Molecular Rotations of Glucides in Relation to their Structures. VI.
Optical Superposition in Methyl Pentoses.[*1]
Presumption of Two Unknown $[M]_D^0$(W)

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Recently, the author discussed $[M]_D^{20}$(W) of pentoses by using PM-method[*2], and concluded that the principle of optical superposition of Kirkwood's idea exists in this group[2)]. In this paper, the author tries to investigate whether this principle exists in methyl pentoses by using the same method.

Molecular Model and Data Used

The names of pentoses and methyl pentoses to which the calculations were applied, with groups in their molecules, and their corresponding molecular rotations are tabulated in Table I.

These pentoses and methyl pentoses except α-D- and β-D-isorhamnoses were concluded to have C 1 conformation by Reeves' experiments of cuprammonium-glycoside complexes[3)][*4]. It is presumed

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[*1] Only the glucides which have the six-membered (pyranose) ring in their molecules, are treated in this article, and so the suffix "-pyranose" of their names is omitted, here.

[*2] Ref.*17 in the previous paper 1.

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

2) S. Yamana, ibid. **30**, 916 (1957).

[*3] Hudson's data is 303.3° (ref. *12 in the previous paper 1).

a) F. J. Bates and Associates, "Polarimetry, Saccharimentry and the Sugars", United States Government Printing Office, Washington (1942), p. 762.

b) ibid. p. 750.

c) ibid. p. 726.

3) R. E. Reeves, *J. Am. Chem. Soc.*, **72**, 1499 (1950).

TABLE I

Name	Unit Groups	$[M]^{20}_{\mathrm{D}}$(W)	Lit.
α-D-xylose	[$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, Ring]	140.5°	(a)
β-L-arabinose	[$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, Ring]	286.1°*3	(a)
α-D-rhamnose	[$(OH)^{1\alpha}$, $(OH)^{2\beta}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_3)^{5\beta}$, Ring]	15.7°	(a)
β-D-rhamnose	[$(OH)^{1\beta}$, $(OH)^{2\beta}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_3)^{5\beta}$, Ring]	−63.0°	(b)
α-D-isorhamnose	[$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_3)^{5\beta}$, Ring]	120.3°	(c)
β-D-isorhamnose	[$(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_3)^{5\beta}$, Ring]		
α-D-fucose	[$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, $(CH_3)^{5\beta}$, Ring]	251.0°	(a)
β-D-fucose	[$(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, $(CH_3)^{5\beta}$, Ring]		

TABLE II

$[\mu]^{20}_{\mathrm{D\,obs}}$, CAUSED BY THE DYNAMICAL COUPLING EFFECT BETWEEN ANY TWO MEMBERS OF UNIT GROUPS (EXCEPT RING) IN MCDONALD AND BEEVERS' MOLECULAR MODEL (WHEN THE OPTICAL CENTER OF (OH) GROUP IS LOCATED AT THE CENTER OF MASS OF ^{r}C—(OH) BOND, AND THAT OF $(CH_3)^{5\beta}$ GROUP IS AT THE CENTER OF MASS OF C^5—$(CH_3)^{5\beta}$ BOND)

	$(CH_3)^{5\beta}$	4β	4α	3β	3α	2β	2α
1α	−2.0 (−4.2)	−0.1	−0.1	5.6	1.3	3.3	26.4
1β	0.4 (0.8)	−0.7	0.6	0.5	−5.8	29.5	−32.3
2α	−0.3 (−0.5)	3.7	1.3	31.0	−25.2		
2β	0.2 (0.4)	0.4	−5.1	−29.8	−3.1		
3α	1.5 (3.2)	2.3	26.8				
3β	−0.6 (−1.2)	28.8	−29.8				
4α	7.3 (15.7)						
4β	−7.6 (−16.4)						

Note: The values of $[\mu]^{20}_{\mathrm{D\,obs}}$ concerning $(CH_3)^{5\beta}$, calculated from Hudson's data of β-L-arabinose (ref. *3), are given in parentheses.

