Articles

Synthesis of 2-Amino-4,6-Di-*O*-Benzoyl-3-*O*-Benzyl-1,2-Dideoxy Mannojirimycin

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Diacetone-D-glucose was converted into 5-azido-6-*O*-benzoyl-3-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose. After removal of isopropylidene and benzoyl protecting groups, hydrogenation performed reduction of azide and subsequent cyclization by reductive amination to give 3-*O*-benzyl-1-deoxy nojirimycin in high yield. The second azide group was introduced on 2-carbon by selective substitution reaction, and reduction of azide to amino group gave titled compound.

Introduction

Inhibitors of α-glucosidase[1] and glycoprotein trimming enzymes have been receiving great attentions these days. They have potential therapeutic uses in diabetic mellitus,[2] tumor metastases,[3] acquired immunodeficiency syndrome,[4] and insecticide.[5]

A number of glucosidase inhibitors have been found. Several plant alkaloids and sugar analogous with nitrogens in the ring instead of oxygen block the processing pathway of protein bound oligosaccharide at the various stages. Therefore, the N-linked oligosaccharide can not be modified beyond a specific stage. This gives rise to glycoproteins having various types of altered oligosaccharide structures.[6]

Deoxynojirimycin inhibits the glucosidase I and II, and its diastereomer deoxymannojirimycin is known as an inhibitor of mannosidase IA/B.[7] α-Homonojirimycin was found recently.[8] Due to their interesting biological activities, a number of nojirimycin derivatives have been developed. Various functional groups (fluoro, alkyl, acyl, acetoamido) were introduced at specific position of the piperidine ring system.[9] Recently, deoxynojirimycin derivatives connected with a glucose by forming α 1-3 glycoside bond showed effective inhibition of endoglucosidase and endomannosidase.[10]

Since the synthesis and biological activities of 2-acetoamido-1,2-dideoxy nojirimycin derivatives were reported, not enough studies on other derivatives of amino dideoxy nojirimycin have been performed in spite of their potency as new glucosidase inhibitors. Recently, synthesis of 6-azido and 6-amino-1,6-dideoxy nojirimycin derivatives as useful intermediates of numerous alkaloids and piperazine or piperidine drug was published.[11] Here we introduce the synthesis of the selectively protected 2-amino-1,2-dideoxy mannojirimycin (**1**), a valuable precursor of various derivatives of 2-amino-1,2-dideoxy mannojirimycin. In our further study, 2-amino group will be used as a site for attaching several functional groups (alkyl, sugar, amino acid, oligopeptide).

Experimental

General

Every reagent was purchased from Aldrich, Merck, Fluka, or Janssen Co. Each solvent was purified and dried before use according to the method in references.[12] ^{1}H NMR and ^{13}C NMR spectra were recorded with Varian VXR-200 or Bruker AW-80 spectrometer on solutions in $CDCl_3$ or CD_3OD. IR spectrums were done with Mattson 3000 FT-IR spectrometer.

Synthesis

3-*O*-benzyl-1,2 : 5,6-di-*O*-isopropylidene-α-D-glucofuranose (3). Diacetone-D-glucose (**2**) (13 g) was dissolved in dioxane, and benzyl chloride (11.5 mL) and KOH (12 g) were added. After stirring 5 hours at 100 ℃, saturated aqueous NH_4Cl was added, and extraction with CH_2Cl_2 was done. The collected organic layer was dried, rotaevaporated, and purified by chromatography. Compound **3** was obtained as syrup. (14.3 g, 82%). ^{1}H NMR ($CDCl_3$, ppm): 7.2 (5H, m), 5.7 (1H, d), 4.2 (2H, m), 4.0 (2H, m), 3.5 (3H, m), 1.2 (3H, s), 1.1 (3H, s). ^{13}C NMR ($CDCl_3$, ppm): 105.3, 82.6, 81.7, 81.3, 72.5, 67.4. IR (cm^{-1}): 2918.13, 2849.86, 1724.20, 1373.24, 1021.20.

