NOTES

Molecular Rotations of Glucides in Relation to their Structures. XI[1]. *β-D-Allomethylose*

By Shukichi YAMANA

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Micheel observed the mutarotation of β-D-allomethylose and obtained the following data[2]: $[M]^{18}_{D}(W)=-19.7°$ (30 sec. after the time of resolution) → $-1.6°$ (85 min. after the time of resolution)

Therefore, it can be expected that the initial $[M]^{20}_{D}(W)$ of β-D-allomethylose is more laevorotatory than $-19.7°$. However, by using his own method of calculation, Whiffen obtained 2° as the $[M]_D(W)$ of β-D-allomethylose[3]. It is apparent that Whiffen's calculated value is incompatible with the values observed by Micheel. The present author will try to apply the PM-method in this case. The names of the carbohydrates to which the calculations are applied, with the unit groups in their molecules, are given in Table I.

TABLE I

Name	Unit group	$[M]_D(W)$	Ref.
β-D-Allo-methylose	$[(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\alpha}$, $(OH)^{4\alpha}$, $(CH_3)^{5\beta}$, Ring]		
β-D-Gulo-methylose	$[(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\alpha}$, $(OH)^{4\beta}$, $(CH_3)^{5\beta}$, Ring]	$-69.4°$[4]	5

Referring to Table I, if the orientation of $(OH)^4$ changes from β to α in β-D-gulomethylose, β-D-allomethylose is obtained. By using the PM-method, $\sum[\mu]^{20}_{D\,obs}$, caused by this orientation change of $(OH)^4$ (that is to say, $[\mu]^{20}_{D\,obs}$ of Yo. Diff. <β-D-allomethylose − β-D-gulomethylose>[6]), is calculated as below:

$$\{(4\alpha)-(4\beta)\}\,\text{⅄}\,\{(1\beta)+(2\alpha)+(3\alpha)+(CH_3)^{5\beta}+R\}^{7)}=(4\alpha)\,\text{⅄}\,(1\beta)+(4\alpha)\,\text{⅄}\,(2\alpha)+(4\alpha)\,\text{⅄}\,(3\alpha)+(4\alpha)\,\text{⅄}\,(CH_3)^{5\beta}+(4\alpha)\,\text{⅄}\,R-\{(4\beta)\,\text{⅄}\,(1\beta)+(4\beta)\,\text{⅄}\,(2\alpha)+(4\beta)\,\text{⅄}\,(3\alpha)+(4\beta)\,\text{⅄}\,(CH_3)^{5\beta}+(4\beta)\,\text{⅄}\,R\}=0.0-0.5+45.4+37.9+(4\alpha)\,\text{⅄}\,R-\{-0.6+7.1+0.6-37.6+(4\beta)\,\text{⅄}\,R\}^{8)}=113.3+(4\alpha)\,\text{⅄}\,R-(4\beta)\,\text{⅄}\,R=43.8^{9)}$$

The corresponding observed value in given by: {$[M]^{20}_{D}(W)$ of β-D-allomethylose} minus {$[M]^{20}_{D}(W)$ of β-D-gulomethylose}. Therefore, if the $[M]^{20}_{D}(W)$ of β-D-allomethylose is x, the observed value of Yo. Diff. <β-D-allomethylose − β-D-gulomethylose> is $(x-(-69.4))$. This observed value should be equal to the above calculated $[\mu]^{20}_{D\,obs}$.

Therefore,

$$x-(-69.4)\equiv 43.8$$

$$\therefore\quad x=-25.6$$

This expected value of $[M]^{20}_{D}(W)$ of β-D-allomethylose, -25.6, is compatible with Micheel's data already mentioned. This fact may indicate the suitability of the PM-method in this case.

Department of Chemistry
Kyoto Gakugei University
Fushimi-ku, Kyoto

1) Part X: S. Yamana, This Bulletin, 35, 1950 (1962).
2) F. Micheel, *Ber.*, 63, 347 (1930).
3) D. H. Whiffen, *Chem. & Ind.*, 1956, 964.
4) This is the observed value at 29°C.
5) P. A. Levene and J. Compton, *J. Biol. Chem.*, 111, 335 (1935).
6) Cf. Ref. 17 in a previous paper, S. Yamana, This Bulletin, 35, 1269 (1962).
7) Cf. Ref. *12 in a previous paper, S. Yamana, This Bulletin, 31, 564 (1958).
8) Table II of the preceding paper[1] was used.
9) Equation 15 of the preceding paper[1] was used.