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Thiosugars. XVIII.[1] Synthesis of 2-Acylamino-1,6-anhydro-2,6-dideoxy-6-thio-β-D-glucopyranose

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As a supplement of our program aimed at the synthesis and reaction of 1,6-anhydro-6-deoxy-6-thio-β-mono- and di-saccharides, those of the corresponding derivative of 2-acylamino-2-deoxy-β-D-glucopyranose (acyl=acetyl or benzoyl) were described.

Synthesis of 1,6-anhydro-2-benzamido-2-deoxy-β-D-glucopyranose and acetolysis products of the diacetate were also reported.

Much attention has been devoted to the chemistry of 1,6-anhydro-β-aldopyranoses[3] owing to the validity of the compounds as starting materials for chemical modification[4] and polymerization[5] of aldopyranoses. However, a little work has been carried out about those of amino sugars.

In 1956, Micheel and Wulff[6] reported, when 3,4,6-tri-O-acetyl-2-*p*-toluenesulfonamide-β-D-glucopyranosyl fluoride was treated with excess hot methanolic sodium methoxide, the formation of 1,6-anhydro-2-deoxy-2-*p*-toluenesulfonamido-β-D-glucopyranose (I), which might be the first reported example of 1,6-anhydro derivative in amino sugars. In 1962, 2-acetamido-1,6-anhydro-2-deoxy-β-D-glucopyranose (II) was firstly synthesized[7] by treatment of 2-acetamido-1,3,4-tri-O-acetyl-2-deoxy-6-O-*p*-toluenesulfonyl-β-D-glucopyranose with methanolic sodium methoxide. In the next year, compound II having almost identical melting point and specific rotation with our preparation was synthesized from I by Micheel and Michaelis.[8] Syntheses of 2-amino-1,6-anhydro-2-deoxy- and 4-amino-1,6-anhydro-4-deoxy-β-D-talopyranoses were reported by Horton, *et al.*[9] Among the reported papers, it is quite interesting to notice that some derivatives of II have recently been pointed out from two different laboratories as a favorable starting material for syntheses of (1→4)-linked disaccharides bearing a 2-acetamido-2-deoxy-D-glucopyranose.[10] However, no paper has been reported about thio analog that has a sulfur atom in the 1,6-anhydro ring.

In this paper we describe the first synthesis of the title compound (acyl=acetyl (VIII), benzoyl (XII)) as a supplement of our program for the study of the synthesis and reactivity of 1,6-anhydro-6-deoxy-6-thio-β-mono- and di-saccharides. The flow sheet of the synthesis (Chart 1) and the method of the structural assignment were almost similar to those of other

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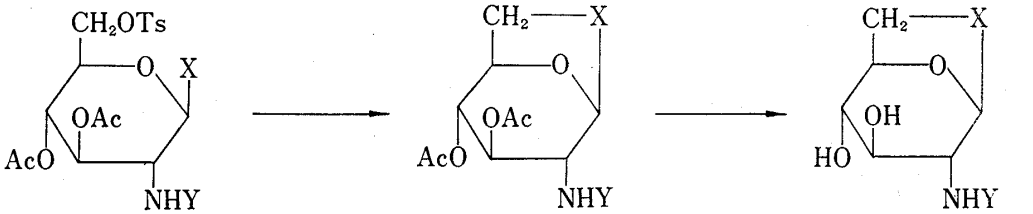

III: X=SSCOEt, Y=Ac
X: X=SSCOEt, Y=Bz
IX: X=OAc, Y=Bz

IV: X=S, Y=Ac
XI: X=S, Y=Bz
XIII: X=O, Y=Bz

VIII: X=S, Y=Ac
XII: X=S, Y=Bz
XIV: X=O, Y=Bz

Bz=benzoyl, Ts=tosyl

Chart 1

1,6-anhydro-6-deoxy-6-thio-β-derivatives in aldopyranoses,[11] lactose,[12] cellobiose,[13] and maltose.[1]

