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Synthesis of ethyl 2-acetamido-6-*S*-(5-amino-5-deoxy-β-D-arabinopyranosyl)-2-deoxy-1,6-dithio-β-D-glucopyranoside: a sulfur-linked 5-amino-5-deoxyglycopyranosyl disaccharide

Katsuhiko Suzuki [1], Hironobu Hashimoto *

Department of Life Science, Faculty of Bioscience and Biotechnology, Tokyo Institute of Technology, Nagatsuta, Midoriku, Yokohama 226-8501, Japan

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Abstract

A novel pseudo-disaccharide having an imino sugar residue at the non-reducing end, namely, a sulfur-linked 5-amino-5-deoxyglycopyranosyl disaccharide, which is a potential specific inhibitor for glycosidases that recognize not only the glycosidic linkage but also the aglycone moiety, was synthesized. Glycosidation of *N*-Boc-5-amino-5-deoxy-D-arabinose with ethyl 2-acetamido-3,4-di-*O*-acetyl-2-deoxy-1,6-dithio-β-D-glucopyranoside in the presence of TsOH gave exclusively the corresponding 1,2-*cis*-linked thioglycoside. The interglycosidic linkage proved stable enough under conditions for the deprotection of the *N*-Boc group with TFA. This pseudodisaccharide was unstable at pH > 5, but stable at lower pH. The sulfur-linked 5-amino-5-deoxyglycopyranosyl disaccharide was shown to be formed from 5-amino-5-deoxy-D-arabinose and ethyl 2-acetamido-2-deoxy-1,6-dithio-β-D-glucopyranoside in an acidic buffer solution.

Keywords: Imino sugar; 5-Amino-5-deoxyglycopyranosyl thioglycoside; Glycosidation; *N*,*S*-acetal

1. Introduction

Glycosidases, among the most important carbohydrate enzymes, are responsible for the control of various biological phenomena. Inhibitors of these enzymes aid in investigations of several important biochemical processes. Such inhibitors are commonly based on naturally occurring or synthetic substrate analogues, wherein the ring oxygen is substituted by other atoms such as nitrogen, sulfur, and carbon. Glycosidases are usually classified as aglycone-specific or non-specific, based on their substrate specificity. Many imino sugars (pseudo-sugars with nitrogen in the ring), or polyhydroxy-piperidines and -pyrrolidines, have remarkable inhibitory activities against exo-glycosidases [1], due to their strong affinities for the carboxylate group in the active site of glycosidases. In general, glycosidases have rather strict recognition requirements for the glycone moiety of their substrate. Imino sugars therefore show specific inhibition against glycosidases that hydrolyze glycosides having the same configuration as the imino sugar [2]. In contrast, most exo-glycosidases are not specific for the aglycone moiety of the substrate glycoside.

* Corresponding author. Tel.: +81-45-924-5704; fax: +81-45-924-5805.

E-mail address: hhashimo@bio.titech.ac.jp (H. Hashimoto)

[1] Present address: College of Science and Engineering, Iwaki Meisei University, Iwaki, Fukushima 970, Japan.

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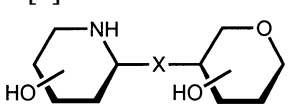
Pseudo-oligosaccharides having a pseudo sugar at the non-reducing end are potential candidates for specific inhibitors of glycosidases that recognize not only the glycosidic linkage but also the aglycone moiety. Recently, we synthesized 5-thio-L-fucose-containing disaccharides having α-(1→6), α-(1→3), or α-(1→4) linkages to GlcNAc, and an α-(1→2) linkage to Gal [3]. Only the α(1→2)-linked disaccharide showed inhibitory activity against *Bacillus* sp. K40T α-L-fucosidase (EC 3.2.1.63), which hydrolyzes the α-L-Fuc-(1→2) linkage specifically.

Some pseudo-oligosaccharides having deoxynojirimycin or an analogue (a 1,5-dideoxy-1,5-iminohexitol) [4] and α-homonojirimycin (a 2,6-dideoxy-2,6-iminoheptitol) [5] at the reducing end have been synthesized. However, an aminal-type pseudo-oligosaccharide having an imino sugar residue at the non-reducing end, even a disaccharide, had not been synthesized prior to our preliminary report [6], because *O*-glycosyl derivatives of imino sugars (*N*,*O*-acetal **1**) are extremely unstable, being prone to elimination giving the corresponding cyclic imines [7]. On the other hand, several stable C-linked pseudo-disaccharides having an imino sugar at the non-reducing end have been reported [8].



1 X = O

2 X = S

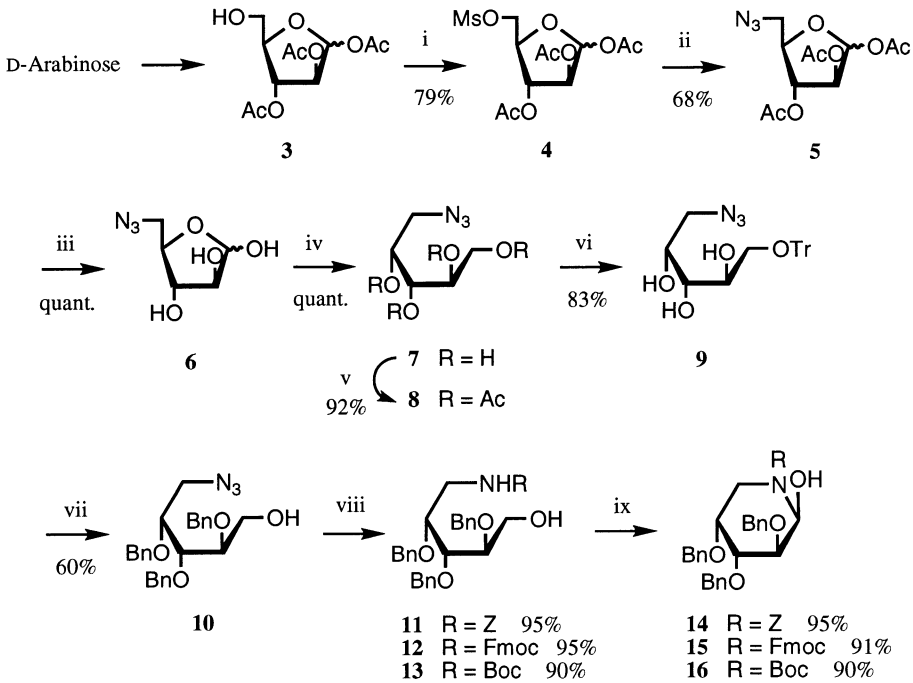
In a previous communication, we reported the synthesis of a novel pseudo-disaccharide **2** having an imino sugar residue at the non-reducing end, linked to the aglycone sugar through a thioaminal linkage [7]. The thioaminal linkage was found to be more stable than the corresponding O-glycosidic (aminal) linkage. In this paper, we describe details of the unique character of a 5-amino-5-deoxyglycopyranosyl (polyhydroxypiperidyl) thioglycoside. In aqueous solution, this thioglycoside of a 5-amino-5-deoxyglycopyranose is unstable at pH > 5; it anomerizes rapidly or is hydrolyzed, but is stable at lower pH. The 5-amino-5-deoxyglycopyranosyl thioglycoside (*N*,*S*-acetal) was formed from a 5-amino-5-deoxyglycopyranose and a 6-thio sugar in an acidic buffer solution.

2. Results and discussion

Our target pseudodisaccharide, namely a 5-amino-5-deoxyglycopyranosyl disaccharide, was synthesized through glycosidation of protected imino sugars with a sugar thiol, followed by deprotection. In this coupling reaction, 5-alkoxycarbonylamino-5-deoxyglycopyranoses were selected as donors, based on their stability under acidic glycosidation conditions [7].

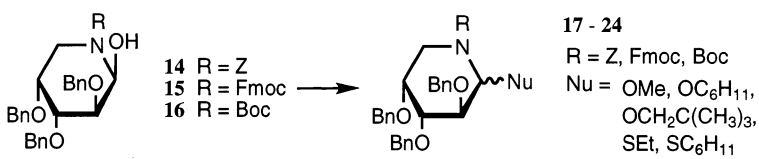
In general, the synthesis of 5-amino-5-deoxypentopyranose can be achieved in shorter steps than for 5-amino-5-deoxyhexopyranoses, because the conversion of the primary hydroxyl into an amino group is easy and prevents stereochemical problems. To examine the glycosidation reaction of imino sugars, N-protected 5-amino-2,3,4-tri-*O*-benzyl-5-deoxy-D-arabinoses **14**, **15**, and **16** were synthesized from D-arabinose as a model imino sugar (Scheme 1). An azido group was introduced by substitution on the 5-O-mesylated furanoside **4** with NaN_3 in Me_2SO. After O-deacetylation, the hemiacetal **6** was reduced with $NaBH_4$ in MeOH to afford 5-azido-5-deoxy-D-arabinitol (**7**), whose structure was confirmed by the NMR spectrum of its tetraacetate **8**. The 1-trityl ether **9**, obtained in high yield by conventional tritylation of **7**, was benzylated to give the tri-benzyl ether **10**. The azido group of **10** was converted into an amino group, which was protected as benzyl carbamate (*N*-Z) **11**, the 9-fluorenylmethyl carbamate (*N*-Fmoc) **12**, and the *tert*-butyl carbamate (*N*-Boc) **13**. The hemiaminals (*N*,*O*-acetals) **14**, **15**, and **16** were constructed by Swern oxidation [9] of the amino alcohols **11**, **12**, and **13**, respectively.

