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Convenient preparation of chiral ethylenediamine linked to D-glucose

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Abstract

A useful preparation of an ethylenediamine derivative linked to D-glucose, 2,3-diaminopropyl β-D-glucopyranoside, has been described. The optically pure compound was obtained conveniently via recrystallization of the diastereomeric mixture of the diazido precursor. The stereochemistry of the ethylenediamino compound was elucidated by X-ray crystallography. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Ethylenediamine; X-ray crystallography; Glucose; Diastereomer separation

1. Introduction

The interaction of carbohydrates with metal ions in living systems is considered to be a very fascinating field in the biological sciences [1–4]. We have already reported the preparation, structure determination, and biological or non-biological functions of several metal complexes of N-glycosylic compounds derived from ethylenediamine, trimethylenediamine, and tris(2-aminoethyl)amine [5–13]. During our studies, we fortunately discovered new sugar transformation reactions by cooperative effects between metal ions and amines. We have also developed antitumor or antifungal metal complexes containing amino sugars. Furthermore, we succeeded in the preparation of sugar–cobalt(II) complexes having molecular recognition ability and N-glycosylic complexes, including unprecedented trinuclear Mn(II)Mn(III)Mn(II) complexes. However, these attractive metal-coordinating ligands are so unstable in the absence of metal ions that N-glycosidation and ligation to the metal ions should be performed in the same flask. Otherwise, a complicated reaction mixture results in some cases, along with decreasing product yields. Thus, it is desired to establish the synthesis of a glycoconjugated ethylenediamine having a stable linker. Substitution of the sugar moiety on a carbon atom in the ethylenediamine molecule introduces a new chiral center, so it is another important problem to control the chirality at that position. Now we describe, herein, the convenient synthesis and characterization of the glycoside of (*S*)-2,3-diaminopropanol from racemic 2,3-dibromopropanol utilizing the benefit of chirality in the sugar unit.

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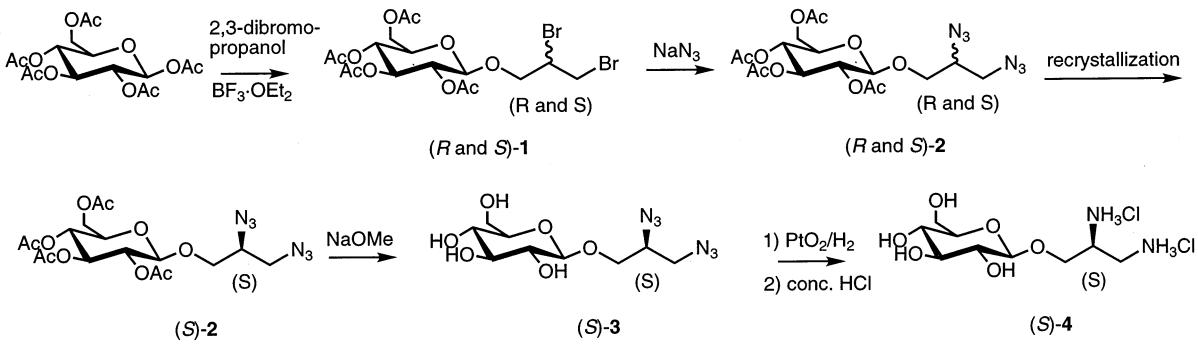

Scheme 1.

Penta-*O*-acetyl-D-glucopyranose was treated with racemic 2,3-dibromopropanol in the presence of boron trifluoride etherate to give (*R*)- and (*S*)-**1** in 99% yield (see Scheme 1). This is a mixture of diastereomers with respect to C-2 on the side chain. These products have already been reported by Marquez et al. from tetra-*O*-acetyl-α-D-glucopyranosyl bromide using mercuric bromide and mercuric cyanide [14]. However, they never mentioned the stereochemistry and/or diastereomeric excess of the products. Judging from the NMR spectrum of the products herein produced, solidified **1** obtained from the present method gave a 56:44 mixture of diastereomers. No remarkable enrichment of the diastereomer was seen in this stage.

