# *Molecular Rotations of Glucides in Relation to their Structures. III. Optical Superposition in Pentoses*

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In 1874, vant't Hoff suggested that the partial rotation contributed by a given asymmetric carbon atom to the total rotation of a molecule containing several such atoms, is independent of the configuration of these other atoms*1. He predicted also that the rotation of arabinose should be equal to the sum of those of xylose, ribose and the expected fourth type of pentose at that time (lyxose), from the standpoint of the orientations of OH groups in their open chain structure(1). His prediction, however, was proved to be invalid by many experiments. Hudson found some interesting facts, suitable for proving van't Hoff's principle of optical superposition*1 in glucides, and he put forward two

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*1 Guye and Gautier (Ph. A. Guye and M. Gautier, *Compt. rend.*, **119**, 740 (1894)) named this idea "principe de la superposition algébrique des effets optiques des carbones asymétriques". This is called generally "vant't Hoff's principle of optical superposition".

1) Van't Hoff, *Bull. Soc. Chim.*, **23**, 298 (1875).

2) C. S. Hudson, *J. Am. Chem. Soc.*, **31**, 66 (1909).

TABLE I

| Name | Unit Groups | $[M]^{20}_{D}$(W) | Lit. |
|---|---|---|---|
| β-L-arabinose | [$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, Ring] | 303.3° | (a) |
| α-L-arabinose | [$(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, Ring] | 133.6° | (a) |
| α-D-xylose | [$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, Ring] | 138.1° | (b) |
| β-D-xylose | [$(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, Ring] | | |
| α-D-ribose | [$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\alpha}$, $(OH)^{4\alpha}$, Ring] | | |
| β-D-ribose | [$(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\alpha}$, $(OH)^{4\alpha}$, Ring] | | |

isorotation rules as set out below[2];

Rule 1—"The rotation of $C^1$- atom in the case of many substances of the sugar group is affected in only a minor degree by changes in the structure of the remainder of the molecule".

Rule 2—"Changes in the structure of $C^1$- atom in the case of many substances of sugar group affect in only a minor degree the rotation of the remainder of the molecule".

But mannose deviates from the first empirical rule. Then, in order to explain this anormality, Hudson assigned to α-D-mannose a five-membered (furanose) ring, whilst admitting the presence of the six-membered (pyranose) ring in glucose and galactose, as well as in β-D-mannose[3]. Nevertheless, his idea was not supported by any independent chemical evidence. In 1929, under the hypothesis that the van't Hoff's principle exists in glucide, that is to say, every one of the asymmetric carbon atoms in the aldopyranose-ring possesses its own definite partial molecular rotation, Isbell calculated the values of these partial molecular rotations by simple algebraic summation and subtraction of $[M]^{20}_{D}$(W)[*2] of several glucides. By using these calculated values, he presumed $[M]^{20}_{D}$(W) of sixteen glucides, then unknown[4]. However, many independent experiments have proved most of them to be inaccurate. Haworth and Hirst attributed these irregularities of rotatory power to the influence of dissimilarities of configuration[5], in accordance with the view of Rosanoff[6] who held that the optical rotatory power of an asymmetric carbon atom depends not only upon the composition and constitution, but also upon the configuration of the glucides. Rosanoff's view was very splendid. But it had no ground of physical theory and was not quantitative. In 1951, the author proposed the application of the calculation-method based on quantum mechanics, to illustrate $[M]^{20}_{D}$(W) of glucides[7]. Lately, the author succeeded in explaining Hudson's first isorotation rule and the deviation of mannose from this[8], on the basis of Kirkwood's polarizability theory of optical rotatory power[9], which adopted the idea that the partial rotation is caused by the dynamical coupling effect between any two unit groups in a molecule.

By using the method which is similar to that used in the previous paper[8], the author tried here to elucidate the relation between the structure of pentoses[*3] and the value of their molecular rotations; this attempt had been continued since the time of van't Hoff without success, and it was found that there exists the principle of optical superposition of Kirkwood's idea in the pentose group.

## Molecular Model and Data Used[*4]

The names of pentoses, to which the calculations were applied, unit groups in their molecules, and their corresponding molecular rotations are tabulated in Table I[*5].

In order to simplify the calculations, the molecular model of an aldopyranose-ring of Reeves' C 1 conformation (the bond length of C–O is 1.42 Å) which was used in the previous paper[8], was also adopted here. (Fig. 1)

The optical data for OH group and H

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3) C. S. Hudson, *J. Am. Chem. Soc.*, **52**, 1680 (1930).

