*Carbohydrate Research*, 228 (1992) 377–398
Elsevier Science Publishers B.V., Amsterdam



# Chemical modification of the sugar part of methyl acarviosin: synthesis and inhibitory activities of nine analogues*

Yasushi Shibata, Yasuhiro Kosuge, Toshimi Mizukoshi, and Seiichiro Ogawa†
*Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Kohoku-ku, Yokohama, 223 (Japan)*

(Received June 20th, 1991; accepted October 25th, 1991)

ABSTRACT

Nine analogues of methyl acarviosin (**1**), the core structure of acarbose and its homologues, the 6-hydroxy- (**2**), 6-azido- (**3**), 6-amino- (**4**), 6-acetamido- (**5**), 6-methoxy- (**6**), 6-hydroxy-2-*O*-methyl- (**8**), and 6-hydroxy-3-*O*-methyl derivatives (**9**), including the 5-methoxycarbonyl analogue (**7**) and 3,6-anhydro derivative (**10**) of **2**, were synthesized by chemical modification of the sugar part of **2** derived by condensation of methyl 3,4-anhydro-α-D-galactopyranoside (**17**) and 4,7:5,6-di-*O*-isopropylidenevalienamine (**26**) or by direct coupling between **26** and the 6-substituted methyl 3,4-anhydro-α-D-galactopyranoside derivatives. Compounds **2** and **8** show notable inhibitory activity against yeast α-D-glucosidase almost comparable to that of **1**. Introduction of a polar substituent at C-6 of **1** decreases the inhibitory activity. Interestingly, inversion of the conformation of the sugar part of **1** by introduction of the 3,6-anhydro bridge elicits almost no effect on the inhibitory activity.

## INTRODUCTION

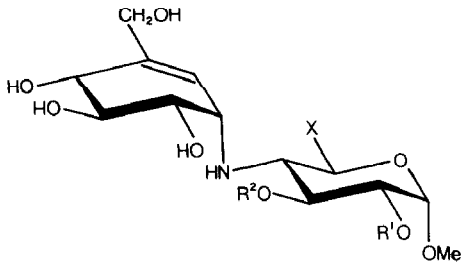
The previous paper[2] reported syntheses and the inhibitory activity of methyl oligobiosaminide, the essential core structure of oligostatins[3], the carba-oligosaccharidic α-D-glucosidase inhibitors, and several deoxy derivatives thereof. Unexpectedly, methyl oligobiosaminide was found to possess only weak activity and therefore we could not obtain successful results from its chemical modification.

Methyl acarviosin[4] (**1**) constitutes the core structure of acarbose[5] and its homologues, containing 4-amino-4,6-dideoxy-D-glucopyranose and a branched-chain unsaturated cyclitol (valienamine), and itself shows powerful inhibitory activity against certain hydrolases. In this paper, we describe a chemical modification of the sugar part of **1**, providing nine related carba-disaccharides **2–10**, which were subjected to biological assay for inhibitory activity against yeast α-glucosidase.

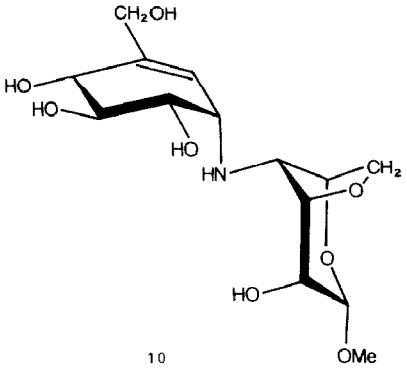
Synthesis of the carba-disaccharides was carried out conventionally coupling of the sugar epoxides with (1*S*)-4,7:5,6-di-*O*-isopropylidenevalienamine[6] (**26**), followed by deprotection. Modification of the 6-hydroxyacarviosin derivative **27** thus readily prepared was also conducted.

* Synthesis of Pseudo-oligosaccharide Glycosidase Inhibitors, Part X. Part IX, see ref. 1.
† Author for correspondence.

0008-6215/92/$ 05.00 



| | $R^1$ | $R^2$ | X |
|---|---|---|---|
| 1 | H | H | $CH_3$ |
| 2 | H | H | $CH_2OH$ |
| 3 | H | H | $CH_2N_3$ |
| 4 | H | H | $CH_2NH_2$ |
| 5 | H | H | $CH_2NHAc$ |
| 6 | H | H | $CH_2OMe$ |
| 7 | H | H | $CO_2Me$ |
| 8 | Me | H | $CH_2OH$ |
| 9 | H | Me | $CH_2OH$ |

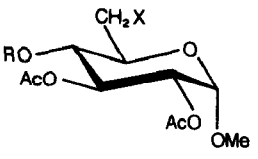


10

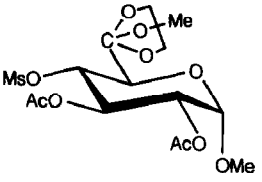
## RESULTS AND DISCUSSION

*Preparation of several 6-substituted derivatives of methyl 3,4-anhydro-α-D-galacto-pyranoside.* — The 4,6-di-*O*-tosyl derivative[7] **12** obtained from methyl 2,3-di-*O*-acetyl-α-D-galactopyranoside[8] (**11**) was treated with sodium azide in *N,N*-dimethylformamide at 60° to give the 6-azido compound **13** (98%) selectively. Treatment of **13** with an excess of methanolic sodium methoxide in 1:1 chloroform–methanol at room temperature produced a single epoxide **18** (86%), which was further characterized as the acetate **19** (97%). Treatment of **11** with a slight excess of chlorotriphenylmethane in pyridine in the presence of 4-dimethylaminopyridine at 60° gave the 6-*O*-trityl derivative, which was successively mesylated to afford the 4-mesylate **14** (73% overall yield). Compound **14** was similarly converted into the expoxide **20**, which was subsequently *O*-methylated with methyl iodide (sodium hydride) in tetrahydrofuran to give the 2-*O*-methyl derivative **21** (85% overall yields). Hydrogenolysis of **21** in the presence of Pd–C afforded the epoxide **22** (74%). *O*-Detritylation of **14** with aqueous acetic acid (→**15**) and successive Jones' oxidation and esterification with 3-hydroxymethyl-3-methyloxene gave the cyclic ortho ester **16** (20% overall yield), which was converted into the epoxide **24** (86%), characterized as the acetate **25**. The OH-2 blocked derivative **23** was obtained in 86% yield by conventional pyranylation of **20**.

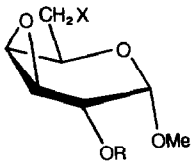
*Synthesis of methyl acarviosin analogues.* — Coupling between a slight excess of methyl 3,4-anhydro-α-D-galactopyranoside[9] (**17**) and (1*S*)-4,7:5,6-di-*O*-isopropylidene-valienamine (**26**) in 2-propanol for 42 h at 120° proceeded smoothly to afford, after chromatography, two condensates **27** (56%) and **44** (44%), which were characterized by conversion into the respective triacetates **28** and **45**. The $^1$H-n.m.r. spectra (270 MHz, $CDCl_3$) of **28** and **45** revealed signals due to the protons of the sugar parts attached to the



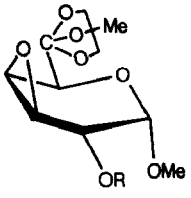
| | R | X |
|---|---|---|
| 11 | H | H |
| 12 | Ts | OTs |
| 13 | Ts | $N_3$ |
| 14 | Ms | OTr |
| 15 | Ms | OH |



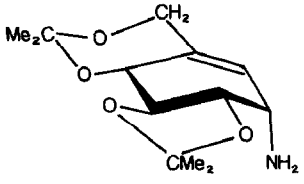
16



| | R | X |
|---|---|---|
| 17 | H | OH |
| 18 | H | $N_3$ |
| 19 | Ac | $N_3$ |
| 20 | H | OTr |
| 21 | Me | OTr |
| 22 | Me | OH |
| 23 | THP | OTr |



24 R = H
25 R = Ac



26

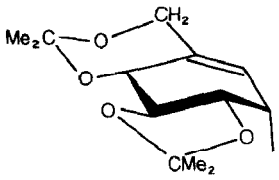
carbon atoms bearing the imino linkage as a triplet and a broad singlet at $\delta$ 2.99 ($J_{3,4}$ 10.5 Hz) and 2.91 ($J_{2,3}$ ~ 0 Hz), respectively, which indicated that the sugar residue of **28** possesses the *gluco* configuration and that of **45** has the *gulo* configuration. The coupling involves a somewhat favored diequatorial opening of the epoxide ring with the amine, in which the 6-hydroxyl group may conceivably play a role via hydrogen bonding with the epoxide-ring oxygen in the transition state.

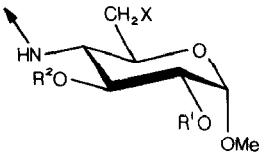
Similar coupling of **18** and **26** produced a pair of the condensates: **38** (21%) and **46** (31%), the product ratio being predicted by the Fürst–Plattner rule. The structure of **46** was confirmed by transforming it into the diacetate **47**. Likewise, coupling of **20, 21**, and **22** with **26** gave **39** (26%) and **48** (39%), **40** (28%) and **49** (47%), and **41** (37%) and **50** (47%), respectively.

Coupling **23** and **26** produced a mixture (83%) of **42** and **51**, which was conventionally *O*-methylated to the respective 3-*O*-methyl derivatives **43** (18%, based on **26** used) and **52** (44%).

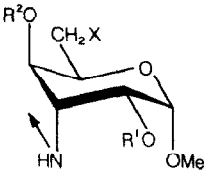
However, coupling of **24** and **26** proceeded exclusively in diaxial-opening fashion to give **53** (33%) as the sole condensate, which was characterized by conversion into the hexaacetyl methylcarboxylate **54** by conventional deblocking and acetylation. Therefore, modification of the readily accessible **27** seemed in this case the more convenient route to the *gluco* isomer.

Isopropylidenation of **27** with 2-methoxypropene in *N,N*-dimethylformamide in the presence of *p*-toluenesulfonic acid gave the tri-*O*-isopropylidene derivative **29** (62%), which was converted into the 6-tosylate **30** (86%) in the usual way. Compound



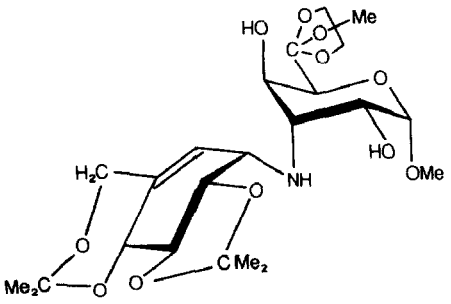


27 – 43

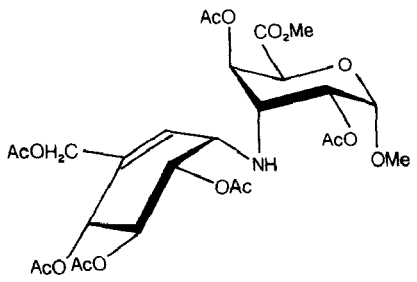


44 – 52

| | $R^1$ | $R^2$ | X |
|---|---|---|---|
| 27, 44 | H | H | OH |
| 28, 45 | Ac | Ac | OAc |
| 29 | $CMe_2$ | | OH |
| 30 | $CMe_2$ | | OTs |
| 31 | H | H | OTs |
| 32 | Ts | Ac | OTs |
| 33 | $CMe_2$ | | I |
| 34 | $CMe_2$ | | H |
| 35 | $CMe_2$ | | $N_3$ |
| 36 | $CMe_2$ | | $NH_2$ |
| 37 | $CMe_2$ | | OMe |
| 38, 46 | H | H | $N_3$ |
| 47 | Ac | Ac | $N_3$ |
| 39, 48 | Ac | Ac | OTr |
| 40, 49 | Me | H | OTr |
| 41, 50 | Me | Ac | OAc |
| 42, 51 | THP | H | OTr |
| 43, 52 | THP | Me | OTr |



53



54

**27** was treated with 2.8 molar equivalents of tosyl chloride in pyridine at 0°→room temperature to give the 6-tosylate **31** (66%) and the 2,6-ditosylate (31%), characterized as the acetate **32**. Compound **31** was readily convertible into **30** (96%). Treatment of **30** with sodium iodide in DMF at 100° gave the iodide **33** (91%), which was reduced with lithium triethylborohydride in THF to give the 6-deoxy compound **34** (55%). Similar treatment of **30** with sodium azide gave the azide **35** (92%), which was reduced with hydrogen sulfide in aqueous pyridine to give the amine **36**. *O*-Deisopropylidenation of **36** with aqueous acetic acid followed by chromatography on a column of an Amberlite CG-50 ($NH_4^+$) with aqueous ammonia as an eluent gave **4** (56%). *O*-Methylation of **29** with methyl iodide in DMF in the presence of sodium hydride gave the methyl ether **37** (85%) as a syrup.

