Carbohydrate Research, 75 (1979) C17–C20

Preliminary communication

Isolation and characterization of D-acosamine from a basic antibiotic, Sporaviridin

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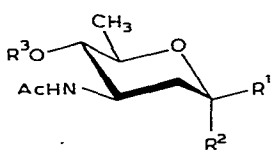
(Received April 20th, 1979; accepted for publication in revised form June 10th, 1979)

Sporaviridin is a broad-spectrum, basic antibiotic produced by *Streptosporangium viridogriseum* nov. sp.[1], and contains an oligosaccharide as a structural component. We describe here the first identification of a naturally occurring 3-amino-2,3,6-trideoxy-D-*arabino*-hexose, D-acosamine, as its methyl *N*-acetyl glycoside, obtained by methanolysis of *N*-acetylsporaviridin.

N-Acetylsporaviridin obtained by treating sporaviridin with acetic anhydride in methanol, was boiled under reflux with 5% hydrogen chloride in methanol. The solution was made neutral, evaporated, and the residue was extracted with ethyl acetate. A water-soluble fraction was evaporated and the residue acetylated with acetic anhydride in pyridine. The resulting acetyl derivatives were separated by chromatography on silica gel to give an anomeric pair of methyl *N,O*-diacetyl glycosides, (**1** and **2**), $C_{11}H_{19}NO_5$, together with anomeric pairs of four other methyl glycosides*. Physical data for **1** and **2** are as follows:



1 : R^1 = H R^2 = OMe R^3 = Ac

2 : R^1 = OMe R^2 = H R^3 = Ac

3 : R^1 = H R^2 = OMe R^3 = H

Compound **1** was obtained as colorless needles, m.p. 162–163°, $[\alpha]_D^{20}$ +204° (*c* 0.3, methanol); ν_{max}^{KBr} 3310, 1735, 1655, and 1555 cm^{-1}; $C_{11}H_{19}NO_5$ (mol.wt. 245); *m/e* c.i. (isobutane): 246 (MH^+, base peak) and 214 ($MH^+ - CH_3OH$); *m/e* c.i. (NH_3): 263 ($M \cdot NH_4^+$, base peak), 246 (MH^+), and 214 ($MH^+ - CH_3OH$)..

Compound **2** was isolated as colorless needles, m.p. 184–186°, $[\alpha]_D^{20}$ +39° (*c* 0.3, methanol); ν_{max}^{KBr} 3285, 1740, 1660, and 1555 cm^{-1}; $C_{11}H_{19}NO_5$ (mol.wt. 245); *m/e* c.i. (isobutane): 246 (MH^+, base peak) and 214 ($MH^+ - CH_3OH$); *m/e* c.i. (NH_3): 263 ($M \cdot NH_4^+$), 246 (MH^+, base peak), and 214 ($MH^+ - CH_3OH$).

The ^{13}C-n.m.r. spectra of **1** and **2** (Table I) allowed differentiation of the α-anomer (**1**, 98.7 p.p.m.) from the β-anomer (**2**, 102.2 p.p.m.) by the chemical shifts of the

*They are 6-deoxy-D-glucose (D-quinovose), D-glucose, 3-amino-2,3,6-trideoxy-3-*C*-methyl-L-*lyxo*-hexose (vancosamine), and 4-amino-4,6-dideoxy-D-glucose (viosamine). Further details concerning these sugars will be discussed in a full paper.

TABLE I

CARBON-13 CHEMICAL SHIFTS OF COMPOUNDS 1, 2 AND 3[a]

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	OCH_3	$NHCOCH_3$	$NHCOCH_3$	$OCOCH_3$	$OCOCH_3$
1	98.73	36.60	47.07	77.04	66.96	18.03	54.87	22.71	172.02[b]	20.71	172.65[b]
2	102.24	37.96	49.85	76.85	72.22	18.08	56.72	22.66	172.21[c]	20.71	172.70[c]
3	98.73	36.86	49.65	76.45	69.50	18.29	54.66	22.81	173.18	–	–

[a] ^{13}C-n.m.r. spectra were recorded with a JEOL JNM-FX100 n.m.r. spectrometer at 25.05 MHz in CD_3OD with Me_4Si as internal reference. [b,c] Assignments may be reversed.

TABLE II

^{1}H-n.m.r. SPECTRA OF COMPOUNDS 1, 2 AND 3[a]

	Chemical shifts (δ)[b] *(first-order couplings, Hz, in parentheses)*											
Compound	*H-1* ($J_{1,2ax}$)	*H-2eq* ($J_{1,2eq}$)	($J_{2eq,2ax}$)	*H-2ax* ($J_{2ax,3}$)	*H-3* ($J_{2eq,3}$)	*H-4* ($J_{3,4}$)	*H-5* ($J_{4,5}$)	*H-6* ($J_{5,6}$)	OCH_3	*NH* ($J_{3,NH}$)	N-*Ac*	O-*Ac*
1	4.66dd (3.5)	2.23ddd (1.0)	(13.0)	1.61m (11.5)	←4.20–4.58m→ (4.5)	(10.0)	3.86dq (10.0)	1.15d (6.5)	3.30s	5.76d (7.0)	1.88s	2.03s
2	4.50dd (9.5)	2.32ddd (2.0)	(13.0)	1.60dt (13.0)	4.26m (5.0)	4.52t (9.5)	3.70dq (9.5)	1.24d (6.5)	3.49s	6.24d (9.0)	1.91s	2.06s
3	4.72dd (3.5)	2.07ddd (1.0)	(12.5)	1.63dt (12.5)	4.13m (5.0)	3.07t (9.5)	3.71dq (9.5)	1.26d (6.5)	3.33s	6.67d (8.0)	2.00s	–

