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Synthesis and biological activities of methyl oligobiosaminide and some deoxy isomers thereof*

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ABSTRACT

Methyl oligobiosaminide (**1**) the core structure of oligostatin C, and five analogues, the 6-hydroxy- (**2**), 2-deoxy- (**3**), 2-deoxy-6-hydroxy- (**4**), 3-deoxy- (**5**), and 3-deoxy-6-hydroxy derivatives (**6**), were synthesized by coupling the protected pseudo-sugar epoxide **46** with suitable methyl 4-amino-4-deoxy-α-D-hexopyranoside derivatives. Compounds **3** and **6** showed notable inhibitory activity against α-D-glucosidase and α-D-mannosidase, respectively, whereas compound **1** had almost no activity.

INTRODUCTION

The antibiotic oligostatin, isolated[2] from the fermentation broth of *Streptomyces myxogenes* nov. sp. SF-1130, is one of a homologous series of pseudo-oligosaccharidic α-D-glucosidase inhibitors[3] containing common structural units composed of 4-amino-4-deoxy-D-glucopyranose and a branched-chain cyclitol. Methanolysis of oligostatin C produced[4] methyl acarviosin instead of the core structure, methyl oligobiosaminide (**1**). It was of interest to prepare **1** and related compounds to study their biological properties. The first synthesis of the hepta-*O*-acetyl derivative of **1** was reported[5] by one of us before, but, biological assay of the free form has not yet been performed. In this paper, we describe synthesis of **1** and five related pseudo-disaccharides **2**–**6**, and their inhibitory activity against three hydrolases.

RESULTS AND DISCUSSION

Synthesis of methyl 4-amino-2,4-dideoxy- and -2,4,6-trideoxy-α-D-arabino-hexopyranoside. — Methyl 3,4-*O*-isopropylidene-α-D-galactopyranoside[6] (**7**) was treated with 1.5 mol. equiv. of chlorotriphenylmethane and 4-dimethylaminopyridine in pyridine at 60° to give a 90% yield of the 6-*O*-trityl derivative[7] (**8**), the 2-OH group of which was removed via a thiocarbonate[8] to give the deoxy compound **11** (88%). The ^{1}H-n.m.r. spectrum of **11** contained a signal due to H-1 as a doublet of doublets at δ 4.83 with 5-

*Synthesis of Pseudo-oligosaccharide Glycosidase Inhibitors, Part VII. For Part VI, see ref. 1.
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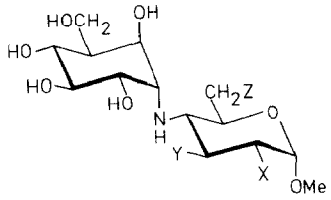
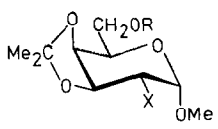


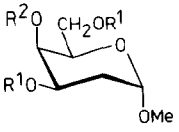
	X	Y	Z
1	OH	OH	H
2	OH	OH	OH
3	H	OH	H
4	H	OH	OH
5	OH	H	H
6	OH	H	OH

and 6.3-Hz spacings, in accord with the expected distorted half-chair coformation. Deprotection of **11** with aqueous acetic acid gave the triol (**12**), which, without isolation, was further treated with 2.5 mol. equiv. of benzoyl chloride in pyridine at ambient temperature to give selectively the 3,6-dibenzoate **13** in quantitative yield. The structure of **13** was confirmed by the ^{1}H-n.m.r. signal of H-3 (δ 5.47, $J_{3,2a}$ 12.5, $J_{3,2e}$ 5.1 Hz). Compound **13** was mesylated and the mesylate **14** treated with sodium azide in *N*,*N*-dimethylformamide at 120° to give the azide **15** (74%), the ^{1}H-n.m.r. spectrum of which showed a doublet of doublets (δ 3.72, J 9.1, 10.1 Hz) attributable to the axial H-4. Zemplén deacetylation of **15** with methanolic sodium methoxide afforded the diol **16**, the 6-OH group of which was selectively chlorinated with sulfuryl chloride in pyridine, and the crude chloride **17** was hydrogenolyzed with Raney nickel in ethanol containing potassium hydroxide to give the amine **18** in 33% overall yield. Compound **18** was characterized as the di-*N*,*O*-acetyl derivative **19**, whose ^{1}H-n.m.r. spectrum contained a three-proton doublet (δ 1.24, J 6.2 Hz) due to 5-methyl group. Similar hydrogenolysis of **16** gave the amine **20** in 97% yield. The ^{1}H-n.m.r. spectrum of the tri-*N*,*O*-acetyl derivative (**21**) of **20** fully established the assigned structure.

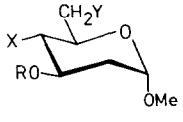
Synthesis of methyl 4-amino-3,4-dideoxy- and 3,4,6-trideoxy-α-D-ribo-*hexopyranoside*. — Compound **8** was benzylated to the benzyl ether **9**, which was hydrolyzed with aqueous acetic acid to give the triol **22**. Compound **22** was treated with an excess of *p*-toluenesulfonyl chloride in pyridine followed by acetylation to give the ditosylate **24** in 89% overall yield from **8**. Direct benzylation of **7** gave the dibenzyl ether **10**, *O*-deisopropylidenation of which gave a diol that was selectively tosylated and acetylated to the monotosylate **25** in 80% yield. Removal of the tosyloxy function at C-3 of **24** was carried out by reduction with sodium borohydride[9] in 2-propanol at reflux temperature to afford a complex mixture of products from which the acetate **26** was isolated in 47% yield. In contrast, similar reaction of **25** with sodium borohydride proceeded smoothly to give the acetate **28** (63%) and the 4-epimer **30** (7%), together with a 31% yield of methyl 3-acetoxymethyl-2,5-di-*O*-benzyl-3-deoxy-*α*-D-xylofuranoside (**38**) formed by ring contraction. Hydrogenolysis of **38** with Pd–C and successive acetylation gave the triacetate **39** (71%). The structures of **38** and **39** were assigned on the basis of ^{1}H-n.m.r. spectral data, in comparison with data for related compounds[9].



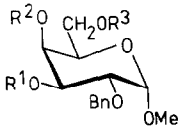
	R	X
7	H	OH
8	Tr	OH
9	Tr	OBn
10	Bn	OBn
11	Tr	H



	R^1	R^2
12	H	H
13	Bz	H
14	Bz	Ms



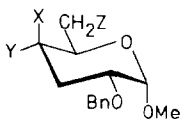
	R	X	Y
15	Bz	N_3	OBz
16	H	N_3	OH
17	H	N_3	Cl
18	H	NH_2	H
19	Ac	NHAc	H
20	H	NH_2	OH
21	Ac	NHAc	OAc



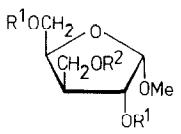
	R^1	R^2	R^3
22	H	H	H
23	H	H	Bn
24	Ts	Ac	Ts
25	Ts	Ac	Bn

Compound **26** was *O*-deacetylated and the resultant alcohol **27** was treated with sulfuryl chloride in pyridine to give 55% yield of the chloride **32**, which was treated with sodium azide in *N*,*N*-dimethylformamide at 100° to give the azide **33** in 40%, together with 33% of an elimination product, the 4-enopyranoside **40**. The structure of **33** was supported by the ^{1}H-n.m.r. spectrum, which contained a doublet of doublets of doublets (δ 2.97, J 4.4, 9.7, and 12.1 Hz) due to H-4. The ^{1}H-n.m.r. spectrum of **40** contained one and two-proton narrow multiplets at δ 4.51 and 2.19, attributable to H-4 and H-3,3, respectively. Alternatively, the alcohol **29** obtained from **28** was first converted into the mesylate **34** (96%), and the product was treated with sodium benzoate in *N*,*N*-dimethylformamide to give the benzoate **35** (70%). Chlorination of **29** with sulfuryl chloride resulted in elimination to give only the 4-enopyranoside **41**. Another alcohol (**31**), obtained from **30** or **35**, was mesylated and conventional treatment of the product (**36**) with azide ion gave the azide **37** (59%). Hydrogenolysis of **33** with Pd–C gave the amine **42** (66%), which was characterized as the di-*N*,*O*-acetyl derivative **43**. The ^{1}H-n.m.r. spectrum of **43** contained two well-resolved signals (δ 4.58, J 3.7, 4.8, and 11.7 Hz) and δ 3.91, J 4.4, 10.3, and 11.7 Hz) due to H-2 and H-4, respectively. Similarly, **37** was converted into the amine **44** in 86% yield. The ^{1}H-n.m.r. spectrum of the tri-*N*,*O*-acetyl derivative **45**, also supported the structure assigned.

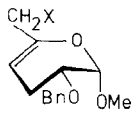
Synthesis of pseudo-disaccharides. — Coupling of (1*R*, 2*S*, 5*R*, 7*R*, 8*R*, 9*R*, 10*R*)-8,9-dibenzyloxy-5-phenyl-4,6,11-trioxatricyclo[8.1.0.$0^{2,7}$]undecane[10] (**46**) with a slight excess of methyl 4-amino-4,6-dideoxy-α-D-glucopyranoside[11] (**47**) was performed in 2-propanol in a sealed tube for 92 h at 120° to afford a mixture of the protected pseudo-disaccharides, which was successively hydrogenolyzed in the presence of 10% Pd–C in ethanol followed by acetylation, giving, after fractionation on a column of silica gel, the hepta-*O*-acetyl derivatives **49** (34%) and **55** (11%), which were identified by comparison with authentic samples[5], on the basis of the ^{1}H-n.m.r. spectral data (Table I), and from their optical rotations.