*2 $[M]^{20}_{D}$(W) is a notation which represents the optical molecular rotation of the plane polarized light of wave-length of D line at 20°C by an aqueous solution.

4) H. S. Isbell, *Bureau of Standards. J. Res.*, **3**, 1041 (1929).

5) W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, **1930**, 2615.

6) M. A. Rosanoff, *J. Am. Chem. Soc.*, **28**, 525 (1906); **29**, 536 (1907).

7) S. Yamana, Presentation and Discussion at the XIIth International Congress of Pure and Applied Chemistry. September (1951), New York.

8) S. Yamana, This Bulletin, **30**, 207 (1957).

9) J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937).

*3 In the cases of hexose and methyl pentose, there are $CH_2OH$ and $CH_3$ groups which combine with $C^5$-atom of the aldopyranose-ring, respectively. Then, the calculations become very complicated. In order to avoid this intricacy, only the pentose group is treated in this article. (Concerning the problem of hexose and methyl pentose, refer to Part IV of this study.

*4 Abbreviated symbols and notations, used in this paper, are the same as those in the previous paper (8).

*5 According to Reeves' continued investigations of cuprammonium-glycoside complexes (R. E. Reeves, *J. Am. Chem. Soc.*, **72**, 1499 (1950)), all of the following pentoses are of the C1 conformation of ring structure in their aqueous solutions, but the one remaining pentose (lyxose) is of both C1 and 1C conformations in its aqueous solution. Reeves, however, did not speak of the value of the quantitative ratio between these two types of conformation. Accordingly, it is impossible to try to make the calculation on lyxose in this paper.

a) E. Montogomery and C. S. Hudson, *J. Am. Chem. Soc.*, **56**, 2074 (1934).

b) J. K. Wolfe, R. M. Hann and C. S. Hudson, ibid., **64** 1493 (1942).

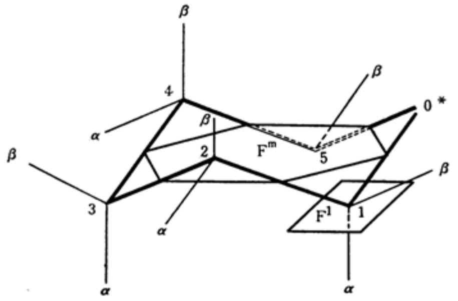

Fig. 1. Perspective drawing of the molecular model of an aldopyranose-ring of Reeves' C 1 conformation.
$F^m$………(Flar)$^m$-plane
$F^1$………(Flar)$^1$-plane

atom, used in the previous paper[10], were employed again without any correction. The refractive indices of the aqueous solutions of pentoses under question are presumed to be nearly equal (1.34)*[6].

## Method Proposed

The principle of the method of calculation is similar to that used in the previous paper[8]. The outline of this method is as follows;

(i)—The molecular model of pentose was divided into unit groups*[7].

(ii)—$[\mu]^{20}_{\mathrm{Dcalcd}}(3/n^2+2)$, caused by the dynamical coupling effect between any two members of these unit groups were calculated according to Kirkwood's polarizability theory*[8].

(iii)—$[\mu]^{20}_{\mathrm{Dobs}}$ was calculated from $[\mu]^{20}_{\mathrm{Dcalcd}}(3/n^2+2)$, above obtained*[9].

(iv)—In order to avoid the difficulty, caused by the impossibility of calculation of the terms with which the aldopyranose-ring is concerned, quasi-empirical methods were devised by using the experimental data of $[M]^{20}_{D}(W)$ of β-L-arabinose, α-L-arabinose and α-D-xylose.

(v)—By algebraic summation of $[\mu]^{20}_{\mathrm{Dobs}}$s, above obtained, $[M]^{20}_{D}(W)$s of β-D-xylose, α-D-ribose and β-D-ribose were calculated.

(vi)—These calculated values were compared with the molecular rotations which have been observed under such conditions as close to $[M]^{20}_{D}(W)$ as possible.