3-*O*-benzyl-1,2-*O*-isopropylidene-5,6-di-*O*-methanesulphonyl-α-D-glucofuranose (4). Compound **3** (14.3 g) was dissolved in 80 mL aqueous acetic acid solution (HOAc : H_2O=3 : 2). After stirring 10 hours at room temperature, toluene was added and solvent was rotaevaporated. The resulting syrup was dried under the vacuum for 1 day, and 100 mL of dry pyridine was added. The reaction mixture was placed in ice bath, and MsCl (8.6 mL) was slowly added. After stirring 6 hours at room temperature, water was added and extraction with CH_2Cl_2 was done. The collected organic layer was dried, evaporated, and recrystallized in $CHCl_3$/pet ether to yield compound **4** (16.2 g, 87%). ^{1}H NMR ($CDCl_3$, ppm): 7.3 (5H, m), 5.8 (1H, d, J=4.0 Hz), 5.0 (2H, m), 4.2 (4H, m), 3.8 (4H, m), 3.0 (3H, s), 1.4 (3H, s), 1.2 (3H, s). IR (cm^{-1}) 3032.88, 2938.31, 1747.40, 1360.70, 1200.23.

5,6-anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-idofuranose (5). Compound **4** (16.2 g) was dissolved in

dry DMF and reaction flask was placed in ice bath. After KO_2 (12 g) and 18-crown-6 ether (4 g) were added, the reaction mixture was stirred at room temperature for 1 day. After adding water, the reaction mixture was extracted with CH_2Cl_2, and the collected organic layer was dried and evaporated to yield crude compound **5** (10 g, 96%). ^1H NMR ($CDCl_3$, ppm): 7.3 (5H, m, aromatic H), 5.8 (1H, d, J=3.9 Hz, H-1), 4.85 (1H, d, J=12.2 Hz, $PhCH_2$), 4.82 (1H, d, J=12.2 Hz, $PhCH_2$), 4.5 (1H, d), 3.95 (1H, d), 3.8 (1H, m), 3.3 (1H, m), 2.75 (1H, m), 2.65 (1H, m), 1.2 (3H, s), 1.1 (3H, s). ^{13}C NMR ($CDCl_3$, ppm): 137.1, 128.2, 127.7, 127.4, 111.6, 105.2, 82.5, 81.9, 71.6, 49.9, 42.8, 26.6, 26.1. IR (cm^{-1}): 2988.5, 2933.5, 1725.2, 1490, 1400.

6-*O*-benzoyl-3-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-methanesulphonyl-β-L-idofuranose (6). Crude compound **5** (3.5 g) and NaOBz (4 g) were dissolved in dry DMF and stirred at 120 ℃ for 10 hours. After adding water, extraction with CH_2Cl_2 was performed. The collected organic layer was dried, and evaporated. The resulting crude syrup was dried under the vacuum for 1 day and dissolved in dry pyridine with MsCl (2.5 mL). The reaction mixture was stirred for 2 hours at room temperature. After adding water, extraction was done with CH_2Cl_2, and the collected organic layer was dried and evaporated to yield crude compound **6** (5.2 g, 84%). ^1H NMR ($CDCl_3$, ppm): 8.0 (2H, m, aromatic H), 7.2 (8H, m, aromatic H), 5.8 (1H, d, J=4.0 Hz, H-1), 5.1 (1H, m, H-5), 4.5 (6H, m), 3.9 (1H, d), 3.1 (3H, s, CH_3S), 1.2 (3H, s, CH_3), 1.1 (3H, s, CH_3). IR (cm^{-1}): 2986.0, 1722.5, 1452.5, 1357.9, 1271.2, 1176.6.

