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SYNTHESIS AND CRYSTAL STRUCTURE OF 7-ACETAMIDO-6,7,8-TRIDEOXY-1,2:3,4-DI-*O*-ISOPROPYLIDENE-α-D-*glycero*-D-*galacto*-OCTOPYRANOSE

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ABSTRACT

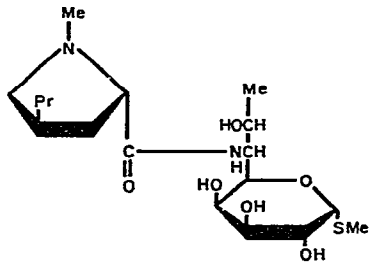
7-Acetamido-6,7,8-trideoxy-1,2:3,4-di-*O*-isopropylidene-α-D- and -β-L-*glycero*-D-*galacto*-octopyranoses (**8**) and (**9**), intermediates for the synthesis of analogs of the antibiotic lincomycin, have been synthesized from *cis*-6,7,8-trideoxy-1,2:3,4-di-*O*-isopropylidene-7-*C*-nitro-α-D-*galacto*-oct-6-enose (**4**). The configuration of C-7 in compound **8** was determined by X-ray crystallography. The crystals are orthorhombic, space group $P2_12_12_1$ with $Z = 4$, in a unit cell of dimensions $a = 2.457(1)$ nm, $b = 1.380(1)$ nm, and $c = 526(1)$ pm. The conformation of compound **8** in the solid state is ${}^{\circ}S_2$, slightly distorted towards ${}^{\circ}H_5$.

INTRODUCTION

Lincomycin (**1**) is an antibiotic produced by the actinomycete *Streptomyces lincolnensis* var. *lincolnensis*[1]. Several approaches towards synthesis of lincosamine (**2**), an intermediate in the synthesis of lincomycin, have been reported[2–8]. A total synthesis of methyl 6-amino-6,8-dideoxy-1-thio-α-D-*erythro*-D-*galacto*-octopyranoside (**3**), the sugar portion of lincomycin, has been described[9]; compound **3** was acylated[10] with L-*trans*-4-propylhygric acid[11] to give lincomycin. Structural modifications of lincomycin have been reviewed[12]. The sugar moiety has been modified by esterification[12], and by varying the substituents[12–15] at C-1, C-2, and C-7. Analogs of lincomycin having different configurations[12,16] at C-2, C-3, C-4, and C-5 have been prepared. A number of syntheses of derivatives of lincosamine, isomeric at C-6 and C-7, have been reported[2,5,8,9,12,14,17]. The amino acid component of lincomycin has been modified by varying the alkyl substituents[12] at N-1′ and C-4′. Syntheses of *C*-3′- and *C*-5′-alkyl-*C*-4′-depropyl-lincomycins have been reported[12].

RESULTS AND DISCUSSION

The starting material in the present synthesis, *cis*-6,7,8-trideoxy-1,2:3,4-di-*O*-isopropylidene-7-*C*-nitro-α-D-*galacto*-oct-6-enose (**4**), prepared[6] from D-galactose,



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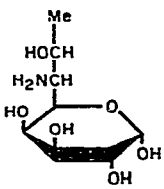

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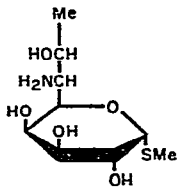

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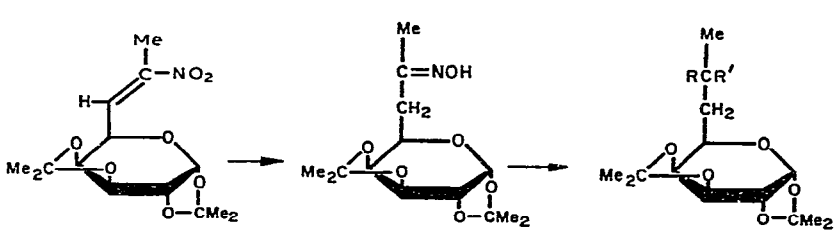
was hydrogenolyzed in the presence of palladium-on-charcoal, to give 6,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-octos-7-ulose oxime (**5**). Catalytic hydrogenation of compound **5** afforded a mixture of the D- and L-*glycero* amines (**6** and **7**, respectively). The mixture of amines was *N*-acetylated, and the products were chromatographed on silica gel, to give the 7-acetamido-6,7,8-trideoxy-1,2:3,4-di-*O*-isopropylidene-α-D- and -β-L-*glycero*-D-*galacto*-octopyranoses (**8**) and (**9**), respectively, in the ratio 3.3:2.