Reaction of the 1-acetates of the aminals **14**, **15**, and **16** with a simple alcohol or a thiol in the presence of Me_3SiOTf (1 equiv) in CH_2Cl_2 gave the corresponding glycosides **17**–**21** (Table 1, entries 1–5). While the yields of the *N*-Z and *N*-Fmoc derivatives were good, that of the *N*-Boc derivative (entry 5) was lower due to partial decomposition of the Boc



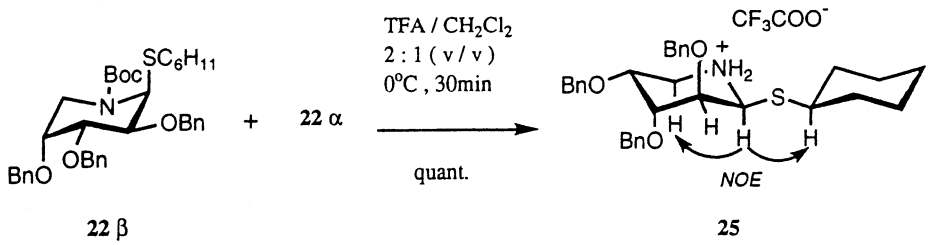
Scheme 1. Synthesis of N-protected 5-amino-2,3,4-tri-*O*-benzyl-5-deoxy-D-arabinoses **14**–**16**. Reagents: (i) MsCl, pyridine; (ii) NaN_3, Me_2SO; (iii) NaOMe, MeOH; (iv) $NaBH_4$, MeOH; (v) Ac_2O, pyridine; (vi) TrCl, pyridine; (vii) (a) BnBr, NaH, DMF, (b) 70% aqueous AcOH; (viii) $LiAlH_4$, THF then H_2O, ZCl or FmocCl or Boc_2O; (ix) $(COCl)_2$, Me_2SO, Et_3N, CH_2Cl_2.

Table 1
Glycosylation with N-protected 5-amino-5-deoxy-D-arabinose



Entry	Donor	Acceptor (NuH)	Method [a]	Yield (%)	β:α [b]	Product
1	**14**	$(CH_3)_3CCH_2OH$	A	quant.	1:0	**17** R = Z, Nu = $OCH_2C(CH_3)_3$
2	**14**	EtSH	A	quant.	3:1	**18** R = Z, Nu = SEt
3	**15**	EtSH	A	79	2.8:1	**19** R = Fmoc, Nu = SEt
4	**15**	$C_6H_{11}SH$	A	73	3.1:1	**20** R = Fmoc, Nu = SC_6H_{11}
5	**16**	EtSH	A	40	3.8:1	**21** R = Boc, Nu = SEt
6	**16**	$C_6H_{11}SH$	B	72	7.3:1	**22** R = Boc, Nu = SC_6H_{11}
7	**16**	$C_6H_{11}OH$	B	73	1:0	**23** R = Boc, Nu = OC_6H_{11}
8	**16**	MeOH	B	88	1:0	**24** R = Boc, Nu = OMe

[a] (A) (i) Ac_2O, pyridine; (ii) NuH, Me_3SiOTf (1.1 equiv), 4 Å molecular sieves, CH_2Cl_2; (B) NuH, TsOH (1 equiv), CH_2Cl_2.
[b] Ratio was determined by intensities of ^1H NMR signals of H-1.



Scheme 2. Conformational change of the thioglycoside **22b** of 5-amino-5-deoxy-D-arabinose from $^1C_4$ to $^4C_1$ (**25**) by N-deprotection.

group under the coupling conditions. We then found that the free aminal **16** reacted readily with alcohols in the presence of TsOH (1 equiv) as catalyst, giving the glycosides **22**–**24** in satisfactory yields (entries 6–8). This glycosylation reaction with an N-protected imino sugar using TsOH is extremely convenient. In the reaction with alcohols, the more thermodynamically stable β-*O*-glycosides were obtained exclusively. The stereoselectivities in these glycosylations can be explained by an enhanced anomeric effect in N–C–S systems compared with the O–C–O system [10].

The *N*-Boc group of the thioglycoside was successfully removed, whereas deprotection of the *N*-Z and *N*-Fmoc groups was unsuccessful because of ensuing decomposition of the glycoside. Treatment of the *N*-Boc thioglycoside **22** (β:α = 7.3:1) with 2:1 TFA–CH_2Cl_2 gave the N-unprotected glycoside **25** as the pure β anomer in good yield (Scheme 2). The thioaminal structure of **25** is supported by the characteristic ^{13}C NMR signal of the anomeric carbon (δ 60.04). It is noteworthy that the deprotection followed by salt formation causes a conformational change from $^1C_4$ of **22β** to $^4C_1$ of **25**. The $^1C_4$ conformation of **22β** is confirmed by the ^1H NMR data for $J_{2,3}$ 9.9 Hz, $J_{4,5e} < 0.3$ Hz, and $J_{4,5a} < 0.3$ Hz. In contrast, a large value for one of two coupling constants between H-4 and H-5 ($J_{4,5a}$ 11.6 Hz) for **25** indicates a conformational change of the iminopyranose ring from $^1C_4$ to $^4C_1$. The NOE correlation observed between H-1 and H-5 in the ^1H NMR spectrum of **25** also supports the $^4C_1$ conformation and 1,2-*cis*-glycoside. For the *O*-glycoside **24**, deprotection of the *N*-Boc group caused successive eliminations to give 3-benzyloxypyridine and benzyl alcohol. The stability of the thioglycoside can be interpreted in terms of the lower basicity of the sulfur atom. The preference for the $^4C_1$ conformation in **25** is attributed to the positive charge on the ring nitrogen atom, which causes an effect similar to that originally reported in the case of exocyclic quaternary substituents and termed the reverse anomeric effect [11]. The change of anomeric ratio indicates the anomerization of **22** or **25** under these deprotection conditions.

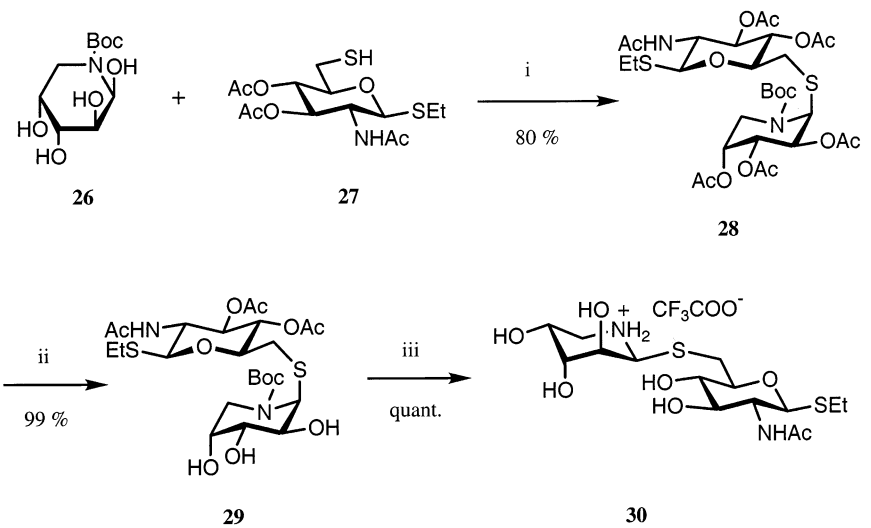
The aforementioned glycosylation was applied to the synthesis of a pseudo-disaccharide. 5-Azido-5-deoxy-D-arabinose (**6**) was converted into *N*-Boc-5-amino-5-deoxy-D-arabinose (**26**) in good yield by catalytic hydrogenation in the presence of Boc_2O. Ethyl 2-acetamido-3,4-di-*O*-acetyl-2-deoxy-1,6-dithio-β-D-glucopyranoside (**27**) was obtained from ethyl 2-acetamido-2-deoxy-1-thio-β-D-glucopyranoside [12]. Condensation of the aminal **26** with the 6-thio sugar **27** in the presence of TsOH (1 equiv) gave the corresponding thioglycoside as a single anomer in 80% yield, and this was converted into the pentaacetate **28** quantitatively. The conformation of the 5-amino-5-deoxyglycopyranose ring was confirmed to be $^1C_4$ by the small coupling constants between H-4 and the two H-5 protons. The $J_{1',2'}$ value of 4.6 Hz therefore indicates an axial–equatorial relationship between H-2 and H-1, that is, a 1,2-*cis* glycosidic linkage. The ^{13}C NMR spectrum of the pentaacetate **28** in $CDCl_3$ shows two signals of the thioaminal C1′ (δ 61.60 and 60.95) due to a 1:1 mixture of E and Z isomers of the *N*-Boc group [7]. Exclusive formation of the β-linked disaccharide in this glycosidation seems to be caused by the bulkiness of the 6-thio sugar **27**.

O-Deacetylation of the thioglycoside **28**, followed by deprotection of the *N*-Boc group of **29** with 2:1 TFA–CH_2Cl_2 gave **30** quantitatively (Scheme 3). The conformational change

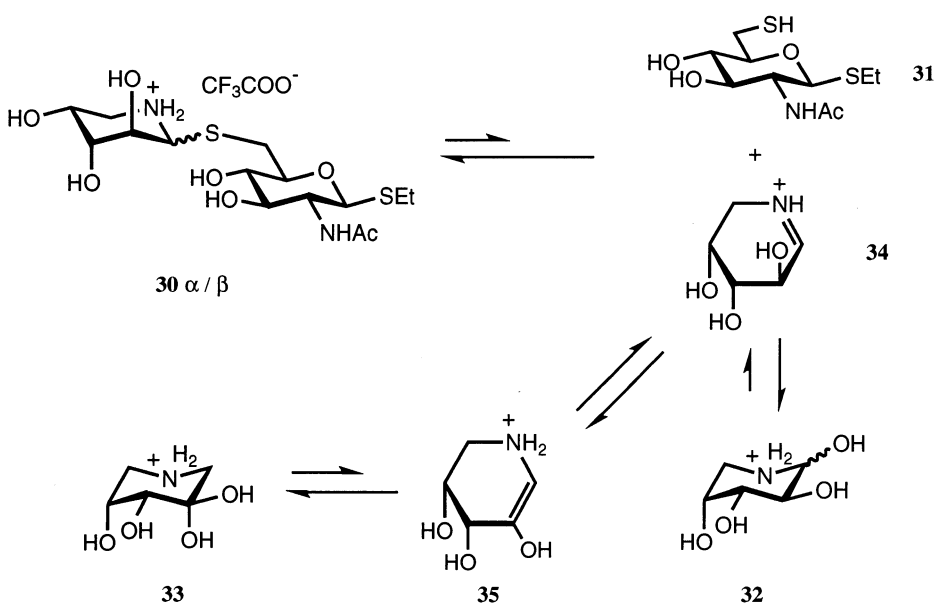
of the 5-amino-5-deoxyglycopyranose ring from $^1C_4$ to $^4C_1$ was similar to that observed from **22** to **25**. Thus, the disaccharide having an imino sugar residue at the non-reducing end was synthesized by linking the glycone and aglycone part through a thioglycosidic linkage.

