Molecular Rotations of Glucides in Relation to their Structures. X[1]. *On the ζ-Coefficient of the Hydroxyl Group in Pentose and Methylpentose*

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In the analysis of the $[M]_D^{20}$(W) by using the PM-method reported on in previous papers[1,2], the following two facts became apparent:

(1) The product of the ζ-coefficients of the hydroxyl and methyl groups, $\zeta_{OH}\zeta_{CH_3}$, is nearly definite and constant, regardless either of the kind of ring or of the number of hydroxyl groups in the molecule in which they are contained.

(2) When there are only two hydroxyl groups in a molecule, the value of $\zeta_{OH}{}^2$ is also nearly constant, regardless of the kind of ring in the molecule.

On the other hand, the value of $\zeta_{OH}{}^2$ when there are more than three hydroxyl groups in a molecule does not seem to be so simple. That value was calculated as $3.6402\{3/(n^2+2)\}$ (for polyhydroxycyclohexane[3]) and $2.4897\{3/(n^2+2)\}$ (for pentose, etc.[4]).

These two values show that the value of $\zeta_{OH}{}^2$ is not nearly constant in this case. Therefore, it is necessary in this article to examine the value of $\zeta_{OH}{}^2$ in pentose, etc.

New Treatment Applied

The value of $\zeta_{OH}{}^2$ in pentose, etc., $2.4897\cdot\{3/(n^2+2)\}$, was obtained in a previous paper[5] on the assumption that every one of the hydroxyl groups in a carbohydrate molecule has the same ζ_{OH} value. However, it is well-known that the chemical character of the hydroxyl group which combines with the C^1-atom of the aldopyranose-ring, $(OH)^1$ [6], is quite different from that of the other hydroxyl groups in the carbohydrate molecule. Therefore, it may be appropriate to presume that the optical character of $(OH)^1$ may also be different from that of the other hydroxyl group[7]. In

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[1] Part IX: S. Yamana, This Bulletin, 35, 1421 (1962).

[2] S. Yamana, ibid., 35, 1269 (1962).

[3] S. Yamana, ibid., 33, 1741 (1960).

[4] Eq. 11 in a previous paper[5].

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

[6] The reducing group, $(OH)^1$, of a cyclic sugar, although alcoholic in form, is in fact a cyclic semi-acetal group ("Advances in Carbohydrate Chemistry", Vol. 5, Academic Press, New York (1950), p. 145).

[7] In his own method of the calculation of the $[M]_D^{20}$-(W) of carbohydrates, Whiffen treated the glycosidic O-atom, O_g, as of a different optical character from the other O-atom (D. H. Whiffen, *Chem. & Ind.*, 1956, 964).