The structure of compound **8** was determined by X-ray diffraction studies, and solved by direct methods using a two-dimensional routine[18] that requires the unit-cell origin at $\frac{1}{4},0,0$ with respect to the standard setting of the space group ($P2_12_12_1$) according to the *International Tables*[19]. With this choice of origin, the equivalent positions of the space group are: x, y, z; $\bar{x}, \bar{y}, \frac{1}{2} + z$; $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$; and $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.



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6 R = NH_2, R′ = H
7 R = H, R′ = NH_2
8 R = NHAc, R′ = H
9 R = H, R′ = NHAc

TABLE I

FRACTIONAL, ATOMIC COORDINATES ($\times 10^4$) AND ISOTROPIC, THERMAL PARAMETERS ($\times 10^3$) FOR COMPOUND **8**

Atom[a]	*x/a*	*y/b*	*z/c*	U_{iso}
O-1	6427(3)	9055(5)	2381(14)	
O-2	5740(3)	9459(5)	−304(16)	
O-3	4826(3)	7752(6)	2616(18)	
O-4	5093(3)	6521(5)	32(17)	
O-5	6062(3)	7515(5)	2700(13)	
O-6	6991(4)	4757(6)	4121(14)	
N	6975(4)	5127(7)	−38(22)	59(3)
C-1	5967(6)	8497(10)	3154(24)	47(3)
C-2	5488(4)	8940(8)	1715(22)	48(3)
C-3	5116(5)	8195(9)	562(25)	53(3)
C-4	5398(5)	7355(9)	−692(23)	47(3)
C-5	5995(4)	7256(8)	14(24)	48(3)
C-6	6213(5)	6243(9)	−318(27)	56(4)
C-7	6825(4)	6147(8)	235(25)	51(3)
C-8	7188(6)	6764(12)	−1404(31)	76(5)
C-9	7039(5)	4502(8)	1910(26)	51(3)
C-10	7194(5)	3479(8)	1171(24)	62(4)
C-11	6257(4)	9793(8)	600(24)	52(3)
C-12	4676(5)	6802(10)	1805(29)	80(4)
C-13	6665(5)	9836(9)	−1506(25)	69(4)
C-14	6190(5)	10742(9)	1964(28)	74(4)
C-15	4145(6)	6796(12)	539(35)	111(6)
C-16	4738(8)	6060(14)	3900(39)	147(7)
H-N[b]	7073(45)	4914(83)	−1299(222)	89(9)
H-1	5997(58)	8511(101)	4529(217)	
H-2	5264(40)	9456(78)	3135(235)	
H-3	4787(44)	8586(79)	−596(243)	
H-4	5409(45)	7358(88)	−2265(269)	
H-5	6261(46)	7671(81)	−700(244)	
H-6(1)	5967(45)	5790(81)	662(256)	
H-6(2)	6173(48)	6004(89)	−1788(252)	
H-7	6876(42)	6369(78)	1988(242)	
H-8(1)	7038(41)	7542(81)	−376(241)	
H-8(2)	7115(49)	6905(94)	−2950(265)	
H-8(3)	7514(48)	6751(80)	−1034(239)	
H-10(1)	7173(5)	3445(8)	−879(24)	
H-10(2)	6915(5)	2958(8)	1980(24)	
H-10(3)	7603(5)	3314(8)	1785(24)	
H-11(1)	6512(5)	10433(9)	−2625(25)	
H-11(2)	6715(5)	9208(9)	−2709(25)	
H-11(3)	7054(5)	10032(9)	−691(25)	
H-14(1)	6585(5)	10931(9)	2707(28)	
H-14(2)	5900(5)	10702(9)	3508(28)	
H-14(3)	6060(5)	11288(9)	621(28)	
H-15(1)	3890(6)	6999(12)	2125(35)	
H-15(2)	4108(6)	6027(12)	201(35)	
H-15(3)	4018(6)	7187(12)	−1139(35)	
H-16(1)	4442(8)	6538(14)	4756(39)	
H-16(2)	5093(8)	6016(14)	5108(39)	
H-16(3)	4563(8)	5347(14)	3677(39)	

[a]Atoms are numbered as shown in Fig. 1. [b]H of HNAc.

