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Nucleosides and Nucleotides. XXXXV.[1] Facile Deoxygenation of Neplanocin A and Nucleosides by the Use of Tri-*n*-butyltin Hydride

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2′(*R*)-Halogeno-2′-deoxyneplanocin A's were hydrogenated with tri-*n*-butyltin hydride to yield 2′-deoxyneplanocin A. The same compound was obtained by reduction of the 2′-*O*-(1-imidazolyl)thiocarbonyl derivative of neplanocin A. This procedure was also applicable to the synthesis of 2′-deoxyadenosine and -guanosine from the corresponding ribosides. Treatment of a neplanocin 2′,3′-*O*-cyclic thiocarbonate with tri-*n*-butyltin hydride gave 3′-deoxyneplanocin selectively in high yield.

Keywords——neplanocin A; nucleoside antibiotic; 2′-deoxyneplanocin A; 3′-deoxyneplanocin A; tri-*n*-butyltin hydride; radical reduction; 2′-deoxyribonucleosides; NMR; 2′-deoxyadenosine; 2′-deoxyguanosine

Neplanocin A (**1**), a new antibiotic from *Ampullariella regularis* A11079,[3] exhibits remarkable antitumor activity against L-1210 leukemia,[3] and its structure was elucidated as [1*R*-(1α, 2α, 3β)]-3-(6-amino-9*H*-purin-9-yl)-5-(hydroxymethyl)-4-cyclopentene-1,2-diol.[4] The unique feature of **1** is that this compound has a cyclopentenol structure in place of a furanose at the sugar portion of the adenine nucleoside. In order to study the mechanism of antitumor action of **1** as well as to increase the activities, the preparation of 2′-or 3′-modified derivatives of **1** seems to be very important. As reported in previous papers,[1,5] we have developed a facile synthesis of 2′-substituted derivatives of **1**, including the 2′-halogeno compounds. This paper describes in detail the 2′-deoxygenation of **1** and ribonucleosides.[5] The 3′-deoxygenation of **1** is also described.

The 2′-deoxygenation of ribonucleosides has been studied for a long time by several workers,[6] but almost all of the procedures were unsuitable for preparative purposes, especially for purine nucleosides. The radical reduction of organohalogen compounds by the use of tri-*n*-butyltin hydride has been recognized as an effective method, if one can easily convert the hydroxyl group to a halogeno group. In fact, the deoxygenation of certain amino sugars *via* halo-amino intermediate by the use of tri-*n*-butyltin hydride and a catalytic amount of azobisisobutyronitrile (AIBN) is documented.[7] Since we have developed a facile synthesis of 2′-halogeno-2′-deoxy neplanocin A's,[5] these compounds were used for this purpose.

Treatment of a 2′-halogeno-2′-deoxyneplanocin A (**5** or **6**)[1,5] with tri-*n*-butyltin hydride and AIBN in refluxing benzene afforded the corresponding product (**7** or **8**). The reaction proceeded smoothly without affecting the double bond at the 4′-5′ position. The structure of **7** was readily determined by nuclear magnetic resonance (NMR) analysis. As shown in Fig. 1, the protons at the 2′-position of **7** were observed clearly at δ 2.3—2.6 as two sets of octets. Deprotection of **7** (**8**) gave the 2′-deoxyneplanocin A **9** (**10**). For more direct conversion of **1** to **9** the procedure developed by Barton and co-workers[8] was adapted. Treatment of **3**[5] with *N*,*N*′-thiocarbonyldiimidazole afforded **11** in 65% yield. The radical reduction of **11** with the hydride proceeded readily to give a 63% yield of **7**.

The present sequence for the 2′-deoxygenation of neplanocin A seems to be applicable to common ribonucleosides. Treatment of protected adenosine or guanosine (**13a, b**) with *N*,*N*′-thiocarbonyldiimidazole followed by reduction of **14** with tri-*n*-butyltin hydride afforded the corresponding 2′-deoxynucleosides (**15**). In the case of inosine, the 2′-deoxy derivative was