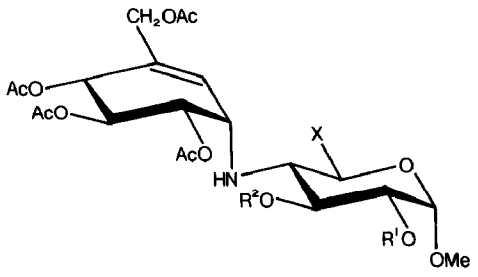
Compound **27** was selectively tritylated followed by acetylation (→**60**) and then *O*-detritylated with aqueous 80% acetic acid to give the 6-hydroxyl derivative **61** (82%), Jones' oxidation of which, followed by esterification with diazomethane, gave the methyl ester **62** (37%).

The structures of the protected carba-disaccharides **28, 34, 35, 36, 37, 40,** and **43** were further assigned and characterized by conversion into the corresponding per-O-acetyl derivatives **56, 55, 57, 58, 59, 63,** and **64**, on the basis of $^1$H-n.m.r. spectra (Table I).

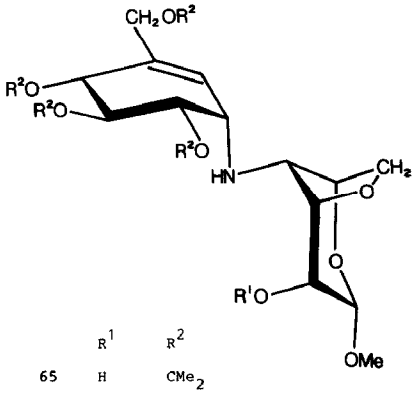
Treatment of **31** with methanolic M sodium methoxide for 3 h at 50° gave the 3,6-anhydride **65** (95%) characterized as the acetate **66**. Compound **65** was *O*-deisopropylidenated to give **10** quantitatively. Compound **10** was converted into the pentaacetate **67** and the structure was evidenced by the $^1$H-n.m.r. data (Table I).

The modified methyl acarviosins **56, 57, 58, 59, 62, 63,** and **64** thus obtained were *O*-deacetylated under Zemplén conditions and purified on a column of an Amberlite CG-50 ($NH_4^+$) resin to give the respective free bases **2, 3, 5, 6, 7, 8,** and **9**, which were directly subjected to biological assay.

*Biological-assay.* — The inhibitory activities of the nine carba-disaccharides **2–10** against yeast α-D-glucosidase were determined, methyl acarviosin (**1**) being used as a reference compound, and the data are listed in Table II. Compounds **2** and **8** possess inhibitory activity comparable with that of **1**. Apparently, introduction of polar substituents at C-6 decreases the activity. The very weak activity of **9** suggests that the 3-hydroxyl function plays a role in the enhancement of the activity. However, most interestingly, inversion ($^4C_1 \rightarrow {}^1C_4$) of the conformation of the sugar part of **2** by introduction of the 3,6-anhydro bridge into it does not seriously affect the inhibitory




| | $R^1$ | $R^2$ | X |
|---|---|---|---|
| 55 | Ac | Ac | $CH_3$ |
| 56 | Ac | Ac | $CH_2OAc$ |
| 57 | Ac | Ac | $CH_2N_3$ |
| 58 | Ac | Ac | $CH_2NHAc$ |
| 59 | Ac | Ac | $CH_2OMe$ |
| 60 | Ac | Ac | $CH_2OTr$ |
| 61 | Ac | Ac | $CH_2OH$ |
| 62 | Ac | Ac | $CO_2Me$ |
| 63 | Me | Ac | $CH_2OAc$ |
| 64 | Ac | Me | $CH_2OAc$ |




| | $R^1$ | $R^2$ |
|---|---|---|
| 65 | H | $CMe_2$ |
| 66 | Ac | Ac |

TABLE I

H-N.m.r. data (270 MHz, $CDCl_3$) for compounds **57–64** and **67**

| *Proton* | *Chemical shifts* ($\delta$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **57** | **58** | **59** | **60** | **61** | **62** | **63** | **64** | **67** |
| H-1 | 4.91d | 4.85d | 4.91d | 5.00d | 4.89d | | 4.88d | 4.85d | 4.96d |
| H-2 | 4.85dd | 4.79dd | 4.87dd | 4.92dd | 4.81dd | | 3.30dd | 4.87dd | |
| H-3 | 5.31t | 5.30t | 5.30t | 5.20t | 5.33t | 5.30t | 5.23t | 3.48t | 4.29m |
| H-4 | 2.79q | 2.62m | 2.95t | 2.96t | 2.89dd | 3.09q | 2.69t | 2.71t | 3.05m |
| H-5 | 3.65ddd | | 3.59–351 | 3.59–3.49 | 3.52dt | 4.07d | 3.65ddd | 3.62ddd | 4.31m |
| H-6 | 3.57dd | 3.61–3.41 | | | 3.80m | | 4.37dd | 4.40dd | 4.17d |
| H-6 | 3.46dd | | 3.71dd | 3.12dd | | | 3.46dd | 3.24dd | 3.92dd |
| H-1′ | 3.71t | 3.74t | 3.74t | 3.35t | 3.75t | 3.43m | 3.70dd | 3.91dd | 4.70m |
| H-2′ | 6.04d | 6.03d | 6.03d | 5.00d | 6.06d | 5.93d | 5.98d | 6.03d | |
| H-4′ | 5.62d | 5.62–5.53 | 5.64–5.60 | 5.41d | 5.61d | | 5.66–5.61 | 5.56d | 5.55m |
| H-5′ | 5.63m | | | 5.24dd | 5.61m | 5.60d | | 5.62dd | 5.61t |
| H-6′ | 4.94m | 4.93dd | 4.97m | 4.82dd | 4.96m | 5.50dd | 4.93dd | 5.08dd | |
| H-7′ | 4.68d | 4.69d | 4.71d | 4.47d | 4.67d | 4.71d | 4.64d | 4.66d | 4.96d |
| H-7′ | 4.25d | 4.40d | 4.36d | 3.99d | 4.42d | 4.37d | 4.37d | 4.36d | 4.69d |
| OMe | 3.41s | 3.37s | 3.38s | 3.40s | 3.38s | 3.41s | 3.44s | 3.50s | 3.53s |
| | | | 3.35s | | | | 3.42s | 3.37s | |
| **Ac** | 2.11 | 2.11 | 2.11 | 2.10[a] | 2.11 | 2.11 | 2.12 | 2.15 | 2.14 |
| | 2.08 | 2.07[a] | 2.07 | 2.05 | 2.069 | 2.06[a] | 2.10 | 2.09[a] | 2.08 |
| | 2.07 | 2.06 | 2.05 | 2.03 | 2.067 | 2.04 | 2.07 | 2.07 | 2.06 |
| | 2.06 | 2.03 | 2.04 | 1.99 | 2.05 | 2.02 | 2.06 | 2.05 | 2.03[a] |
| | 2.02[a] | | 2.02[a] | 1.84 | 2.023 | 2.01 | 2.05 | 2.04 | |
| | | | | | 2.02 | | 2.02 | | |

*Coupling constants (Hz)*

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $J_{1,2}$ | 3.3 | 3.3 | 3.7 | 3.7 | 3.5 | | 3.3 | 3.7 | 3.3 |
| $J_{2,3}$ | 9.9 | 9.9 | 9.9 | 10.1 | 9.9 | 10 | 9.9 | 9.9 | |
| $J_{3,4}$ | 9.9 | 9.9 | 9.9 | 10.1 | 9.9 | 10 | 9.9 | 9.9 | |
| $J_{4,5}$ | 9.9 | | 9.9 | | 10.3 | 10 | 9.9 | 9.9 | |
| $J_{5,6}$ | 2.9 | | 3.3 | 4.9 | 3.1 | | 2.2 | 4.8 | 0 |
| $J_{5,6}$ | 4.6 | | | | | | 4.8 | | 2.9 |
| $J_{6,6}$ | 13 | | 10.3 | 9.9 | | | 11.7 | | 10.6 |
| $J_{4,NH}$ | 9.9 | | | | | 10 | | | |
| $J_{1',2'}$ | 5.5 | 4.8 | 5.1 | 4.4 | 5.2 | 5.4 | 5.5 | 5.1 | 3.5 |
| $J_{4',5'}$ | 7.7 | | 7.7 | 5.9 | 7.3 | 6.8 | | 5.9 | 7.3 |
| $J_{5',6'}$ | | 9.9 | 7.7 | 9.5 | | 7.3 | 7 | 9.2 | 7.3 |
| $J_{1',6'}$ | 5.5 | 4.8 | 5.1 | 4.4 | 5.2 | | 5.1 | 4 | |
| $J_{7',7'}$ | 13.2 | 13.1 | 12.6 | 12.8 | 13.2 | 13 | 12.8 | 13.2 | 12.2 |

[a] Singlet for two methyl groups.

TABLE II

Inhibitory activity of pseudo-disaccharides **1–10** against α-D-glucosidase[a]

| *Compound* | *Final concentration (μg/mL)* | | |
|---|---|---|---|
| | *100* | *10* | |
| **1** | 88.2 | 83.7 | (0.38)[b] |
| **2** | 85.9 | 80.7 | (0.98) |
| **3** | 85.9 | 79.9 | (1.25) |
| **4** | 22.8 | 12.1 | |
| **5** | 68.0 | 29.6 | |
| **6** | 81.6 | 53.1 | |
| **7** | 90.6 | 53.7 | (8.8) |
| **8** | 89.6 | 83.3 | (0.75) |
| **9** | 52.7 | 18.1 | |
| **10** | 91.8 | 83.6 | (1.45) |

[a] Yeast α-D-glucosidase, 0.66mM *p*-nitrophenyl α-D-glucopyranoside, 100mM phosphate buffer saline, pH 6.8. [b] Inhibition (*I*%); numbers in parentheses denotes $IC_{50}$ (concentrations required to cause 50% inhibition, μg/mL) values.

activity. These results might suggest that adoption of the $^1C_4$ conformation, although a thermodynamically less-stable structure, might be important when the inhibitors interact with the enzyme, conceivably, via binding to the active site.

## EXPERIMENTAL

*General methods.* — Melting points were determined with a Mel-Temp capillary melting-point apparatus and are uncorrected. Optical rotations were measured with a Jasco DIP-4 or DIP-370 polarimeter. I.r. spectra were measured with a Jasco A-202 spectrometer. $^1$H-N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal $Me_4Si$) with Jeol JNM EX-90 (90 MHz) or Jeol JNM GSX-270 (270 MHz) instruments. T.l.c. was performed on silica gel 60 GF (E. Merck) with detection by charring with $H_2SO_4$. Column chromatography was conducted on Wakogel C-300 (300 mesh). Organic solutions were dried over anhydrous $Na_2SO_4$ and evaporated at $< 50°$ under diminished pressure.

