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Thiosugars. XIV.[1] Studies on the Syntheses of 1,2-Dideoxy-1,2-dithioimidocarbonyl-β-D-mannopyranose and 1,2-Dideoxy-1,2-trithiocarbonyl-β-D-mannopyranose

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1,2-Dideoxy-1,2-dithioimidocarbonyl-β-D-mannopyranose (III) was prepared in 76% yield by treatment of 1,2-dideoxy-1,2-(N,N-dimethylammonium)dithiocarbonyl-β-D-mannopyranose methanesulfonate (II) with methanolic ammonia. Some acyl derivatives of III were also described.

Treatment of a suspension of III in ethanol containing glacial acetic acid with hydrogen sulfide afforded 1,2-dideoxy-1,2-trithiocarbonyl-β-D-mannopyranose (XII) in 78% yield. The product was also obtainable in 98% yield from II with the same procedure.

Acetylation of XII gave triacetate (XIII) which was also prepared in 61% yield by reflux of II and potassium thiolacetate in acetone, followed by acetylation.

In the previous paper of this series[3] the authors have reported the formation of an unsaturated sugar, 2-N,N-dimethyldithiocarbamoyl-2-deoxy-3,4,6-tri-O-acetyl-D-arabino-hexopyranose-1-ene from 2-O-mesyl-3,4,6-tri-O-acetyl-β-D-glucopyranosyl N,N-dimethyldithiocarbamate (I) and put forward the mechanism of the formation. The crystalline cyclic intermediate, 1,2-dideoxy-1,2-(N,N-dimethylammonium)dithiocarbonyl-β-D-mannopyranose methanesulfonate (II) may be quite interesting because of the potential reactivities toward nucleophilic reagents. As an extension of the studies on the syntheses of thiosugars having antitumor activity[4] the authors were now able to synthesize, starting from I or II, sugar derivatives in which heterocyclic rings fused on glycopyranose ring at C_1 and C_2. The present paper describes full details of this work.

One of the starting material (II) was prepared from 2-O-mesyl-3,4,6-tri-O-acetyl-α-D-glucopyranosyl bromide and sodium N,N-dimethyldithiocarbamate with a slight modification of the previous method. As the modified method proceeds without isolation and purification of the intermediate (I), which improves the yield and simplifies the procedure.

Reaction of chilled methanolic ammonia upon II overnight gave crystals (III), mp 175—176°, $[\alpha]_D^{20}$ −102°, in 76% yield. The product was also obtainable from I with a low yield (34%). The infrared (IR) spectra in nujol suggested the presence of hydroxyl, imino and carbon-nitrogen double bond, while showed neither absorption near 7.50 nor 8.43 μ corresponding to that of methanesulfonyl.

Acetylation or benzoylation of III gave crystalline tetraacetate (IV) or tetrabenzoate (V) in good yield. The nuclear magnetic resonance spectroscopy (NMR) of IV or V, measured in chloroform-d, revealed the presence of three O-acetyl and one N-acetyl or four benzoyls, respectively. The IR spectra of IV and V indicated, in each case, the presence of carbon-nitrogen double bond at 6.70 μ.

Mesylation of III with 1.1 mole of methanesulfonyl chloride (MsCl) in pyridine and successive acetylation of the reaction mixture gave a sirup, from which two crystalline products

1) Part XIII: S. Ishiguro and S. Tejima, *Chem. Pharm. Bull.* (Tokyo), **16**, 1567 (1968).
2) Location: *Kita-12-jo, Nishi-5-chome, Sapporo.*
3) S. Ishiguro and S. Tejima, *Chem. Pharm. Bull.* (Tokyo), **15**, 1478 (1967).
4) M. Akagi, S. Tejima, M. Haga, Y. Hirokawa, M. Yamada, M. Ishiguro, and D. Mizuno, *Yakugaku Zasshi*, **87**, 287 (1967).