TABLE I

Name	Unit group	$[M]_{\mathrm{D}}^{20}$(W)	Ref.
β-L-Arabinose	$[(OH)^{1\alpha}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\beta}$, Ring]	303.3°	9
α-L-Arabinose	$[(OH)^{1\beta}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\beta}$, Ring]	133.6°	9
α-D-Xylose	$[(OH)^{1\alpha}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\alpha}$, Ring]	140.5°	10
β-D-Xylose	$[(OH)^{1\beta}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\alpha}$, Ring]		
α-D-Fucose	$[(OH)^{1\alpha}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\beta}, (CH_3)^{5\beta}$, Ring]	251.0°	10
β-D-Fucose	$[(OH)^{1\beta}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\beta}, (CH_3)^{5\beta}$, Ring]		
α-D-Isorhamnose	$[(OH)^{1\alpha}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\alpha}, (CH_3)^{5\beta}$, Ring]	163.7°	11
β-D-Isorhamnose	$[(OH)^{1\beta}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\alpha}, (CH_3)^{5\beta}$, Ring]		
α-D-Rhamnose	$[(OH)^{1\alpha}, (OH)^{2\beta}, (OH)^{3\beta}, (OH)^{4\alpha}, (CH_3)^{5\beta}$, Ring]	15.7°	10
β-D-Rhamnose	$[(OH)^{1\beta}, (OH)^{2\beta}, (OH)^{3\beta}, (OH)^{4\alpha}, (CH_3)^{5\beta}$, Ring]	−63.0°	10
α-D-Talomethylose	$[(OH)^{1\alpha}, (OH)^{2\beta}, (OH)^{3\beta}, (OH)^{4\beta}, (CH_3)^{5\beta}$, Ring]		
β-D-Talomethylose	$[(OH)^{1\beta}, (OH)^{2\beta}, (OH)^{3\beta}, (OH)^{4\beta}, (CH_3)^{5\beta}$, Ring]		
α-D-Galactose	$[(OH)^{1\alpha}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\beta}, (CH_2)^{5\beta}, (OH)^{6}$, Ring]	271.5°	10
β-D-Galactose	$[(OH)^{1\beta}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\beta}, (CH_2)^{5\beta}, (OH)^{6}$, Ring]	95.1°	10
α-D-Glucose	$[(OH)^{1\alpha}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\alpha}, (CH_2)^{5\beta}, (OH)^{6}$, Ring]	202.1°	10
β-D-Glucose	$[(OH)^{1\beta}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\alpha}, (CH_2)^{5\beta}, (OH)^{6}$, Ring]	33.7°	10
α-D-Mannose	$[(OH)^{1\alpha}, (OH)^{2\beta}, (OH)^{3\beta}, (OH)^{4\alpha}, (CH_2)^{5\beta}, (OH)^{6}$, Ring]	52.8°	10
β-D-Mannose	$[(OH)^{1\beta}, (OH)^{2\beta}, (OH)^{3\beta}, (OH)^{4\alpha}, (CH_2)^{5\beta}, (OH)^{6}$, Ring]	−30.6°	10
α-D-Talose	$[(OH)^{1\alpha}, (OH)^{2\beta}, (OH)^{3\beta}, (OH)^{4\beta}, (CH_2)^{5\beta}, (OH)^{6}$, Ring]	122.5°	10
β-D-Talose	$[(OH)^{1\beta}, (OH)^{2\beta}, (OH)^{3\beta}, (OH)^{4\beta}, (CH_2)^{5\beta}, (OH)^{6}$, Ring]	23.8°	10

Note: In order to simplify the calculations, all of these aldopyranoses may be assumed to be entirely of C1 conformation

this article, the ζ-coefficient of $(OH)^1$ is symbolized as $\zeta_{(OH)^1}$ and is distinguished from the general ζ_{OH}.

Molecular Model and Data Used

McGeachin and Beevers' molecular model[8] of C1 conformation, used in a previous paper[2], is again employed here. The unit groups in the molecules of several aldopyranoses and the corresponding values of molecular rotations are shown in Table I.

A part of Table I is a repetition of Table I of a previous paper[2]. The optical properties of the unit groups (except for the value of the ζ-coefficient) used in a previous paper[2] are adopted here without any correction. The optical center of a unit group is located at the center of the mass of its corresponding bond.

Method Proposed

$[\mu]_{\mathrm{D\,calcd}}^{20}\{3/(n^2+2)\}$, caused by the dynamical coupling effect between any two members of the unit groups (except the ring) has already been calculated; it is given in Table III of a previous paper[2]. That table is applicable for this article without any correction.

Moreover, the equation which indicates the relation between ζ_{OH} and ζ_{CH_3} in pentose and methylpentose has already been obtained in a previous paper[2]:

$$\zeta_{OH}\zeta_{CH_3}=1.5440\{3/(n^2+2)\} \qquad (1)^{12)}$$

Now, some new equations concerning $\zeta_{(OH)^1}$ can be obtained as follows:

$$\begin{aligned}
&[\mu]_{\mathrm{D\,obs}}^{20} \text{ of the An. Diff. of D-rhamnose}^{13)}\\
&=\{(1\alpha)-(1\beta)\}\lambda\{(2\beta)+(3\beta)+(4\alpha)\\
&\quad+(CH_3)^{5\beta}+R\}^{15)}=\{(1\alpha)\lambda(2\beta)\\
&\quad+(1\alpha)\lambda(3\beta)+(1\alpha)\lambda(4\alpha)\\
&\quad+(1\alpha)\lambda(CH_3)^{5\beta}+(1\alpha)\lambda R\}\\
&\quad-\{(1\beta)\lambda(2\beta)+(1\beta)\lambda(3\beta)\\
&\quad+(1\beta)\lambda(4\alpha)+(1\beta)\lambda(CH_3)^{5\beta}\\
&\quad+(1\beta)\lambda R\}=[\{1.51\zeta_{(OH)^1}\zeta_{OH}\\
&\quad+2.54\zeta_{(OH)^1}\zeta_{OH}+0.02\zeta_{(OH)^1}\zeta_{OH}\\
&\quad-5.57\zeta_{(OH)^1}\zeta_{CH_3}\}-\{12.60\zeta_{(OH)^1}\zeta_{OH}\\
&\quad-0.82\zeta_{(OH)^1}\zeta_{OH}+0.02\zeta_{(OH)^1}\zeta_{OH}\\
&\quad+1.26\zeta_{(OH)^1}\zeta_{CH_3}\}]\{(n^2+2)/3\}\\
&\quad+(1\alpha)\lambda R-(1\beta)\lambda R^{16)}=(-7.73\zeta_{(OH)^1}\zeta_{OH}\\
&\quad-6.83\zeta_{(OH)^1}\zeta_{CH_3})\{(n^2+2)/3\}\\
&\quad+(1\alpha)\lambda R-(1\beta)\lambda R
\end{aligned}$$

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[8] H. Mc. D. McGeachin and C. A. Beevers, *Acta Crys.*, **10**. 227 (1957).

[9] E. Montgomery and C. S. Hudson, *J. Am. Chem. Soc.*, **56**, 2074 (1934).

[10] F. J. Bates et al., "Polarimetry, Saccharimetry and the Sugars", United States Government Printing Office, Washington (1942).

[11] E. Zissis, N. K. Richtmyer and C. S. Hudson, *J. Am. Chem. Soc.*, **73**, 4714 (1951).

[12] Eq. 4′ in a previous paper[2].

[13] Cf. Ref. *21 in a previous paper[14].

[14] S. Yamana, This Bulletin, **31**, 564 (1958).

[15] Table I is used.

[16] Table III in a previous paper[2] is used.

TABLE II. $[\mu]^{20}_{\mathrm{D}\,\mathrm{obs}}$, CAUSED BY THE DYNAMICAL COUPLING EFFECT BETWEEN ANY TWO MEMBERS OF UNIT GROUPS (EXCEPT RING) IN McGEACHIN AND BEEVERS' MOLECULAR MODEL

	$(\mathrm{CH_3})^{5\beta}$	4β	4α	3β	3α	2β	2α
1α	− 5.6	0.1	0.0	6.0	− 4.5	3.6	28.6
1β	1.3	− 0.6	0.0	− 1.9	− 3.5	29.6	−28.7
2α	− 0.9	7.1	− 0.5	40.2	−40.5		
2β	2.0	− 2.4	− 6.6	−41.1	1.1		
3α	5.6	0.6	45.4				
3β	0.4	41.9	−43.7				
4α	37.9						
4β	−37.6						

The corresponding ovserved value is given by, $\{[M]^{20}_{\mathrm{D}}(\mathrm{W})$ of α-D-rhamnose$\}$ minus $\{[M]^{20}_{\mathrm{D}}(\mathrm{W})$ of β-D-rhamnose$\}$. This is $15.7-(-63.0)$15) $=78.7$. As these two values should be equal to each other,

$$(-7.73\zeta_{(\mathrm{OH})^1}\zeta_{\mathrm{OH}}-6.83\zeta_{(\mathrm{OH})^1}\zeta_{\mathrm{CH_3}})\{(n^2+2)/3\} + (1\alpha)\text{⅄}\mathrm{R}-(1\beta)\text{⅄}\mathrm{R}\equiv 78.7 \tag{2}$$

By using a method similar to that mentioned above, another equation is obtained for $[\mu]^{20}_{\mathrm{D}\,\mathrm{obs}}$ of the An. Diff. of L-arabinose:

$$28.06\zeta_{(\mathrm{OH})^1}\zeta_{\mathrm{OH}}\{(n^2+2)/3\} + (1\alpha)\text{⅄}\mathrm{R}-(1\beta)\text{⅄}\mathrm{R}\equiv 169.7 \tag{3}$$

From Eq. 3 minus Eq. 2 17):

$$(35.79\zeta_{(\mathrm{OH})^1}\zeta_{\mathrm{OH}}+6.83\zeta_{(\mathrm{OH})^1}\zeta_{\mathrm{CH_3}}) \times\{(n^2+2)/3\}=91.0 \tag{4}$$

Now, in order to calculate the values of ζ_{OH}, $\zeta_{\mathrm{CH_3}}$, and of $\zeta_{(\mathrm{OH})^1}$ in pentose and methylpentose, another new equation (besides Eqs. 1 and 4) is necessary.