TABLE III

$[\mu]^{20}_{\mathrm{D\,obs}}$, CAUSED BY THE DYNAMICAL COUPLING EFFECT BETWEEN ANY TWO MEMBERS OF UNIT GROUPS (EXCEPT RING) IN MCDONALD AND BEEVERS' MOLECULAR MODEL (WHEN THE OPTICAL CENTER OF (OH) GROUP IS LOCATED AT O ATOM, AND THAT OF $(CH_3)^{5\beta}$ GROUP IS AT C ATOM)

	$(CH_3)^{5\beta}$	4β	4α	3β	3α	2β	2α
1α	−2.7 (−5.7)	−0.6	−0.1	7.6	1.9	2.9	25.7
1β	0.4 (0.8)	−0.9	0.6	0.4	−8.0	29.4	−32.8
2α	−0.3 (−0.6)	6.0	1.2	31.2	−24.1		
2β	0.2 (0.5)	0.7	−7.2	−30.4	−2.8		
3α	2.0 (4.4)	2.1	25.2				
3β	−0.5 (−1.1)	28.5	−28.4				
4α	7.3 (15.7)						
4β	−7.6 (−16.4)						

Note: The values of $[\mu]^{20}_{\mathrm{D\,obs}}$ concerning $(CH_3)^{5\beta}$, calculated from Hudson's data of β-L-arabinose (ref. *3), are given in parentheses.

that α-D- and β-D-isorhamnoses have also C 1 conformation because their corresponding aldohexoses(α-D- and β-D-glucoses) were determined to have C 1 conformation. McDonald and Beevers' molecular model, used in the previous papers 1 and 4, is used again in this article. The optical data for OH group and H atom, used in the previous paper 1, are also employed without any correction. It is supposed that CH_3 group has its optical axis of cylindrical symmetry directed along its bond to the atom with which it combines*5 and the optical center of $(CH_3)^{5\beta}$ group is located at the center of mass of C^5—$(CH_3)^{5\beta}$ bond*6. Values of mean polarizability α and of anisotropy ratio β of CH_3 group are 2.27×10^{-24}(cc)[d] and 0.35[e] respectively. The refractive indices of the aqueous solutions of pentoses and methyl pentoses under question are presumed to be nearly equal (1.34)*7.

Method Proposed

If the orientation of $(OH)^4$ in α-D-fucose changes from β to α, α-D-isorhamnose is obtained*8,*9. Therefore, it is appropriate to treat $[M]^{20}_D$(W)-change, caused by the orientation-change of $(OH)^4$*10 in these two sugars at first. The unit groups which can couple with $(OH)^4$ dynamically in α-D-fucose, are $(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(CH_3)^{5\beta}$ and Ring*8. Then, $\sum[\mu]^{20}_{D\text{obs}}$, caused by the dynamical coupling effect of $(OH)^4$ in α-D-fucose, is given by the following equation,

$$\begin{aligned}&(4\beta)\Lambda\{(1\alpha)+(2\alpha)+(3\beta)+(CH_3)^{5\beta}+R\}^{*11}\\&\quad=(4\beta)\Lambda(1\alpha)+(4\beta)\Lambda(2\alpha)+(4\beta)\Lambda(3\beta)\\&\quad+(4\beta)\Lambda(CH_3)^{5\beta}+(4\beta)\Lambda R\equiv E\end{aligned}$$

In the same way, the value in α-D-isorhamnose is as below,

$$\begin{aligned}&(4\alpha)\Lambda\{(1\alpha)+(2\alpha)+(3\beta)+(CH_3)^{5\beta}+R\}\\&\quad=(4\alpha)\Lambda(1\alpha)+(4\alpha)\Lambda(2\alpha)+(4\alpha)\Lambda(3\beta)\\&\quad+(4\alpha)\Lambda(CH_3)^{5\beta}+(4\alpha)\Lambda R\equiv F\end{aligned}$$

Accordingly, $[\mu]^{20}_{D\text{obs}}$-change, caused by the orientation-change of $(OH)^4$ in α-D-fucose from β to α (that is to say, $[\mu]^{20}_{D\text{obs}}$ of Yo. Diff. among α-D-isorhamnose and α-D-fucose), is $(F-E)$. The corresponding observed value is given by, $\{[M]^{20}_D$(W) of α-D-isorhamnose$\}$ minus $\{[M]^{20}_D$(W) of α-D-fucose$\}$.

