[Chem. Pharm. Bull. 15(9)1367~1372(1967)] UDC 547.455.07

175. Takao Maki and Setsuzo Tejima: Thiosugars. XI.*1 Further Studies on Thiolevoglycosans.

(*Faculty of Pharmaceutical Sciences, Hokkaido University**2)

2-Deoxy-1,6-anhydro-1,6-sulfide-β-D-glucopyranose (2-Deoxy-thiolevoglucosan) (IX), m.p. 189~192°, $[\alpha]_D^{22}$ −71.7°, and 2-deoxy-1,6-anhydro-1,6-sulfide-3,4-anhydro-β-D-altrose (2-Deoxy-3,4-anhydro-thiolevoaltrosan) (XIV), m.p. 69~72°, $[\alpha]_D^{28}$ −108°, were synthesized by starting with D-glucal (II), followed by treatment of the intermediate 2-deoxy-6-O-tosyl-3,4-di-O-acetyl-β-D-glucopyranosyl ethylxanthate (VI) and 3-bromo-4-O-acetyl-6-O-tosyl-2,3-dideoxy-β-D-glucopyranosyl ethylxanthate (XIII), respectively, with sodium methoxide.

The preparation of 6-O-tosyl-3,4-di-O-acetyl-D-glucal (III), m.p. 106~107°, $[\alpha]_D^{22}$ +14°, which is a key intermediate in this paper, and the addition of hydrogen bromide upon III were also described.

(Received November 30, 1966)

In 1963 our laboratory reported the synthesis of 1,6-anhydropyranose with sulfur in the 1,6-anhydro ring, and designated the product as thiolevoglucosan.[1] The product has presumably been the first thio analogue of 1,6-anhydroglycosans hitherto been described.[2] Recently, the preparation of 6-thio-1,6-anhydro-β-D-galactopyranose has also been reported by Whistler and Seib[3] which must be the second example of the series.

Incidentally, several papers on levoglycosans, parent compounds of thiolevoglycosans, have been reported in literature in this year.[4] Since levoglucosan is an easily accessible D-glucose derivative preserving the 1C conformation, it can conceivably be useful as a potential intermediate in synthetic works.

As part of a program in this laboratory on the synthesis of thiosugars, the thiolevoglucosan formation has now been extended to 2-deoxy-D-glucose in which a neighboring group participation at the anomeric position by the oxy anion at C2 is eliminated. The present work describes the preparation of 2-deoxy-thiolevoglucosan and 2-deoxy-3,4-anhydro-thiolevoaltrosan both of which have been prepared by starting with 3,4,6-tri-O-acetyl-D-glucal (I).*3

Tosylation of D-glucal (II) with an equimolecular amount of tosyl chloride in pyridine, followed by acetylation, yielded 3,4-di-O-acetyl-6-O-tosyl-D-glucal (III), m.p. 106~107°, $[\alpha]_D^{22}$+14°, in 74% yield. The structure was characterized by infrared spectrum in nujol which showed the presence of tosyl (1175 cm^{-1}) and carbon-carbon double bond (1650 cm^{-1}), and by the satisfactory elemental analysis. In addition, the tosyl was easily replaced with potassium acetate in boiling acetic anhydride to regenerate the starting material (I). The fact shows that III has a primary tosyl group. The replacement con-

---

*1 Part X. S. Ishiguro, S. Tejima: This Bulletin, **15**, 255 (1967).

*2 Kita-15-jo, Nishi-7-chome, Sapporo (槇 孝雄, 手島節三).

*3 Regarding the addition products of I, following papers have been reported from our laboratory. M. Akagi, S. Tejima, H. Nakamura: Yakugaku Zasshi, **82**, 1337 (1962); H. Nakamura, S. Tejima, M. Akagi: This Bulletin, **12**, 1302 (1964); **14**, 648 (1966); T. Maki, H. Nakamura, S. Tejima, M. Akagi: *Ibid.*, **13**, 764 (1965).

1) M. Akagi, S. Tejima, M. Haga: This Bulletin, **11**, 58 (1963).

2) J. Staněk, M. Černý, J. Kocourek, J. Pacák: "The Monosaccharides" 363 (1963), Academic Press Inc., New York and London; H. Paulsen: Angew. Chem., **78**, 501 (1966).

