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Facile Syntheses of *Pseudo*-α-D-arabinofuranose, and Two *Pseudo*-D-arabinofuranosylnucleosides, (+)-Cyclaradine and (+)-1-*Pseudo*-β-D-arabinofuranosyluracil, from D-Arabinose[1]

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Abstract: An optically active *pseudo*-sugar, *pseudo*-α-D-arabinofuranose, was efficiently synthesized from D-arabinose by using a stereoselective nitromethane addition reaction to form a branched nitropyranose (**6**) as a key step. Furthermore, two biologically active *pseudo*-β-D-arabinofuranosylnucleosides, (+)-cyclaradine and (+)-1-*pseudo*-β-D-arabinofuranosyluracil, were also synthesized from the nitrocyclopentene derivative (**12**), which was prepared from a synthetic intermediate of *pseudo*-arabinofuranose, *via* Michael-type reaction introducing nucleic acid base moieties.

INTRODUCTION

Since the pioneering syntheses of a racemic *pseudo*-sugar (carba-sugar), *pseudo*-α-DL-talopyranose[2], and the racemic *pseudo*-nucleoside (carba-nucleoside), the carbocyclic analogue of adenosine[3], and subsequent isolation of *pseudo*-α-D-galactopyranose[4] from *Streptomyces* sp. M-4145 and (-)-aristeromycin[5] from *Streptomyces citricolor* nov. sp., the syntheses, biological activities, physiological properties, and metabolic pathways in this class of compounds have been an area of intense interest and investigation. After extensive modifications on sugar moieties in nucleosides, *pseudo*-nucleosides have displayed wide range of biological activities and have attracted particular attention as anti-tumor and anti-viral agents. (+)-Cyclaradine (**16**) has been known as a synthetic *pseudo*-nucleoside of a well known antiviral agent 9-β-D-arabinofuranosyladenine (Ara-A).[6] Since **16** is resistant to adenosine deaminase, a serum enzyme which limits the clinical utility of Ara-A, it shows more superior activity against *Herpes simplex* virus than Ara-A. Furthermore, (+)-cyclaradine (**16**) shows activity against trifluorothymidine- or acycloguanosine(acyclovir)-resistant *Herpes simplex* virus mutants. On the other hand, the (-)-enantiomer of **16** was completely uneffective for inhibition of virus replication.[7] Since recent studies on *pseudo*-nucleoside have revealed that biological activities of *pseudo*-nucleoside reside mostly in the "natural-type" enantiomer,[8] many efforts have been made to synthesize enantiomerically pure *pseudo*-nucleosides.[9] During the course of our chemical transformation studies starting from carbohydrates as optically pure starting materials, we successfully synthesized optically active *pseudo*-hexopyranoses,[10] *pseudo*-pentofuranoses,[11] and *pseudo*-aminosugars.[12] Furthermore, we have synthesized *pseudo*-nucleosides such as (-)-9-*pseudo*-β-D-glucopyranosyladenine,[13] (-)-9-*pseudo*-β-L-idopyranosyladenine,[13] (+)-9-*pseudo*-β-L-xylo-furanosyladenine,[14] (+)-cyclaradine (**16**),[14] and (-)-aristeromycin[15] utilizing the Michael-type addition of purine base to nitro-cyclohexenes and nitro-cyclopentenes which were readily prepared from the synthetic intermediates of those *pseudo*-sugars. However, in our previous syntheses of *pseudo*-α-D-arabinofuranose

(**11**) and (+)-cyclaradine (**16**), the overall yields were reduced because of no enantioselectivity in preparation of the nitrocyclitol. Furthermore, the Michael-type addition of pyrimidine bases to nitroolefins have never been accomplished. Therefore, we have engaged in constructing more facile synthetic routes of **11** and **16** and synthesis of a *pseudo*-nucleoside containing pyrimidine base residue as an extention of our synthetic studies for converting carbohydrates to *pseudo*-sugars and *pseudo*-nucleosides. In this paper, we describe a full account of the effective synthesis of *pseudo*-α-D-arabinofuranose (**11**) from D-arabinose (**1**) *via* a stereoselective formation of branched nitropyranose and also reported the syntheses of two *pseudo*-β-D-arabinofuranosylnucleosides, (+)-cyclaradine (**16**) and (+)-1-*pseudo*-β-D-arabinofuranosyluracil (**20**), by use of a Michael-type addition reaction of nucleic acid base and a nitro-cyclopentene derivative prepared from the synthetic intermediate of *pseudo*-D-arabinofuranose (**11**).[1]

RESULTS AND DISCUSSION

Synthesis of pseudo-α-D-arabinofuranose(11)

The starting material, methyl 3,4-*O*-isopropylidene -β -D-arabinopyranoside (**2**),[16] was prepared from D-arabinose (**1**) according to a literature procedure. Compound **2** was quantitatively benzylated with benzyl chloride in *N,N*-dimethylformamide(DMF) in the presence of NaH to provide **3**. Removal of the isopropylidene group in **3** with 80 % aqueous acetic acid at 50 °C gave a diol which was treated with dibutyltin oxide(*n*-Bu_2SnO) followed by selective benzylation[17] with benzyl bromide in DMF in the presence of cesium fluoride (CsF) to give methyl 2,3-di-*O*-benzyl-β-D-arabinopyranoside (**4**) quantitatively. The infrared (IR) spectrum of **4** showed hydroxyl absorption band, whereas the proton nuclear magnetic resonance (^{1}H-NMR) spectrum showed the signals due to two pairs of benzylmethyl groups and ten protons in aromatic rings. In the fast atom bombardment mass (FAB-MS) spectrum of **4**, the quasimolecular ion peak was observed at m/z 367$(M+Na)^+$. Swern oxidation[18] of **4** gave an unstable ketone (**5**) which was immediately treated with nitromethane in DMF in the presence of KF and 18-crown-6 to provide a nitromethane adduct (**6**) in 72 % from **4**. The IR spectrum of **6** showed absorption bands due to hydroxyl and nitro groups at 3470, 1560 and 1380 cm^{-1}, while nitromethyl proton signal appeared at 4.70 ppm (2H, br s) in its ^{1}H NMR. The absolute configuration on C-4 in **6** was corroborated by nuclear Overhauser effect spectrometry (NOESY) experiments. Namely, NOEs were observed between 3-H and 5β-H, 3-H and the nitromethyl proton (6-H_2). This finding indicated that nitromethane addition reaction took place from the less sterically hindered equatorial side of the carbonyl group in **5**. The alcohol (**6**) was acetylated and subsequently subjected to deacetoxyhydrogenation with $NaBH_4$ in ethanol to furnish **7** involving inversion of the nitromethyl group. In the ^{1}H NMR study of **7**, intense analysis of the coupling constants on 3-H (δ 4.01, dd, *J*=5.6, 9.5 Hz) and 5-H_2 (δ 3.51, dd, *J*=3.0, 12.2 Hz; δ 3.84, dd, *J*=2.3, 12.2 Hz) using detailed homo-nuclear decoupling experiments disclosed the configuration on C-4 position of **7**. The stereochemical outcome from **6** to **7** could be rationalized by the following plausible reaction pathway. Namely, the acetate of **6** would be first lead to nitroolefine intermediates and subsequent nucleophilic attack of hydride from less hindered β-side of the pyranose ring resulted in exclusive formation of **7**. Acidic hydrolysis of **7** with conc. HCl and acetic acid gave a branched nitropyranose (**8**). Aldol-type ring transformation catalyzed with CsF furnished an epimeric mixture of nitrocyclopentanes(**9**). Ethoxyethylation of **9** with ethyl vinyl ether in