This pseudo-disaccharide **30** was found to be stable at low pH, but was hydrolyzed rapidly at pH > 5 to afford ethyl 2-acetamido-2-deoxy-1,6-dithio-β-D-glucopyranoside (**31**). Under the mild acidic conditions, the N-unprotected imino sugar **32** gradually changed into 1,5-imino-1,5-dideoxy-D-*erythro*-pentulose hydrate **33** via **34** or **35** by an Amadori rearrangement, and the α anomer of **30** also exists in the mixture (Scheme 4). These changes can be traced by ^{1}H NMR spectroscopy.

The α anomer of **30** is deduced to be formed by a reversible addition of thiol to imine in aqueous solution. Therefore, the iminopyranosyl disaccharide can be formed by mixing 5-amino-5-deoxy-D-arabinose **32** and



Scheme 3. Synthesis of ethyl 2-acetamido-6-*S*-(5-amino-5-deoxy-D-arabinopyranosyl)-2-deoxy-1,6-dithio-D-glucopyranoside (**30**). Reagents (i) (a) TsOH, CH_2Cl_2, (b) Ac_2O, pyridine; (ii) NaOMe, MeOH; (iii) TFA, CH_2Cl_2.



Scheme 4. Equilibrium between the pseudo-disaccharide **30** and its component sugars, that is, the imino sugar **32** and the thio sugar **31**.

31 in an acidic buffer solution. Recently, novel isomeric *N*,*S*-acetalic disaccharides having an endocyclic sulfur atom and an exocyclic nitrogen atom were synthesized by Pinto and coworkers [13], and were found to exist as anomeric mixtures in aqueous solution. They proposed that anomerization proceeds by endocyclic C–S bond cleavage to give the intermediate iminium ions. Epimerization of some thiazoline derivatives in an aqueous solution has also been reported [14].

Then, we examined the formation of 5-amino-5-deoxyglycopyranosyl thioglycoside-type disaccharides in aqueous solution in order to prove our above described hypothesis. *N*-Acetyl-6-thio-D-glucosaminide (**31**) was prepared by deacetylation of **27** using aqueous ammonia in the presence of dithiothreitol. 5-Amino-5-deoxy-D-arabinose (**32**) was prepared from 5-azido-5-deoxy-D-arabinose **6** via *N*-Boc-5-amino-5-deoxypyranose. The 500 MHz NMR spectrum of the major compound formed in a 1:1 mixture of **32** and **31** in an acidic buffer (CD_3COOD–CD_3COONa, pD about 3.4) after 30 min was found to be in good agreement with that of the synthesized disaccharide **30**. The formation of 1,5-imino-1,5-dideoxy-D-*erythro*-pentulose hydrate (**33**) was also confirmed by the signal of the H-4 proton, which was assigned by comparison of an authentic sample. Under this condition, the disaccharide exists as a mixture of anomeric isomers ($\alpha:\beta = 1:1$).

Thus, the reversible conversions between the *N*,*S*-acetal **30** and its plausible degradative components (the sugar thiol **31** and the cyclic imine **34**) were confirmed. The formation of the imine **34** was further supported by its hydrated product **32** and 1,5-dideoxy-1,5-imino-D-*erythro*-pentulose (**33**), which was formed by an Amadori rearrangement via the enaminol **35**, as shown in Scheme 4.

In general, construction of the glycosylic linkage in the aqueous solution, so-called acid reversion, is of no practical use. Therefore, this unique character found here, that the 5-amino-5-deoxyglycopyranosyl thioglycoside-type pseudodisaccharide is easily formed from N-unprotected 5-amino-5-deoxyglycopyranose and thio sugar in a mild acidic condition seems to be worthy of notice.

In this paper, the first synthesis of the 5-amino-5-deoxyglycopyranosyl thioglycoside-type pseudo-disaccharide having an imino sugar residue at the non-reducing end was described. Glycosidation of an *N*-Boc aminal **26** with a 6-thio-sugar **27** in the presence of TsOH gave the corresponding 1,2-*cis*-linked thioglycoside exclusively. The interglycosidic thioaminal linkage was proven to be stable enough under the deprotection condition of the *N*-Boc group with TFA. This pseudodisaccharide was unstable at $pH > 5$, but easily formed from 5-amino-5-deoxy-D-arabinose (**32**) and *N*-acetyl-6-thio-D-glucosaminide (**31**) in a mild acidic buffer solution.

3. Experimental

General methods.—Melting point are uncorrected. ^1H NMR spectra were recorded at 270 MHz (Jeol JMN-EX-270) and at 500 MHz (Jeol JMN-GX-500). ^{13}C NMR spectra were recorded at 67.5 MHz (Jeol JMN-EX-270) with the solvent peak ($CDCl_3$; 77.0 ppm) or acetone (30.6 ppm in D_2O) as the reference. Mass spectra were obtained on JMS-700MS (Jeol) or JMS-HX110 (Jeol) spectrometers. Optical rotations were measured at 589 nm with a JascoJIP-4 digital polarimeter (at 24 °C). IR spectra were recorded using NaCl plates on a Hitachi 270-30. Thin-layer chromatography (TLC) was performed on Kieselgel 60 F254 (E. Merck) plates and detected by charring with 5% H_2SO_4 solution or 1% $Ce(SO_4)_2$–1.5% $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$–10% H_2SO_4. Silica gel column chromatography was conducted on E. Merck Silica Gel 60 (70–230 mesh).

1,2,3-Tri-O-acetyl-5-O-methylsulfonyl-D-arabinofuranose (**4**).—To a pyridine (50 mL) solution of **3** [15] (22.5 g, 86.8 mmol) was added MsCl (8.1 mL, 0.10 mol) dropwise over 5 min at 0 °C. After stirring for 15 min at room temperature (rt), the mixture was poured into satd aq $NaHCO_3$, diluted with EtOAc, and washed with brine and water. The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by silica-gel column chromatography (2:1 hex-

ane–EtOAc) to afford 24.3 g of **4** (79%) as an anomeric mixture (α:β = 1.9:1); ^{1}H NMR ($CDCl_3$): δ 6.21 (s, 0.7 H, H-1α), 5.23 (d, 0.7 H, $J_{2,3}$ 1.3 Hz, H-2α), 5.05 (dd, 0.7 H, $J_{3,4}$ 4.6 Hz, H-3α), 6.39 (d, 0.3 H, $J_{1,2}$ 4.3 Hz, H-1β), 5.37–5.28 (m, 0.7 H, H-2β, 3β), 4.54–4.20 (m, 3 H, H-4,5a,5b), 3.07 (s, 3 H, OMs), 2.15, 2.13, 2.10 (each s, 12 H, OAc). Anal. Calcd for $C_{12}H_{18}O_{10}S$: C, 40.67; H, 5.12; Found: C, 40.92; H, 5.15.

1,2,3-Tri-O-*acetyl-5-azido-5-deoxy*-D-*arabinofuranose* (**5**).—To a solution of **4** (5.0 g, 14.1 mmol) in Me_2SO (80 mL) was added NaN_3 (2.0 g, 31.0 mmol). After being stirred at 60 °C for 24 h, the mixture was diluted with EtOAc and washed with water. The organic layer was dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica-gel column chromatography (2:1 hexane–EtOAc) to afford 2.88 g of **5** (68%) as an anomeric mixture (α:β = 1:1); $[\alpha]_D$ + 73.6° (*c* 0.46, $CHCl_3$); IR (KBr) ν_{max} 2110, 1743 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.41–6.40 (m, 0.5 H, H-1β), 6.22 (s, 0.5 H, H-1α), 5.38–5.36 (m, 1 H, H-2β, 3β), 5.22 (d, 0.5 H, $J_{2,3}$ 1.3 Hz, H-2α), 5.05 (dd, 0.5 H, $J_{3,4}$ 4.6 Hz, H-3α), 4.30 (ddd, 0.5 H, $J_{4,5a}$ 3.3, $J_{4,5b}$ 4.6 Hz, H-4α), 4.14 (br s, 0.5 H, H-4β), 3.70 (dd, 0.5 H, $J_{5a,5b}$ 13.5 Hz, H-5aα), 3.52 (dd, 0.5 H, $J_{4,5a}$ 3.6, $J_{5a,5b}$ 13.2 Hz, H-5aβ), 3.47 (dd, 0.5 H, $J_{4,5b}$ 2.3 Hz, H-5bβ), 3.46 (dd, 0.5 H, H-5bα), 2.14, 2.13, 2.12, 2.11, 2.09 (each s, 12 H, OAc). Anal. Calcd for $C_{11}H_{15}N_3O_7$: C, 43.86; H, 5.02; N, 13.95. Found: C, 43.78; H, 4.87; N, 13.86.

5-Azido-5-deoxy-D-*arabinofuranose* (**6**).—To a solution of **5** (2.88 g, 9.58 mmol) in MeOH (15 mL) was added NaOMe (50 mg, 0.93 mmol). After being stirred for 5 h with sonication, the mixture was neutralized with Dowex 50W-X8 resin, and evaporated in vacuo to afford **6** (1.67 g, 100%) as an anomeric mixture. (α:β = 1:1); $[\alpha]_D$ + 5.9° (*c* 0.23, MeOH); IR (KBr disk) ν_{max} 3400, 2926, 2110 cm^{-1}; ^{1}H NMR (D_2O): δ 5.33 (dd, 0.5 H, *J* 0.7, *J* 3.3 Hz, H-1α), 5.28 (d, 0.5 H, $J_{1,2}$ 3.0 Hz, H-1β), 4.24–3.90 (m, 3 H, H-2, 3, 4), 3.68 (dd, 0.5 H, *J* 3.6, *J* 13.7 Hz, H-5α), 3.63 (dd, 0.5 H, *J* 3.3, *J* 13.7 Hz, H-5a); 3.48 (dd, 0.5 H, *J* 6.0 Hz, H-5b), 3.46 (dd, 0.5 H, *J* 6.3 Hz, H-5b). Anal. Calcd for $C_5H_9N_3O_4$: C, 34.29; H, 5.18; N, 23.99. Found: C, 34.68; H, 5.17; N, 23.72.