TABLE II

$[\mu]^{20}_{\mathrm{Dobs}}$, CAUSED BY THE DYNAMICAL COUPLING EFFECT BETWEEN ANY TWO MEMBERS OF UNIT GROUPS (EXCEPT RING)

| | 4β | 4α | 3β | 3α | 2β | 2α |
|---|---|---|---|---|---|---|
| 1α | 0 | 0 | 6.8 | 0 | 0 | 26.8 |
| 1β | 0 | 0 | 0 | −6.8 | 26.8 | −26.8 |
| 2α | 6.8 | 0 | 26.8 | −26.8 | | |
| 2β | 0 | −6.8 | −26.8 | 0 | | |
| 3α | 0 | 26.8 | | | | |
| 3β | 26.8 | −26.8 | | | | |

This method of calculation is illustrated by an example. The $[\mu]^{20}_{\mathrm{Dobs}}$, caused by dynamical coupling effect between any two members of unit groups in α-D-xylose molecule, are*[7] (1α)⅄(2α)*[10], (1α)⅄(3β), (1α)⅄(4α), (1α)⅄R*[11], (2α)⅄(3β), (2α)⅄(4α), (2α)⅄R, (3β)⅄(4α), (3β)⅄R and (4α)⅄R. Then, $[M]^{20}_{D}(W)$ of α-D-xylose, 138.1[b], should be equal to the sum of these $[\mu]^{20}_{\mathrm{Dobs}}$s*[12]. This relation is given by the following equation. (ref. Table II)

$$\begin{aligned}138.1 &\equiv \sum[\mu]^{20}_{\mathrm{Dobs}} = 26.8+6.8+0\\ &\quad +(1\alpha)\text{⅄}\mathrm{R}+26.8+0+(2\alpha)\text{⅄}\mathrm{R}\\ &\quad -26.8+(3\beta)\text{⅄}\mathrm{R}+(4\alpha)\text{⅄}\mathrm{R}\\ &= 33.6+(1\alpha)\text{⅄}\mathrm{R}+(2\alpha)\text{⅄}\mathrm{R}\\ &\quad +(3\beta)\text{⅄}\mathrm{R}+(4\alpha)\text{⅄}\mathrm{R} \qquad (1)\end{aligned}$$

Owing to the symmetry of the aldopyranose-ring,

$$(3\beta)\text{⅄}\mathrm{R} \equiv 0 \qquad (2)$$

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10) S. Yamana, This Bulletin, **30**, 203 (1957).

*6 Ref. *8 in the previous paper (8).

*7 Ref. Table 1 in this article.

*8 Concerning the method of calculation, refer to the previous paper (10).

*9 According to the previous paper(8), $[\mu]^{20}_{\mathrm{Dcalcd}}$, caused by the dynamical coupling effect between two OH groups in an aldopyranose molecule of C1 conformation in aqueous solution, becomes equal to $[\mu]^{20}_{\mathrm{Dobs}}$, when multiplied by $\kappa=12.37/n^2+2$. Then, in order to obtain $[\mu]^{20}_{\mathrm{Dobs}}$ from $[\mu]^{20}_{\mathrm{Dcalcd}}(3/n^2+2)$, the latter must be multiplied by $(n^2+2/3)(12.37/n^2+2)=12.37/3=4.123$. Consequently, the table of $[\mu]^{20}_{\mathrm{Dobs}}$, caused by the dynamical coupling effect between any two OH groups in this case, can be made by multiplying the values of $[\mu]^{20}_{\mathrm{Dcalcd}}(3/n^2+2)$ in Table I of the previous paper (8) with this coefficient, 4.123. But, in order to obtain the first significant decimal figures of $[\mu]^{20}_{\mathrm{Dobs}}$ more precisely, the absolute values, 1.66 and 6.50, should be used instead of 1.7 and 6.5 of the previous paper, respectively. It is important that the coefficient 4.123 was obtained by using the data of $[M]^{20}_{D}(W)$ of four hexoses(α-D-glucose, β-D-glucose, α-D-mannose and β-D-mannose), indifferent to those of pentoses.

*10 The notation X was used in the previous papers (10) (8) to represent $[\mu]^{20}_{\mathrm{Dcalcd}}(3/n^2+2)$, caused by the dynamical coupling effect between two unit groups. But, in this paper, $[\mu]^{20}_{\mathrm{Dobs}}$ is used instead of $[\mu]^{20}_{\mathrm{Dcalcd}}(3/n^2+2)$ for the algebraic summation course. Then, the other notation becomes necessary. The symbol, ⅄, was devised for this reason. This is inverted Y [wai] and is called "iaw [iɔ:]". $(1\alpha)\overset{20}{\underset{D}{\text{⅄}}}(2\alpha)$ means $[\mu]^{20}_{\mathrm{Dobs}}$, caused by the dynamical coupling effect between $(\mathrm{OH})^{1\alpha}$ and $(\mathrm{OH})^{2\alpha}$. But 20 and D in $\overset{20}{\underset{D}{\text{⅄}}}$ were omitted generally for convenience.