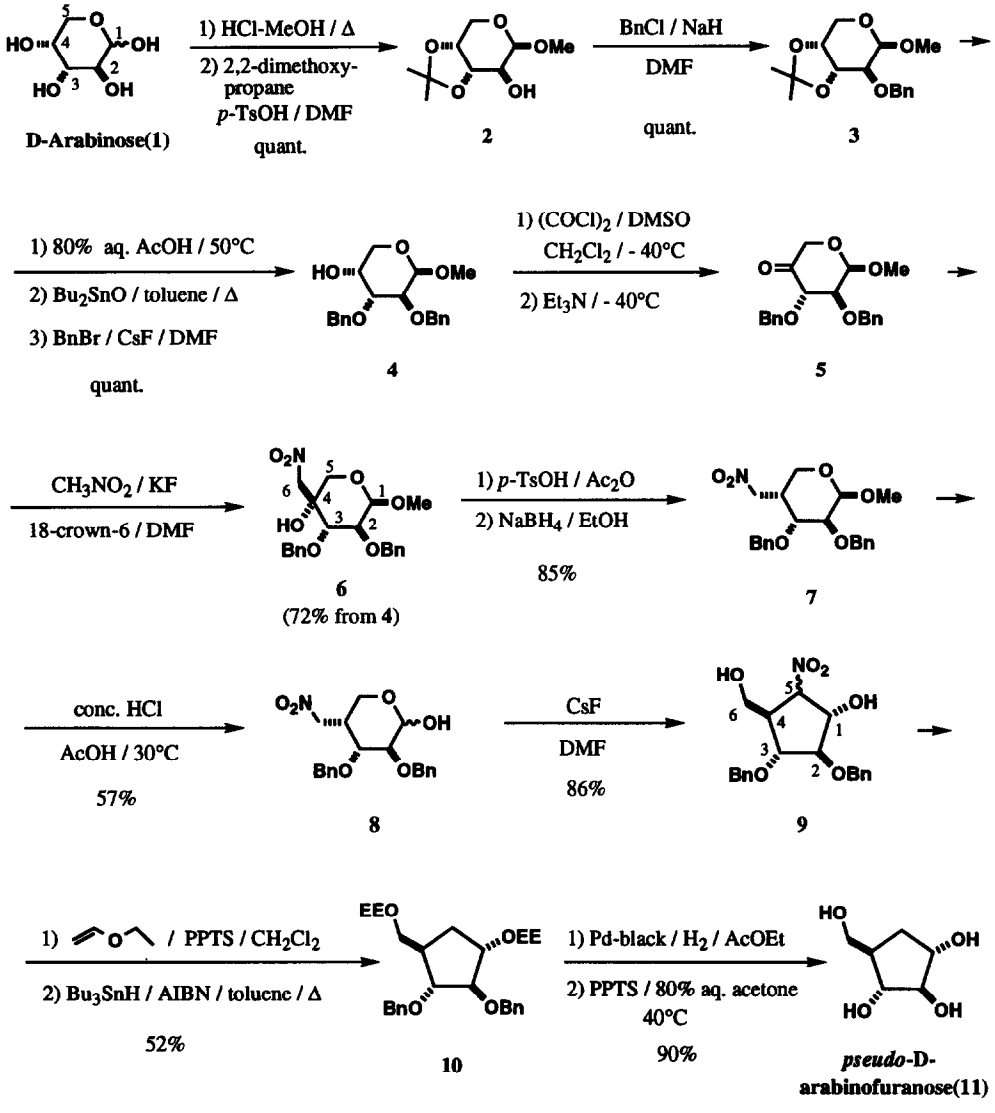

D-Arabinose(1)
1) HCl-MeOH / Δ
2) 2,2-dimethoxy-propane
p-TsOH / DMF
quant.
2
BnCl / NaH
DMF
quant.
3
1) 80% aq. AcOH / 50°C
2) Bu2SnO / toluene / Δ
3) BnBr / CsF / DMF
quant.
4
1) (COCl)2 / DMSO
CH2Cl2 / - 40°C
2) Et3N / - 40°C
5
CH3NO2 / KF
18-crown-6 / DMF
6
(72% from 4)
1) p-TsOH / Ac2O
2) NaBH4 / EtOH
85%
7
conc. HCl
AcOH / 30°C
57%
8
CsF
DMF
86%
9
1) / PPTS / CH2Cl2
2) Bu3SnH / AIBN / toluene / Δ
52%
10
1) Pd-black / H2 / AcOEt
2) PPTS / 80% aq. acetone
40°C
90%
pseudo-D-arabinofuranose(11)

Chart 1

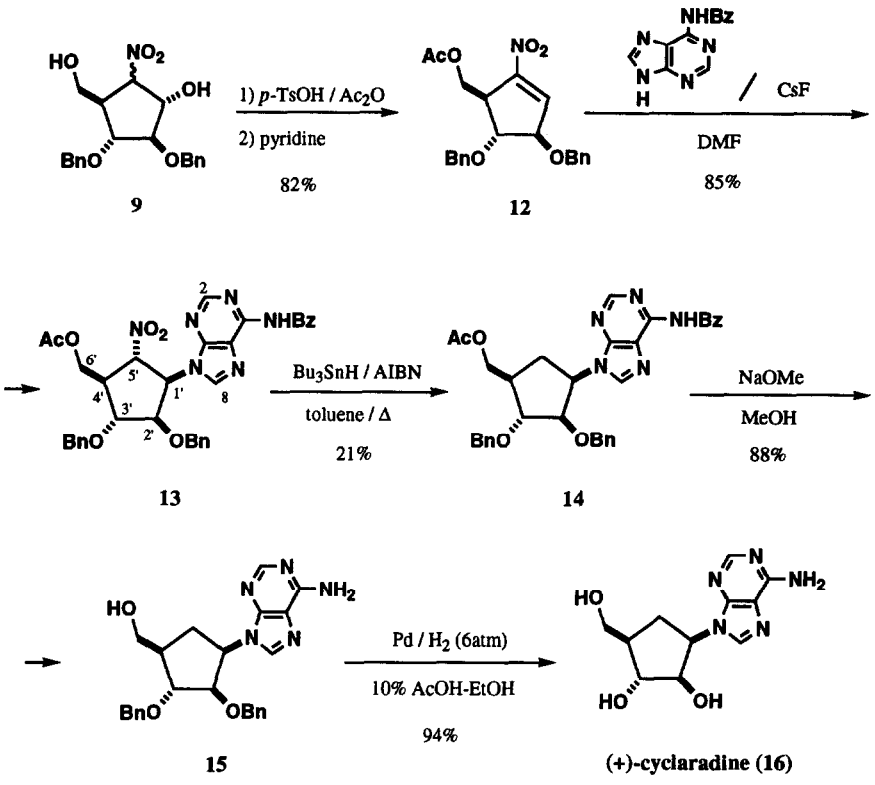
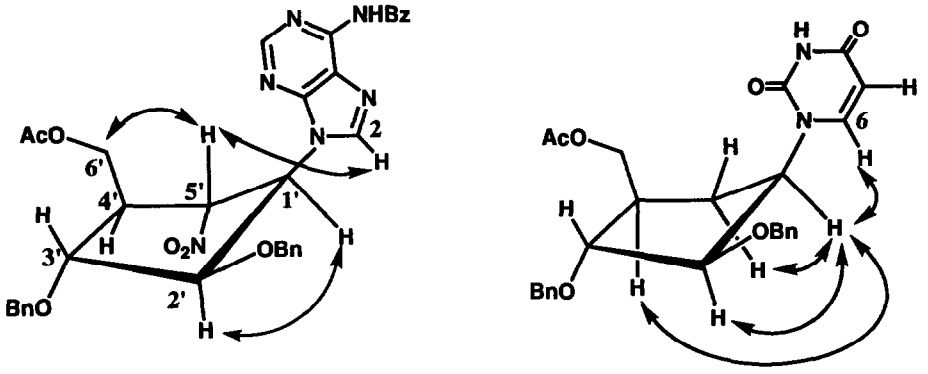