5-Azido-5-deoxy-D-*arabinitol* (**7**).—To a MeOH (10 mL) solution of **6** (100 mg, 0.57 mmol) was added $NaBH_4$ (43 mg, 1.14 mmol). After being stirred for 30 min at rt, the mixture was neutralized with a large excess of AcOH and evaporated. The residue was purified by silica-gel column chromatography (9:1 $CHCl_3$–MeOH) to afford **7** (99.7 mg, 100%) as crystals: mp 86–88 °C; $[\alpha]_D$ + 2.3° (*c* 0.6, MeOH); ^{1}H NMR (D_2O): δ 3.99–3.88 (m, 2 H), 3.70–3.47(m, 5 H); ^{13}C NMR (D_2O): δ 70.70, 69.99, 69.72, 63.02, 53.71. Anal. Calcd for $C_5H_{11}N_3O_4$: C, 33.90; H, 6.26; N, 23.72. Found: C, 33.85; H, 6.16; N, 23.26.

1,2,3,4-Tetra-O-*acetyl-5-azido-5-deoxy*-D-*arabinitol* (**8**).—To a pyridine (5 mL) solution of **7** (100 mg, 0.56 mmol) was added Ac_2O (0.27 mL, 2.80 mmol). After being stirred for 5 h at rt, the mixture was quenched by a large excess of MeOH and evaporated. The residue was purified by silica-gel column chromatography (3:1 hexane–EtOAc) to afford **8** (178 mg, 92%) as a syrup: $[\alpha]_D$ + 41.9° (*c* 0.6, $CHCl_3$); IR (KBr disk) ν_{max} 2968, 2110, 1743, 1440 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.42–5.34 (m, 2 H, H-2,3), 5.13 (ddd, H, $J_{3,4}$ 8.6, $J_{4,5a}$ 3.3, $J_{4,5b}$ 5.6 Hz, H-4), 4.25 (dd, H, $J_{1a,1b}$ 11.9, $J_{1a,2}$ 5.3 Hz, H-1a), 3.95 (dd, 1 H, $J_{1b,2}$ 7.0 Hz, H-1b), 3.50 (dd, 1 H, $J_{5a,5b}$ 13.5 Hz, H-5a), 3.32 (dd, 1 H, H-5b), 2.15, 2.10, 2.08, 2.05 (each s, 12 H, OAc × 4); ^{13}C NMR ($CDCl_3$): δ 170.15, 169.79, 169.49, 169.38, 68.81, 68.59, 67.80, 61.57, 50.42, 20.45, 20.40, 20.34. Anal. Calcd for $C_{13}H_{19}N_3O_8$: C, 45.22; H, 5.55; N, 12.17. Found: C, 45.46; H, 5.72; N, 11.69.

5-Azido-5-deoxy-1-O-*triphenylmethyl*-D-*arabinitol* (**9**).—To a pyridine (50 mL) solution of **7** (4.50 g, 25.6 mmol) was added TrCl (8.56 g, 30.7 mmol). After being stirred for 48 h at rt, the mixture was quenched by a large excess of MeOH and evaporated. The residue was purified by silica-gel column chromatography (3:1 hexane–EtOAc) to afford **9** (8.9 g, 83%) as crystals: mp 97–102 °C; $[\alpha]_D$ + 3.9° (c 0.68, MeOH); ^{1}H NMR ($CDCl_3$): δ 7.30 (m, 15 H, Ph), 3.97 (br s, 1 H), 3.79 (m, 1 H), 3.55–3.39 (m, 4 H), 3.30 (dd, 1 H). Anal. Calcd for $C_{24}H_{25}N_3O_4$: C, 68.70; H, 6.01; N, 10.03. Found: C, 68.64; H, 6.01; N, 9.83.

5-Azido-2,3,4-tri-O-*benzyl-5-deoxy*-D-*arabinitol* (**10**).—To a DMF (100 mL) solution of **9** (8.5 g, 20.3 mmol) was added 55% NaH (3.4 g, 0.14 mol) at 0 °C and the mixture was stirred for 30 min at rt. To the mixture was added BnBr (8.1 mL, 0.10 mol) dropwise slowly and stirred for 3 h at rt, then quenched by a large excess of NaOMe at 0 °C. The reaction mixture was poured into H_2O and diluted with EtOAc. The organic layer was washed with brine, followed by extraction with EtOAc, dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by silica-gel column chromatography (6:1 hexane–EtOAc) to afford the benzylated compound (13.3 g, 95%). A suspension of this compound (13.0 g, 18.9 mmol) in 70% aq AcOH (300 mL) was stirred for 4 h at 60 °C, the mixture was filtrated through a Celite and the filtrate concentrated in vacuo. The residue was purified by silica-gel column chromatography (3:1 hexane–EtOAc) to afford **10** (5.32 g, 63%): mp 48–49 °C; $[\alpha]_D$ −6.7° (*c* 0.99, $CHCl_3$); IR (KBr disk) ν_{max} 3478, 3059, 3028, 2878, 2104, 1497, 1452, 1401 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.33–7.17 (m, 15 H, Ph), 4.71, 4.65, 4.63, 4.62, 4.54, 4.48 (each d, 6 H, *J* 11.9 Hz, benzyl), 3.85–3.46 (m, 7 H, H-1a,1b,2,3,4,5a,5b), 2.12 (br s, 1 H, OH); ^{13}C NMR ($CDCl_3$): δ 138.01, 137.79, 137.48, 128.41, 128.16, 127.94, 127.89, 127.82, 78.99, 78.91, 78.62, 74.27, 72.60, 72.44, 61.33, 50.98. Anal. Calcd for $C_{26}H_{29}N_3O_4$: C, 69.78; H, 6.53; N, 9.39. Found: C, 69.81; H, 6.43; N, 9.29.

2,3,4-Tri-O-*benzyl-5-benzyloxycarbonylamino-5-deoxy*-D-*arabinitol* (**11**).—To a THF (20 mL) solution of **10** (495 mg, 1.11 mmol) was added $LiAlH_4$ (84 mg, 2.22 mmol). The mixture was stirred at rt until the starting material disappeared on TLC, and poured into ice–water (30 mL). To the solution was added Z–Cl (317×10^{-3} mL, 2.22 mmol) dropwise at 0 °C. The mixture was separated and the aqueous layer extracted with $CHCl_3$. The combined extracts were washed with water, dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by silica-gel column chromatography (2:1 hexane–EtOAc) to afford **11** (585 mg, 95%) as a colorless syrup: $[\alpha]_D$ +18.6° (*c* 0.76, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.33–7.25 (m, 20 H, Ph), 5.12 (br s, 1 H, NH), 5.09, 5.04 (each d, 2 H, *J* 12.2 Hz, benzyl), 4.73–4.49 (m, 6 H, benzyl), 3.84–3.43 (m, 7 H), 2.19 (br s, 1 H, OH); ^{13}C NMR ($CDCl_3$): δ 156.44, 138.04, 137.93, 137.68, 136.53, 128.37, 128.21, 128.10, 127.92, 127.84, 127.75, 127.58, 79.71, 79.14, 77.77, 74.29, 72.78, 71.81, 66.51, 61.21, 40.65. Anal. Calcd for $C_{34}H_{37}NO_6$: C, 73.49; H, 6.71; N, 2.52. Found: C, 73.98; H, 6.88; N, 2.45.

2,3,4-Tri-O-*benzyl-5-deoxy-5-(9-fluorenylmethyloxycarbonylamino)*-D-*arabinitol* (**12**).—Compound **12** was obtained by reacting **10** with FmocCl in place of Z–Cl in the same manner as described for **11**, and purified by silica-gel column chromatography (2:1 hexane–EtOAc) to afford a colorless syrup (95%): $[\alpha]_D$ +12.4° (*c* 0.84, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.75–7.24 (m, 23 H, aromatic), 5.10 (br s, 1 H, NH), 4.73–4.53 (m, 6 H, benzyl), 4.38–4.35 (br d, 2 H, FmocCH_2), 4.17 (dd, 1 H, *J* 6.76 Hz, FmocC*H*), 3.83–3.40 (m, 7 H), 2.02 (br s, 1 H, OH); ^{13}C NMR ($CDCl_3$): δ 156.44, 143.83, 141.19, 138.01, 137.93, 137.70, 128.37, 128.27, 128.21, 128.07, 127.98, 127.84, 127.78, 127.73, 127.55, 126.92, 124.94, 119.86, 79.75, 79.174, 77.85, 74.27, 72.76, 71.90, 66.49, 61.15, 47.14, 40.72. Anal. Calcd for $C_{41}H_{41}NO_6$: C, 76.49; H, 6.42; N, 2.18. Found: C, 76.22; H, 6.44; N, 1.97.

2,3,4-Tri-O-*benzyl-5*-tert-*butyloxycarbonylamino-5-deoxy*-D-*arabinitol* (**13**).—Compound **13** was obtained by reacting **10** with Boc_2O in place of Z–Cl in the same manner as described for **11**. Compound **13** was purified by silica-gel column chromatography (2:1 hexane–EtOAc) to afford a colorless syrup (90%): $[\alpha]_D$ +17.6° (*c* 2.56, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.34–7.24 (m, 15 H, Ph), 4.90 (br s, 1 H, NH), 4.72, 4.66 (each d, 2 H, *J* 11.2 Hz, benzyl), 4.62 (s, 2 H, benzyl), 4.57, 4.50 (each d, 2 H, *J* 11.7 Hz, benzyl), 3.84–3.64 (m, 5 H), 3.46–3.42 (m, 2 H), 2.16 (br s, 1 H, OH), 1.42 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$): δ 155.96, 138.10, 137.99, 137.81, 128.28, 128.09, 127.78, 127.73, 127.64, 79.68, 79.17, 79.01, 77.83, 74.27, 72.72, 71.68, 61.22, 39.98, 28.27. Anal. Calcd for $C_{31}H_{39}NO_6$: C, 71.38; H, 7.54; N, 2.69. Found: C, 70.98; H, 7.06; N, 2.22.

