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SYNTHESIS AND CRYSTAL STRUCTURES OF 7-ACETAMIDO-7,8-DIDEOXY-1,2:3,4-DI-*O*-ISOPROPYLIDENE-β-L-*threo*-D-*galacto*-OCTOPYRANOSE AND 7-ACETAMIDO-6-*O*-ACETYL-7,8-DIDEOXY-1,2:3,4-DI-*O*-ISOPROPYLIDENE-α-D-*erythro*-D-*galacto*-OCTOPYRANOSE

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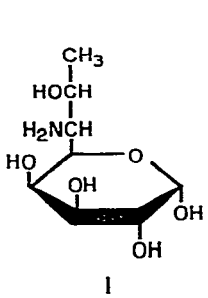
ABSTRACT

7-Acetamido-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*erythro*- (**14**) and -*threo*- and -β-L-*erythro*- and -*threo*- (**17**) octopyranose, intermediates for the synthesis of analogs of the antibiotic lincomycin, have been synthesized from a mixture of 7,8-dideoxy-7-*C*-nitro-octoses prepared from D-galactose. *O*-Acetylation of **14** gave the 6-acetate (**18**). The configurations of C-6 and C-7 in compounds **17** and **18** were determined by X-ray crystallography. The crystals of compound **17** are monoclinic, space group C2, with $Z = 4$, in a unit cell of dimensions $a = 1.825(1)$ nm, $b = 947(1)$ pm, and $c = 1.123(1)$ nm. The crystals of compound **18** are orthorhombic, space group $P2_12_12_1$, with $Z = 12$, in a unit cell of dimensions $a = 2.814(2)$ nm, $b = 1.302(1)$ nm, and $c = 1.713(1)$ nm.

INTRODUCTION

Lincosamine (**1**), an intermediate in the preparation of the antibiotic lincomycin (**2**), has been the subject of several communications[1–7]. The synthesis of the sugar moiety of lincomycin, methyl 6-amino-6,8-dideoxy-1-thio-α-D-*erythro*-D-*galacto*-octopyranoside (**3**), has been reported[8]. Recently, the synthesis of two analogs



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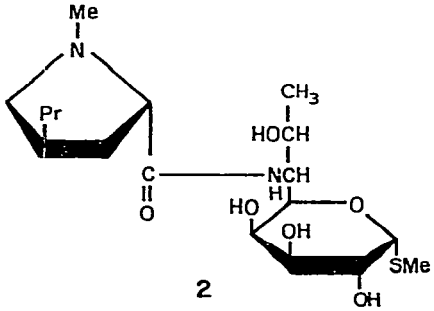

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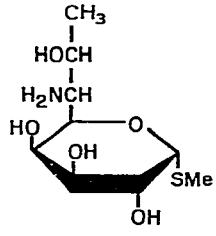
Pr=Me(CH$_2$)$_2$—



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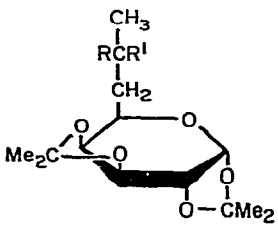
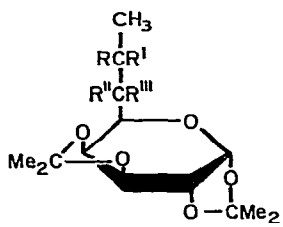
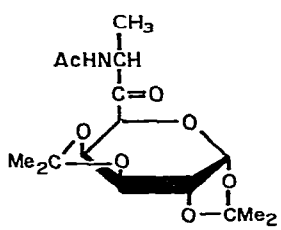
related to lincosamine, namely, 7-acetamido-6,7,8-trideoxy-1,2:3,4-di-*O*-isopropylidene-α-D- and -β-L-*glycero*-D-*galacto*-octopyranoses (**4**) and (**5**), was reported[9]. The configuration of C-7 in the D-*glycero* isomer **4** was determined[9] by X-ray crystallography. The synthesis of four isomers related to lincosamine (**1**), but having the hydroxyl and amino groups at C-6 and C-7, respectively, is described herein. These isomers were characterized as the *N*-acetates.



4 R = NHAc, R^I = H
5 R = H, R^I = NHAc



6 R = NO_2, R^I = H, R^{II} = OH, R^{III} = H
7 R = NO_2, R^I = H, R^{II} = H, R^{III} = OH
8 R = H, R^I = NO_2, R^{II} = H, R^{III} = OH
9 R = H, R^I = NO_2, R^{II} = OH, R^{III} = H
10 R = NH_2, R^I = H, R^{II} = OH, R^{III} = H
11 R = NH_2, R^I = H, R^{II} = H, R^{III} = OH
12 R = H, R^I = NH_2, R^{II} = H, R^{III} = OH
13 R = H, R^I = NH_2, R^{II} = OH, R^{III} = H
14 R = NHAc, R^I = H, R^{II} = OH, R^{III} = H
15 R = NHAc, R^I = H, R^{II} = H, R^{III} = OH
16 R = H, R^I = NHAc, R^{II} = H, R^{III} = OH
17 R = H, R^I = NHAc, R^{II} = OH, R^{III} = H
18 R = NHAc, R^I = H, R^{II} = OAc, R^{III} = H