Reductive desulfurization of 2-acetamido-3,4-di-O-acetyl-1,6-anhydro-2,6-dideoxy-6-thio-β-D-glucopyranose (IV), followed by de-O-acetylation, afforded crystalline 2-acetamido-1,5-anhydro-2,6-dideoxy-D-glucitol (VI). Acetolysis of IV effected cleavage of the 1,6-anhydro-6-thio ring to give 2-acetamido-1,3,4-tri-O-acetyl-6-S-acetyl-2,6-dideoxy-6-thio-α-D-glucopyranose (VII) in 68% yield. On the one hand, acetolysis of 3,4-di-O-acetyl-1,6-anhydro-2-benzamido-2,6-dideoxy-6-thio-β-D-glucopyranone (XI) gave a complex mixture as judged by thin-layer chromatography (TLC). Therefore, further detail is under investigation.

From the correlation of elucidation of the acetolysis mentioned above, we synthesized 3,4-di-O-acetyl-1,6-anhydro-2-benzamido-2-deoxy-β-D-glucopyranose (XIII) and investigated the acetolysis products. When it was carried out under moderate condition, 4,5-(3,4,6-tri-O-acetyl-2-deoxy-D-glucopyrano)-2-phenyl-Δ^2-oxazoline (XV)[14,15] and 2-acetamido-3,4,6-tri-O-acetyl-1-O-benzoyl-2-deoxy-α-D-glucopyranose (XVI)[16] were separated in almost equal amounts. While prolonged the reaction time made disappearance of XV and yielded XVI in 73% as the sole product.

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and uncorrected. Solutions were evaporated in a rotary evaporator below 50° under vacuum. Optical rotations were measured with a Yanagimoto Model OR-10 polarimeter. Infrared (IR) spectra were recorded with a Jasco Model IR-S spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded, unless otherwise noted, at 60 MHz with a Jeol Model JNM-MH-60 spectrometer. Tetramethylsilane was used as the internal standard in $CDCl_3$. TLC and preparative TLC on Silica Gel GF_{254} (E. Merck, Darmstadt, Germany) activated at 110° was performed with solvent systems (A) 3: 1 (v/v) $CHCl_3$–acetone, (B) 6: 1 $CHCl_3$–acetone. Detection was effected with H_2SO_4 or ultraviolet (UV) light (short wave length). Column chromatography was performed on a column of Wako-gel C-200 as the adsorbent.

2-Acetamido-3,4-di-O-acetyl-2-deoxy-6-O-*p*-toluenesulfonyl-β-D-glucopyranosyl Ethylxanthate (III)—To a stirred solution of 2-acetamido-1,3,4-tri-O-acetyl-2-deoxy-6-O-*p*-toluenesulfonyl-β-D-glucopyranose[7] (11 g) in dry $CHCl_3$ (66 ml) was added dropwise a solution of $TiCl_4$ (4.4 g) in dry $CHCl_3$ (13 ml) at room temperature. The mixture, protected from moisture, was boiled under reflux for 5 hr, cooled, and then poured into ice-H_2O (100 ml). The organic layer was separated, washed with ice-H_2O (3×100 ml), dried ($CaCl_2$), and evaporated to give a sirup, which was used without further purification. Yield 10 g. $[\alpha]_D^{15}$ +82.9° (c= 1.5, $CHCl_3$).

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To the sirupy chloride were added potassium ethylxanthate (3.4 g) and EtOH (60 ml). The mixture was refluxed for 15 min on a steam bath, cooled, and then poured into ice-H_2O (800 ml), which was kept for 15 hr at 5° to solidify. The solid was collected by filtration, air-dried, and recrystallized twice from EtOH to give III (8.4 g, 68%), mp 176—177° (decomp.), $[\alpha]_D^{20}$ +20.5° (c=0.8, $CHCl_3$). TLC: *Rf* 0.40 (solvent A). UV λ_{max}^{EtOH} mμ (ε): 275 (10700). NMR ($CDCl_3$) δ ppm: 1.44 (3H, t, J=6 Hz, CH_3–$C\underline{H}_3$), 1.94 (3H, s, NAc), 2.05 (6H, s, 2×Ac), 2.46 (3H, s, C_6H_4–$C\underline{H}_3$), 5.51 (1H, d, $J_{1,2}$=7 Hz, H-1), 6.19 (1H, br. d, J=8 Hz, NH, disappeared with addition of D_2O). *Anal.* Calcd. for $C_{22}H_{29}O_{10}NS_3$: C, 46.88; H, 5.18; N, 2.48. Found: C, 46.62; H, 5.25; N, 2.39.