2,3,4-Tri-O-benzyl-5-benzyloxycarbonylamino-5-deoxy-β-D-arabinose (**14**).—A solution of Me_2SO (1.71 g, 14.96 mmol) in CH_2Cl_2 (5 mL) was added to a solution of $(COCl)_2$ (951 mg, 7.48 mmol) in CH_2Cl_2 (50 mL) under an argon atmosphere at −78 °C. To this mixture was added after 10 min a solution of **11** (416 mg, 0.748 mmol) in CH_2Cl_2 (5 mL), and then after stirring for 30 min a solution of Et_3N (1.51 g, 14.96 mmol) in CH_2Cl_2 (5 mL). The mixture was diluted with $CHCl_3$, washed successively with satd aq $NaHCO_3$ and water, and dried over $MgSO_4$. The organic layer was concentrated, diluted with Et_2O and washed with water. The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by silica-gel column chromatography (5:1–3:1 hexane–EtOAc) to afford **14** (392 mg, 95%) as a syrup: $[\alpha]_D$ −32.2° (*c* 1.10, $CHCl_3$); ^1H NMR (Me_2SO-d_6 at 373 K): δ 7.40–7.28 (m, 20 H, Ph), 5.86 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 5.14, 5.08 (d, 1 H, *J* 12.7 Hz, benzyl), 4.76–4.52 (m, 6 H, benzyl), 4.14 (dd, 1 H, $J_{4,5e}$ 2.3, $J_{5a,5e}$ 14.2 Hz, H-5e), 3.97 (br s, 1 H, H-4), 3.93 (dd, 1 H, $J_{2,3}$ 9.6 Hz, H-2), 3.79 (dd, 1 H, $J_{3,4}$ 3.5 Hz, H-3), 3.18 (d, 1 H, H-5a); ^{13}C NMR (Me_2SO-d_6 at 373 K): δ 154.05, 138.58, 138.46, 138.31, 136.32, 127.75, 127.62, 127.57, 127.48, 127.42, 127.15, 126.97, 126.85, 126.79, 126.74, 126.58, 76.97, 76.23, 74.70, 72.98, 71.09, 70.87, 70.35, 65.92, 39.66. Anal. Calcd for $C_{34}H_{35}NO_6$: C, 73.76; H, 6.37; N, 2.53. Found: C, 73.90; H, 6.32; N, 2.50.

2,3,4-Tri-O-benzyl-5-deoxy-5-(9-fluorenylmethyloxycarbonylamino)-β-D-arabinose (**15**).—Compound **15** was obtained from **12** in the same manner as described for **14**, and purified by silica-gel column chromatography (5:1–3:1 hexane–EtOAc) to afford a syrup (91%): $[\alpha]_D$ −27.8° (*c* 1.26, $CHCl_3$); ^1H NMR (Me_2SO-d_6 at 373 K): δ 7.87–7.26 (m, 23 H, aromatic), 5.78 (dd, 1 H, $J_{1,2}$ 3.5, $J_{1,OH}$ 4.0 Hz, H-1), 5.60 (d, 1 H, OH), 4.72–4.24 (m, 9 H, benzyl, FmocCH_2 and C*H*), 4.02 (br d, 1 H, $J_{5a,5e}$ 14.2 Hz, H-5e), 3.92 (br s, 1 H, H-4), 3.90 (dd, 1 H, $J_{2,3}$ 9.4, $J_{3,4}$ 3.0 Hz, H-3), 3.74 (dd, H-2), 3.11 (d, H-5a); ^{13}C NMR ($CDCl_3$) δ 154.02, 143.45, 143.31, 140.31, 138.56, 138.44, 138.29, 127.46, 127.01, 126.81, 126.74, 126.60, 126.56, 126.51, 126.47, 124.28, 119.41, 76.84, 76.32, 74.54, 72.80, 71.04, 70.87, 70.12, 66.18, 46.40, 39.02. Anal. Calcd for $C_{41}H_{39}NO_6$: C, 76.73; H, 6.13; N, 2.18. Found: C, 77.07; H, 6.06; N, 2.20.

2,3,4-Tri-O-benzyl-5-tert-butyloxycarbonylamino-5-deoxy-β-D-arabinose (**16**).—Compound **16** was obtained from **13** in the same manner as described for **14**, and purified by silica-gel column chromatography (5:1–3:1 hexane–EtOAc) to afford a syrup (90%): $[\alpha]_D$ −49.6° (*c* 0.84, $CHCl_3$); ^1H NMR (Me_2SO-d_6 at 373 K): δ 7.41–7.28 (m, 15 H, Ph), 5.79 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.71–4.54 (m, 6 H, benzyl), 4.08 (br d, 1 H, $J_{5a,5e}$ 14.2 Hz, H-5e), 3.93 (br s, 1 H, H-4), 3.87 (dd, 1 H, $J_{2,3}$ 9.2, $J_{3,4}$ 3.3 Hz, H-3), 3.76 (dd, H-2), 3.09 (d, H-5a), 1.41 (s, 9 H, *t*-Bu); ^{13}C NMR (Me_2SO-d_6 at 373 K): δ 169.45, 153.23, 138.65, 138.55, 138.42, 127.60, 127.41, 126.96, 126.90, 126.83, 126.70, 126.56, 125.91, 78.66, 77.07, 76.28, 73.14, 71.02, 70.80, 70.23, 59.03, 27.53, 13.43. Anal. Calcd for $C_{31}H_{37}NO_6$: C, 71.65; H, 7.18; N, 2.70. Found: C, 71.53; H, 7.27; N, 2.83.

Neopentyl 2,3,4-tri-O-benzyl-5-benzyloxycarbonylamino-5-deoxy-β-D-arabinopyranoside (**17**).—To a solution of **14** (93 mg, 0.168 mmol) in pyridine (2 mL) was added Ac_2O (1 mL). The mixture was concentrated and the residue was dissolved in dry CH_2Cl_2 (5 mL). To this solution was added neopentenyl alcohol (44 mg, 0.504 mmol) and 4 Å molecular sieves (100 mg), and then after 1 h, Me_3SiOTf (36×10^{-3} mL, 0.185 mmol), and the mixture was stirred for 5 min at 0 °C. The reaction was stopped by addition of a large excess of Et_3N. The solution was filtered through a Celite pad and the filtrate evaporated in vacuo. The residue was purified by silica-gel column chromatography (5:1 hexane–EtOAc) to afford **17** (104.5 mg, quant.) as a syrup: $[\alpha]_D$ −42.8° (*c* 0.30, $CHCl_3$); ^1H NMR (Me_2SO-d_6 at 373 K): δ 7.32–7.23 (m, 20 H, Ph), 5.55 (br s, 1 H, H-1), 5.09 (br s, 2 H, benzyl), 4.73–4.51 (m, 6 H, benzyl), 4.16 (br d, 1 H, $J_{5a,5e}$ 14.5 Hz, H-5e), 3.97 (br s, 1 H, H-4), 3.88–3.85 (m, 2 H, H-2,3), 3.08–2.95 (m, 3 H, H-5a, –CH_2-*t*-Bu), 0.87 (s, 9 H, *t*-Bu); ^{13}C NMR (Me_2SO-d_6 at 373 K): δ 154.39, 138.46, 138.22, 136.14, 127.75, 127.64, 127.57, 127.44, 127.26, 127.15, 126.97, 126.83, 126.72, 126.65, 126.60, 126.56, 82.00, 77.56, 76.89, 76.07, 72.99, 71.02,

70.89, 70.41, 66.13, 31.00, 25.88, 25.70. Anal. Calcd for $C_{39}H_{45}NO_6$: C, 75.09; H,7.27; N, 2.25. Found: C, 74.84; H, 7.54; N, 2.18.

Ethyl 2,3,4-tri-O-*benzyl-5-benzyloxycarbonylamino-5-deoxy-1-thio*-D-*arabinopyranoside* (**18**).—Compound **18** was obtained from **14** in the same manner as described for **17** using EtSH as a nucleophile instead of neopentyl alcohol, and purified by silica-gel column chromatography (5:1 hexane–EtOAc) to afford a syrup quantitatively (α:β = 1:3); ^{1}H NMR (Me_2SO-d_6 at 373 K): δ 7.39–7.27 (m, 20 H, Ph), 5.96 (d, 0.75 H, $J_{1,2}$ 3.0 Hz, H-1b), 5.58 (br s, 0.25 H, H-1a), 5.18–5.07 (br s, 2 H, benzyl), 4.76–4.49 (m, 6 H, benzyl), 4.25 (br d, 0.75 H, $J_{5a,5e}$ 14.0 Hz, H-5e), 4.06 (dd, 0.75 H, $J_{2,3}$ 9.9, $J_{3,4}$ 5.3 Hz, H-3), 3.96 (br s, 0.75 H, H-4), 3.71 (dd, 0.75 H, H-2), 3.26 (d, 0.75 H, H-5a), 2.47–2.36 (m, 2 H, S-CH_2CH$_3$), 1.16 (t, 3 H, S-CH$_2$CH_3); ^{13}C NMR (Me_2SO-d_6 at 373 K): δ 154.25, 138.37, 138.15, 138.04, 137.97, 137.90, 137.34, 136.05, 135.96, 127.76, 127.66, 127.58, 127.48, 127.33, 127.21, 127.08, 127.03, 126.99, 126.90, 126.83, 126.72, 126.61, 77.92, 76.98, 75.10, 73.84, 72.71, 72.15, 71.61, 71.00, 70.89, 70.61, 70.44, 69.60, 66.51, 66.36, 60.61, 58.69, 39.95, 39.34, 37.20, 25.52, 22.54, 14.25, 14.13. Anal. Calcd for $C_{36}H_{39}NO_5S$: C, 72.33; H,6.58; N, 2.34. Found: C, 72.82; H, 6.35; N, 2.28.

