Molecular Rotations of Glucides in Relation to their Structures. V. The Internal Conformation of C^6—O Bond in D*-Galactopyranose in the Aqueous Solution and the Direction of the Optical Axis of Methylol Group*

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On the basis of Kirkwood's polarizability theory, the author explained the physical meaning of the empirical rule which had been found by Hudson about isorotation among anomers of aldoses[1]. In this explanation, the author used a simple molecular model of hypothetically ideal shape for simplification of calculation and also assumed that the orientation of OH group of $(CH_2OH)^{5\beta}$ as regards the aldopyranose-ring is definite and similar in D-galactopyranose, D-glucopyranose and D-mannopyranose[*1]. But strictly speaking, the orientation of OH group in $(CH_2OH)^{5\beta}$ is affected by the neighboring atoms and accordingly it may not always be equal in the molecule of D-galactopyranose and D-glucopyranose in aqueous solution[4]. On the other hand, Kirkwood expected that C*-atom with which C_2H_5 group combines in *sec*-butyl alcohol would have a marked effect on the optical axis of C_2H_5 and consequently this axis would be supposed to be placed on the plane of C*-atom and C—C bond in C_2H_5 group, and this axis would be inclined to this C—C bond at the angle between 0° and 54°44′ (one half the tetrahedral angle)[6]. By this conception, the optical axis of $(CH_2OH)^{5\beta}$ in an aldopyranose-molecule is expected to be on the plane of C^5-atom and C^6—O bond and this axis would incline to the C^6—O bond at an angle of θ[*2]. (Fig. 1)

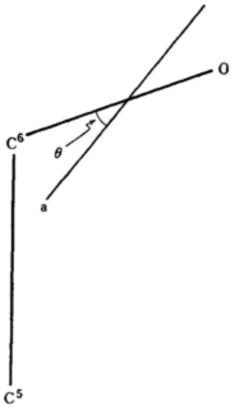

Fig. 1. Direction of the optical axis of $(CH_2OH)^{5\beta}$
a……optical axis.

According to this presumption, the author tried in this article, to calculate the values of the anomeric differences[*3] in molecular models of aldopyranoses[*4].

Molecular Model and Data Used

In the present calculation, Mc Donald

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[1] S. Yamana, This Bulletin, **30**, 207 (1957).

[*1] By this treatment, $[\mu]^{20}_{\mathrm{D\,calcd}}$, caused by the dynamical coupling effect of $(CH_2OH)^{5\beta}$ disappeared. Moreover, in order to simplify the calculations, the author assumed also in the previous papers[1-4] that, indifferently to its orientation, OH group has an optical axis of cylindrical symmetry directed along its bond to C atom with which it combines at resting state. In this case, OH group is treated as a single particle, like so-called pseudo-atom (ref. 5) of atomic weight, 17.008, indifferently to the position of H atom in this group. This state of OH group was called "isotropic" in the previous papers (1) (2). But, it never means that OH group is "optically isotropic".

[2] S. Yamana, ibid., **30**, 203 (1957).

[3] S. Yamana, ibid., **30**, 916 (1957).

[4] S. Yamana, ibid., **30**, 920 (1957).

[5] C. A. Coulson, *Quart. Rev.*, **1**, 144 (1947).

[6] J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937).

[*2] The value of this angle θ may be expected to lie between 0° and 54°44′ (one half the tetrahedral angle).

[*3] Ref. *2 in the previous paper 1. The anomeric difference is abbreviated to An. Diff., hereafter.

[*4] Then, it became possible to presume the internal conformation of C^6-O bond in D-galactopyranose in aqueous solution and the angle of inclination of the optical axis, θ, of $(CH_2OH)^{5\beta}$.

TABLE I

Name	Unit Groups	$[M]^{20}_{D}$(W)	Ref.[*10]
α-D-glucose	[$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_2OH)^{5\beta.\mathrm{ma}}$[*10], Ring]	202.1°	a)
β-D-glucose	[$(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_2OH)^{5\beta.\mathrm{ma}}$, Ring]	33.7°	a)
α-D-mannose	[$(OH)^{1\alpha}$, $(OH)^{2\beta}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_2OH)^{5\beta.\mathrm{ma}}$, Ring]	52.8°	a)
β-D-mannose	[$(OH)^{1\beta}$, $(OH)^{2\beta}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_2OH)^{5\beta.\mathrm{ma}}$, Ring]	−30.6°	a)
α-D-galactose	[$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, $(CH_2OH)^{5\beta.\mathrm{ga}}$[*11], Ring]	271.5°	a)
β-D-galactose	[$(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, $(CH_2OH)^{5\beta.\mathrm{ga}}$, Ring]	95.1°	a)
β-L-arabinose	[$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, Ring]	286.1°	a)
α-L-arabinose	[$(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, Ring]	115.6°[*12]	a)

and Beevers' molecular model[*5] was used. Unit groups in the molecules of several aldopyranoses and corresponding values of molecular rotations are shown in Table I[*7,*8].