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RESULTS AND DISCUSSION

Hydrogenation of a mixture of 7,8-dideoxy-7-*C*-nitro-octoses (**6–9**), prepared[5] from D-galactose, in the presence of Raney nickel afforded a mixture of 7-amino-octoses (**10–13**). Compound **10**, 7-amino-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*erythro*-D-*galacto*-octopyranose, was isolated from the mixture of amino-octoses by crystallization. The remaining mixture of amino-octoses was *N*-acetylated, and the products were chromatographed on silica gel, to give 7-acetamido-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*erythro*- and -*threo*- and -β-L-*erythro*- and -*threo*-octopyranose (**14**, **15**, **16**, and **17**, respectively). *N*-Acetylation of compound **10** gave **14**. *O*-Acetylation of **14** gave 7-acetamido-6-*O*-acetyl-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*erythro*-D-*galacto*-octopyranose (**18**). A sample of compound **14** was oxidized with dimethyl sulfoxide–acetic anhydride, to give 7-acetamido-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-octos-6-ulose (**19**). Reduction of the 7-acetamido-octosulose **19** with sodium borohydride gave a mixture of the 7-acetamido-octoses (**14** and **15**). Compounds **14** and **15**, therefore, have the same configuration at C-7 and are isomeric at C-6.

The structures of compounds **17** and **18** were determined by X-ray diffraction studies. Crystal data and details of intensity measurements and data reductions are given in Table I.

The structure of compound **17** was obtained unambiguously by a two-dimensional, direct-methods procedure[10], and refined by full-matrix least-squares. The SHELX-76 program system[11] was used for all crystallographic computations.

TABLE I

CRYSTAL DATA AND DETAILS OF INTENSITY MEASUREMENTS FOR COMPOUNDS **17** AND **18**

Property	*Compound* **17**	*Compound* **18**
Formula	$C_{16}H_{27}NO_7 \cdot 0.5\ H_2O$	$C_{18}H_{29}NO_8$
Space group	C2	$P2_12_12_1$
a	1.825(1) nm	2.814(2) nm
b	947(1) pm	1.302(1) nm
c	1.123(1) nm	1.713(1) nm
β	102.5(1)°	
U	1.895 nm^3	6.276 nm^3
Z	4	12
F(000)	764	2 496
$\mu(MoK_\alpha)$	0.61 cm^{-1}	0.60 cm^{-1}
$\omega/2\theta$ scan	$3 \leqslant \theta \leqslant 20°$	$3 \leqslant \theta \leqslant 22°$
Scan width	0.9°	0.7°
Scan rate	0.03°s^{-1}	0.02°s^{-1}
B.G. scan	30s	35s
Corrections	Lp	Lp
F cut-off	1σ	1.25σ
Observed intensities	1 684	1 029

TABLE II

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$), AND ISOTROPIC, THERMAL PARAMETERS ($\times 10^3$) FOR COMPOUND **17**

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
O-1	1426(2)	3132(8)	2996(4)	[a]
O-2	1198(3)	1827(7)	1253(4)	
O-3	2758(3)	3410(7)	273(4)	
O-4	3600(3)	1789(8)	1269(4)	
O-5	2682(2)	3238(6)	2919(4)	
O-6	3730(3)	0000(0)	3722(4)	
O-7	2461(3)	3510(7)	5973(4)	
O-8	0000(0)	3363(10)	5000(0)	
N	2846(3)	1406(8)	5392(5)	
C-1	1947(4)	3608(9)	2327(6)	47(2)
C-2	1688(4)	2947(10)	1051(7)	53(2)
C-3	2322(4)	2274(10)	582(7)	53(2)
C-4	2889(4)	1408(9)	1520(6)	47(2)
C-5	2840(4)	1760(8)	2824(6)	36(2)
C-6	3549(4)	1459(9)	3763(6)	41(2)
C-7	3502(4)	1956(9)	5035(6)	47(2)
C-8	4212(5)	1604(12)	5995(8)	63(2)
C-9	2368(4)	2219(9)	5841(6)	44(2)
C-10	1709(4)	1514(10)	6206(7)	55(2)
C-11	861(4)	2284(9)	2243(7)	59(2)
C-12	3509(4)	2921(9)	409(6)	54(2)
C-13	166(5)	3184(13)	1744(8)	88(3)
C-14	699(5)	1020(10)	2926(8)	76(3)
C-15	4036(6)	4095(12)	936(10)	79(3)
C-16	3646(7)	2366(13)	−802(10)	87(3)
H-N[b]	2478(58)	587(41)	5311(56)	78(5)[c]
H-O[d]	−278(50)	3799(91)	4397(68)	
H-O-6	3429(36)	−759(62)	3985(57)	
H-1	1977(40)	4865(92)	2274(66)	
H-2	1503(42)	3683(86)	492(68)	
H-3	2115(40)	1741(87)	−150(69)	
H-4	2852(41)	376(91)	1377(71)	
H-5	2361(42)	1228(81)	3041(64)	
H-6	4029(42)	1946(82)	3562(62)	
H-7	3466(39)	2925(94)	5013(61)	
H-8(1)	4600(45)	2257(85)	5829(63)	
H-8(2)	4149(38)	1987(83)	6812(68)	
H-8(3)	4149(38)	1987(83)	6812(68)	
H-10(1)	1389(4)	2166(10)	6698(7)	
H-10(2)	1903(4)	584(10)	6738(7)	
H-10(3)	1358(4)	1203(10)	5344(7)	
H-13(1)	−226(5)	2492(13)	1162(8)	
H-13(2)	323(5)	4031(13)	1205(8)	
H-13(3)	−93(5)	3618(13)	2441(8)	
H-14(1)	450(5)	1399(10)	3654(8)	
H-14(2)	1170(5)	344(10)	3300(8)	
H-14(3)	288(5)	429(10)	2281(8)	
H-15(1)	3948(40)	4214(80)	1753(77)	