Ethyl 2,3,4-tri-O-*benzyl-5-deoxy-5-(9-fluorenylmethyloxycarbonylamino)-1-thio*-D-*arabinopyranoside* (**19**).—Compound **19** was obtained from **15** in the same manner as described for **18**, and purified by silica-gel column chromatography (5:1 hexane–EtOAc) to afford a syrup (79%, α:β = 1:2.8); ^{1}H NMR (Me_2SO-d_6 at 393 K): δ 7.87–7.22 (m, 23 H, aromatic), 5.80–5.20 (broad, 1 H, H-1α and β), 4.70–4.26 (m, benzyl and Fmoc); ^{13}C NMR (Me_2SO-d_6 at 393 K): δ 143.51, 143.36, 143.33, 143.25, 140.45, 138.33, 138.13, 137.97, 137.85, 127.66, 127.59, 127.50, 127.42, 126.96, 126.87, 126.79, 126.72, 126.69, 126.63, 126.58, 126.49, 126.44, 124.01, 123.97, 119.37, 119.34, 77.67, 75.13, 73.84, 72.51, 71.54, 70.93, 70.26, 70.12, 69.58, 66.09, 60.40, 46.47, 39.34, 36.89, 25.59, 22.43, 14.00. Anal. Calcd for $C_{43}H_{43}NO_5S$: C, 75.30; H, 6.32; N, 2.04. Found: C, 75.76; H, 6.20; N, 2.05.

Cyclohexyl 2,3,4-tri-O-*benzyl-5-deoxy-5-(9-fluorenylmethyloxycarbonyl-amino)-1-thio*-D-*arabinopyranoside* (**20**).—Compound **20** was obtained from **15** in the same manner as described for **17** using cyclohexanethiol as the nucleophile instead of neopentyl alcohol, and purified by silica-gel column chromatography (3:1 hexane–EtOAc) to afford a syrup (73%, α:β = 1:3.1): ^{1}H NMR (Me_2SO-d_6 at 393 K): δ 7.85–7.27 (m, 23 H, aromatic), 5.76, 5.57 (broad, 1 H, H-1α and β), 4.73–4.28 (m, benzyl and Fmoc); ^{13}C NMR (Me_2SO-d_6 at 393 K): δ 153.86, 143.40, 143.20, 143.11, 140.33, 138.31, 138.11, 137.95, 137.92, 137.86, 137.23, 127.50, 127.42, 127.32, 127.28, 127.24, 126.83, 126.78, 126.74, 126.69, 126.60, 126.56, 126.45, 126.40, 126.35, 126.27, 123.92, 123.83, 123.78, 119.19, 77.85, 77.04, 75.29, 73.97, 72.76, 72.20, 71.47, 70.96, 70.69, 70.39, 70.16, 69.60, 66.13, 59.91, 46.49, 46.44, 43.58, 41.33, 37.07, 33.61, 33.01, 32.85, 30.14, 24.71, 24.66, 24.55, 24.48, 24.15, 21.19, 12.89. Anal. Calcd for $C_{47}H_{49}NO_5S$: C, 76.29; H, 6.67; N, 1.89. Found: C, 76.53; H, 6.63; N, 1.83.

Ethyl 2,3,4-tri-O-*benzyl-5*-tert-*butoxycarbonylamino-5-deoxy-1-thio*-D-*arabinopyranoside* (**21**).—Compound **21** was obtained from **16** in the same manner as described for **18**, and purified by silica-gel column chromatography (6:1 hexane–EtOAc) to afford a syrup (40%, α:β = 1:3.8); ^{1}H NMR (Me_2SO-d_6 at 373 K): δ 7.41–7.25 (m, 15 H, Ph), 5.93 (br s, 0.8 H, H-1), 4.76–4.51 (m, 6 H, benzyl), 4.21 (br d, 0.8 H, $J_{5a,5e}$ 14.2 Hz, H-5e), 4.02 (dd, 0.8 H, $J_{2,3}$ 9.9, $J_{3,4}$ 5.6 Hz, H-3), 3.95–3.91 (m, 0.8 H, H-4), 3.69 (dd, 0.8 H, $J_{1,2}$ 3.1 Hz, H-2), 3.17 (d, 0.8 H, H-5a), 2.63–2.40 (m, 2 H, SCH_2CH$_3$), 1.41 (s, 9 H, *t*-Bu), 1.23 (t, 3 H, SCH$_2$CH_3); ^{13}C NMR (Me_2SO-d_6 at 373 K): δ 153.33, 138.44, 138.28, 138.11, 138.08, 138.01, 137.47, 127.62, 127.57, 127.46, 127.42, 127.19, 127.08, 126.88, 126.79, 126.69, 126.61, 126.58, 118.89, 79.43, 79.23, 77.99, 77.04, 75.10, 74.04, 72.82, 72.24, 71.59, 70.87, 70.80, 70.41, 70.28, 69.53, 60.13, 58.22, 39.05, 27.53, 27.44, 27.37, 26.33, 25.54, 22.38, 14.45, 14.31. Anal. Calcd for $C_{33}H_{41}NO_5S$: C, 70.31; H, 7.33; N, 2.48. Found: C, 69.84; H, 7.30; N, 2.53.

Cyclohexyl 2,3,4-tri-O-*benzyl-5*-tert-*butyloxycarbonylamino-5-deoxy-1-thio*-D-*arabinopyranoside* (**22**).—To a solution of **16** (23 mg, 41 μmol) and cyclohexanethiol (15 μmol) in

CH_2Cl_2 (0.5 mL) was added $TsOH \cdot H_2O$ (7.8 mg, 41 μmol) and the mixture was stirred for 1 h at rt. The mixture was loaded on a column of silica gel and fractionated (6:1 hexane–EtOAc) to afford **22** (18.2 mg, 72%, α:β = 1:7.3) as a syrup; ^{1}H NMR (Me_2SO-d_6 at 373 K): δ 7.53–7.36 (m, 15 H, Ph), 6.10 (br s, 0.9 H, H-1), 4.87–4.63 (m, 6 H, benzyl), 4.34 (br d, 0.9 H, $J_{5a,5e}$ 14.2 Hz, H-5e), 4.16 (dd, 0.9 H, $J_{2,3}$ 9.9, $J_{3,4}$ 5.3 Hz, H-3), 4.03 (br s, 0.9 H, H-4), 3.81(dd, 0.9 H, $J_{1,2}$ 3.0 Hz, H-2), 3.36 (d, 0.9 H, H-5a), 2.78–2.61 (m, 1 H, cyclohexyl–C*H*), 2.17–1.31 (m, 10 H, cyclohexyl CH_2), 1.55 (s, 9 H, *t*-Bu); ^{13}C NMR (Me_2SO-d_6 at 373 K): δ 153.08, 138.49, 138.28, 138.11, 138.08, 138.01, 127.57, 127.50, 127.41, 126.90, 126.83, 126.72, 126.63, 126.51, 79.28, 79.14, 78.13, 77.27, 75.19, 74.11, 73.01, 72.35, 71.52, 71.00, 70.78, 70.43, 70.32, 69.54, 43.54, 41.15, 39.36, 33.37, 33.27, 32.96, 27.52, 27.43, 27.37, 25.25, 25.16, 25.00, 24.89, 24.82. Anal. Calcd for $C_{37}H_{47}NO_5S$: C, 71.93; H, 7.67; N, 2.27. Found: C, 71.73; H, 7.60; N, 2.29.

Cyclohexyl 2,3,4-tri-O-*benzyl-5*-tert-*butyloxycarbonylamino-5-deoxy-β-*D-*arabinopyranoside* (**23**).—Compound **23** was obtained from **16** in the same manner as described for **22** using cyclohexanol as the nucleophile, and purified by silica-gel column chromatography (5:1 hexane–EtOAc) to afford a syrup (73%): $[\alpha]_D$ −33.9° (*c* 0.53, $CHCl_3$); ^{1}H NMR (Me_2SO-d_6 at 373 K): δ 7.34–7.27 (m, 15 H, Ph), 5.64 (br s, 1 H, H-1), 4.72–4.52 (m, 6 H, benzyl), 4.10 (br d, 1 H, H-5e, $J_{5a,5e}$ 13.9 Hz), 3.95 (br s, 1 H, H-4), 3.86 (dd, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 3.1 Hz, H-3), 3.77 (dd, 1 H, $J_{1,2}$ 3.6 Hz, H-2), 3.39 (m, 1 H, cyclohexyl–C*H*), 1.82–1.22 (m, cyclohexyl–CH_2), 1.40 (s, 9 H, *t*-Bu); ^{13}C NMR (Me_2SO-d_6 at 373 K): δ 138.64, 138.49, 138.35, 135.38, 133.75, 130.24, 128.75, 128.48, 128.05, 128.02, 127.44, 126.88, 126.78, 126.70, 126.67, 126.58, 126.52, 118.12, 79.00, 77.15, 75.83, 73.12, 71.05, 70.80, 70.23, 56.59, 40.27, 34.76, 32.17, 30.35, 27.53, 27.44, 24.87, 24.75, 23.06, 22.92, 22.66. Anal. Calcd for $C_{37}H_{47}NO_6$: C, 73.85; H, 7.87; N, 2.33. Found: C, 74.30; H, 7.94; N, 2.35.

Methyl 2,3,4-tri-O-*benzyl-5*-tert-*butyloxycarbonylamino-5-deoxy-β-*D-*arabinopyranoside* (**24**).—Compound **24** was obtained from **16** in the same manner as described for **22** using MeOH as the nucleophile, and purified by silica-gel column chromatography (3:1 hexane–EtOAc) to afford a syrup (88%): $[\alpha]_D$ −23.1° (*c* 1.00, $CHCl_3$); ^{1}H NMR (Me_2SO-d_6 at 373 K): δ 7.38–7.23 (m, 15 H, Ph), 5.39 (br s, 1 H, H-1), 4.74–4.53 (m, 6 H, benzyl), 4.11 (br d, 1 H, $J_{5a,5e}$ 14.4 Hz, H-5e), 3.93 (br s, 1 H, H-4), 3.86–3.77 (m, 2 H, H-2, 3), 3.23 (s, 3 H, OMe), 2.87 (d, 1 H, H-5a), 1.41 (s, 9 H, *t*-Bu); ^{13}C NMR (Me_2SO-d_6 at 373 K): δ 138.56, 138.46, 138.33, 127.48, 127.42, 126.83, 126.70, 126.60, 126.56, 79.16, 77.13, 75.92, 72.99, 71.31, 70.84, 70.26, 54.38, 27.44. Anal. Calcd for $C_{32}H_{39}NO_6$: C, 72.02; H, 7.37; N, 2.62. Found: C, 72.06; H, 7.72; N, 2.58.

