2292 (1930). [h] J. K. Dale and C. S. Hudson, *J. Am. Chem. Soc.*, **52**, 2534 (1930). [i] B. Helferich and H. Bredereck, *Ann. Chem.*, **465**, 166 (1928). [j] C. S. Hudson and H. O. Parker, *J. Am. Chem. Soc.*, **37**, 1589 (1915). [k] J. Compton and M. L. Wolfrom, *ibid.*, **56**, 1157 (1934). [l] B. Helferich and E. S. Hillebrecht, *Ber.*, **66**, 378 (1933). [m] H. H. Schlubach and I. Wolf, *ibid.*, **62**, 1507 (1929). [n] C. S. Hudson and J. K. Dale, *J. Am. Chem. Soc.*, **37**, 1264 (1915). [o] E. Fischer and K. Delbrück, *Ber.*, **42**, 2778 (1909). [p] W. A. Bonner, *J. Am. Chem. Soc.*, **80**, 3372 (1958). [q] J. K. Dale, *ibid.*, **46**, 1046 (1924). [r] B. Helferich and S. Winkler, *Ber.*, **66**, 1556 (1933). [s] W. W. Zorbach and S. Saeki, *Naturwiss.*, **50**, 93 (1963). [t] W. W. Pigman and H. S. Isbell, *J. Res. Natl. Bur. Std.*, **19**, 189 (1937). [u] Unknown. [v] This was assumed from the M_D, which had been observed in the neighborhood of 20°. [w] In ethanol.

TABLE II

M^{20}_D (IN CHLOROFORM) OF POLY-*O*-ACETYLKETOPYRANOSYL COMPOUNDS

Derivatives of 1,3,4,5-tetra-*O*-acetyl-	M^{20}_D for X at C-2[f] OH	OCH$_3$	OC$_6$H$_5$	OAc
β-D-Fructose	−319.0[a]	−452.9[b]	−619.6[c]	−471.9[b]
α-L-Sorbose	−74.2[d]	−190.6[d]	*e*	−220.5[d]

[a] C. S. Hudson and D. H. Brauns, *J. Am. Chem. Soc.*, **37**, 2736 (1915). [b] E. Pacsu and F. B. Cramer, *ibid.*, **57**, 1944 (1935). [c] See footnote *l* in Table I. [d] H. H. Schlubach and G. Graefe, *Ann. Chem.*, **532**, 211 (1937). [e] Unknown. [f] 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.

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(1) Part I: S. Yamana, *J. Org. Chem.*, **31**, 3698 (1966).

(2) 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 the molecular rotation against the atomic refraction of X. This fact is indifferent to the configuration at the 1 position.

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

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

(3) The M^{20}_D − R_D (for halogen) lines of the fully acetylated glycopyranosyl compounds, already given in Figures 1 and 4 of the previous paper,[1] are named "Standard Lines" and used in this article as Figure 1.[4]

(4) Symbols are as follows: Ar, arabinose derivative; Fr, fructose derivative; Ga, galactose derivative; G, glucose derivative; M, mannose derivative; Rh, rhamnose derivative; Ri, ribose derivative; So, sorbose derivative; Ta, talose derivative; Xy, xylose derivative.

(5) O. Arndt, *Ann. Chem.*, **695**, 184 (1966).

(6) In order to compare the sugars which have the common kind of aglycon moiety in each, the kinds of radicals used are limited to a few. In this article, four radicals (OH, OAc, OCH_3, and OC_6H_5) are examined.