TABLE II *(continued)*

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
H-15(2)	4010(42)	4533(88)	208(76)	
H-15(3)	4602(45)	3690(81)	1103(66)	
H-16(1)	4178(43)	1980(84)	−614(63)	
H-16(2)	3591(43)	3131(97)	−1201(67)	
H-16(3)	3250(44)	1674(97)	−1146(65)	

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O-1	42(3)	73(4)	53(3)	−24(3)	−4(2)	−2(3)
O-2	51(3)	77(4)	57(3)	−21(3)	11(2)	−18(3)
O-3	58(3)	58(3)	54(3)	11(3)	5(3)	−5(3)
O-4	57(3)	70(4)	66(3)	27(3)	22(3)	12(3)
O-5	41(3)	34(3)	54(3)	1(3)	−1(2)	−4(2)
O-6	52(3)	30(3)	67(3)	9(3)	19(3)	7(3)
O-7	62(3)	39(3)	79(4)	−9(3)	24(3)	3(3)
O-8	63(5)	56(6)	79(6)	0(0)	−1(5)	0(0)
N	51(4)	33(3)	55(4)	−1(3)	20(3)	1(3)

[a]Anisotropic, thermal-vibration parameters of the oxygen and nitrogen atoms.
The U_{ij} are coefficients in the expression
$T = \exp[-2\pi^2\Sigma_i\Sigma_j h_i h_j a_i^* a_j^* U_{ij}]$.
[b]H of HNAc. [c]Common, isotropic, thermal-vibration parameter for all hydrogen atoms. [d]H of 0.5 H_2O.

In order to locate the hydrogen atoms by difference synthesis, it was necessary to refine the anisotropic, thermal-vibration parameters for all oxygen atoms. The refinement of some hydrogen atoms had to be constrained in order to avoid unrealistic parameter-shifts. Convergence was reached at $R = 0.064$, and the residual electron-density nowhere exceeded 0.04 e.nm^{-3}. The refined parameters are given in Table II. The numbering scheme for non-hydrogen atoms is shown in Fig. 1. Hydrogen atoms are numbered according to the atoms to which they are bonded. The internal, molecular coordinates are shown in Figs. 1–3. These compare well with those[9] of the related 7-acetamido-6,7,8-trideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-octopyranose (**4**). The conformations of the pyranose and isopropylidene rings, as defined[12] by their parameters of pucker[13] (see Table III), are also the same for the two compounds; this was to be expected, as only the side chains are different.

Although a solution to the phase problem for compound **18** was readily found by conventional, direct methods, refinement would not progress beyond $R \sim 0.20$. Careful, photographic re-examination of the crystals showed that this arises from the existence of a superstructure having a *c*-axis three times as long as that initially determined; this is illustrated by the oscillation photograph reproduced as Plate 1. Efforts to record the intensities of the weak layer-lines have thus far not been success-

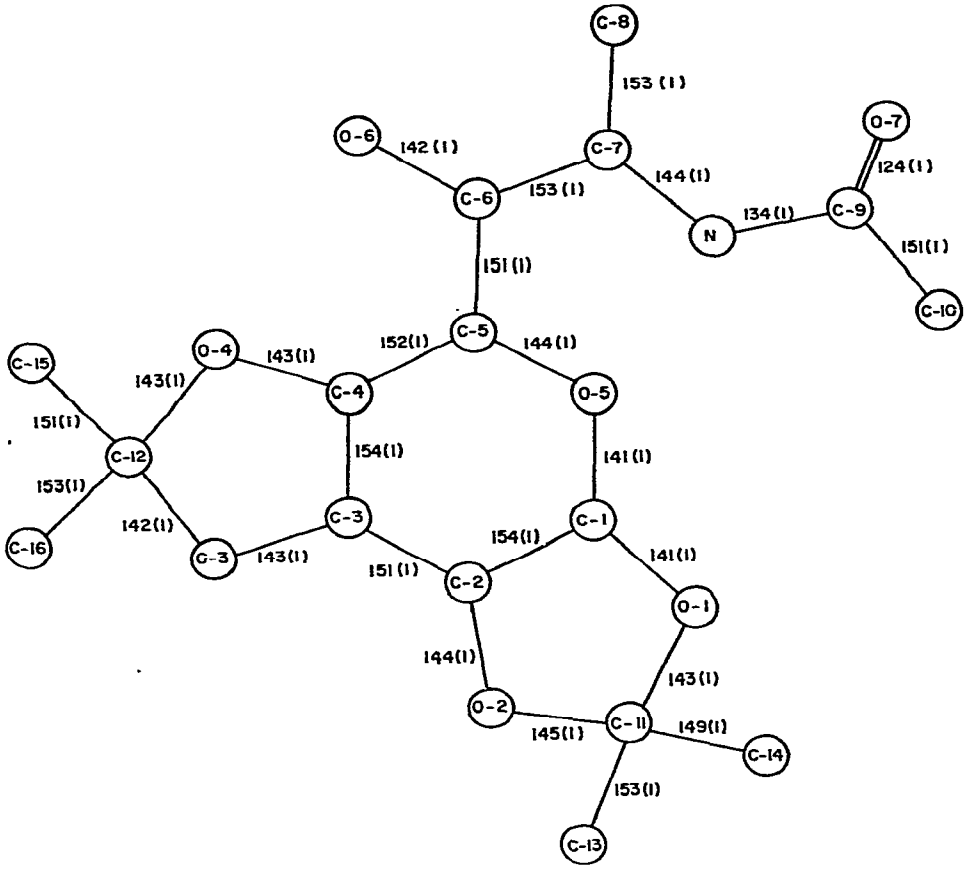

Fig. 1. Compound **17**. (Atom-numbering scheme, and bond lengths in pm.)

ful, and refinement of the tripled asymmetric unit by use of the data available was only partially successful. At $R = 0.145$, the three independent molecules are, however, sufficiently resolved to settle the configurations of C-6 and C-7 in compound **18**.

