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Structural Investigation of the Antibiotic Sporaviridin. VI.[1] Structures of Individual Sugar Components

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The structural assignment of each of five sugar components from a basic antibiotic, sporaviridin, is described: two are neutral monosaccharides, D-quinovose and D-glucose, and the remaining three are amino sugars, D-viosamine, D-acosamine and L-vancosamine. D-Acosamine is only the second example of a 3-amino-2,3,6-trideoxyhexose having D-configuration to be isolated from nature (D-angolosamine was the first).

Keywords——sporaviridin; *Streptsporangium*; D-viosamine; D-acosamine; L-vancosamine; X-ray analysis; ^{1}H-NMR

Sporaviridin (SVD) is a basic and water-soluble antibiotic produced by *Streptosporangium viridogriseum* nov. sp. and was first isolated in 1963.[2] Although it is active against gram-positive bacteria, acid-fast bacteria and trichophyton, it is also a highly toxic compound with hemolytic activity, and a fish poison. Its biological properties are similar to those of saponins.[3] Thus it seems to be a glycosidic compound containing amino sugars. In this paper we describe the structures of the individual sugar components of SVD.

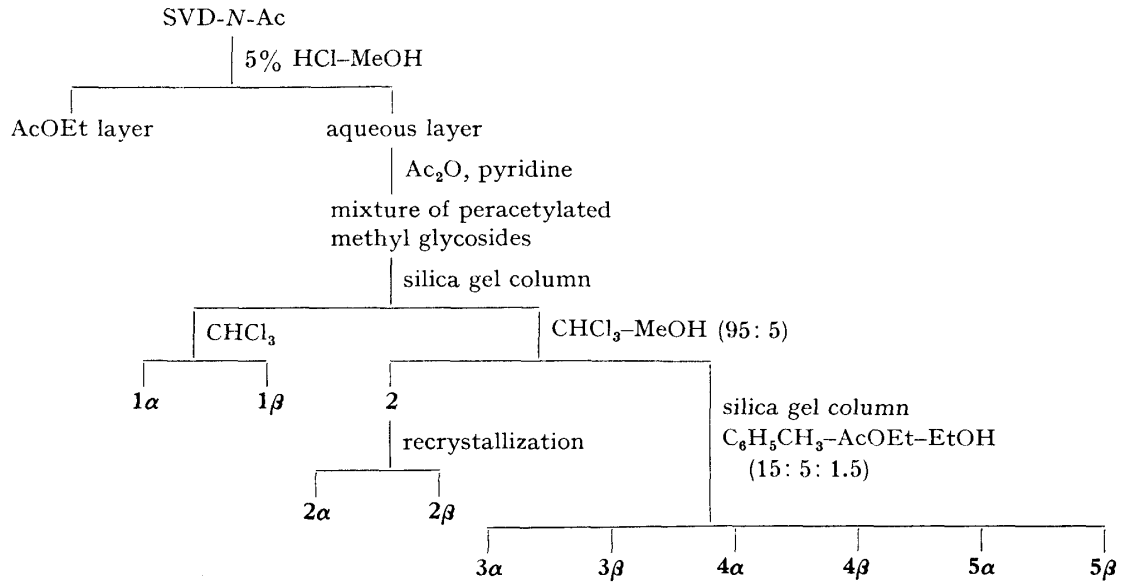


Chart 1. Isolation of the Peracetylated Methyl Glycosides from SVD-*N*-Ac

N-Acetylsporaviridin (SVD-*N*-Ac), a derivative obtained by treating SVD with acetic anhydride in methanol, was heated under reflux 5% hydrogen chloride in methanol. The solution was made neutral, then concentrated, and the residue was partitioned between water and ethyl acetate. The water-soluble fraction was evaporated to dryness and the residue was acetylated with acetic anhydride in pyridine. The resulting acetyl derivatives were separated by repeated chromatographies on a silica gel column as shown in Chart 1 to yield five anomeric pairs of peracetylated methyl glycosides (**1**—**5**). The physicochemical

