Molecular Rotations of Glucides in Relation to their Structures. VII.[1] *Internal Conformation of $O^{1\alpha}$—C^m Bond in $(OCH_3)^{1\alpha}$ of Methyl α-D-Xylopyranoside and of Methyl β-L-Arabinopyranoside in Aqueous Solutions*[2]

By Shukichi Yamana

(Received October 21, 1958)

Although the internal conformation of $O^{1\alpha}$—C^m bond[3] in $(OCH_3)^{1\alpha}$ of methyl α-D-xylopyranoside[5,6] or of methyl β-L-arabinopyranoside[6,7] in crystalline state has been studied from the standpoint of X-ray analysis, those in the aqueous solutions have not yet been determined owing to the lack of a suitable method. (Fig. 1)

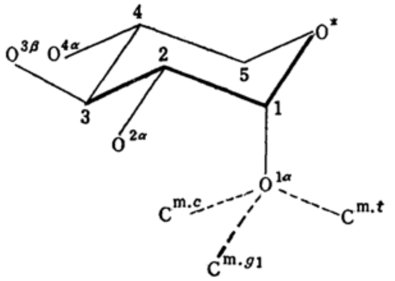


Fig. 1. Perspective drawing of the molecular model of methyl α-D-xylopyranoside: *t*—*trans* ($\phi_{1\alpha}=0°$), *g*1—*gauche* 1 ($\phi_{1\alpha}=120°$), *c*—*cis* ($\phi_{1\alpha}=180°$).

Hudson empirically observed the existence of a certain quantitative relationship between the structure of methyl glycosides and their molecular rotations, $[M]_D^{20}(W)$[8], but no one has attempted to utilize these $[M]_D^{20}(W)$ values for the determination of the internal conformation of their $O^{1\alpha}$—C^m bonds. Recently, the present author succeeded in presuming the internal conformation of C^6—O bond in D-mannopyranose in its aqueous solution by using $[M]_D^{20}(W)$ values of some glucides[9]. By a similar method, the internal conformation of $O^{1\alpha}$—C^m bond in $(OCH_3)^{1\alpha}$ of methyl α-D-xylopyranoside and of methyl β-L-arabinopyranoside in aqueous solutions has been presumed in this article.

Molecular Model and Data Used.—As the molecular model, the one proposed by McDonald and Beevers was used. The values of bond lengths and valency angles concerning the side chain are assumed as follows; $O^{1\alpha}$—C^m is 1.421 Å[a] and $\angle C^1O^{1\alpha}C^m$ is a tetrahedral angle (109° 28′). The unit groups in the glucide molecules under discussion and their corresponding molecular rotations are given in Table I.

As the optical data for OH, CH_3 and H, the values used in the previous papers[1,4]

TABLE I

Name	Unit groups	$[M]_D^{20}(W)$	Lit.
methyl α-D-xyloside	$[(OCH_3)^{1\alpha,}$[10] $(OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\alpha}$, Ring]	252.6°	(b)
methyl β-L-arabinoside	$[(OCH_3)^{1\alpha}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\beta}$, Ring]	403.0°	(c)
α-D-xylose	$[(OH)^{1\alpha}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\alpha}$, Ring]	140.5°	(b)
β-L-arabinose	$[(OH)^{1\alpha}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\beta}$, Ring]	286.1°[11]	(c)

---

[1] Part VI; S. Yamana, This Bulletin, **31**, 564 (1958).

[2] Reported at the Symposium on the Structural Chemistry, held on October 13, 1958, at Kyoto, under the auspices of the Chemical Society of Japan.

[3] $O^{1\alpha}$ means the O atom which combines with C^1-atom of the aldopyranose-ring in α-orientation, and so on. (Cf. the foot-note *5 in the previous paper[4]). C^m means the C atom in methyl group. Then, $O^{1\alpha}$—C^m bond is the O—C bond in $(OCH_3)^{1\alpha}$. (Ref. Fig. 1).