The preliminary parameters of pucker given in Table III refer to only one of the individuals in the three-fold asymmetric unit, and are given here as a basis for comparison with compound **17**. The side-chain, torsion angles are sufficiently reliable to establish uniquely the configurations of C-6 and C-7 in compound **18**; it is 7-acetamido-6-*O*-acetyl-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*erythro*-D-*galacto*-octopyranose, and compound **17** is 7-acetamido-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-β-L-*threo*-D-*galacto*-octopyranose. Stereoscopic drawings of the molecules of compounds **17** and **18** are provided in Figs. 4 and 5, respectively.

EXPERIMENTAL

General. — Melting points were determined with a Kofler, micro hot-stage

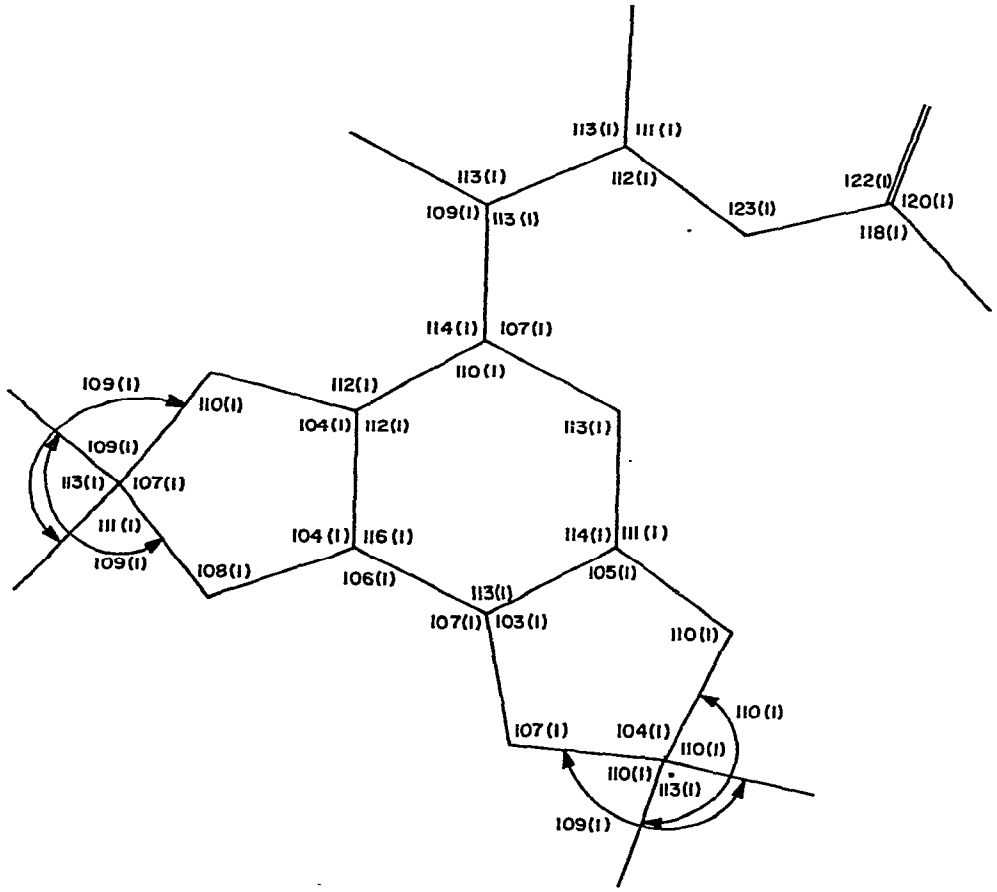

Fig. 2. Bond angles of compound **17**. (The e.s.d. in parentheses refers to the last significant digit.)

apparatus, and are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 polarimeter for solutions in chloroform. I.r. spectra were recorded with a Perkin–Elmer 237 spectrophotometer for 4% dispersions in solid potassium bromide, or 3% solutions in chloroform. P.m.r. spectra were recorded at 35° with a Varian HA-100 spectrometer, for 10% solutions in deuteriochloroform, with tetramethylsilane as the internal reference standard. Coupling constants are given as observed spacings. T.l.c. was performed on plates precoated with a 250-μm layer of Silica Gel 60 F-254 (Merck). Column chromatography was conducted on Silica Gel 60 (70–230 mesh; Merck). The following chromatographic solvents were used: (*A*) 20:1 chloroform–methanol, and (*B*) 2:1 light petroleum–ethyl acetate. The term "light petroleum" refers to the fraction of b.p. 100–120°. Gas–liquid chromatography (g.l.c.) was performed with a Packard 805 chromatograph, with nitrogen as the carrier gas at a flow rate of ~40 ml/min, in a glass column (180 × 0.3 cm) of 1.5% (w/w) of neopentyl glycol succinate supported on Chromosorb W (80–100 mesh), at 215°. Retention times (*T*) are given relative to that of 1,3,5-trinitrobenzene (*T* =

