Molecular Rotations of Glucides in Relation to their Structures. VIII⁽¹⁾*. On the Product of the ζ-Coefficients of the Hydroxyl and the Methyl Groups*

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Recently, the author introduced an adjustable parameter, the ζ-coefficient, in order to make up Kirkwood's polarizability theory of optical rotatory power; he named this manner of the calculation of optical rotation the "PM-method"(2). By using the PM-method, it is possible to explain logically the relation between the $[M]_{\mathrm{D}}^{20}$(W) of some optically active substances (i. e. glucocides, polyhydroxycyclohexanes(4) and menthol-like substances(5)) and their molecular structure. Moreover, the product of the ζ-coefficient of the hydroxyl group and that of the methyl group, $\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}$, was calculated as about $1.6\{3/(n^2+2)\}$ in molecules which have a cyclohexane-ring (i. e. (−)-trans-2-methylcyclohexanol and menthol-like substances(5)). Nevertheless, in the case of carbohydrates which have an aldopyranose-ring in their molecules, the value of $\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}$ had been calculated as either $0.3096\{3/((n^2+2)\}$(6) (when using the $[M]_{\mathrm{D}}^{20}$(W) of β-L-arabinose written in Bates' book(8)) or $0.6671\{3/(n^2+2)\}$(9) (when using the $[M]_{\mathrm{D}}^{20}$(W) of β-L-arabinose observed by Hudson(10)), which values are fairly different from that in the case of molecules which have a cyclohexane-ring, as has been mentioned above. For these reasons, the recalculation of the value of $\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}$ in carbohydrates (methyl pentose) becomes necessary.

New Treatment Applied

Into the "Method Proposed" of the previous paper(7), the following two alterations were introduced:

(i) Molecular Model. — In the previous paper(7), the molecular model which had been determined by McDonald and Beevers(11) from the results of the X-ray analysis of crystalline α-D-glucose (hexose) was used. Strictly speaking, however, the shape of its aldopyranose-ring is not perfectly the same as that in methyl pentose. Therefore, as with the molecular model in this article, the one proposed by Geachin and Beevers(12) in the case of crystalline α-rhamnose monohydrate is used. However, this change in the molecular model will not cause much difference(13).

(ii) The $[M]_{\mathrm{D}}^{20}$(W) of α-D-Isorhamnose. — In this series of studies, the data for $[M]_{\mathrm{D}}^{20}$(W) which are listed in Bates' book(8) have been used preferentially. However, after its publication (1942), new data on the $[M]_{\mathrm{D}}^{20}$(W) of carbohydrates have been reported year after year, and those new data should be taken into account. Particularly, in 1951 Hudson reported 163.7 as the $[M]_{\mathrm{D}}^{20}$(W) of α-D-isorhamnose(15), a value which is far different from that listed in Bates' book, 120.3. Therefore, it should be discussed here which of these two values should be chosen. Generally, the $[M]_{\mathrm{D}}^{20}$(W) of an aldopyranose changes widely as time elapses (this phenomenon is called "mutarotation"), and the determination of the initial $[M]_{\mathrm{D}}^{20}$(W) at the time of resolution is difficult. However, the $[M]_{\mathrm{D}}^{20}$(W) of its methyl glycoside is almost constant and can be easily observed. Therefore, it is desirable that an experimental datum of the $[M]_{\mathrm{D}}^{20}$(W) of an aldopyranose should be examined by using the $[M]_{\mathrm{D}}^{20}$(W) of its methyl glycoside.

On the other hand, concerning $[M]_{\mathrm{D}}^{20}$(W)-Diff<methyl glycoside − cor. al. pyranose(16)>(17), Hudson's empirical rule is well known. This

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1) Part VII: S. Yamana, This Bulletin, **32**, 597 (1959).

2) Footnote* 17 in Ref. 3.

3) S. Yamana, This Bulletin, **31**, 558 (1958).

4) S. Yamana, ibid., **33**, 1741 (1960); **34**, 1212 (1961).

5) S. Yamana, ibid., **34**, 1414 (1961).

6) Eq. 4 in Ref. 7.

7) S. Yamana, This Bulletin, **31**, 564 (1958).

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

9) Eq. 4, in footnote* 17 of Ref. 7.

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

11) T. R. R. McDonald and C. A. Beevers, *Acta Cryst.*, **5**, 654 (1952).

12) H. Mc. D. McGeachin and C. A. Beevers, *Acta Cryst.*, **10**, 227 (1957).

13) Cf. footnote* in Ref. 14.

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

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

16) "cor." and "al." mean "corresponding" and "aldo-" respectively.

17) In order to represent the difference between A and B simply, the abbreviated symbol, Diff <A − B>, will be used hereafter. For example, $[M]_{\mathrm{D}}^{20}$(W)-Diff<methyl α-D-isorhamnoside − α-D-isorhamnose> means the difference in $[M]_{\mathrm{D}}^{20}$(W) between methyl α-D-isorhamnoside and α-D-isorhamnose, and so on.

