Chem. Pharm. Bull. 15(10)1478~1484(1967)

UDC 547.455.07

188. Susumu Ishiguro and Setsuzo Tejima*1 : Thiosugars. XII.*2 Studies on Unsaturated Sugars derived from Glucosyl N,N-Dimethyldithiocarbamate.

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2-O-Mesyl-3,4,6-tri-O-acetyl-β-D-glucopyranosyl N,N-dialkyldithiocarbamate (VI or VII, VI : methyl, VII : ethyl) was prepared starting from the corresponding bromide by treatment with sodium N,N-dialkyldithiocarbamate (III or IV, III : methyl, IV : ethyl). Reflux of a mixture of VI or VII and potassium thiolacetate in acetone-ethanol afforded 2-S-acetyl-2-thio-3,4,6-tri-O-acetyl-β-D-mannopyranosyl N,N-dialkyldithiocarbamate (VIII or IX, VIII : methyl, IX : ethyl) in 30 to 40% yield. The structure was confirmed by UV, IR, NMR and the formation of 3,4,6-tri-O-acetyl-D-hydroglucal.

When a mixture of VI and potassium acetate in acetone-ethanol was refluxed for one hour, crystals (XI), m.p. 104°, $[\alpha]_D^{20}$ +185.8° were obtained in 93% yield. The product was also obtainable by acetylation of 1,2-dideoxy-1,2-(N,N-dimethylammonium)-dithiocarbonyl-β-D-mannopyranose methanesulfonate (XIII) which was prerared starting from VI, by deacetylation and successive evaporation of an aqueous solution of the deacetylated product.

The structure of XI was assigned to be 2-N,N-dimethyldithiocarbamoyl-2-deoxy-3,4,6-tri-O-acetyl-D-arabino-hexopyranose-1-ene, and the reaction mechanism of the formation was discussed.

Deacetylation of XI afforded 2-N,N-dimethyldithiocarbamoyl-2-deoxy-D-arabino-hexopyranose-1-ene (XIV), m.p. 157°, $[\alpha]_D^{20}$ +131.9° which is a new type of unsaturated sugars.

The nuclear magnetic resonance spectroscopy helped greatly in the determination of the structures of compounds in this series.

(Received November 12, 1966)

As one of us has pointed out in the previous paper of this series,[1] the secondary mesyl at C_2 in thiosugars shows high reactivity toward potassium thiolacetate to form the substitution product having vicinal thioacetyls. Since a secondary sulfonyl in carbohydrates generally resists toward nucleophilic substitution, as it has been known by the Oldham and Rutherford rule, our finding appears to provide an interesting and stimulating challenge which may prove to be of value in a variety of thiosugar synthesis.

The progressive studies in our laboratory which aimed at the epimerization of D-glucose derivative to that of D-mannose were unsuccessful, but led to the formation of cyclic dithiocarbonate (II).[2] It seems reasonable to assume that in an initial stage of the reaction, the cyclic intermediate (I) may be formed by neighbouring group participation of the thioketone at C_1 to eject the C_2-mesylate.

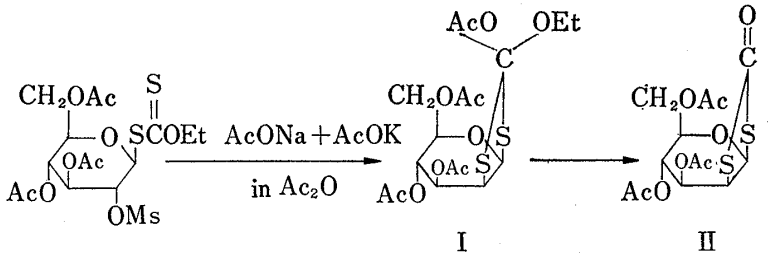


Chart 1.

*1 Kita-15-jo, Nishi-7-chome, Sapporo (石黒 駿, 手島節三).
*2 Part XI. S. Tejima, S. Ishiguro : This Bulletin, **15**, 1367 (1967).
1) H. Nakamura, S. Tejima, M. Akagi : *Ibid.*, **14**, 648 (1966).
2) K. Araki, S. Tejima : *Ibid.*, **14**, 1303 (1966).