[4] S. Yamana, This Bulletin, **30**, 203 (1957).

[5] E. G. Cox, *J. Chem. Soc.*, **1932**, 2535.

[6] H. Braekken, C. J. Koren and N. A. Sörensen, *Z. Krist.*, **88**, 205 (1934).

[7] E. G. Cox and T. H. Goodwin, **85**, 462 (1933); E. G. Cox, T. H. Goodwin and (Miss) A. I. Wagstaff, *J. Chem. Soc.*, **1935**, 978.

[8] C. S. Hudson, *J. Am. Chem. Soc.*, **31**, 66 (1909).

[9] S. Yamana, This Bulletin, **30**, 920 (1957).

[a] D. G. Burkhard and D. M. Dennison. *Phys. Rev.*, **84**, 408 (1951).

[10] The internal conformation of $O^{1\alpha}$—C^m bond in $(OCH_3)^{1\alpha}$ of methyl α-D-xyloside is the same as that of methyl β-L-arabinoside. Concerning this information, refer to "**Method Proposed**" in this article.

[b] F. J. Bates and Associates, "Polarimetry, Saccharimetry and the Sugars", United States Government Printing Office, Washington (1942), p. 759.

[c] Ibid., p. 708.

[11] Hudson's datum is 303.3°. (Ref. the foot-note *12 in the previous paper[12].)

[12] S. Yamana, This Bulletin, **31**, 558 (1958).

are again adopted in this article. In order to simplify the calculations, the optical centers of OH and CH_3 groups are assumed to be located at O and C atoms, respectively[13]. Accordingly, the value of ζ_{CH_3} becomes $0.2880\,(3/n^2+2)^{1/2}$[14]. The refractive indices of the aqueous solutions of these methyl glycosides are presumed to be nearly equal to 1.34[15].

Method Proposed.—If the orientation of $(OH)^4$ in methyl β-L-arabinopyranoside is changed from β to α, methyl α-D-xylopyranoside is obtained[16]. But, throughout the course of this process, the distance between $(CH_3)^{\leftarrow 1\alpha}$[17] and $(OH)^4$ is so much larger[18] than those between $(CH_3)^{\leftarrow 1\alpha}$ and the other atoms (than $(OH)^4$) in the same molecules, that the orientation-change of $(OH)^4$ should not cause any influence on the internal conformation of $O^{1\alpha}—C^m$ bond. In other words, the internal conformation of $O^{1\alpha}—C^m$ bond in $(OCH_3)^{1\alpha}$ of methyl α-D-xylopyranoside is said to be the same as that of methyl β-L-arabinopyranoside in their aqueous solutions. Then, the unit groups which can couple with $(OH)^4$ dynamically in the molecules of methyl α-D-xylopyranoside and of methyl β-L-arabinopyranoside are $(OCH_3)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$ and Ring[16]. Therefore, Yo. Diff.[20] between these two methyl glycosides is given by the following equation,

$$\{(4\alpha)-(4\beta)\}\,\underline{\mathrm{X}}\,\{(OCH_3)^{1\alpha}+(2\alpha)+(3\beta)+\mathrm{R}\}^{21)}=(4\alpha)\,\underline{\mathrm{X}}\,(OCH_3)^{1\alpha}+(4\alpha)\,\underline{\mathrm{X}}\,(2\alpha)+(4\alpha)\,\underline{\mathrm{X}}\,(3\beta)+(4\alpha)\,\underline{\mathrm{X}}\,\mathrm{R}\}-\{(4\beta)\,\underline{\mathrm{X}}\,(OCH_3)^{1\alpha}+(4\beta)\,\underline{\mathrm{X}}\,(2\alpha)+(4\beta)\,\underline{\mathrm{X}}\,(3\beta)+(4\beta)\,\underline{\mathrm{X}}\,\mathrm{R}\}\equiv I$$