Except the position of their optical centers, the optical data for OH group and H atom in the previous paper 2, are used again without any correction. Values of mean polarizability α and of anisotropy ratio β of CH_2OH group are 2.87×10^{-24} (cc)[c)] and 0.35[d)] respectively. It is supposed that CH_2OH group has its optical axis of cylindrical symmetry which is placed on the plane of C^5-atom and its C^6—O bond, and this axis inclines to the C^6—O bond at an angle θ[*2] (cf. Fig. 1). It is also supposed that the optical center of OH group which combines with C atom is located at the center of mass of C—(OH) bond, and the optical center of $(CH_2OH)^{5\beta}$ is at C^6-atom[*13]. The refractive indices

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[*5] Ref. *4 in the previous paper 4. This model seems to show the molecule-shape of an aldopyranose in aqueous solution more accurately than the ideal model[*6] does.

[*6] Ref. "Molecular Model and Data Used." in the previous papers 4 and 1.

[*7] Isbell and Pigman observed $[M]^{20}_{D}$(W) of aldopyranoses in details when studying the mutarotation-curves. In this paper, Isbell and Pigman's data were used. By using their data, it became apparent that An. Diff. of D-galactopyranose is not exactly but approximately equal to that of D-glucopyranose.

[*8] As it has not been confirmed that D-talopyranose has C 1 conformation in its aqueous solution, this sugar is not treated in this paper. If D-talopyranose has C 1 conformation, the following data would be used for α- and β-isomers.

Name	Unit Groups	$[M]^{20}_{D}$(W)	Ref.
α-D-talose	[$(OH)^{1\alpha}$, $(OH)^{2\beta}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, $(CH_2OH)^{5\beta.\mathrm{ga}}$[*9], Ring]	122.5°	a)[*10]
β-D-talose	[$(OH)^{1\beta}$, $(OH)^{2\beta}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, $(CH_2OH)^{5\beta.\mathrm{ga}}$, Ring]	23.8°	a)

[*9] Ref. *11 in this article. When the orientation of $(OH)^2$ of D-galactopyranose changes from α to β, D-talopyranose is obtained. But, the distance between the O atom in $(OH)^2$ and that in C^6-O bond in $(CH_2OH)^{5\beta.\mathrm{ga}}$ is too large to give rise to any influence of the orientation-change of $(OH)^2$ on the internal conformation of C^6-O bond. Therefore, the orientation of OH group in $(CH_2OH)^{5\beta}$ as regards the aldopyranose-ring may be definite and similar in these two sugars in aqueous solutions.

[*10] "ma" means the internal conformation concerning $(CH_2OH)^{5\beta}$ in the molecule of D-mannopyranose in aqueous solution. Accordingly, $(CH_2OH)^{5\beta.\mathrm{ma}}$ means CH_2OH group which combines with 5-position of the aldopyranose-ring in β-orientation, and at the same time, the internal conformation of the C^6-O bond in this CH_2OH group is of mostly *trans* type and sometimes *gauche* II type. (There exists an equilibrium between these two types). Concerning this information, refer to the previous paper 4.

a) F. J. Bates and associates, "Polarimetry, Saccharimetry and the Sugars", United States Government Printing Office, Washington (1942), p. 762.—"Isbell and Pigman Table of Optical Rotation and Mutarotation of the Reducing Sugars."

[*11] "ga" means the internal conformation concerning $(CH_2OH)^{5\beta}$ in the molecule of D-galactopyranose in aqueous solution (cf. *10).

[*12] This is $[M]^{20}_{D}$(W) of α-L-arabinose·$CaCl_2$·$4H_2O$ and not of the pure α-L-arabinose (ref. a)). In order to avoid this defect, it is advisable to use Hudson's data (ref. b)) subsidiarily. ($[M]^{20}_{D}$(W) of β-L-arabinose=303.3°; $[M]^{20}_{D}$(W) of α-L-arabinose =133.6°. By using these Hudson's data, An. Diff. of L-arabinose is (303.3−133.6=169.7). This is very consistent with that, obtained by using Isbell and Pigman's data, (286.1−115.6=170.5).

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

c) Landolt-Börnstein, Physikalisch-Chemische Tabellen, Hw. II. p. 985.

d) Values obtained by Ramakrishna-Rao; see Landolt-Börnstein, Physikalisch-Chemische Tabellen, 5th Ed., Eg. II. p. 91.

[*13] As the rotatory parameter, g, in the theoretical formula (ref. *14) contains the term, $1/R^3_{ik}$, the former is very sensitive to the magnitude of R_{ik}. In other words, a small deviation in the position of the optical center of a unit group causes a great deviation in $[\mu]^{20}_{D\mathrm{calcd}}$, with which this unit group is concerned. Then, concerning the position of the optical

of the aqueous solutions of aldopyranoses under question are presumed to be nearly equal (1.34)*16.

