Carbohydrate Research, 144 (1985) 155–162
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

Synthesis of a core structure of the antibiotic oligostatin*

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(Received December 11th, 1984; accepted for publication, May 18th, 1985)

There has been much interest in the chemistry and biochemistry of the pseudo-oligosaccharidic α-D-glucosidase inhibitors[2] which contain common structural units composed of 4-amino-4-deoxy- or 4-amino-4,6-dideoxy-D-glucopyranose and saturated or unsaturated branched-chain cyclitols. Oligostatin, isolated from the fermentation broth of *Streptomyces myxogenes* nov. sp. SF-1130, is such an inhibitor and also has antibacterial activity[3]. Methanolysis of oligostatin C (**1**) afforded a crystalline methyl α-glycoside (**3**, methyl dehydro-oligobiosaminide[3] or acarviosin[4]). The formation of **3**, instead of the expected core structure methyl oligobiosaminide (**2**), was rationalised in terms of an acid-catalysed dehydration involving the axial hydroxyl group of the inositol moiety, and **3** is five times more potent an α-D-glycosidase inhibitor than the parent pseudo-trisaccharide, acarbose[4]. Therefore, it is of interest to synthesise **2** and related compounds, and to study their biological properties. We now describe a synthesis of the protected derivative (**15**) of **2**, and its 6-hydroxy analogue **11**.

The condensation of methyl 4-amino-4-deoxy-[5] (**5**) or 4-amino-4,6-dideoxy-α-D-glucopyranoside[6] (**7**) with the 5,7-*O*-benzylidene derivative[7] (**8**) of DL-3,4-di-*O*-acetyl-1,2-anhydro-(1,2,4,6/3,5)-1,2,3,4,5-pentahydroxy-6-hydroxymethylcyclohexane was envisaged as a route to a pseudo-disaccharide structure like **2**. Hydrogenation of methyl 4-azido-4-deoxy-α-D-glucopyranoside[5] (**4**) in methanol in the presence of Raney nickel T-4[8] gave 57% of **5**. Treatment of **4** with sulfuryl chloride (2.5 mol) in pyridine at −10° gave 63% of the 6-chloro-6-deoxy derivative **6**, hydrogenation of which in ethanol, in the presence of Raney nickel and potassium hydroxide, gave 92% of **7**.

Condensation of molar equivalents of **5** and **8** in 2-propanol in a sealed tube

*Synthesis of Pseudo-oligosaccharide Glycosidase Inhibitors, Part IV. For Part III, see ref. 12. For Part II and a preliminary report, see ref. 1.
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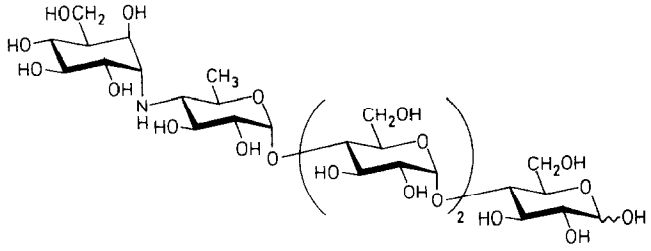

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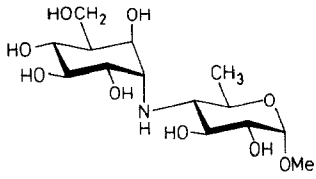

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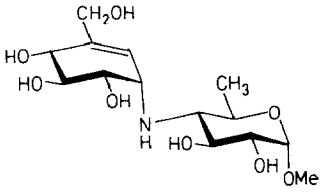

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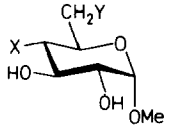
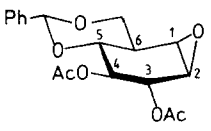


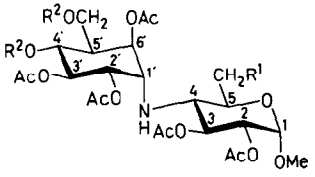
	X	Y
4	N_3	OH
5	NH_2	OH
6	N_3	Cl
7	NH_2	H