2-Acetamido-3,4-di-O-acetyl-1,6-anhydro-2,6-dideoxy-6-thio-β-D-glucopyranose (IV)——A mixture of III (9 g) with 0.7M methanolic sodium methoxide (112.5 ml) was stirred for 30 min at room temperature. After keeping overnight, the mixture was made neutral with AcOH, filtered, and the filtrate was evaporated to dryness. The residue was acetylated with Ac_2O (36 ml) and pyridine (36 ml) for 24 hr at 0°. The completely dried sirup, obtained by repeated azeotropic distillation with toluene, was dissolved in $CHCl_3$ (100 ml), and filtered. The filtrate was washed with ice-H_2O and dried ($MgSO_4$). After treatment with charcoal, the solvent was removed to give an amorphous powder, which crystallized from EtOH–petr. ether (bp 30—70°). After being kept overnight, the crystals (4.2 g) were collected by filtration. Twice recrystallizations from EtOH–petr. ether gave pure IV (3.8 g, 78%), mp 156—157°, $[\alpha]_D^{19}$ −70.4° (c=0.9, $CHCl_3$). TLC: *Rf* 0.32 (solvent A). NMR ($CDCl_3$) δ ppm: 2.05 (3H, s, NAc), 2.13, 2.17 (6H, s, 2×Ac), 5.33 (1H, s, H-1), 6.60 (1H, br. d, J=8 Hz, NH). *Anal.* Calcd. for $C_{12}H_{17}O_6NS$: C, 47.52; H, 5.65; N, 4.62. Found: C, 47.77; H, 5.71; N, 4.67.

2-Acetamido-3,4-di-O-acetyl-1,5-anhydro-2,6-dideoxy-D-glucitol (V)——A mixture of IV (200 mg) and freshly activated Raney Ni catalyst, prepared from 220 mg of alloy, in AcOEt (4 ml) was boiled under reflux for 3 hr. The Ni was removed by filtration and washed with $CHCl_3$. The combined filtrate and washings were evaporated to dryness to afford a sirup, which crystallized from EtOH–petr. ether. The crystals were collected by filtration and recrystallized from the same solvent to yield pure V (90 mg, 45%), mp 162—163°, $[\alpha]_D^{19}$ +3° (c=1.2, $CHCl_3$). TLC: *Rf* 0.33 (solvent A). NMR ($CDCl_3$) δ ppm: 1.28 (3H, d, $J_{5,6}$=6 Hz, C–CH_3), 2.00 (3H, s, NAc), 2.12 (6H, s, 2×Ac), 6.45 (1H, br. d, J=8 Hz, NH). *Anal.* Calcd. for $C_{12}H_{19}O_6N$: C, 52.74; H, 7.01; N, 5.13. Found: C, 52.80; H, 7.06; N, 5.10.

2-Acetamido-1,5-anhydro-2,6-dideoxy-D-glucitol (VI)——To a chilled solution of V (100 mg) in dry MeOH (2 ml) was added 0.7M methanolic sodium methoxide (0.2 ml) at 0°. The mixture was kept for 15 hr at 5°. Dry Amberlite IR-120 (H^+) resin was added, the suspension was stirred for 30 min, filtered, and removal of the solvent afforded an amorphous solid, which crystallized from EtOH–petr. ether. Recrystallization from the same solvent gave pure VI (50 mg, 76%), mp 177—178°, $[\alpha]_D^{14}$ −19.3° (c=0.3, H_2O). IR ν_{max}^{Nujol} cm^{-1}: 3400—3200 (OH), 1640, 1540 (CONH). *Anal.* Calcd. for $C_8H_{15}O_4N$: C, 50.76; H, 7.99; N, 7.41. Found: C, 50.59; H, 8.07; N, 7.35.