Method Proposed

Recently, the author proposed a possible method of estimating the approximate value of the molecular rotation $[M]^{20}_{\mathrm{D}}(\mathrm{W})$ of a glucide. The principle of this method is to calculate the partial molecular rotation, $[\mu]^{20}_{\mathrm{D}\,\mathrm{calcd}}$ (or $[\mu]^{20}_{\mathrm{D}\,\mathrm{calcd}}(3/n^2+2)$, for convenience), according to Kirkwood's polarizability theory at first, and next, to multiply this calculated value with a definite coefficient which can be obtained by using experimental data of some glucides, to get the true partial molecular rotation, $[\mu]^{20}_{\mathrm{D}\,\mathrm{obs}}$. By summing up all of these possible $[\mu]^{20}_{\mathrm{D}\,\mathrm{obs}}$ in a molecule, we can get the calculated value of $[M]^{20}_{\mathrm{D}}(\mathrm{W})$ of this substance*17. This method has its ground on the following equation

$$[\mu]^{20}_{\mathrm{D}\,\mathrm{obs}} = \kappa[\mu]^{20}_{\mathrm{D}\,\mathrm{calcd}}, \qquad (1)$$

where κ is a proportionality-constant and is always positive, and Eq. 1 is derived from the formerly presented equation

$$[M]^{20}_{\mathrm{D}\,\mathrm{obs}} = \kappa[M]^{20}_{\mathrm{D}\,\mathrm{calcd}}{}^{*18}$$

At any rate*19, a multiplying coefficient κ was found important to perform the semi-empirical application of Kirkwood's theory. But now, it seems appropriate to use a new auxiliary coefficient ζ*21, as below; In the case of the dynamical coupling between two unit groups, A and B, it is assumed that κ is the product of two coefficients, ζ_{A} and ζ_{B}, which are derived from the groups A and B, respectively. This is expressed in the following equation

$$\kappa = \zeta_{\mathrm{A}}\zeta_{\mathrm{B}}{}^{*22,*23}. \qquad (2)$$

Then, from Eqs. 1 and 2,

$$[\mu]^{20}_{\mathrm{D}\,\mathrm{obs}} = \zeta_{\mathrm{A}}\zeta_{\mathrm{B}}[\mu]^{20}_{\mathrm{D}\,\mathrm{calcd}} \qquad (3)^{*24}$$

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center, a special precaution should be taken. In some of his calculations, Kirkwood located the optical center of a unit group at its center of mass. This manner of treatment was used even in the case of CH_3 group which combines with the three-membered ring in 2,3-epoxybutane (ref. 7). On the other hand, from the standpoint of bond-interaction, Murakami located the optical center of a bond at its center of mass (ref. 8). According to Murakami's treatment, OH group which combines with the aldopyranose-ring is to be divided into $^{\mathrm{r}}$C—O*15 and O—H bonds. But, on account of lack of data for these two bonds, we were forced to treat OH group as a single particle (ref. *11 in the previous paper 2 and *1 in this article). However, the contribution of $^{\mathrm{r}}$C—O bond (strictly speaking, σ orbitals of $^{\mathrm{r}}$C- and O-atoms in this bond) to the degree of polarization of $^{\mathrm{r}}$C—O—H system, is far greater than that of O—H bond. Then, it may be appropriate to locate the optical center of this system (generally speaking, the optical center of OH group) between $^{\mathrm{r}}$C- and O-atoms (or at the center of mass of $^{\mathrm{r}}$C—(OH) bond, for convenience). Analogously, the optical center of $(CH_2OH)^{5\beta}$ is to be placed at the weighed center of the system of C^5—C^6, C^6—(OH), and two C^6—H bonds, that is to say, in the vicinity of C^6-atom.

*14 Ref. "Theoretical Formulae" in the previous paper 2.

7) W. W. Wood, W. Fickett and J. G. Kirkwood, *J. Chem. Phys.*, **20**, 561 (1952).

8) H. Murakami, This Bulletin, **27**, 246 (1954); **28**, 583 (1955).

*15 $^{\mathrm{r}}$C-atom means the C atom which constitutes the aldopyranose-ring.

*16 Ref. *8 in the previous paper 1.

*17 Ref. "Method Proposed." in the previous paper 3. This method is called "Polarizability-Multiplying method (or abbreviated to PM-method)" by the author, hereafter.

*18 Eq. 4 in the previous paper 2.

*19 It has already been demonstrated that, in the calculation of the optical rotatory power by Kirkwood's polarizability theory, a small deviation in atomic distance or in valency angles causes only a small deviation in the calculated value of optical rotatory power. (ref. *7 in the previous paper 2). Then, the comparatively large value of κ, $(12.37/n^2+2)$*20, can not be due to the imperfectness of the molecular model, used for calculation. It may be due either to the inadequate location of the optical center of OH group, or to the changes of the values of $\alpha_i\beta_i$ or $\alpha_k\beta_k$ in the theoretical formula (ref. *14) which are caused by solvation (ref. *13 in the previous paper 2).