5-azido-6-*O*-benzoyl-3-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (7). Crude compound **6** (5.2 g) and NaN_3 (7 g) were dissolved in dry DMSO and heated at 120 ℃ for 1 day. After DMSO was rotaevaporated, the remaining mixture was dissolved in CH_2Cl_2 and washed with water several times. The collected organic layer was dried and evaporated to yield crude compound **7** (3.8 g, 88%). ^1H NMR ($CDCl_3$, ppm): 8.0 (2H, m, aromatic H), 7.2 (8H, m, aromatic H), 5.9 (1H, d, J=4.0 Hz, H-1), 4.0-4.9 (8H, m), 1.3 (3H, s, CH_3), 1.2 (3H, s, CH_3). IR (cm^{-1}): 2988.5, 2935.4, 2102.3, 1731.9.

5-azido-3-*O*-benzyl-5-deoxy-D-glucofuranose (8). To compound **7** (3.8 g) dissolved in MeOH was added 0.1 M NaOMe (16 mL) slowly at room temperature. After stirring 12 hours, DOWEX 50X8-100 ion exchange resin 1 g was added and the reaction mixture was filtered and rotaevaporated. The resulting syrup dissolved in CH_3CN was added aqueous trifluoroacetic acid (7 mL). After stirring 2 days at 50 ℃, solvent was rotaevaporated. The resulting syrup was chromatographed to yield compound **8** (1.42 g, 56%, α, β mixture). β form: ^1H NMR ($CDCl_3$, ppm): 7.3 (5H, m, aromatic H), 4.9 (1H. s, H-1), 4.6 (2H, dd, J=11.6 Hz, $PhCH_2$), 4.25 (1H, broad s), 3.9 (5H, broad m), 3.5 (1H, m), 2.9 (2H, broad s). ^{13}C NMR ($CDCl_3$, ppm): 137.5, 127.8, 108.7, 82.6, 79.7, 77.8, 71.7, 64.1, 63.3. α form: ^1H NMR ($CDCl_3$, ppm): 7.3 (5H, m, aromatic H), 5.1 (1H. d, J=4.4 Hz, H-1), 4.6 (2H, dd, J=11.5 Hz, $PhCH_2$), 4.2 (1H, m), 4.0 (1H, m), 3.7 (5H, m), 3.3 (2H, broad s). ^{13}C NMR ($CDCl_3$, ppm): 137.2, 127.7, 101.3, 83.3, 77.7 75.4, 71.5, 64.6, 63.2. IR (cm^{-1}): 3507.3, 2988.5, 2936.4, 2522.7, 2101.3, 1455.2, 1163.9.

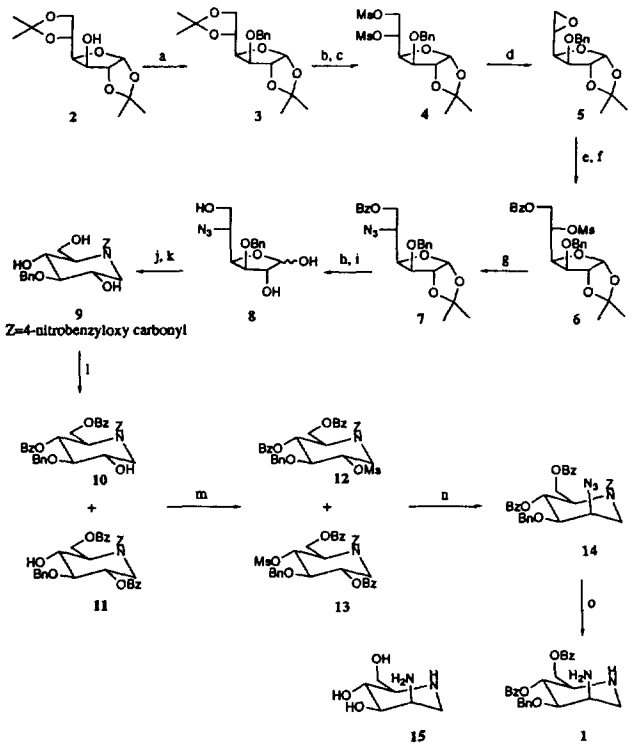
3-*O*-benzyl-1-deoxy-*N*-*p*-nitrobenzyloxycarbonyl-nojirimycin (9). Compound **8** (1.42 g) was dissolved in aq MeOH (MeOH : H_2O=1 : 1), and catalytic amount 5% Pd/c was added. H_2 gas was bubbled for 20 min and the reaction mixture was stirred under atmospheric H_2 pressure for 1 day. After filtering through celite pad, solvent was rotaevaporated. To the resulting solid dissolved in THF were added aq Na_2CO_3 solution and p-nitrobenzylchloroformate. After stirring 30 min at 0 ℃, saturated aq NaCl solution was added and extraction was performed with CH_2Cl_2. The collected organic layer was dried, evaporated, and chromatographed to yield compound **9** (1.2 g, 45%) ^1H NMR ($CDCl_3$, ppm): 7.9-7.2 (10H, m), 5.1 (1H, d), 4.7 (1H, d), 4.6 (1H, d), 3.0-4.1 (m).

