

## Syntheses of 1-Deoxynojirimycin-Trehalamine-Fused and -Linked Compounds and Their Biological Activities

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Received 11 September 1998; accepted 14 October 1998

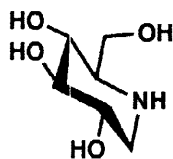
**Abstract:** 1-Deoxynojirimycin-trehalamine-fused and -linked compounds (**10**, **19a** and **19b**) were synthesized from 1-deoxy-2,3,4,6-tetra-*O*-benzylnojirimycin and trehazoline, which was obtained from natural trehazolin as a degradation product. None of these synthetic compounds exceeded 1-deoxynojirimycin in the inhibitory activities towards rat intestinal maltase and yeast  $\alpha$ -D-glucosidase. © 1998 Elsevier Science Ltd. All rights reserved.

**Keywords:** *Amino sugars, Carbohydrates, Thioureas, Enzyme inhibitors*

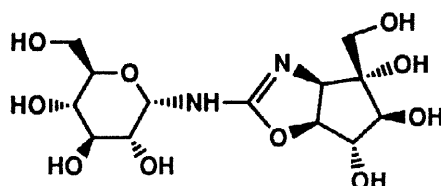
### Introduction

$\alpha$ -Glucosidases catalyze the regiospecific hydrolysis of  $\alpha$ -glucosidic linkages of oligo- and polysaccharides such as starch. Many  $\alpha$ -D-glucosidase inhibitors for therapeutic use have been investigated to control diabetes, obesity, HIV, metastasis of cancer, and so on. Practically, acarbose [1,2,3] and AO-128 (voglibose) [4] have been used clinically as drugs controlling hyperglycemia. 1-Deoxynojirimycin was found to be a potent inhibitor of intestinal oligo- and disaccharidases of mammals [5]. And trehazolin, which is a pseudodisaccharide consisting of an  $\alpha$ -glucosyl group and a unique aglycon moiety (trehalamine), exhibited powerful inhibitory activity towards various trehalases [6]. We were interested in the structure and D-glycosidase inhibitory activity of both 1-deoxynojirimycin-trehalamine-fused and -linked compounds as

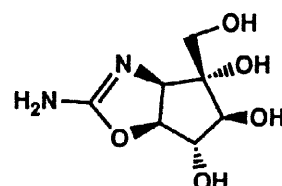
pseudodisaccharides. Here we describe the syntheses of these compounds (**10**, **19a** and **19b**) [7] and their biological activities towards rat intestinal maltase.



1-Deoxynojirimycin



Trehazolin



Trehalamine

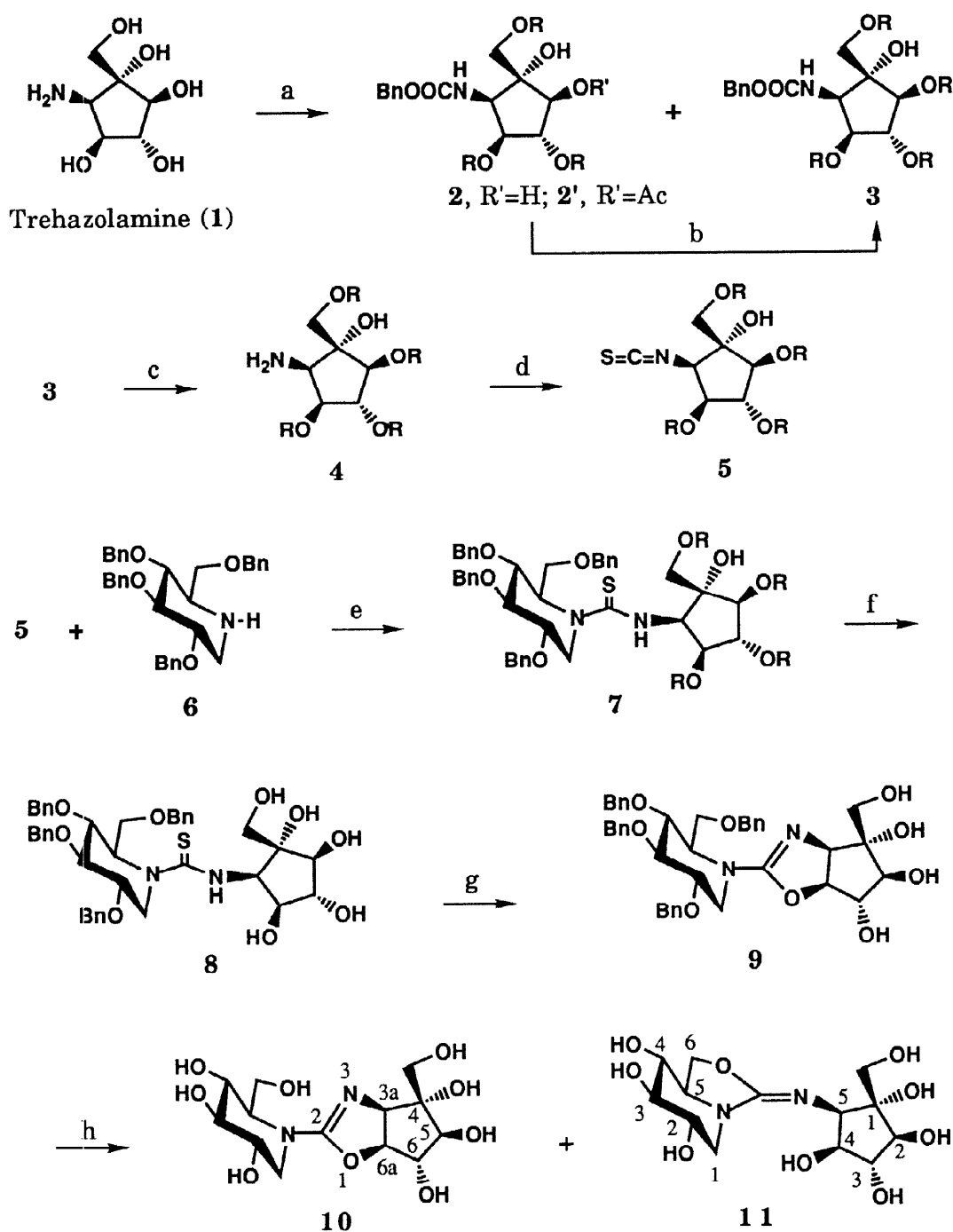
## Results and Discussion

### [Syntheses]

Trehazolamine (**1**), trehazolin aminocyclitol moiety, obtained by hydrolysis of natural trehazolin [8] was treated with benzyl chloroformate in THF-H<sub>2</sub>O containing pyridine at 0–5 °C, and the resulted *N*-benzyloxycarbonyl compound was converted to the tri-*O*-silylated compound **2** (11%) and the tetra-*O*-silylated compound **3** (34%) with *tert*-butyldimethylsilyl chloride and 4-dimethylaminopyridine (DMAP) in *N,N*-dimethylformamide (DMF). Compound **2** was also silylated at 20–25 °C for four days to give **3** in 62% yield accompanying the recovery of **2** (38%). The silylated position of **2** was determined from the <sup>1</sup>H NMR analysis of **2'** after acetylation of the secondary alcohol of **2** by acetic anhydride-pyridine. That is, the C2 proton of **2'** appeared at  $\delta$  4.98 as a doublet ( $J=6.2$  Hz). This shows that the remaining secondary hydroxy group of **2** was at the C2 position. Hydrogenolysis of **3** using palladium on carbon as a catalyst gave **4** (92%). Treatment of **4** with carbon disulfide, triethylamine and 2-chloro-1-methylpyridinium iodide in dichloromethane gave isothiocyanate **5** (87%) [9] as a solid (mp 47–49 °C) after silica gel chromatography. Reaction of compound **5** with 1-deoxy-2,3,4,6-tetra-*O*-benzylnojirimycin **6**, prepared by the reported method [7], in a small volume of tetrahydrofuran (THF) using triethylamine as a catalyst gave thiourea **7** (68%). Treatment of **7** with tetrabutylammonium fluoride gave pentaol **8** (93%). Treatment of **8** with 2-chloro-3-ethylbenzoxazolium tetrafluoroborate and triethylamine in acetonitrile gave a 1-deoxynojirimycin-trehalamine fused oxazoline compound **9** (95%) [10]. Hydrogenolysis of the benzyl groups of **9** using palladium hydroxide on carbon as a catalyst gave an inseparable mixture of **10** and **11** after chromatography using Amberlite CG-50 (NH<sub>4</sub><sup>+</sup> type/H<sup>+</sup> type = 3/2) followed by lyophilization.