*20 Ref. "Method Proposed" in the previous paper 1.

*21 The author chose ζ, a Greek letter which corresponds to z, to represent the new coefficient. Thus, the notations in PM-method, X, Λ and ζ were suggested by x, y and z. (ref. *10 in the previous paper 3).

*22 From the viewpoint of its physical meaning, ζ should be always positive.

*23 The proportionality constant κ was suggested by the Murakami's report (8) on the study of polypeptides of alanine. But here, κ loses its original physical meaning, and the physical meaning of κ is specified in such a way that its value changes when one of two unit groups, A or B, changes.

*24 As was already described in the previous paper 3, the following equation is given in the case of the dynamical coupling of two OH groups,

$$[\mu]^{20}_{\mathrm{D}\,\mathrm{obs}} = 4.123[\mu]^{20}_{\mathrm{D}\,\mathrm{calcd}}(3/n^2+2)$$

In this case,

$$\kappa = \zeta^2_{\mathrm{OH}} = 4.123(3/n^2+2)$$

$$\therefore\ \zeta_{\mathrm{OH}} = 2.0305(3/n^2+2)^{1/2}$$

TABLE II

$[\mu]^{20}_{\text{Dcalcd}}(3/n^2+2)$, CAUSED BY THE DYNAMICAL COUPLING EFFECT BETWEEN ANY TWO MEMBERS OF UNIT GROUPS (EXCEPT $(CH_2OH)^{5\beta}$ AND RING) IN MC DONALD AND BEEVERS' MOLECULAR MODEL

	4β	4α	3β	3α	2β	2α
1α	−0.06 (−0.13)	−0.05 (−0.03)	2.23 (1.76)	0.52 (0.45)	1.31 (0.68)	10.62 (5.96)
1β	−0.29 (−0.20)	0.25 (0.14)	0.21 (0.10)	−2.33 (−1.85)	11.86 (6.81)	−12.97 (−7.59)
2α	1.48 (1.38)	0.51 (0.27)	12.47 (7.23)	−10.11 (−5.59)		
2β	0.17 (0.17)	−2.04 (−1.66)	−11.96 (−7.04)	−1.26 (−0.64)		
3α	0.93 (0.48)	10.76 (5.83)				
3β	11.58 (6.59)	−11.97 (−6.57)				

The values, calculated by supposing that the optical center of OH group is located at its O atom, are given in parentheses.

TABLE III

$[\mu]^{20}_{\text{Dcalcd}}(3/n^2+2)$, CAUSED BY THE DYNAMICAL COUPLING EFFECT OF $(OH)^1$ IN D-GLUCOPYRANOSE

	2α	3β	4α	5β.ma	R
1α	10.62	2.23	−0.05	$(1\alpha)\times(5\beta.\text{ma})$*26	$(1\alpha)\times R$
1β	−12.97	0.21	0.25	$(1\beta)\times(5\beta.\text{ma})$	$(1\beta)\times R$

TABLE IV

$[\mu]^{20}_{\text{Dobs}}(3/n^2+2)$, CAUSED BY THE DYNAMICAL COUPLING EFFECT OF $(OH)^1$ IN D-GLUCOPYRANOSE

	2α	3β	4α	5β.ma	R
1α	$10.62\zeta^2_{\text{OH}}$*27	$2.23\zeta^2_{\text{OH}}$	$-0.05\zeta^2_{\text{OH}}$	$\{(1\alpha)\times(5\beta.\text{ma})\}\zeta_{\text{OH}}\zeta_{\text{CH}_2\text{OH}}$	$\{(1\alpha)\times R\}\zeta_{\text{OH}}\zeta_{\text{R}}$
1β	$-12.97\zeta^2_{\text{OH}}$	$0.21\zeta^2_{\text{OH}}$	$0.25\zeta^2_{\text{OH}}$	$\{(1\beta)\times(5\beta.\text{ma})\}\zeta_{\text{OH}}\zeta_{\text{CH}_2\text{OH}}$	$\{(1\beta)\times R\}\zeta_{\text{OH}}\zeta_{\text{R}}$

On the other hand, $[\mu]^{20}_{\text{Dcalcd}}$, caused by the dynamical coupling effect between any two members of unit groups (except $(CH_2OH)^{5\beta}$ and ring) in the aldopyranose-molecule, can be calculated by using the theoretical formulae*14. The results of calculation are shown in Table II.