3) R. L. Whistler, P. A. Seib: Carbohydrate Research, **2**, 93 (1966).

4) D. Horton, J. S. Jewell: *Ibid.*, **2**, 251 (1966); E. R. Ruckel, C. Schuerch: J. Org. Chem., **31**, 2233 (1966); G. G. S. Dutton, K. N. Slessor: Can. J. Chem., **44**, 1069 (1966).

dition was the similar to that reported by Helferich and Gnüchtel[5] who replaced the primary mesyl in methyl 2,3,4,6-tetra-O-mesyl-α-D-glucopyranoside.

Although few papers have been reported on sulfonated D-galactal[6] and pseudoglycals,[7] regarding partly sulfonated D-glucals, so far as we know, not yet have been referred in literature. Accordingly, the product (Ⅲ) must be an useful intermediate for studies on unsaturated sugars which have now been exciting remarkable interests.*[1,8] Therefore, with the aim of establishing a simpler preparative method of Ⅲ, a modification involving the reduction of 6-O-tosyl-2,3,4-tri-O-acetyl-α-D-glucopyranosyl bromide[9] with zinc in acetic acid was designed, while it was unsuccessful.

Attempts were next made to synthesize 2-deoxy-6-O-tosyl-3,4-di-O-acetyl-β-D-glucopyranosyl ethylxanthate (Ⅵ). Product (Ⅲ) was treated with a saturated solution of hydrogen bromide in benzene for thirty minutes at 0°, and then the excess bromide removed completely to give a sirup (Ⅴ), $[\alpha]_D^{16}+111.3°$. The procedure was in the similar fashion to that used by Novák and Šorm[10] in the addition of hydrogen bromide upon I. A mixture of Ⅴ and potassium ethylxanthate in dry acetone was refluxed for fifteen minutes. Crystals (Ⅵ), m.p. 110~112°, $[\alpha]_D^{20}-35.5°$, were obtained from the reaction mixture. The identical product was also formed by starting with 2-deoxy-D-glucopyranosyl ethylxanthate (Ⅳ),[11] *via* one mole tosylation and sequential acetylation. An ethanolic solution of Ⅵ showed the absorption maximum at 274 mμ, characteristic of the thiocarbonyl, and the infrared spectrum in nujol showed the presence of tosyl (1180 cm^{-1}), which were in consistent with the postulated structure.

Recently, Lundt and Pedersen[12] have reported on the addition of hydrogen fluoride upon acylated D-glucals in benzene with the aim of separating stable acylated 2-deoxy-D-glucopyranosyl fluorides. However, in contrast to their expectation, stable fluorides could not be isolated, while unstable sirups which were believed to be 2,3-didehydro-2,3-dideoxy-4,6-di-O-acyl-D-erythrohexosyl fluorides were obtained. The finding would be of interest as compared with that of hydrogen bromide.

Treatment of Ⅵ with sodium methoxide with a similar procedure for the preparation of thiolevoglucosan[1] gave 2-deoxy-thiolevoglucosan in 84% yield, which was isolated as a crystalline diacetate (Ⅶ), m.p. 79~81°, $[\alpha]_D^{23}-128°$. The product showed neither tosyl (1180 cm^{-1}) by infrared nor thiocarbonyl (274 mμ) by ultraviolet. Reductive desulfurization with Raney nickel gave 1,5-anhydro-2,6-dideoxy-3,4-di-O-acetyl-D-glucitol (Ⅷ), m.p. 39~40°, $[\alpha]_D^{22}+45.5°$ in 85% yield.

Deacetylation of Ⅵ with cold methanolic ammonia afforded 2-deoxy-thiolevoglucosan (Ⅸ) in 80% yield. The product, m.p. 189~192°, $[\alpha]_D^{22}-71.7°$, was easily recrystallizable from ethyl acetate and showed a satisfactory elemental analysis.

Thus, the facile formation of 2-deoxy-thiolevoglucosan from Ⅵ not only indicates that 1,6-anhydro-1,6-sulfide ring formation involves direct participation of the sulfur atom on C1 as has been mentioned in the previous papers from our laboratory,[1,13] but also the β-configuration of the xanthate group in Ⅵ.