Substance **1** was converted to the azido compound **2** with sodium azide in DMF at 70 °C. Repeated recrystallization of the product with ethanol afforded diastereomerically pure **2** in 11% yield (from the diastereomeric mixture of **1**), whose absolute configuration was determined to be 2-(*S*) by X-ray crystallography (Fig. 1). The crystal data and experimental details, final positional parameters and B_{eq} for non-hydrogen atoms are listed in Tables 1 and 2. The puckering of sugar unit was of the β-$^4C_1$ chair conformation.

Deprotection of (*S*)-**2** by excess sodium methoxide in methanol gave (*S*)-**3** quantitatively. Reduction of the azido moiety in compound (*S*)-**3** to amine by PtO_2/H_2 in methanol at atmospheric pressure, followed by treatment with HCl, afforded the final product (*S*)-**4**·2HCl in 40% yield.

Thus, the glycoside of (*S*)-2,3-diaminopropanol [(*S*)-**4**] was obtained from penta-*O*-acetyl-D-glucopyranose and racemic 2,3-dibromopropanol in four steps. The key step was the separation of the diastereomeric mixture of diazido compound **2** utilizing the sugar as a chiral auxiliary. Since the opposite stereoisomer was found reluctant to crystallize, the (*R*)-isomer was not suitable for convenient preparation of the diastereomerically pure compound.

The ability of the present ethylendiamine compound to function as a ligand was evidenced by the formation of the *cis*-dichloroplatinum(II) complex. Circular dichroism spectra of the complex clearly indicated the coordination of the chiral ligand to the platinum atom. Detailed studies of this platinum complex and the other metal com-

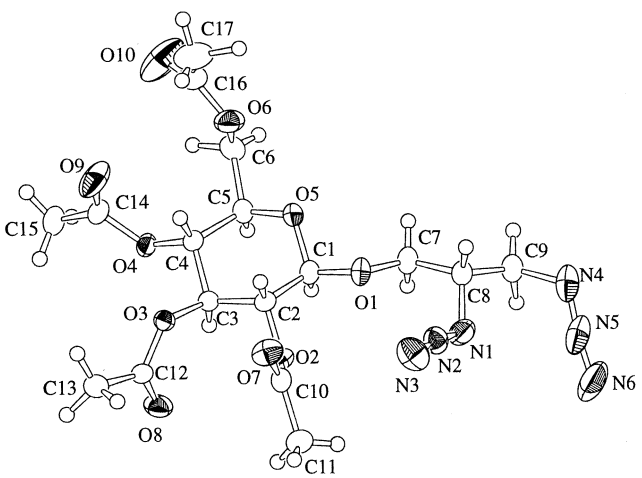

Fig. 1. ORTEP diagram of (*S*)-**2**. Selected bond distances (Å) and angles (°); O-1–C-1 = 1.394(2), O-1–C-7 = 1.429(3), O-5–C1 = 1.413(3), C-1–C-2 = 1.527(3), O-1–C-1–O-5 = 108.0(2), O-1–C-1–C-2 = 108.9(2), O-5–C-1–C-2 = 108.4(2), C-1–O-1–C-7 = 112.1(2), O-1–C-7–C-8 = 108.3(2), N-1–C-8–C-7 = 110.8(2), N-1–C-8–C-9 = 106.5(2), N-4–C-9–C-8 = 112.1(2), C-7–C-8–C-9 = 108.3(2), N-2–N-1–C-8 = 115.5(2), N-5–N-4–C-9 = 114.0(2), N-1–N-2–N-3 = 172.2(3), N-4–N-5–N-6 = 173.5(3).