Then, $[\mu]^{20}_{\text{Dcalcd}}(3/n^2+2)$ and $[\mu]^{20}_{\text{Dobs}}(3/n^2+2)$, caused by the dynamical coupling effects between $(OH)^1$*25 and the other unit groups in D-glucopyranose are as shown in Tables III and IV, respectively. Now, $[\mu]^{20}_{\text{Dobs}}$ of An. Diff.*3 of D-glucopyranose is as follows;

$$\begin{aligned}&[10.62\zeta^2_{\text{OH}}+2.23\zeta^2_{\text{OH}}-0.05\zeta^2_{\text{OH}}\\ &\quad+\{(1\alpha)\times(5\beta.\text{ma})\}\zeta_{\text{OH}}\zeta_{\text{CH}_2\text{OH}}\\ &\quad+\{(1\alpha)\times R\}\zeta_{\text{OH}}\zeta_{\text{R}}]\,(n^2+2/3)\\ &\quad-[-12.97\zeta^2_{\text{OH}}+0.21\zeta^2_{\text{OH}}+0.25\zeta^2_{\text{OH}}\\ &\quad+\{(1\beta)\times(5\beta.\text{ma})\}\zeta_{\text{OH}}\zeta_{\text{CH}_2\text{OH}}\\ &\quad+\{(1\beta)\times R\}\zeta_{\text{OH}}\zeta_{\text{R}}]\,(n^2+2/3)\\ &\quad=(25.31\zeta^2_{\text{OH}}+A+B)\,(n^2+2/3)\end{aligned}$$

where

$$\begin{aligned}A\equiv&\{(1\alpha)\times(5\beta.\text{ma})\\ &-(1\beta)\times(5\beta.\text{ma})\}\zeta_{\text{OH}}\zeta_{\text{CH}_2\text{OH}}\end{aligned}\qquad(4)$$

$$B\equiv\{(1\alpha)\times\text{R}-(1\beta)\times\text{R}\}\zeta_{\text{OH}}\zeta_{\text{R}}\qquad(5)$$

The corresponding observed value is given by, $\{[M]^{20}_{\text{D}}(\text{W})$ of α-D-glucose$\}$ minus $\{[M]^{20}_{\text{D}}(\text{W})$ of β-D-glucose$\}$. This is $(202.1-33.7)$*28$=168.4$. Of course, this observed value should be equal to its corresponding $[\mu]^{20}_{\text{Dobs}}$. Then,

$$168.4=(25.31\zeta^2_{\text{OH}}+A+B)\,(n^2+2/3)\qquad(6)$$

By using the method like that mentioned above, three other equations are obtained. From D-mannopyranose,

$$83.4=(-8.83\zeta^2_{\text{OH}}+A+B)\,(n^2+2/3)\qquad(7)$$

This is ζ-coefficient of OH group in the aldopyranose-molecule of C 1 conformation in aqueous solution, calculated by using the ideal model and Riiber's data of $[M]^{20}_{\text{D}}(\text{W})$, supposing that the optical center of (OH) group is located at its O atom. This value of ζ_{OH} is nearly equal to that, obtained by using Mc Donald and Beevers' model and Isbell and Pigman's data of $[M]^{20}_{\text{D}}(\text{W})$, supposing that the optical center of OH group is at its O atom. (ref. *44 in this article.)

*25 $(OH)^1$ means OH group, which combines with 1-position of the ring, and so on.

*26 $(5\beta.\text{ma})$ is an abbreviated symbol of $(CH_2OH)^{5\beta.\text{ma}}$, and so on.

*27 Eq. 3 is used, here.

*28 Ref. Table 1 in this article.

From D-galactopyranose,

$$176.4 = (25.84\zeta_{\mathrm{OH}}^2 + A' + B)(n^2+2/3) \qquad (8)$$

and from L-arabinopyranose,

$$170.5 = (25.84\zeta_{\mathrm{OH}}^2 + B)(n^2+2/3) \qquad (9)^{*29}$$

where

$$A' \equiv \{(1\alpha)\times(5\beta.\mathrm{ga}) - (1\beta)\times(5\beta.\mathrm{ga})\}\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_2OH}} \qquad (10)$$

From Eq. 6 minus 7,

$$85.0 = 34.14\zeta_{\mathrm{OH}}^2(n^2+2/3)$$

$$\therefore\ \zeta_{\mathrm{OH}}^2 = 2.4897(3/n^2+2) \qquad (11)$$

$$\text{or}\ \ \zeta_{\mathrm{OH}} = 1.5779(3/n^2+2)^{1/2}\ {}^{*22,*30} \qquad (12)$$