TABLE II

ANISOTROPIC, THERMAL PARAMETERS ($U_{ij} \times 10^3$) OF THE OXYGEN ATOMS OF COMPOUND **8**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O-1	53(4)	54(4)	54(5)	11(5)	−17(4)	−11(4)
O-2	51(4)	50(4)	37(4)	3(4)	−3(4)	−11(4)
O-3	51(5)	52(5)	74(6)	2(5)	2(5)	−14(4)
O-4	85(5)	77(6)	76(6)	−32(6)	38(6)	−36(5)
O-5	60(4)	42(4)	33(4)	2(4)	−6(4)	−4(4)
O-6	97(7)	85(6)	29(5)	2(5)	1(5)	−3(6)

After anisotropic refinement of the oxygen thermal-parameters, the hydrogen atoms were all located on difference Fourier maps. A common, isotropic, thermal parameter was refined for all hydrogen atoms, and the coordinates of those on some of the methyl groups had to be constrained to ensure meaningful refinement. At the termination of refinement, when all parameter shifts were less than 0.1 of a standard deviation, the maximum excursions from zero nowhere exceeded 0.03 electron.nm^{-3} (0.3 e.Å^{-3}). The final, conventional $R = 0.077$. The refined parameters are listed in Tables I and II, according to the numbering scheme shown in Fig. 1.

The molecular parameters calculated are shown in Figs. 1–3. A stereoscopic view of the molecule is provided in Fig. 4, which shows that compound **8** has the D-*glycero* configuration at C-7, and is therefore 7-acetamido-6,7,8-trideoxy-1,2:3,4-

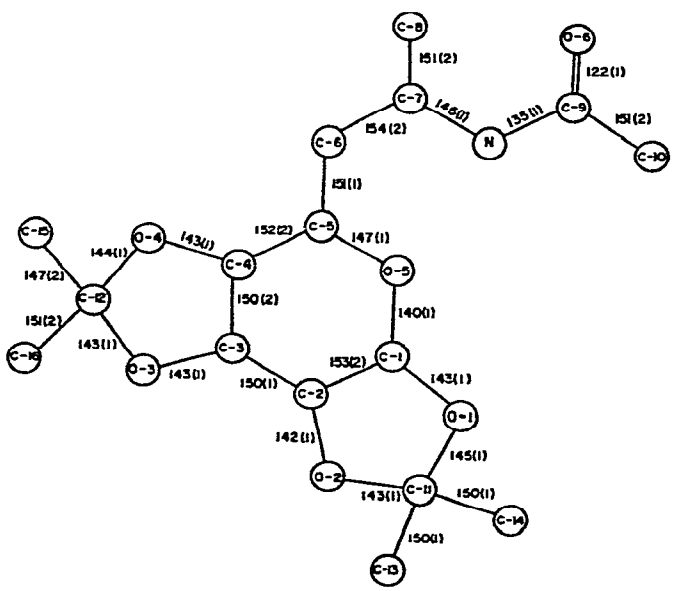

Fig. 1. Compound **8**. (Atomic numbering scheme, and bond lengths in pm.)

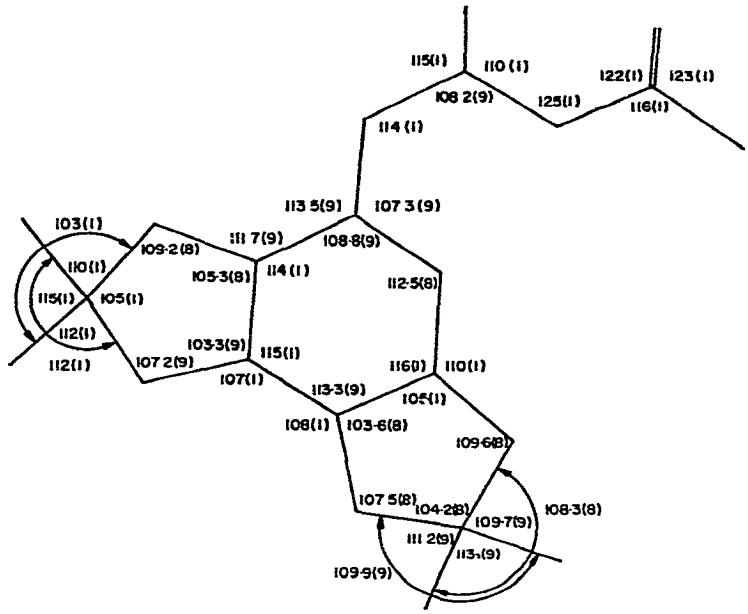

Fig. 2. Bond angles of compound 8. (The estimated s.d. in parentheses refers to the last significant digit.)