*Methyl 2,3-di-*O*-acetyl-6-azido-6-deoxy-4-*O*-p-tolylsulfonyl-α-D-glucopyranoside* (**13**). — A mixture of methyl 2,3-di-*O*-acetyl-4,6-di-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside[7] (**12**, 0.72 g, 1.22 mmol), $NaN_3$ (160 mg, 2.46 mmol), and *N,N*-dimethylformamide (DMF) (10 mL) was heated for 7 h at 60°, and then evaporated. The residue was taken up with EtOAc (80 mL), washed with water (80 mL), dried, and evaporated. Column chromatography (23 g) of the products with 1:25 butanone–PhMe gave **13** (0.55 g, 98%) as plates, m.p. 112–113° (from EtOH); $[\alpha]_D^{25}$ +98° (*c* 1.2, $CHCl_3$); $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 7.78 and 7.35 (2 d, each 2 H, *J* 9 Hz, $MeC_6H_4$), 5.53 (dd, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 9.4 Hz, H-3), 4.95 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.82 (dd, 1 H, H-2), 4.70 (t, 1 H, $J_{4,5}$ 9.4 Hz, H-4), 3.93

(ddd, 1 H, $J_{5,6}$ 3, $J_{5,6'}$ 5.7 Hz, H-5), 3.41 (s, 3 H, OMe), 3.42 (m, 2 H, H-6), 2.45 (s, 3 H, $SO_2Me$), 2.08 and 1.90 (2 s, each 3 H, 2 Ac); $\nu_{max}$ 2110 ($N_3$), 1755 (C = O) $cm^{-1}$.

*Anal.* Calc. for $C_{18}H_{23}N_3O_9S$: C, 47.26; H, 5.07; N, 9.18. Found: C, 47.05; H, 4.92; N, 9.30.

*Methyl 3,4-anhydro-6-azido-6-deoxy-α-D-galactopyranoside* (**18**) *and its acetate* (**19**). — Compound **13** (84 mg, 0.18 mmol) was treated with methanolic M NaOMe (0.2 mL) in 1:1 $CHCl_3$–MeOH (2 mL) for 4 h at room temperature. The mixture was neutralized with AcOH and evaporated. Column chromatography (1.2 g) of the products with 1:8 butanone–PhMe gave **18** (32 g, 86%) as needles, m.p. 87–88° (from EtOH); $[\alpha]_D^{24}$ + 34° (*c* 1.2, $CHCl_3$); $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 4.69 (dd, 1 H, $J_{1,2}$ 4.9, $J_{1,3}$ 1 Hz, H-1), 4.08 (m, 1 H, H-5), 3.83 (d, 1 H, $J_{2,3}$ ~ 0 Hz, H-2), 3.50 (s, 3 H, OMe), 3.46 (m, 2 H, H-6), 3.26 (dd, 1 H, $J_{3,4}$ 4, $J_{4,5}$ 1.2 Hz, H-4), 3.16 (dd, 1 H, H-3), 2.54 (d, 1 H, $J_{2,OH}$ 10.5 Hz, OH).

*Anal.* Calc. for $C_7H_{11}N_3O_4$: C, 41.79; H, 5.51; N, 20.89. Found: C, 41.89; H, 5.34; N, 20.93.

Compound **18** (15 mg, 0.072 mmol) was treated with $Ac_2O$ (1.5 mL) in pyridine (1.5 mL) overnight at room temperature. The mixture was evaporated and the residue was eluted from a short column of silica gel with 1:6 butanone–PhMe to give **19** (17 mg, 97%) as a syrup; $[\alpha]_D^{28}$ + 63° (*c* 0.8, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 4.88 (dd, 1 H, $J_{1,2}$ 4.9, $J_{1,3}$ 0.7 Hz, H-1), 4.78 (d, 1 H, $J_{2,3}$ ~ 0 Hz, H-2), 4.13 (ddd, 1 H, $J_{4,5}$ 1.1, $J_{5,6}$ 5.1, $J_{5,6'}$ 7.7 Hz, H-5), 3.60 (dd, 1 H, $J_{6,6}$ 12.5 Hz) and 3.44 (dd, 1 H) (H-6), 3.49 (s, 3 H, Me), 3.29 (dd, 1 H, $J_{3,4}$ 4 Hz, H-4), 3.22 (dd, 1 H, H-3), 2.17 (s, 3 H, Ac).

*Anal.* Calc. for $C_9H_{13}N_3O_5$: C, 44.44; H, 5.39; N, 17.28. Found: C, 44.71; H, 4.98; N, 17.36.

*Methyl 2,3-di-O-acetyl-4-O-(methylsulfonyl)-6-O-triphenylmethyl-α-D-glucopyranoside* (**14**). — Methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside[8] (**11**, 5.86 g, 21.1 mmol) was heated in a mixture of $Ph_3CCl$ (7 g, 25.1 mmol) and 4-dimethylaminopyridine (DMAP, 0.77 g, 6.33 mmol) in pyridine (50 mL) for 14 h at 60°. The mixture was evaporated, the residue dissolved in $CHCl_3$ (100 mL), and the solution washed with water (50 mL), dried, and evaporated. The product was eluted from a column of silica gel with 1:2 butanone–PhMe containing a trace of $Et_3N$ to give the trityl ether (9.6 g) as a yellow syrup. This compound was treated with $MeSO_2Cl$ (2.87 mL, 37.1 mmol) for 3 h at room temperature. After evaporation, the residue was taken up with EtOAc (100 mL), washed with water (50 mL), dried, and evaporated. The product (10.2 g) was crystallized from EtOAc–EtOH to give **14** (9.2 g, 73%) as needles, m.p. 188–189° (dec.); $[\alpha]_D^{29}$ + 66° (*c* 1, $CHCl_3$); $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 7.54–7.18 (m, 15 H, $CPh_3$), 5.54 (dd, 1 H, $J_{3,4}$ 9.1, $J_{4,5}$ 10 Hz, H-4), 5.04 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.88 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 4.67 (dd, 1 H, H-3), 3.99 (ddd, 1 H, $J_{5,6}$ 2.8, $J_{5,6'}$ 5.4 Hz, H-5), 3.50 (s, 3 H, OMe), 3.42 (dd, 1 H, $J_{6,6}$ 10.9 Hz) and 3.25 (dd, 1 H) (H-6), 2.50 (s, 3 H, Ms), 2.08 and 2.06 (2 s, each 3 H, 2 Ac).

*Anal.* Calc. for $C_{31}H_{34}O_{10}$: C, 62.20; H, 5.72. Found: C, 62.19; H, 5.72.

*Methyl 3,4-anhydro-6-O-triphenylmethyl-α-D-galactopyranoside* (**20**). — Compound **14** (1 g, 1.67 mmol) was treated with methanolic M NaOMe (3 mL) in 1:1

$CHCl_3$–MeOH (40 mL) for 2 h at room temperature. The mixture was processed as described in the preparation of **18**, to give crude **20** (0.8 g) as a syrup; $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 7.53–7.19 (m, 15 H, $CPh_3$), 4.61 (bd, 1 H, $J_{1,2}$ 4.9 Hz, H-1), 3.98 (bt, 1 H, $J_{5,6} = J_{5,6'} = 6.9$ Hz, H-5), 3.78 (dd, 1 H, $J_{2,OH}$ 10.1 Hz, H-2), 3.44 (s, 3 H, Me), 3.41–3.18 (m, 4 H, H-3,4,6,6'), 2.46 (d, 1 H, OH).

*Methyl 3,4-anhydro-2-*O*-methyl-6-*O*-triphenylmethyl-α-*D*-galactopyranoside* (**21**). — A mixture of **20** (0.8 g), 60% NaH (115 mg, 2.88 mmol), 98% MeI (0.18 mL, 2.83 mmol), and tetrahydrofuran (20 mL) was stirred for 2 h at room temperature. To the solution was added MeOH and the mixture was evaporated and the residue was extracted with EtOAc. Column chromatography (40 g) of the products with 1:20 butanone–PhMe containing $Et_3N$ gave **21** (0.68 mg, 85%) as a syrup; $[\alpha]_D^{28}$ −4.5° (*c* 0.7, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 7.49–7.15 (m, 15 H, $CPh_3$), 4.68 (dd, 1 H, $J_{1,2}$ 4.2, $J_{1,3}$ 1.1 Hz, H-1), 4.02 (td, 1 H, $J_{4,5}$ 0.7, $J_{5,6} = J_{5,6'} = 6.6$ Hz, H-5), 3.50 and 3.43 (2s, each 3 H, 2 Me), 3.40–3.29 (m, 4 H, H-2,4,6,6'), 3.26 (dd, 1 H, $J_{2,3}$ 4.2 Hz, H-3).

*Anal.* Calc. for $C_{27}H_{28}O_5$: C, 75.00; H, 6.53. Found: C, 74.79; H, 6.24.

*Methyl 3,4-anhydro-2-*O*-methyl-α-*D*-galactopyranoside* (**22**). — Compound **21** (0.52 g, 1.21 mmol) was treated 10% Pd–C (0.5 g) under an atmospheric pressure of $H_2$ for 2 h at room temperature. The mixture was filtered, and the filtrate was evaporated. The residue was eluted from a column of silica gel (7 g) with PhMe→1:5 butanone–PhMe to give **22** (170 mg, 74%) as thin needles, m.p. 88–89° (from EtOH); $[\alpha]_D^{28}$ +64° (*c* 1.1, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 4.76 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-1), 4.07 (dd, 1 H, $J_{4,5} \sim 0$, $J_{5,6}$ 5.5, $J_{5,6'}$ 6.2 Hz, H-5), 3.89–3.85 (m, 2 H, H-6), 3.54 and 3.49 (2 s, each 3 H, 2 OMe), 3.42 (d, 1 H, $J_{2,3} \sim 0$ Hz, H-2), 3.25 (s, 2 H, $J_{3,4} \sim 0$ Hz, H-3,4), 2.11 (bt, 1 H, $J_{6,OH}$ 5.6 Hz, OH).

*Anal.* Calc. for $C_8H_{14}O_5$: C, 50.52; H, 7.42. Found: C, 50.21; H, 7.10.

*Methyl 2,3-di-*O*-acetyl-4-*O*-(methylsulfonyl)-α-*D*-glucopyranoside* (**15**). — A solution of **14** (2 g, 3.39 mmol) in aq. 80% AcOH (40 mL) was heated for 2.5 h at 70°, and evaporated. Column chromatography (40 g) of the product with PhMe→1:2 butanone–PhMe gave **15** (1.32 g, ~100%) as a syrup, $[\alpha]_D^{29}$ +120° (*c* 0.8, $CHCl_3$); $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 5.49 (t, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 4.88 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.77 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2), 4.69 (t, 1 H, H-3), 3.86–3.61 (m, 3 H, H-5,6), 3.11 (s, 3 H, OMe), 3.06 (s, 3 H, $SO_2Me$), 2.44–2.20 (m, 1 H, OH), 2.09 and 2.08 (2 s, each 3 H, 2 Ac).

*Anal.* Calc. for $C_{12}H_{20}SO_{10}\cdot H_2O$: C, 39.45; H, 5.79. Found: C, 39.41; H, 5.35.

*Cyclic ortho ester of methyl 2,3-di-*O*-acetyl-4-*O*-(methylsulfonyl)-α-*D*-glucopyranosiduronic acid with 2-hydroxymethyl-2-methyl-1,3-propanediol* (**16**). — To a solution of **15** (1.32 g, 3.70 mmol) in $Me_2CO$ (30 mL) was added dropwise Jones' reagent [a solution of chromic acid (2.67 g) and $H_2SO_4$ (2.3 mL) in water (10 mL), 4.2 mL] at 0° and then the mixture was stirred for 2.5 h at room temperature. The mixture was poured into water (100 mL) and extracted with $CHCl_3$ (100 mL), and the extract was washed with water (100 mL × 3) and evaporated to give an uronic acid (0.88 g), which was treated with 3-hydroxymethyl-3-methyloxene (1.04 g, 10.2 mmol) in the presence of *N,N*-dicyclohexylcarbodiimide (0.58 g, 2.81 mmol) and DMAP (0.34 g, 2.78 mmol) in $CH_2Cl_2$ (40 mL) for 4 h at room temperature. The mixture was filtered and the filtrate

was evaporated and the residue was extracted with EtOAc. Column chromatography (40 g, 30 g) of the products with 1:4 butanone–PhMe gave a crude uronate (417 mg, 25% based on **15**) as an amorphous powder.