Chart 2

dichloromethane (CH_2Cl_2) in the presence of pyridinium *p*-toluenesulfonate (PPTS) as a catalyst followed by denitrohydrogenation with tributyltin hydride(*n*-Bu_3SnH) and 2,2'-azobisisobutyronitrile (AIBN) in toluene gave a completely protected *pseudo*-D-arabinopyranose (**10**). Finally, debenzylation of **10** with palladium black in EtOH-EtOAc under hydrogen atmosphere and successive acidic treatment with PPTS in 80 % acetone furnished *pseudo*-α-D-arabinofuranose (**11**) in 14 % overall yield from **1**. Compound **11** was identified by detailed comparisons of the ^1H NMR and IR data with those for authentic sample prepared in our previous synthesis.[11] The present conversion method for *pseudo*-D-arabinose (**11**) seems to be significant due not only to the simplicity but also to an improved overall yield which is superior to the previously presented methods.[12,19]

Syntheses of (+)-Cyclaradine (16) and (+)-1-Pseudo-β-D-arabinofuranosyluracil [(+)-C-Ara-U, 20]

In the course of our synthetic studies on *pseudo*-nucleosides, we have utilized nitroolefins readily obtained from nitrocyclitols as acceptors in the Michael type additions of various nitrogen nucleophiles and found the addition reactions toward nitrocyclopentenes to provide thermodynamically stabler adducts, in



13 18

Fig. 1. NOEs Observed in 13 and 18

which the introduced 1-amino group possessed the same orientation as the 4-acyloxymethyl group.[15] Treatment of the nitro-cyclitol (**9**) with acetic anhydride and *p*-TsOH•H_2O provided a mixture of nitro-cyclopentene (**12**) and the 1,5-diacetate of **9**. The mixture was fairly converted to the nitro-cyclopentene by treatment with pyridine. Treatment of **12** with N^6-benzoyladenine in DMF in the presence of CsF at 0 °C provided the 1', 4'-cis adduct (**13**) in 85 % yield. The absorption bands characteristic of the nitro group (1560 cm^{-1}) and the purine base residue (1610, 1590 cm^{-1}) were observed in the IR spectrum of **13**, while the ^1H NMR spectrum newly showed the signals attributable to two methine protons bearing the nitro group (δ 5.46, dd, *J*=7.9, 10.2 Hz, 5'-H) and benzoyladenine residue (δ 5.93, dd, *J*=4.9, 10.2 Hz, 1'-H) respectively. Detailed comparison of spectral data for **13** with those for the homologs described previously[14,15] assumed **13** to possess 1'-R configuration. Additionally, NOE enhancements appeared in the following pairs of protons (1'-H & 2'-H, 5'-H & 6'-H_2, 5'-H & 2-H) in the NOESY spectrum. The enhancements was presumably attributed to the *syn* orientation between the purine base and acetoxymethyl group, and also E conformation of the cyclopentane ring as shown in Fig. 1. The stereostructure of **13** was, therefore, clarified as shown. Denitrohydrogenation of **13** as described above for the conversion from **9** to **10** gave **14**, which was subjected to elimination of the acetyl and *N*-benzoyl groups to yield **15**. The benzyl groups of **15** were finally removed to furnish (+)-cyclaradine (**16**). It was identified by comparison of its physical data with those of authentic sample.[14]

Next, treatment of **12** with a silylated uracil[20] in DMF in the presence of CsF proceeded with the same predominance in diastereoselectivity to afford the 1', 4'-cis adduct (**17**). Reductive elimination of the nitro group of **17** gave **18** and the absolute stereochemistry was corroborated by the ^1H NMR examinations including differencial NOE experiments of **18** as described in Fig 1. Compound **18** was subjected to successive deprotection to furnish 1-(+)-*pseudo*-β-D-arabinofuranosyluracil (**20**). Consideration of the

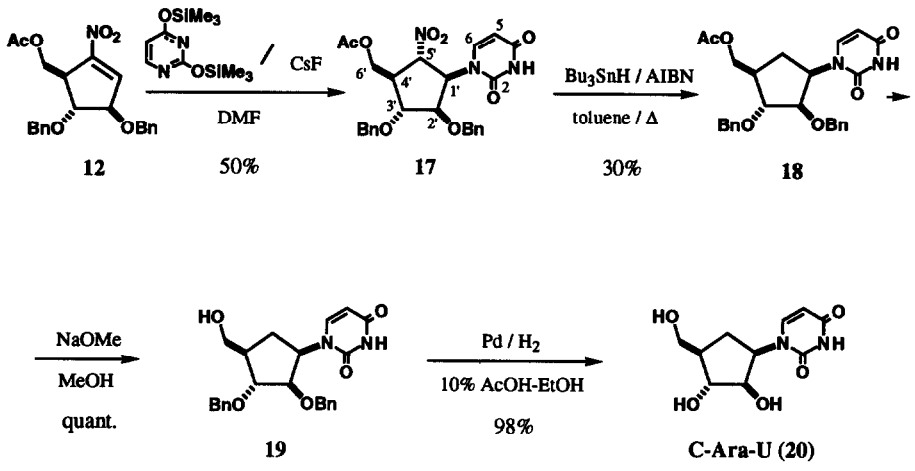


Chart 3

spectral data including the detailed decoupling experiment in the ^1H NMR spectrum of **20** led us to determine the structure **20**. Thus, a facile and enantiospecific syntheses of *pseudo*-α-D-arabinofuranose (**11**), (+)-cyclaradine (**16**), and (+)-1-*pseudo*-β-D-arabinofuranosyluracil [(+)-C-Ara-U, **20**] from D-arabinose (**1**) have been accomplished. The synthetic method may be applied to the synthesis of other *pseudo*-nucleosides, and we are currently extending this approach for the syntheses of other optically active *pseudo*-nucleosides.