Table 1
Crystallographic and experimental data for (*S*)-**2**

Formula	$C_{17}H_{24}N_6O_{10}$
Formula weight	472.41
Color	colorless
Size (mm)	$0.10 \times 0.30 \times 0.80$
Crystal system	monoclinic
Space group	$P2_1$ (no. 4)
No. refs used for cell determination lattice const.	25 ($29.8 < 2\theta < 30.0$)
a (Å)	11.075(2)
b (Å)	7.605(2)
c (Å)	13.357(2)
β (°)	100.21(1)
V (Å^3)	1107.2(3)
Z	2
D_{calc} (g cm^{-1})	1.417
μ (Mo Kα) (cm^{-1})	1.18
Diffractometer	Rigaku AFC7R
Radiation	Mo Kα ($\lambda = 0.71069$ Å)
Monochromator	graphite
T (°C)	−120
2θ range (°)	$4 < 2\theta < 55$
h, k, l range	$+h$, $+k$, $\pm l$
Scan method	ω–2θ
Scan speed (°/min)	8
Solution	direct methods (SAPI91)
Refinement	full-matrix least-squares: all non-hydrogen atoms with anisotropic temperature factors
Hydrogen atoms	included and not refined
Function minimized	$\Sigma w(\|F_o\| - \|F_c\|)^2$
Weighting scheme	$1/\sigma^2(F_o)$
Anomalous dispersion	all non-hydrogen atoms
No. unique reflections	2744
No. observed unique reflections	2572 ($I > 1\sigma(I)$)
No. variables	299
Data/parameter ratio	8.60
R[a]	0.035
R_w[b]	0.048
GOF[c]	1.49

[a] $R = \Sigma\||F_o| - |F_c|\|/\Sigma|F_o|$.
[b] $R_w = [\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$).
[c] GOF $= [\Sigma\, w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$ (N_o = no. data, N_p = no. variables).

plexes utilizing (*S*)-**4** are now in progress in our laboratory.

In summary, we have established a method to obtain a stereocontrolled ethylenediamine compound linked to a glucose moiety via a stable glycoside linker, which should be a very useful ligand in the preparation of sugar-linked functional metal complexes having a chiral carbon in proximity to the metal center.

2. Experimental

General methods.—Melting points were determined on a Yanaco MP-S3 micro hot-stage. TLC was carried out on E. Merck precoated Silica Gel 60 F_{254} plates using UV light and/or 8% H_2SO_4 for visualization. ^{1}H and ^{13}C NMR spectra were measured on a Varian GEMINI 2000 spectrometer at 300

Table 2
Final positional parameters and B_{eq} for non-hydrogen atoms of (*S*)-**2**[a]

Atom	x	y	z	B_{eq}[b]
O-1	0.5227(1)	0.0880(8)	0.37494(9)	2.71(2)
O-2	0.5375(1)	−0.1330(8)	0.20929(9)	2.41(2)
O-3	0.30774(10)	−0.1610(8)	0.06539(9)	2.19(2)
O-4	0.20058(10)	0.1837(8)	0.02137(8)	2.29(2)
O-5	0.3501(1)	0.2150(8)	0.28774(8)	2.53(2)
O-6	0.1075(1)	0.2630(9)	0.2704(1)	4.16(3)
O-7	0.4699(1)	−0.3889(8)	0.2649(1)	3.51(3)
O-8	0.4481(1)	−0.1595(9)	−0.0385(1)	3.30(3)
O-9	0.0076(1)	0.1064(9)	0.0314(1)	5.07(4)
O-10	−0.0734(2)	0.3746(9)	0.1960(2)	7.48(6)
N-1	0.7579(1)	0.0381(9)	0.4897(1)	3.39(3)
N-2	0.7158(2)	−0.1126(9)	0.4805(1)	3.12(3)
N-3	0.6891(2)	−0.2556(9)	0.4684(2)	4.49(4)
N-4	0.8467(2)	0.2776(9)	0.6484(1)	4.14(4)
N-5	0.9425(2)	0.2181(9)	0.6257(1)	4.90(5)
N-6	1.0352(2)	0.1658(10)	0.6144(2)	7.13(7)
C-1	0.4597(2)	0.1272(8)	0.2776(1)	2.37(3)
C-2	0.4261(1)	−0.0443(8)	0.2200(1)	2.14(3)
C-3	0.3552(1)	−0.0008(9)	0.1140(1)	2.02(3)
C-4	0.2461(1)	0.1165(9)	0.1217(1)	2.07(3)
C-5	0.2839(2)	0.2745(9)	0.1919(1)	2.44(3)
C-6	0.1745(2)	0.3776(9)	0.2137(1)	3.42(4)
C-7	0.5873(2)	0.2370(9)	0.4228(1)	2.83(3)
C-8	0.6739(2)	0.1743(9)	0.5164(1)	2.56(3)
C-9	0.7543(2)	0.3293(9)	0.5603(1)	2.98(4)
C-10	0.5481(2)	−0.3062(9)	0.2344(1)	2.50(3)
C-11	0.6697(2)	−0.3741(9)	0.2176(2)	3.28(4)
C-12	0.3614(1)	−0.2271(9)	−0.0103(1)	2.25(3)
C-13	0.2994(2)	−0.3921(9)	−0.0514(1)	2.91(3)
C-14	0.0780(2)	0.1710(9)	−0.0160(1)	2.66(3)
C-15	0.0460(2)	0.2492(9)	−0.1190(1)	3.24(4)
C-16	−0.0157(2)	0.2737(9)	0.2551(2)	4.40(5)
C-17	−0.0698(3)	0.1445(10)	0.3167(2)	6.01(7)