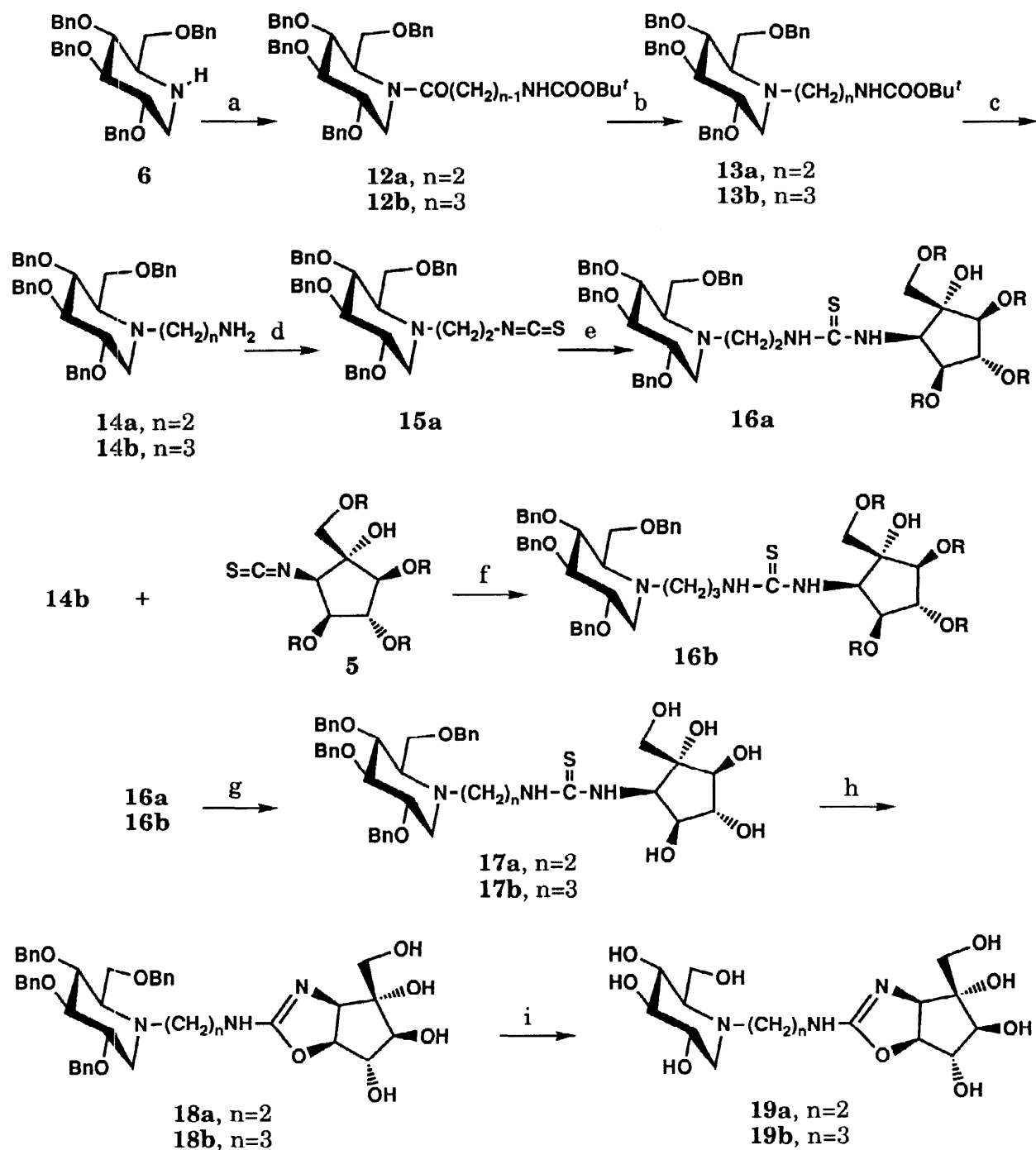
In the <sup>1</sup>H NMR, the spectral peak intensity of **10** gradually increased during 4 days, while that of **11** gradually decreased, and the mixture of **10** and **11** in an NMR tube (D<sub>2</sub>O) was initially 1 : 4, and finally reached an equilibrium at the ratio 4 : 1. <sup>1</sup>H-<sup>13</sup>C long range couplings were observed between C2-carbon (169.8 ppm) and 3a, 6a—two protons of compound **10**. In the <sup>1</sup>H- and <sup>13</sup>C-NMR studies, it is coincident with the structure of **11** that the chemical shifts of C6—two protons and C6-carbon of 1-deoxynojirimycin moiety of **11** are shifted to lower fields than those of **10**. That is, the chemical shifts of the C6-protons of **10** are  $\delta$  3.62 and 3.80, and those of **11** are  $\delta$  4.30 and 4.44. The chemical shift of the C6-carbon of **10** is  $\delta$  61.7 and that

## Scheme 1



Reagents and conditions: R = *tert*-BuMe<sub>2</sub>Si; a) ClCOOBn, pyridine, H<sub>2</sub>O-THF (2:1), 0–5 °C, 30 min, concentrated; then *tert*-BuMe<sub>2</sub>SiCl, DMAP, DMF, 20–25 °C, 16 h, **2**, 34%, **3**, 11%; b) *tert*-BuMe<sub>2</sub>SiCl, DMAP, DMF, 20–25 °C, 4 days, ca. 62% (recovery **2**, 38%); c) H<sub>2</sub>, Pd/C, THF, 24 °C, 8 h, quant.; d) CS<sub>2</sub>, Et<sub>3</sub>N, 2-chloro-1-methylpyridinium iodide, CH<sub>2</sub>Cl<sub>2</sub>, 24 °C, 2.5 h, 87%; e) Et<sub>3</sub>N, THF, 60–65 °C, 3 h, 68% (recovery of **5**, 22% and **6**, 19%); f) *n*-Bu<sub>4</sub>NF, THF, 24 °C, 3 h, 93%; g) 2-chloro-3-ethylbenzoxazolium tetrafluoroborate, Et<sub>3</sub>N, MeCN, 0 °C, 10 min, 95%; h) H<sub>2</sub>, Pd(OH)<sub>2</sub>/C, MeOH, 60 °C, 40 min, an inseparable 4:1 equilibrium mixture of **10** and **11**, 32%.

## Scheme 2



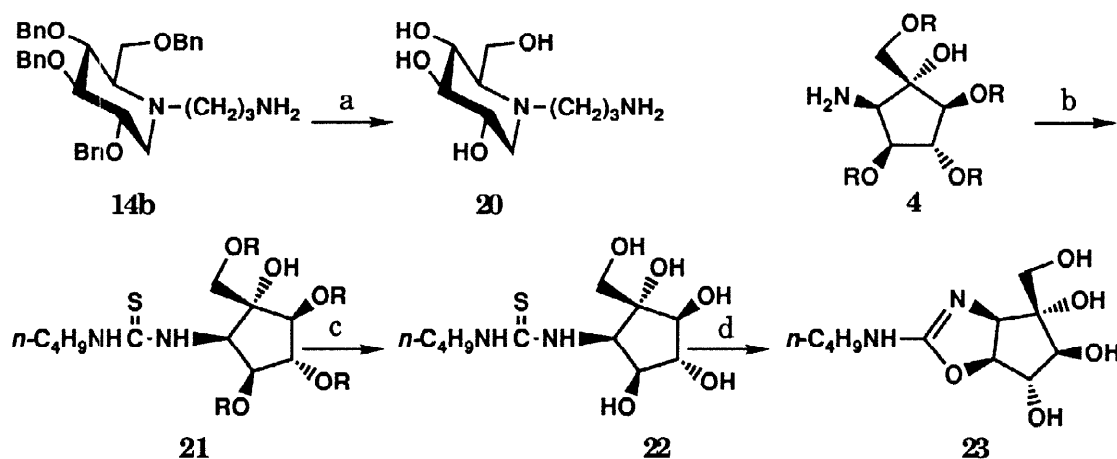
Reagents and conditions: R = *tert*-BuMe<sub>2</sub>Si; a) *N*-Boc-glycine or *N*-Boc-β-alanine, DCC, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, 24 °C, 6 h, 12a, 100%, 12b, 98%; b) BH<sub>3</sub>-THF complex, THF, 24 °C, 16 h, 13a, 62%, 13b, 98%; c) CF<sub>3</sub>COOH, CH<sub>2</sub>Cl<sub>2</sub>, 24 °C, 45 min, 14b, 95%; d) CS<sub>2</sub>, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, 24 °C, 1 h, then Et<sub>3</sub>N, 2-chloro-1-methylpyridinium iodide, two steps 41%; e) 4, cat. Et<sub>3</sub>N, THF, 20–25 °C, 2 days, 87%; f) THF, 60–65 °C, 3 h, 83%; g) HCl-MeOH, 24 °C, 16 h, quant.; h) 2-chloro-3-ethylbenzoxazolium tetrafluoroborate, Et<sub>3</sub>N, MeCN, 0 °C, 30 min, 18a, 67%, 18b, 77%; i) H<sub>2</sub>, Pd(OH)<sub>2</sub>/C, MeOH, 60–65 °C, 8 h, 19a, 72%, 50–55 °C, 24 h, 19b, 98%.

of **11** is  $\delta$  70.7. And also the chemical shift of the C6a-carbon (90.2 ppm) of the trehalamine part of **10** is shifted to a lower field than that of **11** (88.1 ppm). This type of 2-amino-2-oxazoline ring migration reaction from **10** to **11** should be possible according to our previous studies [11,12].

The compounds **19a** and **19b** were synthesized as follows. Condensation of **6** with *N*-*tert*-butoxycarbonylglycine or *N*-*tert*-butoxycarbonyl- $\beta$ -alanine using 1,3-dicyclohexylcarbodiimide (DCC) and DMAP gave **12a** or **12b** in good yields. Reduction of amide-carbonyl of **12a** or **12b** was performed using  $\text{BH}_3$ -THF complex to yield amine **13a** or **13b**. Deprotection of *N*-*tert*-butoxycarbonyl group from **13a** or **13b** was accomplished by treatment with trifluoroacetic acid to give **14a** or **14b**. The amine part of **14a** was converted to an isothiocyanate **15a** by treatment with  $\text{CS}_2$ ,  $\text{Et}_3\text{N}$ , and 2-chloro-3-ethylbenzoxazolium tetrafluoroborate. Reaction of **15a** with amine **4** in THF at 20–25 °C for 2 days using  $\text{Et}_3\text{N}$  as a catalyst gave thiourea **16a**. On the other hand, reaction of amine **14a** with isothiocyanate **5** in THF at 60–65 °C gave thiourea **16b**. Deprotection of *tert*-butyldimethylsilyl groups on trehazolamine moiety of **16a** and **16b** by  $\text{HCl}$ -MeOH gave tetraols **17a** and **17b**, respectively. Oxazoline formation of **17a** and **17b** by 2-chloro-3-ethylbenzoxazolium tetrafluoroborate and  $\text{Et}_3\text{N}$  in MeCN yielded **18a** and **18b**, respectively. Hydrogenolysis of benzyl groups of **18a** and **18b** gave **19a** and **19b**, respectively.

