

## Communications to the Editor

[Chem. Pharm. Bull.]  
[11 (8) 1081 ~ 1082]

UDC 547.458.2

**A Novel Synthesis of Trehalose-Type Thiodisaccharides. An Anomalous Reaction of Potassium Methyl- and Benzyl-xanthates with Halogeno-O-acetyl Sugars in Acetone**

Up to the present time, several sugar xanthates (acylated glycosyl xanthates) have been studied<sup>1)</sup> as an important intermediate for the preparation of thiosugars.<sup>2)</sup> Recently the increasing interests are directed to the sugar xanthates from the view point of optical rotatory dispersion.<sup>3)</sup>

Usually the sugar xanthates are prepared by the condensation of acetohalogeno-sugars with potassium xanthates in proper solvents such as ethanol or acetone.

In this communication the authors wish to describe that potassium methyl- and benzylxanthates reacted abnormally with halogeno-O-acetylsugars in acetone to give acylated diglycosyl sulfides (trehalose-type thiodisaccharides) in good yield different from other potassium xanthates.

The condensation of 2,3,4,6-tetra-O-acetyl- $\alpha$ -D-glucopyranosyl bromide (I) with potassium ethyl-, propyl-, butyl-, and cyclohexyl-xanthates in hot acetone gave the corresponding sugar xanthates in good yield, respectively. That is, 2,3,4,6-tetra-O-acetyl- $\beta$ -D-glucopyranosyl ethylxanthate (II), m.p. 75~76°,  $[\alpha]_D^{18} +30.0$  (c=1.2, CHCl<sub>3</sub>),<sup>4)</sup> *Anal.* Calcd. for C<sub>17</sub>H<sub>24</sub>O<sub>10</sub>S<sub>2</sub>: C, 45.09; H, 5.35. Found: C, 45.26; H, 5.32. 2,3,4,6-Tetra-O-acetyl- $\beta$ -D-glucopyranosyl propylxanthate (III), m.p. 90~91°,  $[\alpha]_D^{18} +31.0$  (c=2.0, CHCl<sub>3</sub>), *Anal.* Calcd. for C<sub>18</sub>H<sub>26</sub>O<sub>10</sub>S<sub>2</sub>: C, 46.34; H, 5.62. Found: C, 46.17; H, 5.63. 2,3,4,6-Tetra-O-acetyl- $\beta$ -D-glucopyranosyl butyl xanthate (IV), m.p. 114~115°,  $[\alpha]_D^{18} +28.8$  (c=1.0, CHCl<sub>3</sub>), *Anal.* Calcd. for C<sub>19</sub>H<sub>28</sub>O<sub>10</sub>S<sub>2</sub>: C, 48.32; H, 5.87. Found: C, 48.39; H, 5.59. 2,3,4,6-Tetra-O-acetyl- $\beta$ -D-glucopyranosyl cyclohexyl xanthate (V), m.p. 111~112°,  $[\alpha]_D^{18} +97.0$  (c=2.0, CHCl<sub>3</sub>), *Anal.* Calcd. for C<sub>21</sub>H<sub>30</sub>O<sub>10</sub>S<sub>2</sub>: C, 49.19; H, 5.97. Found: C, 49.43; H, 5.76.

On the other hand, the condensation of potassium methyl- and benzyl-xanthates with (I) under the same condition did not afford sugar xanthates but bis(2,2',3,3',4,4',6,6'-octa-O-acetyl- $\beta,\beta'$ -D-glucopyranosyl)sulfide (VI),<sup>5)</sup> m.p. 175~176°,  $[\alpha]_D^{18} -38.0$  (c=1.0, CHCl<sub>3</sub>), *Anal.* Calcd. for C<sub>28</sub>H<sub>38</sub>O<sub>18</sub>S: C, 48.41; H, 5.51. Found: C, 48.24; H, 5.56., was obtained in 93% yield.

Similarly, 2,3,4,6-tetra-O-acetyl- $\alpha$ -D-galactopyranosyl bromide (VII) reacted with potassium methyl and benzyl-xanthates under the same condition to give bis(2,2',3,3',4,4',6,6'-octa-O-acetyl- $\beta,\beta'$ -D-galactopyranosyl)sulfide (VIII), m.p. 201~202°,  $[\alpha]_D^{18} -21.0$  (c=1.0, CHCl<sub>3</sub>), *Anal.* Calcd. for C<sub>28</sub>H<sub>38</sub>O<sub>18</sub>S: C, 48.41; H, 5.51. Found: C, 48.22; H, 5.63., in 82% yield. With potassium ethylxanthate, VII reacted normally to give 2,3,4,6-tetra-O-acetyl- $\beta$ -D-galactopyranosyl ethylxanthate (IX), m.p. 81~82°,  $[\alpha]_D^{18} +92.0$  (c=1.0, CHCl<sub>3</sub>), *Anal.* Calcd. for C<sub>17</sub>H<sub>24</sub>O<sub>10</sub>S<sub>2</sub>: C, 45.09; H, 5.35. Found: C, 45.12; H, 5.24.