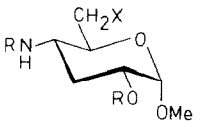
	X	Y	Z
26	H	OAc	H
27	H	OH	H
28	H	OAc	OBn
29	H	OH	OBn
30	OAc	H	OBn
31	OH	H	OBn
32	Cl	H	H
33	H	N_3	H
34	H	OMs	OBn
35	OBz	H	OBn
36	OMs	H	OBn
37	H	N_3	OBn



	R^1	R^2
38	Bn	Ac
39	Ac	Ac



40 X = H
41 X = OBn



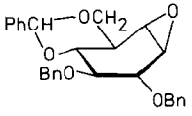
	R	X
42	H	H
43	Ac	H
44	H	OH
45	Ac	OAc

Likewise, coupling of **46** and methyl 4-amino-4-deoxy-α-D-glucopyranoside[11] (**48**), and successive hydrogenolysis and acetylation afforded the pseudo-disaccharide octaacetates **50** and **56** in 43 and 9% isolated yields. They were similarly identified by comparison with authentic samples[5].

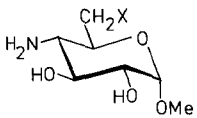
Condensation of the protected amino sugars **18**, **20**, **42**, **44** with **46** was performed under the conditions already described to give, after conventional processing, the corresponding totally *O*-acetylated pseudo-disaccharides **51**, **52**, **53**, and **54** in 44–57% yields, along with the minor products **57**, **58**, **59**, and **60** in 5–10% yields. The structures of new pseudo-disaccharides were established mainly by comparison of the ^{1}H-n.m.r. spectral data (Table I) with the parent compounds **49**, **50**, **55**, and **56**.

Compounds **49**–**54** were *O*-deacetylated with methanolic sodium methoxide followed by purification over a column of Dowex 50W-X2 (H^+) resin to afford the respective free pseudo-disaccharides **1**–**6**, in quantitative yields. These were directly assayed for inhibitory activity against three hydrolydases.

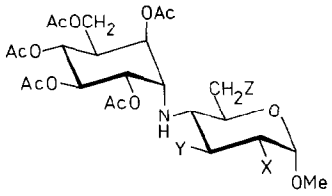
Biological assay. — The inhibitory activities of the six pseudo-disaccharides **1**–**6** against α- and β-D-glucosidases, and α-D-mannosidase, were determined, nojirimycin **B** (ref. 12) being used as a reference compound, and the data are listed in Table II. Interestingly methyl oligobiosaminide (**1**), the core structure of oligostatin, has almost no inhibitory activity, whereas compounds **3** and **6** possess appreciable activity against α-D-glucosidase and α-D-mannosidase, respectively. The structure–inhibitory activity relationship of these pseudo-disaccharides will be discussed in our forthcoming paper[13], where they will be compared with the results for acarviosin analogues.



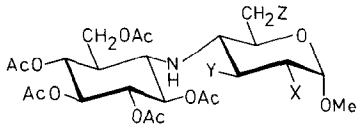
46



47 X = H
48 X = OH



49 - 54



55 - 60

	X	Y	Z
49,55	OAc	OAc	H
50,56	OAc	OAc	OAc
51,57	H	OAc	H
52,58	H	OAc	OAc
53,59	OAc	H	H
54,60	OAc	H	OAc

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 polarimeter. ^{1}H-N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) or D_2O (internal acetone) 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 (Merck) with detection by charring with H_2SO_4. Column chromatography was conducted on Wakogel C-200 (200 mesh) or C-300 (300 mesh). Organic solutions were dried over anhydrous Na_2SO_4 and evaporated at $< 50°$ under diminished pressure.

*Methyl 3,4-*O*-isopropylidene-6-*O*-triphenylmethyl-α-*D*-galactopyranoside* (**8**). — Methyl 3,4-*O*-isopropylidene-α-D-galactopyranoside[6] (**7**, 1.0 g, 4.28 mmol) was heated with Ph_3CCl (1.8 g, 6.46 mmol) and 4-dimethylaminopyridine (0.12 g, 1.06 mmol) in pyridine (20 mL) for 14 h at 60°. The mixture was evaporated, and the residue was diluted with $CHCl_3$ (100 mL), washed with water (50 mL), dried and then evaporated. Column chromatography (C-200, 60 g) of the residue (2.82 g) with 1:5 butanone–PhMe gave **8** (1.48 g, 90.4%) as an amorphous powder; $[\alpha]_D^{24}$ +42° (*c* 0.9, $CHCl_3$); [lit.[7] $[\alpha]_D^{23}$ + 52° (*c* 1, $CHCl_3$)]; ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.80–7.15 (m, 15 H, Tr), 4.37 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 3.45 (s, 3 H, OMe), 2.34 (d, 1 H, $J_{2,OH}$ 6.5 Hz, O*H*), 1.45 and 1.32 (2 s, each 3 H, CMe_2).

Anal. Calc. for $C_{29}H_{32}O_6 \cdot 0.5H_2O$: C, 71.73; H, 6.85. Found: C, 71.16; H, 6.53.

*Methyl 2-deoxy-3,4-*O*-isopropylidene-6-*O*-triphenylmethyl-α-*D*-lyxo-hexopyranoside* (**11**). — Compound **8** (0.86 g, 1.80 mmol) was stirred with imidazole (2.0 mg, 0.029 mmol) and 60% NaH (0.81 g, 13.5 mmol) in tetrahydrofuran (10 mL) for 30 min

TABLE I

^{1}H-N.m.r. data (270 MHz, $CDCl_3$) of compounds **49**–**54**

Proton	*Chemical shifts (δ)*					
	49	**50**	**51**	**52**	**53**	**54**
H-1	4.83d	4.84d	4.73dd	4.79d	4.76d	4.81d
H-2	4.79dd	4.80dd			4.78ddd	4.79ddd
H-2a						
H-2e						
H-3	5.29t	5.34t	5.07ddd	5.10ddd		
H-3a					1.43q	1.48q
H-3e						
H-4	2.59q	2.97q	2.46q	2.81q	2.33m	2.70m
H-5	3.62dq	3.71ddd	3.59dq	3.20ddd	3.49dq	3.61ddd
H-6		4.51dd		4.47dd		4.39dd
H-6		4.26dd		4.31dd		4.32dd
CH_3	1.34d		1.34d		1.34d	
H-1	3.48dd	3.46dd	3.60dd	3.59dd	3.27dd	3.24dd
H-2	5.16dd	5.18dd	5.19dd	5.24dd	5.22dd	5.22dd
H-3	5.33dd	5.26dd	5.34dd	5.30dd	5.33dd	5.29dd
H-4	5.15dd	5.20dd	5.16dd	5.23dd	5.19dd	5.21dd
H-5	2.76dddd	2.57dddd	2.80dddd	2.61dddd	2.81dddd	2.69dddd
H-6	5.21bt	5.25bt	5.23bt	5.24bt	5.16bt	5.13dd
H-7	4.08dd	4.20dd	4.08dd	4.20dd	4.08dd	4.18dd
H-7	4.00dd	3.91dd	3.99dd	3.92dd	3.99dd	3.92dd
OMe	3.39	3.40	3.33	3.34	3.43	3.34
Ac	2.14	2.15	2.15	2.15	2.14	2.133
	2.07	2.13	2.04	2.14	2.07	2.128
	2.04	2.08	2.03[a]	2.04[a]	2.04[a]	2.08
	2.038	2.04	1.99	2.03	2.03	2.05
	2.03	2.035	1.95	1.99	2.00	2.04
	1.99	2.02		1.96		2.035
	1.94	1.99				2.00
		1.95				

[a] Singlet for two methyl groups.

at 0°. To this solution was added CS_2 (0.23 mL, 3.69 mmol) and then the mixture was stirred for 1 h at the same temperature. After treatment with MeI (0.23 mL, 3.69 mmol), the mixture was poured into ice–water (30 mL), extracted with EtOAc (60 mL), dried, and then evaporated to give a syrup (1.1 g), which was heated at reflux with Bu_3SnH (1 mL, 3.72 mmol) in PhMe (15 mL) under Ar for 2.5 h. Column chromatography (C-200, 26 g) of the product with 1:5 EtOAc–hexane gave **11** (0.73 g, 88%) as plates; m.p. 159–160° (from EtOH), $[\alpha]_D^{30}$ +5.2° (*c* 0.7, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.83–7.02 (m, 15 H, Tr), 4.83 (dd, 1 H, $J_{1,2}$ 5, $J_{1,2'}$ 6.3 Hz, H-1), 4.43 (ddd, 1 H, $J_{2,3}$ 5, $J_{2',3}$ 4, $J_{3,4}$ 7 Hz, H-3), 4.11 (dd, 1 H, $J_{4,5}$ 2 Hz, H-4), 3.83 (td, 1 H, $J_{5,6}$ 6.3 Hz, H-5), 3.40 (s, 3 H, OMe), 2.19 (dt, 1 H, $J_{2,2'}$ 9.7 Hz, H-2), 1.66 (ddd, 1 H, H-2'), 1.43 and 1.30 (2 s, each 3 H, CMe_2).

Anal. Calc. for $C_{29}H_{32}O_5$: C, 75.62; H, 7.00. Found: C, 75.94; H, 6.94.