TABLE I. $[M]^{20}_{\mathrm{D}}$(W)-DIFF.<METHYL GLYCOSIDE −COR. AL. PYRANOSE[16]>[17]

Name	$[M]^{20}_{\mathrm{D}}$(W) of methyl glycoside	$[M]^{20}_{\mathrm{D}}$(W) of cor. al. pyranose	$[M]^{20}_{\mathrm{D}}$(W)-Diff.
β-L-Arabinose	403.0[8]	303.3[10]	99.7
α-L-Arabinose	28.4[8]	133.6[10]	−105.2
α-D-Xylose	252.6[8]	140.5[8]	112.1
α-D-Fucose	351.2[21]	251.0[8]	100.2
β-D-Fucose	−25.3[21]		
α-D-Isorhamnose	272.1[22]	163.7[15]	108.4
β-D-Isorhamnose	−97.3[22]		
α-D-Rhamnose	111.4[8]	15.7[8]	95.7
β-D-Rhamnose	−170.0[8]	−63.0[8]	−107.0
α-D-Galactose	380.5[8]	271.5[8]	109.0
β-D-Galactose	0.0[8]	95.1[8]	−95.1
α-D-Glucose	308.6[8]	202.1[8]	106.5
β-D-Glucose	−66.4[8]	33.7[8]	−100.1
α-D-Mannose	153.8[8]	52.8[8]	101.0
β-D-Mannose	−135.5[8]	−30.6[8]	−104.9
		Mean of the absolute value	103.5

rule says that the absolute value of this $[M]^{20}_{\mathrm{D}}$(W)-Diff. is not far from 100[18-20].

By using this rule, the approximate value of the $[M]^{20}_{\mathrm{D}}$(W) of α-D-isorhamnose can be obtained by the following equation:

$$272.1^{23,18)} - 100 = 172.1$$

Accordingly, Hudson's datum of the $[M]^{20}_{\mathrm{D}}$(W) of α-D-isorhamnose, 163.7, seems to be more reliable than that in Bates' book, 120.3.

Data Used

Therefore, Table I of the previous paper[7] is rewritten as Table II of this article.

The optical data of the unit groups used in the previous paper[7] are adopted again without any correction[24]. An optical center of the unit group is located at the center of the mass of the bond with which it is combined.

Re-calculation

$\zeta_{OH}\zeta_{CH_3}$.—By using Table II in this article, Eqs. 1, 2 and 3 of the previous paper[7] can be

TABLE II

Name	Unit groups	$[M]^{20}_{\mathrm{D}}$(W)	Lit.
α-D-Xylose	$[(OH)^{1\alpha}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\alpha}, \mathrm{Ring}]$	140.5°	8)
β-L-Arabinose	$[(OH)^{1\alpha}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\beta}, \mathrm{Ring}]$	303.3°	10)
α-D-Isorhamnose	$[(OH)^{1\alpha}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\alpha}, (CH_3)^{5\beta}, \mathrm{Ring}]$	163.7°	15)
β-D-Isorhamnose	$[(OH)^{1\beta}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\alpha}, (CH_3)^{5\beta}, \mathrm{Ring}]$		
α-D-Fucose	$[(OH)^{1\alpha}, (OH)^{2\alpha}, (OH)^{3\beta}, (OH)^{4\beta}, (CH_3)^{5\beta}, \mathrm{Ring}]$	251.0°	8)

TABLE III. $[\mu]^{20}_{\mathrm{D}\,\mathrm{calcd}}\{3/(n^2+2)\}$, CAUSED BY THE DYNAMICAL COUPLING EFFECT BETWEEN ANY TWO MEMBERS OF UNIT GROUPS (EXCEPT RING) IN McGEACHIN AND BEEVERS' MOLECULAR MODEL

	$(CH_3)^{5\beta}$	4β	4α	3β	3α	2β	2α
1α	−5.57 (−4.32)	0.05 (0.15)	0.02 (0.01)	2.54 (2.20)	−1.93 (−1.83)	1.51 (0.76)	12.17 (6.64)
1β	1.26 (0.65)	−0.26 (−0.18)	0.02 (0.01)	−0.82 (−0.44)	−1.47 (−1.33)	12.60 (7.00)	−12.22 (−6.42)
2α	−0.61 (−0.31)	1.96 (1.65)	−0.15 (−0.08)	11.05 (6.28)	−11.12 (−6.28)		
2β	1.28 (0.82)	−0.66 (−0.64)	−1.80 (−1.53)	−11.28 (−6.37)	0.31 (0.17)		
3α	3.62 (3.00)	0.17 (0.08)	12.46 (6.93)				
3β	0.25 (0.12)	11.52 (6.18)	−12.01 (−6.52)				
4α	24.52 (12.37)						
4β	−24.38 (−12.50)						

Note: The values, calculated by supposing that the optical center of (OH) group is located at its O atom, and that of $(CH_3)^{5\beta}$ group is at its C atom, are given in parentheses.