On the other hand, it has already been pointed out that the values of ζ_{OH} in the carbohydrate which has only two hydroxyl groups in its molecule (i. e., hydro-D-xylal) is nearly equal to that in the polyhydroxycyclohexane which has only two hydroxyl groups in the molecule (i. e., (−)1/2-cyclohexanediol)1). Therefore, it may be presumed that the ζ_{OH} value of some hydroxyl groups in pentose or methylpentose may be nearly equal to that in the polyhydroxycyclohexane which has more than three hydroxyl groups in the molecule, $1.9079\{3/(n^2+2)\}^{1/2}$ 3). Therefore, in order to simplify the calculations, the author assumes, in pentose and methylpentose, the next equation:

$$\zeta_{\mathrm{OH}}=1.9079\{3/(n^2+2)\}^{1/2} \tag{5}$$

or

$$\zeta_{\mathrm{OH}}{}^2=3.6402\{3/(n^2+2)\} \tag{6}$$

Combining Eqs. 1, 4 and 5, the following values of ζ-coefficients can be obtained:

$$\zeta_{\mathrm{CH_3}}=0.8093\{3/(n^2+2)\}^{1/2} \tag{7}$$

$$\zeta_{(\mathrm{OH})^1}=1.2329\{3/(n^2+2)\}^{1/2} \tag{8}$$

$$\zeta_{(\mathrm{OH})^1}\zeta_{\mathrm{OH}}=2.3522\{3/(n^2+2)\}^{18)} \tag{9}$$

$$\zeta_{(\mathrm{OH})^1}\zeta_{\mathrm{CH_3}}=0.9978\{3/(n^2+2)\} \tag{10}$$

By combining Eqs. 1, 6, 9 and 10 with Table III of a previous paper2), a table of $[\mu]^{20}_{\mathrm{D}\,\mathrm{obs}}$ in pentose and methylpentose can be produced19). This is Table II.

In order to test the correctness of Table II, the $[M]^{20}_{\mathrm{D}}(\mathrm{W})$ values of some carbohydrates have been calculated by using it, and those calculated values have then been tested by using Hudson's methyl glycoside rule20) or another new method, devised by the author.

Calculation of $[M]^{20}_{\mathrm{D}}(\mathrm{W})$

Pentose21).—At first, by using the experimental data of $[M]^{20}_{\mathrm{D}}(\mathrm{W})$ of β- and α-L-arabinoses, the value of $\{(1\alpha)\text{⅄}\mathrm{R}-(1\beta)\text{⅄}\mathrm{R}\}$ can be calculated as below:

$$\begin{aligned}&[\mu]^{20}_{\mathrm{D}\,\mathrm{ob}} \text{ of the An. Diff. of L-arabinose}\\ &=\{(1\alpha)-(1\beta)\}\text{⅄}\{(2\alpha)+(3\beta)+(4\beta)\\ &\quad+\mathrm{R}\}^{13)}=(1\alpha)\text{⅄}(2\alpha)+(1\alpha)\text{⅄}(3\beta)\\ &\quad+(1\alpha)\text{⅄}(4\beta)+(1\alpha)\text{⅄}\mathrm{R}-\{(1\beta)\text{⅄}(2\alpha)\\ &\quad+(1\beta)\text{⅄}(3\beta)+(1\beta)\text{⅄}(4\beta)+(1\beta)\text{⅄}\mathrm{R}\}\end{aligned}$$

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17) Eq. 3 is used for the purpose of cancelling the $\{(1\alpha)\text{⅄}\mathrm{R}-(1\beta)\text{⅄}\mathrm{R}\}$ term in Eq. 2.