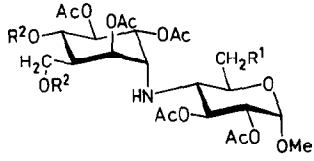


8

at 120° for 5 days, followed by acetylation and column chromatography, afforded two *O*-benzylidenated pseudo-disaccharide derivatives **10** (18%) and **17** (7%); ~50% of **5** was recovered and ~50% of **8** was hydrolysed. A homogeneous mixture of the other products was treated with aqueous acetic acid and then acetylated. Chromatography of the products gave the acetylated pseudo-disaccharide derivatives **11** (16%), $[\alpha]_D$ +101° (chloroform), and **20** (7%), $[\alpha]_D$ +65° (chloroform). Compounds **10** and **17** were similarly converted into the octa-acetates **12**, $[\alpha]_D$ +35° (chloroform), and **19**, $[\alpha]_D$ +77° (chloroform), respectively. Two pairs of diastereoisomers may be obtained by cleavage of the epoxide ring with **5**, when there is no neighbouring-group participation. It is assumed, by analogy with the results of the reaction of **8** with azide ion[7], that the conformation of the cyclohexane ring is fixed by the cyclic acetal group, and that the pseudo-equatorial AcO-3 group cannot attack C-2 and is not a participating group in the reaction of **8** with **5** and **7**. Compounds **11** and **12** gave similar ^{1}H-n.m.r. spectra, as did **19** and **20**,

and it is concluded that they are pairs formed by diaxial and diequatorial ring-opening, respectively. The 200-MHz spectrum of **11** (Table I) supported the structure assigned. In particular, the signal (dd, J 3.6 and 4 Hz) for H-1′*e* at δ 3.45 indicated that **11** and **12** were formed by preferential diaxial-opening of the epoxide ring. In contrast, the signal (t, J 9–9.5 Hz) for H-1′ of **19** and **20** at δ 2.95 indicated an axial,axial,axial arrangement of H-2′,1′,6′. These compounds were derived by diequatorial opening of the epoxide ring, and a neighbouring-group participation mechanism was excluded by analogy with previous work[7] with **8**.

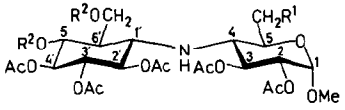


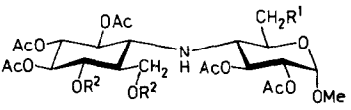


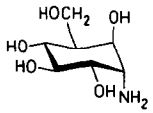
	R^1	R^2		R^1	R^2
9	OAc	>CHPh	**10**	OAc	>CHPh
11	OAc	Ac	**12**	OAc	Ac
13	H	>CHPh	**14**	H	>CHPh
15	H	Ac	**16**	H	Ac

The absolute structures of **11** and **12** were tentatively assigned on the basis of the empirical rules for the optical rotations of cyclitols[9]. Thus, the cyclitol moiety of **11** was deduced to make a dextrorotatory contribution, which was supported by the fact that hydroxyvalidamine[10] (**25**), (1*S*)-(+)-(1,2,4/3,5,6)-2,3,4,6-tetra-hydroxy-5-hydroxymethylcyclohexylamine, has $[\alpha]_D$ +81° (water). The cyclitol moiety of **12** will therefore make a negative contribution, and hence the isomer with the more positive rotation is assigned structure **11**. Similar assignments have been made for related pseudo-di- and -tri-saccharide derivatives[1,11,12]. On the other hand, since the cyclitol moieties of **19** and **20** may have small rotatory contributions[11], the absolute structures could not be assigned.