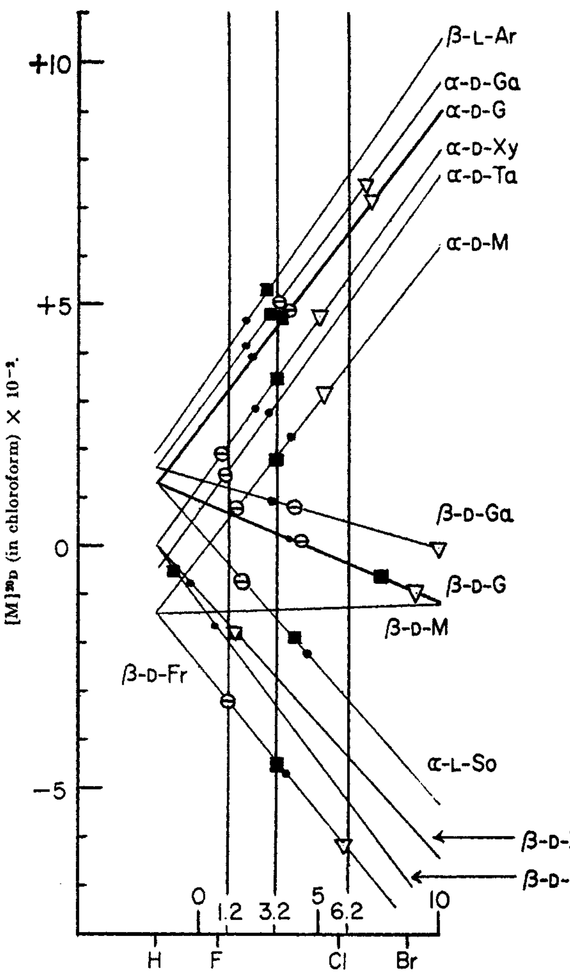

Figure 1.—Position of molecular rotation of acetylated glycopyranoside on the standard line:[3,4] ⊖ ····· (OH); ■ ····· (OCH_3); ▽ ····· (OC_6H_5); ● ····· (OAc).

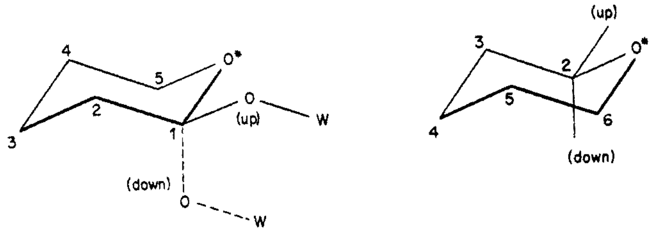

Figure 2.

TABLE III

$M^{20}D$ (IN WATER) OF ALDOPYRANOSYL COMPOUNDS

Derivatives of	H	F	OH	OCH_3	OC_6H_5
	$M^{20}D$ for X at C-1				
β-L-Arabinose	132.3[a]	276.9[b]	303.3[c]	402.2[d]	549.7[e,dd]
α-L-Arabinose	132.3[a]	*cc*	133.6[c]	27.9[d]	13.6[e,dd]
α-D-Xylose	0.0[f]	115.6[g,ee]	140.5[h]	252.8[d]	427.6[i]
β-D-Xylose	0.0[f]	*cc*	−30.0[j,ee]	−106.7[d]	−111.8[i]
α-D-Rhamnose	−124.2[k]	*cc*	15.7[h]	111.4[l]	254.7[m,dd]
β-D-Rhamnose	−124.2[k]	*cc*	−63.0[n]	−170.0[o]	−210.2[m,dd]
α-D-Galactose	125.7[p]	*cc*	271.5[q]	380.6[d]	556.1[r,dd]
β-D-Galactose	125.7[p]	78.3[s]	97.7[q]	1.9[d]	−112.7[t,dd]
α-D-Glucose	70.3[k]	176.1[u,dd]	200.2[v]	308.8[d]	448.4[w]
β-D-Glucose	70.3[k]	45.5[x,dd]	31.5[v]	−66.0[d]	−181.9[w]
α-D-Mannose	−82.6[y]	29.1[z]	52.8[h]	153.4[d]	290.8[aa]
β-D-Mannose	−82.6[y]	*cc*	−30.6[h]	−130.1[bb]	−183.5[aa]