*N*-Aminoalkyl derivative of 1-deoxynojirimycin (**20**) and *N*-alkyltrehalamine (**23**), which are lacking respective counterparts, were also prepared to compare the biological activities of these compounds with that of 1-deoxynojirimycin. Hydrogenolysis of benzyl group of **14b** yielded **20**, and the procedure of preparation of **23** was as follows. Reaction of the amine **4** with butyl isothiocyanate in THF using  $\text{Et}_3\text{N}$  as a catalyst gave thiourea **21** (mp 141–142 °C). Subsequent desilylation of **21** with  $\text{HCl}$ -MeOH gave tetraol **22**. Treatment of **22** with 2-chloro-3-ethylbenzoxazolium tetrafluoroborate and  $\text{Et}_3\text{N}$  in MeCN yielded **23**.

### Scheme 3



Reagents and conditions: R = *tert*-BuMe<sub>2</sub>Si; a)  $\text{H}_2$ ,  $\text{Pd}(\text{OH})_2/\text{C}$ , MeOH, 50–55 °C, 16 h, 86%; b) *n*-C<sub>4</sub>H<sub>9</sub>N=C=S,  $\text{Et}_3\text{N}$ , THF, rt, 16 h, 73%; c)  $\text{HCl}$ -MeOH, 24 °C, 4 h; d) 2-chloro-3-ethylbenzoxazolium tetrafluoroborate,  $\text{Et}_3\text{N}$ , MeCN, 0 °C, 30 min, two steps 46%.

[Biological Activities]

Inhibition of glycosidases (rat intestinal maltase and yeast  $\alpha$ -D-glucosidase) by synthetic compounds (a mixture of **10** and **11**, **19a**, **19b**, 1-deoxynojirimycin, **20**, and **23**) was assayed.

For the measurement of rat intestinal maltase, a glucose oxidase-peroxidase system [13,14] was applied. For dilution, 20 mM phosphate buffer (pH 6.2) was used, and the reactions for assay were carried out at 37 °C for 20 min in a 96-well microtiter plate in a total volume of 150  $\mu$ L, composed from 60  $\mu$ L of phosphate buffer, 10  $\mu$ L of varying concentrations of inhibitors, 20  $\mu$ L of 39.5 mM maltose, 20  $\mu$ L of  $1 \times 10^{-3}$  units of rat intestinal maltase (added last), and glucose assay solution (diluted with 40  $\mu$ L of phosphate buffer) containing 3 units of glucose oxidase (Boehringer Mannheim), 0.13 units of horseradish peroxidase (Boehringer Mannheim), 40  $\mu$ g of phenol and 20  $\mu$ g of 4-aminoantipyrine (Sigma). Then, colorimetric changes at 492 nm were measured by micoplate reader, and the amount of glucose released was calculated. The enzyme inhibitory activities of a mixture of **10** and **11**, **19a**, **19b**, **20**, **23**, and 1-deoxynojirimycin exhibited IC<sub>50</sub> values of 0.68, 4.2, 1.5, 1.4, 9.1, and 0.023  $\mu$ g/mL, respectively.

For the measurement of yeast  $\alpha$ -glucosidase inhibition, 20 mM phosphate buffer (pH 6.2) was used to dilute the reagents, and the reactions for assay were carried out at 37 °C for 10 min in a 96-well microtiter plate in a total volume of 150  $\mu$ L composing from 70  $\mu$ L of phosphate buffer, 10  $\mu$ L of varying concentrations of inhibitors, 50  $\mu$ L of 10 mM 4-nitrophenyl  $\alpha$ -D-glucopyranoside, and 20  $\mu$ L of yeast  $\alpha$ -D-glucosidase (0.03 U/mL, added finally). Then, 20  $\mu$ L of 4M sodium glycinate buffer (pH 10.4) was added to stop the reactions, and colorimetric changes at 415 nm being directly proportional to the amount of liberated 4-nitrophenol were measured by micoplate reader. The enzyme inhibitory activities of a mixture of **10** and **11**, **19a**, **19b**, **20**, **23**, and 1-deoxynojirimycin exhibited IC<sub>50</sub> values of >200, >200, >200, >200, 42, and 13  $\mu$ g/mL, respectively.

## Conclusion

We have synthesized the 1-deoxynojirimycin-trehalamine-fused and -linked compounds **10**, **19a** and **19b**, and also the *N*-aminoalkyl derivative of 1-deoxynojirimycin (**20**) and *N*-alkyltrehalamine (**23**), which are lacking respective counterparts. And the biological activities of these compounds were compared with those of 1-deoxynojirimycin. None of them exceeded 1-deoxynojirimycin in the inhibitory activities towards rat intestinal maltase and yeast  $\alpha$ -D-glucosidase.

## Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. <sup>1</sup>H NMR (270, 400 and 500 MHz) spectra were recorded with JEOL JNM-270, JEOL JNM-GSX 400 and JEOL GSX 500 spectrometers using TMS as an internal standard. IR absorption spectra were determined with a IR A-2 spectrophotometer, and mass spectra were obtained with a JMS-700 mass spectrometer. Optical rotations were obtained by the use of a Perkin-Elmer 241 polarimeter. Elemental analyses were performed by the

Institute of Science and Technology, Inc. Separation of the compounds by column chromatography was done with silica gel 60 (230–400 mesh ASTM, E. Merck) under a slightly elevated pressure (1.2–1.5 atm) for easy elution, and the quantity of silica gel used was 50–100 times of the weight charged on the column. Preparative TLC was performed on silica gel plates (Merck, Silica Gel 60 F<sub>245</sub>). Detection involved spraying the chromatogram with a solution of 17% H<sub>2</sub>SO<sub>4</sub> in water (w/w), containing ammonium molybdate (2.3%) and ceric sulfate (0.9%) (Hanesian dip), and heating the plate for several minutes at ca 180 °C. Tetrahydrofuran (THF) was distilled from LiAlH<sub>4</sub> and used immediately. Dichloromethane was dried by being passed through an ICN Alumina B-Super I. *N,N*-Dimethylformamide (DMF) and pyridine were dried by storage over 4Å molecular sieves. Acetonitrile was dried by storage over 3Å molecular sieves.

**[1R-(1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\beta$ )]-5-*tert*-Butoxycarbonylamino-1-(*tert*-butyldimethylsilyloxy-methyl)-3,4-bis(*tert*-butyldimethylsilyloxy)cyclopentan-1,2-diol (2) and [1R-(1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\beta$ )]-5-*tert*-Butoxycarbonylamino-1-(*tert*-butyldimethylsilyloxymethyl)-2,3,4-tris(*tert*-butyldimethylsilyloxy)cyclopentan-1-ol (3).** To a solution of trehazamine (1) [8] (3.60 g, 20.1 mmol) in H<sub>2</sub>O-THF (2:1, 165 ml) and pyridine (14 g, 177 mmol) was added ClCOOBn (11.0 g, 64.5 mmol) at 0–5 °C with vigorous stirring. The stirring was continued for 30 min at this temperature, then the mixture was concentrated *in vacuo*, and dried with a high vacuum pump. The residue was dissolved in DMF (20 ml), and to this solution were added DMAP (18.0 g, 147 mmol) and *t*-BuMe<sub>2</sub>SiCl (18.0 g, 119 mmol). The mixture was stirred for 16 h at 20–25 °C, diluted with excess EtOAc, washed sequentially with aqueous 0.5M HCl, H<sub>2</sub>O, sat. NaHCO<sub>3</sub>, and brine, dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo* to give a mixture, which was chromatographed on a silica gel column. Elution with cyclohexane-EtOAc (10:1) gave 3 (5.29 g, ca 34% yield, containing a small amount of *t*-BuMe<sub>2</sub>SiOBn), and further elution with cyclohexane-EtOAc (4:1) gave 2 (1.40 g, 11% yield). Physical data of 3: IR  $\nu_{\text{max}}$ (film) 3450, 3400, 1725, 1708 cm<sup>-1</sup>. 270 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.06–0.12 (24H, m), 0.88 (9H, s), 0.89 (9H, s), 0.90 (18H, s), 3.06 (1H, s, OH), 3.74–3.79 (2H, m), 3.93 (1H, d, *J*=2.0 Hz), 4.08 (1H, s), 4.12 (2H, s), 5.06, 5.12 (2H, AB-q, *J*=12.5 Hz), 6.10 (1H, d, *J*=7.2 Hz, NH), 7.22–7.40 (5H, m). FAB MS (positive); *m/z* 770 [M+H]<sup>+</sup>. Anal. Calcd. for C<sub>38</sub>H<sub>75</sub>NO<sub>7</sub>Si<sub>4</sub> (770.4): C, 59.25; H, 9.81; N, 1.82. Found: C, 58.97; H, 9.60; N, 1.86. Physical data of 2: IR  $\nu_{\text{max}}$ (film) 3420, 2950, 2920, 2880, 2860, 1700 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.06–0.11 (18H, m), 0.87 (9H, s), 0.88 (18H, s), 2.78 (1H, d, *J*=4.3 Hz, OH), 3.24 (1H, s, OH), 3.79–3.92 (4H, m), 4.03–4.09 (2H, m), 5.09 (2H, s), 7.32 (5H, bs). FAB MS (positive); *m/z* 656 [M+H]<sup>+</sup>. Anal. Calcd. for C<sub>32</sub>H<sub>61</sub>NO<sub>7</sub>Si<sub>3</sub> (656.1): C, 58.58; H, 9.37; N, 2.14. Found: C, 58.24; H, 9.16; N, 2.11.

**[1R-(1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\beta$ )]-5-*tert*-Butoxycarbonylamino-1-(*tert*-butyldimethylsilyloxymethyl)-2,3,4-tris(*tert*-butyldimethylsilyloxy)cyclopentan-1-ol (3).**

To a solution of 2 (926 mg, 1.41 mmol) in DMF (8 ml) were added DMAP (259 mg, 2.11 mmol) and *t*-BuMe<sub>2</sub>SiCl (320 mg, 2.11 mmol). The mixture was stirred for 4 days at 20–25 °C, diluted with excess EtOAc, washed with aqueous 0.5M HCl, H<sub>2</sub>O, sat. NaHCO<sub>3</sub>, and brine, dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo* to give a residue, which was chromatographed on a silica gel column. Elution with cyclohexane-EtOAc (10:1) gave 3 (679 mg, ca. 62%), which contained a small amount of benzyl *tert*-

butyldimethylsilyl ether. This mixture was also employed for the next reaction without further purification. Recovery of the starting **2** was 356 mg (38%).