Condensation of **7** and **8** in 2-propanol, followed by acetylation and chromatography, gave only 16% of the penta-acetate **14**. Mild, acid hydrolysis of the inseparable mixture of **13, 21**, and **22**, followed by acetylation, gave, after







	R^1	R^2		R^1	R^2
17	OAc	>CHPh	**18**	OAc	>CHPh
19	OAc	Ac	**20**	OAc	Ac
21	H	>CHPh	**22**	H	>CHPh
23	H	Ac	**24**	H	Ac

25

TABLE I

^{1}H-N M R DATA (200 MHz, $CDCl_3$) OF COMPOUNDS **11**, **15**, AND **16**

Proton	*Chemical shifts (δ)*			*Coupling constants (Hz)*			
	11	**15**	**16**		**11**	**15**	**16**
H-1	4.85(d)	4.80(d)	4.81(d)	$J_{1,2}$	3.6	3.8	3.6
H-2	4.77(dd)	4.77(dd)	4.75(dd)	$J_{2,3}$	10	9.8	8
H-3	5 32(t)	5.26(t)	5.18(dd)	$J_{3,4}$	10	9.8	10
H-4	2.95(t)	2.58(t)	2.52(t)	$J_{4,5}$	10	9.8	10
H-5	3.69(ddd)	3.61(t)	3.65(dq)	$J_{5,6a}$	2		
H-6a	4.50(dd)			$J_{5,6b}$	5		
H-6b	4.23(dd)			J_{5,CH_3}		6.2	6.2
CH_3		1.33(d)	1.31(d)	J_{6gem}	12		
H-1′	3.45(dd)	3 46(t)	3.34(dd)	$J_{1',2'}$	3.6	3.6	3.6
H-2′	5.14(dd)	5.13(dd)	5.15–5.04	$J_{2',3'}$	10	10	10
H-3′	5.28(dd)	5.31(dd)	5.34(dd)	$J_{3',4'}$	9	9	9
H-4′	5.17(t)	5.12(t)	5.18(t)	$J_{4',5'}$	9	9	9
H-5′	2.65–2.49	2.83–2.66	2.64–2.44	$J_{5',6'}$	—	4	—
H-6′	—	5.17(dd)	5.15–5.04	$J_{1',6'}$	4	3.6	3.6
H-7′a	4.18(dd)	4.09(d)	4.19(dd)	$J_{5',7'a}$	7.4	0	8.4
H-7′b	3.90(dd)	3.96(dd)	3 92(dd)	$J_{5',7'b}$	4	5	4.4
OCH_3	3.38(s)	3.37(s)	3.37(s)	$J_{7'gem}$	11	11.2	11.2
$OCOCH_3$	2.14	2.12	2.11				
	2.12	2.06	2.06[a]				
	2.06	2 02[a]	2.03				
	2.01[a]	1.98	2.01				
	1.97	1.92	1.96				
	1.93						

[a]Singlet for three methyl groups.

chromatography, the hepta-acetates **15** (15%), $[\alpha]_D$ +101° (chloroform); **23** (7%), $[\alpha]_D$ +71° (chloroform); and **24** (7%), $[\alpha]_D$ +67° (chloroform). Compound **14** was converted into **16**, $[\alpha]_D$ +29° (chloroform). Comparison of their ^{1}H-n.m.r. spectra and optical rotations with those of the corresponding 6-acetoxymethyl compounds allowed tentative assignment of their structures. The absolute structures of only **15** and **16** could be deduced.

Attempted acid-catalysed dehydration of crude **2** (obtained from **15**), under conditions similar to those used for **1**, failed.

EXPERIMENTAL

General methods. — Melting points were determined with a Büchi 510 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) with Varian EM-390 (90 MHz) and JEOL FX-200 (200 MHz) spectrometers. T.l.c. was performed on Silica Gel 60 F_{254} (Merck) and column chromatography on Wakogel C-300 (300 Mesh) (Wako Co.).

Organic solutions were dried (Na_2SO_4) and concentrated at <50° under reduced pressure.

Methyl 4-amino-4-deoxy-α-D-glucopyranoside (**5**). — Methyl 4-azido-4-deoxy-α-D-glucopyranoside[5] (**4**; 210 mg, 0.96 mmol) was hydrogenated at room temperature overnight in methanol (6 mL) in the presence of Raney nickel T-4[8] (0.5 mL) at an initial hydrogen pressure of 3.4 kg/cm^2. The product was crystallised from ethanol–2-propanol to give **5** (106 mg, 57%) as needles, m.p. 163–165.5°, $[\alpha]_D^{25}$ +149° (*c* 1, methanol); lit.[5] m.p. 166–166.5°.