[a] H. G. Fletcher, Jr., and C. S. Hudson, *J. Am. Chem. Soc.*, **69**, 1672 (1947). [b] A. Klemer and J. Ridder, *Diplomarbeit, Münster*, 1958. [c] E. Montgomery and C. S. Hudson, *J. Am. Chem. Soc.*, **56**, 2074 (1934). [d] E. L. Jackson and C. S. Hudson, *ibid.*, **59**, 994 (1937). [e] B. Helferich, S. Winkler, R. Gootz, O. Peters, and E. Günther, *Z. Physiol. Chem.*, **208**, 91 (1932). [f] H. G. Fletcher, Jr., and C. S. Hudson, *J. Am. Chem. Soc.*, **69**, 921 (1947). [g] F. Micheel, A. Klemer, M. Nolte, H. Nordiek, L. Tork, and H. Westermann, *Chem. Ber.*, **90**, 1612 (1957). [h] H. S. Isbell and W. W. Pigman, *J. Res. Natl. Bur. Std.*, **18**, 141 (1937). [i] See footnote *c* in Table I. [j] E. Yanovsky and C. S. Hudson, *J. Am. Chem. Soc.*, **39**, 1013 (1917). [k] R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **72**, 4547 (1950). [l] E. Fischer, *Ber.*, **28**, 1158 (1895). [m] B. Helferich, H. Appel, and R. Gootz, *Z. Physiol. Chem.*, **215**, 277 (1933). [n] E. L. Jackson and C. S. Hudson, *J. Am. Chem. Soc.*, **59**, 1076 (1937). [o] See footnote *f* in Table I. [p] H. G. Fletcher, Jr., and C. S. Hudson, *J. Am. Chem. Soc.*, **70**, 310 (1948). [q] C. N. Riiber, J. Minsaas, and R. T. Lyche, *J. Chem. Soc.*, 2173 (1929). [r] B. Helferich and H. Appel, *Z. Physiol. Chem.*, **205**, 231 (1932). [s] F. Micheel, A. Klemer, G. Baum, P. Ristić, and F. Zumbülte, *Chem. Ber.*, **88**, 475 (1955). [t] B. Helferich, S. Demant, J. Goerdeler, and R. Bosse, *Z. Physiol. Chem.*, **283**, 179 (1948). [u] B. Helferich, K. Bäuerlein, and F. Wiegand, *Ann. Chem.*, **447**, 27 (1926). [v] A. Neuberger and R. P. Rivers, *J. Chem. Soc.*, 122 (1939). [w] T. G. Bonner, E. J. Bourne, and S. McNally, *ibid.*, 761 (1926). [x] F. Micheel and A. Kelemer, *Chem. Ber.*, **85**, 187 (1952). [y] H. G. Fletcher, Jr., and H. W. Diehl, *J. Am. Chem. Soc.*, **74**, 3175 (1952). [z] F. Micheel and D. Borrmann, *Chem. Ber.*, **93**, 1143 (1960). [aa] See footnote *r* in Table I. [bb] R. E. Reeves, *J. Am. Chem. Soc.*, **72**, 1499 (1950). [cc] Unknown. [dd] This was assumed from the MD, which had been observed in the neighborhood of 20°. [ee] In ethanol.

TABLE IV

$M^{20}D$ (IN WATER) OF KETOPYRANOSYL COMPOUNDS

Derivative of	H	F	OH	OCH_3	OC_6H_5
	$M^{20}D$ for X at C-2[i]				
β-D-Fructose	−82.6[a]	−216.8[b]	−239.6[c]	−334.2[c]	−538.1[d]
α-L-Sorbose	70.3[e]	*h*	−77.8[f]	−172.2[g]	*h*

[a] 1,5-Anhydro-D-mannitol; see footnote *y* in Table III. [b] F. Micheel, A. Klemer, M. Nolte, H. Nordiek, L. Tork, and H. Westermann, *Chem. Ber.*, **90**, 1612 (1957). [c] C. S. Hudson and D. H. Brauns, *J. Am. Chem. Soc.*, **38**, 1216 (1916). [d] See footnote *l* in Table I. [e] 1,5-Anhydro-D-glucitol; see footnote *k* in Table III. [f] H. H. Schlubach and J. Vorwerk, *Ber.*, **66**, 1251 (1933). [g] See footnote *d* in Table II. [h] Unknown. [i] 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.

pyranosyl compounds[7] (see Figure 1), are all nearly equal to *ca.* 3.2 which is apparently different from the atomic refraction, RD, of the methoxy radical, 7.417.[8] This phenomenon is similar to the case of the hydrogen atom in the hydrides, already described in rules 2 and 3,[2] and here we are forced to assume that the abscissa of Figure 1 (also in all the figures of the previous paper[1]) corresponds, in general, to some new optical property (*S*) and not to the atomic refraction, RD, itself, and that only for halogen groups is the *S* value proportional to the RD value and only in this case can RD be used as the abscissa.