This is $(120.3-251.0)^{*8}=-130.7$. As these two values should be equal to each other,

$$\begin{aligned}&-130.7=\text{Yo. Diff.}=(F-E)=\{(4\alpha)\Lambda(1\alpha)\\&\quad+(4\alpha)\Lambda(2\alpha)+(4\alpha)\Lambda(3\beta)+(4\alpha)\Lambda(CH_3)^{5\beta}\\&\quad+(4\alpha)\Lambda R\}-\{(4\beta)\Lambda(1\alpha)+(4\beta)\Lambda(2\alpha)\\&\quad+(4\beta)\Lambda(3\beta)+(4\beta)\Lambda(CH_3)^{5\beta}+(4\beta)\Lambda R\}\end{aligned}\qquad(1)^{*12}$$

By using the method similar to that mentioned above, the following equation is obtained from Yo. Diff. among α-D-xylose and β-L-arabinose.

$$\begin{aligned}&\{(4\alpha)-(4\beta)\}\Lambda\{(1\alpha)+(2\alpha)+(3\beta)+R\}\\&\quad=\{(4\alpha)\Lambda(1\alpha)+(4\alpha)\Lambda(2\alpha)+(4\alpha)\Lambda(3\beta)\\&\quad+(4\alpha)\Lambda R\}-\{(4\beta)\Lambda(1\alpha)+(4\beta)\Lambda(2\alpha)\end{aligned}$$

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*4 There are sixteen kinds of methyl pentose of D-series and the conformations of α-D- and β-D-rhamnoses and of α-D- and β-D-fucoses have been decided. But, the rest of them have not yet been determined.

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

*5 This is C^5-atom, in this case (ref. Fig. 1 in the previous paper 4).

*6 cf. *13 in the previous paper 1.

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

e) Values obtained by Cabannes and Granier; see Landolt-Börnstein, "Physikalisch-Chemische Tabellen", 5th Ed. Eg. II, p. 90.

*7 Ref. *8 in the previous paper 5.

5) S. Yamana, This Bulletin, **30**, 207 (1957).

*8 Ref. Table I in this article.

*9 Generally, the diastereomer at C^1-atom is called "anomer" and that at C^2-atom is called "epimer" (ref. 6). Now, the author proposes to use the names of "miner [miːmə]" and "yomer [jɔːmə]" to represent the diastereomers at C^3- and C^4-atoms, respectively. "mi-" and "yo-" mean 3 and 4 in Japanese, respectively. The reason for using the oriental language and not European in this case, is to avoid their confusion with the names of polymers ("trimer" etc.). Then, it can be said that α-D-fucose and α-D-isorhamnose are "yomer" to each other.

6) Tollens-Elsner, "Kurzes Handbuch der Kohlenhydrate", Johann Ambrosius Barth, Verlag Leipzig (1935), p. 16, 20.

*10 This is called "yomeric difference (or abbreviated to Yo. Diff.)" by the author (ref. *9 in this article cf. *3 in the previous paper 1).

*11 Ref. *10 in the previous paper 2.

*12 The right side of Eq. 1 can be rewritten as below,

$$\begin{aligned}&\{(4\alpha)\Lambda(1\alpha)+(4\alpha)\Lambda(2\alpha)+(4\alpha)\Lambda(3\beta)\\&\quad+(4\alpha)\Lambda(CH_3)^{5\beta}+(4\alpha)\Lambda R\}-\{(4\beta)\Lambda(1\alpha)\\&\quad+(4\beta)\Lambda(2\alpha)+(4\beta)\Lambda(3\beta)+(4\beta)\Lambda(CH_3)^{5\beta}\\&\quad+(4\beta)\Lambda R\}=(4\alpha)\Lambda\{(1\alpha)+(2\alpha)+(3\beta)\\&\quad+(CH_3)^{5\beta}+R\}-(4\beta)\Lambda\{(1\alpha)+(2\alpha)+(3\beta)\\&\quad+(CH_3)^{5\beta}+R\}=\{(4\alpha)-(4\beta)\}\Lambda\{(1\alpha)+(2\alpha)\\&\quad+(3\beta)+(CH_3)^{5\beta}+R\}\end{aligned}$$

($\because$ the notation Λ can be treated in the same way as the multiplication-symbol × of the algebra.) Then, it can be said that $\{(4\alpha)-(4\beta)\}\Lambda\{\cdots\cdots\}$ is a formula of $[\mu]^{20}_{D\text{obs}}$ of Yo. Diff.

$$+(4\beta)\text{⅄}(3\beta)+(4\beta)\text{⅄}\mathrm{R}\}=-145.6^{*13} \qquad (2)$$