This compound (330 mg, 0.73 mmol) was stirred in dichloroethane (10 mL) in the presence of $BF_3$–$Et_2O$ (22 $\mu$L, 0.18 mmol) for 30 min at room temperature. After neutralization with $Et_3N$, the mixture was evaporated. Column chromatography (21 g) of the product with 1:3 butanone–PhMe gave the ortho ester **16** (257 mg, 78% based on the crude uronate) as needles, m.p. 147° (dec.) (from EtOH); $[\alpha]_D^{28}$ +89° (*c* 1, $CHCl_3$); $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 5.56 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.9 Hz, H-4), 5.03 (t, 1 H, $J_{2,3}$ 9.9 Hz, H-3), 5.01 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.84 (dd, 1 H, H-2), 3.97 (s, 6 H, 3 C$H_2$O), 3.86 (d, 1 H, H-5), 3.43 (s, 3 H, OMe), 2.98 (s, 3 H, $SO_2$Me), 2.09 and 2.04 (2 s, each 3 H, 2 Ac), 0.84 (s, 3 H, ortho ester Me).

*Anal.* Calc. for $C_{17}H_{26}SO_{12}$: C, 44.93; H, 5.77. Found: C, 44.79; H, 5.35.

*Cyclic ortho ester of methyl 3,4-anhydro-α-*D*-galactopyranosiduronic acid with 2-hydroxymethyl-2-methyl-1,3-propanediol* (**24**) *and its acetate* (**25**). — Compound **16** (330 mg, 0.73 mmol) was treated with methanolic M NaOMe (1.2 mL) in 1:1 $CHCl_3$–MeOH (12 mL) for 6 h at room temperature and the mixture was processed as described in the preparation of **19**. Column chromatography (6.5 g) of the products with 3:2 butanone–PhMe containing $Et_3N$ gave crude **24** (171 mg, ~86%) as an amorphous powder; $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 4.84 (d, 1 H, $J_{1,2}$ 4.8 Hz, H-1), 4.00 (s, 6 H, C$H_2$O), 3.50 (s, 3 H, OMe), 3.38 (d, 1 H, $J_{3,4}$ 3.9 Hz) and 3.16 (dd, 1 H, $J_{2,3}$ 1.3 Hz) (H-3,4), 2.52 (d, 1 H, $J_{2,OH}$ 10.5 Hz, OH),0.84 (s, 3 H, ortho ester Me).

Compound **24** (20 mg) was acetylated conventionally to give **25** (16 mg, 71%) as an amorphous powder, $[\alpha]_D^{26}$ +57° (*c* 0.9, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): 5.02 (dd, 1 H, $J_{1,2}$ 4.8, $J_{1,3}$ 0.9 Hz, H-1), 4.89 (d, 1 H, $J_{2,3}$ ~0 Hz, H-2), 4.01 (s, 6 H, C$H_2$O), 3.44 (s, 3 H, OMe), 3.19 (dd, 1 H, $J_{3,4}$ 4 Hz, H-3), 2.13 (s, 3 H, Ac), 0.85 (s, 3 H, ortho ester Me).

*Anal.* Calc. for $C_{14}H_{20}O_8$: C, 53.16; H, 6.16. Found: C, 53.18; H, 6.37.

*Methyl 3,4-anhydro-2-O-tetrahydropyranyl-6-O-triphenylmethyl-α-*D*-glucopyranoside* (**23**). — Compound **20** (1.21 g) obtained from **14** (1.5 g, 2.51 mmol) was treated with 2,3-dihydro-4*H*-pyran (1 mL, 11.0 mmol) in the presence of pyridinium *p*-toluenesulfonate (0.22 g, 0.86 mmol) in $CH_2Cl_2$ (30 mL) for 5 h at room temperature. The mixture was diluted with $CH_2Cl_2$ (70 mL), washed with water (50 mL), and evaporated. Column chromatography (50 g) of the products with 1:15 EtOAc–PhMe containing $Et_3N$ gave **23** (1.15 g, 91%) as a syrup; $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 7.54–7.16 (m, 15 H, $CPh_3$), 3.44 and 3.42 (2 s, total 3 H, Me), 1.83–1.42 (m, 6 H, THP).

*Anal.* Calc. for $C_{31}H_{34}O_6$: C, 74.08; H, 6.82. Found: C, 73.79; H, 6.66.

*4′,7′:5′,6′-Di-O-isopropylidene derivative* (**27**) *of methyl 4-deoxy-4-[(1*S*)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-*D*-glucopyranoside and that* (**44**) *of methyl 3-deoxy-3-[(1*S*)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-*D*-gulopyranoside.* — A mixture of methyl 3,4-anhydro-α-D-galactopyranoside[9] (**17**, 165 mg, 0.94 mmol), (1*S*)-4,7;5,6-di-*O*-isopropylidenevalienamine[6] (**26**, 200 mg, 0.78 mmol), and 2-propanol (1 mL) was heated in a sealed

tube for 42 h at 120°, and evaporated. Column chromatography (35 g) of the products with 2:3 $Me_2CO$–PhMe gave, first, **44** (149 mg, 44% based on **26** used) as an amorphous powder; $[\alpha]_D^{23}$ + 105° (*c* 0.8, $CHCl_3$). Eluted second was **27** (149 mg, 56% based on **26** used) as an amorphous powder; $[\alpha]_D^{23}$ + 114° (*c* 1, $CHCl_3$). Compound **27** (20 mg, 0.046 mmol) was acetylated conventionally to give the triacetate **28** (25 mg, 97%) as an amorphous powder; $[\alpha]_D^{23}$ + 115° (*c* 1.3, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 5.49 (d, 1 H, $J_{1',2'}$ 4.4 Hz, H-2'), 5.38 (t, 1 H, $J_{2,3} = J_{3,4}$ = 10.5 Hz, H-3), 4.89–4.83 (m, 2 H, H-1,2), 4.47–4.41 (m, 2 H, H-4',7'), 4.42 (d, 2 H, $J_{5,6}$ 3.3 Hz, H-6), 4.14 (d, 1 H, $J_{7',7'}$ 14.3 Hz, H-7'), 3.95 (dd, 1 H, $J_{4',5'}$ 8.2 Hz, $J_{5',6'}$ 9.9 Hz, H-5'), 3.73 (dt, 1 H, $J_{4,5}$ 10.5 Hz, H-5), 3.68 (t, 1 H, $J_{1',6'}$ 4.1 Hz, H-1'), 3.50 (dd, 1 H, H-6'), 3.40 (s, 3 H, OMe), 2.99 (t, 1 H, 10.5 Hz, H-4), 2.11, 2.07, 2.06 (3 s, each 3 H, 3 Ac), 1.54, 1.44, and 1.41 (3 s, 3, 6, and 3 H, 2 $CMe_2$).

*Anal.* Calc. for $C_{26}H_{39}NO_{12}$: C, 55.99; H, 7.05; N, 2.51. Found: C, 55.96; H, 6.60; N, 2.27.

Likewise, **44** (20 mg, 0.046 mmol) was converted into **45** (24 mg, 93%) as an amorphous powder; $[\alpha]_D^{23}$ + 111° (*c* 1.2, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 5.69 (d, 1 H, $J_{1',2'}$ 3.6 Hz, H-2'), 5.30 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 4.8 Hz, H-2), 4.86 (d, 1 H, H-1), 4.77 (d, 1 H, *J* 2.6 Hz, H-4), 4.54 (d, 1 H, $J_{4',5'}$ 7.7 Hz, H-4'), 4.50–4.44 (m, 2 H, H-6,7'), 4.27–4.14 (m, 3 H, H-6,5',7'), 4.11 (dd, 1 H, $J_{5,6}$ 5.9, $J_{6,6}$ 11.4 Hz, H-6), 3.59–3.43 (m, 2 H, H-3,5), 3.38 (s, 3 H, OMe), 3.29 (t, 1 H, $J_{1',6'}$ 3.6 Hz, H-1'), 2.91 (bs, 1 H, H-3), 2.13, 2.12, and 2.09 (3 s, each 3 H, 3 Ac), 1.56, 1.49, and 1.43 (3 s, 3, 6, and 3 H, 2 $CMe_2$).

*Anal.* Found: C, 55.73; H, 6.98; N, 2.17.

*4',7':5',6'-Di-*O*-isopropylidene derivative* **38** *of methyl 6-azido-4,6-dideoxy-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-*D*-glucopyranoside and that* (**46**) *of methyl 6-azido-3,6-dideoxy-3-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-*D*-gulopyranoside.* — A mixture of **18** (0.43 g, 2.14 mmol), **26** (0.45 g, 1.76 mmol), and 2-propanol (2.5 mL) was heated in a sealed tube for 42 h at 120° and evaporated. Column chromatography (45 g) of the products with 2:3 butanone–PhMe gave, first, **46** (246 mg, 31% based on **26** used) as an amorphous powder; $[\alpha]_D^{25}$ + 77° (*c* 1.4, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 5.45 (d, 1 H, $J_{1',2'}$ 3.7 Hz, H-2'), 4.72 (d, 1 H, $J_{1,2}$ 2.9 Hz, H-1), 4.19 (d, 1 H, $J_{7',7'}$ 13.9 Hz, H-7'), 4.05 (ddd, 1 H, $J_{4,5}$ 1.1, $J_{5,6}$ 4.8, $J_{5,6'}$ 7.3 Hz, H-5), 3.90 (dd, 1 H, $J_{4',5'}$ 8.2, $J_{5',6'}$ 9.3 Hz, H-5'), 3.75 (bs, 1 H, H-1'), 3.59 (dd, 1 H, $J_{6,6}$ 12.8 Hz) and 3.37 (dd, 1 H) (H-6), 3.46 (s, 3 H, OMe), 3.18 (t, 1 H, $J_{2,3} = J_{3,4}$ = 3.8 Hz, H-3), 1.57, 1.52, 1.48 and 1.46 (4 s, each 3 H, 2 $CMe_2$).

Compound **46** (246 mg) was acetylated conventionally to give **47** (234 mg, 82%) as plates; m.p. 111–112° (from EtOH); $[\alpha]_D^{23}$ + 95° (*c* 1.1, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 5.66 (d, 1 H, $J_{1',2'}$ 2.9 Hz, H-2'), 5.03 (dd, 1 H, $J_{1,2}$ 3.9, $J_{2,3}$ 4.8 Hz, H-2), 4.88 (d, 1 H, H-1), 4.71 (d, 1 H, $J_{3,4}$ 2.9 Hz, H-4), 4.54 (d, 1 H, $J_{4',5'}$ 8.1 Hz, H-4'), 4.47 (d, 1 H, $J_{7',7'}$ 14.3 Hz, H-7'), 4.41 (dd, 1 H, $J_{1',6'}$ 2.6, $J_{5',6'}$ 9.2 Hz, H-6'), 4.24 (d, 1 H, H-7'), 4.22–4.16 (m, 1 H, H-5'), 3.59–3.53 (m, 2 H, H-3,5), 3.48 (dd, 1 H, $J_{5,6}$ 9, $J_{6,6}$ 12.8 Hz, H-6), 3.42 (s, 3 H, OMe), 3.30–3.28 (m, 1 H, H-1'), 3.15 (dd, 1 H, $J_{5,6}$ 3.7 Hz, H-6), 2.94 (s, 1 H, NH), 2.14 and 2.13 (2 s, each 3 H, 2 Ac), 1.56, 1.49, 1.48, and 1.44 (4 s, each 3 H, 2 $CMe_2$).

Eluted second was **38** (166 mg, 21% based on **26** used), isolated as an amorphous powder; $[\alpha]_D^{22}$ + 143° (*c* 1.2, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 5.52 (d, 1 H, $J_{1',2'}$ 4.8

Hz, H-2'), 4.79 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.17 (d, 1 H, $J_{7',7'}$ 13.9 Hz, H-7'), 3.83 (dd, 1 H, $J_{4',5'}$ 8.1, $J_{5',6'}$ 9.9 Hz, H-5'), 3.75 (t, 1 H, $J_{1',6'}$ 4.8 Hz, H-1'), 3.45 (s, 3 H, OMe), 2.62 (t, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 1.56, 1.53, 1.49, and 1.42 (4 s, each 3 H, 2 $CMe_2$).

Compound **38** was isopropylidenated as described in the preparation of **29** to give **35**.