On the one hand, there has been considerable interest in recent years in the studies of neighbouring group reactions which have been of importance utility in achieving an inversion of sugar hydroxyl[3] or synthesis of *cis*-substituted sugars.[4]

From these standpoints we designed further extension of the nucleophilic substitution of the secondary mesyl in thiosugars. In this paper the authors used glucosyl N,N-dialkyldithiocarbamates ($\left(\begin{matrix}R\\R\end{matrix}\!>\!N\text{-}\overset{\overset{S}{\|}}{C}\text{-}S\text{-}R'\right.$, R=methyl or ethyl, R′=D-glucopyranosyl$\left.\right)$ which also contained a thioketone similar to glucosyl xanthates, and the preparation of which had already been reported in the preceding paper of this series. The present paper dealt with the formation of unsaturated sugars from mesylated glucosyl N,N-dimethyldithiocarbamate.

Reaction of sodium N,N-dialkyldithiocarbamate (Ⅲ or Ⅳ, Ⅲ: methyl, Ⅳ: ethyl) with 2-O-mesyl-3,4,6-tri-O-acetyl-α-D-glucopyranosyl bromide (Ⅴ)[5] in dry acetone afforded crystalline 2-O-mesyl-3,4,6-tri-O-acetyl-β-D-glucopyranosyl N,N-dialkyldithiocarbamate (Ⅵ or Ⅶ, Ⅵ: methyl, Ⅶ: ethyl). The structure was characterized by the satisfactory elementary analyses, and the infrared spectra which showed clearly the presence of dithiocarbamate[6] (λ_{max}^{Nujol} μ: *ca.* 6.65) and mesyl (*ca.* 7.50 and 8.43). Its ethanolic solution exhibited the absorption maxima at 239 and 278, or 242 and 281 mμ, respectively, which were characteristic of glycosyl dithiocarbamates.*[2]

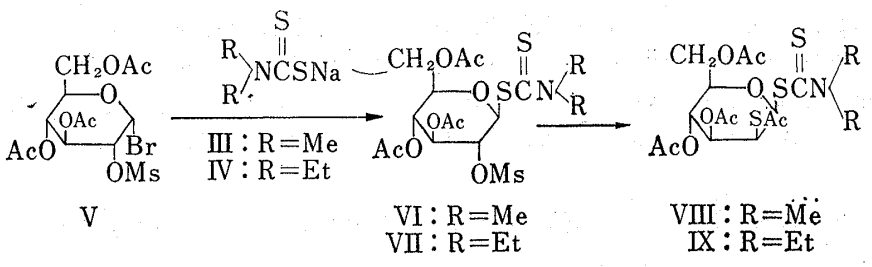
The nuclear magnetic resonance spectroscopy (NMR) helped greatly in the determination of the structure of compounds in this series.

The NMR of Ⅵ at 60 Mc. showed a doublet at τ4.08 (anomeric proton) with the coupling constant ($J_{1,2}$=11.0 c.p.s.). This large value was in agreement with an axial-axial oriented protons at C_1 and C_2 which clearly confirmed the β-configuration. However, in Ⅶ the region of the anomeric proton was masked by a multiplet owing to the presence of the methylen in N,N-diethyl at C_1, thus we could not analyse. In any case, the small dextrorotatory value of Ⅵ or Ⅶ may be consistent with the β-configuration.

Reflux of Ⅵ or Ⅶ with potassium thiolacetate in acetone-ethanol for thirty minutes afforded crystals (Ⅷ or Ⅸ) in 30 to 40% yield. The elementary analyses were in good agreement with that of $C_{17}H_{25}O_8NS_3$ or $C_{19}H_{29}O_8NS_3$. The ethanolic solution exhibited absorption maxima at 242 and 278 mμ (dithiocarbamate), and the infrared spectra showed no absorption at *ca.* 7.50 and 8.43 (mesyl), but showed the bands assignable to thioacetyl (*ca.* 5.85) and dithiocarbamate (*ca.* 6.65). Reductive desulfurization of Ⅷ or Ⅸ gave a similar compound, 3,4,6-tri-O-acetyl-D-hydroglucal (Ⅹ)[7] in nearly 80% yield. The NMR spectra showed a singlet at τ7.61 corresponding to one thioacetyl. A doublet at τ4.20 (anomeric proton) with a coupling constant ($J_{1,2}$=2.5 c.p.s.) indicated an equatorially oriented C_2 proton having a projected angle of 60° with an axial C_1 proton.

Summing up the data mentioned above, Ⅷ or Ⅸ was assigned to be 2-S-acetyl-2-thio-3,4,6-tri-O-acetyl-β-D-mannopyranosyl N,N-dialkyldithiocarbamate (Ⅷ: methyl, Ⅸ: ethyl).