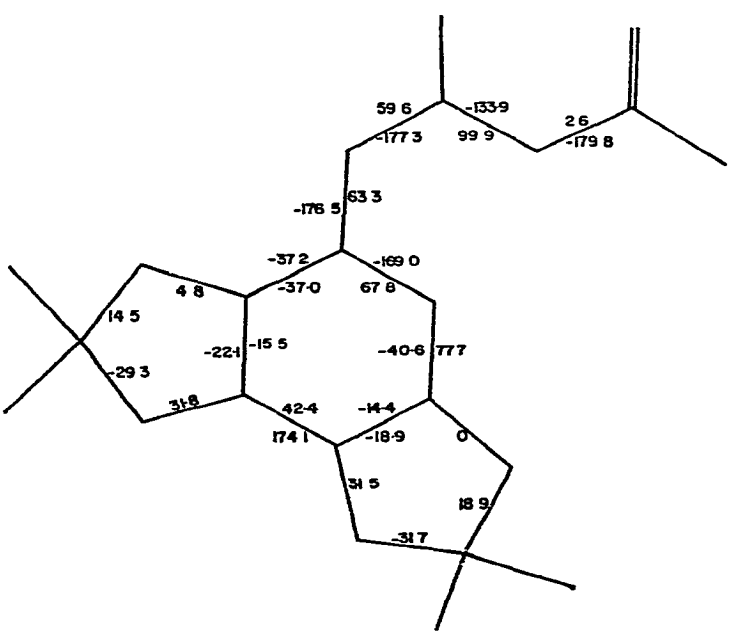

Fig. 3. A selection of torsion angles that define the conformation of compound 8.

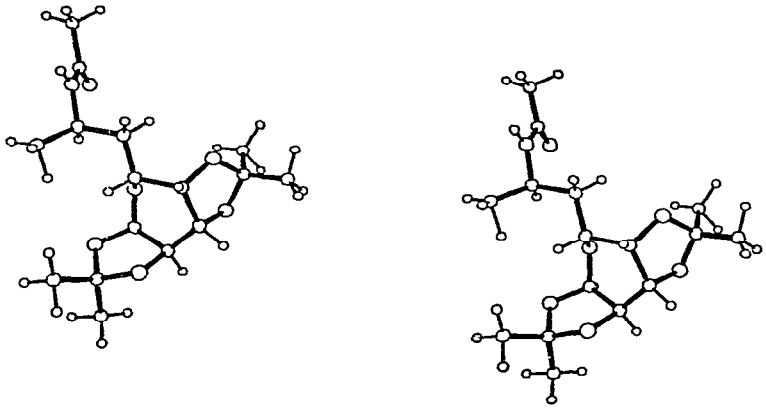

Fig. 4. A stereoscopic drawing of the molecule of compound **8**.

di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-octopyranose. Compound **9** (being isomeric with compound **8** at C-7) is 7-acetamido-6,7,8-trideoxy-1,2:3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-octopyranose.

The bond lengths and angles are in excellent agreement with the mean values[20] derived from several analyses on related compounds, and also with those for the only other di-*O*-isopropylidene-*galacto*-octopyranose whose structure is known[20,21].

The conformation of compound **8** was analyzed by using a computer program based on the method of Cremer and Pople[22] for the calculation of parameters of puckering. The polar parameters for the pyranose ring are Q = 65 pm, $\phi(2) = 329°$, and $\theta = 81°$. These establish the conformation[23] as ${}^{\circ}S_2$ ($\phi = 330°$, $\theta = 90°$), slightly distorted towards ${}^{\circ}H_5$ ($\theta = 51°$), which is drastically different from the chair conformation of α-D-galactopyranose[24]. This difference is caused by the presence of the two isopropylidene rings. In the comparable dithiepan derivative[20], the pyranose ring is even more distorted, but, as discussed later, this is caused by steric factors.