EXPERIMENTAL SECTION

General

Optical rotations were measured with a JASCO DIP-370 digital polarimeter and a Horiba SEPA-200 digital polarimeter. Low- and high-resolution EI mass spectra (MS) were taken on a Hitachi M-80 spectrometer. Low- and high-resolution FAB mass spectra were taken on a JEOL JMS-SX102 spectrometer. IR spectra were obtained by using Shimadzu FT-IR DR-8000 or Hitachi 260-30 grating spectrometer. ^1H NMR spectra were recorded on JEOL EX-270 (270 MHz) or JEOL JNM GX-500 (500 MHz) spectrometers with $(CH_3)_4Si$ as the internal standard. ^{13}C NMR spectra were determined on JEOL EX-270 (67.5 MHz) or JEOL JNM GX-500 (125 MHz) spectrometers with $(CH_3)_4Si$ (0 ppm) as the internal standard. UV spectra were determined with Shimadzu UV-1200 spectrometer. The following experimental conditions were used for chromatography : column chromatography, silica gel BW-200 (Fuji-Davidson Chemical); analytical and preparative thin-layer chromatography (TLC), precoated silica gel 60 F_{254} plates (Merck, 0.25 and 0.5 mm layer thickness).

Methyl 3,4-O-isopropylidene-β-D-arabinofuranoside (2)

A solution of D-arabinose (**1**,10.0 g, 66.6 mmol) in 9 % HCl-dry MeOH (10 ml) was heated under reflux for 15 h. The reaction mixture was neutralized with Amberlite IRA-400 ($^-$OH form) and the resin was removed by filtration. Removal of the solvent from the filtrate under reduced pressure gave a product. The product was dissolved in DMF (87 ml) and the solution was treated with 2,2-dimethoxypropane (41.3 ml, 33.6 mmol) and *p*-TsOH•H_2O (62 mg, 0.33 mmol). After stirring at room temperature (25 °C) for 4 h, the reaction mixture was neutralized with Amberlite IRA-400 ($^-$OH form) and the resin was removed by filtration. Removal of the solvent from the filtrate under reduced pressure furnished **2** (14.0 g, quant.) which was identified by comparing the IR, ^{1}H NMR and MS data with reported values.[16] **2**, a colorless oil, $[\alpha]_D^{22}$ -197.0° (*c*=1.00, $CHCl_3$). High resolution FAB MS; Calcd for $C_9H_{17}O_5$ $(M+H)^+$: 205.1076. Found: 205.1073. IR (film): 3460, 2930, 1090, 1060 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 1.36, 1.53 (3H each, both s, isopropylidene), 3.44 (3H, s, OCH_3), 3.78 (1H, m, 2-H), 3.93 (2H, br s, 5-H), 4.17 - 4.26 (2H, m, 3, 4-H), 4.72 (1H, d, *J*=4.0 Hz, 1-H). MS (m/z, %): 189 (M^+-CH_3, 43.8), 59 (100). FAB MS (m/z, positive): 205 $(M+H)^+$.

Benzylation of 2

A solution of **2** (9.4 g, 46.1 mmol) in DMF (27 ml) was treated with NaH (5.56 g, 232 mmol, defatted with dry ether prior to use) and benzyl chloride (16 ml, 139 mmol) in an ice-cooling bath. After stirring at room temperature (25 °C) for 1 h, the reaction mixture were poured into ice-water and the whole was extracted with AcOEt. The AcOEt was washed with brine, then dried over $MgSO_4$ and the solvent was evaporated to dryness under reduced pressure. The residue was purified by column chromatography [SiO_2 400 g, benzene-AcOEt (10:1)] to give **3** (14.3 g, quant.). **3**, a colorless oil, $[\alpha]_D^{22}$ -109.1° (*c*=1.0, $CHCl_3$). High resolution EI-MS; Calcd for $C_{16}H_{22}O_5$ (M^+): 294.1465. Found: 294.1436. IR (film): 2930, 1460, 1090, 740, 700 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 1.36, 1.41 (3H each, both s, isopropylidene), 3.39 (3H, s, OCH_3), 3.52 (1H, dd, *J*=3.3, 7.9 Hz, 2-H), 3.91 (2H, br s, 5-H_2), 4.21 (1H, m, 4-H), 4.33 (1H, dd, *J*=5.6, 7.9 Hz, 3-H), 4.64 (1H, d, *J*=3.3 Hz, 1-H), 4.71, 4.83 (2H, ABq, *J*=12.5 Hz, $PhCH_2$), 7.26 - 7.39 (5H, m, $PhCH_2$). MS (m/z, %): 294 (M^+, 0.4), 91 ($PhCH_2^+$, 100).

Treatment of 3 with 80 % aq. AcOH followed by benzylation

A solution of **3** (12.6 g, 42.9 mmol) in 80 % aq. AcOH (40 ml) was stirred at 50 °C for 8 h and then, the solvent was evaporated under reduced pressure. The product (930 mg) was dissolved in toluene (22 ml) and the solution was treated with *n*-Bu_2SnO (1.09 g, 4.39 mmol). The mixture was heated under reflux for 3 h. After a removal of solvent from the reaction mixture under reduced pressure, the residue, thus obtained, was mixed with CsF (778 mg, 5.12 mmol) and the mixture was dried at 40 °C under reduced pressure for 1.5 h. The suspension of them in DMF (22 ml) was treated with benzyl bromide (0.96 ml, 8.07 mmol) and stirred at room temperature (25 °C) for 2 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt extract was washed with brine, then dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a product which was purified by column chromatography [SiO_2 20 g, benzene-AcOEt (3:1)] to furnish **4** (1.23 g, quant.). **4**, a colorless oil, $[\alpha]_D^{22}$ -64.2°(*c*=1.0, $CHCl_3$). High resolution FAB MS; Calcd for $C_{20}H_{24}O_5Na$ $(M+Na)^+$: 367.1521. Found: 367.1535. IR (film): 3480, 2930,

1100, 1070, 740, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 3.37 (3H, s, OCH_3), 3.71 (2H, m, 5-H), 3.87 (2H, m, 2, 3-H), 3.98 (1H, m, 4-H), 4.68 (1H, d, *J*=3.3 Hz, 1-H), 4.65 - 4.82 (4H, m, $PhCH_2$ x2), 7.25 - 7.37 (10H, m, $\underline{Ph}CH_2$ x2). MS (m/z, %): 312 (M^+-CH_3OH, 1.5), 253 (M^+-$PhCH_2$, 14), 91 ($PHCH_2^+$, 100). FAB MS (m/z, positive): 367 $(M+Na)^+$.

Swern oxidation of 4

A stirred solution of $(COCl)_2$ (10.8 ml, 124 mmol) in CH_2Cl_2 (100 ml) was cooled to -40 °C and treated with DMSO (14.6 ml, 206 mmol). A solution of **4** (14.2 g, 41.3 mmol) in CH_2Cl_2 (6.6 ml) was added dropwise to the reaction mixture and the whole mixture was stirred at -40 °C for 6 h. The reaction solution was then treated with Et_3N (72 ml, 517 mmol) and stirred at room temperature (25 °C) for 30 min.. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt extract was washed with brine, then dried over $MgSO_4$ and the solvent was evaporated under reduced pressure to give the crude ketone **5**. Due to its unstability, the product was used in next reaction without purification. A part of the crude product of **5** was purified by preparative TLC [benzene-AcOEt (3:1)] for obtaining its physical data. **5**, a colorless oil, $[\alpha]_D^{22}$ -78.2°(*c*=2.0, $CHCl_3$). High MS; Calcd for $C_{20}H_{22}O_5$ (M^+): 342.1465. Found: 342.1456. IR (film): 3030, 1730, 740, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 3.48 (3H, s, OCH_3), 3.80 (1H, dd, *J*=3.0, 10.0 Hz, 2-H), 3.90, 4.14 (2H, ABq, *J*=15.0 Hz, 5-H_2), 4.44 (1H, d, *J*=10.0 Hz, 3-H), 4.76 (1H, d, *J*=3.0 Hz, 1-H), 4.68, 4.87 (2H, ABq, *J*=12.0 Hz, $PhCH_2$), 4.72, 5.00 (2H, ABq, *J*=11.0 Hz, $PhCH_2$), 7.28 - 7.46 (10H, m, $\underline{Ph}CH_2$ x2). MS (m/z, %): 342 (M^+, 0.1), 251 (M^+-$PhCH_2$, 4.8), 91 ($PhCH_2^+$, 100).