**[1R-(1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\beta$ )]-2-Acetoxy-5-*tert*-butoxycarbonylamino-1-(*tert*-butyldimethylsilyloxymethyl)-3,4-bis(*tert*-butyldimethylsilyloxy)cyclopentane-1-ol (2')** A solution of **2** (10 mg) in pyridine (0.4 ml) and acetic anhydride (0.2 ml) was allowed to stand overnight at room temperature. The reaction mixture was concentrated *in vacuo* to give a residue, which was chromatographed on a silica gel small column. Elution with cyclohexane-EtOAc (4:1) gave **2'** (8 mg, 75%) as an oil. IR  $\nu_{\text{max}}$ (film) 3448, 2950, 2925, 2885, 2860, 1727  $\text{cm}^{-1}$ . 270 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.03 (3H, s), 0.04 (3H, s), 0.08 (3H, s), 0.10 (6H, s), 0.91 (9H, s), 0.92 (9H, s), 0.93 (9H, s), 2.14 (3H, s), 3.59, 3.75 (2H, AB-q,  $J=10.2$  Hz), 4.08–4.18 (2H, m), 4.30 (1H, dd,  $J=7.7, 8.1$  Hz), 4.98 (1H, d,  $J=6.2$  Hz, C2-H), 5.14 (2H, s), 5.68 (1H, d,  $J=8.1$  Hz), 7.36 (5H, bs). FAB MS (positive);  $m/z$  720  $[\text{M}+\text{Na}]^+$ , 698  $[\text{M}+\text{H}]^+$ . Anal. Calcd. for  $\text{C}_{34}\text{H}_{63}\text{NO}_8\text{Si}_3$  (698.1): C, 58.50; H, 9.10; N, 2.01. Found: C, 58.55; H, 9.15; N, 2.05.

**[1R-(1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\beta$ )]-5-Amino-1-(*tert*-butyldimethylsilyloxymethyl)-2,3,4-tris(*tert*-butyldimethylsilyloxy)cyclopentane-1-ol (4).** A solution of **3** (1.36 g, 1.77 mmol) in THF (100 ml) containing 10% Pd on carbon (0.7 g) as catalyst was stirred for 8 h at 24 °C under an atmosphere of hydrogen, and filtered, concentrated *in vacuo* to give **4** (1.12 g, quantitative) as a solid. mp 79–82 °C. IR  $\nu_{\text{max}}$ (Nujol) 3560 (w), 3400 (w)  $\text{cm}^{-1}$ . 270 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.09–0.11 (24H, m), 0.89 (9H, s), 0.90 (9H, s), 0.91 (9H, s), 0.93 (9H, s), 1.66 (2H, bs,  $\text{NH}_2$ ), 3.00 (1H, bs, OH), 3.14 (1H, d,  $J=5.2$  Hz, C5-H), 3.76, 3.99 (2H, AB-q,  $J=10.3$  Hz), 3.83 (1H, d,  $J=3.4$  Hz, C2-H), 3.90 (1H, dd,  $J=3.4, 3.8$  Hz), 4.00 (1H, dd,  $J=3.8, 5.2$  Hz). FAB MS (positive);  $m/z$  636  $[\text{M}+\text{H}]^+$ . Anal. Calcd. for  $\text{C}_{30}\text{H}_{69}\text{NO}_5\text{Si}_4$  (636.2): C, 56.64; H, 10.93; N, 2.20. Found: C, 56.60; H, 10.79; N, 2.14.

**[1R-(1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\beta$ )]-1-(*tert*-Butyldimethylsilyloxymethyl)-5-isothiocyanato-2,3,4-tris(*tert*-butyldimethylsilyloxy)cyclopentane-1-ol (5).** To a solution of **4** (508 mg, 0.798 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml) were added  $\text{CS}_2$  (122 mg, 1.60 mmol) and  $\text{Et}_3\text{N}$  (202 mg, 2.00 mmol) at 24 °C under nitrogen. The solution was stirred for 1 h, and then to this solution were added  $\text{Et}_3\text{N}$  (162 mg, 1.60 mmol) and 2-chloro-1-methylpyridinium iodide (307 mg, 1.20 mmol). This solution was stirred for 2.5 h at 24 °C under nitrogen, concentrated *in vacuo*, diluted with EtOAc, washed with sat.  $\text{NaHCO}_3$ ,  $\text{H}_2\text{O}$ , brine, dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo* to give a mixture, which was chromatographed on a silica gel column. Elution with cyclohexane-EtOAc (24:1) gave **5** (473 mg, 87%). IR  $\nu_{\text{max}}$ (film) 3520 (w), 2960, 2935, 2900, 2860, 2125  $\text{cm}^{-1}$ . 270 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.09–0.11 (24H, m), 0.89 (9H, s), 0.91 (9H, s), 0.93 (9H, s), 0.95 (9H, s), 3.44 (1H, bs, OH), 3.73, 3.95 (2H, AB-q,  $J=10.3$  Hz), 3.83–3.90 (2H, m), 3.96 (1H, d,  $J=5.6$  Hz), 4.10 (1H, dt,  $J<1, 4.0$  Hz). FAB MS (positive);  $m/z$  678  $[\text{M}+\text{H}]^+$ , 620. Anal. Calcd. for  $\text{C}_{31}\text{H}_{67}\text{NO}_5\text{SSi}_4$  (678.3): C, 54.89; H, 9.96; N, 2.07; S, 4.73. Found: C, 54.59; H, 9.69; N, 2.09; S, 4.51.

**N-[[1R-(1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\beta$ )]-[1-(*tert*-Butyldimethylsilyloxymethyl)-1-hydroxy-2,3,4-tris(*tert*-butyldimethylsilyloxy)cyclopent-5-yl]aminothiocarbonyl]-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (7).** A THF solution of **5** (52.4 mg, 0.100 mmol) and 2,3,4,6-



tetra-*O*-benzyl-1-deoxynojirimycin (**6**, 67.8 mg, 0.100 mmol) was concentrated *in vacuo*. To the residue were added THF (0.10 ml) and Et<sub>3</sub>N (9.5 mg). The mixture was maintained at 60–65 °C for 3 h with stirring, and after evaporation, the residue was chromatographed on a silica gel TLC plate. Development with cyclohexane-EtOAc (10:1) gave **7** (82 mg, 68%) at R<sub>f</sub>=0.41, starting **5** (15 mg, 22% recovery) and tetra-*O*-benzyl-1-deoxynojirimycin (10 mg, 9% recovery). IR ν<sub>max</sub>(film) 3365, 2955, 2930, 2888, 2859 cm<sup>-1</sup>. 270 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.09 (3H, s), 0.12 (3H, s), 0.15 (3H, s), 0.17–0.19 (12H, m), 0.24 (3H, s), 0.88 (9H, s), 0.92 (9H, s), 0.96 (9H, s), 1.00 (9H, s), 3.16 (1H, s, OH), 3.59–3.75 (3H, m), 3.81–3.93 (3H, m), 3.96–4.07 (2H, m), 4.10 (1H, s), 4.21 (1H, m), 4.38–4.85 (11H, m), 4.98 (1H, m), 7.11 (1H, d, *J*=6.6 Hz, NH), 7.34 (20H, s). FAB MS (positive); *m/z* 1202, 1201 [M+H]<sup>+</sup>. Anal. Calcd. for C<sub>65</sub>H<sub>104</sub>N<sub>2</sub>O<sub>9</sub>SSi<sub>4</sub> (1202.0): C, 64.95; H, 8.72; N, 2.33; S, 2.67. Found: C, 65.28; H, 8.75; N, 2.34; S, 2.63.

***N*-[[1*R*-(1α,2β,3α,4β,5β)]-1-Hydroxymethyl-1,2,3,4-(tetrahydro)cyclopent-5-yl]aminothiocarbonyl]-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (**8**).** To a solution of **7** (148 mg, 0.123 mmol) in THF (6 ml) was added 1M THF solution of *n*-Bu<sub>4</sub>NF (1.20 ml, 1.20 mmol). The solution was stirred for 3 h at 24 °C, diluted with EtOAc, washed with brine, dried over MgSO<sub>4</sub>, and filtered, and the filtrate was concentrated *in vacuo* to give a residue, which was chromatographed on a silica gel column. Elution with EtOAc, and then 5% MeOH in EtOAc gave **8** (85 mg, 93%). IR ν<sub>max</sub>(film) 3360, 2924, 2870 cm<sup>-1</sup>. 270 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.46–3.80 (10H, m), 3.96–4.04 (3H, m), 4.31–4.73 (8H, m), 4.84 (1H, t, *J*=6.2 Hz, changed to a doublet on addition of D<sub>2</sub>O), 7.15–7.31 (21H, m, containing NH). FAB MS (positive); *m/z* 745 [M+H]<sup>+</sup>. Anal. Calcd. for C<sub>41</sub>H<sub>48</sub>N<sub>2</sub>O<sub>9</sub>S (744.9): C, 66.11; H, 6.94; N, 3.76; S, 4.30. Found: C, 66.25; H, 6.87; N, 3.77; S, 4.12.