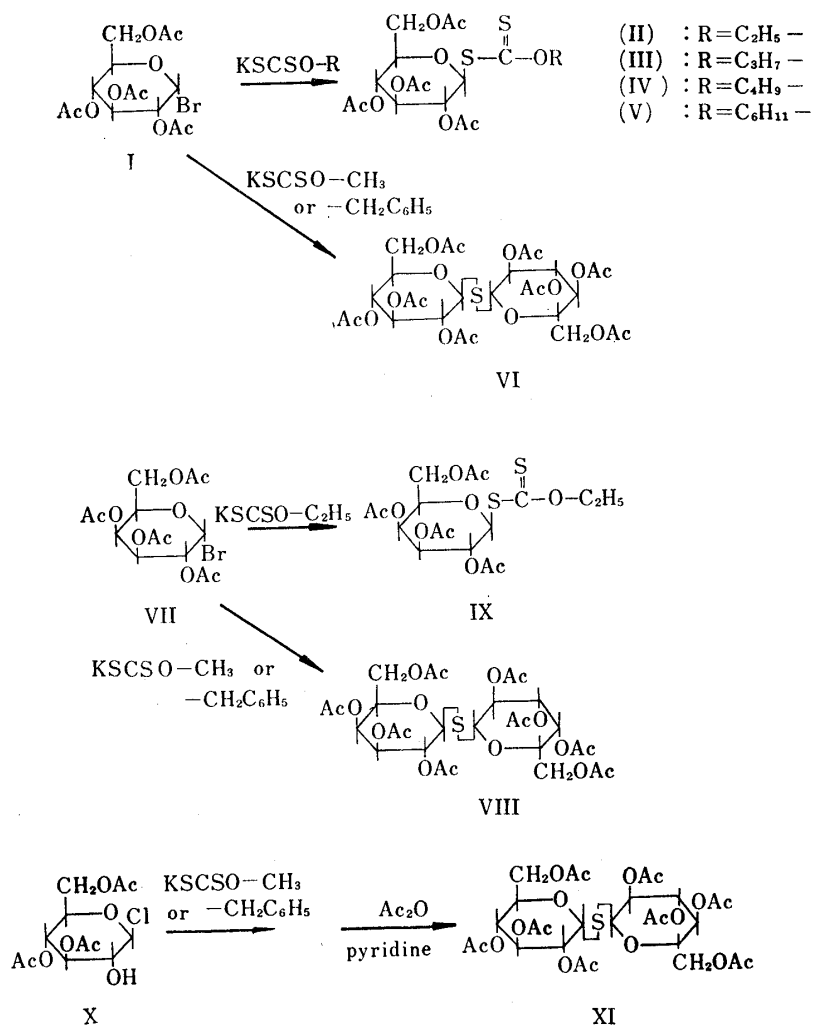
1) M. Akagi, S. Tejima, M. Haga: This Bulletin, 9, 360 (1961).

2) A. L. Raymond: "Advances in Carbohydrate Chemistry," 1, 129 (1945) Academic Press Inc., New York, N. Y.

3) C. Djerassi: "Optical Rotatory Dispersion, Application to Organic Chemistry," Chap. 14 (1960) McGraw-Hill Inc., New York, N. Y.

4) W. Schneider, R. Gille, K. Eisefeld: Ber., 61, 1244 (1928).

5) W. Schneider, F. Wrede: *Ibid.*, 50, 793 (1917).



The condensation of 3,4,6-tri-O-acetyl- $\beta$ -D-glucopyranosyl chloride (X)<sup>6)</sup> with potassium methyl- and benzyl-xanthates in hot acetone and successive acetylation gave bis-(2,2',3,3',4,4',6,6'-octa-O-acetyl- $\alpha,\alpha'$ -D-glucopyranosyl)sulfide (XI), m.p. 191~192°,  $[\alpha]_D^{18} +259.2$  ( $c=2.0$ , CHCl<sub>3</sub>), *Anal.* Calcd. for C<sub>28</sub>H<sub>38</sub>O<sub>16</sub>S: C, 48.41; H, 5.51. Found: C, 48.49; H 5.48., in good yield.

Faculty of Pharmaceutical Sciences,  
School of Medicine, Hokkaido University  
Nishi-5-chome, Kita-12-jo, Sapporo.

Masuo Akagi (赤木満洲雄)  
Setsuzo Tejima (手島節三)  
Masanobu Haga (羽賀正信)  
Masakatsu Sakata (阪田正勝)

Received May 16, 1963

6) P. Brigl: *Z. physiol. Chem.*, **116**, 1 (1921).