Nitromethane treatment of 5

A solution of crude **5** (11.1 g, 32.5 mmol) in DMF (61 ml) was treated with KF (2.8 g, 48.2 mmol) and 18-crown-6 (8.55 g, 32.3 mmol) and stirred at room temperature (25 °C) for 30 min. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt extract was washed with brine, then dried over $MgSO_4$. The solvent was evaporated under reduced pressure to give a product which was purified by column chromatography [SiO_2 700 g, *n*-hexane-AcOEt (3:1)] to furnish **6** (9.36 g, 72 % from **3**). **6**, a colorless oil, $[\alpha]_D^{22}$ -20.8°(*c*=1.0, $CHCl_3$). High resolution FAB MS; Calcd for $C_{21}H_{25}NO_7Na$ $(M+Na)^+$: 426.1529. Found: 426.1536. IR (film): 3470, 1560, 1380, 1080, 740, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 3.47 (1H, dd, *J*=3.0, 7.9 Hz, 2-H), 3.49 (3H, s, OCH_3), 3.60, 3.70 (2H, ABq, *J*=11.6 Hz, 5-H_2), 3.89 (1H, d, *J*=7.9 Hz, 3-H), 4.51, 4.69 (2H, ABq, *J*=11.9 Hz, $PhCH_2$), 4.60 (1H, d, *J*=3.0 Hz, 1-H), 4.68, 4.78 (2H, ABq, *J*=11.2 Hz, $PhCH_2$), 4.70 (2H, br s, CH_2NO_2), 7.27 - 7.39 (10H, m, $\underline{Ph}CH_2$ x2). MS (m/z, %): 342 (M^+-CH_3NO_2, 0.1), 312 (M^+-$PhCH_2$, 2.9), 251 (M^+-CH_3NO_2-$PhCH_2$, 2.9), 91 ($PhCH_2^+$, 100). FAB MS (m/z, positive): 426 $(M+Na)^+$.

Conversion from 6 to 7

A solution of **6** (1.02 g, 2.53 mmol) in Ac_2O (18 ml) was treated with *p*-TsOH•H_2O (430 mg, 2.26 mmol) and stirred at room temperature (25 °C) for overnight. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt extract was successively washed with sat. aq. $NaHCO_3$ and brine, then dried over $MgSO_4$ and the solution was evaporated to dryness under reduced

pressure. A solution of the residue (1.48 g) in EtOH (25 ml) was treated with $NaBH_4$ (126 mg, 3.33 mmol) and stirred at room temperature (25 °C) for 1 h. The reaction mixture was poured into ice-water followed by salting out with NaCl and the whole was extracted with AcOEt. The AcOEt extract was washed with brine, then dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a product which was purified by column chromatography [SiO_2 50 g, benzene-AcOEt (50:1)] to furnish **7** (840 mg, 85 %). **7**, a colorless oil, $[\alpha]_D^{22}$ -54.0° (*c*=1.0, $CHCl_3$). High resolution FAB MS; Calcd for $C_{21}H_{25}NO_6Na$ $(M+Na)^+$: 410.1580. Found: 410.1562. IR (film): 1560, 1380, 1110, 740, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 2.91(1H, m, 4-H), 3.36 (1H, dd, *J*=3.6, 9.5 Hz, 2-H), 3.40 (3H, s, OCH_3), 3.51 (1H, dd, *J*=3.0, 12.2 Hz, 5-H), 3.84 (1H, dd, *J*=2.3, 12.2 Hz, 5-H), 4.01 (1H, dd, *J*=5.6, 9.5 Hz, 3-H), 4.52 (1H, dd, *J*=9.8, 13.1 Hz, CH_2NO_2), 4.61 (1H, d, *J*=3.6 Hz, 1-H), 4.63, 4.77 (2H, ABq, *J*=11.9 Hz, $PhCH_2$), 4.69 (1H, dd, *J*=5.0, 13.1 Hz, CH_2NO_2), 4.69 (2H, br s, $PhCH_2$), 7.26 - 7.38 (10H, m, $\underline{Ph}CH_2$ x2). MS (m/z, %): 355 (M^+-CH_3OH, 0.1), 296 (M^+-$PhCH_2$, 4.3), 91 ($PhCH_2^+$, 100). FAB MS (m/z, positive): 410 $(M+Na)^+$.

Demethylation of 7

A solution of **7** (230 mg, 0.594 mmol) in acetic acid (6.4 ml) was treated with conc. HCl (3.2 ml) and stirred at room temperature (30 °C) for overnight. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt extract was washed with sat. aq. $NaHCO_3$, brine and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a product which was purified by column chromatography [SiO_2 10 g, *n*-hexane-acetone (4:1)] to furnish **8** (133 mg, 57 %). **8**, a colorless oil, $[\alpha]_D^{22}$ -7.4° (*c*=1.0, $CHCl_3$). High resolution FAB MS; Calcd for $C_{20}H_{23}NO_6Na$ $(M+Na)^+$: 396.1423. Found: 396.1436. IR (film): 3400, 3030, 1560, 1380, 1090, 740, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 2.93 - 2.98 (1H, m, 4-H), 3.39 - 3.91(4H, 2, 3-H, 5-H_2), 4.27 - 4.75 (7H, 1-H, CH_2NO_2, $PhCH_2$), 7.25 - 7.39 (10H, m, $\underline{Ph}CH_2$ x2). MS (m/z, %): 282 (M^+-$PhCH_2$, 2.8), 91 ($PHCH_2^+$, 100). FAB MS (m/z, positive): 396 $(M+Na)^+$.

Nitromethane cyclization of 8

A solution of **8** (3.0 g, 8.0 mmol) in DMF (30 ml) was treated with CsF (2.43 g, 16.0 mmol) and stirred at room temperature (25 °C) for 3 h. The reaction mixture was poured into ice-water followed by salting out with NaCl and the whole was extracted with AcOEt. Work-up of the AcOEt extract in the usual manner and removal of the AcOEt under reduced pressure yielded a product (3.2 g). The product (1.0 g) was purified by column chromatography [SiO_2 50 g, $CHCl_3$-acetone (10:1)] to furnish **9** (807 mg, 86 %). **9**, a colorless oil, $[\alpha]_D^{22}$ -8.4° (*c*=1.0, $CHCl_3$). High resolution FAB MS; Calcd for $C_{20}H_{23}NO_6Na$ $(M+Na)^+$: 396.1423. Found: 396.1434. IR (KBr): 3400, 3030, 1560, 1380, 1070, 740, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 2.70 - 3.11 (1H, m, 4-H), 3.57 - 4.05 (4H, m, 2, 3-H, 6-H_2), 4.47 - 4.95 (6H, m, 1-H, 5-H, $PhCH_2$ x2), 7.26 - 7.39 (10H, m, $\underline{Ph}CH_2$ x2). MS (m/z, %): 355 (M^+-H_2O, 0.1), 282 (M^+-$PhCH_2$, 6.2), 91 ($PHCH_2^+$, 100). FAB MS (m/z, positive): 396 $(M+Na)^+$.