3) B. R. Baker: "Methods in Carbohydrate Chemistry" Vol. Ⅱ, 447 (1963). Academic Press Inc., New York and London; E. J. Reist, L. V. Fisher, D. E. Gueffroy, L. Goodman: J. Org. Chem., **31**, 1506 (1966).
4) B. R. Baker, T. L. Hullar: *Ibid.*, **30**, 4053 (1965); B. R. Baker, K. Hewson, L. Goodman, A. Benitez: J. Am. Chem. Soc., **80**, 6577 (1958).
5) B. Helferich, J. Zinner: Chem. Ber., **95**, 2604 (1962).
6) L. J. Bellamy: "The Infra-red Spectra of Complex Molecules," 357 (1958). Methuen & Co., Ltd. London.
7) E. Fischer: Ber., **47**, 196 (1914).



V VI : R=Me VII : R=Et VIII : R=Me IX : R=Et

Chart 2.

In the course of the reaction, only one molecule substitution involving the Walden inversion might have occurred at the C_2-mesyl, while the carbamoyl radical at C_1 did not accept the substitution toward potassium thiolacetate. The finding was not identical with that of the corresponding ethylxanthate which had been able to undergo two molecules substitution at C_1 and C_2 to form 1,2-di-S-acetyl-1,2-dithio-3,4,6-tri-O-acetyl-β-D-mannopyranose.[1)]

In the next step, the authors projected the synthesis of β-D-mannopyranosyl N,N-dialkyldithiocarbamates starting from VI or VII, followed by epimerization of the C_2-mesyl with potassium acetate and successive deacetylation.

Reflux of VI and potassium acetate in acetone-ethanol for one hour gave colorless crystals (XI), m.p. 104°, $[\alpha]_D^{20}$ +185.8° in 94% yield. Contrary to expectation, the elementary analyses were not in agreement with those of 2,3,4,6-tetra-O-acetyl-β-D-mannopyranosyl N,N-dimethyldithiocarbamate, $C_{17}H_{25}O_9NS_2$. On the other hand, the extremely large dextrorotatory value (+185.8°) compared to the starting material (+8.3°), led us to an assumption that some significant structural change might have occurred during the reaction.

The infrared spectra showed no absorption at *ca.* 7.50 and 8.43 (mesyl), but showed the bands assignable to carbon-carbon double bond (6.17) and dithiocarbamate (6.65). Reductive desulfurization with Raney nickel afforded 3,4,6-tri-O-acetyl-D-hydroglucal which was identical with a sample prepared by desulfurization of VIII or IX.

The NMR spectrum showed signals at τ7.94 corresponding to three acetyls. A sharp singlet which was due to the anomeric proton could be observed at very low fields, τ3.16.

It is quite interesting to notice that while the N,N-dimethylamino protons in VI occurred as a sharp doublet at τ6.47, those of XI showed a singnal having a characteristic broad area (τ6.40 to 6.70), looked like humps of camels. Recently, Valega[8)] has described in the NMR study of some N,N-dimethylcarbamates that the N,N-dimethylamino protons show only one peak when there is an essentially free rotation of the dimethylamino group about the carbon-nitrogen bond in these compounds, while cause a splitting of the methyl protons if the linkage in the >N-C=O increases the double bond character. If we refer to his interpretation, though we cannot yet completely explain the reason why XI shows such a broad signal, the phenomenon appears to imply that in XI the dipolar form (>$\overset{+}{N}$=C-) less contribute than VI.

The authors speculated on the structure of XI to be 2-N,N-dimethyldithiocarbamoyl-2-deoxy-3,4,6-tri-O-acetyl-D-arabino-hexopyranose-1-ene, which fulfills completely the data mentioned above, and the elementary analyses were in quite agreement with that of $C_{15}H_{21}O_7NS_2$.

8) T. M. Valega : J. Org. Chem., **31**, 1150 (1966).

To extend the validity of the postulated structure, we measured the NMR spectra of 3,4,6-tri-O-acetyl-D-glucal*3 and 2,3,4,6-tetra-O-acetyl-2-hydroxy-D-glucal, then made a comparison with the spectrum of XI.

The anomeric proton of the acetylated glucal occurred as a doublet at τ 3.50, while that of the 2-hydroxy-D-glucal, a singlet at τ3.41. Thus the anomeric proton of XI (singlet, τ3.16) has a structural similarity with the latter, but not with the former, and the structure postulates for the absence of a proton at C_2, consequently, the dithiocarbamoyl radical must be situated at C_2.