(VI and VII) were separated in 28 and 9% yield. The NMR of VI revealed a singlet (3H) at τ 6.85, which was assgined to N–mesyl. Two singlets at τ 7.87 (6H) and 7.91 (3H) were assigned to three acetyls at C_3, C_4, and C_6. The analysis of the sulfur content suggested the presence of one mesyl group in VI. On the one hand, VII included three singlets at τ 6.85 (3H), 6.90 (3H), and 7.88 (6H) which were assigned to N–mesyl, O–mesyl and two O–acetyl, respectively. The elemental analyses suggested the presence of two mesyl groups in VII which was in consistent with the result from NMR. Further, one mesyloxy in VII was substituted with iodine in theoretical yield to give crystalline iodide (VIII). The NMR of VIII included two singlets at τ 6.85 (3H) and 7.88 (6H) which were assignable to N–mesyl and two O–acetyls; no O–mesyl group was evident.

Reaction of phenylhydrazine acetate upon III afforded crystalline phenylhydrazone (IX) in 94% yield. Acetylation of IX gave crystalline triacetate (X), mp 156°, $[\alpha]_D^{20}$ −440°.

From the data mentioned above, the authors assigned III as 1,2–dideoxy–1,2–dithioimidocarbonyl–β–D–mannopyranose.

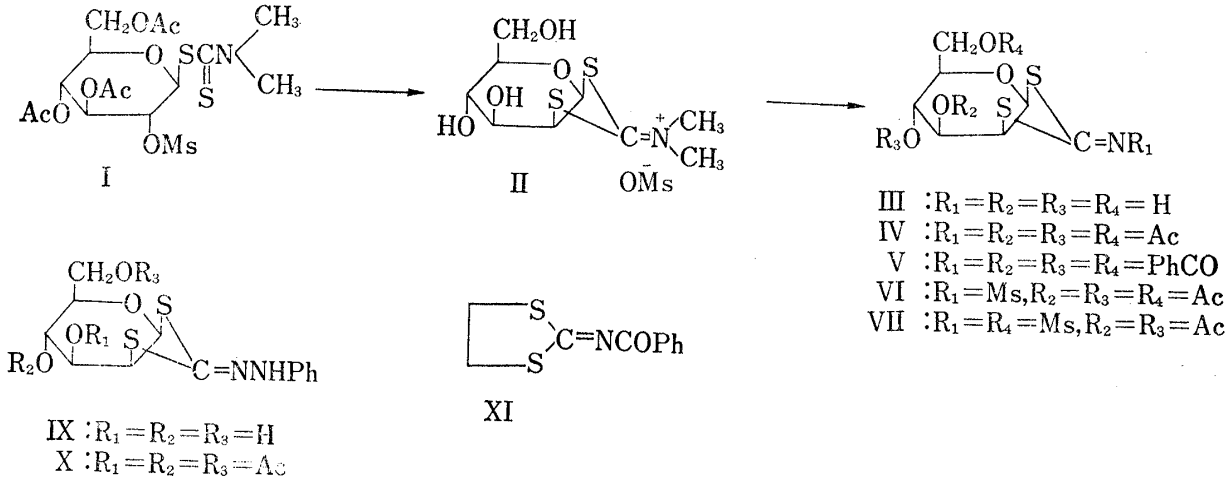

Chart 1

It is quite interesting to notice that in III a cyclic ethylene dithiocarbonate group fused on the pyranose ring at C_1 and C_2, which should be a new type of sugar derivatives has not yet been reported in the literature.

On the one hand, not so many papers have been referred on dithioimidocarbonates. In 1964, Addor[5] reported a new synthetic method of cyclic dithioimidocarbonate and extended the method to the syntheses of several compounds of this series.[6] The same author also reported the nematocidal effect of the analogs.[7] He describes that an IR absorption band assignable to the C=N group of 2–imido–1,3–dithiolane falls to 1560 cm^{-1}. This value is low in comparison to that found for most C=N groups. The fact may be attributed to the mesomeric and inductive effects provided with the two sulfur atoms.

It is noteworthy to describe that the same shift of C=N absorption bands were observed in the IR spectrum of III (ν_{max}^{Nujol} cm^{-1}: 1560, 1580).