Methyl 4-azido-6-chloro-4,6-dideoxy-α-D-glucopyranoside (**6**). — To a stirred solution of **4** (810 mg, 3.7 mmol) in dry pyridine (10 mL) was added sulfuryl chloride (0.8 mL, 10 mmol) dropwise at −10°. After 10 min at −10°, the mixture was poured into ice–water and extracted with ethyl acetate. The extract was concentrated, and the residue was eluted from a column of silica gel with 2-butanone–toluene (1:2) to give **6** (560 mg, 63%) as a white powder, m.p. 144–145°, $[\alpha]_D^{23}$ +240° (*c* 1.1, methanol).

Anal. Calc. for $C_7H_{12}ClN_3O_4$: C, 35.38; H, 5.09; Cl, 14.92; N, 17.68. Found: C, 35.47; H, 5.01; Cl, 15.10; N, 17.71.

Methyl 4-amino-4,6-dideoxy-α-D-glucopyranoside (**7**). — A solution of **6** (884 mg, 3.72 mmol) in ethanol (10 mL) containing potassium hydroxide (0.76 g) was hydrogenated in the presence of Raney nickel T-4 (3 mL) at room temperature for 5 h. The product was eluted from a column of Dowex 50W-X2 (H^+) resin with aqueous 1% ammonia to give **7** (605 mg, 92%) as needles (from chloroform–ether), m.p. 115–116°, $[\alpha]_D^{23}$ +142° (*c* 0.87, water); lit.[6] m.p. 117–118°, $[\alpha]_D^{23}$ +143° (*c* 0.85, water).

4′,7′-O-Benzylidene derivative (**9**) *of methyl 2,3,6-tri-O-acetyl-4-deoxy-4-[(1S)-(1,2,4/3,5,6)-2,3,6-triacetoxy-4-hydroxy-5-hydroxymethyl-1-cyclohexylamino]-α-D-glucopyranoside and its diastereoisomer* (**10**), *5′,7′-O-benzylidene derivative* (**17**) *of methyl 2,3,6-tri-O-acetyl-4-deoxy-4-[(1S)-(1,3,5/2,4,6)-2,3,4-triacetoxy-5-hydroxy-6-hydroxymethyl-1-cyclohexylamino]-α-D-glucopyranoside and its diastereoisomer* (**18**), *methyl 4-deoxy-4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-hydroxymethyl-1-cyclohexylamino]-α-D-glucopyranoside octa-acetate* (**11**) *and its diastereoisomer* (**12**), *and methyl 4-deoxy-4-[(1S)-(1,3,5/2,4,6)-2,3,4,5-tetrahydroxy-6-hydroxymethyl-1-cyclohexylamino]-α-D-glucopyranoside octa-acetate* (**19**) *and its diastereoisomer* (**20**)*. — A mixture of **5** (84 mg, 0.44 mmol) and **8**[7] (153 mg, 0.44 mmol) in 2-propanol (0.8 mL) was heated in a sealed tube at 120° for 117 h and then concentrated, and the residue was treated with acetic anhydride (2 mL) and pyridine (2 mL) at room temperature overnight. The mixture was concentrated and the residue was eluted from a column of silica gel (20 g) with 2-butanone–toluene (2:9). Eluted first was the tetra-acetate (79 mg) formed by hydrolysis of **8** followed by acetylation.

Eluted second was a mixture (77 mg) of **9** and **18**.

*The structures of **17** and **19**, and **18** and **20** may be reversed.

Eluted third was **17** (22 mg, 7%), isolated as prisms (from ethanol), m.p. 201–202°, $[\alpha]_D^{23}$ +82° (*c* 1.1, chloroform).

Anal. Calc. for $C_{33}H_{43}NO_{16}$: C, 55.85; H, 6.11; N, 1.97. Found: C, 55.98; H, 6.01; N, 2.13.