It is interesting to notice that the product (XI) was also obtainable by acetylation of 1,2-dideoxy-1,2-(N,N-dimethylammonium)-dithiocarbonyl-β-D-mannopyranose methanesulfonate (XIII) with acetic anhydride and pyridine. The compound (XIII) was prepared after evaporation of an aqueous solution of 2-O-mesyl-β-D-glucopyranosyl N,N-dimethyldithiocarbamate (XII) which was obtained by deacetylation of the corresponding 2-O-mesyl-carbamate (VI) with chilled methanolic ammonia.

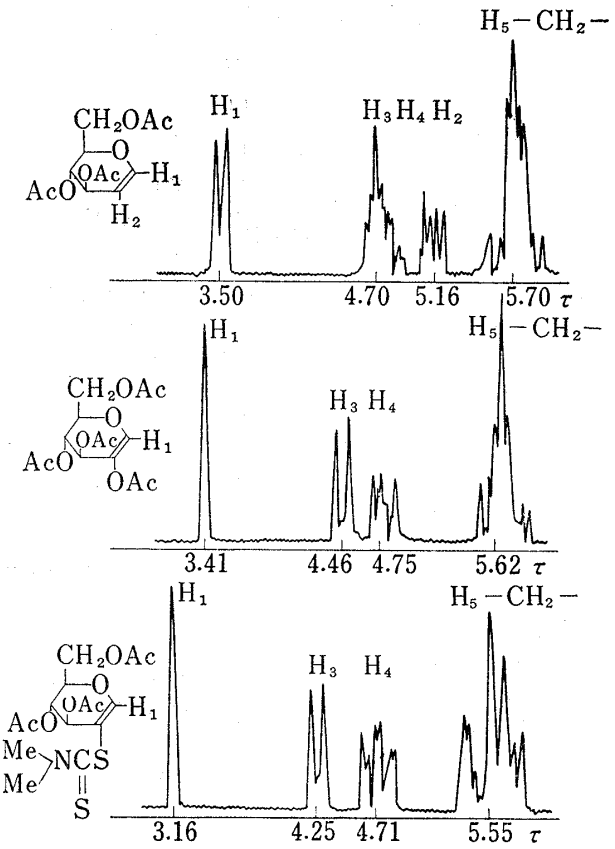


Fig. 1. Nuclear Magnetic Resonance Spectra in $CDCl_3$

The finding prompts us to induce the interpretation that the methanesulfonate (XIII) must be the intermediate of the unsaturated sugar formation. We speculate the reaction mechanism as follows.

Recently, Baker, *et al.*[9] have reported a view that in a basic medium a sugar derivative possessing a nucleophilic neighbouring group, such as thioureido, and a suitable leaving group in a *trans*-diequatorial disposition cyclized to form a five membered thiazoline. This is in accordance with our interpretation which requires the formation of five membered sulfonate (XIII) in the initial stage of the reaction.

Deacetylation of XI with chilled methanolic ammonia gave 2-N,N-dimethyldithiocarbamoyl-2-deoxy-D-arabino-hexopyranose-1-ene (XIV), m.p. 157°, $[\alpha]_D^{20}$ +131.9° which is a new type of unsaturated sugars has not yet been reported in literature.

There has been considerable interest in recent years in the studies of sugars with exocyclic double bond,[10] double[11] or triple bond[12] in pyranose or furanose ring. However, few examples have been referred on the unsaturated sugars possessing some substitution group attached directly on the carbon-carbon double bond.[13] Concering to

*3 Detailed studies of the NMR have been reported by L. D. Hall : J. Org. Chem., **29**, 297 (1964); "Advances in Carbohydrate Chemistry," Vol. 19, 51 (1964). Academic Press, Inc., New York and London.

9) B. R. Baker, T. Neilson : J. Org. Chem., **29**, 1051 (1964); B. R. Baker, T. L. Hullar : *Ibid.*, **30**, 4038, 4045, 4049 (1965).
10) D. Horton, W. N. Turner : Carbohydrate Research, **1**, 444 (1965).
11) E. F. L. J. Anet : *Ibid.*, **1**, 95 (1965); R. S. Tipson, A. Cohen : *Ibid.*, **1**, 338 (1965).
12) C. D. Hurd, H. Jenkins : *Ibid.*, **2**, 240 (1966).
13) R. J. Ferrier : "Advances in Carbohydrate Chemistry," Vol. 20, 68 (1965), Academic Press Inc., New York and London.