Ethoxyethylation of 9 followed by denitrohydrogenation

A solution of **9** (20 mg, 0.054 mmol) in CH_2Cl_2 (2.5 ml) was treated with ethyl vinyl ether (0.05 ml, 0.52 mmol) and PPTS (50 mg, 0.20 mmol), and stirred at room temperature (25 °C) for 2h. The reaction

mixture was poured into ice-water and the whole was extracted with AcOEt. Work-up of the AcOEt extract as described above for the preparation of **8** gave the product (34.2 mg). A solution of the product (30.5 mg) in toluene (6.0 ml) was treated with *n*-Bu_3SnH (0.16 ml, 0.60 mmol) and AIBN (15 mg, 0.091 mmol), and heated under reflux for 15 min. The reaction mixture was cooled to room temperature (25 °C) and added $CHCl_3$. Removal of the solvent from the whole mixture under reduced pressure gave the residue which was purified by column chromatography [SiO_2 10 g, *n*-hexane-acetone (15:1)] to furnish **10** (14.5 mg, 52 %). **10**, a colorless oil, IR (film): 2980, 1130, 1060, 740, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 1.15 - 1.36 (12H, m, CH_3 x4), 1.78 - 2.40 (4H, m, 3, 4-H, 5-H_2), 3.35 - 4.16 (5H, m, 1, 2, 3-H, 6-H_2), 4.58 - 4.80 (4H, m, $PhCH_2$ x2), 7.24 - 7.40 (10H, m, $\underline{Ph}CH_2$ x2). MS (m/z, %): 399 (M^+-CH_3CHOEt, 1.1), 73 (CH_3CHOEt^+, 100).

Conversion from 10 to pseudo-α-D-arabinofuranose (11)

A solution of **10** (6.5 mg, 0.014 mmol) in AcOEt (3.5 ml) was hydrogenated in the presence of Pd-black (65 mg, 0.61 mmol) at ordinary temperature and pressure for 1 h. The catalyst was filtered off, and the solvent of the filtrate was evaporated under reduced pressure to gave a product (3.8 mg). A solution of the product (3.1 mg) in 80 % aq. acetone (0.5 ml) was treated with PPTS (22.5 mg, 0.0895 mmol) and stirred at 40 °C for 30 min. The reaction mixture was neutralized with IRA-400 (^-OH form) and the resin was removed by filtration. Removal of the solvent from the filtrate under reduced pressure gave *pseudo*-α-D-arabinofuranose (**11**, 1.8 mg, 90 %) which was confirmed to be identical with an authentic sample[11] by IR (KBr) and ^1H NMR (d5-pyridine - D_2O).

Acetylation of 9 followed by deacetoxyhydrogenation

A solution of **9** (200 mg, 0.0536 mmol) and *p*-TsOH•H_2O (1.70 g, 8.94 mmol) in Ac_2O (3.0 ml) was stirred at room temperature (25 °C) for 30 min. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. Work-up of the AcOEt extract as described above for the preparation of **8** gave a product (226 mg). The product was dissolved in pyridine (3.0 ml), and the whole mixture was stirred at room temperature (25 °C) for 1 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. Work-up of the AcOEt extract as described for the preparation of **8** gave a product which was purified by column chromatography [SiO_2 10 g, *n*-hexane-benzene-AcOEt (10:1:1 – 5:1:1)] to furnish **12** (174 mg, 82 %). **12**, a colorless oil, $[\alpha]_D^{22}$ -82.5° (*c*=1.0, $CHCl_3$). High MS; Calcd for $C_{20}H_{23}NO_6$ $(M)^+$: 397.1524. Found: 397.1527. IR (film): 3030, 1740, 1530, 1350, 1230, 740, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 1.96 (3H, s, CH_3CO), 3.38 (1H, m, 4-H), 4.12 (1H, m, 3-H), 4.38 (2H, d, *J*=4.6 Hz, 6-H_2), 4.57 (1H, m, 2-H), 4.59 (4H, br s, $PhCH_2$ x2), 6.45 (1H, br s, 1-H), 7.32 - 7.42 (10H, m, $\underline{Ph}CH_2$ x2). MS (m/z, %): 397 (M^+, 8.6), 91 ($PHCH_2^+$, 100).

Michael-type addition reaction of 12 with N^6-benzoyladenine to give 13

A solution of **12** (500 mg, 1.26 mmol) in DMF (12.5 ml) was treated with N^6-benzoyladenine (361 mg, 1.51 mmol) and CsF (230 mg, 1.51 mmol), and the whole mixture was stirred in an ice-cooling bath for 1 h. The reaction mixture was poured into ice-water followed by salting out with NaCl, and the whole was extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave a product which was purified

by column chromatography [SiO_2 13 g, *n*-hexane-acetone (2:1)] to furnish **13** (679 mg, 85 %). **13**, a white powder, $[\alpha]_D^{22}$ +65.7° (*c*=1.0, $CHCl_3$). High resolution FAB MS; Calcd for $C_{34}H_{32}N_6O_7$ $(M+H)^+$: 637.2411. Found: 637.2412. IR (KBr): 1740, 1700, 1610, 1590, 1560, 1370, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 2.02 (3H, s, CH_3CO), 3.20 (1H, m, 4'-H), 3.89 (1H, dd, *J*=1.3, 3.3 Hz, 3'-H), 4.15 (1H, d, *J*=4.9 Hz, 2'-H), 4.33 (2H, d, *J*=6.9 Hz, 6'-H), 4.25, 4.39 (2H, ABq, *J*=11.6 Hz, $PhCH_2$), 4.59 (2H, br s, $PhCH_2$), 5.46 (1H, dd, *J*=7.9, 10.2 Hz, 5'-H), 5.93 (1H, dd, *J*=4.9, 10.2 Hz, 1'-H), 6.91 - 8.08 (15H, m, $\underline{Ph}CH_2$ x2, PhCO), 8.24 (1H, s, 8-H), 8.77 (1H, s, 2-H), 9.10 (1H, br s, NH). ^{13}C NMR (67.5 MHz, $CDCl_3$, δ): 20.3 ($\underline{C}H_3CO$), 47.6 (4'-C), 58.6 (1'-C), 63.0 (6'-C), 71.7 ($Ph\underline{C}H_2$), 72.3 ($Ph\underline{C}H_2$), 79.4 (3'-C), 80.5 (2'-C), 87.1 (5'-C), 122.4 (5-C), 127.6 - 136.5 (17C, $\underline{Ph}CH_2$ x2, $\underline{Ph}CO$), 141.9 (8-C), 149.5 (6-C), 152.1 (2-C), 152.4 (4-C), 164.9 (PhCO), 170.4 (CH_3CO). MS (m/z, %): 398 (M^+-N^6-benzoyladenine, 0.2), 91 ($PHCH_2^+$, 100). FAB MS (m/z, positive): 637 $(M+H)^+$.