2-Acetamido-1,3,4-tri-O-acetyl-6-S-acetyl-2,6-dideoxy-6-thio-α-D-glucopyranose (VII)——Compound IV (230 mg) was dissolved in acetolysis mixture (4.6 ml; 70:30:1 (v/v) Ac_2O–AcOH–H_2SO_4). After stirring for 17 hr at room temperature, the solution was poured into ice-H_2O (100 ml). The mixture was stirred for 4 hr, neutralized with $NaHCO_3$, and then extracted with $CHCl_3$ (3×10 ml). The combined extracts were washed with H_2O, dried, and decolorized with charcoal. Removal of the solvent afforded an amorphous powder, which crystallized from EtOH–petr. ether. The crystals were collected by filtration and recrystallized from the same solvent to afford pure VII (210 mg, 68%), mp 170—171°, $[\alpha]_D^{18}$ +88.5° (c=0.9, $CHCl_3$). TLC: *Rf* 0.28 (solvent A). IR ν_{max}^{Nujol} cm^{-1}: 3270 (NH), 1745 (OAc), 1685 (SAc), 1655, 1545 (CONH). NMR ($CDCl_3$) δ ppm: 1.94 (3H, s, NAc), 2.05, 2.10, 2.19 (9H, s, 3×Ac), 2.37 (3H, s, SAc), 6.15 (1H, d, $J_{1,2}$=3.5 Hz, H-1), 6.28 (1H, br. d, J=9 Hz, NH). *Anal.* Calcd. for $C_{16}H_{23}O_9NS$: C, 47.40; H, 5.72; N, 3.45. Found: C, 47.16; H, 5.68; N, 3.46.

2-Acetamido-1,6-anhydro-2,6-dideoxy-6-thio-β-D-glucopyranose (VIII)——De-O-acetylation of IV (1 g) was similarly performed as described for the preparation of VI to yield a solid. Recrystallization from EtOH gave pure VIII (0.5 g, 69%), mp 174—175°, $[\alpha]_D^{18}$ −26.6° (c=1.3, H_2O). IR ν_{max}^{Nujol} cm^{-1}: 3400—3200 (OH), 1630, 1525 (CONH). Negative Fehling test. *Anal.* Calcd. for $C_8H_{13}O_4NS$: C, 43.80; H, 5.98; N, 6.39. Found: C, 43.78; H, 5.93; N, 6.39.

1,3,4-Tri-O-acetyl-2-benzamido-2-deoxy-6-O-*p*-toluenesulfonyl-β-D-glucopyranose (IX)——To a chilled solution of 1,3,4-tri-O-acetyl-2-amino-2-deoxy-6-O-*p*-toluenesulfonyl-β-D-glucopyranose hydrochloride[7] (11 g) in dry pyridine (66 ml) was added dropwise benzoyl chloride (4.5 g) under stirring at −10°. After stirring for 3 hr at 0°, the mixture was poured into ice-H_2O (500 ml) and then the mixture was kept for 15 hr at 5° to afford an amorphous powder, which was collected by filtration, air-dried, and recrystallized from EtOH to give pure IX (11 g, 88%), mp 163—164° (decomp.), $[\alpha]_D^{16}$ +43° (c=1.3, $CHCl_3$). TLC: *Rf* 0.49 (solvent A). IR ν_{max}^{Nujol} cm^{-1}: 3340 (NH), 1655, 1525 (CONH). NMR ($CDCl_3$) δ ppm: 2.05, 2.10, 2.15 (9H, s, 3×Ac), 2.54 (3H, s, C_6H_4–CH_3), 5.85 (1H, d, $J_{1,2}$=7.5 Hz, H-1), 7.10—7.85 (9H, m, C_6H_4+C_6H_5). *Anal.* Calcd. for $C_{26}H_{29}O_{11}NS$: C, 55.41; H, 5.19; N, 2.49. Found: C, 55.44; H, 5.10; N, 2.35.