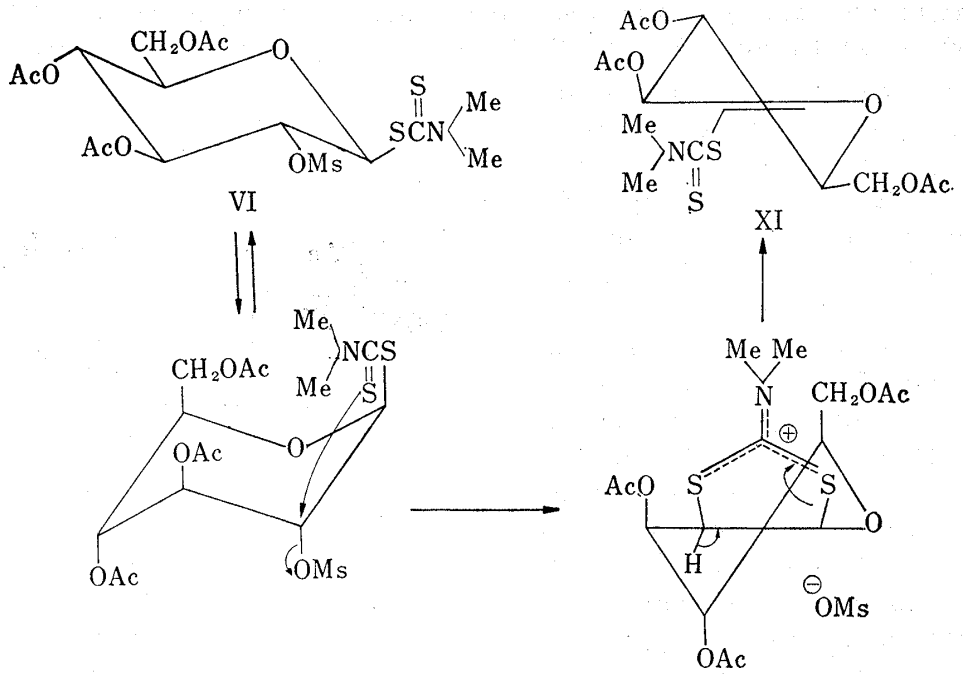


Chart 3.

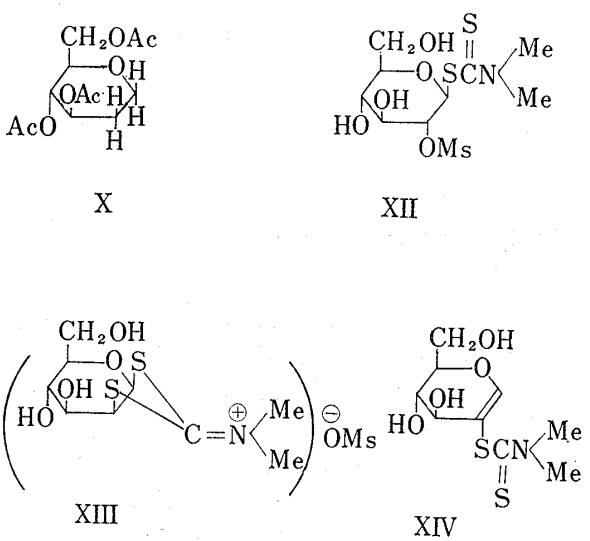


Chart 4.

unsaturated sugars derived from sulfur containing sugar derivatives, four papers have been referred in literature. Christensen and Goodman[14] have reported the formation of methyl 4,6-O-benzylidene-2,3-dideoxy-α-D-erythro-hex-2-enoside (XV) when methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-epithio-α-D-alloside is treated with trimethylphosphite. Two papers, reported by Horton, *et al.*,[15] are the formation of the similar compound (XV) by treatment of methyl 2,3-di-O-mesyl-4,6-O-benzylidene-α-D-glucopyranoside with potassium ethylxanthate in boiling 1-butanol. They speculate that the corresponding 2,3-episulfide may be the intermediate of the reaction. The formation of XV has also been reported by another worker.[16]

Thus, the unsaturated sugars herein reported by us may be quite fascinating if we consider the structure and the machanism of formation. The product also seems to offer an attractive one for further elucidation of special reactivities in thiosugars.

Experimental

Unless stated otherwise, solvents were evaporated *in vacuo* at a bath temperature of 40° in a rotary evaporator. Thin-layer chromatography (TLC) was performed by ascending method on silica gel G (E. Merck,

14) J. E. Christensen, L. Goodman: J. Am. Chem. Soc., **83**, 3827 (1961).
15) D. Horton, W. N. Turner: Tetrahedron Letters, 2531 (1964); E. Albano, D. Horton, T. Tsuchiya: Carbohydrate Research, **2**, 349 (1966).
16) R. D. Gutherie, D. Murphy: J. Chem. Soc., **1965**, 6666.