2-azido-3-*O*-benzyl-4,6-di-*O*-benzoyl-1,2-dideoxy-*N*-*p*-nitrobenzyloxycarbonyl-mannojirimycin (14). Compound **9** (180 mg) was dissolved in THF. Pyridine (1.2 mL) and benzoyl chloride (0.07 mL) were added at −20 ℃. After stirring 2 hours at room temperature, ice water was added to quench the reaction. Extraction with $CHCl_3$ was done and the collected organic layer was dried and evaporated to yield 1 : 1 mixture of **10** and **11**. Without separation, mixture of **10** and **11** was dissolved in pyridine (12 mL), and MsCl (0.1 mL) was added in ice bath. After stirring 2 hours at 0 ℃, water was added and extraction with $CHCl_3$ was performed. The organic layer was collected, dried, and evaporated to yield 1 : 1 mixture of **12** and **13**. Without separation, crude mixture was dissolved in dry DMSO. After adding 300 mg of NaN_3, the reaction mixture was heated at 90 ℃ for 8 hours. After cooling the reaction mixture, water was added and extraction was done with $CHCl_3$. The collected organic layer was dried, evaporated, and chromatographed to yield compound **14** (79.8 mg, 27.6%). ^1H NMR ($CDCl_3$, ppm): 7.0-8.0 (m, aromatic H), 5.4 (1H, m), 5.1 (1H, m), 4.8 (4H, m), 4.5 (1H, dd), 4.3 (1H, dd), 4.0 (2H, m), 3.8 (2H, m). ^{13}C NMR ($CDCl_3$, ppm): 105.3, 104.7, 155.4, 143.0, 136.4, 133.3, 129.8, 129.5, 129.3, 128.8, 128.4, 127.8, 123.8, 123.2, 74.9, 74.4, 74.1, 73.7, 68.8, 67.7, 65.9, 60.5, 55.0, 53.7. IR (cm^{-1}): 2922.3, 2852.9, 2104.5, 1720.6, 1602.9, 1521.9, 1452.4, 1345.4, 1255.3.

2-amino-3-*O*-benzyl-4,6-di-*O*-benzoyl-1,2-dideoxy-mannojirimycin (1). Compound **14** (60 mg) was dissolved in dry ethanol, and catalytic amount of 5% Pd/c was added. Under atmospheric H_2 pressure, the reaction mixture were stirred for 1 hour at room temperature. The reaction mixture was filtered through celite bed, and solvent was evaporated. Final purification was performed with preparative TLC to yield pure compound **1** (37.1 mg, 83%). ^1H NMR ($CDCl_3$, ppm) 7.1-8.0 (15H, aromatic H), 5.46 (1H, t, J=9.38 Hz, H-4), 4.59 (1H, d, J=12.17 Hz, $PhC\underline{H}_2$), 4.43 (2H, m, $PhC\underline{H}_2$, 6a), 4.20 (1H, dd, J=11.4 Hz, 6.05 Hz, H-6b), 3.57 (1H, m, H-2), 3.53 (1H, dd, J=3.71 Hz, H-3), 3.03 (2H, m, H-1a, 5), 2.75 (1H, d, J=12.63 Hz, H-1b). ^{13}C NMR ($CDCl_3$, ppm): 166.5, 166.1, 138.0, 133.3, 133.2, 130.2, 130.1, 130.0, 129.9, 128.5, 128.5, 127.9, 80.8, 71.4, 70.6, 65.0, 58.8, 49.3, 48.7. IR (cm^{-1}): 2922.3, 2855.7, 1720.6, 1501.0, 1452.5, 1315.5, 1275.0, 1109.1.