Cyclohexyl 5-amino-2,3,4-tri-O-*benzyl-5-deoxy-1-thio-β-*D-*arabinopyranoside TFA salt* (**25**).—To a solution of **22** in CH_2Cl_2 (0.35 mL) was added TFA (0.7 mL). The mixture was stirred for 22 h and concentrated to give **25**; ^{1}H NMR ($CDCl_3$): δ 7.42–7.19 (m, 15 H, Ph), 4.82–4.31 (m, 6 H, benzyl), 4.56 (br s, 1 H, H-1), 4.11–4.08 (m, 1 H, H-4), 3.58–3.65 (m, 2 H, H-2, 3), 3.42 (dd, 1 H, $J_{4,5e}$ 4.6, $J_{5a,5e}$ 11.9 Hz, H-5e), 3.31 (dd, 1 H, $J_{4,5a}$ 11.6 Hz, H-5a), 3.10 (m, 1 H, S–C*H* <), 2.28–1.18 (m, 10 H, cyclohexyl-CH_2–); ^{13}C NMR ($CDCl_3$): δ 135.57, 137.25, 136.48, 129.31–127.17, 77.86, 74.12, 73.80, 72.74, 72.09, 70.03, 60.04, 44.15, 42.61, 34.47, 33.01, 25.82, 25.43; HRMS (FAB$^+$, JMS-700MS) Calcd for $C_{32}H_{40}NO_3S$ $[M+H]^+$: 518.2731; Found: 518.2728.

*5-*tert-*Butoxycarbonylamino-5-deoxy-β-*D-*arabinose* (**26**).—To a methanol (43 mL) solution of **20** (1.5 g, 8.57 mmol) was added Boc_2O (3.7 g, 17.14 mmol) and 10% Pd–C (∼ 220 mg). The mixture was stirred for 24 h under an atmosphere of hydrogen, filtered through a Celite pad and the filtrate concentrated in vacuo. The residue was purified by silica-gel column chromatography (9:1 CH_2Cl_2–MeOH) to afford **26** (1.25 g, 59%): $[\alpha]_D$ −21.9° (*c* 0.90, MeOH); ^{1}H NMR (D_2O) δ 5.80 (br s, 1 H, H-1), 4.10 (br s, 1 H, H-4), 4.03–3.97 (m, 1 H, H-5a), 3.90 (dd, 1 H, $J_{2,3}$ 10.3, $J_{3,4}$ 3.2 Hz, H-3), 3.81 (dd, 1 H, $J_{1,2}$ 3.8 Hz, H-2), 3.30(br d, 1 H, $J_{5a,5b}$ 13.9 Hz, H-5b), 1.53 (s, 9 H, *t*-Bu); ^{13}C NMR (D_2O): δ 82.56, 69.20, 68.32, 67.97, 27.50. Anal. Calcd for $C_{10}H_{19}NO_6$: C, 48.19; H, 7.68; N, 5.62. Found: C, 48.09; H, 7.16; N, 5.48.

*Ethyl 2-acetamido-3,4,-di-*O*-acetyl-2-deoxy-1,6-dithio-β-*D*-glucopyranoside* (**27**).—To a pyridine (50 mL) solution of ethyl 2-acetamido-2-deoxy-1-thio-β-D-glucopyranoside [11] was added TsCl (6.62 g, 34.8 mmol). The mixture was stirred for 1 h at rt. The reaction was stopped by addition of a large excess of MeOH. The solution was concentrated and dried. To a pyridine (50 mL) solution of this residue was added Ac_2O (30 mL) and 4-dimethylaminopyridine (DMAP, 177 mg, 1.45 mmol). The mixture was stirred for 12 h at rt and concentrated. The residue was purified by silica-gel column chromatography (1:3 hexane–EtOAc) to afford 6-tosylate (4.74 g, 65%). To a DMF (5 mL) solution of the 6-tosylate (1.29 g, 2.54 mmol) was added KSAc (581 mg, 5.08 mmol). After being stirred for 3 h at 80 °C, the mixture was diluted with EtOAc and washed with brine. The organic layer was dried over ($MgSO_4$), and concentrated in vacuo. The residue was purified by silica-gel column chromatography (1:3 hexane–EtOAc) to afford 6-thioacetate (818 mg, 79%): $[\alpha]_D$ −25.2° (*c* 1.56, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.54 (d, 1 H, $J_{2,NH}$ 9.57 Hz, NH), 5.13 (dd, 1 H, $J_{2,3}$ 9.89, $J_{3,4}$ 9.57 Hz, H-3), 4.99 (dd, 1 H, $J_{4,5}$ 9.57 Hz, H-4), 4.54 (d, 1 H, $J_{1,2}$ 10.23 Hz, H-1), 4.09 (ddd, 1 H, H-2), 3.60 (ddd, 1 H, $J_{5,6a}$ 2.97, $J_{5,6b}$ 7.26 Hz, H-5), 3.27 (dd, 1 H, $J_{6a,6b}$ 14.18 Hz, H-6a), 3.03 (dd, 1 H, H-6b), 2.79–2.65 (m, 2 H, SCH_2CH$_3$), 2.34 (s, 3 H, SAc), 2.09, 2.03, 1.95 (each s, 9 H, OAc), 1.27 (t, 3 H, SCH$_2$CH_3). Anal. Calcd for $C_{16}H_{25}NO_7S_2$: C, 47.16; H, 6.18; N, 3.44. Found: C, 47.54; H, 6.29; N, 3.51.

To a solution of 6-thioacetate (200 mg, 0.489 mmol) in MeCN (10 mL) was added 2-aminoethanethiol (45 mg, 0.587 mmol) and stirred for 30 min at 70 °C under argon. The reaction mixture was concentrated in vacuo and the residue purified by silica-gel column chromatography (1:2 hexane–EtOAc) to afford **27** (172 mg, 96%): $[\alpha]_D$ −23.2° (*c* 1.28, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.51 (d, 1 H, $J_{2,NH}$ 9.6 Hz, NH), 5.16 (dd, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 9.41 Hz, H-3), 5.03 (dd, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 4.61 (d, 1 H, $J_{1,2}$ 9.2 Hz, H-1), 4.10 (ddd,1 H, H-2), 3.55 (ddd, 1 H, $J_{5,6a}$ 3.0, $J_{5,6b}$ 7.3 Hz, H-5), 2.82–2.63 (m, 4 H, H-6a, 6b, SCH_2-CH$_3$), 2.05, 2.03, 1.96 (each s, 9 H, OAc), 1.78 (dd, 1 H, $J_{6,SH}$ 8.6 Hz, SH), 1.29 (t, 3 H, SCH$_2$CH_3). Anal. Calcd for $C_{14}H_{23}NO_6S_2$: C, 46.01; H, 6.34; N, 3.83. Found: C, 46.44; H, 6.40; N, 3.83.

*Ethyl 2-acetamido-3,4-di-*O*-acetyl-6-*S*-(2,3,4-tri-*O*-acetyl-5-*tert*-butoxycarbonylamino-5-deoxy-β-*D*-arabinopyranosyl)-2-deoxy-1,6-dithio-β-*D*-glucopyranoside* (**28**).—A mixture of **26** (78.7 mg, 0.316 mmol), **27** (232.2 mg, 0.632 mmol) and $TsOH{\cdot}H_2O$ (60 mg, 0.316 mmol) in CH_2Cl_2 was stirred for 1 h to give a thioglycoside. After purification by silica-gel column chromatography (9:1 CH_2Cl_2–MeOH), the thioglycoside was dissolved in pyridine (3 mL). To this mixture was added Ac_2O (1.5 mL) and DMAP (4 mg, 31.6 μmol) and stirred for 12 h at rt. The reaction was stopped by addition of MeOH, and the solution was concentrated in vacuo. The residue was purified by silica-gel column chromatography (EtOAc) to give **28** (183 mg, 80%): $[\alpha]_D$ −26.9° (*c* 0.20, $CHCl_3$); ^{1}H NMR ($C_6D_5NO_2$ at 393 K): δ 6.45 (br d, 1 H, $J_{1',2'}$ 4.6 Hz, H-1′), 6.12 (br d, 1 H, $J_{2,NH}$ 9.2 Hz, NH), 5.61–5.48 (m, 4 H, H-3, 2′, 3′,4′), 5.18 (dd, 1 H, $J_{3,4} = J_{4,5}$ 9.4 Hz, H-4), 5.06 (d, 1 H, $J_{1,2}$ 10.2 Hz, H-1), 4.50 (br d, 1 H, $J_{5'a,5'e}$ 14.8 Hz, H-5′e), 4.29 (ddd, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 3.91 (m, 1 H, H-5), 3.70 (br d, 1 H, H-5′a), 2.99–2.79 (m, 4 H, H-6a, 6b, SCH_2CH$_3$), 2.16, 2.14, 2.12, 2.09, 2.08, 2.07 (each s, 18 H, Ac), 1.61 (s, 9 H, *t*-Bu), 1.36 (t, 3 H, SCH$_2$CH_3); ^{13}C NMR ($CDCl_3$): δ 84.26 (C-1), 83.97 (C-1), 77.25 (C-5), 76.53 (C-5), 73.96, 73.62, 71.64, 71.03, 68.80, 68.53, 68.05, 67.91, 67.71, 67.19 (C-3,4,2′,3′,4′), 61.60 (C-1′), 60.95 (C-1′), 53.19 (C-2), 53.10 (C-2), 40.68 (C-5′), 39.59 (C-5′). Anal. Calcd for $C_{30}H_{46}N_2O_{14}S_2$: C, 49.85; H, 6.41; N, 3.88; S, 8.87. Found: C, 50.01; H, 6.41; N, 3.81; S, 8.62.