Darmstadt, Germany) or Wakogel B-5. Spots were located on silica gel plates by irradiating with UV lamp or by spraying with 50% H_2SO_4. The NMR spectra were measured by JNM-3H-60-spectrometer (Japan Electron Optics Laboratory Co., Ltd.), Varian A60 (Varian Associates) or H-6013 (Hitachi Ltd., Tokyo) in $CDCl_3$ at 60 Mc. with Me_4Si as an internal standard. Chemical shifts were given in τ values and coupling constants (J) c.p.s.

Sodium N,N-diethyldithiocarbamate (Ⅳ) which was recrystallized from 5 parts of boiling acetone was prepared from NaOH, CS_2 and Et_2NH by a slight modification of Kulka[17] for the preparation of Na-N,N-dimethyldithiocarbamate (Ⅲ).

2-O-Mesyl-3,4,6-tri-O-acetyl-β-D-glucopyranosyl N,N-Dimethyldithiocarbamate (Ⅵ)——A mixture of Ⅲ (6 g.) and 2-O-mesyl-3,4,6-tri-O-acetyl-α-D-glucopyranosyl bromide (Ⅴ) (20 g.)[5] in dry acetone (60 ml.) was refluxed for few min. After cooling, the mixture was poured into ice-H_2O (1 L), then allowed to stand overnight at room temperature. The resulting white solid was separated by filtration, dried, and recrystallized from MeOH to give crystals (8.8 g., 40%), m.p. 111~114°, $[\alpha]_D^{20}$ +8.3° (c=1.19, $CHCl_3$), UV λ_{max}^{EtOH} mμ (ε): 239 (9400), 278 (9000), IR ν_{max}^{Nujol} μ: 6.65 (dithiocarbamate[6]), 7.50, 8.43 (OMs). *Anal.* Calcd. for $C_{16}H_{25}O_{10}NS_3$: C, 39.41; H, 5.17; N, 2.87; S, 19.73. Found: C, 39.13; H, 5.03; N, 2.98; S, 19.77.

2-O-Mesyl-3,4,6-tri-O-acetyl-β-D-glucopyranosyl N,N-Diethyldithiocarbamate (Ⅶ)——A mixture of Ⅳ (15 g.) and Ⅴ (30 g.) in dry acetone (150 ml.) was treated with the same procedure as for the preparation of Ⅵ. Recrystallization from EtOH gave crystals (20 g., 58%), m.p. 111~112°, $[\alpha]_D^{20}$ +4° (c=1.48, $CHCl_3$), UV λ_{max}^{EtOH} mμ (ε): 242 (9600), 281 (9500), IR λ_{max}^{Nujol} μ: 6.70 (dithiocarbamate), 7.50, 8.43 (OMs). *Anal.* Calcd. for $C_{18}H_{29}O_{10}NS_3$: C, 41.93; H, 5.67; N, 2.72; S, 18.66. Found: C, 41.55; H, 5.58; N, 2.67; S, 18.36.

2-S-Acetyl-2-thio-3,4,6-tri-O-acetyl-β-D-mannopyranosyl N,N-Dimethyldithiocarbamate (Ⅷ)——A mixture of Ⅵ (4 g.) in dry acetone (20 ml.) and AcSK (2 g.) in abs. EtOH (30 ml.) was refluxed for 30 min. The mixture became turbid and K-methanesulfonate precipitated in the course of the reaction. After cooling, the mixture was poured into ice-H_2O (300 ml.) and extracted with $CHCl_3$. The $CHCl_3$-layer was washed with H_2O, dried over Na_2SO_4, then filtered. The filtrate was evaporated to give a sirup which dissolved in warm EtOH, treated with charcoal and filtered. Crystals began to deposite when the filtrate was standing for 1 hr. at room temperature. After standing overnight in a refrigerator, the precipitates were separated by filtration and recrystallized from EtOH to give colorless needles (1.5 g., 39%), m.p. 182~183°, $[\alpha]_D^{20}$ +67.2° (c=1.38, $CHCl_3$), UV λ_{max}^{EtOH} mμ (ε): 242 (10400), 278 (8500), IR λ_{max}^{Nujol} μ: 5.85 (SAc), 6.65 (dithiocarbamate). *Anal.* Calcd. for $C_{17}H_{25}O_8NS_3$: C, 43.66; H, 5.39; N, 3.00; S, 20.57. Found: C, 43.64; H, 5.40; N, 3.07; S, 20.75. The NMR spectrum of Ⅷ showed a singlet at τ 7.61 corresponding to one SAc. A doublet at τ 4.20 (anomeric proton) with a coupling constant ($J_{1,2}$=2.5 c.p.s.) indicated an equatorially oriented C_2 proton having a projected angle of 60° with an axial C_1 proton.