Result and Discussion

Our synthesis commenced with diacetone-D-glucose (**2**) because it is cheap and easily accessible (Scheme 1). The benzylation of the remaining 3-OH of diacetone-D-glucose (**2**) with benzyl chloride gave **3**. Terminal isopropylidene pro-



Scheme 1. a) KOH, BnCl, dioxane, 100 ℃, 5 hr. b) AcOH/H_2O(3/2), rt, 10 hr. c) 2.5 eq MsCl, py, rt, 6 hr. d) KO_2, 18-crown-6, DMF, rt, 1 day. e) 4 eq NaOBz, DMF, 120 ℃, 10 hr. f) MsCl, py, rt, 2 hr. g) NaN_3, DMSO, 120 ℃, 1 day. h) NaOMe, MeOH, rt, 12 hr. i) TFA/H_2O(1/1), CH_3CN, 50 ℃, 2 days. j) H_2 (1 atm), 5% Pd/c, MeOH/H_2O(1/1), rt, 1 day. k) Na_2CO_3, ZCl, THF/H_2O(3/1), 0 ℃, 30 min. l) BzCl, py, −20 ℃-rt, 2 hr. m) MsCl, py, 0 ℃, 2 hr. n) NaN_3, DMF, 90 ℃, 8 hr. o) H_2 (1 atm), 5% Pd/c, EtOH, rt, 1 hr.

tecting group of **3** was selectively removed by stirring in aqueous acetic acid at room temperature, and the resulting two free OH groups were converted into mesyl groups. Subsequently two mesyl groups of **4** were converted into epoxide **5** with KO_2 and 18-crown-6 ether.[13] The merits of KO_2 reaction were mild reaction condition, high efficiency, and complete inversion of stereochemistry. Therefore, the stereochemistry of 5-carbon in **4** was completely inverted in **5**.

When **5** was treated with sodium benzoate in DMF, benzoate anion attacked 6-carbon and the epoxide ring was opened. The resulting OH group on 5-carbon was converted into mesyl group to yield **6**. By treating with sodium azide, 5-mesyl group in **6** was substituted by azide anion to yield **7**, and the stereochemistry on 5-carbon was inverted again. The terminal benzoyl protecting group of **7** was removed by reaction with sodium methoxide, and the isopropylidene group was also deprotected by hydrolysis with trifluoroacetic acid to yield **8**. Under hydrogen atmosphere, azido group of **8** was reduced to amino group, which performed intramolecular cyclization forming piperidine ring system by reductive amination of hemiacetal. The similar methodologies have been applied to construct piperidine ring systems.[14] It was interesting that no cyclized product was obtained when there was a benzyl or benzoyl protection group on 6-OH of **8**. It is conceived steric hindrance caused by 6-O-protecting group may destabilize the proper molecule geometry for intramolecular cyclization. The nitrogen on the resulting piperidine ring was protected by the reaction with 4-nitrobenzyl chloroformate to yield **9**.

We initially expected reactivity differences between 2- and 4-hydroxyl groups of **9** toward benzoyl chloride, because 2-hydroxyl group seemed to be less sterically congested. Therefore, the reaction of **9** with benzoyl chloride was expected to yield **11** as a major product. However, the result was 1 : 1 mixture of **10** and **11**. Low temperature reaction condition and slow addition of benzoyl chloride failed to improve the product ratio.