Similarly, the other kinds of aglycon moiety (*i.e.*, OAc and OC_6H_5, etc.) are treated and the results are given in Figure 1, in which it is apparent that the abscissal values of these kinds of radicals are not strictly constant (even in both α-D- (or β-L-) aldopyranosyl and β-D- (or α-L-) keptopyranosyl series). Thus, Arndt's conclusion (that, indifferent to their configurations at the 1 position of the pyranose ring, OAc and OC_6H_5 have their own abscissal values, respectively) is limited only to the D-glucose series and apparently has no generality.

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[7] It is apparent from the geometries of the molecules, that the aglycon moiety is axial in α-D- (or β-L-) aldopyranosyl or β-D- (or α-L-) ketopyranosyl compounds, but it is equatorial in β-D- (or α-L-) aldopyranosyl compounds. (See Figure 2).

[8] A. I. Vogel, *J. Chem. Soc.*, 1833 (1948).

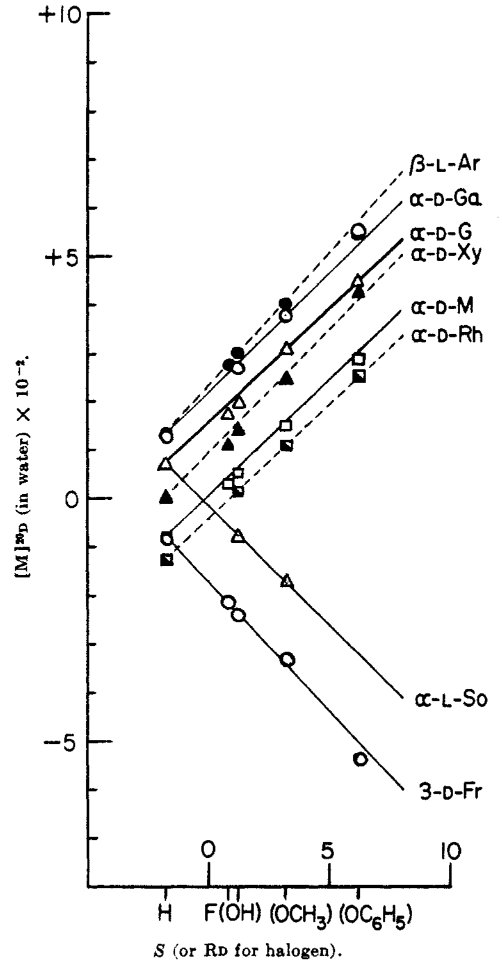

Figure 3. Molecular rotation of unacetylated glycopyranoside which has an axial radical attached to the ring carbon atom, next to the ring oxygen, as a function of S value of the radical.[4,11]

Axial Radical.—It can be seen in Figure 1, however, that for each of axial aglycon moieties (*i.e.*, OH, OAc, or OC_6H_5), the fluctuation in the abscissal values is small. This suggests that these axial radicals (as well as OCH_3 already mentioned) can have their own definite S values (*i.e.*, abscissal values) when in unacetylated sugars, but these values are changed in acetylated sugars owing to the interactions between these aglycon moieties and the closely situated, bulky acetoxy groups in the molecule.[9]

In order to test the validities of these assumptions and S values, tentatively given here,[9] the M^{20}_D values of unacetylated glycopyranosyl compounds (which have no bulky acetoxy groups in the molecule) are plotted against these S values. The results are given in Figure 3.[10,11]

The perfectly straight lines obtained here may prove that each of the axial OH and OC_6H_5 moieties (as well as that of OCH_3) has its own seemingly definite S values.[12] By plotting M^{20}_D values of poly-*O*-acetylglycopyranosyl compounds, each having an axial radical at the 1 position of the ring, against these S values, Figure 4 is obtained, in which the plot of $M^{20}_D - S$ (or R_D for halogen) is not straight but zigzag. This shape must tell something concerning the manner of interactions between the axial radical at the 1 position and the acetoxy groups in the remainder of the molecule.