Eluted fourth was **10** (55 mg, 18%), isolated as a white powder, $[\alpha]_D^{23}$ +46° (*c* 2.7, chloroform).

Anal. Found: C, 56.02; H, 6.26; N, 1.92.

Eluted fifth was methyl 4-acetamido-2,3,6-tri-*O*-acetyl-4-deoxy-α-D-glucopyranoside (82 mg, 52%), isolated as a syrup.

Compound **10** (42 mg) was treated with aqueous 80% acetic acid (4 mL) at 90° for 90 min. The mixture was concentrated, the residue was acetylated in the usual way, and the product was eluted from a column of silica gel with chloroform to give **12** (40 mg, 96%) as a syrup, $[\alpha]_D^{23}$ +35° (*c* 2, chloroform). ^{1}H-N.m.r. data (90 MHz): δ 3.36 (s, 3 H, OMe), 3.20 (t, 1 H, $J_{1',2'} = J_{1',6'} = 3.6$ Hz, H-1′), 2.82 (t, 1 H, $J_{3,4} = J_{4,5} = 10$ Hz, H-4 appeared on deuteration), 2.09, 2.08, 2.05, 2.02, 2.00, and 1.95 (6 s, 3, 9, 3, 3, 3, and 3 H, 8 OAc).

Anal. Calc. for $C_{30}H_{43}NO_{18}$: C, 51.06; H, 6.14; N, 1.98. Found: C, 50.84; H, 5.99; N, 1.88.

Compound **17** (50 mg, 0.07 mmol) was similarly *O*-debenzylidenated and then acetylated to give **19** (47 mg, 95%) as a syrup, $[\alpha]_D^{23}$ +77° (*c* 1.1, chloroform). ^{1}H-N.m.r. data (90 MHz): δ 3.32 (s, 3 H, OMe), 2.94 (t, 2 H, *J* 9.5 Hz, H-4,1′), 2.11, 2.07, 2.02, 2.00, 1.99, 1.97, and 1.95 (7 s, 3, 6, 3, 3, 3, 3, and 3 H, 8 OAc).

Anal. Found: C, 50.66; H, 5.83; N, 1.81.

The mixture of **9** and **18** (69 mg, 0.097 mmol) was *O*-debenzylidenated and then acetylated. Elution of the product from a column of silica gel with 2-butanone–toluene (1:3) and recrystallisation of the product from methanol gave **20** (18 mg, 7%) as prisms, m.p. 166–168°, $[\alpha]_D^{23}$ +64.5° (*c* 0.7, chloroform). ^{1}H-N.m.r. data (90 MHz): δ 3.34 (s, 3 H, OMe), 2.95 (t, 2 H, $J_{1',2'} = J_{1',6'} = 9$ Hz, H-1′,4 appeared on deuteration), 2.13, 2.09, 2.06, 2.03, 1.97, and 1.94 (6 s, 3, 6, 3, 3, 3, and 6 H, 8 OAc).

Anal. Found: C, 50.78; H, 6.05; N, 1.99.

The mother liquor of **20** gave **11** (44 mg, 16%) as a syrup, $[\alpha]_D^{23}$ +101° (*c* 1.1, chloroform). For the ^{1}H-n.m.r. data (200 MHz), see Table I.

Anal. Found: C, 51.17; H, 6.19; N, 1.83.

4′,7′-O-Benzylidene derivative (**13**) *of methyl 2,3-di-O-acetyl-4,6-dideoxy-4-[(1S)-(1,2,4/3,5,6)-2,3,6-triacetoxy-4-hydroxy-5-hydroxymethyl-1-cyclohexylamino]-α-D-glucopyranoside and its diastereoisomer* (**14**), *the 5′,7′-O-benzylidene derivative* (**21**) *of methyl 2,3-di-O-acetyl-4,6-dideoxy-4-[(1S)-(1,3,5/2,4,6)-2,3,4-triacetoxy-5-hydroxy-6-hydroxymethyl-1-cyclohexylamino]-α-D-glucopyranoside and its diastereoisomer* (**22**), *methyl 4,6-dideoxy-4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-hydroxymethyl-1-cyclohexylamino]-α-D-glucopyranoside hepta-acetate* (**15**) *and its diastereoisomer* (**16**), *and methyl 4,6-dideoxy-4-[(1S)-(1,3,5/2,4,6)-2,3,4,5-tetrahydroxy-6-hydroxymethyl-1-cyclohexylamino]-α-D-glucopyranoside*