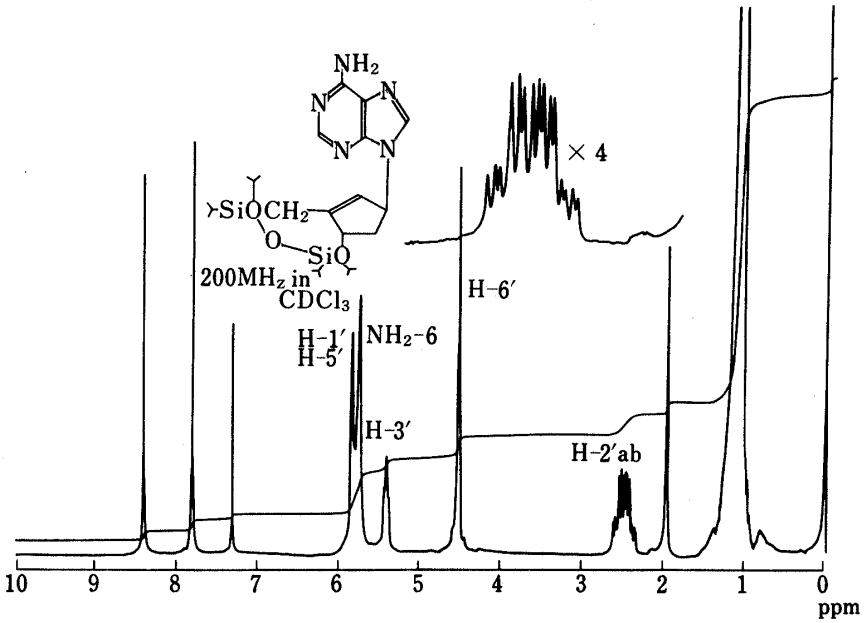


Fig. 1. NMR Spectrum of 2′-Deoxy-3′,6′-*O*-(tetraisopropyldisiloxane-1,3-diyl)neplanocin A (7) in $CDCl_3$

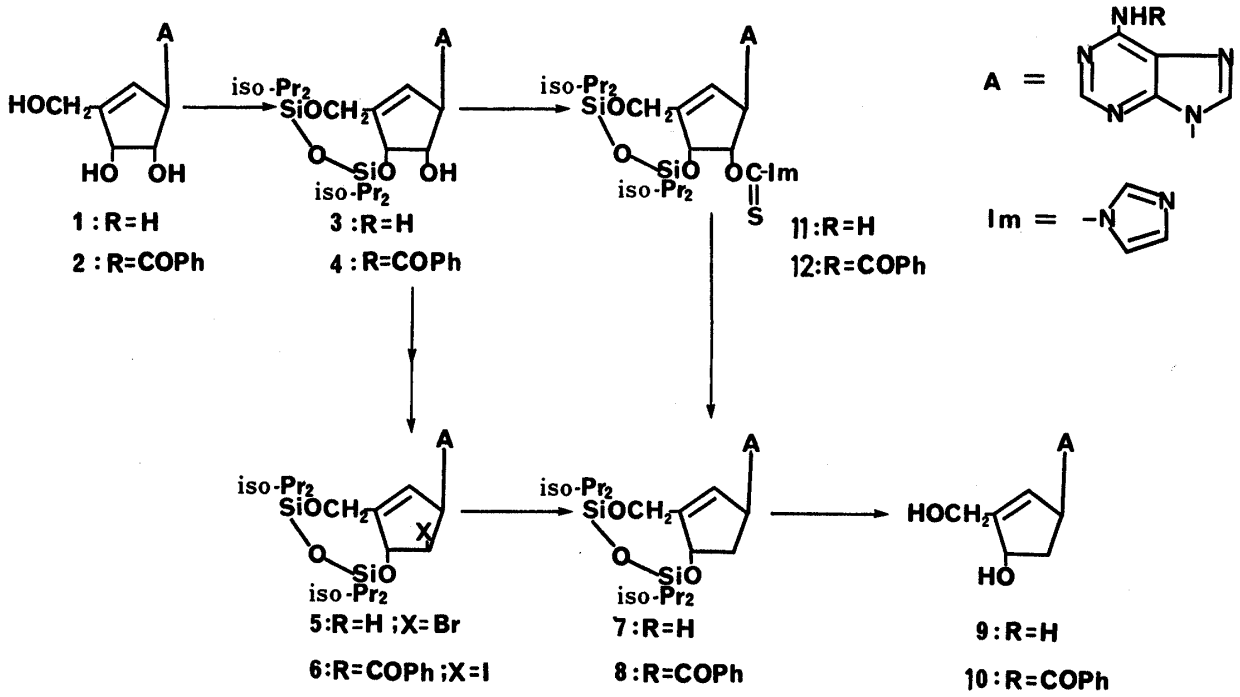
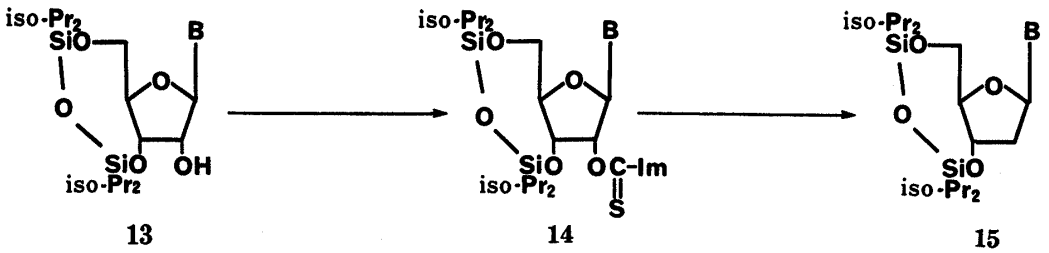