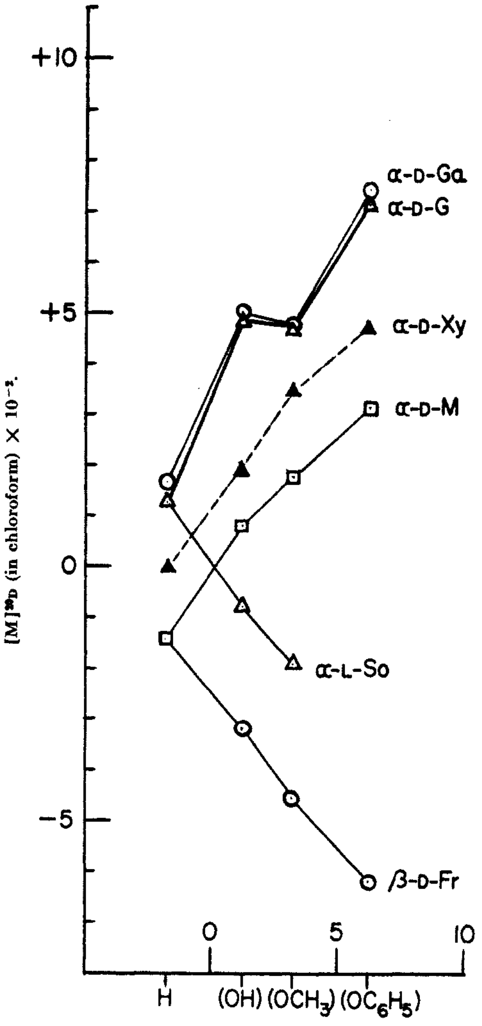

Figure 4.—Molecular rotation of acetylated glycopyranoside which has an axial radical attached to the ring carbon atom, next to the ring oxygen, as a function of S value of the radical.[4] (Concerning $[M]^{20}_D$ data of hydrides, see Table I of ref 1.)

Equatorial Radical.—Next, β-D- (or α-L-) aldopyranosyl compounds (whether acetylated or unacetylated) which have an equatorial radical at the 1 position are treated. Figures 5 and 6[13] are obtained by plotting the M^{20}_D values of these compounds against the S values of the radicals at the 1 position.[13] These $M^{20}_D - S$ plots are, apparently, not straight but zigzag and in order to interpret their slopes by their molecular structures, it is convenient to examine these plots (in Figures 5 and 6), by dividing them into several sections, as follows.

A. From H to OH.—It is clear in Figures 5 and 6, that with regard to the axis of abscissa, the $M^{20}_D - S$·

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(9) According to Figure 1, the mean value of the abscissal values of an axial radical at the 1 position of the pyranose ring is as follows:[7] OH has a value of *ca.* 1.2, OAc a value of *ca.* 2.5, and OC_6H_5 a value of *ca.* 6.2. These values are taken tentatively as the S values of these radicals.

(10) As the M_D data of acetyl glycopyranosides are unknown, the abscissal value of OAc at the 1 position cannot be examined.

(11) For comparison, the fluorides which have the F atom at the 1 position are also examined here. As F is a halogen, the S value of F is equal to its R_D, 0.81.[8] On the other hand, the S value of H is −1.8.[2]

(12) These values can not be related directly to their corresponding atomic refractions (R_D of OH is 2.546; R_D of OC_6H_5 is 27.123).[8]

(13) The $M^{20}_D - s$ lines of the acetylated compounds (in Figure 5) resemble those of the corresponding unacetylated compounds (in Figure 6) in shape, but the slopes of the former are steeper than those of the latter.