***N*-[[3*aR*-(3α,4α,5β,6α,6α)]-4-Hydroxymethyl-3*a*,5,6,6*a*-tetrahydro-4,5,6-trihydroxy-4*H*-cyclopentoxazol-2-yl]-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (**9**).**

To a solution of **8** (52 mg, 0.070 mmol) in MeCN (3.5 ml) was added 2-chloro-3-ethylbenzoxazolium tetrafluoroborate (34.7 mg, 0.129 mmol) at 0 °C. After stirring for 1 h at 0 °C, Et<sub>3</sub>N (35 mg, 0.347 mmol) was added to this solution at 0 °C. After stirring for 10 min at 0 °C, the reaction mixture was concentrated *in vacuo*, and chromatographed on a silica gel column. Elution with 10% MeOH in EtOAc gave **9** (47 mg, 95%). IR ν<sub>max</sub>(film) 3280 (broad), 1641 cm<sup>-1</sup>. 270 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>+DMF-d<sub>7</sub>+D<sub>2</sub>O) δ 3.62–4.83 (22H, m), 7.21–7.32 (20H, m). FAB MS (positive); *m/z* 733 [M+Na]<sup>+</sup>, 711 [M+H]<sup>+</sup>. Anal. Calcd. for C<sub>41</sub>H<sub>46</sub>N<sub>2</sub>O<sub>9</sub> (710.8): C, 69.28; H, 6.52; N, 3.94. Found: C, 69.17; H, 6.31; N, 3.90.

***N*-[[3*aR*-(3α,4α,5β,6α,6α)]-4-Hydroxymethyl-3*a*,5,6,6*a*-tetrahydro-4,5,6-trihydroxy-4*H*-cyclopentoxazol-2-yl]-1,5-dideoxy-1,5-imino-D-glucitol (**10**) and *N*,6-*O*-[(trehazolaminy]iminomethylidene]-1-deoxynojirimycin (**11**).** A solution of **9** (50 mg, 0.070 mmol) in MeOH (10 ml) containing Pd(OH)<sub>2</sub> on carbon (1.0 g, wet, Degussa type, Pd content 20%) was stirred for 40 min at 60 °C under an atmosphere of hydrogen. The mixture was filtered. The catalyst was washed with MeOH (5 ml). The combined filtrate was concentrated *in vacuo*. The residue was chromatographed on Amberlite CG 50 (NH<sub>4</sub><sup>+</sup> type/H<sup>+</sup> type = 3/2, 20 ml). Elution with 0.5 M NH<sub>3</sub> aqueous solution (4 ml each) gave an inseparable mixture of **10** and **11** (8.0 mg, 32%) as a powder after lyophilization. The mixture of **10** and **11** in an NMR tube (D<sub>2</sub>O) equilibrated at 4 : 1 after 4 days. IR ν<sub>max</sub>(Nujol) 3370,

1665 (shoulder), 1640 cm<sup>-1</sup>. FAB MS (positive); *m/z* 351. High resolution FAB MS (positive); Calcd. for C<sub>13</sub>H<sub>23</sub>N<sub>2</sub>O<sub>9</sub>: 351.1403. Found: 351.1383. 500 MHz <sup>1</sup>H and <sup>13</sup>C NMR data of **10**: trehalamine part; <sup>1</sup>H NMR (D<sub>2</sub>O) δ 3.77 (1H, m, C4CHHOH), 3.87 (1H, m, C4CHHOH), 3.96 (1H, m, C5H), 4.25 (1H, m, C6H), 4.25 (1H, d, *J*<sub>3a,6a</sub>=8.9 Hz, C3aH), 5.00 (1H, d, *J*<sub>3a,6a</sub>=8.9 Hz, C6aH); 1-deoxynojirimycin part; δ 2.44 (1H, d, *J*<sub>geminal</sub>=11.4 Hz, C1HHN), 2.52 (1H, m, C5H), 3.10 (1H, dd, *J*=4.7, 11.4 Hz, C1HHN), 3.22 (1H, *J*<sub>3,4</sub>=9.5 Hz, C4H), 3.32 (1H, t, *J*=9.5 Hz, C3H), 3.45 (1H, dd, *J*=4.7, 9.5 Hz, C2H), 3.62 (1H, m, C6HHOH), 3.80 (1H, m, C6HHOH); trehalamine part; <sup>13</sup>C NMR (D<sub>2</sub>O) δ 62.3 (C4CH<sub>2</sub>OH), 65.6 (C3a), 82.8 (C5), 83.2 (C6), 85.4 (C4), 90.2 (C6a); 1-deoxynojirimycin part: δ 51.7 (C1), 61.7 (C6), 63.7 (C5), 70.5 (C2), 74.2 (C4), 81.8 (C3). 500 MHz <sup>1</sup>H and <sup>13</sup>C NMR data of **11**: trehalamine part; <sup>1</sup>H NMR (D<sub>2</sub>O) δ 3.58 (1H, m, CHHOH), 3.75 (1H, m, CHHOH), 3.90 (1H, m, C3H), 4.17 (1H, m, C2H), 4.33 (1H, m, C5H), 4.92 (1H, m, C4H); 1-deoxynojirimycin part; δ 2.84 (1H, m, C1HHN), 3.38 (1H, m, C4H), 3.42 (1H, m, C3H), 3.53 (1H, m, C5H), 3.63 (1H, m, C5H), 3.87 (1H, m, C1HHN), 4.30 (1H, m, C6H), 4.44 (1H, m, C6H); trehalamine part; <sup>13</sup>C NMR (D<sub>2</sub>O) δ 61.8 (C1CH<sub>2</sub>OH), 77.0 (C5-N), 83.0 (C3), 83.2 (C2), 88.1 (C4), 80-90 (C1); 1-deoxynojirimycin part: δ 48.3 (C1), 70.7 (C6), 72.0 (C2), 74.5 (C4), 76.6 (C5), 79.8 (C3). In this 500 MHz NMR, the partial structures, determined by the <sup>1</sup>H-<sup>1</sup>H connectivity, were elucidated by the double quantum filtered COSY and total correlation spectroscopy. The assignment of <sup>13</sup>C signals directly bonded to those protons was determined by the heteronuclear multiple-quantum correlation spectrum.

***N*-[*N*-(*tert*-Butoxycarbonyl)glycyl]-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (**12a**).** To a solution of **6** (524 mg, 1.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) were added *N*-(*tert*-butoxycarbonyl)glycine (210 mg, 1.20 mmol), and DCC (248 mg, 1.20 mmol). The mixture was stirred for 16 h at 24 °C, filtered, and the filtrate was diluted with EtOAc. The solution was washed with 1M aqueous HCl solution, H<sub>2</sub>O, sat. aqueous NaHCO<sub>3</sub>, and brine, dried over MgSO<sub>4</sub>, and filtered. The filtrate was concentrated *in vacuo*, and chromatographed on a silica gel column. Elution with cyclohexane-EtOAc (3:1) gave **12a** (727 mg, containing a small amount of 1,3-dicyclohexylurea) as a gum, which was employed for the next reaction without further purification. IR ν<sub>max</sub>(film) 3425, 3340 (broad), 1711, 1651 cm<sup>-1</sup>. 270 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.45 (9H, s), 3.37-3.74 (6H, m), 3.86-4.19 (2H, m), 4.29-4.76 (10H, m), 5.52 (1H, bs, NH), 7.21-7.35 (20H, m). FAB MS (positive); *m/z* 681 [M+H]<sup>+</sup>, 703 [M+Na]<sup>+</sup>. High resolution FAB MS (positive); *m/z* Calcd. for C<sub>41</sub>H<sub>49</sub>N<sub>2</sub>O<sub>7</sub>: 681.3540. Found: 681.3574.

***N*-[3-(*tert*-Butoxycarbonylamino)propionyl]-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (**12b**).** To a solution of **6** (524 mg, 1.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) were added *N*-(*tert*-butoxycarbonyl)-β-alanine (227 mg, 1.20 mmol), DMAP (147 mg, 1.20 mmol) and DCC (248 mg, 1.20 mmol). The mixture was stirred for 6 h at 24 °C, filtered, concentrated *in vacuo*, and chromatographed on a silica gel column. Elution with cyclohexane-EtOAc (3:2) gave **12b** (683 mg, 98%) as a gum. IR ν<sub>max</sub>(film) 3584-2869, 1711, 1642 cm<sup>-1</sup>. 270 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.42 (9H, s), 1.75 (1H, broad, NH), 2.53 (2H, bs), 3.32-4.12 (8H, m), 4.25-4.80 (9H, m), 5.31-5.38 (1H, m), 7.21-7.34 (20H, m). Anal. Calcd. for C<sub>42</sub>H<sub>50</sub>N<sub>2</sub>O<sub>7</sub>: C, 72.60; H, 7.25; N, 4.03. Found: C, 72.13; H, 7.31; N, 4.07.

***N*-[2-(*tert*-Butoxycarbonylamino)ethyl]-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (13a).** A solution of the above obtained **12a** (727 mg) in 1M BH<sub>3</sub>-THF complex (30 ml) was stirred for 16 h at 24 °C, and diluted with EtOAc (400 ml). This solution was washed with 1M aqueous HCl (43 ml) by vigorous stirring, and then neutralized with sat. NaHCO<sub>3</sub> (60 ml). The organic layer was dried over MgSO<sub>4</sub>, filtered, concentrated *in vacuo*, and chromatographed on a silica gel column. Elution with cyclohexane-EtOAc (3:1) gave **13a** (412 mg, 62% for two steps, containing a small amount of 1,3-dicyclohexylurea) as a gum. IR  $\nu_{\text{max}}$ (film) 3360 (broad), 1711, 1655 cm<sup>-1</sup>. 270 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.43 (9H, s), 2.17 (1H, t, *J*=10.9 Hz), 2.40 (1H, d, *J*=8.9 Hz), 2.47 (1H, td, *J*=4.9, 13.3 Hz), 2.81-2.91 (1H, m), 3.05-3.25 (3H, m), 3.45-3.66 (5H, m), 4.33-4.98 (8H, m), 5.13 (1H, bs, NH), 7.09-7.13 (2H, m), 7.24-7.36 (18H, m). FAB MS (positive); *m/z* 667 [M+H]<sup>+</sup>. High resolution FAB MS (positive); Calcd. for C<sub>41</sub>H<sub>51</sub>N<sub>2</sub>O<sub>6</sub>: 667.3744. Found: 667.3754. Anal. Calcd. for C<sub>41</sub>H<sub>50</sub>N<sub>2</sub>O<sub>6</sub> (666.9): C, 73.85; H, 7.56; N, 4.20. Found: C, 73.46; H, 7.55; N, 4.15.