Similarly, Yo. Diff. between α-D-xylopyranose and β-L-arabinopyranose is given by,

$$\{(4\alpha)-(4\beta)\}\,\underline{\mathrm{X}}\,\{(1\alpha)+(2\alpha)+(3\beta)+\mathrm{R}\}=\{(4\alpha)\,\underline{\mathrm{X}}\,(1\alpha)+(4\alpha)\,\underline{\mathrm{X}}\,(2\alpha)+(4\alpha)\,\underline{\mathrm{X}}\,(3\beta)+(4\alpha)\,\underline{\mathrm{X}}\,\mathrm{R}\}-\{(4\beta)\,\underline{\mathrm{X}}\,(1\alpha)+(4\beta)\,\underline{\mathrm{X}}\,(2\alpha)+(4\beta)\,\underline{\mathrm{X}}\,(3\beta)+(4\beta)\,\underline{\mathrm{X}}\,\mathrm{R}\}\equiv J$$

Accordingly, $I-J^{22)}=\{(4\alpha)\,\underline{\mathrm{X}}\,(OCH_3)^{1\alpha}-(4\beta)\,\underline{\mathrm{X}}\,(OCH_3)^{1\alpha}\}-\{(4\alpha)\,\underline{\mathrm{X}}\,(1\alpha)-(4\beta)\,\underline{\mathrm{X}}\,(1\alpha)\}=(4\alpha)\,\underline{\mathrm{X}}\,(OCH_3)^{1\alpha}-(4\beta)\,\underline{\mathrm{X}}\,(OCH_3)^{1\alpha}\}-\{(4\alpha)\,\underline{\mathrm{X}}\,(OH)^{1\alpha}-(4\beta)\,\underline{\mathrm{X}}\,(OH)^{1\alpha}\}^{23)}$ (1)

$(OCH_3)^{1\alpha}$ may be considered to occur by replacing $H^{\leftarrow 1\alpha}$-atom[25] in $(OH)^{1\alpha}$ by $CH_3{}^{\leftarrow\alpha}$ group. And because of the small polarizability of $H^{\leftarrow 1\alpha}$, $(4\alpha)\,\underline{\mathrm{X}}\,H^{\leftarrow 1\alpha}\simeq 0$ and $(4\beta)\,\underline{\mathrm{X}}\,H^{\leftarrow 1\alpha}\simeq 0$. Therefore, Eq. 1 can be simplified as below;

$$I-J=[(4\alpha)\,\underline{\mathrm{X}}\,\{O^{1\alpha}+(CH_3)^{\leftarrow 1\alpha}\}-(4\beta)\,\underline{\mathrm{X}}\,\{O^{1\alpha}+(CH_3)^{\leftarrow 1\alpha}\}]-[(4\alpha)\,\underline{\mathrm{X}}\,\{O^{1\alpha}+H^{\leftarrow 1\alpha}\}-(4\beta)\,\underline{\mathrm{X}}\,\{O^{1\alpha}+H^{\leftarrow 1\alpha}\}]\simeq(4\alpha)\,\underline{\mathrm{X}}\,(CH_3)^{\leftarrow 1\alpha}-(4\beta)\,\underline{\mathrm{X}}\,(CH_3)^{\leftarrow 1\alpha\ 26)}$$

The value of this $\{(4\alpha)\,\underline{\mathrm{X}}\,(CH_3)^{\leftarrow 1\alpha}-(4\beta)\,\underline{\mathrm{X}}\,(CH_3)^{\leftarrow 1\alpha}\}$ was calculated by PM-method[27] as a function of $\phi_{1\alpha}$[19]. These values, $[\mu]^{20}_{\mathrm{D\,obs}}$ for $(I-J)$ are shown in Table II.