Although compound **10** and **11** could be separated by chromatography, the mixture was used for the further reaction with mesyl chloride in pyridine to yield 1 : 1 mixture of **12** and **13**. The mesyl groups in **12** and **13** were forced to be substituted with azide anion by treating with sodium azide in DMSO. Almost one product was obtained and identified as **14**, and unreacted **13** was recovered. Because S_N2 reactions are much more sensitive to steric hindrance, less hindered 2-mesyl group in compound **12** could be selectively substituted. Finally **14** was placed under hydrogen atmosphere with catalytic amount of 5% Pd/charcoal. The azido group was reduced to amino group and at the same time *N*-4-nitrobenzyl carbamate group was removed to yield **1**. The structure of **1** was confirmed by ^1H NMR, ^{13}C NMR, COSY, FT-IR spectrum, and high resolution FAB mass spectoscopy.

In our further studies, various mono or oligosaccharide molecules, or specially designed linker molecules are planed to be connected with 2-amino group of **1** to enhance reactivity and selectivity as new mannosidase inhibitors. Therefore, protecting groups on 3, 4, 6-OH are necessary for further reactions. Although our first synthetic target was **1**, compound **15** which can be easily obtained by debenzylation and debenzoylation of **1** would be an attractive compound, and interesting biological activities are expected. We also have a plan to prepare and study the nature of **15**.

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SERS on Silver Formed in Anodic Aluminum Oxide Nanotemplates

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A strong SERS effect has been observed on silver surfaces which were prepared by Ag deposition in anodic aluminum oxide nanotemplates and subsequent partial removal of the oxide layers. The advantage of these surfaces for SERS studies is that the controlled size and dispersion of Ag particles can be achieved.

Introduction

Surface-enhanced Raman Scattering (SERS) spectroscopy[1,2] is a well-established method for studying properties of molecules adsorbed on specially prepared surfaces of metals, such as silver, gold, and copper. For SERS experiments, various SERS-active surfaces have been used. Examples of these are surfaces of colloidal metal particles,[3] vacuum-deposited metal films,[4] electrochemically roughened electrodes,[5] chemically prepared films,[6] and HNO_3-roughened metal foils.[7] However, surfaces with controlled particle size and dispersion have not been reported. When anodized in an electrolytic acid solution, aluminum forms a porous oxide with highly uniform-size and parallel pores open only on one end.[8] Its pores can function as nanotemplates in which small metal or semiconductor particles can be electrochemically deposited. As electrodeposition continues, metal fills the pore from the bottom upward.[9] Metal wires can be fabricated in this manner with lengths in excess of 2 μm and with diameters between approximately 10 and 200 nm. Surfaces prepared in this way have been studied in a wide spectrum of scientific and technological fields, from catalysis to magnetic data storage.[8,10]

In this paper we present a strong SERS effect observed on surfaces of silver particles deposited in anodic aluminum oxide pores whose oxide layers were partly removed after the deposition of silver.

Experimental

0.25 mm-thick aluminum sheet was used as a substrate material. Prior to the anodization, several steps were taken to ensure a clean non-oxidized surface of the aluminum. The air-oxidized surface of the aluminum sheet was etched in an aqueous solution of sodium carbonate (25 g/L) at 80 ℃ for 1 minute.

The sheet was then rinsed in distilled water for 30 seconds, dipped into 1 : 1 nitric acid/water solution for 15 seconds in order to neutralize the sodium carbonate, and finally rinsed in distilled water for 1 minute.

Cleaned aluminum sheets were anodized in an aqueous solution of H_3PO_4 (10% (w/w)) at room temperature (20-25 ℃) for 30 minutes at 20 V DC. [The porous anodic aluminum oxide is made during this anodization process.] The cathode of the electrochemical cell was a graphite sheet.

Silver/alumina/aluminum sheets were prepared from an aqueous mixture of silver nitrate (1.51 g/L) buffered with boric acid (45 g/L). The silver metal was deposited in the anodic aluminum oxide pores using a sinusoidal 20 V AC for 40 seconds. The counterelectrodes were graphite sheets. The silver/alumina/aluminum sheet was then rinsed in distilled water for several minutes.

The oxide surface prepared by anodization on silver/alumina/aluminum sheet was partly removed by etching in an aqueous solution of sodium carbonate (25 g/L) at 80 ℃ for