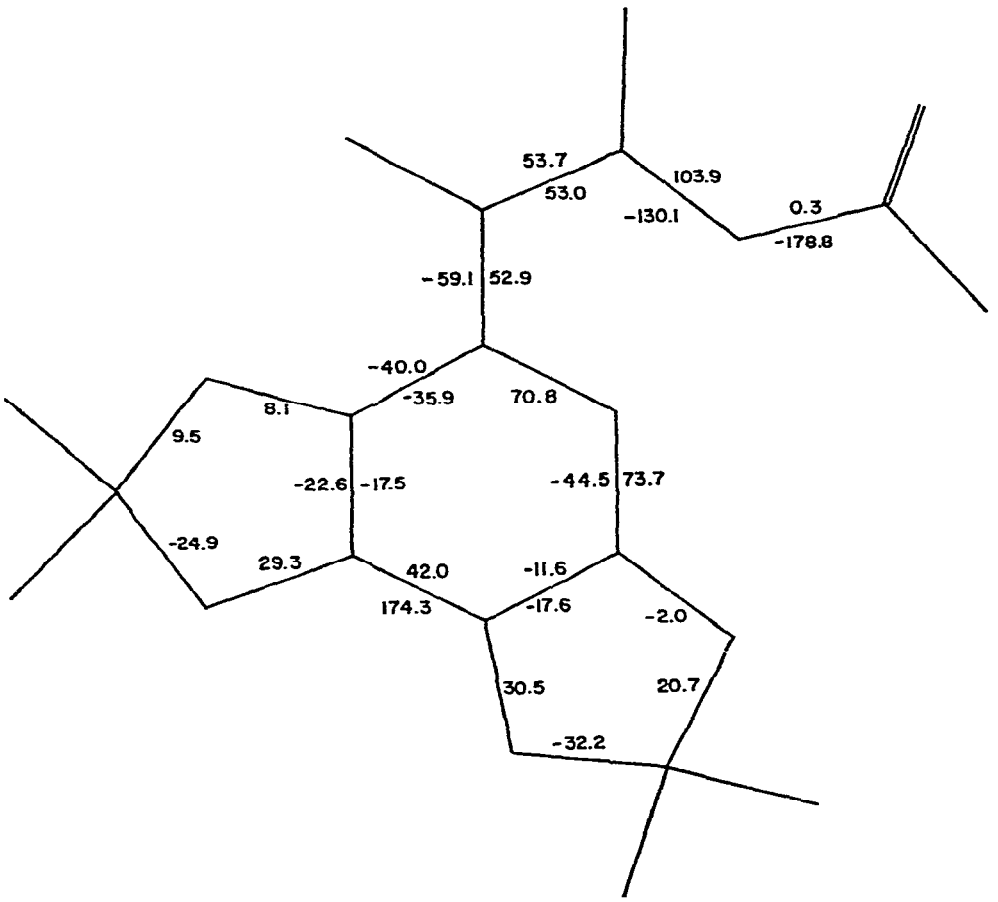

Fig. 3. A selection of torsion angles that define the conformation of compound **17**.

TABLE III

POLAR PARAMETERS OF PUCKERING, AND CONFORMATIONS, OF COMPOUNDS **17** AND[12] **18**

Compound	*Ring*	*Q (pm)*	*θ (degrees)*	*φ (degrees)*	*Conformation*
17	Pyranose (O-5–C-1–C-2–C-3–C-4–C-5)	65	81	332	$^1S_6 \leftrightarrow {}^1T_3$
	1,2-isopropylidene (O-1–C-11–O-2–C-2–C-1)	30		250	$_3{}^2T \leftrightarrow {}_3E$
	3,4-isopropylidene (O-3–C-12–O-4–C-4–C-3)	27		342	$_5{}^1T$
18	Pyranose	77	70	309	$^1S_6 \leftrightarrow {}^1T_3 \leftrightarrow B_{3,6}$
	1,2-isopropylidene	65		223	$_3{}^2T \leftrightarrow {}^2E$
	3,4-isopropylidene	66		360	^1E

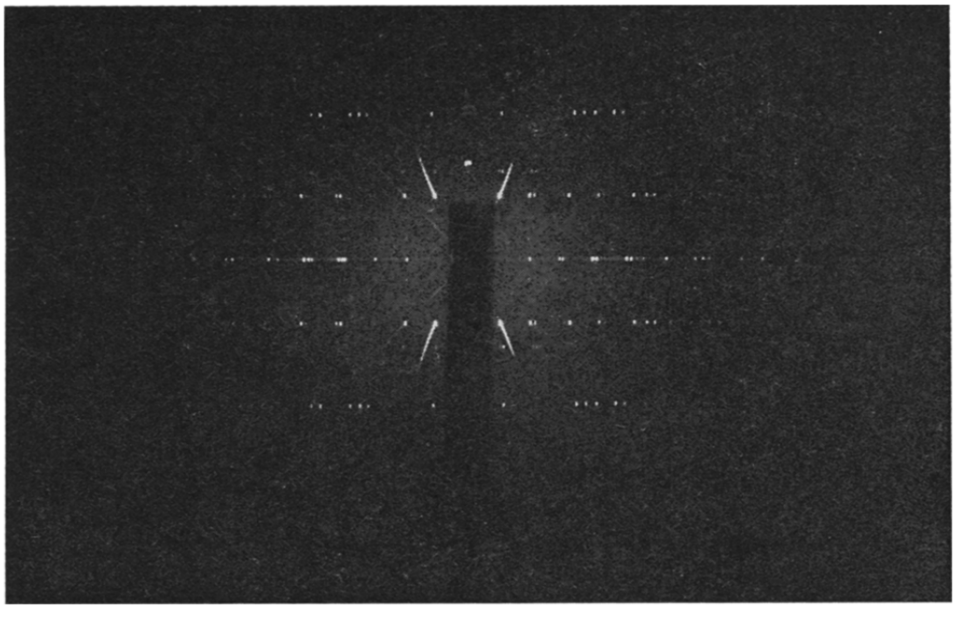

Plate 1. Oscillation photograph of the X-ray diffraction pattern exhibited by crystals of compound **18**.