5) B. Helferich, A. Gnüchtel: Ber., **71**, 712 (1938).
6) A.B. Foster, W.G. Overend, M. Stacey, L. Wiggins: J. Chem. Soc., **1949**, 2542.
7) S. Laland, W.G. Overend, M. Stacey: *Ibid.*, **1950**, 738; D.M. Cimen, R.J. Ferrier, W.G. Overend: *Ibid.*, **1966**, 446.
8) R.J. Ferrier: "Advances in Carbohydrate Chemistry" Vol. 20, 67 (1965), Academic Press Inc., New York and London.
9) J. Compton: J. Am. Chem. Soc., **60**, 395 (1938).
10) J.J.K. Novák, F. Šorm: Collection Czechoslov. Chem. Communs., **27**, 902 (1962).
11) T. Maki, H. Nakamura, S. Tejima, M. Akagi: This Bulletin, **13**, 764 (1965).
12) I. Lundt, C. Pedersen: Acta Chem. Scand., **20**, 1369 (1966).
13) M. Akagi, S. Tejima, M. Haga: This Bulletin, **10**, 905, 1039 (1962).

In 1920 Fischer, *et al.*[14] recorded that when I and hydrogen bromide were treated in acetic acid gave a crystalline "diacetyl D-glucal hydrobromide", which on reacetylation yielded a "triacetyl D-glucal hydrobromide". Later, Davoll and Lythgoe[15] reinvestigated Fisher's work, however, they were unable to isolate the compound Fischer described.

Accordingly, it is noteworthy to describe that when a solution of III in glacial acetic acid containing hydrogen bromide was left to stand for three hours at room temperature, crystals (X), m.p. 113.5~114°, $[\alpha]_D^{24}$ +126°, were obtained in 75% yield. The product was not identical with the sirupy bromide (V), obtained from III by treatment with hydrogen bromide in benzene.

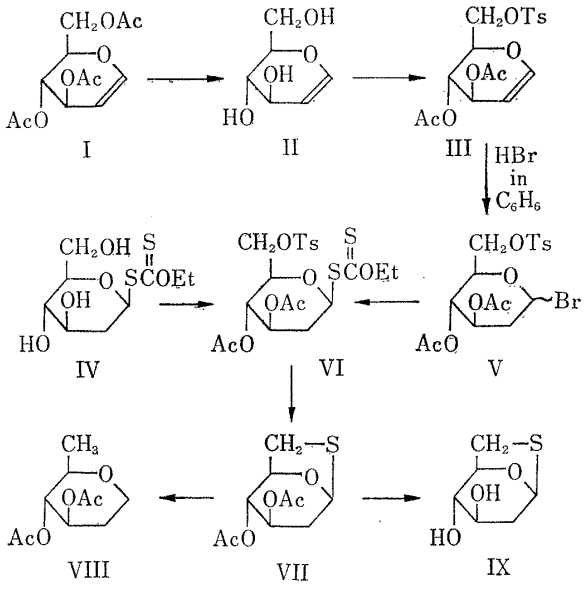

Chart 1.

The product (X) showed a violet coloration with the Dische reagent for 2-deoxysugars,[16] and involved an active bromine which was easily replaceable with methoxy by the Koenigs-Knorr glycosidation to give a crystalline glycoside (XI), m.p. 132°, $[\alpha]_D^{16}$ −10°. It is of interest to notice the resulted glycoside still involved a bromine atom. The nuclear magnetic resonance spectrum of X exhibited a triplet at τ 3.65 (anomeric proton), a multiplet at τ 7.21 (methylene at C2), a singlet at τ 7.53 (methyl in tosyl),and a singlet at τ 7.88 corresponding to one acetyl. The elemental analyses of X and XI were in good agreement with that of $C_{15}H_{18}Br_2O_6S$ and $C_{16}H_{21}BrO_7S$, respectively. From the data mentioned above, the authors postulated the structure of X to be 2-deoxy-3-bromo-3-deoxy-D-hexopyranosyl bromide. The comparatively large dextrorotatory value would suggest the α-configuration of the anomeric bromide. According to nuclear magnetic resonance studies of the bromination of I[17] have shown that tri-O-acetyl-2-bromo-2-deoxy-α-D-glucopyranosyl bromide (60%) and tri-O-acetyl-2-bromo-2-deoxy-α-D-mannopyranosyl bromide (30%) are the main products. Thus, it is remarkable that the 2-deoxy glycosyl halides having an axial halogen atom are, presumably, formed preferentially, which would support our α-configuration.