TABLE I. Physicochemical Properties of **1**—**8**

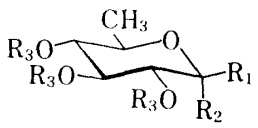
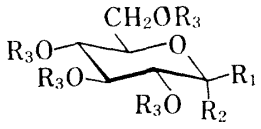
Compound	mp (°C) (lit.)	Appearance (Recryst. solvent)	Formula	Analysis (%) Calcd (Found) C	H	N	MS (*m/z*) CI (iso-C_4H_{10}) CI(NH_3)	$[\alpha]_D^{25}$(°) [lit.]	IR (cm^{-1}) (KBr)
1α	76—78	Colorless prisms	$C_{13}H_{20}O_8$	51.31	6.63		305 (MH^+)	+133.0 (c=0.3, $CHCl_3$)	1750
	(81—82)[4]	(Et_2O–hexane)		(51.20	6.59)		322 $(M+NH_4)^+$	[+112.0 (c=1.24, $CHCl_3$)][4]	
1β	103—105	Colorless prisms	$C_{13}H_{20}O_8$	51.31	6.63		305 (MH^+)	−23.0 (c=0.3, EtOH)	1755
	(100)[5]	(Et_2O–hexane)		(51.15	6.69)		322 $(M+NH_4)^+$	[−19.0 (c=1.0, EtOH)][5]	
2α	102—104	Colorless needles	$C_{15}H_{22}O_{10}$	49.72	6.12		363 (MH^+)	+133.0 (c=0.3, EtOH)	1740
	(101)[6,7]	(Et_2O–hexane)		(49.72	6.32)		380 $(M+NH_4)^+$	[+137.3 (c=2.0, EtOH)][6,7]	
2β	103—105	Colorless needles	$C_{15}H_{22}O_{10}$	49.72	6.12		363 (MH^+)	−30.3 (c=0.3, EtOH)	1740
	(104—105)[6,7]	(Et_2O–hexane)		(49.87	6.29)		380 $(M+NH_4)^+$	[−24.6 (c=1.5, EtOH)][6,7]	
3α	169—173	Colorless needles	$C_{13}H_{21}NO_7$	51.48	6.98	4.62	304 (MH^+)	+193.0 (c=0.3, $CHCl_3$)	3300 1740
	(169—170)[11]	(Benzene–hexane)		(51.25	6.95	4.57)	321 $(M+NH_4)^+$	[+190.0 (c=1.585, $CHCl_3$)][11]	1655 1555
3β	203—205	Colorless needles	$C_{13}H_{21}NO_7$	51.48	6.98	4.62	304 (MH^+)	+3.5 (c=0.2, $CHCl_3$)	3310 1745
	(198—200)[12]	(Benzene–AcOEt)		(51.40	7.02	4.57)	321 $(M+NH_4)^+$	[+15.0 (c=1.0, $CHCl_3$)][12]	1655 1540
4α	162—163	Colorless needles	$C_{11}H_{19}NO_5$	53.86	7.81	5.71	246 (MH^+)	+204.0 (c=0.3, MeOH)	3310 1735
	(162—163)[22]	(Et_2O–hexane)		(53.94	8.03	5.62)	263 $(M+NH_4)^+$	[+194.0 (c=0.59, MeOH)][22]	1655 1555
4β	184—186	Colorless needles	$C_{11}H_{19}NO_5$	53.86	7.81	5.71	246 (MH^+)	+3.0 (c=0.3, $CHCl_3$)	3285 1740
	(180)[20]	(Benzene–hexane)		(53.90	8.63	5.64)	263 $(M+NH_4)^+$	[+7.4 (c=0.4, $CHCl_3$)][20]	1660 1550
5α	166—168	Colorless needles	$C_{12}H_{21}NO_5$	55.58	8.16	5.40	260 (MH^+)	−220.0 (c=0.3, MeOH)	3290 1730
		(Benzene–cyclohexane)		(55.75	8.40	5.32)	277 $(M+NH_4)^+$		1650 1110
5β	123—124	Colorless needles	$C_{12}H_{21}NO_5$	55.58	8.16	5.40	260 (MH^+)	−83.0 (c=0.3, MeOH)	3300 1740
		(Benzene–cyclohexane)		(55.97	8.38	5.39)	277 $(M+NH_4)^+$		1650 1560
6α	162—163	Colorless needles	$C_9H_{17}NO_4$	53.19	8.43	6.89	204 (MH^+)	+139.3 (c=0.3, MeOH)	3600—3200
	(160—161)[22]	(Et_2O–benzene)		(53.08	8.55	6.85)	221 $(M+NH_4)^+$	[+137.5 (c=1.0, MeOH)][22]	3290 1640
									1560
6β	224—225.5	Colorless needles	$C_9H_{17}NO_4$	53.19	8.43	6.89	204 (MH^+)	−56.6 (c=0.3, H_2O)	3600—3150
	(224—226)[20]	(AcOEt–MeOH)		(52.90	8.81	6.78)	221 $(M+NH_4)^+$	[−57.6 (c=0.95, H_2O)][20]	3275 1640
									1560
7α	122—124	Colorless prisms	$C_{10}H_{19}NO_4$	55.28	8.82	6.45	218 (MH^+)	−159.0 (c=0.3, MeOH)	3350 3270
		(Benzene–cyclohexane)		(55.12	9.23	6.33)	235 $(M+NH_4)^+$		1640
8α	168—170	Colorless needles	$C_{22}H_{25}NO_5$	68.91	6.57	3.65	384 (MH^+)	−180.0(c=0.3, MeOH)	3400 1720
	(168—169)[26]	(Benzene–cyclohexane)		(68.88	6.50	3.74)	401 $(M+NH_4)^+$	[−191.0 (c=0.1, MeOH)][26]	1700 1660