Chart 1



B=a: adenine, b: guanine

Chart 2

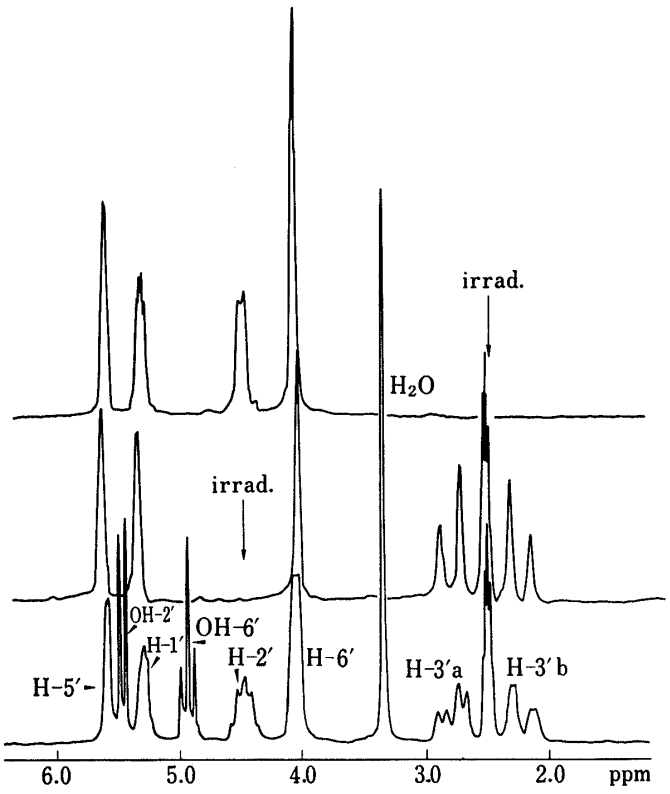


Fig. 2. NMR Spectrum of 3′-Deoxyneplanocin A (**19**) in DMSO-d_6 and the Results of decoupling after Addition of D_2O

not obtained due to extensive hydrolysis to hypoxanthine during the work-up. This system may be adaptable for the conversion of various other nucleosides, including pyrimidine nucleosides.[9]

It has been reported[10] that the radical reduction of the 2′,3′-cyclic thiocarbonate of a ribonucleoside gave both 2′-and 3′-deoxy derivatives. This method seemed suitable for the synthesis of 3′-deoxyneplanocin A, since in the case of **1** a selective 3′-deoxygenation would be expected due to the presence of an allyl alcohol system involving the 3′-oxy function (but not the 2′-oxy function), and this was found to be the case. Perbenzoylation followed by deacetonation of 2′,3′-*O*-isopropylidene neplanocin A afforded N^6,6′-*O*-dibenzoylneplanocin A (**16**). Treatment of **16** with *N*,*N*′-thiocarbonyldiimidazole gave **17** in high yield. The homolytic cleavage of **17** with the butyltin hydride and AIBN with careful exclusion of moisture proceeded to give **18** as a main product. Debenzoylation of **18** afforded 3′-deoxyneplanocin A (**19**), an analog of cordycepin.[11] The structure of **19** was confirmed by