Coupling constants (Hz)

	49	50	51	52	53	54
$J_{1,2}$	3.7	3.7			3.7	3.7
$J_{1,2a}$			2.6	2.2		
$J_{1,2e}$			~0	~0		
$J_{2,3}$	9.7	10.1				
$J_{2a,3}$			11.2	9.9		
$J_{2e,3}$			5.1	5.1		
$J_{2,3a}$					11.7	11.7
$J_{2,3e}$					4.6	4.6
$J_{3,4}$	9.7	10.1	9.5	10.1		
$J_{3a,4}$					11.7	11.7
$J_{3e,4}$						
$J_{4,5}$	9.7	10.1	9.5	10.1	9.5	10.3
$J_{5,6}$	6.2	2.2	6.2	2.4	6.2	2.4
$J_{5,6}$		4.6		4.8		4.8
$J_{6,6}$		11.7		11.7		11.7
$J_{4,NH}$	9.7	10.1	9.5	10.1		
$J_{1',2'}$	4.4	4.0	4.8	4	4.4	4
$J_{2',3'}$	10.6	10.6	10.6	10.3	10.4	10.3
$J_{3',4'}$	9.5	9.5	9.5	9.2	9.4	9.5
$J_{4',5'}$	11	11.4	11.7	11	11.7	11
$J_{5',6'}$	2.9	3.7	2.9	3.7	2.2	2.9
$J_{1',6'}$	4	3.7	3.7	3.7	3.7	3.3
$J_{5',7'}$	9.5	7.5	9.3	7.5	9.2	8.1
$J_{5',7'}$	4.4	4	4.4	4	4.4	4
$J_{7',7'}$	11	11.4	11	11.4	11.4	11.5

TABLE II

Inhibitory activity of pseudo-disaccharides **1**–**6** against three enzymes

Compound	*α-D-Glucosidase*[a]	*β-D-Glucosidase*[b]	*α-D-Mannosidase*[c]
1	5.9[d]	6.2	1.8
2	11.1	3.6	2.7
3	65.4 (47.5)	6.7	7.2
4	11.2	4.5	11.7
5	7.3	4.5	0.6
6	10.5	6.4	43.9
Nojirimycin B	10.0	91.0 (1.0)	93.0 (7.3)

[a] Yeast α-D-glucosidase, 0.66mM *p*-nitrophenyl α-D-glucopyranoside, 100mM phosphate-buffered saline, pH 6.8.[b] Almond β-D-glucosidase, 0.33mM *p*-nitrophenyl β-glucopyranoside, 100mM acetate buffer, pH 5.0; [c] Jack bean α-D-mannosidase, 100 mM acetate buffer, pH 4.5.[d] Inhibition (*I*%) determined at the final concentration of 100 $\mu g.mL^{-1}$; numbers in parentheses denote IC_{50} (concentrations required to cause 50% inhibition, $\mu g.mL^{-1}$) values.

*Methyl 3,6-di-*O*-benzoyl-2-deoxy-α-*D*-lyxo-hexopyranoside* (**13**). — Compound **11** (1 g, 2.17 mmol) was treated with aq. 80% AcOH (30 mL) for 45 min at 55° and then evaporated. The residue was diluted with water (50 mL), washed with EtOAc (25 mL) and then evaporated to give the triol **12** (0.40 g, ~100%) as a syrup. To a solution of

crude **12** in pyridine (10 mL) was added BzCl (0.62 mL, 5.34 mmol) at 0° and then the mixture was stirred for 13 h at room temperature. After evaporation, column chromatography (C-300, 40 g) of the product (1.33 g) with 1:12 butanone–toluene gave **13** (0.84 g, ~100%) as a syrup; $[\alpha]_D^{28}$ +45° (*c* 0.8, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 8.04 (d-like, 4 H, *J* 7.7 Hz), 7.57 (t-like, 2 H, *J* 7.7 Hz), and 7.44 (t-like, 4 H, *J* 7.7 Hz) (2 COPh), 5.47 (ddd, 1 H, $J_{2a,3}$ 12.5, $J_{2e,3}$ 5.1, $J_{3,4}$ 2.9 Hz, H-3), 4.96 (d, 1 H, $J_{1,2a}$ 3.3, $J_{1,2e}$ ~0 Hz, H-1), 4.62 (dd, 1 H, $J_{5,6}$ 5.9, $J_{6,6'}$ 11.4 Hz) and 4.53 (dd, 1 H, $J_{5,6'}$ 6.6 Hz) (H-6), 4.23 (t, 1 H, $J_{4,5}$ ~0 Hz, H-5), 4.19 (d, 1 H, H-4), 2.30 (td, 1 H, $J_{2,2}$ 12.5 Hz, H-2*a*), 2.23 (m, 1 H, OH), and 2.05 (dd, 1 H, H-2*e*).

Anal. Calc. for $C_{21}H_{22}O_7$: C, 63.79; H, 5.86. Found: C, 64.16; H, 5.68.

*Methyl 4-azido-3,6-di-*O*-benzoyl-2,4-dideoxy-α-*D-arabino-*hexopyranoside* (**15**). — Compound **13** (0.82 g, 2.12 mmol) was treated with CH_3SO_2Cl (0.33 mL, 4.26 mmol) in pyridine (5 mL) for 2 h at room temperature. To the mixture was added water (25 mL) and extracted with EtOAc (50 mL), and the extract was washed successively with aqueous $NaHCO_3$ (25 mL) and water (25 mL) and then evaporated to give the mesylate **14** (0.91 g, ~93.0%) as a syrup, which was heated with NaN_3 (0.77 g, 11.8 mmol) in *N*,*N*-dimethylformamide (10 mL) for 16 h at 120°. The mixture was evaporated and the residue taken up in EtOAc (50 mL), washed with water (25 mL) and evaporated. Column chromatography (C-300, 35 g) of the residue (0.70 g) with 1:12 EtOAc–PhMe gave **15** (0.64 g, 74% based on **13**) as a syrup; $[\alpha]_D^{28}$ +57°, (*c* 0.7, $CHCl_3$); ν_{max}^{film} 2110 (N_3) and 1725 (C=O) cm^{-1}; ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 8.42–7.32 (m, 10 H, 2 COPh), 5.52 (ddd, 1 H, $J_{2a,3}$ 11.8, $J_{2e,3}$ 5.1, $J_{3,4}$ 9.1 Hz, H-3), 4.89 (dd, 1 H, $J_{1,2a}$ 3.6, $J_{1,2e}$ 1.3 Hz, H-1), 4.72 (dd, 1 H, $J_{5,6}$ 2.9, $J_{6,6'}$ 12 Hz) and 4.57 (dd, 1 H, $J_{5,6'}$ 4 Hz) (H-6), 3.90 (ddd, 1 H, $J_{4,5}$ 10.1 Hz, H-5), 3.72 (dd, 1 H, H-4), 3.39 (s, 3 H, OMe), 2.50 (ddd, 1 H, $J_{2,2}$ 12.9 Hz, H-2*e*), 1.84 (ddd, 1 H, H-2*a*).

Anal. Calc. for $C_{21}H_{21}N_3O_6$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.11; H, 5.23; N, 10.03.

*Methyl 4-azido-2,4-dideoxy-α-*D-arabino-*hexopyranoside* (**16**). — Compound **15** was treated with methanolic 0.2M NaOMe (6 mL) for 2 h at room temperature, and then made neutral with Amberlite IRA-120B (H^+) resin. The mixture was evaporated to give a syrup (0.58 g) that was eluted from a column of silica gel (C-300, 8 g) with PhMe→1:6 EtOH–PhMe to give **16** (272 mg, ~100%); m.p. 83–85° (from EtOH), $[\alpha]_D^{27}$ + 177° (*c* 0.9, MeOH).

Anal. Calc. for $C_7H_{13}N_3O_4$: C, 41.38; H, 6.45; N, 20.50. Found: C, 41.27; H, 6.17; N, 20.50.

*Methyl 4-amino-2,4,6-trideoxy-α-*D-arabino-*hexopyranoside* (**18**) *and its di-*N,O-*acetyl derivative* (**19**). — Compound **16** (443 mg, 2.18 mmol) was stirred with SO_2Cl_2 (0.35 mL, 4.36 mmol) in pyridine (5 mL) for 1 h at −15°. The mixture was poured into ice–water (50 mL) and extracted with EtOAc (100 mL × 2) and the extract was evaporated. Column chromatography (C-300, 15 g) of the residue (470 mg) with 1:10 butanone–PhMe gave the chloride **17** (232 mg). This compound was hydrogenolyzed in EtOH (7 mL) in the presence of Raney nickel T-4 and KOH (135 mg, 3.84 mmol) in Parr apparatus (3.4 kg.cm^{-2} of initial hydrogen pressure) for 36 h at room temperature. The

mixture was filtered and the filtrate eluted from a column of Dowex 50W-X2 (H^+) resin (14 mL) with MeOH→5% NH_4OH–MeOH to give **18** (115 mg, ~33% based on **16**) as a crude amorphous powder.

The crude **18** (53 mg) was acetylated with pyridine and Ac_2O (0.5 mL each) overnight at room temperature. Column chromatography (C-300, 5 g) of the product (98 mg) with 1:10 EtOH–PhMe gave **19** (51 mg, 70%) as needles; m.p. 145–146° (from EtOAc), $[\alpha]_D^{30}$ +176° (*c* 1.2, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 5.44 (d, 1 H, $J_{4,NH}$ 9.9 Hz, NH), 5.16 (ddd, 1 H, $J_{2a,3}$ 11.7, $J_{2e,3}$ 5.1, $J_{3,4}$ 9.9 Hz, H-3), 4.80 (dd, 1 H, $J_{1,2a}$ 3.7, $J_{1,2e}$ 1.5 Hz, H-1), 3.84 (q, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 3.63 (dq, 1 H, $J_{5,6}$ 6.2 Hz, H-5), 3.33 (s, 3 H, OMe), 2.10 (ddd, 1 H, $J_{2,2}$ 12.8 Hz, H-2*e*), 2.03 and 1.95 (2 s, each 3 H, NAc and OAc), 1.85 (ddd, 1 H, H-2*a*), and 1.24 (d, 3 H, H-6).

Anal. Calc. for $C_{11}H_{19}NO_5$: C, 53.87; H, 7.81; N, 5.71 Found: C, 54.08; H, 7.56; N, 5.70.