*Ethyl 2-acetamido-6-*S*-(5-*tert*-butoxycarbonylamino-5-deoxy-β-*D*-arabinopyranosyl)-2-deoxy-1,6-dithio-β-*D*-glucopyranoside* (**29**).—To a solution of **28** (109.4 mg, 0.151 mmol) in MeOH (5 mL) was added NaOMe powder (10 mg, 0.185 mmol). The mixture was stirred for 1 h, neutralized with resin (Dowex 50W-X8), filtered, and concentrated in vacuo to give **29** (76.6 mg, 99%): $[\alpha]_D$ −14.4° (*c* 1.39, MeOH); ^{1}H NMR (Me_2SO-d_6: D_2O = 4:1 at 373 K): δ 5.57 (br d, 1 H, $J_{1',2'}$ 3.6 Hz, H-1′),

4.42 (d, 1 H, $J_{1,2}$ 10.2 Hz, H-1), 1.82 (s, 3 H, Ac), 1.39 (s, 9 H, *t*-Bu), 1.15 (t, 3 H, SCH_2CH_3); ^{13}C NMR (Me_2SO-d_6: $D_2O = 4:1$ at 373 K): δ 154.66, 152.51, 133.80, 121.78, 84.10, 80.61, 80.54, 75.49, 73.86, 70.87, 68.30, 67.77, 65.59, 55.21, 43.71, 32.98, 28.27, 23.96, 22.86, 14.97. Anal. Calcd for $C_{20}H_{36}N_2O_9S_2$: C, 46.86; H, 7.08; N, 5.46; S, 12.51. Found: C, 45.67; H, 6.68; N, 5.49; S, 12.33.

*Ethyl 2-acetamido-6-*S*-(5-amino-5-deoxy-β-*D*-arabinopyranosyl)-2-deoxy-1,6-dithio-β-*D*-glucopyranoside TFA salt* (**30**).—To a solution of **29** (8.4 mg, 16.3 μmol) in CH_2Cl_2 (0.5 mL) was added TFA (1 mL) at 0 °C and stirred for 30 min. The mixture was stirred for 30 min at rt, and concentrated to give **30** quantitatively: ^1H NMR (D_2O): δ 4.66 (d, 1 H, $J_{1,2}$ 11.0 Hz, H-1), 4.57 (br s, 1 H, H-1′), 4.17–4.09 (m, 2 H, H-2′, 4′), 3.91 (br s, 1 H, H-3′), 3.68–3.45 (m, 4 H, H-2, 3, 4, 5), 3.34 (dd, 1 H, $J_{4',5'e}$ 4.6, $J_{5'a,5'e}$ 12.1 Hz, H-5′e), 3.20 (d, 1 H, $J_{6a,6b}$ 13.5 Hz, H-6a), 3.15 (d, 1 H, H-6b), 3.11 (dd, 1 H, $J_{4',5'a}$ 10.6 Hz, H-5′a), 2.71–2.57 (m, 2 H, SCH_2CH_3), 1.92 (s, 3 H, Ac), 1.15 (t, 3 H, SCH_2CH_3); ^{13}C NMR (D_2O): δ 174.43, 84.58, 79.10, 74.56, 70.39, 69.26, 64.32, 62.27, 54.83, 42.90, 30.07, 29.78, 25.25, 22.23, 14.51; HRMS (FAB^+, JMS-700MS) Calcd for $C_{15}H_{29}N_2O_7S_2$ $[M+H]^+$: 413.1418; Found: 413.1429.

*Ethyl 2-acetamido-2-deoxy-1,6-dithio-β-*D*-glucopyranoside* (**31**).—A solution of **27** (90 mg, 0.244 mmol), dithiothreitol (DTT, 376 mg, 2.44 mmol), aq ammonia (28%, 6 mL) and MeOH (1 mL) was stirred for 16 h at the rt. The mixture was concentrated and purified by silica-gel column chromatography (19:1 EtOAc–MeOH) to afford **31** (50 mg, 64%): $[\alpha]_D$ −0.3° (*c* 0.7, MeOH); ^1H NMR (CD_3CO_2D–CD_3CO_2Na in D_2O pD = 3.4 buffer): δ 4.65 (d, 1 H, $J_{1,2}$ 10.4 Hz, H-1), 3.79 (dd, 1 H, $J_{2,3}$ 9.9 Hz, H-2), 3.61–3.46 (m, 3 H, H-3, 4, 5), 3.01 (br d, 1 H, $J_{6a,6b}$ 14.52 Hz, H-6a), 2.84–2.66 (m, 3 H, H-6b, SCH_2CH_3), 2.04 (s, 3 H, Ac), 1.27 (t, 3 H, SCH_2CH_3); ^{13}C NMR (CD_3CO_2D–CD_3CO_2Na in D_2O pD = 3.4 buffer): δ 174.36, 84.20, 80.25, 75.20, 72.40, 55.00, 25.64, 24.74, 22.32, 14.66. HRMS (FAB^+, JMS-HX110) Calcd for $C_{10}H_{20}NO_4S_2$ $[M+H]^+$: 282.0833; Found: 282.0829.

*Cyclohexyl 5-*tert*-butoxycarbonylamino-5-deoxy-1-thio-*D*-arabinopyranoside*.—A mixture of **26** (58 mg, 0.233 mmol) and cyclohexanethiol (85×10^{-3} mL, 0.699 mmol) in CH_2Cl_2 (3 mL) was added to $TsOH \cdot H_2O$ (44 mg, 0.233 mmol) and stirred for 10 min at rt. The solution was neutralized by addition of Et_3N and concentrated. The residue was purified by silica-gel column chromatography (3:1 hexane–EtOAc–EtOAc only) to afford the corresponding thioglycoside (72 mg, 85%): $[\alpha]_D$ −64.7° (*c* 0.93, MeOH); ^1H NMR (Me_2SO-d_6: $D_2O = 5:1$ at 353 K): δ 5.58 (br s, 1 H, H-1), 3.86–3.74 (m, 3 H, H-3,4,5a), 3.38 (dd, 1 H, $J_{1,2}$ 3.30, $J_{2,3}$ 9.90 Hz, H-2), 3.16 (1 H, br d, $J_{5a,5b}$ 13.86 Hz, H-5b), 2.56–2.49 (m, 1 H, cyclohexyl-CH<), 2.00–1.20 (m, 10 H, cyclohexyl–CH_2–), 1.38 (s, 9 H, *t*-Bu); ^{13}C NMR (Me_2SO-d_6: $D_2O = 5:1$ at 353 K): δ 80.24, 70.89, 68.02, 67.78, 42.41, 34.22, 33.93, 28.22, 25.99, 25.72, 25.48. Anal. Calcd for $C_{16}H_{29}NO_5S$: C, 55.31; H, 8.41; N, 4.03. Found: C, 55.22; H, 8.30; N, 3.72.

*5-Amino-5-deoxy-*D*-arabinopyranose TFA salt* (**32**).—The thioglycoside just described (72 mg) was treated with TFA (0.8 mL) in CH_2Cl_2 (0.4 mL) for 30 min at 0 °C and for an additional 30 min at rt to give the cyclohexyl 5-amino-5-deoxy-1-thio-D-arabinopyranoside TFA salt; ^1H NMR (CF_3COOD): δ 5.17 (d, 1 H, $J_{1,2}$ 3.30 Hz, H-1), 4.70–4.63 (m, 2 H, H-2,4), 4.30–4.04 (m, 1 H, H-3), 3.89 (br d, 1 H, $J_{5a,5b} = 13.19$ Hz, H-5a), 3.69 (dd, 1 H, $J_{4,5b}$ 6.11 Hz, H-5b), 3.11 (m, 1 H, cyclohexyl–CH<), 2.08–1.37 (m, 10 H, cyclohexyl–CH_2–); HRMS (FAB^+, JMS-700MS) Calcd for $C_{11}H_{22}NO_3S$ $[M+H]^+$: 248.1320; Found: 248.1307.

The imino sugar thioglycoside thus obtained was treated in CH_2Cl_2–water (1:1) for 24 h, and then the water layer was concentrated to give the title free imino sugar as the TFA salt **32** quantitatively (α:β = 1.7:1); ^1H NMR (D_2O): δ 5.19 (br s, 0.4 H, H-1β), 4.62 (d, 0.6 H, $J_{1,2}$ 8.75 Hz, H-1α), 4.25–4.21 (m, 1 H, H-4α and H-4β), 4.00–3.99 (m, 0.8 H, H-2β,3β), 3.87 (dd, 0.6 H, $J_{2,3}$ 9.74 Hz, H-2α), 3.72 (dd, 0.6 H, $J_{3,4}$ 3.47 Hz, H-3α), 3.45–3.19 (m, 2 H, H-5a,5b); ^{13}C NMR (D_2O): δ 82.42 (C-1α), 78.86 (C-1β), 72.41 (C-3α), 71.41 (C-2α), 69.45, 68.78 (C-2β,3β), 66.46 (C-4α), 65.51 (C-4β), 45.62 (C-5α), 42.62 (C-5β).

1,5-Dideoxy-1,5-imino-D-erythro-*pentulose hydrate* (**33**).—An acidic buffer (CD_3CO_2D–CD_3CO_2Na–D_2O buffer, pD = 3.4) solution of **32** was kept in the sample tube for 24 h to gave **33** quantitatively: ^{1}H NMR (CD_3CO_2D–CD_3CO_2Na/D_2O buffer, pD = 3.4): δ 4.19 (ddd, 1 H, $J_{3,4}$ 2.81, $J_{4,5a}$ 10.56 Hz, $J_{4,5e}$ 4.73 Hz, H-4), 3.85 (d, 1 H, H-3), 3.23 (dd, 1 H, $J_{5a,5e}$ 12.21 Hz, H-5e), 3.20 (d, 1 H, $J_{1a,1b}$ 16.17 Hz, H-1a), 3.14 (d, 1 H, H-1b), 3.05 (dd, 1 H, H-5a); ^{13}C NMR (CD_3CO_2D–CD_3CO_2Na/D_2O buffer, pD = 3.4): δ 92.02, 71.61, 64.38, 64.31, 42.57. HRMS (FAB$^+$, JMS-HX110) Calcd for $C_5H_{12}O_4N$ $[M+H]^+$: 150.0766; Found: 150.0761.

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