According to the chemistry of imidates,[8] acid anhydrides and acid chlorides convert imidates to the acylated imidates. Thus, the structures of IV, V, VI and VII were assigned as 1,2–dideoxy–1,2–(N–acetyl)dithioimidocarbonyl–3,4,6–tri–O–acetyl–β–D–mannopyranose, 1,2–dideoxy–1,2–(N–benzoyl)dithioimidocarbonyl–3,4,6–tri–O–benzoyl–β–D–mannopyranose, 1,2–dideoxy–1,2–(N–mesyl)dithioimidocarbonyl–3,4,6–tri–O–acetyl–β–D–mannopyranose and

5) R. W. Addor, *J. Org. Chem.*, **29**, 738 (1964).
6) R.W. Addor, S.D. Levy, and R.J. Magee, Belg. Patent 637658 (1964) [*C.A.*, **62**, 6490 (1965)].
7) D.S. Cannon and R.W. Addor, U.S. Patent 3183148 (1965) [*C.A.*, **64**, 737 (1966)].
8) R. Roger, D.G. Neilson, *Chem. Rev.*, **61**, 179 (1961).

1,2-dideoxy-1,2-(N-mesyl)dithioimidocarbonyl-3,4-di-O-acetyl-6-O-mesyl-β-D-mannopyranose, respectively. The results of the elemental analyses, IR and NMR were consistent with the assigned structures.

Recently, Neidlein and Haussmann[9] have reported the synthesis of N-benzoylimido-1,3-dithiolane (XI), which possesses the structural similarity with V.

As a mesyloxy group in a primary alcoholic hydroxyl is substituted with iodine by reflux with sodium iodide, the structure of VIII was assigned as 1,2-dideoxy-1,2-(N-mesyl)-dithioimidocarbonyl-3,4-di-O-acetyl-6-deoxy-6-iodo-β-D-mannopyranose.

Schmidt[10] records the isolation of phenylhydrazone from simple imidate by condensation with phenylhydrazine hydrochloride. Thus, it should be quite reasonable to assign the structures of IX and X as 1,2-dideoxy-1,2-dithiocarbonyl-β-D-mannopyranose phenylhydrazone and 1, 2-dideoxy-1, 2-dithiocarbonyl-3,4,6-tri-O-acetyl-β-D-mannopyranose phenylhydrazone.

In 1965, Corey, *et al.*[11] have reported that 1,2-trithiocarbonates were formed in good yield when dithioimidocarbonates were heated with hydrogen sulfide in ethanol. The authors, in the next step, projected the synthesis of glycosyl 1,2-trithiocarbonate starting from III.

A suspension of III in ethanol containing glacial acetic acid was treated with hydrogen sulfide for three days at room temperature to afford yellow needles (XII) in 78% yield. The product, UV λ_{max}^{EtOH} mμ (ε): 318 (13000), $[\alpha]_D^{20}$ +173°, did not melt or change its appearance by 360°. It is noteworthy to describe that the product was also obtainable from II with the same procedure in 98% yield.

Acetylation of XII with acetic anhydride-pyridine gave yellow acetate (XIII), mp 121°, $[\alpha]_D^{20}$ +47°, UV λ_{max}^{EtOH} mμ (ε): 316 (16000). The product was also obtainable in 61% yield by reflux of II with potassium thiolacetate, followed by acetylation of the reaction product. The anomeric proton of XIII was shown as a doublet ($J_{1,2}$=2.5 cps) by NMR at τ 4.17. Two singlets at τ 7.86 (6H) and 7.88 (3H) were assigned as acetyls at C_3, C_4 and C_6, respectively.