*Methyl 4-amino-2,4-dideoxy-α-*D-arabino-*hexopyranoside* (**20**) *and its tri-*N,O-*acetyl derivative* (**21**). — Compound **16** (302 mg, 1.49 mmol) was hydrogenolyzed in MeOH (5 mL) in the presence of Raney nickel T-4 in Parr apparatus (3.4 kg.cm^{-2} initial hydrogen pressure) for 18 h at room temperature. The mixture was filtered and the filtrate was evaporated to give **20** (255 mg, 96.7%) as an amorphous powder; $[\alpha]_D^{30}$ +127° (*c* 1, MeOH).

Compound **20** (20 mg, 0.11 mmol) was acetylated conventionally to give **21** (36 mg, ~100%) as needles; m.p. 119–120° (from EtOAc); $[\alpha]_D^{30}$ +115° (*c* 1.1, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 5.66 (d, 1 H, $J_{4,NH}$ 10.1 Hz, NH), 5.22 (ddd, 1 H, $J_{2a,3}$ 11.7, $J_{2e,3}$ 5.1, $J_{3,4}$ 10.1 Hz, H-3), 4.88 (dd, 1 H, $J_{1,2a}$ 2.9, $J_{1,2e}$ 1.5 Hz, H-1), 4.27–4.17 (m, 2 H, H-6), 4.04 (q, $J_{4,5}$ 10.1 Hz, H-4), 3.76 (ddd, 1 H, $J_{5,6}$ 2.9, $J_{5,6'}$ 5.1 Hz, H-5), 3.34 (s, 3 H, OMe), 2.13 (ddd, 1 H, $J_{2,2}$ 12.8 Hz, H-2*e*), 2.10, 2.04, and 1.94 (3 s, each 3 H, NAc and 2 OAc), and 1.87 (ddd, 1 H, H-2*a*).

Anal. Calc. for $C_{13}H_{21}NO_7$: C, 51.48; H, 6.98; N, 4.62. Found: C, 51.42; H, 6.76; N, 4.70.

*Methyl 4-*O*-acetyl-2-*O*-benzyl-3,6-di-*O*-*p*-tolylsulfonyl-α-*D*-galactopyranoside* (**24**). — Compound **8** (5.50 g, 11.5 mmol) was stirred with $PhCH_2Br$ (1.54 mL, 13.0 mmol) in the presence of 60% NaH (0.65 g, 16.2 mmol) in tetrahydrofuran (50 mL) for 30 min at room temperature. To the mixture was added MeOH (a few drops) and it was evaporated. The residue dissolved in EtOAc (150 mL), washed with water (75 mL × 2) and then evaporated. The benzyl ether **9** (6.60 g) so obtained was heated in aq. 80% AcOH (50 mL) for 3 h at 70° and evaporated. The syrupy residue was diluted with water (150 mL), washed with hexane (75 mL) and evaporated to give the triol **22** (3.62 g). To a solution of **22** in pyridine (35 mL) was added *p*-toluenesulfonyl chloride (6 g, 31.5 mmol) at 0°, and the mixture was stirred for 2 days at room temperature and evaporated. The residue was acetylated and the acetate (8.31 g) recrystallized from EtOH to give **24** (6.50 g, 89% based on **8**) as needles; m.p. 148–148.5°, $[\alpha]_D^{28}$ +41° (*c* 1, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 7.77 and 7.75 (2 d, each 2 H, *J* 8.4 Hz, MeC_6H_4), 7.35–7.17 (m, 9 H, CH_2Ph and MeC_6H_4), 5.44 (bd, 1 H, $J_{3,4}$ 3.7, $J_{4,5}$ ~0 Hz, H-4), 4.87 (dd, 1 H, $J_{2,3}$ 10.1 Hz, H-3), 4.58 (d, 1 H, $J_{1,2}$ 3,7 Hz, H-1), 4.47 and 4.34 (2 d, each 1 H, *J* 12.1 Hz, CH_2Ph), 4.09

(bdd, 1 H, $J_{5,6}$ 5.5, $J_{5,6'}$ 6.6 Hz, H-5), 3.97–3.95 (m, 2 H, H-6), 3.72 (dd, 1 H, H-2), 3.30 (s, 3 H, OMe), 2.45 and 2.38 (2 s, each 3 H, 2 Ts), and 2.05 (s, 3 H, Ac).

Anal. Calc. for $C_{30}H_{34}O_{11}S_2$: C, 56.77; H, 5.40. Found: C, 56.50; H, 5.21.

Methyl 4-O-acetyl-2,6-di-O-benzyl-3-O-p-tolylsulfonyl-α-D-galactopyranoside (**25**). — Compound **7** (2.0 g, 8.54 mmol) was treated with $PhCH_2Br$ (2.44 mL, 20.5 mmol) and 60% NaH (1 g, 25.0 mmol) in *N*,*N*-dimethylformamide (20 mL) as in the preparation of **9**. The product was heated in aq. 80% AcOH (20 mL) for 3 h at 70° and the residue processed as described in the preparation of **22**. Compound **23** (3.36 g) was stirred with *p*-toluenesulfonyl chloride (1.95 g, 10.2 mmol) in pyridine (50 mL) for 3 days at room temperature and then acetylated to give **25** (4.10 g, 80% based on **7**) as needles; m.p. 128–129° (from EtOH), $[\alpha]_D^{23}$ +37° (*c* 1, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 7.79 (d, 2 H, *J* 8.4 Hz, MeC_6H_4), 7.32–7.22 (m, 12 H, 2 CH_2Ph and MeC_6H_4), 5.53 (dd, 1 H, $J_{3,4}$ 3.7, $J_{4,5}$ 0.8 Hz, H-4), 4.94 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-3), 4.62 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.51, 4.41 and 4.38 (3 d, 2, 1 and 1 H, *J* 12.1 Hz, 2 CH_2Ph), 4.03 (bt, 1 H, $J_{5,6}$ 6.1 Hz, H-5), 3.78 (dd, 1 H, H-2), 3.45–3.43 (m, 2 H, H-6), 3.34 (s, 3 H, OMe), 2.38 (s, 3 H, Ts), and 2.06 (s, 3 H, Ac).

Anal. Calc. for $C_{30}H_{34}O_9S$: C, 63.14; H, 6.01. Found: C, 63.13; H, 5.97.

Methyl 4-O-acetyl-2-O-benzyl-3,6-dideoxy-α-D-ribo-hexopyranoside (**26**). — Compound **24** (6.50 g, 10.2 mmol) was refluxed with $NaBH_4$ (4.70 g, 0.12 mol) in 2-propanol (75 mL) for 24 h and then evaporated. The residue was acetylated conventionally and the product purified by column chromatography (C-300, 96 g) with 1:20 butanone–PhMe to give **26** (1.40 g, 47%) as a syrup; $[\alpha]_D^{25}$ +75° (*c* 1.7, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 7.34 (s, 5 H, CH_2Ph), 4.64 and 4.53 (2 d, each 1 H, *J* 12.1 Hz, CH_2Ph), 4.61 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.46 (ddd, 1 H, $J_{3a,4}$ 11.7, $J_{3e,4}$ 4.8, $J_{4,5}$ 9.9 Hz, H-4), 3.75 (dq, 1 H, $J_{5,6}$ 6.2 Hz, H-5), 3.56 (ddd, 1 H, $J_{2,3a}$ 11.7, $J_{2,3e}$ 4.8 Hz, H-2), 3.42 (s, 3 H, OMe), 2.27 (dt, 1 H, $J_{3,3}$ 11.7 Hz, H-3*e*), 2.05 (s, 3 H, Ac), 1.27 (q, 1 H, H-3*a*), and 1.13 (d, 3 H, H-6).

Anal. Calc. for $C_{16}H_{22}O_5$: C, 65.09; H, 7.54. Found: C, 64.70; H, 7.31.

Methyl 4-O-acetyl-2,6-di-O-benzyl-3-deoxy-α-D-ribo-hexopyranoside (**28**) *and -xylo-hexopyranoside* (**30**) *and methyl 3-acetoxymethyl-2,5-di-O-benzyl-3-deoxy-α-D-xylofuranoside* (**38**). — Compound **25** (200 mg, 0.35 mmol) was refluxed with $NaBH_4$ (80 mg, 2.11 mmol) in 2-propanol (5 mL) for 2 h. The mixture was processed as described in the preparation of **26**. Column chromatography (C-300, 6.9 g) of a mixture (138 mg) of the products with 1:20 EtOAc–PhMe gave first **28** (88 mg, 63%) as a syrup; $[\alpha]_D^{30}$ +65° (*c* 1, $CHCl_3$), ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 7.35 (s, 10 H, 2 CH_2Ph), 4.75 (ddd, 1 H, $J_{3a,4}$ 12.1, $J_{3e,4}$ 5.1, $J_{4,5}$ 10.3 Hz, H-4), 4.62 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.57, 4.55, 4.45 and 4.37 (4 d, each 1 H, *J* 12.1 Hz, 2 CH_2Ph), 3.71 (dt, 1 H, $J_{5,6}$ 2.9, $J_{5,6'}$ 4.1 Hz, H-5), 3.52 (ddd, 1 H, $J_{2,3a}$ 12.1, $J_{2,3e}$ 4.8 Hz, H-2), 3.46 (dd, 1 H, $J_{6,6}$ 10.6 Hz) and 3.40 (dd, 1 H) (H-6), 3.37 (s, 3 H, OMe), 2.27 (dt-like, 1 H, $J_{3,3}$ 12.1 Hz, H-3*e*), 1.84 (s, 3 H, Ac), and 1.78 (q, 1 H, H-3*a*).

Anal. Calc. for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05. Found: C, 68.63; H, 6.90.