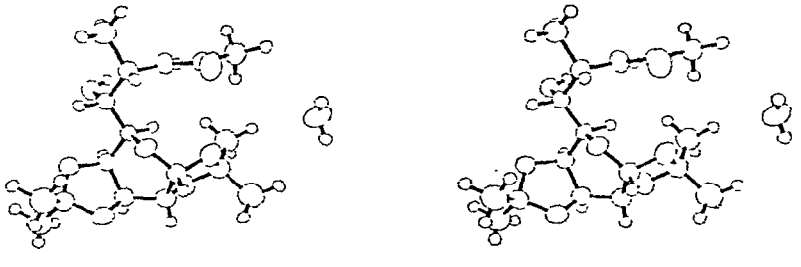

Fig. 4. A stereoscopic drawing of a molecule of compound **17**.

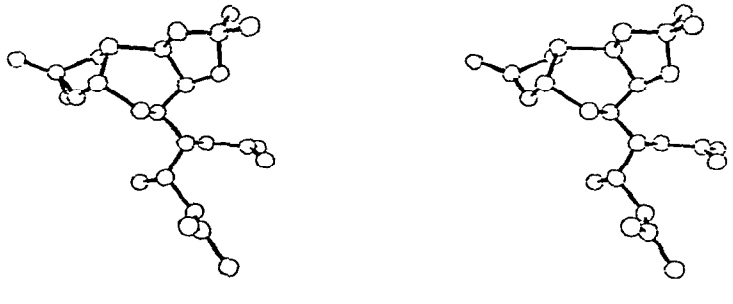

Fig. 5. A stereoscopic drawing of a molecule of compound **18**.

1.00). Mass spectra were recorded with an A.E.I. MS9 instrument, using the direct-insertion method. Crystallographic examinations were carried out in a Philips PW1100 diffractometer equipped with a graphite-crystal monochromator, and MoKα radiation was used.

*7-Acetamido-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-*D-erythro- *and* -threo- *and* -β-L-erythro- *and* -threo-D-galacto-*octopyranose* (**14**, **15**, **16**, and **17**). — To a solution of a mixture (6.0 g) of the isomeric nitro-octoses[5] (**6–9**, prepared from D-galactose) in methanol (200 ml) was added freshly prepared Raney nickel (1 g), and the mixture was shaken under hydrogen at atmospheric pressure for 40 h. The suspension was filtered, and the filtrate was evaporated to a syrup. A solution of the residue in chloroform was extracted with iced, M sulfuric acid, and the extract was made alkaline with M sodium hydroxide, and extracted with chloroform. The extract was washed with water, dried (Na_2SO_4), and evaporated, to give a mixture of amines **10–13** (4.2 g, 77%), part of which crystallized from ethyl acetate–light petroleum. Recrystallization from the same solvent mixture gave the amino-octose **10** as needles (620 mg), m.p. 133–134°, $[\alpha]_D^{20}$ −62° (*c* 2.6); ν_{max}^{KBr} 3600–3300 (OH, NH_2), 1380 and 1370 cm^{-1} (CMe_2); *m/e* 303 (M^+), 288 (M^+ − 15); p.m.r. data: τ 4.51 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 5.38 (q, 1 H, $J_{3,4}$ 7.8 Hz, H-3), 5.55 (q, 1 H, $J_{4,5}$ 1 Hz, H-4), 5.71 (q, 1 H, $J_{2,3}$ 2.0 Hz, H-2), 6.32 (m, 2 H, H-5,6), 6.73 (m, 1 H, H-7), 7.75 (br s, 3 H, D_2O-exchangeable, OH-6, NH_2-7), 8.47, 8.54, 8.63, and 8.68 (4 s, 3 H each, 2 CMe_2), and 8.93 (d, 3 H, $J_{7,8}$ 6.0 Hz, Me-7); c.d. [*c* 1.33 mg.mol.L^{-1}; 21°; carbon tetrachloride containing Pr(dmp)$_3$]: Δε (340 nm) 0, (321) −0.66, (314) 0, (300) + 3.01, and (290)0.

Anal. Calc. for $C_{14}H_{25}NO_6$: C, 55.4; H, 8.3; N, 4.6. Found: C, 55.4; H, 8.4; N, 4.6.

The mother liquor from **10** was evaporated to a syrup. To a solution of the mixed amines (**10–13**) in methanol (75 ml) was added acetic anhydride (4 ml), and the mixture was kept for 2 h at room temperature. Pyridine (4 ml) was added, and the solvents were removed under diminished pressure. The residue was partitioned between chloroform and iced, M sulfuric acid. The chloroform layer was successively washed with saturated sodium hydrogencarbonate solution and water, dried (Na_2SO_4), and evaporated. The resulting syrup was applied to a column of silica gel (1.5 kg), and eluted with solvent *A*.