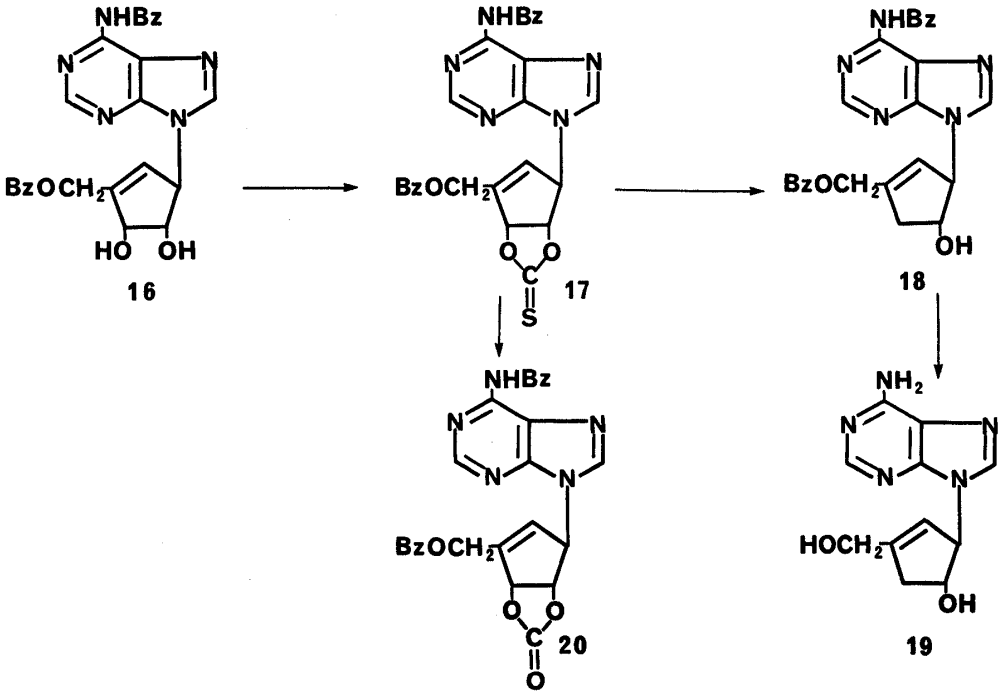


Chart 3

the instrumental analyses. The NMR spectrum of **19** showed the 3′-protons as a signal with dABq-type splitting. Irradiation of the 2′-proton changed the 3′-proton signal to an AB quartet. In the course of the reductive cleavage at the 3′-position, some rearrangement of the allyl radical which would lead to a 5′-deoxy-3′,4′-ene derivative was possible, but such a product was not detected in the reaction mixture.

When the radical cleavage of **17** was carried out with no precaution to exclude moisture, a simple hydrolytic desulfurization took place to give the 2′,3′-cyclic carbonate (**20**) of neplanocin A.

The biological activities of 2′- and 3′-deoxyneplanocin A's are currently under investigation and will be reported separately.

Experimental

All melting points were determined on Yanagimoto micromelting point apparatus (MP-3) and are uncorrected. The ^{1}H NMR spectra were recorded on a JEOL FX-100-FT or FX-200-FT spectrometer in chloroform-d_1 or DMSO-d_6 with tetramethylsilane as an internal standard. Chemical shifts are reported in ppm (δ), and signals are described as s(singlet), d(doublet), t(triplet), q(quartet), br(broad), or m(multiplet). All exchangeable protons were confirmed by addition of D_2O. Ultraviolet (UV) spectra were recorded on a Shimadzu UV-300 spectrophotometer and infrared (IR) spectra with a Hitachi 215 spectrophotometer. Mass spectra (MS) were measured on a JEOL JMS D-300 spectrometer. Thin-layer chromatography (TLC) was carried out on Merck pre-coated $60F_{254}$ plates, and silica gel chromatography was performed on Wako-gel C-200. Tri-*n*-butyltin hydride was purchased from Ventron Corp.