Denitrohydrogenation of 13

A solution of **13** (200 mg, 0.31 mmol) in toluene (40 ml) was treated with *n*-Bu_3SnH (0.8 ml, 3.0 mmol) and AIBN (76 mg, 0.46 mmol), and heated under reflux for 1 h. The reaction mixture was cooled to room temperature (25 °C) and added $CHCl_3$. Removal of the solvent from the reaction mixture under reduced pressure gave a product which was purified by column chromatography [SiO_2 60 g, benzene-acetone (5:1)] to furnish **14** (38 mg, 21 %). **14**, a white powder, $[\alpha]_D^{22}$ +47.7° (*c*=1.0, $CHCl_3$). High MS; Calcd for $C_{34}H_{33}N_5O_5$ (M^+): 591.2479. Found: 591.2508. IR (KBr): 1740, 1700, 1610, 1580, 1250, 740 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 2.05 (3H, s, CH_3CO), 2.13 (1H, m, 5'-H), 2.48 (2H, m, 4', 5'-H), 3.85 (1H, br s, 3'-H), 4.08 (1H, d, *J*=4.6 Hz, 2'-H), 4.19 (2H, d, *J*=6.6 Hz, 6'-H), 4.20, 4.38 (2H, ABq, *J*=11.4 Hz, $PhCH_2$), 4.53, 4.59 (2H, ABq, *J*=12.2 Hz, $PhCH_2$), 5.30 (1H, m, 1'-H), 6.95 - 8.02 (15H, m, $\underline{Ph}CH_2$ x2, PhCO), 8.25 (1H, s, 8-H), 8.77 (1H, s, 2-H), 9.12 (1H, br s, NH). ^{13}C NMR (67.5MHz, $CDCl_3$, δ): 20.8 ($\underline{C}H_3CO$), 31.3 (5'-C), 42.2 (4'-C), 54.8 (1'-C), 65.8 (6'-C), 71.7 ($Ph\underline{C}H_2$), 71.9 ($Ph\underline{C}H_2$), 81.4 (2'-C), 82.6 (3'-C), 122.4 (5-C), 123.0 - 137.6 (18C, $\underline{Ph}CH_2$ x2, $\underline{Ph}CO$), 142.9 (8-C), 149.2 (6-C), 152.4 (2-C), 152.5 (4-C), 164.6 ($Ph\underline{C}O$), 170.9 ($CH_3\underline{C}O$). MS (m/z, %): 591 (M^+, 1.9), 500 (M^+-$PhCH_2$, 21), 91 ($PHCH_2^+$, 100).

Conversion from 14 to 15

A solution of **14** (38 mg, 0.064 mmol) in 10 % NaOMe-MeOH (2.0 ml) was stirred at room temperature (25 °C) for 6 h. The reaction mixture was poured into ice-water and the whole was extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed with brine then dried over $MgSO_4$. Removal of the solvent from the extract under reduced pressure gave a product which was purified by column chromatography [SiO_2 3 g, $CHCl_3$-MeOH (20:1)] to furnish **15** (25 mg, 88 %). **15**, a white powder, $[\alpha]_D^{22}$ +60.2° (*c*=1.00, $CHCl_3$). High MS; Calcd for $C_{25}H_{27}N_5O_3$ (M^+): 445.2112. Found: 445.2121. IR (KBr): 3300, 1650, 1600, 1070, 740, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ): 2.20 (1H, m, 5'-H), 2.40 (2H, m, 4', 5'-H), 3.72 (1H, dd, *J*=5.6, 10,9 Hz, 6'-H), 3.79 (1H, dd, *J*=4.6, 10.9 Hz, 6'-H), 3.93 (1H, br s, 3'-H), 4.08 (1H, dd, *J*=1.3, 4.6 Hz, 2'-H), 4.18, 4.34 (2H, ABq, *J*=11.5 Hz, $PhCH_2$), 4.53, 4.61 (2H, ABq, *J*=11.9 Hz, $PhCH_2$), 5.21 (1H, m, 1'-H), 5.65 (2H, br s, NH_2), 6.95 - 7.40 (10H, m, $\underline{Ph}CH_2$ x2), 8.04 (1H, s, 8-H), 8.33 (1H, s, 2-H). MS (m/z, %): 445 (M^+, 0.7), 354 (M^+-$PhCH_2$, 33), 232 (100), 91 ($PHCH_2^+$, 80).

Conversion from 15 to (+)-cyclaradine (16)

A solution of **15** (11 mg, 0.025 mmol) in 10 % AcOH-EtOH (v/v) (11ml) was hydrogenated in the presence of Pd-black (110 mg, 1.0 mmol) at room temperature (25 °C) at a hydrogen pressure of 6 atmospheres for 1 h. The catalyst was filtered off and the solvent was removed from the filtrate under reduced pressure to gave a product which was purified by column chromatography [SiO_2 2 g, $CHCl_3$-MeOH-H_2O (7:3:1, lower phase)] to furnish (+)-cyclaradine (**16**, 25 mg, 94 %). **16**, a white powder, $[\alpha]_D^{22}$ +50.9° (*c*=1.0, MeOH). High MS (m/z); Calcd for $C_{11}H_{15}N_5O_3$ (M^+): 265.1173. Found: 265.1190. IR (KBr): 3350, 1660, 1610 cm^{-1}. ^1H NMR (270 MHz, CD_3OD, δ): 2.16 (1H, m, 4'-H), 2.19 (1H, ddd, *J*=2.6, 10.7, 11.9 Hz, 5'-H), 2.48 (1H, ddd, *J*=4.3, 7.6, 11.9 Hz, 5'-H), 3.72 (1H, dd, *J*=5.9, 10.6 Hz, 6'-H), 3.79 (1H, dd, *J*=5.3, 10.6 Hz, 6'-H), 3.96 (1H, dd, *J*=3.0, 4.6 Hz, 3'-H), 4.08 (1H, dd, *J*=3.0, 5.0 Hz, 2'-H), 5.18 (1H, ddd, *J*=2.6, 5.0, 7.8 Hz, 1'-H), 8.39 (1H, s, 8-H), 8.50 (1H, s, 2-H). EI-MS (m/z, %): 265 (M^+, 3.8), 234 (M^+-CH_2OH, 6.0), 135 (adenine, 100). The ^1H NMR spectrum was previously taken in d_6-DMSO. The physicochemical properties other than the NMR data have never been described.