From Eq. 1 minus 2,

$$(4\alpha)\text{⅄}(\mathrm{CH_3})^{5\beta}-(4\beta)\text{⅄}(\mathrm{CH_3})^{5\beta}=14.9$$

This equation can be rewritten as below[*14],

$$\{(4\alpha)\times(\mathrm{CH_3})^{5\beta}-(4\beta)\times(\mathrm{CH_3})^{5\beta}\}$$
$$\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}(n^2+2/3)=14.9 \qquad (3)^{*13}$$

On the other hand, the value of $(4\alpha)\times(\mathrm{CH_3})^{5\beta}$ and $(4\beta)\times(\mathrm{CH_3})^{5\beta}$ in Eq. 3 can be calculated by using the theoretical formulae[*15] as 23.58 and −24.54 respectively. By using these values in Eq. 3,

$$\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}=0.3096\ (3/n^2+2) \qquad (4)^{*13}$$

But, ζ_{OH} was already calculated and its value is 1.5779 $(3/n^2+2)^{1/2}$[*16]. Then

$$\zeta_{\mathrm{CH_3}}=0.3096(3/n^2+2)/1.5779(3/n^2+2)^{1/2}$$
$$=0.1962(3/n^2+2)^{1/2} \qquad (5)^{*17,*18}$$

Thus, ζ-coefficient of $\mathrm{CH_3}$ group which is indispensable in calculation of $[\mu]^{20}_{\mathrm{Dobs}}$ concerning $\mathrm{CH_3}$ group, can be obtained quasi-empirically. Next, an attempt has been made to examine whether this value of $\zeta_{\mathrm{CH_3}}$ is suitable or not, as follows; at first, by combining these values of $\zeta_{\mathrm{CH_3}}$ and ζ_{OH} with Table II of the previous paper 1, the tables of $[\mu]^{20}_{\mathrm{Dobs}}$ in the methyl pentose-molecule can be made[*19]. They are Tables II and III.

The unit groups which can couple with $(\mathrm{OH})^1$ dynamically in D-rhamnose, are $(\mathrm{OH})^{2\beta}$, $(\mathrm{OH})^{3\beta}$, $(\mathrm{OH})^{4\alpha}$, $(\mathrm{CH_3})^{5\beta}$ and Ring[*8]. Then, $\sum[\mu]^{20}_{\mathrm{Dobs}}$-change, caused by the orientation-change of $(\mathrm{OH})^1$ in this sugar from β to α (that is to say $[\mu]^{20}_{\mathrm{Dobs}}$ of An. Diff.[*20] of D-rhamnose), is represented as below,

$$\{(1\alpha)-(1\beta)\}\text{⅄}\{(2\beta)+(3\beta)+(4\alpha)+(\mathrm{CH_3})^{5\beta}$$
$$+\mathrm{R}\}^{*21}=\{(1\alpha)\text{⅄}(2\beta)+(1\alpha)\text{⅄}(3\beta)$$
$$+(1\alpha)\text{⅄}(4\alpha)+(1\alpha)\text{⅄}(\mathrm{CH_3})^{5\beta}+(1\alpha)\text{⅄}\mathrm{R}\}$$
$$-\{(1\beta)\text{⅄}(2\beta)+(1\beta)\text{⅄}(3\beta)+(1\beta)\text{⅄}(4\alpha)$$
$$+(1\beta)\text{⅄}(\mathrm{CH_3})^{5\beta}+(1\beta)\text{⅄}\mathrm{R}\}=\{3.3+5.6$$
$$-0.1-2.0+(1\alpha)\text{⅄}\mathrm{R}\}-\{29.5+0.5+0.6$$
$$+0.4+(1\beta)\text{⅄}\mathrm{R}\}^{*22}=-24.2+(1\alpha)\text{⅄}\mathrm{R}$$
$$-(1\beta)\text{⅄}\mathrm{R}=82.0^{*23,*24}$$

The corresponding observed value is given by, {$[M]^{20}_{\mathrm{D}}$(W) of α-D-rhamnose} minus {$[M]^{20}_{\mathrm{D}}$(W) of β-D-rhamnose}. This is, 15.7−(−63.0)=78.7.