2′-Deoxy-3′,6′-*O*-(tetraisopropyldisiloxane-1,3-diyl)neplanocin A (7)——A solution of **5**[1] (500 mg) in dry benzene (5 ml) was treated with 350 μl of nBu$_3$SnH, and the mixture was heated to reflux under an argon atmosphere. A catalytic amount of AIBN was added and refluxing was continued for 3 h. The solvent was then removed under reduced pressure, and the residue was subjected to silica gel chromatography ($CHCl_3$: EtOH=40 : 1). From the eluate, compound **7** was obtained. Crystallization and recrystallization of **7** from EtOH gave colorless needles of **7**. 385 mg (90%): mp 149—151 °C: Beilstein test (−): UV λ_{max}^{MeOH} nm: 262. NMR (FX-200 in $CDCl_3$); 1.1 (28H, iso-Pr×4), 2.3—2.6 (2H, two sets of octet, H-2′a,b), 4.49 (2H, s, H-6′), 5.39 (1H, dd, H-3′), 5.72 (2H, s, NH_2-6), 5.81 (2H, m, H-1′, H-5′), 7.75 (1H, s, H-2), 8.36 (1H, s, H-8): MS *m/e*; 489 (M^+), 446 (M^+−iso-Pr), 136 (B+2), 135 (B+1).

Anal. Calcd for $C_{23}H_{39}N_5O_3Si_2 \cdot 1/2H_2O$: C, 55.38; H, 8.08; N, 14.04. Found: C, 55.75; H, 7.87; N, 14.09.

N*^{6}-Benzoyl-2′-deoxy-3′,6′-*O*-(tetraisopropyldisiloxane-1,3-diyl)neplanocin A** (8) ***via **6**——A solution of **6**[1] (72 mg) in dry benzene (1 ml) was treated with 48 μl of nBu$_3$SnH and the mixture was heated to 70°C. A catalytic amount of AIBN was then added and the mixture was stirred for 2 h at 70°C. The solvent was evaporated off under reduced pressure, and the residue was subjected to preparative TLC (benzene: AcOEt= 1 : 1) to isolate **8**. 50 mg (84%): Beilstein test (−): MS *m/e*; 593 (M^+), 550 (M^+−iso-Pr).

2′-Deoxyneplanocin A (9)——nBu$_4$NF (300 mg) was added to a solution of **7** (278 mg) in tetrahydrofuran (THF) (5 ml). After 5 min, the reaction mixture was concentrated under reduced pressure, and the residue was crystallized from EtOH to give 115 mg (82%) of **9**. mp 231—234°C: NMR (FX-200 in DMSO-d_6); 2.2—2.4 (2H, m,H-2′a,b), 4.15 (2H,slightly br, H-6′). 4.8—5.0 (2H, t+dd, OH-6′, H-3′), 5.06 (1H, d, OH-3′), 5.64 (1H, m, H-1′), 5.75 (1H, d, H-5′), 7.17 (2H, br, NH_2-6), 7.97 (1H, s, H-2), 8.13 (1H, s, H-8): MS *m/e*; 247 (M^+), 229 (M^+-H_2O), 136 (B+2), 135 (B+1).

Anal. Calcd for $C_{11}H_{13}N_5O_2$: C, 53.43; H, 5.30; N, 28.33. Found: C, 53.43; H, 5.25; N, 28.04.

2′-*O*-(1-Imidazolyl)thiocarbonyl-3′,6′-*O*-(tetraisopropyldisiloxane-1,3-diyl)neplanocin A (11)——A mixture of **3**[1] (280 mg) and *N*,*N*′-thiocarbonyldiimidazole (120 mg) in 5 ml of 1,2-dichloroethane was refluxed with stirring for 3 h. The solvent was removed under reduced pressure. The resulting residue was purified by a silica gel chromatography to give a foam, which was crystallized from ethyl acetate to give 220 mg (65%) of **11**. mp 155—160°C: NMR (FX-200 in $CDCl_3$); 1.1 (28H, iso-Pr×4), 4.57 (2H, slightly br, H-6′), 5.64 (3H, (m, NH_2-6 and H-3′), 5.88 (2H, m, H-2′ and H-1′), 6.04 (1H, d, H-5′), 7.03 (1H, s, imidazole H-4), 7.72 (1H, s, imidazole H-5), 7.84 (1H, s, H-2), 8.33 (1H, s, H-8), 8.40 (1H, s, imidazole H-2): MS *m/e*; 615 (M^+), 572 (M^+−iso-Pr), 136 (B+2), 135 (B+1).