Eluted second was **30** (10 mg, 7.3%), isolated as a syrup; $[\alpha]_D^{23}$ ~0° (*c* 2.3, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 7.32–7.26 (m, 10 H, 2 CH_2Ph), 5.12 (bt, 1 H, H-4), 4.74 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.61, 4.57, 4.53 and 4.43 (4 d, each 1 H, *J* 12.1 Hz, 2 CH_2Ph),

4.03, (dt, 1 H, $J_{4,5}$ 1.5, $J_{5,6} = J_{5,6'} = 10.3$ Hz, H-5), 3.74 (ddd, 1 H, $J_{2,3a}$ 10.3, $J_{2,3e}$ 6.6 Hz, H-2), 3.47 (d, 2 H, H-6), 3.44 (s, 3 H, OMe), 2.08–2.03 (m, 2 H, H-3*a*, 3*e*), and 1.96 (s, 3 H, Ac).

Anal. Found: C, 68.80; H, 6.99.

Last fractions gave **38** (42 mg, 31%), isolated as a syrup; $[\alpha]_D^{30}$ +99° (*c* 1.2, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 7.34 (m, 10 H, 2 CH_2Ph), 4.79 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.61 and 4.52 (2 d, each 1 H, *J* 11.7 Hz) and 4.50 (s, 2 H) (2 CH_2Ph), 4.34 (ddd, 1 H, $J_{3,4}$ 8.8, $J_{4,5}$ 3.7, $J_{4,5'}$ 4.4 Hz, H-4), 4.30 (dd, 1 H, $J_{3,6}$ 5.7, $J_{6,6}$ 11.2 Hz) and 4.21 (dd, 1 H, $J_{3,6'}$ 8.2 Hz) (CH_2OAc), 3.84 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 3.56 (dd, 1 H, $J_{5,5}$ 10.6 Hz) and 3.50 (dd, 1 H) (H-5), 3.41 (s, 3 H, OMe), 2.83 (dddd, 1 H, H-3), and 1.93 (s, 3 H, Ac).

Anal. Found: C, 69.19; H, 7.36.

*Methyl 3-acetoxymethyl-2,5-di-*O*-acetyl-3-deoxy-α-*D*-xylofuranoside* (**39**). — Compound **38** (80 mg, 0.20 mmol) was hydrogenolyzed in EtOH (5 mL) containing AcOH in the presence of 10% Pd–C (80 mg) similarly in a Parr apparatus for 6 h at room temperature. The product was acetylated and purified by column chromatography (C-300, 3 g) with 1:10 butanone–PhMe gave **39** (43 mg, 71%) as a syrup; $[\alpha]_D^{21}$ +183° (*c* 1.3, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 5.12 (d, 1 H, $J_{1,2}$ 4.4 Hz, H-1), 4.82 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.45 (ddd, 1 H, $J_{3,4}$ 8.6, $J_{4,5}$ 3.7, $J_{4,5'}$ 5.1 Hz, H-4), 4.36 (dd, 1 H, $J_{5,5}$ 12.1 Hz) and 4.05 (dd, 1 H) (H-5), 4.28 (dd, 1 H, $J_{3,6}$ 5.7, $J_{6,6}$ 11.5 Hz) and 4.16 (dd, 1 H, $J_{3,6'}$ 8 Hz) (H-6), 3.40 (s, 3 H, OMe), 2.94 (dddd, 1 H, H-3), 2.12, 2.10, and 2.06 (3 s, each 3 H, 3 Ac).

Anal. Calc. for $C_{13}H_{20}O_8$: C, 51.31; H, 6.62. Found: C, 51.19; H, 6.39.

*Methyl 2-*O*-benzyl-4-chloro-3,4,6-trideoxy-α-*D*-xylo-hexopyranoside* (**32**). — Compound **26** (1.40 g, 4.76 mmol) was stirred with M methanolic NaOMe (2 mL) in 1:1 $CHCl_3$–MeOH (20 mL) for 2 h at room temperature. After neutralization with AcOH, the mixture was filtered and the filtrate evaporated to give **27** (1.21 g, ~100%), to a solution of which in pyridine (20 mL) was added SO_2Cl_2 (0.57 mL, 7.09 mmol), and the mixture was stirred for 2 h at room temperature. The mixture was processed as described in the preparation of **17** to give a syrup (0.78 g), which was eluted from a column of silica gel (C-300, 39 g) with 1:25 butanone–PhMe to give **32** (0.71 g, 55% based on **26**) as an amorphous powder; $[\alpha]_D^{26}$ +66° (*c* 1.4, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.32 (s, 5 H, CH_2Ph), 4.68 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.66 and 4.51 (2 d, each 1 H, *J* 12 Hz, CH_2Ph), 4.21–3.85 (m, 3 H, H-2,4,5), 3.40 (s, 3 H, OMe), 2.37–2.16 (m, 2 H, H-3*a*,3*e*), and 1.21 (d, 2 H, $J_{5,6}$ 6.5 Hz, H-6).

Anal. Calc. for $C_{14}H_{19}ClO_3$: C, 62.11; H, 7.07. Found: C, 62.19; H, 7.07.

*Methyl 4-azido-2-*O*-benzyl-3,4,6-trideoxy-α-*D*-ribo-hexopyranoside* (**33**) *and methyl 2-*O*-benzyl-3,4,6-trideoxy-α-*D*-glycero-hex-4-enopyranoside* (**40**). — Compound **32** (0.51 g, 1.87 mmol) was treated with NaN_3 (0.73 g, 11.3 mmol) in *N*,*N*-dimethylformamide (8 mL) for 18 h at 100° and the mixture was processed as described in the preparation of **15**. Column chromatography (C-300, 22 g) of the product (0.44 g) with 1:15 EtOAc–hexane gave first **40** (146 mg, 33.4%) as a syrup; $[\alpha]_D^{25}$ +83° (*c* 1.2, $CHCl_3$); ν_{max}^{film} 1685 cm^{-1} (C=C); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 7.32 (s, 5 H, CH_2Ph), 4.87 (d, 1 H, $J_{1,2}$ 2.6 Hz, H-1), 4.68 and 4.58 (2 d, each 1 H, *J* 12.5 Hz, CH_2Ph), 4.52–4.49 (m, 1 H,

H-4), 3.66 (ddd, 1 H, $J_{2,3a}$ 10.1, $J_{2,3e}$ 7 Hz, H-2), 3.50 (s, 3 H, OMe), 2.28–2.11 (m, 2 H, H-3a, 3e), and 1.73–1.60 (m, 3 H, H-6).

Eluted second was **33** (208 mg, 40.2%), isolated as a syrup; $[\alpha]_D^{25}$ +67° (*c* 1.1, $CHCl_3$); ν_{max}^{film} 2100 cm^{-1} (N_3); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 7.32 (s, 5 H, CH_2Ph), 4.64 and 4.57 (2 d, each 1 H, *J* 12.1 Hz, CH_2Ph), 4.62 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 3.58 (dq, 1 H, $J_{4,5}$ 9.9, $J_{5,6}$ 6.2 Hz, H-5), 3.53 (ddd, 1 H, $J_{2,3a}$ 12.1, $J_{2,3e}$ 4.4 Hz, H-2), 3.41 (s, 3 H, OMe), 2.97 (ddd, 1 H, $J_{3a,4}$ 12.1, $J_{3e,4}$ 4.4 Hz, H-4), 2.20 (dt, 1 H, $J_{3,3}$ 12.1 Hz, H-3*e*), 1.90 (s, 3 H, Ac), and 1.23 (d, 3 H, H-6).

Anal. Calc. for $C_{14}H_{19}N_3O_5$: C, 60.63; H, 6.91; N, 15.15. Found: C, 60.32; H, 6.93; N, 14.46.

*Methyl 2,6-di-O-benzyl-3-deoxy-4-O-(methylsulfonyl)-α-*D-ribo-*hexopyranoside* (**34**). — To a solution of compound **29** (1.15 g, 3.21 mmol), obtained by a treatment of **28** with M methanolic NaOMe, in pyridine (20 mL) was added CH_3SO_2Cl (0.48 mL, 6.20 mmol) at 0° and then the mixture was stirred for 4 h at room temperature. After evaporation, the residue was diluted with EtOAc (100 mg), washed with saturated aq. $NaHCO_3$ (50 mL × 2) and water (50 mL), and evaporated to give a syrup (1.50 g), column chromatography (C-200, 65 h) of which with 1:10 butanone–PhMe gave **34** (1.34 g, 96%) as a syrup; $[\alpha]_D^{25}$ +50° (*c* 0.6, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.30 (s, 10 H, 2 CH_2Ph), 3.45 (s, 3 H, OMe), 2.91 (s, 3 H, Ms), 2.45 (dt-like, 1 H, $J_{3,3}$ 11.9, $J_{2,3e}$ = $J_{3e,4}$ = 6 Hz, H-3e), 2.12 (q, 1 H, $J_{2,3a}$ = $J_{3a,4}$ = 11.9 Hz, H-3*a*).

Anal. Calc. for $C_{22}H_{28}SO_7$: C, 60.53; H, 6.47. Found: C, 60.16; H, 6.40.