The D-*threo* isomer **15** (50 mg) was obtained as a syrup, $[\alpha]_D^{20}$ −12° (*c* 0.6); R_F 0.42 (solvent *A*); $\nu_{max}^{CHCl_3}$ 3600–3200 (OH, NH), 1660 (Amide I), 1523 (Amide II), 1381 and 1370 cm^{-1} (CMe_2); *m/e* 330 (M^+ − 15); p.m.r. data: τ 4.07 (d, 1 H, D_2O-exchangeable, $J_{NH,7}$ 9.0 Hz, NH-7), 4.48 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 5.44 (q, 1 H, $J_{3,4}$ 7.7 Hz, H-3), 5.63 (q, 1 H, $J_{4,5}$ 1.8 Hz, H-4), 5.71 (q, 1 H, $J_{2,3}$ 2.5 Hz, H-2), 5.78 (m, 1 H, $J_{7,8}$ 4.0 Hz, $J_{7,NH}$ 9.0 Hz, H-7), 6.21 (q, 1 H, $J_{6,7}$ 1.7 Hz, H-6), 6.44 (q, 1 H, $J_{5,6}$ 8.5 Hz, H-5), 7.69 (br s, 1 H, D_2O-exchangeable, OH-6), 8.06 (s, 3 H, NAc-7), 8.54 and 8.58 (2s, 3 H each, CMe), and 8.69–8.78 (m, 9 H, CMe, Me-7); c.d. (*c* 909.0 μg.mol.L^{-1}; 20°, MeOH); Δε (230 nm) 0, (220) 0.23, (210) 0.43, and (205) 0.66.

Anal. Calc. for $C_{15}H_{24}NO_7$ (M^+ − 15): *m/e* 330.155. Found: *m/e* 330.155.

The L-*erythro* isomer **16** (80 mg), a syrup, had $[\alpha]_D^{20}$ −40° (c, 1.8); R_F 0.39 (solvent *A*); ν_{max}^{KBr} 3550–3270 (OH, NH), 1640 (Amide I), 1525 (Amide II), 1380 and 1370 cm^{-1} (CMe_2); *m/e* 345 (M^+), 330 (M^+ − 15); p.m.r. data: τ 3.68 (d, 1 H, D_2O-exchangeable, $J_{NH,7}$ 9.0 Hz, NH-7), 4.44 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 5.43 (q, 1 H, $J_{3,4}$ 8.0 Hz, H-3), 5.69 (q, 1 H, $J_{2,3}$ 2.5 Hz, H-2), 5.77 (q, 1 H, $J_{4,5}$ 1.7 Hz, H-4), 5.84 (m, 1 H, $J_{7,8}$ 7.0 Hz, H-7), 6.11 (q, 1 H, $J_{6,7}$ 3.2 Hz, H-6), 6.29 (q, 1 H, $J_{5,6}$ 5.5 Hz, H-5), 6.99 (br s, 1 H, D_2O-exchangeable, OH-6), 8.04 (s, 3 H, NAc-7), 8.50, 8.56 (2s, 3 H each) and 8.68 (s, 6 H, 2 CMe_2), and 8.85 (d, 3 H, Me-7); c.d. (*c* 1.44 mg.mol. L^{-1}; 20°; MeOH): Δε (237 nm) 0, (220) −0.49, (205) −0.90, and (202) −0.74.

Anal. Calc. for $C_{15}H_{24}NO_7$ (M^+ − 15): *m/e* 330.155. Found: *m/e* 330.155.

The L-*threo* isomer **17** (1.4 g) crystallized from ethyl acetate–light petroleum as needles, m.p. 155–157°, $[\alpha]_D^{20}$ −91° (*c* 0.7); R_F 0.32 (solvent *A*); *T* 3.0; $\nu_{max}^{CHCl_3}$ 3610 (OH), 3435 (NH), 1655 (Amide I), 1510 (Amide II), 1382 and 1372 cm^{-1} (CMe_2); *m/e* 345 (M^+), 330 (M^+ − 15); p.m.r. data; τ 3.68 (d, 1 H, D_2O-exchangeable, $J_{NH,7}$ 8.0 Hz, NH-7), 4.52 (d, 1 H, $J_{1,2}$ 5.3 Hz, H-1), 5.39 (q, 1 H, $J_{3,4}$ 7.8 Hz, H-3), 5.55 (q, 1 H, $J_{4,5}$ 1.6 Hz, H-4), 5.71 (q, 1 H, $J_{2,3}$ 2.2 Hz, H-2), 5.97 (m, 1 H, $J_{7,8}$ 7.0 Hz, $J_{7,NH}$ 8.0 Hz, H-7), 6.31 (m, 2 H, H-5,6), 7.73 (br s, 1 H, D_2O-exchangeable, OH), 8.04 (s, 3 H, NAc-7), 8.52, 8.56, 8.65, and 8.68 (4 s, 3 H each, 2 CMe_2), and 8.72 (d, 3 H, Me-7); c.d. (*c* 986.7 μg.mol.L^{-1}; 20°; MeOH): Δε (238 nm) 0, (206) −2.73, and (203) −2.43.

Anal. Calc. for $C_{16}H_{27}NO_7 \cdot 0.5\ H_2O$: C, 54.2; H, 8.0; N, 3.9. Found: C, 54.4; H, 7.9; N, 3.7.