*4',7':5',6'-Di-*O*-isopropylidene derivative* **39** *of methyl 2,3-di-*O*-acetyl-4-deoxy-4-[(1*S*)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-6-*O*-triphenylmethyl-α-*D*-glucopyranoside and that* (**48**) *of methyl 2,4-di-*O*-acetyl-3-deoxy-3-[(1*S*)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-6-*O*-triphenylmethyl-α-*D*-gulopyranoside.* — A mixture of **20** (0.59 g, 1.41 mmol), **26** (300 mg, 1.17 mmol), and 2-propanol (2 mL) was heated in a sealed tube for 41 h at 120° and then evaporated. Column chromatography (46 g) of the products with 1:2 butanone-PhMe containing $Et_3N$ gave two fractions ($R_F$ = 0.48 and 0.31, 2:3 butanone–PhMe). The compound (394 mg) obtained from the first fraction was acetylated conventionally to give **48** (349 mg, 39% based on **26** used) as an amorphous powder; $[\alpha]_D^{31}$ + 76° (*c* 1, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): δ 7.45–7.23 (m, 15 H, $CPh_3$), 5.68 (m, 1 H, H-2'), 4.97 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 4.8 Hz, H-2), 4.80 (d, 1 H, H-1), 4.53 (d, 1 H, $J_{4',5'}$ 8.1 H, H-4'), 4.44 (dd, 1 H, $J_{7',7'}$ 13.9, *J* 0.9 Hz) and 4.20 (d, 1 H) (H-7'), 3.38 (dd, 1 H, $J_{5,6}$ 6.6, $J_{6,6}$ 9.9 Hz) and 3.13 (dd, 1 H, $J_{5,6}$ 6.6 Hz) (H-6), 3.35 (s, 3 H, OMe), 3.23 (bt, 1 H, $J_{1',2'} = J_{1',6'}$ = 3.5 Hz, H-1'), 2.79 (m, 1 H, H-3), 2.10 and 1.96 (2 s, each 3 H, 2 Ac), 1.55, 1.49, and 1.34 (3 s, 3, 3, and 6 H, 2 $CMe_2$).

*Anal.* Calc. for $C_{43}H_{51}NO_{11}$: C, 68.15; H, 6.67; N, 1.85. Found: C, 68.10; H, 6.67; N, 1.77.

Acetylation of the product (245 mg) obtained from the second fraction gave **39** (230 mg, 26% based on **26** used) as needles, m.p. 203–204.5° (from EtOH); $[\alpha]_D^{31}$ + 110° (*c* 1, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): δ 7.51–7.23 (m, 15 H, $CPh_3$), 5.30 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.9 Hz, H-3), 5.20 (d, 1 H, $J_{1',2'}$ 3.6 Hz, H-2'), 4.96 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.90 (dd, 1 H, H-2), 4.34 (d, 1 H, $J_{4',5'}$ 8.1 Hz, H-4'), 4.21 (dd, 1 H, $J_{7',7'}$ 14.3, *J* 0.9 Hz) and 3.74 (d, 1 H) (H-7'), 3.65 (dd, 1 H, $J_{5',6'}$ 9.9 Hz, H-5'), 3.59 (bdd, 1 H, $J_{1',6'}$ 1.8 Hz, H-1'), 3.55 (dd, 1 H, H-6'), 3.45 (s, 3 H, OMe), 3.38 (dd, 1 H, $J_{5,6}$ 4.8, $J_{6,6}$ 9.9 Hz) and 3.22 (dd, 1 H, $J_{5,6}$ 5.3 Hz) (H-6), 3.08 (t, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 2.08 and 2.03 (2 s, each 3 H, 2 Ac), 1.50, 1.38, 1.34, and 1.25 (4 s, each 3 H, 2 $CMe_2$).

*Anal.* Found: C, 67.84; H, 6.94; N, 1.86.

*4',7':5',6'-Di-*O*-isopropylidene derivative* (**40**) *of methyl-4-deoxy-4-[(1*S*)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-2-*O*-methyl-6-*O*-triphenylmethyl-α-*D*-glucopyranoside and that* (**49**) *of methyl 3-deoxy-3-[(1*S*)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-2-*O*-methyl-6-*O*-triphenylmethyl-α-*D*-gulopyranoside.* — A mixture of **21** (407 mg, 0.94 mmol), **26** (200 mg, 0.78 mmol), and 2-propanol (1.5 mL) was heated in a sealed tube for 69 h at 120° and then evaporated. Column chromatography (24 g) of the products with 1:4 butanone-PhMe containing $Et_3N$ gave, first, **49** (250 mg, 47% based on **26** used), as an amorphous powder; $[\alpha]_D^{28}$ + 89° (*c* 2.8, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): δ 7.49–7.24 (m, 15 H, $CPh_3$), 5.49 (d, 1 H, $J_{1',2'}$ 4.4 Hz, H-2'), 4.89 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.51 (d, 1 H, $J_{4',5'}$ 8.1

Hz, H-4'), 4.43 (dd, 1 H, *J* 1.1, $J_{7',7'}$ 13.9 Hz) and 4.12 (d, 1 H) (H-7'), 4.16 (dd, 1 H, $J_{5',6'}$ 9.9 Hz, H-5'), 3.79 (dd, 1 H, $J_{2,3}$ 4.2 Hz, H-2), 3.73 (t, 1 H, $J_{3,4} = J_{4,OH} = 3.3$ Hz, H-4), 3.68 (dd, 1 H, $J_{4,5} \sim 0$, $J_{5,6}$ 4.4, $J_{5,6}$ 4.8 Hz, H-5), 3.54 (dd, 1 H, $J_{1',6'}$ 4.8 Hz, H-6'), 3.49 (dd, 1 H, $J_{6,6}$ 10.3 Hz) and 3.35 (dd, 1 H) (H-6), 3.44 and 3.39 (2 s, each 3 H, 2 OMe), 3.30 (dd, 1 H, H-1'), 3.19 (d, 1 H, OH), 2.75 (br s, 1 H, H-3) 1.54, 1.46, 1.45, and 1.37 (4 s, each 3 H, 2 $CMe_2$).

*Anal.* Calc. for $C_{40}H_{49}NO_9$: C, 69.85; H, 7.13; N, 2.04. Found: C 69.56; H, 7.03; N, 2.02.

Eluted second was **40** (153 mg, 28% based on **26** used), isolated as an amorphous powder; $[\alpha]_D^{28}$ + 63° (*c* 1.9, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 7.50–7.26 (m, 15 H, $Ph_3C$), 4.99 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.75 (s, 1 H, $J_{1',2'} \sim 0$ Hz, H-2'), 4.25 and 4.80 (2 d, each 1 H, $J_{7',7'}$ 13.9 Hz, H-7'), 3.59 and 3.46 (2 s, each 3 H, 2 OMe), 2.78 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.9 Hz, H-4), 1.515, 1.51, 1.45, and 1.37 (4 s, each 3 H, 2 $CMe_2$).

*Anal.* Found: C 69.72; H, 7.08; N, 2.03.

*4',7':5',6'-Di-*O*-isopropylidene derivative* (**41**) *of methyl 3,6-di-*O*-acetyl-4-deoxy-4-[(1*S*)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-2-*O*-methyl-α-*D*-glucopyranoside and that* (**50**) *of methyl 4,6-di-*O*-acetyl-3-deoxy-3-[1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-2-*O*-methyl-α-*D*-gulopyranoside.* — A mixture of **22** (134 mg, 0.71 mmol), **26** (150 mg, 0.59 mmol), and 2-propanol (1 mL) was heated in a sealed tube for 43 h at 120° and then evaporated. The products were acetylated conventionally, and column chromatography (17 g) of the products with 1:5 $Me_2CO$–PhMe gave, first, crude **50** (153 mg), which was eluted from a column of silica gel (7.5 g) with 1:6 $Me_2CO$–PhMe to give **50** (153 mg, 47% based on **26** used), as thin needles, m.p. 142–143° (from EtOH); $[\alpha]_D^{29}$ + 143.8° (*c* 1, $CHCl_3$); $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 5.82–5.69 (m, 1 H, H-2'), 4.86–4.75 (m, 2 H, H-1,4), 3.40 (s, 6 H, 2 OMe), 2.86–2.73 (m, 1 H, H-3), 2.11 and 2.08 (2 s, each 3 H, 2 Ac), 1.56, 1.45, and 1.40 (3 s, 3, 6, and 3 H, 2 $CMe_2$).

*Anal.* Calc. for $C_{25}H_{39}NO_{11}$: C, 56.70; H, 7.42; N, 2.64. Found: C, 56.58; H, 7.12; N, 2.68.

Eluted second was **41** (115 mg, 37% based on **26** used) as an amorphous powder; $[\alpha]_D^{29}$ + 143° (*c* 1, $CHCl_3$); $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 5.50 (d, 1 H, $J_{1',2'}$ 4.5 Hz, H-2'), 5.33 (t, 1 H, $J_{2,3} = J_{3,4}$ = 10 Hz, H-3), 4.89 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.14 (d, 1 H, $J_{7',7'}$ 11.5 Hz, H-7'), 3.97 (t, 1 H, $J_{4',5'} = J_{5',6'}$ = 8 Hz, H-5'), 3.42 (s, 6 H, 2 OMe), 2.87 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 2.10 (s, 6 H, 2 Ac), 1.52 and 1.42 (2 s, 3 and 9 H, 2 $CMe_2$).

*Anal.* Found: C, 56.33; H, 7.15; N, 2.69.

*4',7':5',6'-Di-*O*-isopropylidene derivative* (**42**) *of methyl 4-deoxy-4-[(1*S*)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-2-*O*-tetrahydropyranyl-6-*O*-triphenylmethyl-α-*D*-glucopyranoside and that* (**51**) *of methyl 3-deoxy-3-[(1*S*)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-2-*O*-tetrahydropyranyl-6-*O*-triphenylmethyl-α-*D*-gulopyranoside.* — A mixture of **23** (472 mg, 0.94 mmol), **26** (200 mg, 0.78 mmol), and 2-propanol (1.5 mL) was heated in a sealed tube for 41 h at 120° and then evaporated. Column chromatography (21 g) of the products with 1:5 butanone–PhMe containing of triethylamine gave a mixture of **42** and **51** (492 mg, 83% based on **26** used), as an amorphous powder.

*4′,7′:5′,6′-Di-O-isopropylidene derivative* (**43**) *of methyl 4-deoxy-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-3-O-methyl-2-O-tetrahydropyranyl-6-O-triphenylmethyl-α-D-glucopyranoside and that* (**52**) *of methyl 3-deoxy-3-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-4-O-methyl-2-O-tetrahydropyranyl-6-O-triphenylmethyl-α-D-gulopyranoside.* — A mixture of compounds **42** and **51** (492 mg, 0.65 mmol) was stirred with MeI (0.38 mL, 6.13 mmol) in the presence of 60% sodium hydride (118 mg, 2.83 mmol) in DMF (10 mL) for 19 h at room temperature. The mixture was evaporated and the residue was extracted with $CHCl_3$ (50 mL), and the extract was washed with water (50 mL), and then evaporated. Column chromatography (26 g) of the products with 1:10 butanone-PhMe containing $Et_3N$ gave, first, **52** (301 mg, 44% based on **26** used) as an amorphous powder; $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 7.49–7.21 (m, 15 H, $CPh_3$), 5.58 (d, $J_{1',2'}$ 4.8 Hz) and 5.52 (d, $J_{1',2'}$ 4.4 Hz) (total 1 H, H-2′), 3.40, 3.38, and 3.32 (3 s, total 6 H, 2 OMe), 2.94 and 2.85 (2 bs, total 1 H, H-3), 1.56, 1.51, 1.50, 1.496, 1.48, 1.38, and 1.37 (7 s, total 12 H, 2 $CMe_2$).

*Anal.* Calc. for $C_{45}H_{57}NO_{10}$: C, 70.02; H, 7.44; N, 1.81. Found: C, 69.88; H, 7.31; N, 1.74.