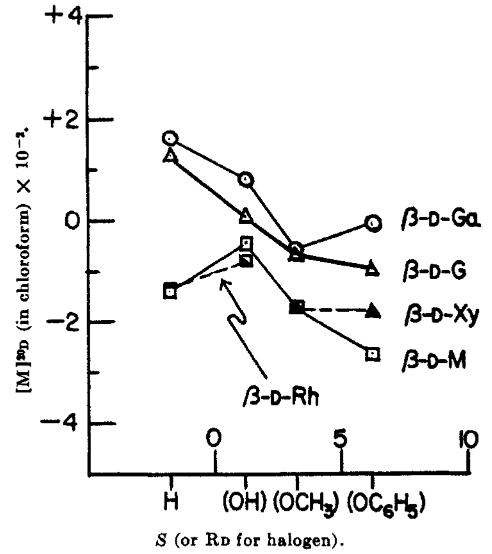

Figure 5.—Molecular rotation of acetylated glycopyranoside which has an equatorial radical attached to the ring carbon atom, next to the ring oxygen, as a function of S value of the radical.[4] (Concerning $[M]^{20}_D$ data of hydrides, see Table I of ref 1.)

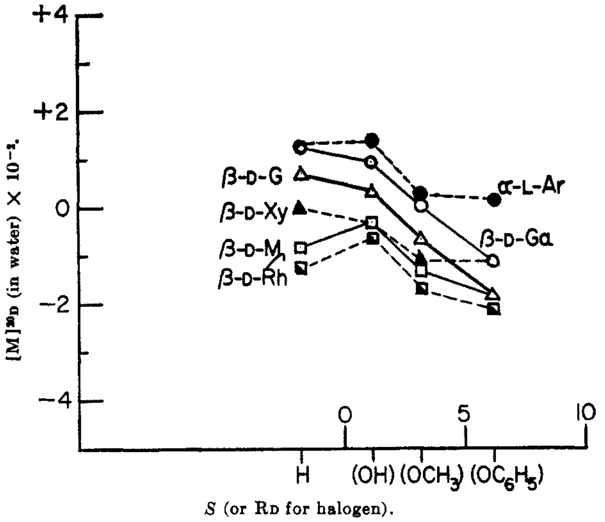

Figure 6.—Molecular rotation of unacetylated glycopyranoside which has an equatorial radical attached to the ring carbon atom, next to the ring oxygen, as a function of S value of the radical.[4]

[H → OH]-1 (up) lines[14] of β-D-Ga and β-D-G are nearly the mirror images of those of β-D-M and β-D-Rh. On the other hand, it is obvious in their structures that the orientation of the group at the 2 position of the ring is "down" in β-D-G and β-D-Ga and "up" in β-D-M and β-D-Rh. In other words, from the standpoint of the relative configurations at the 1 and 2 positions, β-D-G and β-D-Ga are the mirror images of β-D-M and β-D-Rh. This may be the principal reason for the mirror-image relation of the $M^{20}_D - S$[H → OH]-1 (up) lines in Figures 5 and 6.[15] Then, some methods of estimating molecular rotation such as Whiffen's,[17] Brewster's,[18] or the PM methods[19] may be available here.

B. From OH to OCH_3.—As is apparent in Figures 5 and 6, the $M^{20}_D - S$[OH → OCH_3]-1 (up) lines are all nearly parallel to each other and this is almost indifferent to the orientation of the radical at the 2 position (to say nothing of the other positions of the pyranose ring). This phenomenon may indicate that the CH_3 group in the OCH_3 radical at the 1 position is situated too far away from the radical at the 2 position to cause any new, appreciable partial molecular rotations with it.[20,21] This interpretation is consistent with the stereochemical viewpoint. That is to say, stereochemistry demands that the most stable situation of the O-1–CH_3 bond which has the minimal potential to be *trans* to the C-1–C-2 bond (see Figure 2) is the furthest from the 2 position of the ring.[22]

On the other hand, according to Whiffen's method[17] (as well as Brewster's[18] or the PM method[19]), the partial molecular rotation caused by a pair of O-1–CH_3 bond of OCH_3-1 (up) in the *trans* position and a C-1–O* bond in the ring should be negative in sign. This estimation is consistent with the downward slopes of $M^{20}_D - S\cdot$[OH → OCH_3]-1 (up) lines in Figures 5 and 6. Thus, it is concluded here, in the $M^{20}_D - S$ diagram, that although a hydroxy radical can be treated as a quasi-single particle, a methoxy radical should be decomposed into two components, as shown in eq 2.