The corresponding observed value of $(I-J)$, given by $[\{([M]^{20}_{\mathrm{D}}(W)$ of methyl α-D-xylopyranoside) minus $([M]^{20}_{\mathrm{D}}(W)$ of

---

[13] In Eq. 5 of the previous paper[1], ζ_{CH3} was calculated as $0.1962\,(3/n^2+2)^{1/2}$ on the supposition that the optical center of CH_3 group is located at the center of mass of ${}^{r}C—(CH_3)$ bond (cf. the foot-note *13 of the previous paper[12].) But here, since CH_3 group combines with O atom instead of ${}^{r}C$-atom, the above value of ζ_{CH3} is hardly adoptable.

[14] According to Hudson's data of L-arabinoses, $\zeta_{CH3}=0.6206(3/n^2+2)^{1/2}$. (Ref. the foot-note *31 in the previous paper[1]).

[15] The refractive index (n) of an aqueous solution of methyl glycoside is 1.33~1.35[d]. When the value of n changes by 0.01, $(n^2+2/3)$ changes by $\partial/\partial n(n^2+2/3)\,\delta n\simeq 0.007$. The magnitude of this value of $(n^2+2/3)$-change is very small and may be neglected on comparison with that of $(n^2+2/3)\simeq 1.265$. On the other hand, $[\mu]^{20}_{\mathrm{D\,obs}}$ contains the factor n in itself only in the form of $(n^2+2/3)$. (Ref. "**Theoretical Formulae**" in the previous paper[4].) Then, $[\mu]^{20}_{\mathrm{D\,obs}}$, resulting from the dynamical coupling between two definite unit groups may be considered to be constant in that range of $n=1.33\sim1.35$.

[d] "International Critical Tables of Numerical Data", Vol. 7. p. 69.

[16] Ref. Table I in this article.

[17] $(CH_3)^{\leftarrow 1\alpha}$ indicates the CH_3 group which combines with $O^{1\alpha}$-atom, and so on. Therefore, $(CH_3)^{\leftarrow 1\alpha}$ is the CH_3 group in $(OCH_3)^{1\alpha}$. (Ref. Fig. 1).

[18] Since C^1- and C^4-atoms are situated nearly on the opposite ends of a diameter of the aldopyranose-ring together, the distances between C^m-atom[3] in $(CH_3)^{\leftarrow 1\alpha}$ and the O atom in $(OH)^4$ are shown below:

	longest	shortest
$(OH)^{4\alpha}$	5.91 Å (at $\phi_{1\alpha}{}^{19)}=60°$)	3.63 Å (at $\phi_{1\alpha}=240°$)
$(OH)^{4\beta}$	5.60 Å (at $\phi_{1\alpha}=60°$)	4.23 Å (at $\phi_{1\alpha}=240°$)

[19] The author defined an angle $\phi_{1\alpha}$ which determines the internal conformation of $O^{1\alpha}—C^m$ bond as follows; (i) $\phi_{1\alpha}$ is zero at the situation where C^m— and C^2-atoms are in *trans* position each other. (ii) The value of rotation in the positive direction increases with the distance between C^*- and C^m-atoms. (Fig. 1).

[20] Yo. Diff. is an abbreviated symbol of "yomeric difference". This is $[M]^{20}_{\mathrm{D}}(W)$-change of a glucide, caused by the orientaionchange of $(OH)^4$ from β to α. (ref. the foot-note *10 in the previous paper[1].)

[21] Ref. the foot-note *12 in the previous paper[1].

[22] J is adopted only for the purpose of canceling the terms concerning the aldopyranose-ring, R, in I.

[23] Ref. the foot-note *10 in the previous paper[24].

[24] S. Yamana, This Bulletin, 30, 916 (1957).

[25] $H^{\leftarrow 1\alpha}$ means the H atom which combines with $O^{1\alpha}$-atom. (Cf. the foot-note 17 in this article).