Treatment of X with potassium thiolacetate or ethylxanthate in dry acetone afforded crystals (XII) or (XIII), respectively. The product (XII), m.p. 143~145°, $[\alpha]_D^{19}$ −5°, showed the presence of tosyl (1182 cm^{-1}) and thioacetyl (1710 cm^{-1}) by infrared. The product (XIII), m.p.127~128°, $[\alpha]_D^{17}$ −27.1°, showed the presence of tosyl (1175 cm^{-1}) and thioketone (274 mμ) by infrared and ultraviolet, respectively.

Treatment of XIII with sodium methoxide by the similar procedure in the formation of 2-deoxy-thiolevoglucosan, afforded a solid which was recrystallized from cyclohexane to give pure crystals (XIV), m.p. 69~72°, $[\alpha]_D^{23}$ −108° in 70% yield. The product showed neither Beilstein's bromine test, absorptions at 3200~3500 (hydroxyl), 1745 (acetyl), 1175 cm^{-1} (tosyl) by infrared, nor thioketone (274 m) by ultraviolet. However, it showed absorptions at 865, 1165 and 1205 cm^{-1} corresponding to epoxide by infrared. The elemen-

14) E. Fischer, M. Bergmann, H. Schotte : Ber., **53**, 517 (1920).
15) J. Davoll, B. Lythgoe : J. Chem. Soc., **1949**, 2526.
16) R.E. Deriaz, M. Stacey, E.G. Teece, L. Wiggins : *Ibid.*, **1949**, 1222.
17) R.U. Lemieux, B. Fraser-Reid : Can. J. Chem., **42**, 532 (1964); R.U. Lemieux, S. Levine : *Ibid.*, **42**, 1473 (1964).

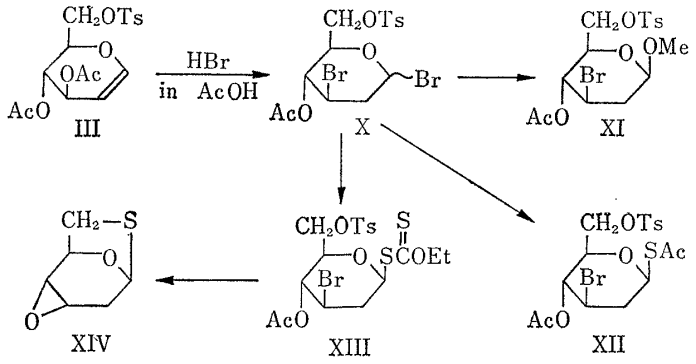

Chart 2.

tal analysis was in good agreement with that of $C_6H_8O_2S$.

Therefore, treatment of XIII with sodium methoxide resulted in simultaneous formation of the epoxide and the 1,6-anhydro-1,6-sulfide rings. The epoxide formation indicates that the orientations of the hydroxyl at C4 and bromine at C3 must be *trans*, thus the bromine at C3 in compounds (X, XI, XII and XIII) must be the same configuration with D-glucose.

The product (XIV) would be of interest as a thio analogue of 3,4; 1,6-dianhydro-β-D-altropyranose, m.p. 104~106°, $[\alpha]_D^{18}$ −76°, which has been reported by **Černý**, *et al.*[18]

Further studies on the addition of hydrogen bromide upon I and III in glacial acetic acid has now been in progress in our laboratory and the details will be reported in future.

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

6-O-Tosyl-3,4-di-O-acetyl-D-glucal (III)——To a solution of D-glucal[19] (3 g.) in dry pyridine (30 ml.) was added gradually, under ice-cooling and stirring, a solution of tosyl chloride (4 g.) in dry pyridine (12 ml.), and the mixture was stirred for further 1 hr. at 0°. After standing for 48 hr. at room temperature protected from moisture, the mixture was treated with Ac_2O (30 ml.) with stirring, then allowed to stand an additional 20 hr. The mixture was poured into ice-H_2O (500 ml.) and the resulted sirupy product solidified by scratching the side of the flask and successive standing for several hours. The solid was separated by filtration and recrystallized from EtOH to give pure material (4 g., 74%), m.p. 106~107°, $[\alpha]_D^{22}$ +14°(c=1, $CHCl_3$). IR λ_{max}^{Nujol} cm^{-1} : 1175 (SO_2-O), 1650 (C=C). *Anal.* Calcd. for $C_{17}H_{20}O_8S$: C, 53.12; H, 5.22. Found : C, 53.07; H, 5.31. The product was not so stable and decomposed in the air for two weeks.