[a] Estimated standard deviations are given in parentheses.
[b] All non-hydrogen atoms were assigned with anisotropic thermal parameters given as the isotropic equivalent displacement parameter defined as $B_{eq} = (8\pi^2/3)(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

MHz and on a Varian UNITY 500 plus spectrometer in $CDCl_3$ (internal Me_4Si, δ 0.00) or Me_2SO-d_6 (internal Me_4Si, δ 0.00) at 25 °C. Optical rotations were determined at room temperature with a Jasco DIP-140 digital polarimeter. Mass spectra were measured on a Jeol JMS-SX 102 mass spectrometer.

2,3-Dibromopropyl 2,3,4,6-tetra-O-*acetyl-β*-D-*glucopyranoside* (**1**).—To a solution of penta-*O*-acetyl-D-glucopyranose (10.3 g, 26.3 mmol) and racemic 2,3-dibromopropanol (8.3 g, 38 mmol) in dry CH_2Cl_2 (70 mL) boron trifluoride etherate (23.6 mL, 167 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 1 h and at room temperature overnight. After the addition of EtOAc, the solution was washed with water, dried, and evaporated to give **1** (14.2 g, 26.0 mmol) in 99% yield as an oil. Solidified **1** has mp 64–69 °C, lit. [14] 94–96 °C; $[\alpha]_D$ −2.30° (*c* 1.0, chloroform), lit. [14] −7.22°; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02 (3H, s, Ac), 2.04 (3H, s, Ac), 2.08 (3H, s, Ac), 2.10 (3H, s, Ac), 3.67–3.96 (4H, m, Glc-H5, α-1, γ), 4.16 (1H, dd, *J* 12.2, 1.8 Hz, Glc-H6a), 4.22–4.33 (3H, m, Glc-H6b, α-2, β), 4.58 (d, 0.44H, d, *J* 7.9 Hz, Glc-H1), 4.60 (d, 0.56H, d, *J* 7.9 Hz, Glc′-H1), 5.0–5.14 (2H, m, Glc-2,4), 5.24 (1H, dd, *J* 9.8, 9.2 Hz, Glc-H3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 20.47, 20.63, 32.07, 33.19, 47.94, 61.72, 68.20, 70.42, 70.95, 71.21, 71.89, 72.41, 72.49, 101.06, 101.27, 169.55, 170.41, 170.82. Anal. Calcd for $C_{17}H_{24}Br_2O_{10}$: C, 37.25; H, 4.41; Br, 29.15. Found: C, 37.10; H, 4.23; Br, 29.75%. FABMS: (Calcd for $C_{17}H_{25}{}^{79}Br^{81}BrO_{10}$ $[M+H]^+$ 548.9795); found *m*/*z* 548.9826.