Eluted second was **43** (108 mg, 16% based on **26** used), isolated as an amorphous powder; $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 7.51–7.26 (m, 15 H, $Ph_3C$), 5.26–5.22 (m, 1 H, H-2′), 4.96 (d, $J_{1,2}$ 3.3 Hz) and 4.94 (d, $J_{1,2}$ 3.7 Hz) (total 1 H, H-1), 3.65 and 3.46 (2s, each 3 H, 2 OMe), 2.91 (t, $J_{3,4} = J_{4,5} = 9.7$ Hz) and 2.89 (t, $J_{3,4} = J_{4,5} = 9.2$ Hz) (total 1 H, H-4), 1.50, 1.43, 1.33, and 1.30 (4 s, each 3 H, 2 $CMe_2$).

*Anal.* Found: C, 69.91; H, 7.28; N, 1.75.

*4′,7′:5′,6′-Di-O-isopropylidene derivative* (**53**) *of cyclic ortho ester of methyl 3-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-D-gulopyranosiduronic acid with 2-hydroxymethyl-2-methyl-1,3-propanediol.* — A mixture of **24** (129 mg, 0.47 mmol), **26** (100 mg, 0.39 mmol), and 2-propanol (1 mL) was heated in a sealed tube for 89 h at 120° and then evaporated. Column chromatography (10 g) of the products with 1:5 $Me_2CO$–PhMe containing a trace of $Et_3N$ gave **53** (69 mg, 33% based on **26** used), as a syrup; $[\alpha]_D^{27}$ + 164° (*c* 1.5, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 5.46 (d, 1 H, $J_{1',2'}$ 4.7 Hz, H-1′), 4.78 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1) 4.46 and 4.18 (2 d, each 1 H, $J_{7',7'}$ 13.9 Hz, H-7′), 4.44 (d, 1 H, $J_{4',5'}$ 7 Hz, H-4′), 4.00 (s, 6 H, $CH_2O$), 3.53 (t, 1 H, $J_{1',6'}$ 4.7 Hz, H-1′), 3.42 (s, 3 H, OMe), 3.17 (bs, 1 H, H-3), 1.56, 1.49, 1.46, and 1.44 (4 s, each 3 H, 2 $CMe_2$), 0.85 (s, 3 H, *ortho* ester Me).

*Anal.* Calc. for $C_{25}H_{39}NO_{11}$: C, 56.70; H, 7.42; N, 2.64. Found: C, 56.46; H, 7.03; N, 2.67.

*Methyl {methyl 2,3,4′,5′,6′,7′-hexa-O-acetyl-3-deoxy-3-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-D-gulopyranosid}uronate* (**54**). — Compound **53** (64 mg, 0.12 mmol) was heated in aq. 80% AcOH (3 mL) for 2 h at 60° and then the mixture was evaporated to give a syrup (52 mg), which was treated with methanolic M NaOMe (0.2 mL) in MeOH (2 mL) at room temperature for 6 h. After neutralization with AcOH, the mixture was filtered and the filtrate was evaporated to give a syrup, which was acetylated conventionally. Column chromatography (3.5 g) of the products with 1:4 butanone–PhMe gave **54** (39 mg, 52%) as an amorphous powder;

$[\alpha]_D^{27}$ +87° (*c* 1.5, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 6.02 (d, 1 H, $J_{1',2'}$ 4.8 Hz, H-2'), 5.60 (d, 1 H, $J_{4',5'}$ 6.6 Hz, H-4'), 5.55 (dd, 1 H, $J_{5',6'}$ 8.9 Hz, H-5'), 5.09–5.04 (m, 3 H, H-1,2,6'), 4.89 (bd, 1 H, $J_{3,4}$ 3.3 Hz, H-4), 4.87 (bd 1 H, $J_{4,5}$ 1.5 Hz, H-5), 4.72 and 4.73 (2 d, each 1 H, $J_{7',7'}$ 13 Hz, H-7'), 3.79 (s, 3 H, COOMe), 3.71 (m, 1 H, H-1'), 3.46 (s, 3 H, OMe), 3.26 (m, 1 H, H-1), 2.78 (bdd, 1 H, *J* 4.4 and 5.1 Hz, NH), 2.09, 2.08, 2.07, 2.068, and 2.05 (5s, 3, 3, 3, 6, and 3 H, 6 Ac).

*Anal.* Calc. for $C_{27}H_{37}NO_{16}$: C, 51.35; H, 5.90; N, 2.22. Found: C, 51.15; H, 5.59; N, 2.18.

*2,3:4',7':5',6'-Tri*-O-*isopropylidene derivative* **29** *of methyl 4-deoxy-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-*D*-glucopyranoside.* — Compound **27** (0.33 g, 0.77 mmol) was treated with 2-methoxypropene (0.37 mL, 3.7 mmol) in the presence of TsOH·$H_2O$ (30 mg, 0.16 mmol) in DMF (3 mL) for 18 h at room temperature. The mixture was neutralized with $NaHCO_3$, diluted with $CHCl_3$, filtered, and the filtrate was evaporated to give a residue (0.39 g), which was stirred in MeOH (3 mL) containing AcOH (0.5 mL) for 2 h at room temperature. The solution was evaporated and column chromatography (18 g) of the residue with 1:4 $Me_2CO$–PhMe gave **29** (0.25 g, 62%) as a syrup; $[\alpha]_D^{30}$ +185° (*c* 1.7, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 5.70 (d, 1 H, $J_{1',2'}$ 4.4 Hz, H-2'), 5.03 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.53 (d, 1 H, $J_{4',5'}$ 8.1, H-4'), 4.45 and 4.21 (2 d, 1 H, $J_{7',7'}$ 13.9 Hz, H-7'), 4.05 (t, 1 H, $J_{1',6'}$ 4.4 Hz, H-1'), 4.03 (dd, 1 H, $J_{5',6'}$ 9.8 Hz, H-5'), 3.91 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.7 Hz, H-3), 3.89–3.81 (m, 2 H, H-6), 3.60 (dd, 1 H, H-6'), 3.48 (dd, 1 H, H-2), 3.45 (s, 3 H, OMe), 3.45–3.39 (m, 1 H, H-5), 3.07 (t, 1 H, $J_{4,5}$ 9.7 Hz, H-4), 1.56, 1.47, 1.46, 1.44, and 1.42 (5 s, 3, 3, 6, 3, and 3 H, 3 $CMe_2$).

*Anal.* Calc. for $C_{23}H_{37}NO_9$: C, 58.58; H, 7.91; N, 2.97. Found: C, 58.43; H, 7.68; N, 2.93.

*2,3:4',7':5',6'-Tri*-O-*isopropylidene derivative* **30** *of methyl 4-deoxy-6-*O-*p-tolylsulfonyl-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]-amino-α-*D*-glucopyranoside.* — To a solution of **29** (29 mg, 0.061 mmol) in pyridine (1 mL) was added *p*-toluenesulfonyl chloride (35 mg, 0.18 mmol) at 0°, and the mixture was stirred for 18 h at room temperature and then evaporated. The residue was extracted with $CHCl_3$. Column chromatography (2 g) of the products with butanone-PhMe gave **30** (33 mg, 86%) as a syrup; $[\alpha]_D^{30}$ +146° (*c* 1, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 7.81 and 7.35 (2 d, each 2 H, *J* 8.1 Hz, $MeC_6H_4$), 5.61 (d, 1 H, $J_{1',2'}$ 4 Hz, H-2'), 4.97 (d, 1 H, $J_{1,2}$ 2.9 Hz, H-1), 4.51 (d, 1 H, $J_{4',5'}$ 8.1 Hz, H-4'), 4.47 (d, 1 H, $J_{7',7'}$ 13.9 Hz, H-7'), 4.42 (dd, 1 H, $J_{5,6}$ 1.8, $J_{6,6}$ 10.3 Hz) and 4.25 (dd, 1 H, $J_{5,6'}$ 5.7 Hz) (H-6), 4.23 (d, 1 H, H-7'), 3.99 (dd, 1 H, $J_{5',6'}$ 9.9 Hz, H-5'), 3.98 (dd, 1 H, $J_{1',6'}$ 4.8 Hz, H-1'), 3.83 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.9 Hz, H-3), 3.54 (dd, 1 H, H-6'), 3.48 (ddd, 1 H, $J_{4,5}$ 9.9 Hz, H-5), 3.42 (dd, 1 H, H-2), 3.40 (s, 3 H, OMe), 2.98 (t, 1 H, H-4), 2.44 (S, 3 H, Ts), 1.57, 1.47, 1.43, 1.40, and 1.38 (5 s, 3, 6, 3, 3, and 3 H, 3 $CMe_2$).

*Anal.* Calc. for $C_{30}H_{43}NO_{11}S$: C, 57.58; H, 6.93; N, 2.24. Found: C, 57.54; H, 6.71; N, 2.11.

*4',7':5',6'-Di*-O-*isopropylidene derivative* **31** *of methyl 4-deoxy-6-*O-*p-tolylsulfonyl-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]-*

*amino-α-*D*-glucopyranoside and that* (**32**) *of methyl 3-*O*-acetyl-4-deoxy-2,6-di-*O*-p-tolylsulfonyl-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-*D*-glucopyranoside.* — Compound **27** (50 mg, 0.12 mmol) was stirred with *p*-toluenesulfonyl chloride (15 mg, 0.17 mmol) in pyridine (1 mL) for 40 min at 0°, and further treated with an additional chloride (15 mg) for 7 h at room temperature. The mixture was processed as described in the preparation of **30**, and column chromatography (4 g) of the products with 1:2 $Me_2CO$–PhMe gave, first, the 2,6-ditosylate ($R_F$ 0.85, 1:1 $Me_2CO$-PhMe, 26 mg, 31%) as a syrup. This compound was characterized as the acetate **32**; $[\alpha]_D^{27}$ + 101° (*c* 0.5, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 7.80, 7.77, and 7.36 (3 d, 2, 2, and 4 H, *J* 8.4 Hz, 2 Ts), 5.45 (d, 1 H, $J_{1',2'}$ 4.8 Hz, H-2'), 5.33 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.9 Hz, H-3), 4.65 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.46 (dd, 1 H, $J_{5,6}$ 1.8, $J_{6,6}$ 10.6 Hz, H-6), 4.44–4.38 (m, 2 H, H-4',7'), 4.35 (dd, 1 H, H-2), 4.26 (dd, 1 H, $J_{5,6'}$ 1.8 Hz, H-6), 4.17 (d, 1 H, $J_{7',7'}$ 14.3 Hz, H-7'), 3.80 (dd, 1 H, $J_{4',5'}$ 8.1, $J_{5',6'}$ 9.9 Hz, H-5'), 3.62–3.55 (m, 2 H, H-5,1'), 3.44 (dd, 1 H, $J_{1',6'}$ 4.8 Hz, H-6'), 3.27 (s, 3 H, OMe), 2.85 (dt, 1 H, $J_{4,5}$ 9.9, $J_{4,NH}$ 7.3 Hz, H-4), 2.45 (s, 6 H, 2 Ts), 1.88 (s, 3 H, Ac), 1.54, 1.43, 1.40, and 1.33 (4 s, each 3 H, 2 $CMe_2$).

*Anal.* Calc. for $C_{36}H_{47}NO_{13}S_2$: C, 55.30; H, 6.06; N, 1.79. Found: C, 55.03; H, 5.80; N, 1.90.

Eluted second was **31** (45 mg, 66%), isolated as a syrup.

Compound **31** (181 mg, 0.31 mmol) was treated with 2-methoxypropene (0.15 mL, 1.5 mmol) in the presence of $TsOH \cdot H_2O$ (6 mg, 0.064 mmol) in DMF (3 mL) for 17 h at room temperature, giving, after the usual work-up, **30** (185 mg, 96%) as a syrup.