3,4-Di-O-acetyl-2-benzamido-2-deoxy-6-O-*p*-toluenesulfonyl-β-D-glucopyranosyl Ethylxanthate (X)——Dry HCl gas was saturated to Ac_2O (18 ml) at 0°. To this chlorination reagent was added IX (1.2 g) in one portion, the suspension was stirred until a solution resulted, and then kept for 2 days at room tem-

perature. Dichloromethane (30 ml) was added, and the mixture was poured into ice-H_2O (100 ml). After stirring for 2 hr at 0°, the organic layer was separated, successively washed with H_2O and aq. $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated to give an amorphous chloride (0.79 g), which was used without further purification.

To the chloride were added potassium ethylxanthate (0.24 g) and dry acetone (6 ml). The mixture was similarly treated as described for the preparation of III to yield crude X. Several recrystallizations from EtOH gave pure X (0.4 g, 36%), mp 182—183° (decomp.), $[\alpha]_D^{25}$ +71.5° (c=0.7, $CHCl_3$). NMR ($CDCl_3$) δ ppm: 1.43 (3H, t, J=6.8 Hz, CH_2–C<u>H</u>$_3$), 2.03, 2.14 (6H, s, 2×Ac), 2.51 (3H, s, C_6H_4–C<u>H</u>$_3$), 5.62 (1H, d, $J_{1,2}$=7 Hz, H-1), 7.06—7.91 (9H, m, C_6H_4+C_6H_5). *Anal.* Calcd. for $C_{27}H_{31}O_{10}NS_3$: C, 51.83; H, 4.99; N, 2.24. Found: C, 51.56; H, 4.92; N, 2.30.

3,4-Di-O-acetyl-1,6-anhydro-2-benzamido-2,6-dideoxy-6-thio-β-D-glucopyranose (XI)——Treatment of X (500 mg) with 0.7M sodium methoxide in MeOH (5 ml) and successive acetylation were similarly as described for the preparation of IV to afford crude XI as an amorphous powder, which contaminated with by-products judged by TLC (solvent B). The main spot, *Rf* 0.74 was isolated by preparative TLC. Pure XI (140 mg, 48%), mp 171—172°, $[\alpha]_D^{22}$ +7° (c=0.7, $CHCl_3$), was obtained by acetone extraction from the adsorbent, removal of the solvent, and finally recrystallization from EtOH–petr. ether. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430 (NH), 1742 (CO), 1666, 1508 (CONH). NMR ($CDCl_3$) δ ppm: 2.20, 2.23 (6H, s, 2×Ac), 5.53 (1H, s, H-1), 7.20—7.85 (5H, m, C_6H_5). *Anal.* Calcd. for $C_{17}H_{19}O_6NS$: C, 55.87; H, 5.24; N, 3.83. Found: C, 55.58; H, 5.38; N, 3.96.

1,6-Anhydro-2-benzamido-2,6-dideoxy-6-thio-β-D-glucopyranose (XII)——Deacetylation of XI (300 mg) as described for the preparation of VI afforded an amorphous powder, chromatographically homogeneous, negative Fehling test, $[\alpha]_D^{22}$ +34.5° (c=0.3, EtOH). IR ν_{max}^{Nujol} cm^{-1}: 3360 (OH), 1645, 1520 (CONH).