***N*-[3-(*tert*-Butoxycarbonylamino)propyl]-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (13b).** To compound **12b** (695 mg, 1.00 mmol) was added 1M BH<sub>3</sub>-THF complex (40 ml). The solution was treated as described above to give **13b** (683 mg, 98%) as a gum. IR  $\nu_{\text{max}}$ (film) 3384-2809, 1711 cm<sup>-1</sup>. 270 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.25 (2H, bs), 1.43 (9H, s), 2.02 (1H, t, *J*=10.4-11.0 Hz), 2.24 (1H, d, *J*=9.1 Hz), 2.37 (1H, m), 2.81 (1H, m), 2.95-3.07 (2H, m), 3.16 (1H, m), 3.43-3.67 (5H, m), 4.34, 4.96 (2H, AB-q, *J*=10.9 Hz), 4.45, 4.54 (2H, AB-q, *J*=12.1 Hz), 4.63, 4.70 (2H, AB-q, *J*=11.6 Hz), 4.82 (2H, t, *J*=11.5 Hz), 5.25 (1H, bs, NH), 7.08-7.13 (2H, m), 7.26-7.34 (18H, m). FAB MS (positive); *m/z* 681 [M+H]<sup>+</sup>. High resolution FAB MS (positive); Calcd. for C<sub>42</sub>H<sub>53</sub>N<sub>2</sub>O<sub>6</sub>: 681.3904. Found: 681.3872. Anal. Calcd. for C<sub>42</sub>H<sub>52</sub>N<sub>2</sub>O<sub>6</sub> (680.9): C, 74.09; H, 7.70; N, 4.11. Found: C, 74.01; H, 7.85; N, 4.10.

***N*-(2-Aminoethyl)-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (14a).** To a solution of the above-obtained **13a** (412 mg) in CH<sub>2</sub>Cl<sub>2</sub> (7 ml) was added CF<sub>3</sub>COOH (3.5 ml). The solution was stirred for 30 min at 24 °C, and diluted with Et<sub>2</sub>O (100 ml), washed with 1 M aqueous NaOH, and dried over MgSO<sub>4</sub>, filtered, concentrated *in vacuo* to give crude **14a** (412 mg) as a powder, which was employed for the next reaction without further purification.

***N*-(3-Aminopropyl)-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (14b).** To a solution of **13b** (360 mg, 0.529 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) was added CF<sub>3</sub>COOH (3 ml). After the solution was stirred for 45 min at 24 °C, the reaction mixture was treated above to give **14b** (291 mg, 95%) as a gum. IR  $\nu_{\text{max}}$ (film) 3600-2780, 1715-1580 (w, broad) cm<sup>-1</sup>. 270 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.53 (1H, m), 1.43 (9H, s), 1.63 (1H, m), 1.85 (2H, bs, NH<sub>2</sub>, D<sub>2</sub>O exchanged), 2.14 (1H, t, *J*=10.6 Hz), 2.27 (1H, d, *J*=9.2 Hz), 2.51 (1H, ddd, *J*=4.6, 8.6, 13.2 Hz), 2.63 (2H, t, *J*=6.6 Hz), 2.79 (1H, m), 3.13 (1H, dd, *J*=4.6, 11.2 Hz), 3.43-3.70 (5H, m), 4.41, 4.87 (2H, AB-q, *J*=10.6 Hz), 4.46 (2H, s), 4.66, 4.71 (2H, AB-q, *J*=11.2 Hz), 4.81, 4.96 (2H, AB-q, *J*=10.6 Hz), 7.13-7.17 (2H, m), 7.24-7.38 (18H, m). FAB MS (positive); *m/z* 581 [M+H]<sup>+</sup>. High resolution FAB MS (positive); Calcd. for C<sub>37</sub>H<sub>45</sub>N<sub>2</sub>O<sub>4</sub>: 581.3373. Found: 581.3388.

***N*-(2-Isothiocyanatoethyl)-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (15a).** To a solution of the crude **14a** (412 mg) obtained above in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) were added CS<sub>2</sub> (100 mg, 1.24 mmol) and Et<sub>3</sub>N (202 mg, 2.00 mmol) at 24 °C under nitrogen. The solution was stirred for 1

h, and then to this solution were added Et<sub>3</sub>N (150 mg) and 2-chloro-1-methylpyridinium iodide (260 mg, 1.02 mmol). This solution was stirred for 2.5 h at 24 °C under nitrogen, and concentrated *in vacuo* to give a mixture, which was diluted with EtOAc, washed with sat. NaHCO<sub>3</sub>, H<sub>2</sub>O, brine, dried over MgSO<sub>4</sub>, and filtered. The filtrate was concentrated *in vacuo* to give a mixture, which was chromatographed on a silica gel column. Elution with cyclohexane-EtOAc (3:1) gave **15a** (156 mg, two steps from **13a**, 41%). IR  $\nu_{\text{max}}(\text{film})$  2170, 2110, 1648, 1590 cm<sup>-1</sup>. 270 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.34 (1H, t, *J*=10.8 Hz), 2.49 (1H, td, *J*=2.9, 9.0 Hz), 2.86 (1H, td, *J*=6.2, 12.0 Hz), 3.00–3.14 (2H, m), 3.38–3.52 (4H, m), 3.57–3.65 (3H, m), 4.44, 4.88 (2H, AB-q, *J*=10.9 Hz), 4.45 (2H, s), 4.65, 4.71 (2H, AB-q, *J*=11.6 Hz), 4.80, 4.95 (2H, AB-q, *J*=10.9 Hz), 7.13–7.19 (2H, m), 7.25–7.40 (18H, m). FAB MS (positive); *m/z* 609 [M+H]<sup>+</sup>. High resolution FAB MS (positive); Calcd. for C<sub>37</sub>H<sub>41</sub>N<sub>2</sub>O<sub>4</sub>S: 609.2830. Found: 609.2803.

**N-[2-[[1R-(1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\beta$ )]-[1-(*tert*-Butyldimethylsilyloxymethyl)-1-hydroxy-2,3,4-tris(*tert*-butyldimethylsilyloxy)cyclopent-5-yl]aminothiocarbonyl]aminoethyl]-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (16a).** A solution of **15a** (31 mg, 0.051 mmol) and **4** (36 mg, 0.057 mmol) in THF (0.5 ml) and Et<sub>3</sub>N (10 mg) was stirred at 20–25 °C for 2 days, concentrated *in vacuo*, and chromatographed on a silica gel plate. Development with cyclohexane-EtOAc (4:1) gave **16a** (55 mg, 87%) as a gum. The R<sub>f</sub> values of two starting materials (**15a** and **4**) and the product (**16a**) were almost same. IR  $\nu_{\text{max}}(\text{film})$  3335, 2955–2930, 1640 (shoulder) cm<sup>-1</sup>. 270 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.09–0.12 (24H, m), 0.90 (27H, broad s), 0.94 (9H, s), 1.53 (1H, m), 2.22 (1H, m), 2.43 (1H, m), 2.66 (1H, m), 3.00 (1H, m), 3.17 (1H, m), 3.43–3.99 (12H, m), 4.37–4.97 (8H, m), 7.09–7.12 (2H, m), 7.25–7.32 (18H, m). FAB MS (positive); *m/z* 1244 [M+H]<sup>+</sup>, 721. High resolution FAB MS (positive); Calcd. for C<sub>67</sub>H<sub>110</sub>N<sub>3</sub>O<sub>9</sub>SSi<sub>4</sub>: 1244.7046. Found: 1244.7064. Anal. Calcd. for C<sub>67</sub>H<sub>109</sub>N<sub>3</sub>O<sub>9</sub>SSi<sub>4</sub> (1245.0): C, 64.64; H, 8.83; N, 3.38; S, 2.58. Found: C, 64.70; H, 8.48; N, 3.39; S, 2.63.

**N-[3-[[1R-(1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\beta$ )]-[1-(*tert*-Butyldimethylsilyloxymethyl)-1-hydroxy-2,3,4-tris(*tert*-butyldimethylsilyloxy)cyclopent-5-yl]aminothiocarbonyl]aminopropyl]-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (16b).** A solution of **14b** (92 mg, 0.158 mmol) and **5** (107 mg, 0.158 mmol) in THF (0.20 ml) was warmed at 60–65 °C for 3 h with stirring, concentrated *in vacuo*, and chromatographed on a silica gel column. Elution with cyclohexane-EtOAc (4:1) gave **16b** (166 mg, 83%) as a gum. IR  $\nu_{\text{max}}(\text{film})$  3100–2800, 2480 (w), 1640 cm<sup>-1</sup>. 270 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.09–0.12 (24H, m), 0.90–0.93 (36H, m), 1.26 (1H, broad), 1.50–1.80 (3H, m), 2.20 (1H, t, *J*=10.7 Hz), 2.32 (1H, t, *J*=9.2 Hz), 2.63 (1H, m), 2.80 (1H, m), 3.11 (1H, dd, *J*=4.7, 11.0 Hz), 3.33 (1H, m), 3.42–3.78 (8H, m), 3.90 (1H, m), 3.97 (1H, s), 4.35–4.97 (8H, m), 7.08–7.11 (2H, m), 7.22–7.38 (18H, m). FAB MS (positive); *m/z* 1260, 1259, 1258 [M+H]<sup>+</sup>, 738, 737, 735, 176. Anal. Calcd. for C<sub>68</sub>H<sub>111</sub>N<sub>3</sub>O<sub>9</sub>SSi<sub>4</sub> (1259.1): C, 64.87; H, 8.89; N, 3.34; S, 2.55. Found: C, 65.08; H, 8.93; N, 3.29; S, 2.59.