Reduction of 11 with nBu$_3$SnH to 7——**11** (120 mg) was dissolved in 2 ml of dry toluene under an argon atmosphere, and 57 μl of nBu$_3$SnH and a catalytic amount of AIBN were added to the solution. The mixture was heated at 100°C with stirring for 3 h to give **7**, which was crystallized and recrystallized from EtOH. 58 mg (63%): Physical properties of this product were identical with those of the product obtained from **5**.

2′-*O*-(1-Imidazolyl)thiocarbonyl-3′,5′-*O*-(tetraisopropyldisiloxane-1,3-diyl)adenosine (14a)——Compound **13a**[12] (200 mg) was treated with *N*,*N*′-thiocarbonyldiimidazole in the same manner as described above to give 116 mg (48%, foam) of **14a**. NMR (FX-100 in $CDCl_3$); 1.1 (28H, iso-Pr×4), 4.0—4.2 (3H, m, H-5′a,b,

H-4′), 5.5—5.7 (3H, m, NH_2-6, H-3′), 6.11 (1H, s, H-1′), 6.44 (1H, d, H-2′), 7.09 (1H, s, imidazole H-4), 7.68 (1H, s, imidazole H-5), 7.92 (1H, s, H-2), 8.29 (1H, s, H-8), 8.39 (1H, s, imidazole H-2): MS *m/e*; 619 (M^+), 576 (M^+−iso-Pr), 136 (B+2), 135 (B+1).

2′-*O*-(1-Imidazolyl)thiocarbonyl-3′,5′-*O*-(tetraisopropyldisiloxane-1,3-diyl)guanosine (14b)——Compound **13b**[12] (200 mg) was treated with *N*,*N*′-thiocarbonyldiimidazole in the same manner as described above to give 190 mg (79%) of crystalline **14b**: mp 242—245°C (dec.) (AcoEt): NMR (FX-200 in $CDCl_3$); 1.1 (28H, iso-Pr×4), 4.0—4.2 (3H, m, H-5′a,b, H-4′), 5.05 (1H, dd, H-3′), 6.02 (1H, s, H-1′), 6.12 (2H, br, NH_2-2), 6.43 (1H, d, H-2′), 7.08 (1H, s, imidazole H-4), 7.67 (1H, s, imidazole H-5), 7.68 (1H, s, H-8), 8.38 (1H, s, imidazole H-2), 11.97 (1H, br, NH-1).

Anal. Calcd for $C_{26}H_{41}N_7O_6SSi_2$; C, 49.11; H, 6.50; N, 15.42; S, 5.04. Found: C, 48.80; H, 6.49; N, 15.15; S, 4.99.

2′-*O*-(1-Imidazolyl)thiocarbonyl-3′,5′-*O*-(tetraisopropyldisiloxane-1,3-diyl)insoine——Treatment of 3′,5′-*O*-(tetraisopropyldisiloxane-1,3-diyl)inosine (300 mg)[12] in the same manner as described above gave 320 mg (88%) of the title compound. mp 242—244°C (EtOH): NMR (FX-100 in $CDCl_3$); 1.1 (28H, iso-Pr×4), 4.0—4.3 (3H, m, H-5′a,b, H-4′), 5.31 (1H, dd, H-3′), 6.16 (1H, s, H-1′), 6.33 (1H, d, H-2′), 7.09 (1H, s, imidazole H-4), 7.69 (1H, s, imidazole H-5), 8.00 (1H, s, H-2), 8.08 (1H, s, H-8), 8.39 (1H, s, imidazole H-2), 13.01 (1H, br, NH-1).

Anal. Calcd for $C_{26}H_{40}N_6O_6SSi_2$: C, 50.29; H, 6.49; N, 13.54; S, 5.16. Found: C, 50.10; H, 6.53; N, 13.54; S, 5.18.

2′-Deoxy-3′,5′-(tetraisopropyldisiloxane-1,3-diyl)adenosine (15a)——Compound **14a** (200 mg) was reduced with n-Bu_3SnH by the same procedure as described before to give **15a**, 135 mg (78%): NMR (FX-200 in $CDCl_3$); 1.1 (28H, iso-Pr×4), 2.70 (2H, m, H-2′a,b), 3.90 (1H, m, H-4′), 4.05 (2H, m, H-5′), 4.96 (1H, m, H-3′), 5.73 (2H, br, NH_2-6), 6.30 (1H, dd, H-1′), 8.03 (1H, s, H-2), 8.32 ((1H, s, H-8): MS *m/e*; 493 (M^+), 450 (M^+−iso-Pr), 136 (B+2), 135 (B+1).