2,3-Diazidopropyl 2,3,4,6-tetra-O-*acetyl-β*-D-*glucopyranoside* (**2**).—A mixture of compound **1** (16.0 g, 29.2 mmol), sodium azide (5.02 g, 77.2 mmol) and DMF (100 mL) was agitated at 70 °C for 2 h. After the addition of EtOAc and washing with water, the solution was dried and evaporated to give **2** (2.40 g, 5.08 mmol). Repeated recrystallization of compound **2** with ethanol afforded diastereomerically pure product (1.44 g, 3.05 mmol, 11% from compound **1**), mp 110–112 °C; $[\alpha]_D$ −20.8° (*c* 1.9, chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.01 (3H, s, Ac), 2.03 (3H, s, Ac), 2.06 (3H, s, Ac), 2.10 (3H, s, Ac), 3.32 (1H, dd, *J* 12.8, 6.1 Hz, γ-1), 3.42 (1H, dd, *J* 12.8, 4.9 Hz, γ-2), 3.63 (1H, dd, *J* 10.1, 7.3 Hz, α-1), 3.69–3.79 (2H, m, Glc-H5, β), 4.00 (1H, dd, *J* 10.1, 4.0 Hz, α-2), 4.17 (1H, dd, *J* Glc-H6a), 4.26 (1H, dd, *J* 12.2, 4.6 Hz, Glc-H6b), 4.59 (1H, d, *J* 7.9 Hz, Glc-H1), 5.03 (1H, dd, *J* 9.5, 7.9 Hz, Glc-H2), 5.10 (1H, dd, *J* 9.8, 9.5 Hz, Glc-H4), 5.22 (1H, t, *J* 9.5, 9.5 Hz, Glc-H3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 20.41, 20.49, 20.56 (CH_3), 51.34 (C-γ), 60.43 (C-β), 61.66 (C-6), 68.18 (C-4), 69.53 (C-α), 70.97 (C-2), 71.97 (C-5), 72.65 (C-3), 100.70 (C-1), 169.46, 169.49, 170.35, 170.74 (C=O). Anal. Calcd for $C_{17}H_{24}N_6O_{10}$: C, 43.22; H, 5.12; N, 17.79. Found: C, 43.16; H, 5.20; N, 17.77%.

2,3-Diazidopropyl β-D-*glucopyranoside* (**3**).—Sodium methoxide was added to a methanolic solution (80 mL) of (*S*)-**2** (1.46 g, 3.09 mmol) until the pH reached 9. The reaction mixture was stirred 1 h at room temperature and neutralized with ion-exchange (H^+) resin. Removal of the solvent gave (*S*)-**3** quantitatively: $[\alpha]_D$ −11.9° (*c* 1.7, methanol); ^{1}H NMR (500 MHz, Me_2SO-d_6): δ 2.97 (1H, dd, *J* 9.0, 7.8 Hz, Glc-H2), 3.05 (1H, dd, *J* 8.8, 8.5 Hz, Glc-H4), 3.12 (1H, ddd, *J* 8.8, 6.1, 2.2 Hz, Glc-H5), 3.16 (1H, dd, *J* 8.8, 8.8 Hz, Glc-H3), 3.45 (1H, dd, *J* 12.2, 5.9 Hz, Glc-H6a), 3.47 (1H, d, *J* 7.6 Hz, γ-1), 3.59 (1H, dd, *J* 7.6, 4.0 Hz, γ-2), 3.60 (1H, dd, *J* 11.0, 6.6 Hz, α-1), 3.68 (1H, dd, *J* 12.2, 2.2 Hz, Glc-H6b), 3.83 (1H, dd, *J* 11.0, 4.9 Hz, α-2), 3.92 (1H, m, β), 4.19 (1H, d, *J* 7.8 Hz, Glc-H1). ^{13}C NMR (500 MHz, Me_2SO-d_6): δ 50.97 (C-γ), 60.47 (C-β), 61.07 (C-6), 68.31 (C-α), 70.05 (C-4), 73.31 (C-2), 76.55 (C-3), 76.93 (C-5), 103.21 (C-1). FABMS: (Calcd for $C_9H_{16}N_6NaO_6$ $[M+Na]^+$ 327.1029); found *m*/*z* 327.1033.