This observed value is almost consistent with the above calculated value, 82.0. This fact indicates that there exists the principle of optical superposition of Kirkwood's idea in methyl pentoses, and also that the values in Table II are all suitable and accordingly the value of $\zeta_{\mathrm{CH_3}}$ in Eq. 5 is almost satisfactory. Next, the unknown $[M]^{20}_{\mathrm{D}}$(W) of β-D-fucose is presumed by using the method, similar to that mentioned above.

$[\mu]^{20}_{\mathrm{Dobs}}$ of An. Diff. of D-fucose is given by the following equation.

$$\{(1\alpha)-(1\beta)\}\text{⅄}\{(2\alpha)+(3\beta)+(4\beta)+(\mathrm{CH_3})^{5\beta}$$
$$+\mathrm{R}\}^{*21}=\{(1\alpha)\text{⅄}(2\alpha)+(1\alpha)\text{⅄}(3\beta)$$
$$+(1\alpha)\text{⅄}(4\beta)+(1\alpha)\text{⅄}(\mathrm{CH_3})^{5\beta}+(1\alpha)\text{⅄}\mathrm{R}\}$$
$$-\{(1\beta)\text{⅄}(2\alpha)+(1\beta)\text{⅄}(3\beta)+(1\beta)\text{⅄}(4\beta)$$
$$+(1\beta)\text{⅄}(\mathrm{CH_3})^{5\beta}+(1\beta)\text{⅄}\mathrm{R}\}=\{26.4+5.6$$
$$-0.1-2.0+(1\alpha)\text{⅄}\mathrm{R}\}-\{-32.3+0.5-0.7$$
$$+0.4+(1\beta)\text{⅄}\mathrm{R}\}=62.0+(1\alpha)\text{⅄}\mathrm{R}$$
$$-(1\beta)\text{⅄}\mathrm{R}=168.2^{*23}$$

The corresponding observed value is obtained by, {$[M]^{20}_{\mathrm{D}}$(W) of α-D-fucose} minus {$[M]^{20}_{\mathrm{D}}$(W) of β-D-fucose}. Then, if $[M]^{20}_{\mathrm{D}}$(W) of β-D-fucose, now unknown, is x,

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[*13] cf. *17 in this article.

[*14] Ref. Eq. 32 in *32 in the previous paper 1.

[*15] Ref. "Theoretical Formulae" in the previous paper 7.

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

[*16] Eq. 12 in the previous paper 1.

[*17] By using Hudson's data of β-L-arabinose (ref. *3),

$$\{(4\alpha)-(4\beta)\}\text{⅄}\{(1\alpha)+(2\alpha)+(3\beta)+\mathrm{R}\}=-162.8 \qquad (2)^*$$
$$\{(4\alpha)\mathrm{X}(\mathrm{CH_3})^{5\beta}-(4\beta)\mathrm{X}(\mathrm{CH_3})^{5\beta}\}\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}(n^2+2/3)=32.1 \qquad (3)^*$$
$$\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH3}}=0.6671\ (3/n^2+2) \qquad (4)^*$$
$$\zeta_{\mathrm{CH_3}}=0.4228\ (3/n^2+2)^{1/2} \qquad (5)^*$$

[*18] It is apparent here that $\zeta_{\mathrm{OH}}>\zeta_{\mathrm{CH_2OH}}>\zeta_{\mathrm{CH_3}}$ (ref. Eq. 20 in the previous paper 1). This fact coincides with the assumption that the magnitude of ζ-coefficient depends mostly upon the degree of change of $\alpha_i\beta_i$ of an unit group by solvation (ref. *19 in the previous paper 1). In other words, the magnitude of ζ indicates roughly the degree of solvation of an unit group. Moreover it is interesting that, when Hudson's data of L-arabinoses are used, $\zeta_{\mathrm{OH}}\zeta_{\mathrm{CH_3}}$ (this is $0.6671\ (3/n^2+2)$) is nearly equal to $\zeta^2_{\mathrm{CH_2OH}}$ (this is $0.6276\ (3/n^2+2)$). (ref. *17 in this article and *43 in the previous paper 1).

[*19] Concerning the procedure of making the table of $[\mu]^{20}_{\mathrm{Dobs}}$, refer to Eq. 3 in the previous paper 1. The values of ζ_{OH} and $\zeta_{\mathrm{CH_3}}$ which are used for Table. III, are given in *44 in the previous paper 1 and *31 in this article.