*Methyl 4-O-benzoyl-2,6-di-O-benzyl-3-deoxy-α-*D-xylo-*hexopyranoside* (**35**). — A mixture of **34** (1.34 g, 3.07 mmol), NaOBz (2 g, 13.9 mmol) and *N,N*-dimethylformamide (50 mL) was heated for 68 h at 120° and then evaporated. The residue was diluted with EtOAc (100 mL), washed with water (50 mL) and evaporated to give a syrup (1.56 g), column chromatography (C-300, 78 g) of which with 1:20 butanone–PhMe gave **35** (1.0 g, 70%) as an amorphous powder; $[\alpha]_D^{25}$ +6.9° (*c* 1, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 8.04–7.89 (m, 1 H), 7.61–7.30 (m, 2 H) (COPh), 7.25 and 7.21 (2 s, each 5 H, 2 CH_2Ph), 5.38 (m, 1 H, H-4), 4.80 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 4.64, 4.56, 4.48 and 4.38 (4 d, each 1 H, *J* 11.5 Hz, 2 CH_2Ph), 4.16 (td, 1 H, $J_{4,5}$ 1.9, $J_{5,6}$ Hz, H-5), 3.84 (ddd, 1 H, $J_{2,3a}$ 9.9, $J_{2,3e}$ 7.1 Hz, H-2), 3.55 (d, 2 H, H-6), 3.47 (s, 3 H, OMe), and 2.37–2.08 (m, 2 H, H-3a, 3*e*).

Anal. Calc. for $C_{28}H_{30}O_6$: C, 72.71; H, 6.54. Found: C, 72.77; H, 6.54.

*Methyl 2,6-di-O-benzyl-3,4-dideoxy-α-*D-glycero-*hex-4-enopyranoside* (**41**). — Compound **29** (41 mg) was treated with SO_2Cl_2 as described in the preparation of **32** to give crude **41** (32 mg, 81%) as a syrup; ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 4.98 (d, 1 H, $J_{1,2}$ 2.2 Hz, H-1), 4.86 (dd, $J_{3,4}$ 2.6, $J_{3',4}$ 5.1 Hz, H-4). This compound could not be purified for elemental analysis. The structure was assigned by comparison of the ^{1}H-n.m.r. data with those of **40**.

*Methyl 2,6-di-O-benzyl-3-deoxy-4-O-(methylsulfonyl)-α-*D-xylo-*hexopyranoside* (**36**). — The alcohol **31** (0.71 g, 1.98 mmol), obtained from **30** or **35**, was stirred with CH_3SO_2Cl (0.32 mL, 4.13 mmol) in pyridine (15 mL) as in the preparation of **34**. Column chromatography (C-200, 45 g) of the crude product (0.89 g) with 1:12 butanone–PhMe gave **36** (0.80 g, 92% based on **35**) as a syrup; $[\alpha]_D^{26}$ +79° (*c* 1, $CHCl_3$);

^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.32 (s, 10 H, 2 CH_2Ph), 4.96 (m, 1 H, H-4), 4.70 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.66 and 4.53 (2 d, each 1 H, J 11 Hz), and 4.52 (s, 2 H) (2 CH_2Ph), 4.20 (td, 1 H, $J_{4,5}$ 1.2, $J_{5,6}$ 6.3 Hz, H-5), 3.79 (ddd, 1 H, $J_{2,3a}$ 11.9, $J_{2,3e}$ 6.9 Hz, H-2), 3.56–3.47 (m, 2 H, H-6), 3.42 (s, 3 H, OMe), 2.87 (s, 3 H, Ms), 2.54–2.23 (m, 1 H, H-3*e*), and 2.09 (ddd, 1 H, $J_{3,3}$ 14 Hz, H-3*a*).

Anal. Calc. for $C_{22}H_{28}O_7S$: 60.53; H, 6.47. Found: C, 60.24; H, 6.43.

*Methyl 4-azido-2,6-di-*O*-benzyl-3,4-dideoxy-α-*D-ribo-*hexopyranoside* (**37**). — Treatment of **36** (0.78 g) with NaN_3 (0.69 g, 10.8 mmol) in *N,N*-dimethylformamide (15 mL) as in the preparation of **15** and column chromatography (C-300, 30 g) of the product (0.61 g) with 1:15 EtOAc–hexane gave **37** (0.40 g, 59%) as a syrup; $[\alpha]_D^{25}$ + 59° (*c* 0.8, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.31 (s, 10 H, 2 CH_2Ph), 4.70 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.64–4-54 (m, 4 H, 2 CH_2Ph), 3.69–3.42 (m, 5 H, H-2, 4,5,6), 3.41 (s, 3 H, OMe), 2.25 (dt, 1 H, $J_{3,3}$ 11.7, $J_{2,3e} = J_{3e,4}$ = 4.9 Hz, H-3*e*), 1.94 (q, 1 H, $J_{2,3a} = J_{3a,4}$ = 11.7 Hz, H-3*a*).

Anal. Calc. for $C_{21}H_{25}N_3O_4$: C, 65.78; H, 6.57; N, 10.96. Found: C, 65.37; H, 6.48; N, 10.88.

*Methyl 4-amino-3,4,6-trideoxy-α-*D-ribo-*hexopyranoside* (**42**) *and its di-*N,O*-acetyl derivative* (**43**). — Compound **33** (0.21 g, 0.75 mmol) was hydrogenolyzed in EtOH (6 mL) containing AcOH (a few drops) in the presence of 10% Pd–C (0.20 g) in Parr apparatus (3.4 kg.cm^{-2} of initial hydrogen pressure) for 24 h at room temperature. The mixture was filtered and the filtrate was eluted from a column of Dowex 50W-X2 (H^+) resin (10 mL) with MeOH→5% NH_4OH–MeOH to give **42** (87 mg, 66%) as a syrup; $[\alpha]_D^{24}$ + 168° (*c* 1, MeOH).

Compound **42** (4.2 mg, 0.0237 mmol) was acetylated conventionally to give **43** (4.8 mg, 83%) as a syrup; $[\alpha]_D^{26}$ +141° (*c* 0.2, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 5.24 (d, 1 H, $J_{4,NH}$ 9.2 Hz, NH), 4.58 (ddd, 1 H, $J_{1,2}$ 3.7, $J_{2,3a}$ 11.7, $J_{2,3e}$ 4.8 Hz, H-2), 4.76 (d, 1 H, H-1), 3.91 (tdd, 1 H, $J_{3a,4}$ 11.7, $J_{3e,4}$ 4.4, $J_{4,5}$ 10.3 Hz, H-4), 3.56 (dq, 1 H, $J_{5,6}$ 6.3 Hz, H-5), 3.41 (s, 3 H, OMe), 2.08 (dt, 1 H, $J_{3,3}$ 11.7 Hz, H-3*e*), 2.08 and 1.99 (2 s, each 3 H, NAc and OAc), 1.76 (q, 1 H, H-3*a*), and 1.20 (d, 3 H, H-6).

Anal. Calc. for $C_{11}H_{19}NO_5 \cdot H_2O$: C, 50.18; H, 8.04; N, 5.31. Found: C, 50.38; H, 7.87; N, 5.12.

*Methyl 4-amino-3,4-dideoxy-α-*D-ribo-*hexopyranoside* (**44**) *and its tri-*N,O*-acetyl derivative* (**45**). — As in the previous experiment, compound **37** (0.40 g, 1.05 mmol) was converted into **44** (160 mg, 86%), isolated as a syrup; $[\alpha]_D^{23}$ +128° (*c* 1.2, MeOH).

Compound **44** (23 mg, 0.13 mmol) was acetylated conventionally to give **45** (27 mg, 68%) as a syrup; $[\alpha]_D^{21}$ +118° (*c* 1.4, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 5.60 (m, 1 H, NH), 4.86 (td, 1 H, $J_{1,2}$ 3.7, $J_{2,3a}$ 11.7, $J_{2,3e}$ 4.8 Hz, H-2), 4.83 (d, 1 H, H-1), 4.25 (dd, 1 H, $J_{5,6}$ 2.2, $J_{6,6}$ 12.1 Hz) and 4.12 (dd, 1 H, $J_{5,6'}$ 6.2 Hz) (H-6), 4.17–4.04 (m, 1 H, H-4), 3.69 (ddd, 1 H, $J_{4,5}$ 10.5 Hz, H-5), 3.42 (s, 3 H, OMe), 2.10, 2.08, and 1.97 (3 s, each 3 H, NAc and 2 OAc), 1.84 (q, 1 H, $J_{3a,4} = J_{3,3}$ = 11.7 Hz, H-3a).

Anal. Calc. for $C_{13}H_{21}NO_7$: C, 51.48; H, 6.98; N, 4.62. Found: C, 51.31; H, 6.61; N, 4.65.

*Methyl 4-[(1*S*)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclo-*

hexyl]amino- (**49**) *and methyl 4-[(1S)-(1,3,5/2,4,6)-2,3,4,5-tetrahydroxy-6-(hydroxymethyl)cyclohexyl]amino-4,6-dideoxy-α-*D*-glucopyranoside heptaacetate* (**55**). — A mixture of (1*R*,2*S*,5*R*,7*R*,8*R*,9*R*,10*R*)-8,9-dibenzyloxy-5-phenyl-4,6,11-trioxatricyclo-[8.1.0.0^{2,7}]undecane[10] (**46**, 0.20 g, 0.45 mmol), methyl 4-amino-4,6-dideoxy-α-D-glucopyranoside (**47**, 96 mg, 0.54 mmol), and 2-propanol (1 mL) was heated in a sealed tube for 92 h at 120°, and then evaporated. Column chromatography (C-300, 18 g) of the syrupy residue (368 mg) with 1:10 EtOH–PhMe gave a mixture (272 mg) of the condensates, which was hydrogenolyzed in EtOH (10 mL) in the presence of 10% Pd–C (270 mg) and AcOH (one drop) in a Parr apparatus for 22 h at room temperature. The mixture was filtered and the filtrate was evaporated to a syrup (252 mg) that was eluted from a column of silica gel (C-300, 13 g) with 1:5 butanone–PhMe to give first **49** (99 mg, 34% based on **46** used) as an amorphous powder; $[\alpha]_D^{26}$ +91° (*c* 1, $CHCl_3$); [lit.[5] $[\alpha]_D^{23}$ +101° (*c* 2.6, $CHCl_3$)]; ^{1}H-n.m.r. (270 MHz, $CDCl_3$), see Table I.

