Molecular Rotations of Glucides in Relation to their Structures. IX[1]*. The Value of the ζ-Coefficient of the Hydroxyl Group in Hydro-D-xylal*

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The value of the ζ-coefficient of the hydroxyl group, ζ_{OH}, in hydro-D-xylal has been calculated. The unit groups in the molecule and its $[M]^{20}_{D}(W)$ are shown in Table I (Fig. 1).

TABLE I

Name	Unit groups	$[M]^{20}_{D}(W)$
Hydro-D-xylal	$[(OH)^{3\beta}, (OH)^{4\alpha}, Ring^{0}]$ [2]	-53.0[3]

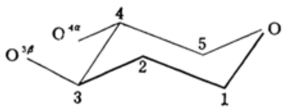

Fig. 1. Perspective drawing of the molecular model of hydro-D-xylal.

In the aldopyranose-ring, R^0 [2], of hydro-D-xylal, the O atom is combined with two methylene radicals, (i. e. $-C^1H_2-$ and $-C^5H_2-$). Therefore, the shape of R^0 is considered to be almost symmetrical. Therefore, in order to simplify the calculations, an ideal model of glucide[4] is used here. By using the PM-method[6],

$[M]^{20}_{D}(W)$ of hydro-D-xylal,

$$-53.0 \equiv \sum [\mu]^{20}_{D\ \mathrm{obs}} \text{ of hydro-D-xylal}$$
$$= (3\beta)\,\mathrm{X}\,(4\alpha) + (3\beta)\,\mathrm{X}\,R^0 + (4\alpha)\,\mathrm{X}\,R^0 \tag{1}$$

As R^0 is symmetrical,

$$(3\beta)\,\mathrm{X}\,R^0 = 0 \tag{2}$$

On the other hand, as the orientation of 4α is almost parallel with the average plane of R^0 (equatorial bond), it is expected that the absolute value of $(4\alpha)\,\mathrm{X}\,R^0$ will be very small[7]. Therefore, for the sake of simplicity of calculation, the next equation is available;

$$(4\alpha)\,\mathrm{X}\,R^0 \simeq 0 \tag{3}$$

Combining Eqs. 1, 2 and 3,

$$-53.0 \simeq (3\beta)\,\mathrm{X}\,(4\alpha) \tag{4}$$

However,

$$(3\beta)\,\mathrm{X}\,(4\alpha) = \{(3\beta)\times(4\alpha)\}\zeta^2_{OH}\{(n^2+2)/3\}^{9)}$$
$$= \{[\mu]^{20}_{D\ \mathrm{calcd}} \text{ between } (OH)^{3\beta} \text{ and } (OH)^{4\alpha}\}$$
$$\times\{3/(n^2+2)\}\zeta^2_{OH}\{(n^2+2)/3\}^{11)}$$
$$= -A\zeta^2_{OH}\{(n^2+2)/3\}^{12)}$$
$$= -11.73\zeta^2_{OH}\{(n^2+2)/3\} \tag{5}$$

From Eqs. 4 and 5,

$$-53.0 \simeq -11.73\zeta^2_{OH}\{(n^2+2)/3\}$$

or

$$\zeta^2_{OH} \simeq 4.5183\{3/(n^2+2)\}$$

This value is almost equal to the value of ζ^2_{OH} in (−)1/2 cyclohexanediol, which has only two hydroxyl groups in its molecule, $4.1091\{3/(n^2+2)\}$[13]. This fact may mean that the value of the ζ-coefficient of a unit group is nearly constant, regardless of the kind of ring in the molecule with which it is concerned.

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1) Part VIII, S. Yamana, This Bulletin, 35, 1269 (1962).
2) $Ring^0$ (or R^0) means an aldopyranose-ring which has not any hydrogen bond producing group at its 1- or 5-position.
3) H. G. Fletcher, Jr. and C. S. Hudson, 71, 3682 (1949).
4) This model can be made from the ideal model of polyhydroxycyclohexane by replacing the C^6-atom of its cyclohexane-ring by the ring-O-atom. (Cf. previous papers[5,6]). For this model, $[\mu]^{20}_{D\ \mathrm{calcd}}\{3/(n^2+2)\}$ is given by Table I of a previous paper[5] and, more precisely, by Table II of a previous paper[6].
5) S. Yamana, This Bulletin, 30, 207 (1957).
6) S. Yamana, ibid., 33, 1741 (1960).
7) Concerning the reason for this deduction from the relative geometry of the unit groups, cf. Eq. 1 of a previous paper[8].
8) S. Yamana, This Bulletin, 30, 203 (1957).
9) Equation 32 of a previous paper[10] is used.
10) S. Yamana, This Bulletin, 31, 558 (1958).
11) Cf. footnote *10 of the previous paper[5].
12) Table II of the previous paper[6] is used.
13) Cf. footnote 4, S. Yamana, This Bulletin, 34, 1414 (1961).