*2,3:4',7':5',6'-Tri-*O*-isopropylidene derivative* **33** *of methyl 4,6-dideoxy-6-iodo-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-*D*-glucopyranoside.* — Compound **30** (27 mg, 0.044 mmol) was heated with NaI (33 mg, 0.22 mmol) in DMF (3 mL) for 1 h at 100° and then the mixture was evaporated. Column chromatography (2 g) of the products with 1:12 butanone–PhMe gave **33** (23 mg, 91%) as a syrup; $[\alpha]_D^{30}$ + 158° (*c* 1.4, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 5.69 (d, 1 H, $J_{1',2'}$ 4.4 Hz, H-2'), 5.07 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.53 (d, 1 H, $J_{4',5'}$ 8.1 Hz, H-4'), 4.48 (dd, 1 H, $J_{7',7'}$ 13.9, *J* 1.5 Hz) and 4.29 (d, 1 H) (H-7'), 4.11 (dd, 1 H, $J_{5',6'}$ 9.9 Hz, H-5'), 4.02 (t, 1 H, $J_{1',6'}$ 4.4 Hz, H-1'), 3.92 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H-3), 3.68 (dd, 1 H, $J_{5,6}$ 2.6, $J_{6,6}$ 10.3 Hz, H-6), 3.58 (dd, 1 H, H-6'), 3.56–3.48 (m, 2 H, H-2,6), 3.49 (s, 3 H, OMe), 3.16 (ddd, 1 H, $J_{4,5}$ 9.5, $J_{5,6'}$ 6.1 Hz, H-5), 2.91 (t, 1 H, 9.5 Hz, H-4), 1.56, 1.48, 1.47, 1.45, 1.44 and 1.43 (6 s, each 3 H, 3 $CMe_2$).

*Anal.* Calc. for $C_{23}H_{36}INO_8$: C, 47.51; H, 6.24; N, 2.41. Found. C, 47.24; H, 6.00; N, 2.26.

*2,3:4',7':5',6'-Tri-*O*-isopropylidene derivative* **34** *of methyl 4,6-dideoxy-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-*D*-glucopyranoside.* — To a solution of **33** (25 mg, 0.042 mmol) in tetrahydrofuran (1 mL) was added M $LiEt_3BH$–tetrahydrofuran solution (0.6 mL, 0.6 mmol) at 0° and then the mixture was stirred for 1 h at 0°. The reaction was quenched by adding MeOH (1 mL) and 35% $H_2O_2$ (1 mL), and the mixture was diluted with $CHCl_3$ (20 mL), washed with water (15 mL × 2), and evaporated. Column chromatography (1 g) of the products with

1:8 butanone–PhMe gave **34** (39 mg, 55%) as a syrup; $[\alpha]_D^{30}$ +108° (*c* 0.9 $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 5.68 (d, 1 H, $J_{1',2'}$ 4.6 Hz, H-2'), 4.98 (d, 1 H, $J_{1,2}$ 2.9 Hz, H-1), 4.53 (d, 1 H, $J_{4',5'}$ 8.4 Hz, H-4'), 4.49 and 4.19 (2 d, each 1 H, $J_{7',7'}$ 13.4 Hz, H-7'), 4.14 (dd, 1 H, $J_{4',5'}$ 8.4 Hz, H-5'), 4.04 (t, 1 H, $J_{1',6'}$ 4.6 Hz, H-1'), 3.85 (t, 1 H, $J_{2,3}$ 9.5 = $J_{3,4}$ = 9.9 Hz, H-3), 3.60 (dd, 1 H, $J_{5',6'}$ 9.9 Hz, H-6'), 3.50 (dd, 1 H, H-2), 3.43 (s, 3H , OMe), 3.43 (dt, 1 H, $J_{4,5}$ 9.5, $J_{5,6}$ 6.2 Hz, H-5), 2.78 (t, 1 H, H-4), 1.57, 1.47, 1.46, 1.44, and 1.41 (5 s, 3, 3, 3, 6, and 3 H, 3 $CMe_2$), 1.34 (d, 3 H, H-6).

*Anal.* Calc. for $C_{23}H_{37}NO_8$: C, 60.64; H, 8.19; N, 3.07. Found: C, 60.52; H, 7.78; N, 2.99.

*2,3:4',7':5',6'-Tri-O-isopropylidene derivative* **35** *of methyl 6-azido-4,6-dideoxy-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-D-gluco-pyranoside.* — Compound **30** (67 mg, 0.11 mmol) was heated with $NaN_3$ (34 mg, 0.54 mmol) in DMF (1 mL) for 1 h at 100° and then the mixture was evaporated. Column chromatography (3 g) of the products with 1:12 butanone–PhMe gave **35** (49 mg, 92%) as a syrup; $[\alpha]_D^{25}$ +160° (*c* 1.7, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 5.64 (d, 1 H, $J_{1',2'}$ 4.4 Hz, H-2'), 5.07 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.52 (d, 1 H, $J_{4',5'}$ 8.2 Hz, H-4'), 4.48 (dd, 1 H, $J_{7',7'}$ 14.3, *J* 1.5 Hz) and 4.20 (d, 1 H) (H-7'), 4.00 (t, 1 H, $J_{1',6'}$ 4.4 Hz, H-1'), 3.86 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H-3), 3.64 (d, 1 H, $J_{6,6}$ 11 Hz, H-6), 3.58 (dd, 1 H, $J_{1',6'}$ 4.4, $J_{5',6'}$ 9.7 Hz, H-6'), 3.52 (d, 1 H, H-6), 3.50 (dd, 1 H, H-2), 3.48 (S, 3 H, OMe), 3.48–3.45 (m, 1 H, H-5), 2.98 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 1.56, 1.47, 1.45, 1.43, and 1.426 (5 s, 3, 3, 6, 3, and 3 H, 3 $CMe_2$).

*Anal.* Calc. for $C_{23}H_{36}N_4O_8$: C, 55.63; H, 7.31; N, 11.28. Found. C, 55.72; H, 7.50; N, 10.99.

*Methyl 6-amino-4,6-dideoxy-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxyme-thyl-2-cyclohexenyl]amino-α-D-glucopyranoside* (**4**) *and its 2,3:4',7':5',6'-tri-O-isopropylidene derivative* **36**. — Compound **35** (23 mg, 0.045 mmol) was stirred for 26 h at room temperature in 1:1 pyridine–water (2 mL) saturated with $H_2S$. The mixture was evaporated and the products were eluted from a column of silica gel (3 g) with PhMe→1:5 EtOH–PhMe to give crude **36** (17 mg) as a syrup.

Compound **36** (17 mg) was treated with aq. 70% AcOH (1 mL) for 2 h at 60°. The product was purified by a column of Amberlite CG-50 ($NH_4^+$) resin (2.5 mL) with 0.5→1.5% $NH_4OH$ as an eluent to give **4** (9 mg, 56%) as prisms, m.p. 173–177° (from EtOH); $[\alpha]_D^{27}$ +171° (*c* 0.3, MeOH).

*2,3:4',7':5',6'-Tri-O-isopropylidene derivative* **37** *of methyl 4-deoxy-6-O-methyl-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-D-gluco-pyranoside.* — A mixture of **29** (17 mg, 0.036 mmol), 98% $CH_3I$ (5 μL × 2, total 0.16 mmol), 60% sodium hydride (3 mg × 2, total 0.15 mmol), and DMF (1 mL) was stirred for 6 h at room temperature and then evaporated. Column chromatography (1 g) of the residue with 1:5 $Me_2CO$–PhMe gave **37** (15 mg, 85%) as a syrup; $[\alpha]_D^{25}$ +156° (*c* 0.7, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 5.69 (d 1 H, $J_{1',2'}$ 4.4 Hz, H-2'), 5.07 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.54 (d, 1 H, $J_{4',5'}$ 8.1 Hz, H-4'), 4.49 and 4.18 (2 d, each 1 H, $J_{7',7'}$ 15.4 Hz, H-7'), 4.16 (dd, 1 H, $J_{5',6'}$ 9.9 Hz, H-5'), 4.03 (t, 1 H, $J_{1',2'}$ 4.4 Hz, H-1'), 3.86 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.9 Hz, H-3), 3.77–3.66 (m, 2 H, H-6), 3.59 (dd, 1 H, H-6'), 3.53 (dd, 1 H, $J_{2,3}$ 9.5

Hz, H-2), 3.45 and 3.40 (2 s, each 3 H, 2 OMe), 3.43–3.36 (m, 1 H, H-5), 3.14 (t, 1 H, $J_{3,4} = J_{4,5} = 9.5$ Hz, H-4), 1.57, 1.47, 1.46, 1.45, and 1.41 (5 s, 3, 3, 3, 3 and 6 H, 3 $CMe_2$).

*Anal.* Calc. for $C_{24}H_{39}NO_9$: C, 59.36; H, 8.10; N, 2.88. Found. C, 59.34; H, 7.71; N, 2.86.

*Methyl 4,6-dideoxy-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexyl]amino-α-D-glucopyranoside* (**1**) *and its hexaacetate* (**55**). — Compound **34** (51 mg, 0.11 mmol) was heated in aq. 70% AcOH (1 mL) for 2 h at 60° and the mixture was evaporated. The residue was eluted from a column of Amberlite IRA-400 ($OH^-$) resin (5 mL) with MeOH and the product was crystallized from EtOH to give **1** (20 mg, 53%) as plates; m.p. 154–157°, [lit.[4], 157° (from MeOH–EtOAc); 225° (dec.) (from $Me_2CO$)]; $[\alpha]_D^{27}$ + 173° (*c* 0.2, MeOH), [lit.[4], $[\alpha]_D^{20}$ + 160° (*c* 0.5, $H_2O$); $[\alpha]_D^{20}$ + 97° (*c* 0.5, EtOH)].

The $^1$H-n.m.r. spectral data (270 MHz, $CDCl_3$) and optical rotation (in $CHCl_3$) of the hexaacetyl derivative **55** of **1** accorded with those reported for an authentic sample.

*Methyl 4-deoxy-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-D-glucopyranoside* (**2**) *and its heptaacetate* (**56**). — Compound **27** (100 mg, 0.18 mmol) was heated in aq. 70% AcOH (1 mL) for 2 h at 60° and the mixture was evaporated to give a residue (84 mg), which was acetylated conventionally. Column chromatography (5 g) of the products with 1:4 butanone–PhMe gave **56** (109 mg, 93%) as an amorphous powder. The $^1$H-n.m.r. spectral data (270 MHz, $CDCl_3$) and optical rotation (in $CDCl_3$) accorded with those reported for an authentic sample[10].

Compound **56** (123 mg, 0.19 mmol) was treated with methanolic M NaOMe (0.2 mL) in MeOH (2 mL) for 1 h at room temperature. The solution was neutralized with Amberlite IRA-120B (H + ) resin and then the mixture was filtered and the filtrate was evaporated to give **2** (61 mg, 89%) as a plates; m.p. 185–187° (from EtOH); $[\alpha]_D^{27}$ + 147° (*c* 0.3, MeOH); [lit.[10], m.p. 185–186° (from EtOH); $[\alpha]_D^{18}$ + 188° (*c* 0.9, $H_2O$).]

*Methyl 6-azido-4,6-dideoxy-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-D-glucopyranoside* (**3**) and its hexaacetate (**57**). — Compound **35** (33 mg, 0.065 mmol) was *O*-deisopropylidenated and acetylated, as described in the preparation of **55**. Column chromatography (1 g) of the products with 1:3 butanone–PhMe gave **57** (39 mg, 94%) as an amorphous powder; $[\alpha]_D^{25}$ + 147° (*c* 1.3, $CHCl_3$).

*Anal.* Calc. for $C_{26}H_{36}N_4O_{14}$: C, 49.68; H, 5.77; N, 8.91. Found: C, 49.21; H, 5.66; N, 8.78.

Compound **57** (85 mg, 0.14 mmol) was *O*-deacetylated with methanolic NaOMe to give **3** (40 mg, 78%) as plates, m.p. 170–173° (from EtOH), $[\alpha]_D^{27}$ + 137° (*c* 0.3, MeOH).

*Methyl 6-acetamido-4,6-dideoxy-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-D-glucopyranoside* (**5**) *and its hexaacetate* (**58**). — Compound **4** (9 mg, 0.026 mmol) was acetylated and then column chromatography (1 g) of the product with 1:10 EtOH–PhMe gave **58** (14 mg, 80%) as a syrup; $[\alpha]_D^{27}$ + 79° (*c* 1.7, $CHCl_3$).

*Anal.* Calc. for $C_{28}H_{40}N_2O_{15}$: C, 52.17; H, 6.25; N, 4.35. Found: C, 52.09; H, 6.25; N, 4.16.

Compound **58** (85 mg, 0.14 mmol) was *O*-deacetylated with methanolic NaOMe to give **5** (56 mg, 92%) as plates; m.p. 203–205° (from EtOH); $[\alpha]_D^{27}$ +143° (*c* 0.3, MeOH).