3,4,6-Tri-O-acetyl-D-glucal (I) from III——A mixture of III (2 g.) and AcOK (2 g.) in Ac_2O (30 ml.) was refluxed for 1 hr. in an oil bath. The mixture was poured into ice-H_2O (200 ml.), allowed to stand for 5 hr. at room temperature, then the solution was extracted with $CHCl_3$ (20 ml. × 3). The organic layer was washed successively with aq. $NaHCO_3$ and H_2O. A sirup which was obtained on solvent removal from the dried extract, crystallized by trituration with a small amount of EtOH and sequential standing in a refrigerator. Recrystallization from EtOH gave pure material (0.8 g., 57%), m.p. 54°, $[\alpha]_D^{20}$ −20°(c=1, $CHCl_3$). The product was indistinguishable with an authentic 3,4,6-tri-O-acetyl-D-glucal (I) by IR.

2-Deoxy-6-O-tosyl-3,4-di-O-acetyl-β-D-glucopyranosyl Ethylxanthate (VI)——a) From 2-deoxy-β-D-glucopyranosyl ethylxanthate (IV)[11] : Preferential tosylation of IV (4 g.) in pyridine (30 ml.) with a solution of tosyl chloride (3.1 g., 1.1 mole) in pyridine (10 ml.) and subsequent acetylation with Ac_2O (30 ml.) according to the preparation of III afforded a solid which recrystallized from EtOH to give pure material (7 g., 93%), m.p. 110~112°, $[\alpha]_D^{20}$ −33° (c=0.5, $CHCl_3$). UV λ_{max}^{EtOH} mμ : 274 (C=S). IR λ_{max}^{Nujol} cm^{-1} : 1180 (SO_2-O). *Anal.* Calcd. for $C_{20}H_{26}O_9S_3$: C, 47.41; H, 5.17; S, 18.99. Found : C, 47.52; H, 5.42; S, 18.94.

b) From 6-O-tosyl-3,4-di-O-acetyl-D-glucal (III) : A solution of III (3 g.) in dry benzene (20 ml.) was saturated with HBr under ice-cooling. After standing at 0° for 30 min. the solvent was evaporated to give a sirup which was dissolved in dry benzene (10 ml.) and evaporated again. The procedure was further repeated twice. The resulted sirupy 2-deoxy-6-O-tosyl-3,4-di-O-acetyl-D-glucopyranosyl bromide (V) had $[\alpha]_D^{16}$ +111.3°

18) M. Černý, J. Pacák, J. Staněk : Collection Czechoslov. Chem. Communs., **30**, 1151 (1965).
19) W. Roth, W. Pigman : "Methods in Carbohydrate Chemistry" Vol. II, 405 (1963). Academic Press Inc., New York and London.

(c=0.79, $CHCl_3$). A mixture of V (3.6 g.) and potassium ethylxanthate (2.7 g.) in dry acetone (25 ml.) was refluxed for 15 min. After cooling, the mixture was poured into ice-H_2O (600 ml.). The resultant precipitate was collected by filtration and recrystallized from EtOH to give pure material (3.2 g., 56%), m.p. 110~113°, $[\alpha]_D^{20}$ −35.5°(c=1, $CHCl_3$). The product was indistinguishable with a sample prepared by method a) by IR.