*11 R is an abbreviated symbol of Ring.

*12 Ref. Eq. (3) in the previous paper (10).

and $$(2\alpha)\lambda R+(4\alpha)\lambda R\equiv 0 \qquad (3)$$

Combining these two conditional equations with Eq. (1),

$$(1\alpha)\lambda R=104.5 \qquad (4)$$

A similar treatment was applied also to the cases of $\beta$-L- and $\alpha$-L-arabinose, and the following two equations were obtained. From $\beta$-L-arabinose,

$$(1\alpha)\lambda R+(2\alpha)\lambda R+(4\beta)\lambda R=209.3 \qquad (5)$$

and from $\alpha$-L-arabinose,

$$(1\beta)\lambda R+(2\alpha)\lambda R+(4\beta)\lambda R=100.0 \qquad (6)$$

By subtracting Eq. (4) from (5),

$$(2\alpha)\lambda R+(4\beta)\lambda R=104.8 \qquad (7)$$

and by subtacting Eq. (7) from (6),

$$(1\beta)\lambda R=-4.8 \qquad (8)$$

Thus, the values of two $[\mu]^{20}_{\mathrm{Dobs}}$s, $\{(1\alpha)\lambda R$ and $(1\beta)\lambda R\}$, and one $\sum[\mu]^{20}_{\mathrm{Dobs}}$, $\{(2\alpha)\lambda R+(4\beta)\lambda R\}$ were shown by Eqs. (4), (8) and (7). These values which were obtained quasi-empirically, seem to be reasonable, from the viewpoint of the geometry of the molecule, as described below:

[1]—The orientation of $1\alpha$ is essentially perpendicular to the hypothetical flat plane which is symbolized by $(\mathrm{Flar})^{\mathrm{m}}$-plane[*13] in Fig. 1 (axial bond), while that of $1\beta$ is almost in parallel with this flat plane (equatorial bond)11). (ref. Fig. 1). Accurately speaking, the direction of $1\beta$ projects out, greatly inclined toward the $(\mathrm{Flar})^{1}$-plane[*14] on the opposite side of $1\alpha$. Then, $(1\alpha)\lambda R$ and $(1\beta)\lambda R$ should be opposite in sign, and the absolute value of the former must be far greater than that of the latter[*15]. These conditions, which are required from the standpoint of the geometry of the molecule, are all satisfied by Eqs. (4) and (8). This indicates that Eqs. (4) and (8) are reasonable in their sign and magnitudes.

[2]—$4\beta$ and $2\alpha$ are axial and equatorial orientations respectively. (ref. Fig. 1). Then, the absolute value of $(4\beta)\lambda R$ must be far greater than that of $(2\alpha)\lambda R$. In other words, the sign of $(2\alpha)\lambda R+(4\beta)\lambda R$ should be the same as that of $(4\beta)\lambda R$....... (Condition A)

On the other hand, the positions of $C^1$- and $C^4$- atoms are on the opposite half of the aldopyranose-ring together, in relation to the symmetrical plane of this ring in which the centers of the ring-O-atom (represented by O*) and $C^3$- atom lie. Of course, the orientations of $\alpha$ and $\beta$ project out to the opposite sides of $(\mathrm{Flar})^{\mathrm{m}}$-plane together; then the second condition is obtained.

$(1\alpha)\lambda R$ and $(4\beta)\lambda R$ must be equal to each other in their sign[*15]....... (Condition B)

Referring to Conditions A and B, it is concluded as below; $\{(2\alpha)\lambda R+(4\beta)\lambda R\}$ and $(1\alpha)\lambda R$ should have the same sign....... (Condition C)

This condition is satisfied by Eqs. (4) and (7). As Eq. (4) has already been proved to be reasonable, above, Eq. (7) is concluded also to be probable.

In spite of the difficulties of calculating them by the purely theoretical procedure, the values of the terms containing R could be thus obtained quasi-empirically.