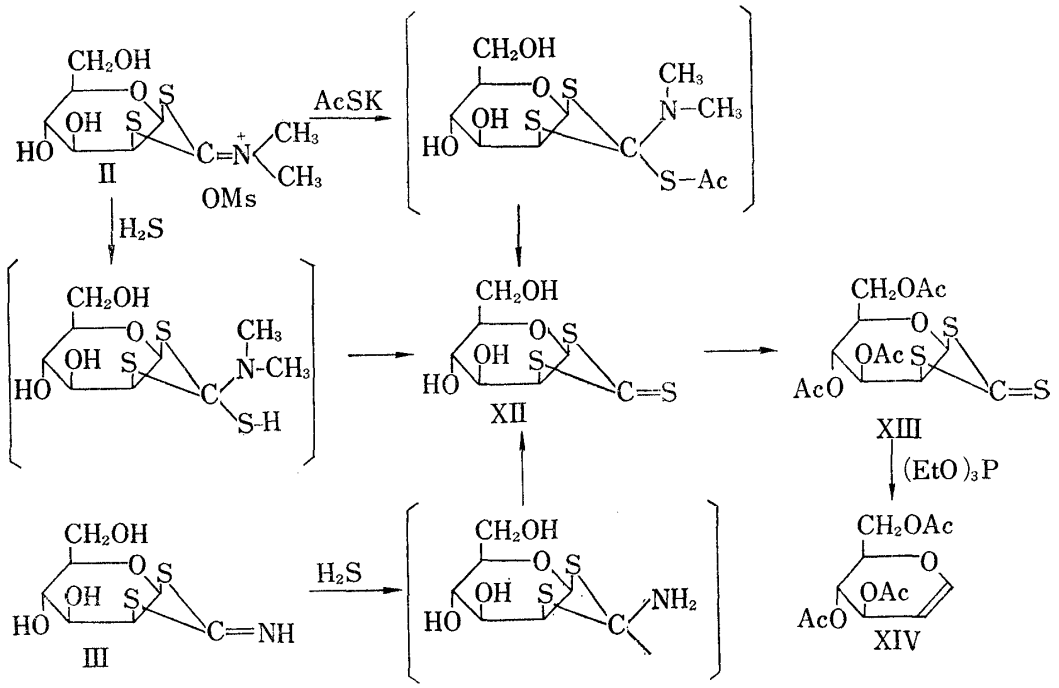

Chart 2

9) R. Neidlein and W. Haussmann, *Chem. Ber.*, **99**, 239 (1966).
10) E. Schmidt, *Chem. Ber.*, **47**, 2545 (1914).
11) E.J. Corey, F.A. Carey, and R.A.E. Winter, *J. Am. Chem. Soc.*, **87**, 934 (1965).

Heating of XIII at 155° with triethylphosphite afforded 3,4,6-tri-O-acetyl-D-glucal (XIV) in 63% yield. According to the studies of Corey, *et al.*[11] trithiocarbonates were converted by trialkylphosphite into the olefine. Recently, Horton, *et al.*[12] reported that sugar thionocarbonate was also converted by trimethylphosphite into the alkene.

From the above mentioned data, the authors assigned the structures of XII and XIII as 1,2-dideoxy-1,2-trithiocarbonyl-β-D-mannopyranose and 1,2-dideoxy-1,2-trithiocarbonyl-3,4,6-tri-O-acetyl-β-D-mannopyranose.

The products (XII and XIII) are the first reported examples of trithiocarbonates in which trithiocarbonyl group fused on the sugar pyranose ring. The authors summarize the courses of the reaction as Chart 2.

Experimental

Unless stated otherwise, solvents were evaporated *in vacuo* at a bath temperature of 40° in a rotatory evaporator. Thin-layer chromatography (TLC) was performed by ascending method with silica gel G (E. Merck, Darmstadt, Germany) as the absorbent using ether–benzene (1:3, v/v) or 28% NH_4OH–PrOH–H_2O (2:6:1) as the solvent. Identification was effected with UV lamp or dil. H_2SO_4. The NMR spectra were measured by JNM-3H-60 spectrometer (Japan Electron Optics Laboratory Co., Ltd.) or H-6013 (Hitachi Ltd., Tokyo) in $CDCl_3$ at 60 Mc with tetramethylsilane as an internal standard. Chemical shifts were given in τ values and coupling constants (J) cps.

1,2-Dideoxy-1,2-(N,N-dimethylammonium)dithiocarbonyl-β-D-mannopyranose Methanesulfonate (II)——A mixture of sodium N,N-dimethyldithiocarbamate[13] (9 g) and 2-O-mesyl-3,4,6-tri-O-acetyl-α-D-glucopyranosyl bromide[14] (30 g) in dry acetone (100 ml) was refluxed for few min. After cooling the mixture was poured into ice–H_2O (1 liter), the resultant mixture was extracted with $CHCl_3$. The organic layer was washed with H_2O, dried over Na_2SO_4, filtered, and the solvent was removed to give a sirup (30 g). Dry NH_3-gas was passed to saturation at 0° through a chilled suspension of the sirup in dry MeOH (200 ml). The mixture was left overnight in a refrigerator, filtered, and then evaporated to dryness to give crystalline residue (13 g). A solution of the product in 20% (v/v) aq. EtOH (100 ml) was refluxed for few min. After cooling the solvent was removed to give a sirup which induced to crystals by addition of a small amount of EtOH and scratching the side of the flask. Recrystallization from MeOH gave pure material (11 g, 44%), mp 186°, which was indistinguishable with authentic sample by mixed mp, TLC and IR.