[*20] Ref. *3 in the previous paper 1.

[*21] It can be said that $\{(1\alpha)-(1\beta)\}\text{⅄}\{\cdots\cdots\}$ is a formula of $[\mu]^{20}_{\mathrm{Dobs}}$ of An. Diff. (cf. *12).

[*22] The values in Table II are used.

[*23] Eq. 13 in the previous paper 1 is used here.

[*24] cf. *30.

the observed value of An. Diff. of D-fucose is $(251.0-x)$. This value should be equal to the above calculated $[\mu]^{20}_{\mathrm{Dobs}}$. Then $251.0-x=168.2$ hence $x=82.8$*24

By using the same method, $[M]^{20}_{\mathrm{D}}$(W) of β-D-isorhamnose, now unknown, is calculated as -46.6*24.

Discussion on the Results

In the previous paper[4], the author presumed the internal conformation of C^6—O bond in D-mannose molecule in aqueous solution by a new method, devised by the author, and the obtained result satisfied the conditions which were required from the viewpoint of the atomic distances in the molecule of D-mannose. By the calculation in reversing the order of this method, it becomes possible to find another method*25 of presuming the unknown $[M]^{20}_{\mathrm{D}}$(W), as below; according to the previous paper 1, the internal conformation of C^6—O bond in D-galactose in aqueous solution seems to be mostly of *gauche* II type. Then, the unit groups which can couple with $(OH)^1$ dynamically in this sugar are $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, $(CH_2OH)^{5\beta \cdot g\mathrm{II}}$ and Ring*26. Therefore, $[\mu]^{20}_{\mathrm{Dobs}}$ of An. Diff. of D-galactose is given by,

$$\begin{aligned}&\{(1\alpha)-(1\beta)\}\lambda\{(2\alpha)+(3\beta)+(4\beta)\\&\quad+(5\beta.g\mathrm{II})+\mathrm{R}\}^{*21}=\{(1\alpha)-(1\beta)\}\lambda\{(2\alpha)\\&\quad+(3\beta)+(4\beta)+\mathrm{R}\}+\{(1\alpha)\\&\quad-(1\beta)\}\lambda(5\beta.g\mathrm{II})\equiv G\end{aligned}$$

Whereas, $[\mu]^{20}_{\mathrm{Dobs}}$ of An. Diff. of D-fucose has already been given by,

$$\begin{aligned}&\{(1\alpha)-(1\beta)\}\lambda\{(2\alpha)+(3\beta)+(4\beta)\\&\quad+(CH_3)^{5\beta}+\mathrm{R}\}=\{(1\alpha)-(1\beta)\}\lambda\{(2\alpha)\\&\quad+(3\beta)+(4\beta)+\mathrm{R}\}+\{(1\alpha)\\&\quad-(1\beta)\}\lambda(CH_3)^{5\beta}\equiv H\end{aligned}$$

Then, the difference between these two $[\mu]^{20}_{\mathrm{Dobs}}$, ($G$ and H), is as follows;

$$\begin{aligned}G-H&=\{(1\alpha)-(1\beta)\}\lambda(5\beta.g\mathrm{II})-\{(1\alpha)\\&\quad-(1\beta)\}\lambda(CH_3)^{5\beta}=\{(1\alpha)\lambda(5\beta.g\mathrm{II})\\&\quad-(1\beta)\lambda(5\beta.g\mathrm{II})\}-\{(1\alpha)\lambda(CH_3)^{5\beta}\\&\quad-(1\beta)\lambda(CH_3)^{5\beta}\}\simeq(1\alpha)\lambda(OH)^{6 \cdot g\mathrm{II}*27}\\&\quad-(1\beta)\lambda(OH)^{6 \cdot g\mathrm{II}}=7.3^{*28}\end{aligned}$$

The corresponding observed value is given by, $(271.5-95.1)^{*26}-(251.0-x)^{*28}=x-74.6$.

As these two values should be equal to each other,

$$7.3=x-74.6 \quad \therefore \quad x=81.9$$

This is the presumed value of $[M]^{20}_{\mathrm{D}}$(W) of β-D-fucose, by the new method without using ζ_{CH_3}. By using the same method*29, $[M]^{20}_{\mathrm{D}}$(W) of β-D-isorhamnose can be calculated to be -43.4*24. These presumed values are not exactly but approximately consistent with those, calculated by using ζ_{CH_3} in "Method Proposed" of this article, (82.8 and -46.6), respectively.