**N-[2-[[1R-(1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\beta$ )]-(1-Hydroxymethyl-1,2,3,4-tetrahydroxycyclopent-5-yl)aminothiocarbonyl]aminoethyl]-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (17a).** To a solution of **16a** (50 mg, 0.040 mmol) in MeOH (5 ml) was added a solution of 10% (w/w) HCl in MeOH (5 mL). The solution was stirred for 16 h at 24 °C, and concentrated *in vacuo* to give a hydrochloride of **17a** (33 mg, quantitative) as a powder. IR  $\nu_{\text{max}}(\text{Nujol})$  3300 (broad), 1550 cm<sup>-1</sup>. 270

MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.80–5.20 (26H, m), 6.87 (2H, bs), 7.07–7.40 (18H, m). FAB MS (positive);  $m/z$  788  $[\text{M}+\text{H}]^+$ . High resolution FAB MS (positive); Calcd. for  $\text{C}_{43}\text{H}_{54}\text{N}_3\text{O}_9\text{S}$ : 788.3579. Found: 788.3586.

***N*-[3-[[1*R*-(1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\beta$ )]-1-Hydroxymethyl-1,2,3,4-(tetrahydroxy)cyclopent-5-yl]aminothiocarbonyl]aminopropyl]-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol Hydrochloride (17b).** The similar treatment of **16b** (473 mg) as described above gave **17b** (314 mg, quantitative) as a powder. IR  $\nu_{\text{max}}$ (Nujol) 3320 (broad), 1682, 1638  $\text{cm}^{-1}$ . 270 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.48–1.60 (2H, m), 2.09 (1H, m), 2.31 (1H, m), 2.46 (1H, m), 2.65–2.80 (2H, m), 3.08 (1H, m), 3.30 (1H, m), 3.40–3.71 (8H, m), 3.87–4.00 (3H, m), 4.32–4.90 (8H, m), 7.08–7.15 (2H, m), 7.21–7.33 (18H, m). FAB MS (positive);  $m/z$  802  $[\text{M}+\text{H}]^+$ . High resolution FAB MS (positive); Calcd. for  $\text{C}_{44}\text{H}_{56}\text{N}_3\text{O}_9\text{S}$ : 802.3735. Found: 802.3748. *Anal.* Calcd. for  $\text{C}_{44}\text{H}_{55}\text{N}_3\text{O}_9\text{S}\cdot\text{HCl}$  (838.5): C, 63.03; H, 6.73; N, 5.01; S, 3.82; Cl, 4.23. Found: C, 62.90; H, 6.76; N, 5.03; S, 3.67; Cl, 4.54.

***N*-[2-[[3*aR*-(3 $\alpha$ ,4 $\alpha$ ,5 $\beta$ ,6 $\alpha$ ,6 $\alpha$ )]-4-Hydroxymethyl-3*a*,5,6,6*a*-tetrahydro-4,5,6-trihydroxy-4*H*-cyclopentoxazol-2-yl]aminoethyl]-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (18a).** To a suspension of the hydrochloride **17a** (56 mg, 0.068 mmol) in MeCN (5 ml) was added 2-chloro-3-ethylbenzoxazolium tetrafluoroborate (42 mg, 0.156 mmol) at 0–5  $^\circ\text{C}$  under nitrogen with stirring. The suspension changed to a solution immediately. After stirring for 1 h at 0  $^\circ\text{C}$ ,  $\text{Et}_3\text{N}$  (170 mg, 1.68 mmol) was added. After stirring for 30 min at 0  $^\circ\text{C}$ , the reaction mixture was concentrated *in vacuo*, and chromatographed on a silica gel column. Elution with 10% MeOH in EtOAc, and MeOH–EtOAc (1:1) gave a mixture of silica gel and **18a**, which was concentrated *in vacuo*, and diluted with EtOAc. The mixture was washed with sat.  $\text{NaHCO}_3$  and brine to remove the silica gel, dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo* to give **18a** (34 mg, 67%) as a yellowish powder. IR  $\nu_{\text{max}}$ (Nujol) 3340 (broad), 1703, 1665  $\text{cm}^{-1}$ . 270 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.16 (1H, t,  $J=10.3$  Hz), 2.32 (1H, m), 2.48 (1H, m), 2.87 (1H, m), 3.10 (1H, m), 3.20–3.30 (2H, m), 3.40–3.48 (2H, m), 3.50–3.67 (3H, m), 3.98 (2H, bs), 4.11 (1H, bs), 4.20 (1H, bs), 4.28–4.36 (2H, m), 4.44–5.09 (8H, m), 7.06–7.09 (2H, m), 7.16–7.40 (18H, m). FAB MS (positive);  $m/z$  754  $[\text{M}+\text{H}]^+$ . High resolution FAB MS (positive); Calcd. for  $\text{C}_{43}\text{H}_{52}\text{N}_3\text{O}_9$ : 754.3705. Found: 754.3704.

***N*-[3-[[3*aR*-(3 $\alpha$ ,4 $\alpha$ ,5 $\beta$ ,6 $\alpha$ ,6 $\alpha$ )]-4-Hydroxymethyl-3*a*,5,6,6*a*-tetrahydro-4,5,6-trihydroxy-4*H*-cyclopentoxazol-2-yl]aminopropyl]-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (18b).** The similar treatment of **17b** (54 mg) as described above gave **18b** (40 mg, 77%) as a yellowish powder.  $^1\text{H}$  NMR ( $\text{CDCl}_3+\text{DMF-d}_7+\text{D}_2\text{O}$ )  $\delta$  3.62–4.83 (22H, m), 7.21–7.32 (20H, m). IR  $\nu_{\text{max}}$ (Nujol) 3340 (broad), 1698  $\text{cm}^{-1}$ . 270 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.50–1.70 (2H, m), 2.04 (1H, broad), 2.25 (1H, m), 2.37 (1H, m), 2.70 (1H, m), 2.98–3.22 (3H, m), 3.37–3.70 (5H, m), 3.86–4.10 (3H, m), 4.20–4.95 (11H, m), 7.05–7.12 (2H, m), 7.20–7.37 (18H, m). FAB MS (positive)  $m/z$  768  $[\text{M}+\text{H}]^+$ . High resolution FAB MS (positive), Calcd. for  $\text{C}_{44}\text{H}_{54}\text{N}_3\text{O}_9$ : 768.3858. Found: 768.3868. *Anal.* Calcd. for  $\text{C}_{44}\text{H}_{53}\text{N}_3\text{O}_9$  (767.9): C, 68.82; H, 6.96; N, 5.47. Found: C, 68.30; H, 6.83; N, 5.48.

***N*-[2-[[3*aR*-(3 $\alpha$ ,4 $\alpha$ ,5 $\beta$ ,6 $\alpha$ ,6 $\alpha$ )]-4-Hydroxymethyl-3*a*,5,6,6*a*-tetrahydro-4,5,6-trihydroxy-4*H*-cyclopentoxazol-2-yl]aminoethyl]-1,5-dideoxy-1,5-imino-D-glucitol (19a).**

A solution of **18a** (34 mg, 0.045 mmol) in MeOH (10 ml) containing  $\text{Pd}(\text{OH})_2$  on carbon (50 mg, wet,

Degussa type, Pd content 20%) as a catalyst was stirred for 8 h at 60–65 °C under an atmosphere of hydrogen. The catalyst was filtered off, and the filtrate was concentrated *in vacuo*. The residue was chromatographed on Amberlite CG 50 (NH<sub>4</sub><sup>+</sup> type/H<sup>+</sup> type = 3/2, 12 ml). Elution with 0.5 M NH<sub>3</sub> aqueous solution (3 ml each), then 1.0 M NH<sub>3</sub> aqueous solution gave **19a** (13 mg, 72%) as a powder after lyophilization. IR  $\nu_{\max}$ (Nujol) 3500–3100 (broad), 1705, 1660 cm<sup>-1</sup>. 400 MHz <sup>1</sup>H NMR (D<sub>2</sub>O)  $\delta$  2.13–2.22 (2H, m, CH<sub>2</sub>-NH), 2.58 (1H, m, N-CH), 2.75 (1H, m, N-CH), 2.88 (1H, dd, *J*=4.9, 11.7 Hz, C1-H), 3.08 (1H, t, *J*=9.3 Hz), 3.10–3.20 (2H, m), 3.18 (1H, m), 3.36 (1H, m), 3.55, 3.65 (2H, AB-q, *J*=11.7 Hz, C6'-H<sub>2</sub>), 3.67 (1H, d, *J*=2.4 Hz), 3.73–3.77 (2H, m), 3.99 (1H, dd, *J*=2.4, 4.4 Hz), 4.16 (1H, d, *J*=8.3 Hz), 4.75 (1H, dd, *J*=1.0, 8.8 Hz). <sup>13</sup>C NMR (D<sub>2</sub>O)  $\delta$  40.5 (CH<sub>2</sub>-NH), 52.6 (CH<sub>2</sub>-N), 58.0 (C1), 59.8 (C6 or C7'), 64.4 (C7' or C6), 71.0, 72.2, 75.8, 80.5, 82.3, 82.6, 85.2, 98.8 (C2, C3, C4, C5, C3a', C5', C6', C6a'), 163.7 (C2'). FAB MS (positive); *m/z* 394 [M+H]<sup>+</sup>. High resolution FAB MS (positive); *m/z* Calcd. for C<sub>15</sub>H<sub>28</sub>N<sub>3</sub>O<sub>9</sub>: 394.1825. Found: 394.1834.