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[18] Cf. Table I.

[19] C. S. Hudson, *J. Am. Chem. Soc.*, **47**, 268 (1925).

[20] The author proposes to name this empirical rule "Hudson's methyl glycoside rule".

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

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

[23] This is the $[M]^{20}_{\mathrm{D}}$(W) of methyl α-D-isorhamnoside.

[24] The mean polarizability, α, of OH is 1.04×10^{-24} cc.; the α of CH_3 is 2.27×10^{-24} cc.; the anisotropy ratio, β, of OH is 0.35 and the β of CH_3 is 0.35. The refractive index, n, is 1.34.

rewritten as the following Eqs., 1′, 2′ and 3′, respectively.

$$
\begin{aligned}
&\text{Yo. Diff.}\langle\alpha\text{-D-isorhamnose}-\alpha\text{-D-fucose}\rangle^{17)}\\
&=163.7-251.0^{25)}=-87.3\equiv(F-E)\\
&=\{(4\alpha)\,\overline{\mathrm{X}}\,(1\alpha)+(4\alpha)\,\overline{\mathrm{X}}\,(2\alpha)+(4\alpha)\,\overline{\mathrm{X}}\,(3\beta)\\
&+(4\alpha)\,\overline{\mathrm{X}}\,(\mathrm{CH_3})^{5\beta}+(4\alpha)\,\overline{\mathrm{X}}\,\mathrm{R}\}\\
&-\{(4\beta)\,\overline{\mathrm{X}}\,(1\alpha)+(4\beta)\,\overline{\mathrm{X}}\,(2\alpha)+(4\beta)\,\overline{\mathrm{X}}\,(3\beta)\\
&+(4\beta)\,\overline{\mathrm{X}}\,(\mathrm{CH_3})^{5\beta}+(4\beta)\,\overline{\mathrm{X}}\,\mathrm{R}\} \qquad (1')
\end{aligned}
$$

$$
\begin{aligned}
&\text{Yo. Diff.}\langle\alpha\text{-D-xylose}-\beta\text{-L-arabinose}\rangle\\
&=140.5-303.3^{25)}=-162.8\equiv\{(4\alpha)-(4\beta)\}\\
&\overline{\mathrm{X}}\,\{(1\alpha)+(2\alpha)+(3\beta)+\mathrm{R}\}=\{(4\alpha)\,\overline{\mathrm{X}}\,(1\alpha)\\
&+(4\alpha)\,\overline{\mathrm{X}}\,(2\alpha)+(4\alpha)\,\overline{\mathrm{X}}\,(3\beta)+(4\alpha)\,\overline{\mathrm{X}}\,\mathrm{R}\}\\
&-\{4\beta)\,\overline{\mathrm{X}}\,(1\alpha)+(4\beta)\,\overline{\mathrm{X}}\,(2\alpha)+(4\beta)\,\overline{\mathrm{X}}\,(3\beta)\\
&+(4\beta)\,\overline{\mathrm{X}}\,\mathrm{R}\} \qquad (2')
\end{aligned}
$$

$$
\begin{aligned}
&\{(4\alpha)\times(\mathrm{CH_3})^{5\beta}-(4\beta)\times(\mathrm{CH_3})^{5\beta}\}\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}\\
&\times\{(n^2+2)/3\}=75.5 \qquad (3')
\end{aligned}
$$

On the other hand, all $[\mu]^{20}_{\mathrm{Dcalcd}}\{3/(n^2+2)\}$, values caused by the dynamical coupling effect between any two members of the unit groups (except the ring) in the molecular model are calculated by using the theoretical formulae of Kirkwood and are shown in Table III.

It is apparent in Table III that $(4\alpha)\times(\mathrm{CH_3})^{5\beta}$ and $(4\beta)\times(\mathrm{CH_3})^{5\beta}$ are 24.52 and −24.38 respectively[26]. By using these values in Eq. 3′,

$$\{24.52-(-24.38)\}\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}\{(n^2+2)/3\}=75.5$$

$$\text{or}\qquad \zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}=1.5440\{3/(n^2+2)\} \qquad (4')$$

The value of $\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}$ in Eq. 4′ is nearly equal to $1.6\{3/(n^2+2)\}$ which was obtained as the values of $\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}$ in the case of those substances which have a cyclohexane-ring.