2-S-Acetyl-2-thio-3,4,6-tri-O-acetyl-β-D-mannopyranosyl N,N-Diethyldithiocarbamate (Ⅸ)——A mixture of Ⅶ (8 g.) and AcSK (3 g.) was treated with the same procedure as for the preparation of Ⅷ. Recrystallization from EtOH gave crystals (2.5 g., 32%), m.p. 131°, $[\alpha]_D^{20}$ +30.7° (c=0.88, $CHCl_3$), UV λ_{max}^{EtOH} mμ (ε): 250 (10300), 280 (9000), IR λ_{max}^{Nujol} μ: 5.90 (SAc), 6.70 (dithiocarbamate). *Anal.* Calcd. for $C_{19}H_{29}O_8NS_3$: C, 46.03; H, 5.90; N, 2.85; S, 19.41. Found: C, 46.06; H, 6.14; N, 2.93; S, 19.38. The NMR spectrum of Ⅸ showed a singlet at τ 7.61 corresponding to one SAc. A doublet at τ 4.18 (anomeric proton) with a coupling constant ($J_{1,2}$=2.5 c.p.s.) indicated an equatorially oriented C_2 proton having a projected angle of 60° with an axial C_1 proton.

3,4,6-Tri-O-acetyl-D-hydroglucal (Ⅹ)——a) From Ⅷ: A mixture of Ⅷ (0.5 g.) and approximately 20 g. of freshly prepared Raney Ni in EtOH (30 ml.) was refluxed for 5 hr. The supernatant solution was then removed, the Ni washed with EtOH, and the combined filtrate and washings were evaporated to give a sirup (0.23 g., 77%), $[\alpha]_D^{20}$ +26.8° (c=5.60, EtOH). Fischer[7] reports $[\alpha]_D$ +35.55° (c=8.41, EtOH) for 3,4,6-tri-O-acetyl-D-hydroglucal.

b) From Ⅸ: A mixture of Ⅸ (1 g.) and approximately 20 g. of Raney Ni in EtOH (50 ml.) was treated with the same procedure as before to give a sirup (0.45 g., 81%), $[\alpha]_D^{20}$ +27.3° (c=11.3, EtOH). The product was identical with an authentic 3,4,6-tri-O-acetyl-D-hydroglucal, prepared by hydrogenation of 3,4,6-tri-O-acetyl-D-glucal[1] by TLC (solvent: MeOH benzene (3:97) or AcOEt-iso. PrOH-H_2O (90:5:5) and IR.

2-N,N-Dimethyldithiocarbamoyl-2-deoxy-3,4,6-tri-O-acetyl-D-arabinohexopyranose-1-ene (Ⅺ)——A mixture of Ⅵ (4 g.) and AcOK (4 g.) in 120 ml. of abs. EtOH-acetone (1:1, v/v) was refluxed for 1 hr. In the course of the reaction, the mixture became turbid and K-methanesulfonate precipitated. Cooling, and after addition of $CHCl_3$ (50 ml.), it was poured into ice-H_2O, and the H_2O-layer extracted with $CHCl_3$. The combined $CHCl_3$-layer was washed with H_2O, dried over Na_2SO_4, then filtered. The filtrate was evaporated to give a sirup which dissolved in warm EtOH, filtered, the filtrate left to stand in a refrigerator overnight to induce crystallization. Crystalline mass was separated by filtration and recrystallized from EtOH to give colorless needles (3 g., 94%), m.p. 104°, $[\alpha]_D^{20}$ +185.8° (c=0.86, $CHCl_3$), UV λ_{max}^{EtOH} mμ (ε): 278 (8000), IR λ_{max}^{Nujol} μ: 6.17 (C=C), 6.65 (dithiocarbamate). *Anal.* Calcd. for $C_{15}H_{21}O_7NS_2$: C, 46.03; H, 5.41; N,

17) M. Kulka: Can. J. Chem., **34**, 1093 (1956).

3.58; S, 16.40. Found: C, 45.94; H, 5.50; N, 3.63; S, 16.02. The NMR spectrum showed a singlet corresponding to one proton at τ 3.16 (anomeric proton).