The D-*erythro* isomer **14** (1.1 g) crystallized from ethyl acetate–light petroleum as needles, m.p. 171–172°, $[\alpha]_D^{20}$ −43° (*c*, 1.1); R_F 0.26 (solvent *A*); *T* 3.5; $\nu_{max}^{CHCl_3}$ 3620 (OH), 3435 (NH), 1655 (Amide I), 1512 (Amide II), 1382 and 1375 cm^{-1} (CMe_2); *m/e* 345 (M^+), 330 (M^+ − 15); p.m.r. data: τ 3.97 (d, 1 H, D_2O-exchangeable, $J_{NH,7}$ 8.1 Hz, NH-7), 4.49 (d, 1 H, $J_{1,2}$ 5.2 Hz, H-1), 5.37 (q, 1 H, $J_{3,4}$ 8.0 Hz, H-3), 5.55 (q, 1 H, $J_{4,5}$ 1.8 Hz, H-4), 5.69 (q, 1 H, $J_{2,3}$ 2.2 Hz, H-2), 5.82 (m, 1 H, $J_{7,8}$ 7.1 Hz, H-7), 6.12 (q, 1 H, $J_{6,7}$ 2.5 Hz, H-6), 6.37 (q, 1 H, $J_{5,6}$ 8.8 Hz, H-5), 8.02 (s, 3 H, NAc-7), 8.49, 8.56, 8.64, 8.68 (4 s, 3 H each, 2 CMe_2), and 8.77 (d, 3 H, Me-7); c.d. (*c* 1.047 mg.mol.L^{-1}; 20°; MeOH): Δε (238 nm) 0, (220) −0.37, (213) −0.58, and (208) −0.26.

Anal. Calc. for $C_{16}H_{27}NO_7$: C, 55.6; H, 7.9; N, 4.1. Found: C, 55.9; H, 7.9; N, 4.1.

N-Acetylation of the amino-octose **10** gave a crystalline product, identical in all respects with compound **14**.

*7-Acetamido-6-O-acetyl-7,8-dideoxy-1,2:3,4-di-O-isopropylidene-α-*D-erythro-D-galacto-*octopyranose* (**18**). — To a solution of compound **14** (250 mg) in pyridine (3 ml) was added acetic anhydride (4 ml), and the mixture was stirred for 24 h at 25°. The solvents were removed under diminished pressure, and the residue was applied to a column of silica gel (100 g), which was eluted with solvent *B*. The 6-acetate **18** (230 mg) crystallized from ethyl acetate–light petroleum as needles, m.p. 107–108°, $[\alpha]_D^{20}$ −82° (*c* 1.0); R_F 0.36 (solvent *A*); $\nu_{max}^{CHCl_3}$ 3410 (NH), 1734 (ester

CO), 1665 (Amide I), 1512 (Amide II), 1383 and 1372 cm^{-1} (CMe_2); *m/e* 372 (M^+ — 15), 327 (M^+ — 60); p.m.r. data: τ 3.73 (d, 1 H, D_2O-exchangeable, $J_{NH,7}$ 8.5 Hz, NH-7), 4.45 (d, 1 H, $J_{1,2}$ 5.2 Hz, H-1), 4.97 (q, 1 H, $J_{5,6}$ 9.5 Hz, H-5), 5.38 (q, 1 H, $J_{3,4}$ 7.9 Hz, H-3), 5.50 (m, 1 H, H-7), 5.65 (q, 1 H, $J_{2,3}$ 2.4 Hz, H-2), 5.79 (q, 1 H, $J_{4,5}$ 2.0 Hz, H-4), 6.15 (q, 1 H, $J_{6,7}$ 1.6 Hz, H-6), 7.92 (s, 3 H, OAc-6), 8.05 (s, 3 H, NAc-7), 8.44, 8.56, 8.65, and 8.68 (4 s, 3 H each, 2 CMe_2), and 8.80 (d, 3 H, Me-7).

Anal. Calc. for $C_{18}H_{29}NO_8$: C, 55.8; H, 7.6; N, 3.6. Found C, 55.9; H, 7.6; N, 3.5.

*7-Acetamido-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-*α*-*D*-glycero-*D*-galacto-octos-6-ulose* (**19**). — To a solution of compound **14** (106 mg) in dimethyl sulfoxide (2 ml) was added acetic anhydride (2 ml), and the mixture was kept for 2 h at 25°. Iced water (5 ml) was added, and the solution was freeze-dried. A solution of the residue in chloroform was washed with water, dried (Na_2SO_4), and filtered, and the filtrate was evaporated to a syrup (86 mg); R_F 0.55 (solvent *B*); ν_{max}^{film} 3340 (NH), 1725 (C=O), 1660 (Amide I), 1520 (Amide II), 1382 and 1372 cm^{-1} (CMe_2); *m/e* 343 (M^+), 328 (M^+ — 15).

Reduction of compound **19**. — A solution of the 7-acetamido-octosulose **19** (75 mg) in aqueous methanol was treated with sodium borohydride (50 mg) for 20 min at 25°. Acetone was added, and the solvents were removed under diminished pressure. Water (5 ml) was added to the residue, the mixture was extracted with chloroform, and the extract was washed with water, dried (Na_2SO_4), and evaporated. The resulting syrup was applied to a column of silica gel (60 g), which was eluted with solvent *A*. The two different products (8 mg) and (49 mg) were identical (by R_F, i.r., m.s.) with compounds **14** and **15**, respectively.

The table of structure factors is deposited with, and can be obtained from, Elsevier Scientific Publishing Company, BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands: reference should be made to No. BBA/DD 094, *Carbohydr. Res.*, 70 (1979) 103–115.

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