2′-Deoxy-3′,5′-*O*-(tetraisopropyldisiloxane-1,3-diyl)guanosine (15b)——Compound **14b** (92 mg) gave **15b** by the same procedure as above. 48 mg (66%): mp >300°C (dec.) (EtOH): NMR (FX-100 in $CDCl_3$+DMSO-d_6); 1.1 (28H, iso-Pr×4), 2.5 (m, H-2′a,b, overlapping with DMSO), 3.8—4.1 (3H, m, H-4′, H-5′a,b), 4.74 (1H, m, H-3′), 5.72 (2H, br, NH_2-2), 6.10 (1H, dd, H-1′), 7.6 5(1H, s, H-8), 10.57 (1H, br, NH-1): MS *m/e*; 509 (M^+), 466 (M^+−iso-Pr).

Anal. Calcd for $C_{22}H_{39}N_5O_5Si_2$: C, 51.83; H, 7.71; N, 13.74. Found: C, 51.66; H, 7.58; N, 13.60.

2′-Deoxyadenosine——Deprotection of **15a** (120 mg) with Bu_4NF gave 2′-deoxyadenosine in 90% yield. mp 187—189°C (ref. 187—189°C[13]): NMR (FX-200 in DMSO-d_6); 2.25 (1H, dq, H-2′a), 2.70 (1H, m, H-2′b), 3.58 (2H, m, H-5′), 3.88 (1H, dd, H-4′), 4.40 (1H, m, H-3′), 5.24 (1H, t, OH-5′), 5.29 (1H, d, OH-3′), 6.34 (1H, dd, H-1′), 7.29 (2H, br, NH_2-6), 8.12 (1H, s, H-2), 8.32 (1H, s, H-8): MS *m/e*; 251 (M^+), 233 (M^+-H_2O), 136 (B+2), 135 (B+1).

Anal. Calcd for $C_{10}H_{13}N_5O_3$: C, 47.80; H, 5.22; N, 27.88; Found: C, 47.64; H, 5.19; N, 27.76.

***N*⁶,6′-Dibenzoylneplanocin A (16)**——Neplanocin A (**1**, 5.0 g) was suspended in dry acetone (200 ml) and 70% $HClO_4$ (4.2 ml) was added to afford a solution. The mixture was stirred for 2 h at room temperature, then neutralization with NH_4OH (pH 8) gave crystals. These were filtered off and washed with acetone. The mother liquor was concentrated under reduced pressure and the residue was chromatographed on silica gel. The combined crystalline material gave 4.59 g (80%) of 2′,3′-isopropylideneplanocin A. mp 256—259°C (MeOH): NMR (FX-100 in DMSO-d_6); 1.28, 1.39 (each s, 3H, 3H, isopropyl), 4.15 (2H, slightly br, H-6′), 4.68 (1H, d, H-3′), 5.07 (1H, t, OH-6′), 5.33 (1H, dd, H-2′), 5.45 (1H, dd, H-1′), 5.71 (1H, d, H-5′), 7.25 (2H, br, NH_2-6), 7.96 (1H, s, H-2), 8.15 (1H, s, H-8).

Anal. Calcd for $C_{14}H_{17}N_5O_3$: C, 55.43; H, 5.65; N, 23.09. Found: C, 55.39; H, 5.77; N, 22.89.

The above isopropylidene derivative (303 mg) was perbenzoylated with benzoyl chloride (0.47 ml) in dry pyridine (10 ml) at room temperature, and the resulting crude product, after silica gel chromatography on a short column ($CHCl_3$), was treated with 70% HCOOH at 60°C for 5 h. The reaction mixture was evaporated to dryness under reduced pressure, and the residue was purified by silica gel chromatography ($CHCl_3$: MeOH=20 : 1) to give **16**. 420 mg (89%): mp 202—205°C (MeOH): NMR (FX-100 in DMSO-d_6); 4.48 (1H, m, H-2′), 4.64 (1H, m, H-3′), 5.02 (2H, slightly br, H-6′), 5.25, 5.34 (each d, OH-2′, OH-3′), 5.58 (1H, dd, H-1′), 6.05 (1H, d, H-5′), 7.4—8.1 (10H, m, Ph×2), 8.45 (1H, s, H-2), 8.71 (1H, s, H-8), 11.13 (1H, br, NH-6): MS *m/e*; 471 (M^+).