$$OCH_3 \doteqdot OH + CH_3 \qquad (2)^{16,23}$$

C. From OCH_3 to OC_6H_5.—It is clear in Figure 5 that the slope of $M^{20}_D - S$[OCH_3 → OC_6H_5]-1 (up) line is greatly dependent on the parent sugar and the same is in Figure 6. Moreover, when comparing Figures 5 and 6, the effects of the acetoxy groups are apparent. The unacetylated compounds which have no acetoxy groups in their molecules show three kinds of slopes of $M^{20}_D - S$[OCH_3 → OC_6H_5]-1 (up) line in Figure 6 (*i.e.* α-L-Ar and β-D-Xy, β-D-Ga and β-D-G, and β-D-M and β-D-Rh). Therefore, the slope of the line can be concluded to be indifferent to the orientation of the hydroxy group at the 4 position of the ring (which is the opposite side of the 1 position, with regard to the center of the ring).

On the other hand, in the case of the acetylated compounds, there are three types of slopes of the lines in Figure 5 (*i.e.*, β-D-Ga, β-D-G and β-D-Xy, and β-D-M). The phenomenon that β-D-G and β-D-Xy belong to the same class may indicate that the slope of the line of the acetylated compound is not influenced very much by the CH_2OAc group at the 5 position.

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(14) Of course, when the X radical is replaced by the X′ radical at the 1 position, the M^{20}_D value of a compound generally changes. The $M^{20}_D - S$ line corresponding to this X → X′ change at the 1 position is symbolized thereafter as the $M^{20}_D - S$ [X → X′]-1 line.

(15) The rough mirror image relation between (β-D-G and β-D-Ga) and β-D-M can already be seen even when the aglycon moiety is an atom.[1] The fact that the $M^{20}_D - s$ line of the β-D halide can not coincide with that corresponding to the H → OH change at the 1 position in (up) proves that, strictly speaking, a hydroxyl radical can not be treated as a single particle.[16]

(16) Strictly speaking, a hydroxy radical should be treated as follows:[15]

$$(OH) \doteqdot O + H.$$

(17) D. H. Whiffen, *Chem. Ind.* (London), 964 (1956).

(18) J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 (1959); *Tetrahedron*, **13**, 106 (1961).

(19) S. Yamana, *Bull. Chem. Soc. Japan*, **31**, 558 (1958); *J. Am. Chem. Soc.*, **86**, 1606 (1964); *Tetrahedron*, **21**, 709 (1965).

(20) In this situation, the partial molecular rotation due to this CH_3 group is mostly caused between this group and the polarizable ring oxygen atom, O*.[21] (In other words, between the O-1–(CH_3) bond in OCH_3-1 (up) and the C-1–O* bond in the ring.)

(21) O* means the ring oxygen atom.

(22) See the anticipations in the previous paper: S. Yamana, *Bull. Chem. Soc. Japan*, **32**, 597 (1959).

(23) This manner of treatment of a complex radical has often been used by the present author. For example, see S. Yamana, *Bull. Chem. Soc. Japan*, **34**, 1414 (1961); ref 22.

Discussion

Now we can conclude that, when any suitable value of S is given to the aglycon moiety, the M^{20}D − S (or RD for halogen) plot can, although it is generally zigzag, be straight under the following special conditions: (1) when an atom (such as H, F, Cl, Br, or I) attaches (whether in the axial or equatorial position) to the 1 position of the pyranose ring (whether acetylated or benzoylated);[1,2] (2) when an axial OCH_3 attaches to the 1 position of the pyranose ring (whether acetylated or unacetylated); (3) when an axial radical (such as OH or OC_6H_5 attaches to the 1 position of the pyranose ring (unacetylated only).

These three conditions are tabulated as Table V.

TABLE V

CONDITIONS FOR THE STRAIGHT LINE OF M^{20}D − S (OR RD FOR HALOGEN) PLOT

Condition	1 Position	Other position
1	Atom, axial or equatorial	OAc or OBz
2	Axial, OCH_3	OH or OAc
3	Axial, OH or OC_6H_5	OH

The details of the physical meanings of these conditions (especially of the first condition) are left for the future. The second and third conditions can, however, be explained qualitatively as follows.