1,2-Dideoxy-1,2-dithioimidocarbonyl-β-D-mannopyranose (III)——a) From 1,2-dideoxy-1,2-(N,N-dimethylammonium) dithiocarbonyl-β-D-mannopyranose methanesulfonate (II): Dry NH_3-gas was passed to saturation at 0° through a chilled suspension of II (5 g) in dry MeOH (100 ml). After keeping overnight in a refrigerator, the mixture was evaporated to give crystalline residue. Recrystallization from MeOH gave pure material (2.5 g, 76%), mp 175—176°, $[\alpha]_D^{20}$ −102° (c=0.8, l=1, N,N-dimethylformamide), IR ν_{max}^{Nujol} μ: 2.85 (OH), 3.15 (NH), 6.32, 6.42 (C=N). *Anal.* Calcd. for $C_7H_{11}O_4NS_2$: C, 35.43; H, 4.67; N, 5.90; S, 27.03. Found: C, 35.53; H, 4.98; N, 5.92; S, 26.78.

b) From 2-O-mesyl-3,4,6-tri-O-acetyl-β-D-glucopyranosyl N,N-dimethyl dithiocarbamate (I): A solution of I (30 g) in 80% (v/v) aq. EtOH (200 ml) was refluxed for 30 min. The solvent was evaporated to give a slight yellow sirup (30 g), $[\alpha]_D^{20}$ −163° (c=1.39, l=1, EtOH). Dry NH_3-gas was passed to saturation at 0° through a chilled solution of the sirup in dry MeOH (200 ml) and the mixture was left overnight in a refrigerator. The solvent was removed to give crystalline residue. Recrystallization from MeOH gave pure material (5 g, 34%), which was indistinguishable with the product prepared by a).

1,2-Dideoxy-1,2-(N-acetyl)dithioimidocarbonyl-3,4,6-tri-O-acetyl-β-D-mannopyranose (IV)——To a chilled mixture of Ac_2O (50 ml) and pyridine (50 ml) was added III (5 g). The mixture was left for 2 days at room temperature, then poured into ice–H_2O (1 liter), and the product was extracted with $CHCl_3$. The organic layer was washed with dil. H_2SO_4, aq. $NaHCO_3$ and H_2O, dried over Na_2SO_4, filtered, and the filtrate was evaporated to give crystalline mass. Recrystallization from EtOH gave pure material (6.5 g, 76%), mp 122° $[\alpha]_D^{20}$ −94.2° (c=2.06, l=1, $CHCl_3$), IR ν_{max}^{Nujol} μ: 5.70 (OAc), 6.00 (NAc), 6.70 (C=N), NMR τ: 4.40—5.28 (4H, multiplet, H_1, H_2, H_3, H_4), 5.80 (2H, multiplet, CH_2 at C_6), 6.20 (1H, multiplet H_5), 7.60 (3H, singlet, $NCOCH_3$), 7.87 (6H, singlet, $2COCH_3$), 7.89 (3H, singlet, CH_3CO at C_6). *Anal.* Calcd. for $C_{15}H_{19}O_8NS_2$: C, 44. 43; H, 4.72; N, 3.45; S, 15.82. Found: C, 44.42; H, 4.76; N, 3.53; S, 15.90.