Eluted second was **55** (32 mg, 11% based on **46** used), isolated as an amorphous powder; $[\alpha]_D^{26}$ +61° (*c* 1.6, $CHCl_3$); [lit.[5] $[\alpha]_D^{23}$ +71° (*c* 1.5, $CHCl_3$)]; ^{1}H-n.m.r. data (270 MHz, $CDCl_3$): δ 5.17–4.98 (m, 4 H, H-3, 2′, 3′, 4′), 4.83–3.76 (m, 3 H, H-1, 2, 5′), 4.34 (d, 2 H, $J_{6',7'}$ 2.2 Hz, H-7′), 3.49 (dq, 1 H, $J_{4,5}$ 9.9, $J_{5,6}$ 6.2 Hz, H-5), 3.36 (s, 3 H, OMe), 3.11 (t, 1 H, $J_{1',2'} = J_{1',6'}$ = 10.6 Hz, H-1′), 2.97 (t, 1 H, $J_{3,4}$ 9.9 Hz, H-4), 2.11, 2.08, 2.07, 2.06, 2.00, 1.98, and 1.97 (7 s, each 3 H, 7 Ac), and 1.31 (d, 3 H, H-6).

Methyl 4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexyl]amino- (**50**) *and methyl 4-[(1S)-(1,3,5/2,4,6)-2,3,4,5-tetrahydroxy-6-(hydroxymethyl)cyclohexyl]amino-4-deoxy-α-*D*-glucopyranoside octaacetate* (**56**). — A mixture of **46** (200 mg, 0.45 mmol), methyl 4-amino-4-deoxy-α-D-glucopyranoside (**48**, 105 mg, 0.54 mmol), and 2-propanol (1 mL) was heated in a sealed tube for 92 h at 120°, and then evaporated. Column chromatography (C-300, 16 g) of the residue (324 mg) with 1:7 EtOH–PhMe gave first a single fraction (59 mg), as an amorphous powder, which was hydrogenolyzed and then acetylated conventionally. The product (68 mg) was eluted from a column of silica gel (C-300, 3.4 g) with 1:4 butanone–PhMe to give **56** (29 mg, 9.1% based on **46** used) as an amorphous powder; $[\alpha]_D^{21}$ + 56° (*c* 1.4, $CHCl_3$); [lit.[5] $[\alpha]_D^{23}$ + 77° (*c* 1.1, $CHCl_3$)]; ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 5.16–5.03 (m, 3 H, H-2′, 3′, 4′), 4.98 (dd, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 9.5 Hz, H-3), 4.83 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.81 (dd, 1 H, H-2), 4.78 (t, 1 H, $J_{4',5'} = J_{5',6'}$ 9.7 Hz, H-5′), 4.39 (dd, 1 H, $J_{6',7'}$ 4.0, $J_{7',7'}$ 12.5 Hz) and 4.30 (dd, 1 H, $J_{6',7'}$ ~0 Hz) (H-7′), 4.35 (dd, 1 H, $J_{5,6}$ 3.3, $J_{6,6}$ 11 Hz) and 4.26 (dd, 1 H, $J_{5,6}$ 1.8 Hz) (H-6), 3.57 (ddd, 1 H, $J_{4,5}$ 9.9 Hz, H-5), 3.47–3.39 (m, 2 H, H-4, 1′), 3.37 (s, 3 H, OMe), 2.95 (m, 1 H, H-6′), 2.16, 2.12, 2.11, 2.10, 2.07, 2.00, and 1.97 (7 s, 3, 3, 3, 3, 3, 3, 3, and 6 H, 8 Ac).

The second single fraction (188 mg) obtained was treated and eluted from a column of silica gel (C-300, 11 g) with 1:4 butanone–PhMe to give **50** (137 mg, 43.2% based on **46** used) as an amorphous powder; $[\alpha]_D^{26}$ +84° (*c* 1, $CHCl_3$); [lit.[5] $[\alpha]_D^{23}$ +101° (*c* 1.1, $CHCl_3$)]. ^{1}H-N.m.r. data (270 MHz, $CDCl_3$) are listed in Table I.

Methyl 4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexyl]amino- (**51**) *and methyl 4-[(1S)-(1,3,5/2,4,6)-2,3,4,5-tetrahydroxy-6-(hydroxymethyl)cyclohexyl]amino-2,4,6-trideoxy-α-*D*-*arabino*-hexopyranoside hexaacetate* (**57**). — A mixture of **18** (100 mg, 0.62 mmol), **46** (200 mg, 0.45 mmol) and 2-propanol (1 mL)

was heated in a sealed tube for 90 h at 120°, and then evaporated. Column chromatography (C-300, 30 g) of the residue (300 mg) with 2:3 EtOAc–PhMe gave first a syrup (47 mg), which was hydrogenolyzed and then acetylated conventionally. Crude **57** (60 mg) obtained was purified by elution from a column of silica gel (C-300, 2 g) with 1:6 butanone–PhMe to give **57** (23 mg, 7.9% based on **46** used) as an amorphous powder; $[\alpha]_D^{20}$ +67° (*c* 1.1, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 5.14–4.85 (m, 4 H, H-2′, 3′, 4′, 5′), 4.78 (ddd, 1 H, $J_{2a,3}$ 11.4, $J_{2e,3}$ 5, $J_{3,4}$ 9.3 Hz, H-3), 4.69 (dd, 1 H, $J_{1,2a}$ 3.1, $J_{1,2e}$ 1.6 Hz, H-1), 4.38–4.27 (m, 2 H, H-7′), 3.45 (dq, 1 H, $J_{4,5}$ 9.3, $J_{5,6}$ 6.5 Hz, H-5), 3.30 (t, 1 H, $J_{1',2'} = J_{1',6'}$ = 10.6 Hz, H-1′), 3.30 (s, 3 H, OMe), 2.18 (ddd, 1 H, $J_{2,2}$ 12.8 Hz, H-2*e*), 2.08 (t, 1 H, H-4), 2.12, 2.08, 2.02, 1.99, and 1.98 (5 s, 3, 3, 3, 6 and 3 H, 6 Ac), 1.58 (ddd, 1 H, H-2a), and 1.33 (d, 1 H, H-6).

Anal. Calc. for $C_{26}H_{39}NO_{14}$: C, 52.97; H, 6.67; N, 2.38. Found: C, 53.15; H, 6.68; N, 2.01.

Similar treatment of the second fraction (160 mg) obtained gave the crude product (260 mg), which was eluted from a column of silica gel (C-300, 8 g) with 1:6 butanone–PhMe to give **51** (135 mg, 51% based on **46** used) as needles; m.p. 162–164° (from EtOH), $[\alpha]_D^{27}$ +92° (*c* 1, $CHCl_3$): ^{1}H-n.m.r. data (270 MHz, $CDCl_3$) are listed in Table 1.

Anal. Found: C, 52.81; H, 6.48; N, 2.26.

Methyl 4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexyl]amino- (**52**) *and methyl 4-[(1S)-(1,3,5/2,4,6)-2,3,4,5-tetrahydroxy-6-(hydroxymethyl)cyclo-hexyl]amino-2,4-dideoxy-α-*D-arabino-*hexopyranoside heptaacetate* (**58**). — A mixture of **20** (120 mg, 0.68 mmol), **46** (210 mg, 0.47 mmol) and 2-propanol (1 mL) was heated in a sealed tube for 90 h at 120° and then evaporated. Column chromatography (C-300, 30 g) of the residue (330 mg) with 2:5 Me_2CO–PhMe gave a single fraction (45 mg), as an amorphous powder, which was hydrogenolyzed and then acetylated conventionally, and the product (45 mg) was eluted from a column of silica gel (C-300, 1.5 g) with 1:6 butanone–PhMe to give **58** (15 mg, 5% based on **46** used) as an amorphous powder; $[\alpha]_D^{23}$ +54° (*c* 0.8, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 5.14–4.81 (m, 5 H, H-3,2′,3′,4′,5′), 4.77 (dd, 1 H, $J_{1,2a}$ 2.6, $J_{1,2e}$ ~0 Hz, H-1), 4.43–4.19 (m, 4 H, H-6,7′), 3.53 (m, 1 H, H-5), 3.31 (s, 3 H, OMe), 3.20 (t, 1 H, $J_{1',2'} = J_{1',6'}$ = 10.8 Hz, H-1′), 3.11 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.7 Hz, H-4), 2.14, 2.13, 2.11, 2.09, 2.02, 1.99, and 1.98 (7 s, each 3 H, 7 Ac).

Anal. Calc. for $C_{28}H_{41}NO_{16}$: C, 51.93; H, 6.38; N, 2.16. Found: C, 51.93; H, 6.27; N, 1.74.

Similar treatment of the second fraction (224 mg) obtained gave the product (330 mg), which was eluted from a column of silica gel (C-300, 10 g) with 1:6 butanone–PhMe to give **52** (160 mg, 43.5% based on **46** used) as an amorphous powder; $[\alpha]_D^{27}$ +73° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$) are listed in Table I.

Anal. Found: C, 51.59; H, 5.89; N, 1.75.