2,3-Diaminopropyl β-D-*glucopyranoside dihydrochloride* (**4**·*2HCl*).—Reduction of the azido moiety in compound (*S*)-**3** (0.92 g, 3.0 mmol) to the amine was carried out by hydrogenation in the presence of PtO_2 (71 mg) in methanol (90 mL) at atmospheric pressure, followed by treatment with HCl to afford 0.40 g (1.2 mmol) of the final product, (*S*)-**4**·2HCl in 40% yield: mp 235 °C (dec); $[\alpha]_D$ −9.44° (*c* 1.2, water); ^{1}H NMR (500 MHz, Me_2SO-d_6): δ 3.06 (1H, dd, *J* 7.7, 7.8 Hz, Glc-H2), 3.07 (1H, dd, *J* 10.7, 9.2 Hz, Glc-H-4), 3.14–3.19 (4H, m, Glc-H3,5, γ), 3.47 (1H, dd, *J* 12.0, 5.8 Hz,

Glc-H6a), 3.67 (1H, m, β), 3.70 (1H, dd, *J* 12.0, 2.0 Hz, Glc-H6b), 3.76 (1H, dd, *J* 11.2, 6.6 Hz, α-1), 4.04 (1H, dd, *J* 11.2, 4.2 Hz, α-2), 4.25 (1H, d, *J* 7.7 Hz, Glc-H1). ^{13}C NMR (500 MHz, Me_2SO-d_6): δ 38.08 (C-γ), 48.64 (C-β), 60.87 (C-6), 66.39 (C-α), 69.88 (C-4), 73.16 (C-2), 76.01 (C-3), 76.95 (C-5), 103.04 (C-1). Anal. Calcd for $C_9H_{22}Cl_2N_2O_6$: C, 33.24; H, 6.82; N, 8.61. Found: C, 32.99; H, 6.87; N, 8.62%.

Single-crystal structural analysis.—Suitable crystals for X-ray crystallography were obtained by a recrystallization of (*S*)-**2** from ethanol. The crystal data and the experimental conditions are listed in Table 1. Intensity data for (*S*)-**2** were collected with graphite-monochromated Mo Kα radiation ($\mu = 1.18$ cm^{-1}, $\lambda = 0.71069$ Å) on a Rigaku AFC-7R diffractometer at -120 °C. Three standard reflections were monitored every 150 reflections and no systematic decrease in intensity was observed. Reflection data were corrected for Lorentz-polarization and absorption (by ψ-scan method) effects. The structure of (*S*)-**2** was solved by direct methods with SAPI91 [15]. Hydrogen atoms were included but not refined. The structure was refined with the full-matrix least-square technique minimizing $\Sigma\, w(|F_o| - |F_c|)^2$. Final refinement with anisotropic thermal parameters for non-hydrogen atoms converged to $R = 0.035$ and $R_w = 0.048$. Final positional parameters and B_{eq} for non-hydrogen atoms are listed in Table 2. Atomic scattering factors, f', and f''' for O, N, and C were taken from the literature [16,17]. All calculations were carried out on a Silicon Graphics Indigo2 workstation with the TEXSAN program [18]. Perspective sketches were drawn using the ORTEP program [19].

3. Supplementary material

Tables of atomic coordinates, bond lengths, and bond angles have been deposited with the Cambridge Crystallographic Data Centre. These tables may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 IEZ, UK.

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