From Eqs. 6 and 11,

$$\begin{aligned} 106.2 &= B(n^2+2/3) \\ &= \{(1\alpha)\times\mathrm{R} - (1\beta)\times\mathrm{R}\}\zeta_{\mathrm{OH}}\zeta_{\mathrm{R}}(n^2+2/3)^{*31} \\ &= (1\alpha)\lambda\mathrm{R} - (1\beta)\lambda\mathrm{R} \qquad (13)^{*32,*29} \end{aligned}$$

from Eqs. 6, 11 and 13,

$$\begin{aligned} -0.8 &= A(n^2+2/3) \\ &= \{(1\alpha)\times(5\beta.\mathrm{ma}) - (1\beta)\times(5\beta.\mathrm{ma})\} \\ &\qquad \zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_2OH}}(n^2+2/3)^{*33,*35} \end{aligned}$$

$$\begin{aligned} \therefore\ \ & \zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_2OH}}(n^2+2/3) \\ &= -0.8/\{(1\alpha)\times(5\beta.\mathrm{ma}) \\ &\quad - (1\beta)\times(5\beta.\mathrm{ma})\} \qquad (14) \end{aligned}$$

and from Eq. 8 minus 9,

$$\begin{aligned} 5.9 &= A'(n^2+2/3) \\ &= \{(1\alpha)\times(5\beta.\mathrm{ga}) - (1\beta)\times(5\beta.\mathrm{ga})\} \\ &\quad \zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_2OH}}(n^2+2/3)\}^{*34} \end{aligned}$$

$$\begin{aligned} \therefore\ \ & \zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_2OH}}(n^2+2/3) \\ &= 5.9/\{(1\alpha)\times(5\beta.\mathrm{ga}) \\ &\quad - (1\beta)\times(5\beta.\mathrm{ga})\} \qquad (15) \end{aligned}$$

As each of ζ_{OH}, $\zeta_{\mathrm{CH_2OH}}$ and $(n^2+2/3)$ in Eqs. 14 and 15 is always positive (ref. *22), the following two inequalities are obtained. From Eq. 14,

$$\{(1\alpha)\times(5\beta\cdot\mathrm{ma}) - (1\beta)\times(5\beta\cdot\mathrm{ma})\} < 0 \qquad \text{(Ineq. 1)}$$

From Eq. 15,

$$\{(1\alpha)\times(5\beta\cdot\mathrm{ga}) - (1\beta)\times(5\beta\cdot\mathrm{ga})\} > 0 \qquad \text{(Ineq. 2)}$$

The left-hand side of Eq. 14 is equal to that of Eq. 15, then the right-hand sides of these two equations should be equal to each other,

$$\begin{aligned} & -0.8/\{(1\alpha)\times(5\beta.\mathrm{ma}) - (1\beta)\times(5\beta.\mathrm{ma})\} \\ &= 5.9/\{(1\alpha)\times(5\beta.\mathrm{ga}) - (1\beta)\times(5\beta.\mathrm{ga})\} \end{aligned}$$

$$\begin{aligned} \therefore\ \ & \{(1\alpha)\times(5\beta.\mathrm{ga}) - (1\beta)\times(5\beta.\mathrm{ga})\} \\ & /\{(1\alpha)\times(5\beta.\mathrm{ma}) - (1\beta)\times(5\beta.\mathrm{ma})\} \\ &= -7.38 \qquad (16) \end{aligned}$$

Eq. 16 indicates that

$$\begin{aligned} & \{(1\alpha)\times(5\beta.\mathrm{ga}) - (1\beta)\times(5\beta.\mathrm{ga})\} \\ & \neq \{(1\alpha)\times(5\beta.\mathrm{ma}) - (1\beta)\times(5\beta.\mathrm{ma})\} \end{aligned}$$

$$\therefore\ \ 5\beta.\mathrm{ga} \neq 5\beta.\mathrm{ma} \qquad (17)^{*36}$$

Now, in order to simplify the following calculations, two simplifications are made as below;

(Simp. I) The internal conformation of C^6—O bond in D-mannopyranose in aqueous solution is only of *trans* type. (ref. *10). Shortly speaking,

$$5\beta.\mathrm{ma} = 5\beta.t^{*37}$$

(Simp. II) The internal conformation of C^6—O bond in D-galactopyranose in aqueous solution is one of the *trans*, *gauche* I or *gauche* II types[*38], and this type is represented by x. Then,

$$5\beta\cdot\mathrm{ga} = 5\beta\cdot\mathrm{x}$$

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*29 Cf. *35 in this article.

*30 If D-talopyranose has C 1 conformation (ref. *8), it is possible to calculate ζ_{OH} by using $[M]_{\mathrm{D}}^{20}(\mathrm{W})$ of D-galactose and of D-talose. The calculated value of ζ_{OH} in this case, is 1.5086 $(3/n^2+2)^{1/2}$. This is nearly equal to the value in Eq. 12.

*31 Eq. 5 is used, here.

*32 When the partial molecular rotation is caused by the dynamical coupling effect between unit groups A and B,

$$[\mu]_{\mathrm{D\,obs}}^{20} = \zeta_{\mathrm{A}}\zeta_{\mathrm{B}}[\mu]_{\mathrm{D\,calcd}}^{20}$$

(Eq. 3 in this article), where

$$[\mu]_{\mathrm{D\,obs}}^{20} = (\mathrm{A})\lambda(\mathrm{B})$$

(ref. *10 in the previous paper 3), and

$$[\mu]_{\mathrm{D\,calcd}}^{20} = \{(\mathrm{A})\times(\mathrm{B})\}(n^2+2/3)$$

(ref. *14 in the previous paper 2). Then,

$$(\mathrm{A})\lambda(\mathrm{B}) = \{(\mathrm{A})\times(\mathrm{B})\}\zeta_{\mathrm{A}}\zeta_{\mathrm{B}}(n^2+2/3). \qquad (32)$$

*33 Eq. 4 is used, here.