*Methyl 4-deoxy-6-*O*-methyl-4-[(1*S*)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-*α*-*D*-glucopyranoside* (**6**) *and its hexaacetate* (**59**). — Compound **37** (66 mg, 0.15 mmol) was *O*-deisopropylidenated, as described in the preparation of **1** to give **6** (47 mg, 99%) as plates; m.p. 174–176° (from EtOH); $[\alpha]_D^{27}$ +194° (*c* 0.2, MeOH).

Compound **6** (10 mg, 0.027 mmol) was acetylated conventionally and then column chromatography (1 g) of the product with 1:3 butanone–PhMe gave **59** (15 mg, 89%) as a syrup; $[\alpha]_D^{25}$ +104° (*c* 0.6, $CHCl_3$).

*Anal.* Calc. for $C_{27}H_{39}NO_{15}$: C, 52.51; H, 6.36; N, 2.27. Found: C, 52.53; H, 6.31; N, 2.22.

*Methyl 2,3-di-*O*-acetyl-4-deoxy-4-[(1*S*)-(1,4,6/5)-4,5,6-triacetoxy-3-acetoxymethyl-2-cyclohexenyl]amino-6-*O*-triphenylmethyl-α-D-glucopyranoside* (**60**). — A mixture of **27** (91 mg, 0.21 mmol), $Ph_3CCl$ (145 mg, 0.52 mmol), DMAP (5 mg, 0.41 mmol), and pyridine (2 mL) was heated for 19 h at 60° and then evaporated. After acetylation, the product was eluted from a column of a silica gel (7 g) with 1:7 butanone–PhMe to give the trityl ether (93 mg, 58%) as needles, m.p. 203–204.5° (from EtOH); $[\alpha]_D^{31}$ +110° (*c* 1, $CHCl_3$).

*Anal.* Calc. for $C_{43}H_{51}NO_{11}$: C, 67.84; H, 6.94; N, 1.86. Found: C, 68.15; H, 6.67; 1.85.

This compound (139 mg, 0.18 mmol) was stirred with $TsOH \cdot H_2O$ (10 mg, 0.053 mmol) in MeOH for 18 h at room temperature. The mixture was neutralized with $NaHCO_3$ and evaporated, and the residue was acetylated. Column chromatography (8 g) of the products with 1:5 butanone–PhMe gave **60** (103 mg, 66%) as a syrup; $[\alpha]_D^{24}$ +72° (*c* 0.4, $CHCl_3$).

*Anal.* Calc. for $C_{45}H_{51}NO_{15}$: C, 63.90; H, 6.08; N, 1.66. Found: C, 64.15; H, 5.84; N, 1.84.

*Methyl 2,3-di-*O*-acetyl-4-deoxy-4-[(1*S*)-(1,4,6/5)-4,5,6-triacetoxy-3-acetoxymethyl-2-cyclohexenyl]amino-α-D-glucopyranoside* (**61**). — Compound **60** (91 mg, 0.11 mmol) was heated in aq. 80% AcOH (2 mL) at 60° for 2 h and then the mixture was evaporated. Column chromatography (3 g) of the product with 1:3 $Me_2CO$–PhMe gave **61** (53 mg, 82%) as a syrup; $[\alpha]_D^{25}$ +130° (*c* 0.5, $CHCl_3$).

*Anal.* Calc. for $C_{26}H_{37}NO_{15}$: C, 51.74; H, 6.18; N, 2.32. Found: C, 51.82; H, 6.07; N, 2.33.

*Methyl {methyl 2,3-di-*O*-acetyl-4-deoxy-4-[(1*S*)-(1,4,6/5)-4,5,6-triacetoxy-3-acetoxymethyl-2-cyclohexenyl]amino-α-D-glucopyranosid}uronate* (**62**). — To a solution of compound **61** (87 mg, 0.15 mmol) in $Me_2CO$ (4 mL) was added 8M Jones' reagent (0.08 mL × 3) at 0–5° and the mixture was stirred for 58 h. After treatment with 2-propanol, the mixture was evaporated to give a residue, which was taken up with water (20 mL) and extracted with dimethylether (30 mL × 3). The extract was evaporated and the product (66 mg) was treated with diazomethane in ether (2 mL) and then column

chromatography (3.5 g) of the product with 1:5 $Me_2CO$–PhMe gave **62** (34 mg, 37%) as a syrup; $[\alpha]_D^{25}$ + 107° (*c* 1.7, $CHCl_3$).

*Anal.* Calc. for: C, 51.35; H, 5.91; N, 2.22. Found: C, 51.57; H, 5.57; N, 2.30.

*Methyl {methyl 4-deoxy-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-6-O-triphenylmethyl-α-D-glucopyranosid}uronate* (**7**). — Compound 62 (19 mg, 0.029 mmol) was *O*-deacetylated with methanolic M NaOMe to give **7** (10 mg, 91%) as an amorphous powder; $[\alpha]_D^{25}$ + 137° (*c* 0.3, MeOH).

*Methyl 4-deoxy-2-O-methyl-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-D-glucopyranoside* (**8**) *and its hexaacetate* (**63**). — Compound **40** (108 mg, 0.065 mmol) was *O*-deisopropylidenated and acetylated, as described in the preparation of **56**. Column chromatography (4.5 g) of the products with 1:3 butanone–PhMe gave **63** (84 mg, 87%) as an amorphous powder; $[\alpha]_D^{32}$ + 146° (*c* 1, $CHCl_3$).

*Anal.* Calc. for $C_{27}H_{39}NO_{15}$: C, 52.51; H, 6.36; N, 2.27. Found: C, 52.24; H, 5.97; N, 2.31.

Likewise, compound **41** (110 mg, 0.21 mmol) was converted into **63** (101 mg, 78%).

Compound **63** (50 mg, 0.081 mmol) was *O*-deacetylated conventionally to give **8** (29 mg, ~ 100%) as an amorphous powder; $[\alpha]_D^{29}$ + 139° (*c* 1, MeOH).

*Methyl 4-deoxy-3-O-methyl-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-D-glucopyranoside* (**9**) *and its hexaacetate* (**64**). — Compound **41** (55 mg, 0.077 mmol) was *O*-deisopropylidenated and acetylated, as described in the preparation of **55**. Column chromatography (1.5 g) of the products with 1:3 butanone–PhMe gave **64** (29 mg, 65%) as an amorphous powder; $[\alpha]_D^{32}$ + 111° (*c* 1, $CHCl_3$).

*Anal.* Calc. for $C_{27}H_{39}NO_{15}$: C, 52.51; H, 6.36; N, 2.27. Found: C, 52.79; H, 6.30; N, 2.32.

Compound **64** (27 mg, 0.043 mmol) was *O*-deacetylated conventionally to give **9** (16 mg, ~ 100%) as an amorphous powder; $[\alpha]_D^{29}$ + 133° (*c* 1, MeOH).

*4',7':5',6'-Di-O-isopropylidene derivative* **65** *of methyl 4-deoxy-3,6-anhydro-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-D-glucopyranoside.* — Compound **31** (62 mg, 0.11 mmol) was treated with methanolic M NaOMe (0.2 mL) in MeOH (2 mL) for 3 h at 50°. The mixture was made neutral with AcOH, insoluble material was filtered off, and the filtrate was evaporated. Column chromatography (6 g) of the products with 2:5 acetone–toluene gave **65** (45 mg, 98%) as an amorphous powder; $[\alpha]_D^{22}$ + 70° (*c* 1.1, $CHCl_3$).

Compound **65** (22 mg, 0.053 mmol) was acetylated conventionally to give the acetate of **66** (21 mg, 90%) as an amorphous powder; $[\alpha]_D^{21}$ + 66° (*c* 1, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): $\delta$ 5.61 (dd, 1 H, $J_{1',2'}$ 5.1, $J_{2',7'}$ 1.5 Hz, H-2'), 5.00–4.97 (m, 1 H, H-2), 4.97 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.53 (d, 1 H, $J_{4',5'}$ 8.4 Hz, H-4'), 4.48 (dd, 1 H, $J_{7',7'}$ 13.9 Hz, H-7'), 4.40 (t, 1 H, $J_{2,3} = J_{3,4}$ = 4.4 Hz, H-3), 4.35 (t, 1 H, $J_{4,5}$ 2.6 Hz, H-5), 4.22 (dd, 1 H, $J_{5',6'}$ 9.9 Hz, H-5'), 4.17 (d, 1 H, $J_{5,6}$ ~ 0, $J_{6,6}$ 10.6 Hz) and 3.93 (dd, 1 H, $J_{5,6}$ 2.6 Hz) (H-6), 4.16 (d, 1 H, H-7'), 3.68–3.63 (m, 1 H, H-1'), 3.54 (dd, 1 H, $J_{1',6'}$ 4 Hz, H-1'), 3.54 (s, 3 H,

OMe), 3.38–3.28 (m, 1 H, H-4), 2.14 (s, 3 H, Ac), 1.56, 1.46, 1.54, and 1.40 (4 s, each 3 H, 4 Me).

*Anal.* Calc. for $C_{22}H_{33}NO_9$: C, 58.01; H, 7.30; N, 3.08. Found: C, 58.26; H, 7.31; N, 3.28.

*Methyl 4-deoxy-3,6-anhydro-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl]amino-α-D-glucopyranoside* **67** *and its pentaacetate* **10**. — Compound **65** (34 mg, 0.081 mmol) was heated in aq. 70% AcOH (2 mL) for 1.5 h at 60°. The mixture was evaporated and the residue obtained was eluted from a column of an Amberlite IRA-400 ($OH^-$) resin (3 mL) to give **10** (27 mg, ~ 100%) as an amorphous powder; $[\alpha]_D^{22}$ + 78° (*c* 1.1, MeOH).

Compound **10** (21 mg, 0.063 mmol) was acetylated conventionally to give **67** (30 mg, 78%) as an amorphous powder; $[\alpha]_D^{22}$ + 59° (*c* 1.3, $CHCl_3$).

*Anal.* Calc. for $C_{24}H_{33}NO_{13}$: C, 53.03; H, 6.12; N, 2.58. Found: C, 53.34; H, 6.04; N, 2.59.

ACKNOWLEDGMENTS

We sincerely thank Mr. H. Arita for elemental analyses, Drs. S. Inouye and T. Machinami (Meiji Seika Kaisha, Yokohama) for bioassay, and Mr. C. Ogawa for preparation of the manuscript. The work was supported, in part, by a grant from the Asahi Glass Foundation for the contribution to industrial technology.

REFERENCES

1 S. Ogawa, C. Uchida, and Y. Shibata, *Carbohydr. Res.*, in press.
2 Y. Shibata, Y. Kosuge, and S. Ogawa, *Carbohydr. Res.*, 199 (1990) 37–54.
3 S. Omoto, J. Itoh, H. Ogino, K. Iwamatsu, N. Nishizawa, and S. Inouye, *J. Antibiot.*, 34 (1981) 1429–1433.
4 B. Yunge, F. R. Heiker, J. Jurz, L. Müller, D. D. Schmidt, and C. Wunsche, *Carbohydr. Res.*, 128 (1984) 235–268.
5 D. D. Schmidt, W. Frommer, B. Junge, L. Müller, W. Wingender, E. Truscheit, and D. Schafer, *Naturwissenschaften*, 64 (1977) 535–536.
6 Y. Shibata and S. Ogawa, *Carbohydr. Res.*, 189 (1989) 309–322.
7 D. M. C. Hull, P. F. Orchard, and L. N. Owen, *Carbohydr. Res.*, 57 (1977) 51–63.
8 R. L. Whistler and S. J. Kazenisc, *J. Am. Chem. Soc.*, 76 (1954) 3044–3046.
9 J. G. Buchanan, *J. Chem. Soc.*, (1958) 2511–2517; S. Ogawa, Y. Iwasawa, T. Toyokuni, and T. Suami, *Carbohydr. Res.*, 141 (1985) 29–40.
10 S. Ogawa, Y. Iwasawa, T. Toyokuni, and T. Suami, *Carbohydr. Res.*, 141 (1985) 29–40.