18) According to the conception that $\zeta_{(\mathrm{OH})^1}$ is different from ζ_{OH}. Eq. 11 in a previous paper5) is rewritten as follows: $\zeta_{(\mathrm{OH})^1}\ \zeta_{\mathrm{OH}}=2.4897\{3/(n^2+2\}$. Note: This value was calculated by using McDonald and Beevers' molecular model (T. R. R. McDonald and C. A. Beevers, *Acta Cryst.*, 5, 654 (1952)) and the $[M]^{20}_{\mathrm{D}}(\mathrm{W})$ value of four hexoses (i. e., α-D-glucose, β-D-glucose, α-D-mannose and β-D-mannose) on the assumption that the internal conformation of the $\mathrm{C^6}$-O bond is definite and similar in those four hexoses.

19) Concerning the making of the table of $[\mu]^{20}_{\mathrm{D}\,\mathrm{obs}}$, cf. Eq. 3 in a previous paper5).

20) Cf. Ref. 20 in a previous paper2).

21) There are four kinds of pentose, arabinose, xylose, lyxose and ribose. However, the exact $[M]^{20}_{\mathrm{D}}(\mathrm{W})$ value of ribose has never been observed, and lyxose is of C1 and 1C conformations in an aqueous solution (R.E.Reeves, *J. Am. Chem. Soc.*, 72, 1499 (1950)). Ribose and lyxose will be discussed by the author in detail in a future paper. Therefore, these two pentoses are not discussed in this article.

$= 28.6 + 6.0 + 0.1 + (1\alpha)\text{⅄}R - \{-28.7 - 1.9$

$- 0.6 + (1\beta)\text{⅄}R\} = 65.9 + (1\alpha)\text{⅄}R$

$- (1\beta)\text{⅄}R$[22] $\equiv 169.7$[23]

or

$$(1\alpha)\text{⅄}R - (1\beta)\text{⅄}R = 103.8 \qquad (11)$$

In a like manner, by using Table II and Eq. 11, the $[\mu]^{20}_{\mathrm{D\,obs}}$ value of the An. Diff. of D-xylose can be calculated as 169.0. Therefore, if the $[M]^{20}_{\mathrm{D}}$(W) of β-D-xylose is x, {$[M]^{20}_{\mathrm{D}}$(W) of α-D-xylose} − {$[M]^{20}_{\mathrm{D}}$(W) of β-D-xylose} $= 140.5 - x$[15] $\equiv 169.0$

$$\therefore \quad x = -28.5$$

This calculated value is approximately equal to Hudson's figure, −30°[24].

Methylpentose. — When the H atom which is combined with the C^5-atom of pentose is replaced by $(CH_3)^{5\beta}$[15], methyl pentose can be obtained. This process can be shown schematically by the following equation:

$$(\text{pentose}) - H^{5\beta} + (CH_3)^{5\beta} = (\text{methylpentose})$$

Because of its small polarizability, the $[\mu]^{20}_{\mathrm{D\,obs}}$ of $H^{5\beta}$ can be neglected. Then, concerning the molecular rotations, the next equation can be obtained:

$$\{[M]^{20}_{\mathrm{D}}(\mathrm{W})\text{ of pentose}\} + \{[\mu]^{20}_{\mathrm{D\,obs}}\text{ of } (CH_3)^{5\beta}\} \simeq \{[M]^{20}_{\mathrm{D}}(\mathrm{W})\text{ of methylpentose}\} \qquad (12)$$

Next, the value of $(CH_3)^{5\beta}\text{⅄}R$ is calculated quasi-empirically as follows: The unit groups which can couple with $(CH_3)^{5\beta}$ in α-D-fucose are $(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$ and ring[15]. Then,

$[\mu]^{20}_{\mathrm{D\,obs}}$ of $(CH_3)^{5\beta}$ in α-D-fucose

$= (CH_3)^{5\beta}\text{⅄}\{(1\alpha) + (2\alpha) + (3\beta) + (4\beta) + R\}$

$= (CH_3)^{5\beta}\text{⅄}(1\alpha) + (CH_3)^{5\beta}\text{⅄}(2\alpha)$

$+ (CH_3)^{5\beta}\text{⅄}(3\beta) + (CH_3)^{5\beta}\text{⅄}(4\beta)$

$+ (CH_3)^{5\beta}\text{⅄}R = -5.6 - 0.9 + 0.4 - 37.6$

$+ (CH_3)^{5\beta}\text{⅄}R = -43.7 + (CH_3)^{5\beta}\text{⅄}R$

The corresponding observed value is given by the following equation:

{$[M]^{20}_{\mathrm{D}}$(W) of α-D-fucose} minus {$[M]^{20}_{\mathrm{D}}$(W) of β-L-arabinose} $= 251.0 - 303.3$[15] $= -52.3$

$$\therefore \quad -43.7 + (CH_3)^{5\beta}\text{⅄}R \equiv -52.3$$

or

$$(CH_3)^{5\beta}\text{⅄}R = -8.6 \qquad (13)$$

Referring to Eq. 12 and the unit groups in the molecules of α-D-xylose and of α-D-isorhamnose, the next equation can be obtained:

$$\{[M]^{20}_{\mathrm{D}}\text{ of }\alpha\text{-D-xylose}\} + \{[\mu]^{20}_{\mathrm{D\,obs}}\text{ of }(CH_3)^{5\beta}\} \simeq \{[M]^{20}_{\mathrm{D}}(\mathrm{W})\text{ of }\alpha\text{-D-isorhamnose}\}$$

In this equation, $[\mu]^{20}_{\mathrm{D\,obs}}$ of $(CH_3)^{5\beta}$ can be given by the following equation:

$(CH_3)^{5\beta}\text{⅄}\{(1\alpha) + (2\alpha) + (3\beta) + (4\alpha) + R\}$[15]

$= (CH_3)^{5\beta}\text{⅄}(1\alpha) + (CH_3)^{5\beta}\text{⅄}(2\alpha)$

$+ (CH_3)^{5\beta}\text{⅄}(3\beta) + (CH_3)^{5\beta}\text{⅄}(4\alpha)$

$+ (CH_3)^{5\beta}\text{⅄}R = -5.6 - 0.9 + 0.4$

$+ 37.9 - 8.6$[22,25] $= 23.2$

Combining this value with Eq. 14, the $[M]^{20}_{\mathrm{D}}$ of α-D-isorhamnose is calculated as 163.7. *This is just equal to the observed value, 163.7*[15]. By using a method similar to that mentioned above, the $[M]^{20}_{\mathrm{D}}$(W) values of two methylpentoses (β-D-fucose and β-D-isorhamnose) which have never been observed are calculated as 88.2 and 1.6 respectively from the $[M]^{20}_{\mathrm{D}}$(W) values of their corresponding pentoses. As the $[M]^{20}_{\mathrm{D}}$(W) values of methyl-β-D-fucoside and of methyl-β-D-isorhamnoside are −25.3[26] and −97.3[27], their respective $[M]^{20}_{\mathrm{D}}$(W)-Diff.< methyl glycoside−cor. al.[28] pyranose >[29] values become −113.5 and −98.9. Therefore, the above expected values of β-D-fucose and β-D-isorhamnose satisfy Hudson's methyl glycoside rule[20]; accordingly, these two expected values seem to be reliable.

Next, by using the experimental data of the $[M]^{20}_{\mathrm{D}}$(W) values of α-D-xylose and β-L-arabinose, the value of $\{(4\alpha)\text{⅄}R - (4\beta)\text{⅄}R\}$ can be calculated as follows:

$[\mu]^{20}_{\mathrm{D\,obs}}$ of Yo. Diff.[30] < α-D-xylose

− β-L-arabinose>[29] $= \{(4\alpha) - (4\beta)\}$

$\text{⅄}\{(1\alpha) + (2\alpha) + (3\beta) + R\}$[31,15]

$= (4\alpha)\text{⅄}(1\alpha) + (4\alpha)\text{⅄}(2\alpha) + (4\alpha)\text{⅄}(3\beta)$

$+ (4\alpha)\text{⅄}R - \{(4\beta)\text{⅄}(1\alpha) + (4\beta)\text{⅄}(2\alpha)$

$+ (4\beta)\text{⅄}(3\beta) + (4\beta)\text{⅄}\}$[22]

$= -93.3 + (4\alpha)\text{⅄}R - (4\beta)\text{⅄}R$

The corresponding observed value is given by the next equation:

{$[M]^{20}_{\mathrm{D}}$(W) of α-D-xylose} − {$[M]^{20}_{\mathrm{D}}$(W) of β-L-arabinose} $= 140.5 - 303.3$[15] $= -162.8$

Then, $-93.3 + (4\alpha)YR - (4\beta)\text{⅄}R \equiv -162.8$

$$\therefore \quad (4\alpha)\text{⅄}R - (4\beta)\text{⅄}R = -69.5 \qquad (15)$$

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[22] Table II is used.