*34 Eq. 10 is used, here.

*35 When using Hudson's data of L-arabinoses (ref. *12 in this article),

$$169.7 = (25.84\zeta^2{}_{\mathrm{OH}} + B)(n^2+2/3) \qquad (9)^*$$

$$105.4 = (1\alpha)\lambda\mathrm{R} - (1\beta)\lambda\mathrm{R} \qquad (13)^*$$

$$\{(1\alpha)\times(5\beta.\mathrm{ma}) - (1\beta)\times5\beta.\mathrm{ma})\}\ \zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_2OH}}(n^2+2/3) = 0$$

$$\text{or}\ \ (1\alpha)\times(5\beta.\mathrm{ma}) - (1\beta)\times(5\beta.\mathrm{ma}) = 0 \qquad (14)^*$$

*36 Strictly speaking, as each of 5β.ga and 5β.ma seems to be the mixture of two types of internal conformation of C^6—O bond (ref. *10), Eq. 17 shows that the quantitative ratio of two types of internal conformation of C^6—O bond is entirely different in D-galactopyranose and in D-mannopyranose in their aqueous solutions.

*37 5β.*t* is an abbreviated symbol of 5β.*trans*.

*38 cf. Fig. 2 in the previous paper 4.

By using these two simplifications, the following two inequalities and two equations are obtained.

From Ineq. 1,

$$\{(1\alpha)\times(5\beta.t)-(1\beta)\times(5\beta.t)\}<0 \quad (\text{Ineq. }1')$$

From (Ineq. 2),

$$\{(1\alpha)\times(5\beta.\mathrm{x})-(1\beta)\times(5\beta.\mathrm{x})\}>0 \quad (\text{Ineq. }2')$$

From Eq. 17,

$$5\beta\cdot\mathrm{x}\neq 5\beta\cdot t \qquad (17')$$[*39]

and from Eq. 16,

$$\{(1\alpha)\times(5\beta.\mathrm{x})-(1\beta)\times(5\beta.\mathrm{x})\}/\{(1\alpha)\times(5\beta.t)-(1\beta)\times(5\beta.t)\}=-7.38 \qquad (16')$$

Next, the value of $\{(1\alpha)\times(5\beta.t)-(1\beta)\times(5\beta.t)\}$ was calculated as a function of the angle θ[*2] which defines the direction of the optical axis of CH_2OH group. The results of calculation are given in the second column of Table V.

TABLE V

$[\mu]^{20}_{\mathrm{Dcalcd}}(3/n^2+2)$-DIFFERENCE AS A FUNCTION OF θ, CALCULATED BY USING MC DONALD AND BEEVERS' MODEL

θ	Diff (t)	Diff $(g\mathrm{I})$	Diff $(g\mathrm{II})$	Diff $(g\mathrm{II})$ /Diff (t)
0°	9.90			
10°	8.21			
20°	5.80			
30°	2.95			
36°	1.18			
40°	0.02			
40°05′	−0.01	−16.54	4.72	−472.00
40°10′	−0.03	−16.52	4.69	−156.33
41°	−0.27	−16.33	4.42	−16.37
41°50′	−0.51	−16.11	4.16	−8.16
42°	−0.55	−16.07	4.09	−7.44
42°10′	−0.60	−16.02	4.04	−6.73
43°	−0.82	−15.79	3.77	−4.60
50°	−2.65	−13.51	1.21	−0.46
54°44′	−3.73	−11.61	−0.66	0.18

Diff (t) ……… $\{(1\alpha)\times(5\beta\cdot t)-(1\beta)\times(5\beta\cdot t)\}$
Diff $(g\ \mathrm{I})$ …… $\{(1\alpha)\times(5\beta\cdot g\ \mathrm{I})-(1\beta)\times(5\beta\cdot g\ \mathrm{I})\}$
Diff $(g\ \mathrm{II})$ … $\{(1\alpha)\times(5\beta\cdot g\ \mathrm{II})-(1\beta)\times(5\beta\cdot g\ \mathrm{II})\}$

Combining these values with (Ineq. 1′), the following conclusion is obtained,

$$40^\circ 05' \leqq \theta \leqq 54^\circ 44'$$

In order to examine *gauche* I type, the value of $\{(1\alpha)\times(5\beta.g\mathrm{I})$[*40]$-(1\beta)\times(5\beta.g\mathrm{I})\}$ was calculated as a function of θ which lies between 40°05′ and 54°44′. The results of calculation are given in the third column in Table V. But these values of $\{(1\alpha)\times(5\beta.g\ 1)-(1\beta)\times(5\beta.g\ 1)\}$ are all negative. Then, by referring Ineq. 2′, it is concluded that

$$5\beta.g1\neq 5\beta.\mathrm{x} \qquad (18)$$[*41]