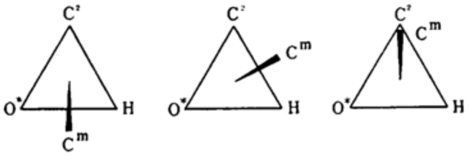
[26] In other expressions, $(OCH_3)^{1\alpha}\simeq(OH)^{1\alpha}+(CH_3)^{\leftarrow 1\alpha}$
$\therefore$ Eq. $1=[(4\alpha)\,\underline{\mathrm{X}}\,(OCH_3)^{1\alpha}-(4\beta)\,\underline{\mathrm{X}}\,(OCH_3)^{1\alpha}]-[(4\alpha)\,\underline{\mathrm{X}}\,(OH)^{1\alpha}-(4\beta)\,\underline{\mathrm{X}}\,(OH)^{1\alpha}]\simeq[(4\alpha)\,\underline{\mathrm{X}}\,\{(OH)^{1\alpha}+(CH_3)^{\leftarrow 1\alpha}\}-(4\beta)\,\underline{\mathrm{X}}\,\{(OH)^{1\alpha}+(CH_3)^{\leftarrow 1\alpha}\}]-[(4\alpha)\,\underline{\mathrm{X}}\,(OH)^{1\alpha}-(4\beta)\,\underline{\mathrm{X}}\,(OH)^{1\alpha}]=(4\alpha)\,\underline{\mathrm{X}}\,(CH_3)^{\leftarrow 1\alpha}-(4\beta)\,\underline{\mathrm{X}}\,(CH_3)^{\leftarrow 1\alpha}$

[27] Ref. the foot-note *17 in the previous paper[12].

TABLE II. $\sum[\mu]^{20}_{\mathrm{Dobs}}$ FOR THE DIFFERENCE BETWEEN TWO YOMERIC DIFFERENCE *I* AND *J*, AS A FUNCTION OF $\phi_{1\alpha}$

$\phi_{1\alpha}$	Isbell and Pigman's data of L-arabinoses	Hudson's data[14] of L-arabinoses
0	5.7	12.2
20	4.5	9.7
40	2.8	5.9
60	1.3	2.8
80	−1.4	−3.0
100	−3.3	−7.2
120	−4.9	−10.5
140	−5.7	−12.3
160	−5.5	−11.9
180	−4.2	−9.1
200	−2.1	−4.6
220	−0.4	−0.8
240	0.0	0.1
260	−0.2	−0.4
280	0.7	1.5
300	2.8	6.1
320	4.9	10.5
340	5.9	12.6

methyl β-L-arabinopyranoside)} minus {([M]$^{20}_{\mathrm{D}}$(W) of α-D-xylopyranose) minus ([M]$^{20}_{\mathrm{D}}$(W) of β-L-arabinopyranose)}], becomes −4.8 on the basis of the Isbell and Pigman's data of L-arabinoses or 12.4 on the basis of the Hudson's data of L-arabinoses[16]. The former value coincides with the calculated value when $\phi_{1\alpha}$ is 120° or 180° as seen in the second column of Table II and the latter value coincides with that when $\phi_{1\alpha}$ is 0° as seen in the third column of Table II. It follows from this result that there are three possible internal conformations of $O^{1\alpha}$—C^m bond as figured in Fig. 2.



trans
$\phi_{1\alpha}=0°$
(Hudson)

gauche 1
$\phi_{1\alpha}=120°$
(Isbell and Pigman)

cis
$\phi_{1\alpha}=180°$
(Isbell and Pigman)

Fig. 2. Internal conformation along $O^{1\alpha}$—C^1 axis.

Discussion of the Results

Among the above three possibilities, it seems difficult for a *cis* form to exist owing to the repulsion between C^2-atom and $(CH_3)^{\leftarrow 1\alpha}$. The internal conformation under consideration, therefore, should be either a *trans*- or a *gauche* 1 form.