Anal. Calcd for $C_{25}H_{21}N_5O_5$: C, 63.68; H, 4.49; N, 14.86. Found: C, 63.70; H, 4.55; N, 14.76.

***N*⁶,6′-Dibenzoylneplanocin A 2′,3′-*O*-Cyclic Thiocarbonate (17)**——A mixture of **16** (200 mg) and *N*,*N*′-thiocarbonyldiimidazole (90 mg) in dry DMF (3 ml) was stirred for 16 h at room temperature. The reaction mixture was poured into ice-water with stirring to give a precipitate, which was separated by filtration and washed with water to give almost pure **17**. 211 mg (97%): NMR (FX-100 in $CDCl_3$); 5.16 (2H, ABq, H-6′a,b), 5.65 (1H, d, H-2′), 5.84 (1H, d, H-1′), 6.14 (1H, d, H-5′), 6.39 (1H, d, H-3′), 7.4—8.1 (11H, m, Ph×2 and H-2), 8.56 (1H, s, H-8), 8.95 (1H, br, NH-6): MS *m/e*; 513 (M^+). This was used for the next step without further purification.

***N*⁶,6-Dibenzoyl-3′-deoxyneplanocin A (18)**——A three-necked flask containing 146 mg of **17** was flushed

with argon, and 30 ml of dry benzene was added. A dry benzene solution (5 ml) of nBu$_3$SnH (0.23 ml) and AIBN (30 mg) was added dropwise to the refluxing solution through a syringe under an argon atmosphere. After 1 h, the mixture was cooled and the solvent was evaporated off under reduced pressure. The residue was purified by preparative TLC ($CHCl_3$: MeOH=20 : 1) to give crystalline **18**. 98 mg (76%): mp 164°C (EtOH): NMR (FX-100 in DMSO-d_6) 2.9—3.1 (2H, m, H-3′a,b), 4.96 (2H, slightly br, H-6′), 5.26 (1H, m, H-2′), 5.50 (1H, dd, H-1′), 5.86 (1H, d, H-5′), 7.4—8.1 (10H, m, Ph×2), 8.48 (1H, s, H-2), 8.72 (1H, s, H-8): MS *m/e*: 455 (M^+).

Anal. Calcd for $C_{25}H_{21}N_5O_4$: C, 65.92; H, 4.65; N, 15.38. Found: C, 65.64; H, 4.69; N, 15.02.

***N*^{6},6′-Dibenzoylneplanocin A 2′,3′-Cyclic Carbonate (20)**——Compound **17** (50 mg) was treated with nBu$_3$SnH and AIBN in toluene at 80°C without precaution against the entry of moisture. Isolation and purification were performed by preparative TLC ($CHCl_3$: MeOH=20 : 1) to give **20**. 18 mg (37%): mp 115—118°C (toluene); 5.14 (2H, ABq, H-6′a,b), 5.44 (1H, d, H-2′), 5.76 (1H, d, H-1′), 6.13 (1H, d, H-5′), 6.16 (1H, d, H-3′), 7.4—8.1 (11H, m, Ph×2 and H-2), 8.58 (1H, s, H-8), 8.96 (1H, br, NH-6): MS *m/e*; 497 (M^+).

3′-Deoxyneplanocin A (19)——**18** (250 mg) in 30 ml of NH_3–MeOH (satd. at 0°C) was kept overnight at room temperature. The solvent was then evaporated off under reduced pressure to afford a crystalline residue, which was recrystallized from EtOH–H_2O to give 110 mg (81%) of **19**. mp 187—189°C: NMR (FX-100 in DMSO-d_6); 2.0—3.0 (2H, dABq, H-3′a,b), 4.06 (2H, slightly br, H-6′), 4.47 (1H, m, H-2′), 4.94 (1H, t, OH-6′), 5.30 (1H, dd, H-1′), 5.46 (1H, d, OH-2′), 5.59 (1H, d, H-5′), 7.19 (2H, br, NH_2-6), 8.01 (1H, s, H-2), 8.14 (1H, s, H-8): MS *m/e*; 247 (M^+).

Anal. Calcd for $C_{11}H_{13}N_5O_2$: C, 53.43; H, 5.30; N, 28.33. Found: C, 53.43; H, 5.43; N, 28.02.

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References and Notes

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