The same method[22] yielded the parameters of puckering q(2) = 30, 29 pm, and $\phi(2) = 253°$, 350° for the 1,2- and 3,4-isopropylidene rings, respectively. These values correspond[25] to conformation ${}_2E$ ($\phi = 252°$) and that lying between ${}^{0}_{4}T$ ($\phi = 342°$) and ${}^{\circ}E$ ($\phi = 0°$) in the pseudo-rotational pathway of furanoses. Comparison of the endocyclic torsion-angles (see Fig. 3) better illustrates the correspondence between the two five-membered rings, and also with the 1,2-isopropylidene ring in the dithiepan derivative of another octopyranose[20]. The 3,4-isopropylidene ring in the latter compound[20] has a totally different conformation, probably because of steric interference with the dithiepan ring. Additional distortion of the pyranose ring also occurs on the side where the 3,4-isopropylidene ring lies. The envelope conformation of the latter, in compound **8**, is probably a minimum-energy conformation, and it resembles the conformation (${}^{2}E$) favored by many furanose compounds.

EXPERIMENTAL

General. — Melting points were determined with a Kofler, micro hot-stage 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. 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*), 1:1 light petroleum–ethyl acetate; (*B*), 2:1 light petroleum–ethyl acetate; and (*C*), 3:1 ethyl acetate–light petroleum. 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, on 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* = 1.00). Mass spectra were recorded with an A.E.I. MS9 instrument, using the direct-insertion method. Crystallographic examination was carried out in a Philips, four-circle diffractometer equipped with a graphite-crystal monochromator, and MoKα radiation was used.

6,8-Dideoxy-1,2:3,4-di-O-*isopropylidene*-α-D-galacto-*octos-7-ulose oxime* (**5**). — To a solution of *cis*-6,7,8-trideoxy-1,2:3,4-di-*O*-isopropylidene-7-*C*-nitro-α-D-*galacto*-oct-6-enose[6] (**4**) (2.6 g) in methanol (100 ml) was added 10% palladium-on-charcoal (500 mg), and the mixture was shaken under hydrogen at atmospheric pressure. After 1 h, t.l.c. (solvent *A*) showed that one major compound (R_F 0.45) had formed. The suspension was filtered, and the filtrate was evaporated to a syrup. A solution of the residue in chloroform (50 ml) was washed successively with iced M sulfuric acid, saturated sodium hydrogencarbonate, and water, dried (Na_2SO_4), filtered, and the filtrate evaporated to a syrup (2.2 g, 89%), which crystallized from ethyl acetate–light petroleum. Recrystallization from this solvent mixture gave the oxime (**5**) as colorless needles (1.8 g), m.p. 144–145°, $[\alpha]_D^{20}$ −61° (*c* 1.0); R_F 0.45 (solvent *A*); ν_{max}^{KBr} 3400 (NOH), 1640 (C=N), 1383 and 1373 cm^{-1} (CMe_2); *m/e* 301 (M^+), 286 (M^+ − 15); p.m.r. data: τ 1.54 (br, s, 1 H, D_2O-exchangeable, 7-NOH), 4.51 (d, 1 H, $J_{1,2}$ 5.1 Hz, H-1), 5.42 (q, 1 H, $J_{3,4}$ 7.8 Hz, H-3), 5.72 (q, 1 H, $J_{2,3}$ 2.4 Hz, H-2), 5.83 (q, 1 H, $J_{4,5}$ 1.8 Hz, H-4), 5.98 (m, 1 H, $J_{5,6}$ 6.9 Hz, $J_{5,6'}$ 6.9 Hz, H-5), 7.50 (d, 2 H, H-6,6'), 8.07 (3-proton s, 7-Me), and 8.48, 8.54, 8.67, and 8.68 (3-proton singlets, 2 CMe_2).

Anal. Calc. for $C_{14}H_{23}NO_6$: C, 55.8; H, 7.7; N, 4.7. Found: C, 55.8; H, 7.6; N, 4.6.

7-Acetamido-6,7,8-trideoxy-1,2:3,4-di-O-*isopropylidene*-α-D- *and* -β-L-glycero-D-galacto-*octopyranose* (**8** *and* **9**). — The oxime **5** (1.7 g) was hydrogenolyzed for

70 h as described for the preparation of **5**. The suspension was filtered, and the filtrate was evaporated to a syrup. A solution thereof 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 **6** and **7** (1.4 g, 86%).