Comparing these calculated values by two different methods with each other,

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*25 In this method, ζ_{CH_3} is needless.

*26 Ref. Table I in the previous paper 1.

*27 $(OH)^{6 \cdot g\mathrm{II}}$ means OH group which combines with C^6-atom in *gauche* II conformation (i.e. OH group in $(CH_2OH)^{5\beta \cdot g\mathrm{II}}$), and so on.

*28 Concerning the process of this simplification, refer to "Method Proposed" in the previous paper 4. And here, the optical center of OH group is located at the center of mass of C—(OH) bond.

*29 $\{[\mu]^{20}_{\mathrm{Dobs}}$ of An. Diff. of D-mannose$\}$ minus $\{[\mu]^{20}_{\mathrm{Dobs}}$ of An. Diff. of D-rhamnose$\}$ $\simeq(1\alpha)\lambda(OH)^{6 \cdot \mathrm{ma}}-(1\beta)\lambda(OH)^{6 \cdot \mathrm{ma}*28}$; $\{[\mu]^{20}_{\mathrm{Dobs}}$ of An. Diff. of D-glucose$\}$ minus $\{[\mu]^{20}_{\mathrm{Dobs}}$ of An. Diff. of D-isorhamnose$\}\simeq(1\alpha)\lambda(OH)^{6 \cdot \mathrm{ma}}-(1\beta)\lambda(OH)^{6 \cdot \mathrm{ma}*28}$ $\therefore$ $\{[\mu]^{20}_{\mathrm{Dobs}}$ of An. Diff. of D-mannose$\}$ minus $\{[\mu]^{20}_{\mathrm{Dobs}}$ of An. Diff. of D-rhamnose$\}=\{[\mu]^{20}_{\mathrm{Dobs}}$ of An. Diff. of D-glucose$\}$ minus $\{[\mu]^{20}_{\mathrm{Dobs}}$ of An. Diff. of D-isorhamnose$\}$. This equation can be rewritten by using the corresponding observed values, as below; $\{[M]^{20}_{\mathrm{D}}$(W) of An. Diff. of D-mannose$\}$ minus $\{[M]^{20}_{\mathrm{D}}$(W) of An. Diff. of D-rhamnose$\}=\{[M]^{20}_{\mathrm{D}}$(W) of An. Diff. of D-glucose$\}$ minus $\{[M]^{20}_{\mathrm{D}}$(W) of An. Diff. of D-isorhamnose$\}$; $\{52.8-(-30.6)\}-\{15.7-(-63.0)\}=\{202.1-33.7\}-\{120.3-x\}^{*8,*24,*26}$ or $x=-43.4$.

*30 When using Hudson's data of L-arabinoses (ref. *17 in this article), $[\mu]^{20}_{\mathrm{Dobs}}$ of An. Diff. of D-rhamnose is 78.6 (Eq. 13* in *35 of the previous paper 1 is used here). (This is just equal to its corresponding observed value, 78.7). The presumed values of $[M]^{20}_{\mathrm{D}}$(W), in this case, are as below; β-D-fucose (86.2) (This is somewhat greater than that, calculated in "Method Proposed" and "Discussion on the Results" in this article.); β-D-isorhamnose (-43.2).

*31 For comparison, the calculated values by supposing that the optical centers of OH and CH_3 groups are located at their respective O and C atoms, are given here (cf. *44 in the previous paper 1),

	Isbell and Pigman's data of L-arabinoses	Hudson's data of L-arabinoses
ζ_{CH_3}	0.2880 $(3/n^2+2)^{1/2}$	0.6206 $(3/n^2+2)^{1/2}$
$[M]^{20}_{\mathrm{D}}$(W) of β-D-fucose	83.6	87.8
$[M]^{20}_{\mathrm{D}}$(W) of β-D-isorhamnose	-46.1	-41.9

$[M]_D^{20}(W)$ of β-D-fucose, and β-D-isorhamnose are presumed to be about 81.9~82.8 and $-46.6\sim-43.4$ respectively*31.

Summary

It was concluded by PM-method that the principle of optical superposition of Kirkwood's idea exists in methyl pentoses, and two $[M]_D^{20}(W)$, formerly unknown, were presumed.

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