Now, $[\mathrm{M}]^{20}_{\mathrm{D}}(\mathrm{W})$ of three pentoses, can be calculated by using the values $[\mu]^{20}_{\mathrm{Dobs}}$s, above obtained. The $[\mu]^{20}_{\mathrm{Dobs}}$ in the case of $\beta$-D-xylose are $(1\beta)\lambda(2\alpha)$, $(1\beta)\lambda(3\beta)$, $(1\beta)\lambda(4\alpha)$, $(1\beta)\lambda R$, $(2\alpha)\lambda(3\beta)$, $(2\alpha)\lambda(4\alpha)$, $(2\alpha)\lambda R$, $(3\beta)\lambda(4\alpha)$, $(3\beta)\lambda R$ and $(4\alpha)\lambda R$[*16]. Then the calculated value of $[\mathrm{M}]^{20}_{\mathrm{D}}(\mathrm{W})$ of $\beta$-D-xylose is to be given by the following equation. (ref. Table II and Eqs. (2), (3), (8)).

$$[\mathrm{M}]^{20}_{\mathrm{D}}(\mathrm{W})=\sum[\mu]^{20}_{\mathrm{Dobs}}=-26.8+0+0+(1\beta)\lambda R+26.8+0+(2\alpha)\lambda R-26.8+(3\beta)\lambda R+(4\alpha)\lambda R=-31.6^{*17}$$

The corresponding observed value of $[\mathrm{M}]^{20}_{\mathrm{D}}(\mathrm{W})$ of $\beta$-D-xylose has not been found in any referential literatures, but Hudson reported that $[\mathrm{M}]^{20}_{\mathrm{D}}$ of this pentose in 80% alcoholic solution is $-30°$c), which is almost equal to the above calculated value. Next, this calculation-method was

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[*13] The molecular model of the aldopyranose-ring, used in this article, is one of Sachse strainless ring conformations and is not perfectly flat. (ref. the previous paper (8)). Then it is improper to use this aldopyranose-ring itself as a standard for comparing the orientations of hydroxyl O atom in the molecule. $(\mathrm{Flar})^{\mathrm{m}}$-plane was devised for this reason. It is a perfectly flat plane in which the middle points of $C^1$—$C^2$, $C^2$—$C^3$, $C^3$—$C^4$, $C^4$—$C^5$, $C^5$—O* and O*—$C^1$ bonds lie. (ref. Fig. 1). "Flar" is an abbreviated symbol of "Flat Aldose Ring".

11) D. H. R. Barton, O. Hassel, K. S. Pitzer and V. Prelog, *Nature*, **172**, 1096 (1953).

[*14] $(\mathrm{Flar})^{1}$-plane, on which the centre of $C^1$ atom lies, is parallel with $(\mathrm{Flar})^{\mathrm{m}}$-plane. (ref. Fig. 1).

[*15] Concerning the reason for these deductions from the relative geometry of unit groups, refer to Eq. (1) of the previous paper (10).

[*16] Ref. Table 1 in this article.

[*17] $[\mu]^{20}_{\mathrm{Dobs}}$s for the anomeric differences (*19) of D-xylose and D-ribose, calculated by using McDonald and Beevers' molecular model, are 168.7 and 171.3, respectively. (Concerning this new molecular model, refer to the next paper, This Bulletin, **30**, 920 (1957). In this case, the presumed value of $[\mathrm{M}]^{20}_{\mathrm{D}}(\mathrm{W})$ of $\beta$-D-xylose becomes −30.6.

c) C. S. Hudson and E. Yanovsky, *J. Am. Chem. Soc.*, **39**, 1013 (1917).

applied to the cases of α-D- and β-D-riboses[*18]. 131.3 and −38.4 were obtained as the calculated values of $[M]_D^{20}(W)$ of α-D- and β-D-riboses, respectively. The value observed for β-D-ribose is −34.7[d]. The datum of $[M]_D(W)$ of α-D-ribose has not been found in any referential literatures, but the calculated value (131.3) is greater than that of β-D-ribose (−38.4) by 169.7. The magnitude of this difference is equal to the observed value of the anomeric difference[*19] of L-arabinose. This fact is to be expected by Hudson's first isorotation rule[*20]. Thus, the calculated values of $[M]_D^{20}(W)$s of β-D-xylose, α-D-ribose and β-D-ribose seem to be all probable. This fact means that the principle of optical superposition of Kirkwood's idea exists in the pentose group.

## Summary

The method of calculation of optical rotatory power, devised by Kirkwood and improved by the author was applied to the pentose group, and it was concluded that the principle of optical superposition of Kirkwood's idea exists in this group.

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[*18] In this case, the conditional equation $(3\alpha)\lambda R = O$ was used in calculation. This was obtained from the symmetry of the Ring.

[d] F. P. Phelps, H. S. Isbell and W. W. Pigman, *J. Am. Chem. Soc.*, **56**, 747 (1934).

[*19] This is the difference in optical rotation of α and β aldoses. (ref. (8)).

[*20] Ref. "Introduction" in this article.