To a solution of the mixed amines in methanol (50 ml) was added acetic anhydride (3 ml), and the mixture was kept for 2 h at room temperature. Pyridine (3 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 (700 g), which was eluted with solvent *C*.

The D-*glycero* isomer **8** (720 mg) crystallized as needles (from ethyl acetate–light petroleum), m.p. 148°, $[\alpha]_D^{20}$ −60° (*c* 1.4); R_F 0.21 (solvent *C*); *T* 1.15; $\nu_{max}^{CHCl_3}$ 3435 (amide NH), 1653 (Amide I), 1523 (Amide II), 1383 and 1375 cm^{-1} (CMe_2); *m/e* 314 (M^+ − 15); p.m.r. data: τ 3.95 (d, 1 H, D_2O-exchangeable, $J_{7,NH}$ 8.0 Hz, 7-NH), 4.51 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 5.42 (q, 1 H, $J_{3,4}$ 7.8 Hz, H-3), 5.72 (q, 1 H, $J_{2,3}$ 2.4 Hz, H-2), 5.82 (q, 1 H, $J_{4,5}$ 1.9 Hz, H-4), 5.91 (m, 1 H, $J_{7,8}$ 6.6 Hz, $J_{7,NH}$ 8.0 Hz, H-7), 6.20 (m, 1 H, $J_{5,6}$ 7.0 Hz, $J_{5,6'}$ 5.4 Hz, H-5), 8.26 (m, 2 H, H-6,6'), 8.06 (3-proton s, 7-NAc), 8.52, 8.55, 8.66, and 8.68 (3-proton singlets, 2 CMe_2), and 8.82 (d, 3 H, 7-Me).

Anal. Calc. for $C_{16}H_{27}NO_6$: C, 58.3; H, 8.3; N, 4.2. Found: C, 58.6; H, 8.1; N, 4.1.

The L-*glycero* isomer **9** (437 mg) crystallized from ethyl acetate–light petroleum as needles, m.p. 140–141°, $[\alpha]_D^{20}$ −64° (*c* 1.1); R_F 0.15 (solvent *C*); *T* 1.35; $\nu_{max}^{CHCl_3}$ 3420 (amide NH), 1660 (Amide I), 1520 (Amide II), 1385 and 1372 cm^{-1} (CMe_2); *m/e* 329 (M^+), 314 (M^+ − 15); p.m.r. data: τ 3.73 (d, 1 H, D_2O-exchangeable, $J_{7,NH}$ 8.0 Hz, 7-NH), 4.48 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 5.41 (q, 1 H, $J_{3,4}$ 7.7 Hz, H-3), 5.70 (q, 1 H, $J_{2,3}$ 2.4 Hz, H-2), 5.90 (m, 1 H, H-7), 5.92 (q, 1 H, $J_{4,5}$ 1.8 Hz, H-4), 6.02 (m, 1 H, $J_{5,6}$ 9.4 Hz, $J_{5,6'}$ 3.6 Hz, H-5), 8.07 (3-proton s, 7-NAc), 8.25 (m, 2 H, H-6,6'), 8.46 (3-proton s), 8.54 (3-proton s), and 8.66 (6-proton s) (2 CMe_2), and 8.79 (d, 3 H, $J_{7,8}$ 6.8 Hz, 7-Me).

Anal. Calc. for $C_{16}H_{27}NO_6$: C, 58.3; H, 8.3; N, 4.2. Found: C, 58.0; H, 8.1; N, 4.3.

Crystal data for compound **8**. — $C_{16}H_{27}NO_6$; orthorhombic; space group $P2_12_12_1$; a = 2.457(1) nm, b = 1.380(1) nm, c = 526(1) pm; U = 1.782 nm^3 (1782 $Å^3$); F(000) = 712; μ(MoKα) = 0.57 cm^{-1}.

Data were collected by scanning each peak in the $\omega - 2\theta$ mode over 0.8°, in steps of 0.025°/s within the limits $3 \leqslant \theta \leqslant 20°$. Background correction was made by counting for half the scan time at each end of the scan and subtracting the total count. Data reduction consisted of Lp correction, merging of equivalent reflexions, and a 2σ(F) cut-off before refinement. In the final refinement, 997 reflexions were used. The program[26] SHELX-76 was used for all of the crystallographic computations.

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/DD069/*Carbohydr. Res.*, 62 (1978) 39–47.

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