1,2-Dideoxy-1,2-(N-benzoyl)dithioimidocarbonyl-3,4,6-tri-O-benzoyl-β-D-mannopyranose(V)——To a chilled stirred solution of III (1.5 g) in pyridine (30 ml) was added dropwise benzoylchloride (7.2 g). The

12) E. Albano, D. Horton, and T. Tsuchiya, *Carbohydrate Res.*, **2**, 349 (1966).
13) M. Kulka, *Can. J. Chem.*, **34**, 1093 (1956).
14) B. Helferich and J. Zinner, *Chem. Ber.*, **95**, 2604 (1962).

mixture, protected from moisture, was stirred for 1 hr at 0°, kept overnight at room temperature, then poured into ice–H_2O (200 ml). The product was extracted with $CHCl_3$, the $CHCl_3$-layer was washed with dil. H_2SO_4, aq. $NaHCO_3$ and H_2O, dried over Na_2SO_4 and filtered. After treatment with charcoal, the solvent was removed to give crystalline mass (3.5 g, 84%). Twice recrystallizations from $CHCl_3$–EtOH gave colorless crystals, mp 211°, $[\alpha]_D^{20}$ −50° ($c=1$, $l=1$, $CHCl_3$), IR ν_{max}^{Nujol} μ: 5.72, 5.78 (OBz), 6.05 (NBz), 6.24 (phenyl), 6.70 (C=N), NMR τ: 1.70–2.80 (20H, multiplet, $4C_6H_5CO$), 3.85—5.02 (4H, multiplet, H_1, H_2, H_3, H_4), 5.40 (2H, multiplet, CH_2 at C_6), 5.70 (1H, multiplet, H_5). *Anal.* Calcd. for $C_{35}H_{27}O_8NS_2$: C, 64.31; H, 4.16; N, 2.14; S, 9.81. Found: C, 64.20; H, 4.00; N, 2.26; S. 9.93.

1,2-Dideoxy-1,2-(N-mesyl)dithioimidocarbonyl-3,4,6-tri-O-acetyl-β-D-mannopyranose (VI) and 1,2-Dideoxy-1,2-(N-mesyl)dithioimidocarbonyl-3,4-di-O-acetyl-6-O-mesyl-β-D-mannopyranose (VII)——To a chilled stirred solution of III (2.85 g) in pyridine (50 ml) was added dropwise MsCl (1.5 g) and the mixture, protected from moisture, was stirred for 1 hr. After addition of Ac_2O (30 ml) at 0°, the mixture was left for 2 days at room temperature, and then poured into ice–H_2O (1 liter). The product was treated with a similar method as in the preparation of V to give a sirup which dissolved in benzene and chromatographied on silica gel (60 g) using benzene and benzene–ether (2:1, v/v) as the solvents. From the first effluent of the benzene–ether, the starting material (IV) (0.2 g, 4%) was recovered after removal of the solvent. From the second parts of the same solvent, a sirup, which crystallized by addition of a small amount of EtOH, was obtained after removal of the solvent. The crystals were collected by filtration and recrystallized from EtOH to give pure material (1.5 g, 28%), mp 173°, $[\alpha]_D^{20}$ −146° ($c=0.54$, $l=1$, $CHCl_3$), IR τ_{max}^{Nujol} μ: 5.67, 5.73 (OAc), 6.60 (C=N), 8.80(NMs), NMR τ: 4.30—5.20 (4H, multiplet, H_1, H_2, H_3, H_4), 5.80 (2H, multiplet, CH_2 at C_6), 6.20 (1H, multiplet, H_5), 6.85 (3H, singlet, NSO_2CH_3), 7.87 (6H, singlet, $2CH_3CO$), 7.91 (3H, singlet, CH_3CO at C_6). The structure was assigned as 1,2-dideoxy-1,2-(N-mesyl)-dithioimidocarbonyl-3,4,6-tri-O-acetyl-β-D-mannopyranose (VI). *Anal.* Calcd. for $C_{14}H_{19}O_9NS_3$: C, 38.09; H, 4.34; N, 3.17; S. 21.77. Found: C, 38.12; H, 4.53; N, 3.02; S, 21.54.