Reductive desulfurization of XI (1 g.) using the similar method as for that of Ⅷ or Ⅸ afforded a sirup (0.4 g., 57%), $[\alpha]_D^{20}$ +29.8° (c=0.84, EtOH) which was indistinguishable by IR and TLC from an authentic sample of 3,4,6-tri-O-acetyl-D-hydroglucal.

2-O-Mesyl-β-D-glucopyranosyl N,N-Dimethyldithiocarbamate (XII)——Dry NH_3-gas was passed to saturation at 0° through a chilled suspension of Ⅵ (5 g.) in dry MeOH (100 ml.). After keeping in a refrigerator, filtered, and the filtrate was evaporated to give a colorless residue. Recrystallization from MeOH gave pure material (3.4 g., 90%), m.p. 120°, $[\alpha]_D^{20}$ +17.1° (c=0.7, pyridine), UV λ_{max}^{EtOH} mμ (ε): 241 (10300), 279 (8800), IR λ_{max}^{Nujol} μ: 2.85 (OH), 6.65 (dithiocarbamate), 7.50, 8.43 (OMs). *Anal.* Calcd. for $C_{10}H_{19}O_7NS_3$: C, 33.23; H, 5.29; N, 3.87; S, 26.61. Found: C, 33.37; H, 5.20; N, 3.52; S, 26.84.

Acetylation of XII (0.5 g.) with pyridine (5 ml.) and Ac_2O (5 ml.) as before gave acetate (0.5 g., 74%) which was identical with Ⅵ in mixed m.p. and IR.

1,2-Dideoxy-1,2-(N,N-dimethylammonium)-dithiocarbonyl-β-D-mannopyranose Methanesulfonate (XIII)——A solution of XII (1.39 g.) in warm H_2O (10 ml.) was evaporated *in vacuo* at 40° to give a crystalline mass which recrystallized from MeOH to give white powder (1.2 g., 85%), m.p. 186°, $[\alpha]_D^{20}$ −186.7° (c=1.20, H_2O), UV λ_{max}^{EtOH} mμ: 245, IR λ_{max}^{Nujol} μ: 3.03 (OH), 6.25 (C=N), 7.50, 8.43 (OMs). *Anal.* Calcd. for $C_{10}H_{19}O_7NS_3$: C, 33.23; H, 5.29; N, 3.87; S, 26.61. Found: C, 33.22; H, 5.30; N, 4.06; S, 26.89.

XI from XIII——To a mixture of pyridine (2 ml.) and Ac_2O (2 ml.) was added XIII (0.2 g.), then left to stand for 20 hr. at room temperature. It was poured into ice-H_2O (50 ml.) and precipitated powders were separated by filtration, dried, and recrystallized from EtOH to give pure material (0.15 g., 69%) which was indistinguishable from XI in mixed m.p. and IR.

2-N,N-Dimethyldithiocarbamoyl-2-deoxy-D-arabino-hexopyranose-1-ene (XIV)——Dry NH_3-gas was passed to saturation at 0° through a chilled suspension of XI (1.7 g.) in dry MeOH (100 ml.). After keeping in a refrigerator overnight, the solvent was removed to give a crystalline residue which recrystallized from EtOH to give pure material (1 g., 87%), m.p. 157°, $[\alpha]_D^{20}$ +131.9° (c=1.32, pyridine), UV λ_{max}^{EtOH} mμ (ε): 278 (9200), IR λ_{max}^{Nujol} μ: 3.10 (OH), 6.17 (C=C), 6.65 (dithiocarbamate). *Anal.* Calcd. for $C_9H_{15}O_4NS_2$: C, 40.74; H, 5.70; N, 5.27. Found: C, 41.04; H, 5.53; N, 5.12. The product was unstable and it decomposed at room temperature for more than a week.

To a mixture of pyridine (5 ml.) and Ac_2O (5 ml.) was added XIV (0.5 g.), then left to stand for 18 hr. at room temperature. It was poured into ice-H_2O (100 ml.) and precipitated powders were separated by filtration, dried and recrystallization from EtOH to give pure material (0.6 g., 80%) which was indistinguishable with XI in mixed m.p. and IR.

The authors are indebted to Mr. S. Shimokawa of School of Technology, Hokkaido University, Dr. M. Haga of National Institutes of Health, Bethesda, U. S. A. and Miss Y. Kishio of this Faculty for NMR studies. Thanks are also due to the Tokyo Laboratory, Kowa Co., Ltd. for a part of elementary analyses.