[23] Cf. Eq. 3.

[24] This is the $[M]^{20}_{\mathrm{D}}$ in an 80% alcoholic solution (E. Yanovsky and C. S. Hudson, *J. Am. Chem. Soc.*, 39, 1013 (1917)).

[25] Eq. 13 is used.

[26] R. C. Hockett, F. P. Phelps and C. S. Hudson, *J. Am. Chem. Soc.*, 61, 1658 (1939).

[27] W. D. Maclay, R. M. Hann and C. S. Hudson, ibid., 61, 1660 (1939).

[28] "cor." and "al." mean "corresponding" and "aldo-".

[29] Cf. Ref. 17 in a previous paper[2].

[30] Cf. Ref. *10 in a previous paper[14].

[31] Cf. Ref. *12 in a previous paper[14].

TABLE III. $[M]^{20}_{\mathrm{D}}$(W)-DIFF. ⟨HEXOSE − COR. METHYLPENTOSE⟩

Series	$[M]^{20}_{\mathrm{D}}$(W) of hexose15)	$[M]^{20}_{\mathrm{D}}$(W) of cor. methyl pentose15)	$[M]^{20}_{\mathrm{D}}$(W)-Diff.
I	α-D-Glucose (202.1)	α-D-Isorhamnose (163.7)	38.4
	α-D-Mannose (52.8)	α-D-Rhamnose (15.7)	37.1
II	β-D-Glucose (33.7)	β-D-Isorhamnose ((1.6))	32.1
	β-D-Mannose (−30.6)	β-D-Rhamnose (−63.0)	32.4
III	α-D-Galactose (271.5)	α-D-Fucose (251.0)	20.5
	α-D-Talose (122.5)	α-D-Talomethylose ((99.6))	22.9
IV	β-D-Galactose (95.1)	β-D-Fucose ((88.2))	6.9
	β-D-Talose (23.8)	β-D-Talomethylose ((20.2))	3.6

Note: The value in (( )) is the calculated value in this article.

By using Eq. 15, the $[M]^{20}_{\mathrm{D}}$(W) of α-D-talomethylose can be calculated as follows:

$$[\mu]^{20}_{\mathrm{D\,obs}} \text{ of Yo. Diff} < \alpha\text{-D-rhamnose} - \alpha\text{-D-talomethylose} > = \{(4\alpha)-(4\beta)\}\,\bar{\lambda}\,\{(1\alpha)+(2\beta)+(3\beta)+(\mathrm{CH_3})^{5\beta}+\mathrm{R}\}^{15,31)} = -83.9^{22)}$$

If the $[M]^{20}_{\mathrm{D}}$(W) value of α-D-talomethylose is y, the corresponding observed value is given by $\{[M]^{20}_{\mathrm{D}}$(W) of α-D-rhamnose$\}$ minus $\{[M]^{20}_{\mathrm{D}}$(W) of α-D-talomethylose$\} = 15.7$15) $- y$

$$-83.9 \equiv 15.7 - y$$

or

$$y = 99.6$$

By using a similar method, the $[M]^{20}_{\mathrm{D}}$(W) value of β-D-talomethylose is calculated as 20.2. However, in these cases, as the $[M]^{20}_{\mathrm{D}}$(W) values of their corresponding methyl glycosides have not yet been observed, examinations by using Hudson's methyl glycoside rule are impossible. Therefore, in order to test the validity of these presumed $[M]^{20}_{\mathrm{D}}$(W) values of methylpentoses, a new method has been devised as follows:

When an $(\mathrm{H})^6$ 32) in $(\mathrm{CH_3})^{5\beta}$ of methylpentose is replaced by $(\mathrm{OH})^6$ 32), hexose can be obtained. This process can be shown schematically by the next equation:

$$(\text{methylpentose}) - (\mathrm{H})^6 + (\mathrm{OH})^6 = (\text{hexose})$$

Owing to its small polarizability, the $[\mu]^{20}_{\mathrm{D\,obs}}$ value of $(\mathrm{H})^6$ can be neglected; the following equation on molecular rotations is obtained:

$$\{[M]^{20}_{\mathrm{D}}(\mathrm{W}) \text{ of methylpentose}\} + \{[\mu]^{20}_{\mathrm{D\,obs}} \text{ of } (\mathrm{OH})^6\} \simeq \{[M]^{20}_{\mathrm{D}}(\mathrm{W}) \text{ of hexose}\}$$

or

$$[M]^{20}_{\mathrm{D}}(\mathrm{W})\text{-Diff.} < \text{hexose} - \text{cor. methylpentose} > \equiv \{[M]^{20}_{\mathrm{D}}(\mathrm{W}) \text{ of hexose}\} - \{[M]^{20}_{\mathrm{D}}(\mathrm{W}) \text{ of methylpentose}\} \simeq [\mu]^{20}_{\mathrm{D\,obs}} \text{ of } (\mathrm{OH})^6 \tag{16}$$

On the other hand, $(\mathrm{OH})^2$ is situated at the opposite end of a diameter of the aldopyranose-ring in relation to the C^5-atom with which $(\mathrm{CH_2OH})^{5\beta}$ is combined, and the distance between $(\mathrm{OH})^2$ and $(\mathrm{OH})^6$ is fairly large34). Therefore, referring to Tschúgaeff's Entfernungssatz35) and Freudenberg's Verschiebungssatz36), the following anticipation is possible:

The value, expressed in Eq. 16, should be almost indifferent to the orientation-change of $(\mathrm{OH})^2$. In short, the $[M]^{20}_{\mathrm{D}}$(W)-Diff. <hexose-cor. methylpentose> of the epimer37) should be nearly equal to each other. (Anticipation 3)

Therefore, if a $[M]^{20}_{\mathrm{D}}$(W) value does not satisfy Anticipation 3, it should be doubtful. Thus, Anticipation 3 can be a new instrument to test the validity of any $[M]^{20}_{\mathrm{D}}$(W) value of hexose or methylpentose.

The concrete values of $[M]^{20}_{\mathrm{D}}$(W)-Diff. <hexose − cor. methylpentose> now available are shown in Table III.

It is apparent in Table III that $[M]^{20}_{\mathrm{D}}$(W)-Diff. < hexose − cor. methylpentose > can be classified into approximately four series and that, moreover, when considering the orientation of $(\mathrm{OH})^2$ 15), the hexoses (or methylpentoses) which belong to the same series are the empimers of each other. Therefore, the values of $[M]^{20}_{\mathrm{D}}$(W) in Table III satisfy Anticipation 3. This fact indicates that the $[M]^{20}_{\mathrm{D}}$(W) values in Table III are almost completely reliable.

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32) Cf. Ref. *10 in a previous paper33).

33) S. Yamana, This Bulletin, **30**, 920(1957).

34) Cf. Ref. *17 in a previous paper33).

35) L. Tschúgaeff, *Ber.*, **31**, 360 (1898).

36) K. Freudenberg and W. Kuhn, ibid., **64**, 726 (1931).

37) Cf. Ref. *9 in a previous paper14).

Summary

As there are four hydroxyl groups in the pentose and methylpentose molecules, the ζ_{OH} values in some of them may be nearly equal to that in the polyhydroxycyclohexane which has four hydroxyl groups in the molecule. In order to satisfy this condition, the ζ-coefficient of $(H)^1$, $\zeta_{(OH)^1}$, was distinguished from that of the other (OH), ζ_{OH}. Next, by using the PM-method, the values of $\zeta_{(OH)}$, ζ_{OH} and ζ_{CH_3} were calculated. Making use of these ζ-coefficients, a table of $[\mu]^{20}_{D\,obs}$ values was made. By using this table, the $[M]^{20}_{D}(W)$ values of some carbohydrates, hitherto unknown, were calculated. The validity of the presumed values was then tested by applying Hudson's methyl glycoside rule and a new anticipation proposed by the author.

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