2-Deoxy-6-thio-3,4-di-O-acetyl-1,6-anhydro-β-D-glucopyranose (2-Deoxy-3,4-di-O-acetyl-thiolevoglucosan) (VII)——A solution of VI (10 g.) in MeOH (125 ml.) containing Na (2 g.) was allowed to stand overnight at room temperature. The mixture was neutralized with 50% AcOH until a drop of the solution was neutral to phenolphthalein. The solvent was removed to dryness. Acetylation was effected overnight at room temperature with Ac_2O (50 ml.) in pyridine (60 ml.) and the solution was poured into ice-H_2O. It was extracted with $CHCl_3$ (40 ml. × 3) and the organic layer was washed successively with ice-cold 3*N*-H_2SO_4, aq. $NaHCO_3$ and H_2O. Moisture was removed with Na_2SO_4 and the solution concentrated to give a sirup which was dissolved in EtOH. On standing in a refrigerator it deposited a crystalline product (4.1 g., 84%). Recrystallization from EtOH gave pure material, m.p. 79~81°, $[\alpha]_D^{23}$ −128° (c=0.5, $CHCl_3$). *Anal.* Calcd. for $C_{10}H_{14}O_5S$: C, 48.76; H, 5.63. Found : C, 48.88; H, 5.63. The product lost a strong absorption of sulfonyl in VI (1180 cm^{-1}) by IR along with that of thiocarbonyl (274 mμ) by UV.

1,5-Anhydro-2,6-dideoxy-3,4-di-O-acetyl-D-glucitol (VIII)——A solution of VII (3 g.) in EtOH (50 ml.) was treated with freshly prepared Raney Ni (40 g. of alloy was activated) and the resulted suspension was refluxed gently for 6 hr. Nickel was removed by filtration and washed throughly with EtOH. The combined filtrate and washings were concentrated to give a colorless oil which was dissolved in dry ether. The insoluble precipitate was removed by filtration and the solvent was evaporated from the filtrate to give an oil (2.3 g., 85%), $[\alpha]_D^{20}$ +43°(c=1, EtOH). The product was dissolved in benzene (10 ml.) and chromatographed on silica gel (25 g.). From the eluate of benzene (150 ml.), crystals, m.p. 39~40°, $[\alpha]_D^{22}$ +45.5°(c=1, EtOH) were obtained afted evaporation of the solvent and successive standing in a vacuum desiccator. *Anal.* Calcd. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found : C, 55.53; H, 7.55.

2-Deoxy-6-thio-1,6-anhydro-β-D-glucopyranose (2-Deoxy-thiolevoglucosan) (IX)——To a chilled MeOH (6 ml.) containing dry NH_3 saturated at 0° was added VII (0.5 g.). The mixture was left to stand overnight at room temperature. The solvent was removed to give a sirup which was triturated with a small amount of AcOEt to crystallize. The crystals were collected by filtration and recrystallized from AcOEt to give pure material (0.2 g., 60%), m.p. 189~192°, $[\alpha]_D^{22}$ −71.7°(c=0.53, MeOH). *Anal.* Calcd. for $C_6H_{10}O_3S$: C, 44.43; H, 6.21; S, 19.77. Found : C, 44.55; H, 6.08; S, 19.85.

3-Bromo-4-O-acetyl-6-O-tosyl-2,3-dideoxy-α-D-glucopyranosyl Bromide (X)——A solution of III (10 g.) in glacial AcOH (55 ml.) containing 32% HBr was left to stand for 3 hr. at room temperature. The mixture was diluted with $CHCl_3$ (200 ml.), and the solution was washed with ice-H_2O, aq. $NaHCO_3$, and H_2O, respectively. Moisture was removed over $CaCl_2$, filtered, and the solvet was removed from the filtrate to afford a sirup. Crystallization was induced by addition of a small amount of dry ether and scratching the side of the flask. The crystals were separated by filtration and recrystallized from dry benzene-petr. ether to give pure material (9.5 g., 75%), m.p. 113.5~114°(decomp.), $[\alpha]_D^{24}$ +126° (c=0.5, $CHCl_3$). The AcOH-solution showed a violet coloration with the Dische test for 2-deoxysugars.[16] *Anal.* Calcd. for $C_{15}H_{18}O_6SBr_2$: C, 37.05; H, 3.73; S, 6.60; Br, 32.87. Found : C, 37.15; H, 3.79; S, 6.76; Br, 32.62. The NMR spectrum showed a triplet at τ 3.65 (anomeric proton), a multiplet at τ 7.21 (methylene protons at C2), a singlet at τ 7.53 (methyl proton in tosyl) and a singlet at τ 7.88 (methyl protons in acetyl).