The last effluent of the same solvent gave a sirup after evaporation of the solvent and crystallization of which was induced by addition of a small amount of EtOH. The crystals were collected by filtration and recrystallized from EtOH to give pure material (0.55 g, 9%), mp 163°, $[\alpha]_D^{20}$ −130° ($c=0.5$, $l=1$, $CHCl_3$), IR ν_{max}^{Nujol} μ: 5.70 (OAc), 6.60 (C=N), 8.50 (OMs), NMR τ: 6.85 (3H, singlet, NSO_2CH_3), 6.90 (3H, singlet, OSO_2-CH_3), 7.88 (6H, singlet, $2CH_3CO$). The structure was assigned as 1,2-dideoxy-1,2-(N-mesyl)dithioimidocarbonyl-3,4-di-O-acetyl-6-O-mesyl-β-D-mannopyranose (VII). *Anal.* Calcd. for $C_{13}H_{19}O_{10}NS_4$: C, 32.69; H, 4.01; N, 2.93; S, 26.86. Found: C, 32.76; H, 4.05; N, 2.97; S, 27.08.

1,2-Dideoxy-1,2-(N-mesyl)-dithioimidocarbonyl-3,4-di-O-acetyl-6-deoxy-6-iodo-β-D-mannopyranose(VIII)——A mixture of VII (0.45 g) and NaI (0.9 g) in Ac_2O (10 ml) was refluxed for 1 hr in an oil bath. After cooling, the mixture was poured into ice–H_2O (100 ml) contaning a few drops of pyridine and the product was extracted with $CHCl_3$. The organic layer was washed with aq. $NaHCO_3$ and H_2O, dried over Na_2SO_4, filtered, and the solvent was removed to give a sirup which was triturated with EtOH to afford crystals. Recrystallization from EtOH gave pure material (0.45 g, 94%), mp 221°, $[\alpha]_D^{20}$−54.7° ($c=0.64$, $l=1$,$CHCl_3$), IR ν_{max}^{Nujol} μ: 5.70 (OAc), 6.60 (C=N), 8.80 (NMs), NMR τ: 6.85 (3H, singlet NSO_2CH_3), 7.88 (6H, singlet, $2CH_3CO$). *Anal.* Calcd. for $C_{12}H_{16}O_7NS_3I$: C, 28.29; H, 3.17; N, 2.75; S, 18.88. Found: C, 28.05; H, 3.30; N, 3.02; S, 19.00.

1,2-Dideoxy-1,2-dithiocarbonyl-β-D-mannopyranose Phenylhydrazone (IX)——To a solution of phenylhydrazine HCl (1.5 g) and AcONa-$3H_2O$ (1.5 g) in H_2O (12 ml) was added a warm solution of III (2 g) in H_2O (60 ml). The mixture was heated to 80° on a steam bath for a few min. While standing at room temperature white powders precipitated. The product was collected by filtration and recrystallized from MeOH to give pure material (2.6 g, 94%), mp 222—223°, IR ν_{max}^{Nujol} μ: 2.85 (OH), 3.05 (NH), 6.24 (phenyl), 6.70 (C=N), 13.4, 14.4 (monosubstituted phenly). *Anal.* Calcd. for $C_{13}H_{16}O_4N_2S_2$: C, 47.55; H, 4.91; N, 8.53; S, 19.53. Found: C, 47.51; H, 5.08; N, 8.78; S, 19.64.

1,2-Dideoxy-1,2-dithiocarbonyl-3,4,6-tri-O-acetyl-β-D-mannopyranose Phenylhydrazone (X)——To a chilled mixture of Ac_2O (26ml) and pyridine (26 ml) was added IX (2.6 g). After standing for 2 days at room temperature, the mixture was poured into ice–H_2O (1 liter) and the resulting solids were separated by filtration and dried in a vacuum desiccator. Recrystallization from EtOH gave pure material (3 g, 83%), mp 156°, $[\alpha]_D^{20}$ −440° ($c=1.07$, $l=1$, $CHCl_3$), IR ν_{max}^{Nujol} μ: 3.10 (NH), 5.70 (OAc), 6.24 (phenyl), 6.70 (C=N), 13.4, 14.4 (monosubstituted phenyl), NMR τ :2.70—3.20 (5H, multiplet, C_6H_5), 3.35 (1H, multiplet, NH), 4.40—5.40 (4H, multiplet, H_1, H_2, H_3, H_4), 5.77 (2H, multiplet, CH_2 at C_6), 6.20 (1H, multiplet, H_5), 7.88 (6H, singlet, $2CH_3CO$), 7.92 (3H, singlet, CH_3CO at C_6). *Anal.* Calcd. for $C_{19}H_{22}O_7N_2S_2$: C, 50.21; H, 4.88; N, 6.16; S, 14.11. Found: C, 49.77; H, 5.06; N, 6.44; S, 14.02.