$[M]^{20}_{\mathrm{D}}$(W) of β-D-Isorhamnose.—In the footnote *29 of a previous paper[7], the author proposed an equation to presume an approximate value of the $[M]^{20}_{\mathrm{D}}$(W) of β-D-isorhamnose, now unknown, without using any ζ-coefficient. That is the {$[M]^{20}_{\mathrm{D}}$(W) of the An. Diff.[27] of D-mannose} minus the {$[M]^{20}_{\mathrm{D}}$(W) of the An. Diff. of D-rhamnose}=the {$[M]^{20}_{\mathrm{D}}$(W) of the An. Diff. of D-glucose} minus the {$[M]^{20}_{\mathrm{D}}$(W) of the An. Diff. of D-isorhamnose} (*29)

On the other hand, some $[M]^{20}_{\mathrm{D}}$(W) values had already been observed, as below[18]:

52.8 (α-D-mannose), −30.6 (β-D-mannose),

15.7 (α-D-rhamnose), −63.0 (β-D-rhamnose),

202.1 (α-D-glucose), 33.7 (β-D-glucose)

and 163.7 (α-D-isorhamnose).

Therefore, if the $[M]^{20}_{\mathrm{D}}$(W) of β-D-isorhamnose is y,

$$
\begin{aligned}
&\{52.8-(-30.6)\}-\{15.7-(-63.0)\}\\
&=\{202.1-33.7\}-\{163.7-y\}\\
&\therefore\quad y=0.0
\end{aligned}
$$

As the $[M]^{20}_{\mathrm{D}}$(W) of methyl β-D-isorhamnoside is −97.3[18], $[M]^{20}_{\mathrm{D}}$(W)-Diff.<methyl β-D-isorhamnoside − β-D-isorhamnose> = −97.3 −0.0 = −97.3.

As the absolute value of this $[M]^{20}_{\mathrm{D}}$(W)-Diff. is about equal to 100, it can be said that the $[M]^{20}_{\mathrm{D}}$(W) of β-D-isorhamnose, presumed above, 0.0, satisfies Hudson's methyl glycoside rule[20] and may be trusted.

Discussion

In the previous paper[7], the value of $\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}$ then obtained was first applied in the calculation of the $[\mu]^{20}_{\mathrm{Dobs}}$ of the An. Diff.[27] of D-rhamnose, and the calculated $[\mu]^{20}_{\mathrm{Dobs}}$ coincided with its corresponding observed value, $[M]^{20}_{\mathrm{D}}$(W). But in that paper, the $[M]^{20}_{\mathrm{D}}$(W) of β-D-isorhamnose was calculated as −46.6[28]. In that case,

$$
\begin{aligned}
&[M]^{20}_{\mathrm{D}}\text{(W)-Diff.}\langle\text{methyl }\beta\text{-D-isorhamnoside}\\
&\quad-\beta\text{-D-isorhamnose}\rangle=-97.3\\
&\quad-(-46.6)=-50.7
\end{aligned}
$$

The absolute value of this $[M]^{20}_{\mathrm{D}}$(W)-Diff., 50.7, deviates greatly from 100. (In other words, −46.6 of the $[M]^{20}_{\mathrm{D}}$(W) of β-D-isorhamnose does not satisfy Hudson's methyl glycoside rule.) Therefore, −46.6 seems to be unreliable as a presumed value of the $[M]^{20}_{\mathrm{D}}$(W) of β-D-isorhamnose. The principal reason for that mis-presumption in the previous paper[7] may be the inadequacy of using 120.3 as the $[M]^{20}_{\mathrm{D}}$(W) of α-D-isorhamnose; accordingly, the value of $\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}$ then obtained, 0.3096 $\{3/(n^2+2)\}$ (or $0.6671\{3/(n^2+2)\}$), may be untrustworthy. Concerning the accidental coincidence of $[\mu]^{20}_{\mathrm{Dobs}}$ with its corresponding $[M]^{20}_{\mathrm{D}}$(W) for the case of the An. Diff. of D-rhamnose in the previous paper[7], further examination will be necessary in the future.

Summary

By using a new molecular model and the new datum concerning the $[M]^{20}_{\mathrm{D}}$(W) of α-D-isorhamnose, the $\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}$ in the case of methyl pentose and the $[M]^{20}_{\mathrm{D}}$(W) of β-D-isorhamnose, now unknown, were re-calculated. The obtained value of $\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}$ was nearly equal to that in the case of substances which have a

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[25] Cf. Table II.

[26] Cf. footnote* 32 in Ref. 3.

[27] This is the difference in optical rotation between the α and β D-aldoses (or the β and L-aldoses).

[28] Without using $\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}$, 'the $[M]^{20}_{\mathrm{D}}$(W) of β-D-isorhamnose was calculated as −43.4 in footnote* 29 of Ref. 7.

cyclohexane-ring. The new value of the $[M]_D^{20}$(W) of β-D-isorhamnose satisfies Hudson's methyl glycoside rule.

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