Combining Eqs. 17′ and 18 with (Simp. II),

$$5\beta\cdot\mathrm{ga}=5\beta\cdot\mathrm{x}=5\beta\cdot g\mathrm{II} \qquad (19)$$

Consequently, the internal conformation of C^6—O bond in D-galactopyranose in aqueous solution is of *gauche* II type[*42]. Then, Eq. 16′ becomes as below;

$$\{(1\alpha)\times(5\beta.g\mathrm{II})-(1\beta)\times(5\beta.g\mathrm{II})\}/\{(1\alpha)\times(5\beta.t)-(1\beta)\times(5\beta.t)\}=-7.38. \qquad (16'')$$

In order to find the suitable value of θ which satisfies Eq. 16″, the value of the left side of this equation was calculated as a function of θ. The results of the calculation are given in the fifth column of Table V, and the value, −7.38, of

$$\{(1\alpha)\times(5\beta.g\mathrm{II})-(1\beta)\times(5\beta.g\mathrm{II})\}/\{(1\alpha)\times(5\beta.t)-(1\beta)\times(5\beta.t)\}$$

can be found at $\theta\simeq 42^\circ$[*43].

It is also apparent in Table V that the value of $\{(1\alpha)\times(5\beta.g\mathrm{II})-(1\beta)\times(5\beta.g\mathrm{II})\}$ which corresponds to the above-found value of θ is 4.09. When this value, Eqs.

[*39] Concretely speaking, the internal conformation of C^6—O bond in D-galactopyranose in aqueous solution is not of *trans* type.

[*40] $5\beta.g$I is an abbreviated symbol of $5\beta.$*gauche* I, and so on.

[*41] Concretely speaking, the internal conformation of C^6—O bond in D-galactopyranose in aqueous solution is not of *gauche* I type.

[*42] This conclusion coincides with that obtained from the viewpoint of the atomic distances between the O atom in $(CH_2OH)^{5\beta}$ (i. e. O^6-atom) and the neighboring atoms. (ref. "Discussion on the Results." in the previous paper 4). The distance between O^6- and $O^{4\beta}$-atoms in D-galactopyranose are as below; *trans* (3.49 Å), *gauche* I (4.16 Å), *gauche* II (2.69 Å) Then, the distance between O^6- and $O^{4\beta}$-atoms in *gauche* II form is the shortest and is equal to the length of a hydrogen bond. Therefore, the movable atom O^6 would be attracted by $O^{4\beta}$-atom and be forced to rest at *gauche* II position.

[*43] The value, 0, of

$$\{(1\alpha)\times(5\beta.\mathrm{ma})-(1\beta)\times(5\beta.\mathrm{ma})\}=\mathrm{Diff}(t),$$

(ref. Eq. 14* in *35) is found at $\theta\simeq 40^\circ 05'$ in Table V, and its corresponding Diff $(g\ \mathrm{II})$ is 4.72. Accordingly,

$$\zeta_{CH_2OH}=0.7922(3/n^2+2)^{1/2} \qquad (20)^*$$

These are the values concerning $(CH_2OH)^{5\beta}$, calculated by using Hudson's data of L-arabinoses. (ref. *12).

19 and 12 are used, Eq. 15 becomes as below;

$$1.5779(3/n^2+2)^{1/2}\zeta_{CH_2OH}(n^2+2/3)=5.9/4.09$$

$$\therefore\ \zeta_{CH_2OH}=0.9142(3/n^2+2)^{1/2}\quad \text{*43,*44} \tag{20}$$

Conclusion

The results of calculation in this paper are as follows:

(1) If the internal conformation of C^6—O bond in D-galactopyranose in aqueous solution is only one of the *trans*, *gauche* I or *gauche* II types, it should be of *gauche* II type.

(2) It is expected that the optical axis of $(CH_2OH)^{5\beta}$ is placed on the plane of C^5-atom and its C^6—O bond, and this optical axis inclines to the C^6—O bond at 42°*43.

(3) ζ-coefficients of OH and CH_2OH groups, in this case, are $1.5779(3/n^2+2)^{1/2}$ and $0.9142(3/n^2+2)^{1/2}$ *43, respectively.

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*44 For comparison, the values, calculated by supposing that the optical center of OH group is located at O atom and that of CH_2OH group is at its center of mass (ref. *13), are given here;

	Isbell and Pigman's data of L-arabinoses	Hudson's data of L-arabinoses
ζ_{OH}	$2.0782(3/n^2+2)^{1/2}$	$2.0782(3/n^2+2)^{1/2}$
ζ_{CH_2OH}	$3.5049(3/n^2+2)^{1/2}$	$3.3936(3/n^2+2)^{1/2}$
θ	34°50′	34°20′