As was already shown in the equatorial radical at the 1 position, the slopes of M^{20}D − S (or RD for halogen) lines can be explained by using the estimation methods of optical rotatory power.[17-19] These methods may be available also in the axial radical at the 1 position. From the standpoint of the stereochemistry, the most stable position of O-1–W bond in the axial OW radical is *trans* to the C-1–C-2 bond (Figure 2), and the partial molecular rotation of the O*–C-1–O-1–W moiety should, owing to the estimation methods of optical rotation,[17-19] be positive in sign. Moreover, the O_1–W bond in this situation is relatively far from the pyranose ring plane and, as O* is the nearest atom to the W atom, the greater part of the partial molecular rotation of W (or O-1–W bond) in OW radical may be the one contributed by this O*–C_1–O_1–W moiety and accordingly it may be almost indifferent to the configurations at the other positions in the ring. This may be the principal reason for the fact that M^{20}D − S (or RD for halogen) plot of the compounds which have an axial radical at the 1 position are nearly parallel and their slopes are positive in sign (*i.e.*, upward). When there are bulky acetoxy radicals at the other position in the ring, however, these acetoxy radicals may be able to interact with OH or OC_6H_5 at the 1 position to cause the zigzag shape of the M^{20}D − S plots.

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Thio Sugars. Synthesis of the Adenine Nucleosides of 4-Thio-D-xylose and 4-Thio-D-arabinose[1]

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The preparation of methyl 2,3-di-*O*-benzoyl-4-*S*-benzoyl-4-thio-α-D-xylopyranoside (**2**) has been accomplished starting from methyl β-L-arabinopyranoside. Acetolysis of **2** effected a ring contraction to give 1,5-di-*O*-acetyl-2,3-di-*O*-benzoyl-4-thio-D-xylofuranose (**4**). A nucleoside condensation of **4** with chloromercuri-6-benzamidopurine gave a mixture of α and β anomers of 9-(4-thio-D-xylofuranosyl)adenine (**5**) which could be separated as their 3,5-*O*-isopropylidene derivatives (**6**). Methylsulfonation of **6**, followed by deacetonation of the resulting mesylate (**7**) and then treatment with sodium methoxide, gave 9-(2,3-anhydro-4-thio-β-D-lyxofuranosyl)adenine (**9**). Reaction of **9** with sodium acetate in *N*,*N*-dimethylformamide (DMF) gave a mixture of 9-(4-thio-β-D-arabinofuranosyl)adenine (**10**) and the isomeric xyloside (**5b**), in the ratio 8:1.

In recent years, a number of monosaccharides have been prepared in our laboratories in which the C-4 hydroxyl has been replaced by a sulfur or nitrogen function in order to prepare ultimately, nucleosides in which the furanose ring oxygen has been substituted by sulfur or nitrogen. We have reported previously on the preparation of 4′-thioadenosine[2] and 4′-acetamidoadenosine[3] as well as 9-(4-acetamido-4-deoxy-β-D-xylofuranosyl)adenine.[4] A report by Bloch[5] described a reduction by 50% in the growth of *Streptococcus faecalis* by a 4.5 × 10^{-7} M solution of 4′-thioadenosine. Evidence was presented that the action was due to interference by thioadenosine with the formation of deoxyadenylates. This activity of a nucleoside of 4-thioribose together with the known biological activity of 9-(β-D-xylofuranosyl)adenine[6] and 9-(β-D-arabinofuranosyl)adenine[7] made it desirable to prepare the sulfur analogs, 9-(4-thio-β-D-xylofuranosyl)adenine (**5b**) and 9-(4-thio-β-D-arabinofuranosyl)adenine (**10**), for biological evaluation. The synthesis of these nucleosides is the subject of this paper.

The sulfonate displacement of methyl 2,3-*O*-benzoyl-4-*O*-(*p*-tolylsulfonyl)-β-L-arabinopyranoside (**1**) by so-

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