[a] Measured at 100 MHz for solutions in $CDCl_3$. [b] Signal multiplicities: d, doublet; m, multiplet; q, quartet; s, singlet; t, triplet.

anomeric carbon atoms. Furthermore, H-1 and H-2 gave rise to an ABX system, which permitted ready distinction of the α-anomer (**1**, $J_{1,2ax}$ 3.5, $J_{1,2eq}$ 1 Hz)[2] and β anomer (**2**, $J_{1,2ax}$ 9.5, $J_{1,2eq}$ 2 Hz) from the ^{1}H-n.m.r. spectra of **1** and **2** (Table II). The signals at δ 1.15 (**1**, 3 H, d, J 6.5 Hz) and 1.24 (**2**, 3 H, d, J 6.5 Hz) were assigned to a 6-CH_3 group. Therefore, this amino sugar was considered to be a 2,6-dideoxyhexose derivative. The chemical shifts of H-3,4, and 5 and the presence of four, consecutive, *trans*-diaxial protons (H-2_{ax}–H-5) displaying large coupling-constants, established that the NHAc and OAc groups are attached to C-3 and C-4, respectively, so that the substituents at C-3, 4, and 5 are equatorially disposed. Accordingly, these results show that **1** is methyl 3-acetamido-4-*O*-acetyl-2,3,6-trideoxy-α-*arabino*-hexopyranoside and **2** is its β anomer.

A naturally occurring 3-amino-2,3,6-trideoxy-*arabino*-hexose was isolated first by Lomakina and co-workers in 1973 as a constituent of an antibiotic, actinoidin[3]. It was named acosamine and has the L configuration. Acosamine, its enantiomer, and several derivatives have been synthesized by several groups[4–11]. The optical rotations reported for methyl *N*,*O*-diacetyl-α-acosaminide and methyl *N*-acetyl-α-acosaminide are shown in Table III.

As already mentioned, our methyl 3-acetamido-4-*O*-acetyl-2,3,6-trideoxy-α-*arabino*-hexopyranoside (**1**) had $[\alpha]_D^{20}$ +204° (*c* 0.3, methanol) and the newly prepared *N*-acetyl derivative **3** had m.p. 162–163°, $[\alpha]_D^{20}$ +139° (*c* 0.3, methanol).

TABLE III

OPTICAL ROTATIONS OF METHYL *N*-ACETYL-α-ACOSAMINIDE AND METHYL *N*,*O*-DIACETYL-α-ACOSAMINIDE

Ref.		*Methyl* N-*acetyl*-α-*acosaminide*		*Methyl* N,O-*diacetyl*-α-*acosaminide*	
		m.p. (°C)	$[\alpha]_D$ (°)	*m.p.* (°C)	$[\alpha]_D$ (°)
L	Lomakina[3]	160–162	−90[a] (*c* 0.1, MeOH)	158–163	−84[a] (*c* 0.5, MeOH)
	Gupta[4]	159–160	−148 (*c* 0.4, MeOH)	–	–
	Lee[5]	160–161	−146 (*c* 0.52, MeOH)	163–164	−191 (*c* 0.52, MeOH)
	Heyns[6]	–	–	153–154	−198 (*c* 2.3, EtOH)
D	Richardson[8]	157.5–158	+137 (*c* 1.55, MeOH)	–	–
	Baer[9]	–	–	162–163	+142 (*c* 1, $CHCl_3$)
	Horton[10]	155–156	+139 (*c* 1, MeOH)	161–162	+184 (*c* 0.9, MeOH)
	Monneret[11]	160–161	+137.5 (*c* 1, MeOH)	162–163	+194 (*c* 0.59, MeOH)

[a] These compounds contained some of the β anomer. See also, note 8 in ref. 6.

The foregoing results establish that one of three amino sugars obtained from sporaviridin is D-acosamine, namely, 3-amino-2,3,6-trideoxy-D-*arabino*-hexose.

The 3-amino-2,3,6-trideoxyhexoses daunosamine (*lyxo*)[12], ristosamine (*ribo*)[2], and acosamine (*arabino*)[3], derived from various antibiotics, all have the L configuration. The present example is the first natural instance of this type of amino sugar to be found having the D configuration, although D-rhodosamine[13] and D-angolosamine[14] (*N,N*-dimethyl derivatives of D-daunosamine and D-acosamine, respectively) have been reported in Nature.

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