Methyl 3-Bromo-4-O-acetyl-6-O-tosyl-2,3-dideoxy-β-D-glucopyranoside (XI)——A mixture of X (1 g.) and Ag_2CO_3 (1.5 g.) in MeOH (8 ml.) was stirred for 30 min. at room temperature. Chloroform (5 ml.) was added to the solution and stirring was continued for further 10 min. After filtration, the solvent was removed to give a solid which was recrystallized from MeOH to give pure material (0.8 g., 90%), m.p. 132°, $[\alpha]_D^{16}$ −10°(c=0.5, $CHCl_3$). *Anal.* Calcd. for $C_{16}H_{21}O_7SBr$: C, 43.94; H, 4.84; S, 7.33; Br, 18.27. Found : C, 44.11; H, 4.95; S, 7.45; Br, 18.15.

1-S-Acetyl-1-thio-3-bromo-4-O-acetyl-6-O-tosyl-2,3-dideoxy-β-D-glucopyranose (XII)——A mixture of X (2 g.) and AcSK (0.56 g.) in dry acetone (15 ml.) was refluxed for 10 min. After cooling, the resulted precipitate was removed by filtration. The filtrate was concentrated to give a sirup which crystallized by addition of EtOH and scratching the side of the flask. Crystals (1.4 g., 73%) were collected by filtration and recrystallized from EtOH to give pure material, m.p. 143~145°, $[\alpha]_D^{19}$ −5 (c=0.5, $CHCl_3$). IR λ_{max}^{Nujol} cm^{-1} : 1182 (O-SO_2), 1710 (SAc). *Anal.* Calcd. for $C_{17}H_{21}O_7S_2Br$: C, 42.41; H, 4.38; S, 13.32; Br, 16.60. Found : C, 42.40; H, 4.51; S, 13.08; Br, 16.94.

3-Bromo-4-O-acetyl-6-O-tosyl-2,3-dideoxy-β-D-glucopyranosyl Ethylxanthate (XIII)——A mixture of X (1 g.) and potassium ethylxanthate (0.4 g.) in dry acetone (8 ml.) was refluxed for 15 min. After cooling, the mixture was poured into ice-H_2O and the resulted solid was separated by filtration (1 g., 92%). Twice recrystallizations from EtOH and finally from dry ether gave pure material, m.p. 127~128°, $[\alpha]_D^{17}$ −27.1° (c=0.6, $CHCl_3$). IR λ_{max}^{Nujol} cm^{-1} : 1175 (O-SO_2). UV λ_{max}^{EtOH} mμ : 274. *Anal.* Calcd. for $C_{18}H_{23}O_7S_3Br$: C, 40.98; H, 4.41; S, 18.24; Br, 15.15. Found : C, 40.95; H, 4.32; S, 18.10; Br, 15.41.

2-Deoxy-6-thio-1,6-anhydro-3,4-anhydro-β-D-altrose (2-Deoxy-3,4-anhydro-thiolevoaltrosan) (XIV)——A mixture of XIII (1 g.) in MeOH (20 ml.) containing Na (0.25 g.) was allowed to stand overnight at room temperature. The mixture was neutralized with 50% AcOH until a drop of the solution was neutral to

phenolphthaleine. The solvent was removed to give a solid which was extracted with $CHCl_3$ and filtered. The filtrate was washed with ice-H_2O, the $CHCl_3$-layer dried over $CaCl_2$ and filtered. The solvent was removed to afford crystals which crystallized after standing in a vacuum desiccator. Recrystallization from dry cyclohexane gave pure material (0.34 g., 70%), m.p. 69~72°, $[\alpha]_D^{23}$ −108°(c=1, $CHCl_3$). IR λ_{max}^{Nujol} cm^{-1}: 865, 1165, 1205 (epoxide). *Anal.* Calcd. for $C_6H_8O_2S$: C, 49.98; H, 5.59; S, 22.24. Found: C, 49.97; H, 5.79; S, 22.39. The product showed neither Beilstein's bromine test, absorptions at 3200~3500 (OH), 1745 (OAc), 1175 cm^{-1} (O-SO_2) by IR nor thioketone (274 mμ) by UV.

The authors indebted to Mr. S. Shimokawa of School of Technology, Hokkaido University 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 elemental analyses.