***N*-[3-[[3a*R*-(3a $\alpha$ ,4 $\alpha$ ,5 $\beta$ ,6 $\alpha$ ,6a $\alpha$ )]-4-Hydroxymethyl-3a,5,6,6a-tetrahydro-4,5,6-trihydroxy-4*H*-cyclopentoxazol-2-yl]aminopropyl]-1,5-dideoxy-1,5-imino-D-glucitol (**19b**).**

A solution of **18b** (50 mg, 0.065 mmol) in MeOH (10 ml) containing Pd(OH)<sub>2</sub> on carbon (55 mg, wet, Degussa type, Pd content 20%) as a catalyst was hydrogenolized for 24 h at 50–55 °C. The reaction mixture was treated as described above to give **19b** (26 mg, 98%) as a powder after lyophilization.  $[\alpha]_D^{24} +56.0^\circ$  (c 0.6, H<sub>2</sub>O). IR  $\nu_{\max}$ (KBr) 3340 (broad), 2926, 2337 (w), 1706, 1659 cm<sup>-1</sup>. 400 MHz <sup>1</sup>H NMR (D<sub>2</sub>O)  $\delta$  1.50–1.57 (2H, m, C-CH<sub>2</sub>-C), 2.03–2.12 (2H, m, C5H-N, N-C1H $\beta$ ), 2.47 (1H, m, N-CHC), 2.59 (1H, m, N-CHC), 2.80 (1H, dd, *J*=5.1, 11.4 Hz, N-C1H $\alpha$ ), 2.98–3.08 (3H, m, N-CH<sub>2</sub>C, C3H), 3.17 (1H, t, *J*=9.5 Hz, C4H), 3.35 (1H, m, C2H), 3.53–3.71 (4H, m, C6H<sub>2</sub>OH, C4'CH<sub>2</sub>OH), 3.78 (1H, d, *J*=4.4 Hz, C5'H), 4.03 (1H, dd, *J*=2.4, 4.4 Hz, C6'H), 4.20 (1H, d, *J*=8.3 Hz, C3a'H), 4.86 (1H, d, *J*=8.3 Hz, C6a'H). 400 MHz <sup>13</sup>C NMR (D<sub>2</sub>O)  $\delta$  25.2, 42.8, 51.4, 57.5, 59.7, 64.0, 67.3, 71.1, 72.2, 73.5, 80.5, 82.1, 82.3, 85.2, 90.9, 163.7. FAB MS (positive); *m/z* 408 [M+H]<sup>+</sup>. High resolution FAB MS (positive); *m/z* Calcd. for C<sub>16</sub>H<sub>30</sub>N<sub>3</sub>O<sub>9</sub>: 408.2027. Found: 408.1952.

***N*-(3-Aminopropyl)-1,5-dideoxy-1,5-imino-D-glucitol (**20**).** Compound **14b** (95 mg) in MeOH (15 ml) was hydrogenolyzed 50–55 °C for 16 h using Pd(OH)<sub>2</sub> on carbon (105 mg). The solution was filtered, and concentrated *in vacuo* to give **20** (31 mg, 86%), which was dissolved in H<sub>2</sub>O, and lyophilized. IR  $\nu_{\max}$ (KBr) 3352 (broad) cm<sup>-1</sup>. 400 MHz <sup>1</sup>H NMR (D<sub>2</sub>O)  $\delta$  1.54 (2H, quintet, *J*=7.2–7.6 Hz), 2.05 (1H, m), 2.07 (1H, t, *J*=11.4 Hz), 2.44 (1H, m), 2.58–2.69 (3H, m), 2.85 (1H, dd, *J*=4.9, 11.4 Hz), 3.07 (1H, t, *J*=9.4 Hz), 3.18 (1H, t, *J*=9.4 Hz), 3.35 (1H, m), 3.65 (1H, dd, *J*=2.7, 12.8 Hz), 3.72 (1H, dd, *J*=2.3, 12.8 Hz). 400 MHz <sup>13</sup>C NMR (D<sub>2</sub>O)  $\delta$  25.71 (H<sub>2</sub>C), 40.94 (H<sub>2</sub>C), 51.40 (H<sub>2</sub>C), 57.42 (H<sub>2</sub>C), 59.58 (H<sub>2</sub>C), 67.44 (HC), 71.05 (HC), 72.24 (HC), 80.58 (HC). FAB MS (positive); *m/z* 221 [M+H]<sup>+</sup>. High resolution FAB MS (positive); *m/z* Calcd. for C<sub>9</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub>: 221.1501. Found: 221.1504.

**[1*R*-(1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\beta$ )]-5-[(Butylaminothiocarbonyl)amino]-1-(*tert*-butyldimethylsilyloxymethyl)-2,3,4-tris(*tert*-butyldimethylsilyloxy)cyclopentane-1-ol (**21**).**

A solution of amine **4** (64 mg, 0.10 mmol), butyl isothiocyanate (20 mg, 0.17 mmol) and Et<sub>3</sub>N (10 mg, 0.10 mmol) in THF (0.5 ml) was allowed to stand at room temperature for 16 h. Reaction mixture was

concentrated *in vacuo*, and chromatographed on a silica gel column. Elution with cyclohexane-EtOAc (9:1) gave **21** (55 mg, 73%) as a solid, mp 141–142 °C (from EtOAc-hexane). IR  $\nu_{\max}$ (Nujol) 3335, 1648  $\text{cm}^{-1}$ . 270 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.07–0.15 (24H, m), 0.85–0.96 (39H, m), 1.31–1.41 (2H, m), 1.51–1.62 (2H, m), 3.24–3.53 (2H, m), 3.68–4.20 (6H, m). FAB MS (positive);  $m/z$  753, 752, 751  $[\text{M}+\text{H}]^+$ . High resolution FAB MS (positive);  $m/z$  Calcd. for  $\text{C}_{35}\text{H}_{78}\text{N}_2\text{O}_5\text{SSi}_4$ : 751.4797. Found: 751.4756.

**[1R-(1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\beta$ )]-5-[(Butylaminothiocarbonyl)amino]-1-hydroxymethyl-cyclopentane-1,2,3,4-tetraol (22).** A solution of amine **21** (44 mg, 0.06 mmol) in MeOH (4 mL) and 10% HCl in MeOH (4 mL, w/w) was stirred at 24 °C for 4 h. Reaction mixture was concentrated *in vacuo* to give **22** (17 mg, quantitatively) as a gum, which was employed for the next reaction without purification. IR  $\nu_{\max}$ (film) 3320, 2959, 2933, 2880, 1620, 1563, 1555  $\text{cm}^{-1}$ . 270 MHz  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3\text{-D}_2\text{O}$ )  $\delta$  0.92 (3H, t,  $J=7.3$  Hz), 1.30–1.42 (2H, m), 1.52–1.63 (2H, m), 3.38–3.64 (3H, m), 3.82 (1H, bs), 3.92 (1H, d,  $J=7.0$  Hz), 3.97 (1H, m), 3.99, 4.14 (2H, AB-q,  $J=9.1$  Hz). FAB MS (positive);  $m/z$  295  $[\text{M}+\text{H}]^+$ . High resolution FAB MS (positive);  $m/z$  Calcd. for  $\text{C}_{11}\text{H}_{22}\text{N}_2\text{O}_5\text{S}$ : 295.1384. Found: 295.1304.

**[3aR-(3 $\alpha$ ,4 $\alpha$ ,5 $\beta$ ,6 $\alpha$ ,6 $\alpha$ )]-2-Butylamino-4-hydroxymethyl-4,5,6,6a-tetrahydro-3aH-cyclopentaoxazole-4,5,6-triol (23).** To a solution of thiourea **22** (17 mg, 0.06 mmol) in MeCN (2 mL) was added 2-chloro-3-ethylbenzoxazolium tetrafluoroborate (29 mg, 0.11 mmol) at 0 °C with stirring under nitrogen atmosphere. After 1 h stirring at 0 °C,  $\text{Et}_3\text{N}$  (50 mg, 0.50 mmol) was added to the mixture. After stirring at 0 °C for 30 min, reaction mixture was concentrated *in vacuo* and was then dissolved in  $\text{H}_2\text{O}$  (2 mL). The aqueous solution was washed with EtOAc (1 mL). The aqueous layer was charged on an Amberlite CG 50 ( $\text{NH}_4^+$  type/ $\text{H}^+$  type = 3/2, 15 mL) column for purification. Elution with 0.5 M aqueous  $\text{NH}_4\text{OH}$  (4 mL  $\times$  10) and then 1.5 M aqueous  $\text{NH}_4\text{OH}$  (4 mL each) gave **23** (7.0 mg, two steps 46%) on the No. 14 as a powder after lyophilization. IR  $\nu_{\max}$ (film) 3375, 2960, 2930, 2870, 1659  $\text{cm}^{-1}$ . 400 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.70 (3H, t,  $J=7.3$  Hz), 1.09–1.18 (2H, m), 1.25–1.36 (2H, m), 2.87–2.99 (2H, m,  $\text{CH}_2\text{N}$ ), 3.52, 3.63 (2H, AB-q,  $J=12.0$  Hz), 3.74 (1H, d,  $J=4.9$  Hz,  $\text{C}_5\text{-H}$ ), 3.95 (1H, dd,  $J=2.5, 4.9$  Hz,  $\text{C}_6\text{-H}$ ), 4.11 (1H, d,  $J=8.8$  Hz,  $\text{C}_{3a}\text{-H}$ ), 4.66 (1H, m,  $\text{C}_{6a}\text{-H}$ ). 400 MHz  $^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  15.3 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_2$ ), 33.1 ( $\text{CH}_2$ ), 44.2 ( $\text{CH}_2\text{-NH}$ ), 64.6 ( $\text{CH}_2\text{OH}$ ), 76.3 ( $\text{C}_{3a}$ ), 82.3, 82.4, 88.9 ( $\text{C}_5, \text{C}_6, \text{C}_{6a}$ ), 85.0 ( $\text{C}_4$ ), 164.1 ( $\text{C}_2$ ). FAB MS (positive);  $m/z$  261  $[\text{M}+\text{H}]^+$ . High resolution FAB MS (positive);  $m/z$  Calcd. for  $\text{C}_{11}\text{H}_{21}\text{N}_2\text{O}_5\text{S}$ : 261.1451. Found: 261.1477.

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