1,2-Dideoxy-1,2-trithiocarbonyl-β-D-mannopyranose (XII)——a) From 1,2-dideoxy-1,2-(N,N-dimethylammonium) dithiocarbonyl-β-D-mannopyranose methanesulfonate (II): Dry H_2S-gas was passed to saturation at room temperature through a suspension of II (3 g) in abs. EtOH (200 ml) containing glacial AcOH (10 ml). After stirring for 3 days at room temperature, the mixture was evaporated to give a yellow crystalline mass. Recrystallization from EtOH gave yellow needles (2.05 g, 98%), mp over 360°, $[\alpha]_D^{20}$ +173° ($c=0.29$, $l=1$, MeOH), UV λ_{max}^{EtOH} mμ (ε): 318 (13000), IR ν_{max}^{Nujol} μ: 2.85 (OH), no NH band near 3.05 nor C=N near 6.40. *Anal.* Calcd. for $C_7H_{10}O_4S_3$: C, 33.10; H, 3.96; S, 37.87. Found: C, 33.53; H, 4.07; S, 35.04.

b) From 1,2-dideoxy-1,2-dithioimidocarbonyl-β-D-mannopyranose (III): The product, XII (2.5 g, 78%) was synthesized from III (3 g) by the same procedure used for a).

1,2-Dideoxy-1,2-trithiocarbonyl-3,4,6-tri-O-acetyl-β-D-mannopyranose (XIII)——a) Acetylation of XII: To a chilled mixture of Ac_2O (5 ml) and pyridine (5 ml) was added XII (0.5 g). The mixture was treated by the same procedure used for the preparation of X. The crude acetate was recrystallized from EtOH to give yellow needles (0.66 g, 87%), mp 121°, $[\alpha]_D^{20}$ +47° (c=0.54, l=1, $CHCl_3$), UV λ_{max}^{EtOH} mμ (ε): 316 (16000), IR ν_{max}^{Nujol} μ: 5.60, 5.80 (OAc), NMR τ: 4.17 (1H, doublet, anomeric proton, $J_{1,2}$=2.5 cps), 4.50–4.70 (3H, multiplet, H_2, H_3, H_4), 5.74 (2H, multiplet, CH_2 at C_6), 6.12 (1H, multiplet, H_5), 7.86 (6H, singlet, $2CH_3$-CO), 7.88 (3H, singlet, CH_3CO at C_6). *Anal.* Calcd. for $C_{13}H_{16}O_7S_3$: C, 41.01; H, 4.24; S, 25.28. Found: C, 41.01; H, 4.24; S, 25.02.

b) From 1,2-dideoxy-1,2-(N,N-dimethylammonium)dithiocarbonyl-β-D-mannopyranose methanesulfonate (II): A combined mixture of II (1.5 g) in dry acetone (25 ml) and AcSK (1.1 g) in abs. EtOH (25 ml) was refluxed for 30 min. In the course of the reaction the mixture became turbid, then precipitated potassium mesylate. After cooling, filtered, and the solvent was removed to give a sirup which was acetylated with Ac_2O (15 ml) pyridine (15 ml). Yellow crystals (0.96 g, 61%), mp 121°, were obtained after treatment of the mixture as described in the preparation of X. The product was indistinguishable with one prepared by a).

3,4,6-Tri-O-acetyl-D-glucal (XIV)——A mixture of XIII (1 g) and triethylphosphite (10 ml) was heated at 105° in an oil bath for 10 min to dissolve XIII. Then the bath temperature was gradually elevated to 155° in a period of 30 min and kept for further 5 min at 155°. After cooling, the mixture was evaporated *in vacuo* at 100—120° to give sirupy residue. Crystallization was induced after treatment of the sirup with a small amount of EtOH and seeding. The crystals were collected by filtration and recrystallized from MeOH–H_2O to give pure product (0.45 g, 63%), mp 54—55°, which was indistinguishable with authentic 3,4,6-tri-O-acetyl-D-glucal by mixed mp and IR.

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