3,4-Di-O-acetyl-1,6-anhydro-2-benzamido-2-deoxy-β-D-glucopyranose (XIII)——Treatment of IX (8 g) with 0.7M methanolic sodium methoxide (80 ml) and successive acetylation were performed as described for the preparation of IV to yield a sirup which crystallized from ether. Recrystallization from EtOH gave pure XIII (1.9 g, 38%), mp 190—191°, $[\alpha]_D^{19}$ −7° (c=0.8, $CHCl_3$). TLC: *Rf* 0.46 (solvent A). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430 (NH), 1745 (CO), 1667, 1508 (CONH). NMR ($CDCl_3$) δ ppm: 2.18, 2.20 (6H, s, 2×Ac), 5.50 (1H, s, H-1), 6.65 (1H, br. d, J=9 Hz, NH), 7.20—7.85 (5H, m, C_6H_5). *Anal.* Calcd. for $C_{17}H_{19}O_7N$: C, 58.45; H, 5.48; N, 4.01. Found: C, 58.21; H, 5.46; N, 3.96.

1,6-Anhydro-2-benzamido-2-deoxy-β-D-glucopyranose (XIV)——Deacetylation of XIII (420 mg) and recrystallization of the deacetylation product from MeOH-ether gave pure XIV (250 mg, 78%), mp 199—201°, $[\alpha]_D^{24}$ +13.7° (c=0.6, H_2O). IR ν_{max}^{Nujol} cm^{-1}: 3400—3200 (OH), 1635, 1512 (CONH). Negative Fehling test. *Anal.* Calcd. for $C_{13}H_{15}O_5N$: C, 58.86; H, 5.70; N, 5.28. Found: C, 58.94; H, 6.02; N, 5.26.

Acetolysis of Compound XIII——1) Compound XIII (500 mg) was dissolved in acetolysis mixture (10 ml, 70: 30: 1 (v/v) Ac_2O–AcOH–H_2SO_4). After stirring for 4 hr at room temperature, the mixture was poured into ice-H_2O (100 ml), stirred for further 1 hr, and extracted with $CHCl_3$ (3×20 ml). The combined extracts were washed with H_2O, dried, and evaporated to afford a sirup (600 mg), which showed two spots by TLC (solvent A). It was dissolved in $CHCl_3$ and the solution chromatographed on a column of silica gel using 30: 1 (v/v) $CHCl_3$–acetone as the elution solvent. Removal of the solvent from the faster moving eluate yielded a sirup (270 mg, 42%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740 (CO), 1645 (C=N). NMR at 100 MHz with a Jeol Model JNM-MH-100 ($CDCl_3$) δ ppm: 2.03, 2.08, 2.15 (9H, s, 3×Ac), 6.24 (1H, d, $J_{1,2}$=7.5 Hz, H-1), 7.33—8.23 (5H, m, C_6H_5). The product was assigned to 4,5-(3,4,6-tri-O-acetyl-2-deoxy-D-glucopyrano)-2-phenyl-Δ^2-oxazoline (XV). (lit.[14] mp 56°, $[\alpha]_D$ +44.7° (pyridine–H_2O 1: 1); lit.[15] sirup).

From the second effluent of the same solvent, another crystals were obtained after removal of the solvent. Recrystallization from MeOH–ether–petr. ether gave pure compound (270 mg, 48%), mp 165—166°, $[\alpha]_D^{26}$ +133° (c=1.3, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420 (NH), 1680, 1505 (CONH). NMR at 100 MHz ($CDCl_3$) δ ppm: 1.93 (3H, s, NAc), 2.09 (9H, s, 3×Ac), 6.46 (1H, d, $J_{1,2}$=3.7 Hz, H-1). The product was assigned to 2-acetamido-3,4,6-tri-O-acetyl-1-O-benzoyl-2-deoxy-α-D-glucopyranose (XVI) by comparison with an authentic sample.

2) A mixture of XIII (340 mg) and the acetolysis mixture (6.8 ml) was stirred for 22 hr at room temperature and then poured into ice-H_2O (70 ml). After stirring for further 4 hr, the mixture was extracted with $CHCl_3$ and the extracts were similarly treated as described in 1). From the eluate of the silica gel column chromatography, only one product (320 mg, 73%), mp 165—166°, indistinguishable with XVI, was isolated.