Methyl 4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexyl]amino- (**53**) *and methyl 4-[(1S)-(1,3,5/2,4,6)-2,3,4,5-tetrahydroxy-6-(hydroxymethyl)cyclohexyl]amino-3,4,6-trideoxy-α-*D-ribo-*hexopyranoside hexaacetate* (**59**). —

A mixture of **42** (87 mg, 0.54 mmol), **46** (200 mg, 0.45 mmol) and 2-propanol (1 mL) was heated in a sealed tube for 165 h at 120° and then evaporated. Column chromatography (C-300, 15 g) of the residue (290 mg) with 1:2 butanone–PhMe gave the first fraction (39 mg), an amorphous powder, which was hydrogenolyzed and then acetylated conventionally, and then the product (31 mg) was eluted from a column of silica gel (C-300, 3.2 g) with 1:5 butanone–PhMe to give **59** (13 mg, 4.9% based on **46** used) as an amorphous powder; $[\alpha]_D^{22}$ +75° (*c* 0.3, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 5.28 (dd, 1 H, $J_{3',4'}$ 8.8, $J_{4',5'}$ 10.6 Hz, H-4'), 5.19 (dd, 1 H, $J_{1',2'}$ 9.5, $J_{2',3'}$ 9.2 Hz, H-2'), 5.15 (dd, 1 H, H-3'), 4.78 (ddd, 1 H, $J_{1,2}$ 3.7, $J_{2,3a}$ 12.1, $J_{2,3e}$ 4.8 Hz, H-2), 4.83 (dd, 1 H, $J_{5',6'}$ 9.9 Hz, H-5'), 4.70 (d, 1 H, H-1), 4.15 (d, 1 H, $J_{6',7'}$ 11.4 Hz) and 4.03 (d, 1 H, $J_{6',7'}$ 4.6 Hz) (H-7'), 3.76 (dq, 1 H, $J_{4,5}$ 9.5, $J_{5,6}$ 6.2 Hz, H-5), 3.39 (s, 3 H, OMe), 3.36 (dd, 1 H, $J_{1',6'}$ 10.6 Hz, H-1'), 3.29 (q, 1 H, $J_{3,3}$ 12.1 Hz, H-3*a*), 2.10, 2.02, 2.01, and 1.98 (4 s, 3, 3, 9, and 3 H, 6 Ac), and 1.06 (d, 3 H, H-6).

Anal. Calc. for $C_{26}H_{39}NO_{14}$: C, 52.97; H, 6.67; N, 2.38. Found: C, 52.75; H, 6.34; N, 2.20.

Similar treatment of the second fraction (137 mg) obtained gave the product (138 mg), which was eluted from a column of silica gel (C-300, 7 g) with 1:4 butanone–PhMe to give **53** (126 mg, 47.5% based on **46** used) as an amorphous powder; $[\alpha]_D^{25}$ +100° (*c* 0.9, $CHCl_3$). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$) are listed in Table I.

Anal. Found: C, 52.71; H, 6.29; N, 2.06.

Methyl 4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexyl]amino- (**54**) *and methyl 4-[(1S)-(1,3,5/2,4,6)-2,3,4,5-tetrahydroxy-6-(hydroxymethyl)cyclohexyl]amino-3,4-dideoxy-α-*D-ribo-*hexopyranoside heptaacetate* (**60**). — A mixture of **44** (106 mg, 0.59 mmol), **46** (220 mg, 0.50 mmol) and 2-propanol (1 mL) was heated in a sealed tube for 112 h at 120° and then evaporated. Column chromatography (C-300, 19 g) of the residue (372 mg) with 1:1 butanone–PhMe gave the first fraction (47 mg), an amorphous powder, which was hydrogenolyzed and then acetylated conventionally, and the product (44 mg) was eluted from a column of silica gel (C-300, 2.2 g) with 1:4 butanone–PhMe to give **60** (31 mg, 10% based on **46** used) as an amorphous powder; $[\alpha]_D^{22}$ +43° (*c* 1.1, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 5.16–5.07 (m, 3 H, H-2',3',4'), 4.89 (dd, 1 H, $J_{4',5'}$ 10.6, $J_{5',6'}$ 9.5 Hz, H-5'), 4.78–4.71 (m, 2 H, H-1,2), 4.38 (dd, 1 H, $J_{5,6}$ 2.2, $J_{6,6}$ 11.7 Hz) and 4.24 (dd, 1 H, $J_{5,6}$ 4.4 Hz) (H-6), 4.36 (dd, 1 H, $J_{6',7'}$ 2.2, $J_{7',7'}$ 11.5 Hz) and 4.10 (dd, 1 H, $J_{6',7'}$ 1.7 Hz) (H-7'), 3.44 (ddd, 1 H, $J_{4,5}$ 10.5 Hz, H-5), 3.39 (s, 3 H, OMe), 2.88 (t, 1 H, $J_{1',2'} = J_{1',6'} = 10.8$ Hz, H-1'), 2.78 (td, 1 H, $J_{3a,4}$ 10.6, $J_{3e,4}$ 4 Hz, H-4), 2.12, 2.10, 2.095, 2.09, 2.01, 2.00, and 1.98 (7 s, each 3 H, 7 Ac), 1.44 (q, 1 H, $J_{2,3a} = J_{3,3} = 10.6$ Hz, H-3*a*).

Anal. Calc. for $C_{28}H_{41}NO_{16}$: C, 51.93; H, 6.38; N, 2.16. Found: C, 51.81; H, 6.25; N, 1.95.

Similar treatment of the second fraction (203 mg) obtained gave the products (218 mg), which was eluted from a column of silica gel (C-300, 11 g) with 1:4 butanone–PhMe gave **54** (181 mg, 56.6% based on **46** used) as an amorphous powder; $[\alpha]_D^{22}$ +78° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data (270 MHz $CDCl_3$) are listed in Table I.

Anal. Found: C, 51.45; H, 6.42; N, 2.12.

*Methyl 4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexyl]amino-4,6-dideoxy-α-*D*-glucopyranoside* (**1**). — Compound **49** (66 mg, 0.10 mmol) was stirred with M methanolic NaOMe (0.2 mL) in methanol (2 mL) for 30 min at 0°. The mixture was eluted from a column of Dowex 50W-X2 (H^+) resin (3 mL) with MeOH→5% NH_4OH–MeOH to give **1** (37 mg, ~100%) as an amorphous powder; $[\alpha]_D^{24}$ +130° (*c* 0.8, MeOH).

*Methyl 4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexyl]amino-4-deoxy-α-*D*-glucopyranoside* (**2**). — Similarly, compound **50** (83 mg, 0.12 mmol) was converted into **2** (40 mg, 91%), isolated as an amorphous powder; $[\alpha]_D^{24}$ +134° (*c* 0.7, MeOH).

*Methyl 4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexyl]amino-2,4,6-trideoxy-α-*D*-*arabino*-hexopyranoside* (**3**). — Similarly, compound **51** (34 mg, 0.068 mmol) was converted into **3** (40 mg, 98%), isolated as an amorphous powder; $[\alpha]_D^{25}$ +128° (*c* 1, MeOH).

*Methyl 4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexyl]amino-2,4-dideoxy-α-*D*-*arabino*-hexopyranoside* (**4**). — Similarly, compound **52** (80 mg, 0.12 mmol) was converted into **4** (43 mg, 99%), isolated as an amorphous powder; $[\alpha]_D^{22}$ +109° (*c* 1, MeOH).

*Methyl 4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexyl]amino-3,4,6-trideoxy-α-*D*-*ribo*-hexopyranoside* (**5**). — Similarly, compound **53** (54 mg, 0.092 mmol) was converted into **5** (37 mg, ~100%), isolated as an amorphous powder; $[\alpha]_D^{25}$ +136° (*c* 0.6, MeOH).

*Methyl 4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexyl]amino-3,4-dideoxy-α-*D*-*ribo*-hexopyranoside* (**6**). — Similarly, compound **54** (100 mg, 0.15 mmol) was converted into **6** (55 mg, ~100%), isolated as an amorphous powder; $[\alpha]_D^{21}$ +113° (*c* 1, MeOH).

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REFERENCES

1 Y. Shibata, S. Ogawa, and T. Suami, *Carbohydr. Res.*, 200 (1990) 486–492.
2 J. Itoh, S. Omoto, T. Shomura, H. Ogino, K. Iwamatsu, S. Inouye, and H. Hidaka, *J. Antibiot.*, 34 (1981) 1424–1428.
3 E. Truscheit, W. Frommer, B. Junge, L. Müller, D. D. Schmidt, and W. Wingender, *Angew. Chem. Int. Ed. Engl.*, 20 (1981) 744–761.
4 S. Omoto, J. Itoh, H. Ogino. K. Iwamatsu, N. Nishizawa, and S. Inouye, *J. Antibiot.*, 34 (1981) 1429–1433.
5 S. Ogawa, Y. Iwasawa, T. Toyokuni, and T. Suami, *Carbohydr. Res.*, 144 (1985) 155–162.
6 V. O. T. Schmidt and E. Wernicke, *Justus Liebigs Ann. Chem.* 558 (1947) 70–80.
7 P. Kaifu, L. C. Plantefaber, and I. J. Goldstein, *Carbohydr. Res.*, 140 (1985) 37–49.

8 D. H. R. Barton and S. W. McCombie, *J. Chem. Soc., Perkin Trans. 1*, (1975) 1574–1585.
9 H. H. Baer, D. J. Astles, H. Chin, and L. Siemsen, *Can. J. Chem.*, 63 (1985) 432–439; R. W. Binkley, *J. Org. Chem.*, 50 (1985) 5646–5649.
10 S. Ogawa and Y. Miyamoto, *J. Chem. Soc., Chem. Commun.*, (1987) 1843–1844; Y. Miyamoto and S. Ogawa, *J. Chem. Soc., Perkin Trans. 1*, (1988) 2675–2680.
11 S. Ogawa, K. Yasuda, T. Takagaki, Y. Iwasawa, and T. Suami, *Carbohydr. Res.*, 141 (1985) 329–334, and references therein.
12 T. Niwa, T. Tsuruoka, H. Goi, Y. Kodama, J. Itoh, S. Inouye, Y. Yamada, T. Niida, M. Nobe, and Y. Ogawa, *J. Antibiot.*, 37 (1984) 1579–1586.
13 Y. Shibata, Y. Kosuge, and S. Ogawa, unpublished results.