hepta-acetate (**23**) *and its diastereoisomer* (**24**)*. — A mixture of **7** (132 mg, 0.745 mmol) and **8** (311 mg, 0.894 mmol) in 2-propanol (0.8 mL) was heated in a sealed tube at 120° for 40 h and then concentrated, and the residue was acetylated in the usual way. The products were eluted from a column of silica gel (30 g) with 2-butanone–toluene (2:9). Eluted first was **8** (98 mg).

Eluted second was the tetra-acetate (104 mg) formed by hydrolysis of **8** and then acetylation.

Eluted third was a mixture (179 mg) of **13, 21**, and **22**, isolated as a syrup.

Eluted fourth was **14** (78 mg, 16%), isolated as a syrup, $[\alpha]_D^{23}$ +44° (*c* 3.1, chloroform).

Eluted fifth was methyl 4-acetamido-2,3-di-*O*-acetyl-4,6-dideoxy-α-D-gluco-pyranoside (77 mg).

Compound **14** (60 mg, 0.092 mmol) was *O*-debenzylidenated and then acetylated to give **16** (55 mg, 92%) as a syrup, $[\alpha]_D^{23}$ +29° (*c* 1.8, chloroform). For the ^{1}H-n.m.r. data (200 MHz), see Table I.

Anal. Calc. for $C_{28}H_{41}NO_{16}$: C, 51.93; H, 6.38; N, 2.16. Found: C, 52.20; H, 6.38; N, 1.99.

The mixture (175 mg) of **13, 21**, and **22** was *O*-debenzylidenated and then acetylated. The products were eluted from a column of silica gel (9 g) with 2-butanone–toluene (1:5). Eluted first was **15** (70 mg, 15%), isolated as a syrup, $[\alpha]_D^{23}$ +101° (*c* 2.6, chloroform). For the ^{1}H-n.m.r. data (200 MHz), see Table I.

Anal. Found: C, 52.29; H, 6.37; N, 2.00.

Eluted second was **24** (36 mg, 7%), isolated as a syrup, $[\alpha]_D^{23}$ +67° (*c* 1.3, chloroform). ^{1}H-N.m.r. data (90 MHz): δ 3.51 (s, 3 H, OMe), 3.09 (bt, 1 H, $J_{3,4}$ = $J_{4,5}$ = 10.5 Hz, H-4), 2.95 (t, 1 H, $J_{1',2'}$ = $J_{1',6'}$ = 9.7 Hz, H-1'), 2.08, 2.05, 2.04, 1.97, and 1.95 (5 s, 3, 3, 3, 6, and 6 Hz, 7 OAc), 1.28 (d, 3 H, $J_{5,6}$ 6.3 Hz, CMe).

Anal. Found: C, 52.15; H, 6.49; N, 2.16.

Eluted third was **23** (36 mg, 7%), isolated as a syrup, $[\alpha]_D^{23}$ +71° (*c* 1.5, chloroform). ^{1}H-N.m.r. data (90 MHz): δ 3.32 (s, 3 H, OMe), 3.05 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, H-4), 2.58 (t, 1 H, $J_{1',2'}$ = $J_{1',6'}$ = 9.4 Hz, H-1'), 2.08, 2.06, 2.05, 2.02, 1.99, 1.96, and 1.94 (7 s, 3, 3, 3, 3, 3, 3, 3, and 3 H, 7 OAc), 1.34 (d, 3 H, $J_{5,6}$ 6.3 Hz, CMe).

Anal. Found: C, 52.17; H, 6.46; N, 2.16.

ACKNOWLEDGMENT

We thank Mr. Saburo Nakada for elemental analyses.

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*The structures of **21** and **23**, and **22** and **24** may be reversed.

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