C^5—O^*—C^1—$O^{1\alpha}$—C^m moiety in methyl α-D-xylopyranoside (Ref. Fig. 1) and also in methyl β-L-arabinopyranoside, is considered to be a kind of polyoxymethylene-chain. The internal conformation of a polyoxymethylene-chain along its C—O axis has been investigated by the methods of measuring the dipole moment, infrared spectrum, etc.[28,29] And it has been concluded that the most stable form of —C—O—C—O—C— chain is a *gauche* type[30]. From these facts, O^*—C^1—$O^{1\alpha}$—C^m moiety in the methyl glycoside under discussion is likely to exist in the conformation which corresponds to $\phi_{1\alpha}=0°$. This leads to the following anticipation.

The position of the minimal potential of $O^{1\alpha}$—C^m bond corresponds to $\phi_{1\alpha}=0°$. (Anticipation 1)

On the other hand, C^2—C^1—$O^{1\alpha}$—C^m moiety in metyl α-D-xylopyranoside and in methyl β-L-arabinopyranoside is a kind of polyethyleneglycol-chain. Because of the non-polar property of its C—C bond and of the steric repulsion between two C-atoms in —C—C—O—C— chain, —C—C—O—C— along its C—O axis is strongly expected to be more stable in a *trans* form than in a *gauche* form. This produces the conclusion that the conformation under discussion would be more advantageous at $\phi_{1\alpha}=0°$ than at $\phi_{1\alpha}=120°$. In other words,

$O^{1\alpha}$—C^m bond has a tendency to keep the position corresponding to $\phi_{1\alpha}=0°$ rather than that corresponding to $\phi_{1\alpha}=120°$. (Anticipation 2)

This anticipation is consistent with Anticipation 1. Therefore, concerning [M]$^{20}_{\mathrm{D}}$(W) of L-arabinoses, Hudson's data seem to be more reliable than Isbell and Pigman's data[31].

---

[28] T. Uchida, Y. Kurita and M. Kubo, *J. Polymer Sci.*, **19**, 365 (1956).

[29] A. R. Philpotts, D. O. Evans and N. Sheppard, *Trans. Faraday Soc.*, **51**, 1051 (1955).

[30] Notice that the shape of a polyoxymethylene-chain shown by the word "*gauche* type" in this case is not the same as that of O^*—C^1—$O^{1\alpha}$—C^m corresponding to the internal conformation of $O^{1\alpha}$—C^m bond of a *gauche* type in Figs. 1 and 2. O^*—C^1—$O^{1\alpha}$—C^m moiety in Figs. 1 and 2 can become a *gauche* type of polyoxymethylene-chain when $\phi_{1\alpha}$ is 0° and become a *trans* type of polyoxymethylene-chain when $\phi_{1\alpha}$ is 120°. (Ref. Fig. 3).

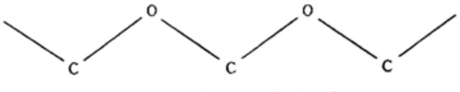


Fig. 3. Polyoxymethylene-chain of *trans* type.

[31] If Isbell and Pigman's data are correct, it must be concluded that the internal conformation of $O^{1\alpha}$—C^m bond corresponds to $\phi_{1\alpha}=120°$. In this case, a kind of the attractive force should be considered between $O^{2\alpha}$-atom and C^m-atom (strictly speaking, the H atom which is combined with C^m-atom).

Summary

By the author's new method, the internal conformation of $O^{1\alpha}$—C^{m} bond in $(OCH_3)^{1\alpha}$ of methyl α-D-xylopyranoside and of methyl β-L-arabinopyranoside in aqueous solutions was presumed. At the same time, Isbell and Pigman's data and Hudson's data of $[M]_{D}^{20}(W)$ of L-arabinoses were discussed.

The author wishes to express his sincere gratitude to Professor S. Tanaka (Kyoto University) and Professor T. Yamamoto (Kyoto University) who is studying in the University of Oregon for their special interests in this series of research.

Department of Chemistry
Kyoto Gakugei University
Fushimi-ku, Kyoto