Michael-type addition reaction of 12 with silylated uracil

A solution of **12** (250 mg, 0.630 mmol) in DMF (7.5 ml) was treated with silylated uracil (230 mg, 0.898 mmol) and CsF (124 mg, 0.816 mmol), and the whole mixture was stirred at room temperature (25 °C) for 1 h. The reaction mixture was poured into ice-water and the whole solution was subjected to salting out with NaCl, and then the whole was extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave a product which was purified by column chromatography [SiO_2 15 g, benzene-acetone (5:1)] to furnish **17** (160 mg, 50 %). **17**, a white powder, $[\alpha]_D^{22}$ +91.3° (*c*=1.0, $CHCl_3$). High MS; Calcd for $C_{26}H_{28}N_3O_8$ $(M+H)^+$: 510.1876. Found: 510.1891. IR (KBr): 3030, 1740, 1690, 1560, 1370, 1240 cm^{-1}. UV λ [nm (ε), $CHCl_3$] : 263 (14000). ^1H NMR (270 MHz, $CDCl_3$, δ): 1.93 (3H, s, CH_3CO), 2.99 (1H, m, 4'-H), 3.69 (1H, dd, *J*=1.7, 4.0 Hz, 3'-H), 4.00 (1H, d, *J*=5.3 Hz, 2'-H), 4.18 (2H, d, *J*=8.0 Hz, 6'-H_2), 4.26, 4.40 (2H, ABq, *J*=11.6 Hz, $PhCH_2$), 4.46, 4.51 (2H, ABq, *J*=11.9 Hz, $PhCH_2$), 5.01 (1H, dd, *J*=8.1, 10.9 Hz, 5'-H), 5.59 (1H, dd, *J*=5.3, 10.9 Hz, 1'-H), 5.63 (1H, d, *J*=8.3 Hz, 5-H), 7.12 - 7.33 (10H, m, $\underline{Ph}CH_2$ x2), 7.35 (1H, d, *J*=8.3 Hz, 6-H), 8.36 (1H, br s, NH). FAB MS (m/z, positive): 510 $(M+H)^+$.

Denitrohydrogenation of 17

A solution of **17** (130 mg, 0.255 mmol) in toluene (27 ml) was treated with *n*-Bu_3SnH (0.74 ml, 2.8 mmol) and AIBN (68 mg, 0.41 mmol), and the whole mixture was stirred at 110 °C for 1 h. The reaction mixture was cooled to room temperature (25 °C) and added $CHCl_3$. Removal of the solvent from the whole mixture under reduced pressure gave a product which was purified by column chromatography [SiO_2 25 g, benzene-acetone (5:1)] and subsequent preparative TLC [benzene-acetone (3:1)] to furnish **18** (35.5 mg, 30 %). **18**, a white powder, $[\alpha]_D^{22}$ +120.5° (*c*=1.0, $CHCl_3$). High resolution FAB MS; Calcd for $C_{26}H_{29}N_2O_6$ $(M+H)^+$: 465.2025. Found: 465.2008. IR (KBr): 3460, 3220, 1740, 1690, 1250, 740, 700 cm^{-1}. UV λ [nm (ε), $CHCl_3$] : 266 (8500). ^1H NMR (270 MHz, $CDCl_3$, δ): 1.84 (1H, dd, *J*=10.2, 12.5 Hz, 5'-H), 2.02 (3H, s, CH_3CO), 2.39 (1H, m, 4'-H), 3.70 (1H, dd, *J*=1.0, 4.3 Hz, 3'-H), 3.99 (1H, d, *J*=5.1 Hz, 2'-H), 4.14 (2H, d, *J*=6.9 Hz, 6'-H_2), 4.31, 4.46 (2H, ABq, *J*=11.6 Hz, $PhCH_2$), 4.47, 4.55 (2H, ABq, *J*=12.0

Hz, $PhCH_2$), 5.10 (1H, ddd, *J*=5.1, 7.3, 12.5 Hz, 1'-H), 5.65 (1H, dd, *J*=2.1, 8.2 Hz, 5-H), 7.12 - 7.38 (10H, m, $\underline{Ph}CH_2$ x2), 7.46 (1H, d, *J*=8.2 Hz, 6-H), 8.53 (1H, br s, NH). MS (m/z, %): 373 (M^+-$PHCH_2$, 9), 91 ($PHCH_2^+$, 100). FAB MS (m/z, positive): 465 $(M+H)^+$.

Conversion of 18 to 19

A solution of **18** (30 mg, 0.065 mmol) in 1 % NaOMe-MeOH (2.0 ml) was stirred at room temperature (25 °C) for 30 min. The reaction mixture was poured into ice-water followed by salting out with NaCl, and the whole was extracted by CH_2Cl_2. The CH_2Cl_2 extract was washed with brine and dried over $MgSO_4$, then removal of the solvent from the extract under reduced pressure yielded **19** (28 mg, quant.). **19**, a white powder, $[\alpha]_D^{22}$ +115.6° (*c*=1.0, $CHCl_3$). High MS; Calcd for $C_{24}H_{26}N_2O_5$ $(M)^+$: 422.1839. Found: 422.1832. IR (KBr): 3420, 3030, 1680, 1070, 740, 700 cm^{-1}. UV λ [nm (ε), $CHCl_3$] : 268 (10800). ^1H NMR (270 MHz, $CDCl_3$, δ): 1.89 (1H, m, 5'-H), 2.14 (1H, m, 5'-H), 2.26 (1H, m, 4'-H), 3.70 (2H, br s, 6'-H), 3.77 (1H, d, *J*=4.3 Hz, 3'-H), 4.00 (1H, d, *J*=5.3 Hz, 2'-H), 4.32, 4.46 (2H, ABq, *J*=11.2 Hz, $PhCH_2$), 4.49, 4.58 (2H, ABq, *J*=11.9 Hz, $PhCH_2$), 5.12 (1H, ddd, *J*=5.3, 6.6, 12.4 Hz, 1'-H), 5.64 (1H, d, *J*=7.9 Hz, 5-H), 7.15 - 7.35 (10H, m, $\underline{Ph}CH_2$ x2), 7.48 (1H, d, *J*=7.9 Hz, 6-H), 8.85 (1H, br s, NH). MS (m/z, %): 422 (M^+, 1.9), 91 ($PHCH_2^+$, 100).

Conversion of 19 to (+)-pseudo-β-D-arabinofuranosyluracil (20)

A solution of **19** (7 mg, 0.017 mmol) in 10 % AcOH-EtOH (7 ml) was hydrogenated in the presence of Pd-black (70 mg, 0.66 mmol) at ordinary temperature and pressure. After 1 h, the catalyst was filtered off and removal of the solvent from the filtrate under reduced pressure gave a product which was purified by column chromatography [SiO_2 2 g, $CHCl_3$-MeOH-H_2O (7:3:1, lower phase)] to furnish (+)-*pseudo*-β-D-arabinofuranosyluracil (**20**, 3.5 mg, 98 %). **20**, a white powder, $[\alpha]_D^{22}$ +112.3° (*c*=0.2, MeOH). High resolution FAB MS; Calcd for $C_{10}H_{15}N_2O_6$ $(M+H)^+$: 243.0981. Found: 243.0995. IR (KBr): 3350, 1690 cm^{-1}. UV λ [nm (ε), MeOH] : 268 (10000). ^1H NMR (270 MHz, CD_3OD, δ): 1.88 (1H, m, 5'-H), 1.99 (1H, m, 4'-H), 2.12 (1H, m, 5'-H), 3.63 (1H, dd, *J*=6.5, 10.7 Hz, 6'-H), 3.74 (1H, dd, *J*=4.9, 10.7 Hz, 6'-H), 3.77 (1H, dd, *J*=2.8, 5.0 Hz, 3'-H), 3.99 (1H, dd, *J*=2.8, 5.6 Hz, 2'-H), 4.96 (1H, ddd, *J*=5.6, 6.9, 12.2 Hz, 1'-H), 5.62 (1H, d, *J*=8.1 Hz, 5-H), 7.72 (1H, d, *J*=8.1 Hz, 6-H). MS (m/z, %): 242 (M^+, 5), 113 ([uracil+H]$^+$, 100). FAB MS (m/z, positive): 243 $(M+H)^+$.

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