TABLE II. ^{1}H-NMR Spectral Data for **1**—**8** (δ Values)[a]

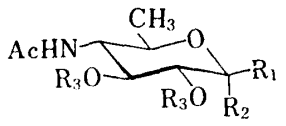
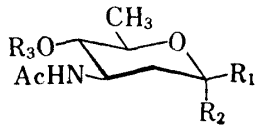
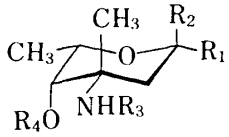
Compound	H-1 ($J_{1,2}$)	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{4,5}$)	H-5 ($J_{5,6}$)	H-6 ($J_{5,6'}$)	H-6′ ($J_{6,6'}$)	OCH_3	$OCOCH_3$		NH ($J_{4,NH}$)	$NHCOCH_3$
1α	4.84 d	4.81 dd	5.41 t	4.74 t	3.84 dq	1.28 d	—	3.36 s	1.97 s	2.01 s	—	—
	(3.5)	(9.5)	(9.5)	(9.5)	(6.0)				2.03 s			
1β	4.35 d	5.01 dd	5.15 t	4.75 t	3.52 dq	1.23 d	—	3.43 s	1.95 s	1.99 s	—	—
	(8.0)	(9.5)	(9.5)	(9.5)	(6.0)							
2α	4.88 d	4.83 dd	5.45 t	5.01 t	3.93 ddd	4.27 dd	4.02 dd	3.38 s	1.97 s	1.99 s	—	—
	(3.5)	(9.5)	(9.5)	(9.5)	(4.5)	(2.5)	(12.0)		2.04 s	2.05 s		
2β	4.38 d	←——4.76—5.23 m——→			3.66 ddd	4.27 dd	4.05 dd	3.43 s	1.94 s	1.96 s	—	—
	(7.5)	(9.5)	(9.5)	(9.5)	(4.5)	(2.5)	(12.0)		1.98 s	2.03 s		
3α	4.87d	4.83 dd	5.23 t	3.96 q	3.66 dq	1.23 d	—	3.35 s	2.00 s	2.02 s	5.76 d	1.91 s
	(3.5)	(9.5)	(9.5)	(9.5)	(6.0)						(9.5)	
3β	4.39d	←4.81—5.27 m→		3.96 q	3.43 dq	1.30 d	—	3.49 s	2.03 s		5.80 d	1.94 s
	(8.0)	(9.5)	(9.5)	(9.5)	(6.0)						(9.5)	

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 ($J_{5,6}$)	C_3–CH_3	OCH_3	$OCOCH_3$	NH ($J_{3,NH}$)	$NHCOCH_3$
4α	4.66 dd	2.23 ddd		1.61m	←—4.20—4.58m—→		3.86 dq	1.15 d	—	3.30 s	2.03 s	5.76 d	1.88 s
	(3.5)	(1.0)	(13.0)	(11.3)	(4.5)	(10.0)	(10.0)	(6.5)				(7.0)	
4β	4.50 dd	2.32 ddd		1.60 dt	4.26m	4.52 t	3.56 dq	1.24 d	—	3.49 s	2.06 s	6.24 d	1.91 s
	(9.5)	(2.0)	(13.0)	(13.0)	(5.0)	(9.5)	(9.5)	(6.5)				(9.0)	
5α	4.74 dd	2.35 dd		1.99 dd	—	4.89 s	4.09 q	1.13 d	1.70s	3.30 s	2.16 s	5.59 s	1.85 s
	(4.0)	(1.0)	(13.0)	(13.0)				(6.0)					
5β	4.50 dd	←——1.57—2.44 m——→			—	4.96 s	3.85 q	1.19 d	1.63s	3.49 s	2.16 s	5.41 s	1.88 s
	(10.0)	(2.5)	(13.0)					(6.0)					

a) Measured in $CDCl_3$ at 100 MHz with TMS as an internal standard. s, singlet; d, doublet; dd, double doublets; dt, doubletriplets; dq, double quartets; ddd, double double doublets; t, triplet; q, quartet; m, multiplet. J values are expressed in Hz.

1α: R_1=H, R_2=OCH_3, R_3=Ac
1β: R_1=OCH_3, R_2=H, R_3=Ac
2α: R_1=H, R_2=OCH_3, R_3=Ac
2β: R_1=OCH_3, R_2=H, R_3=Ac

3α: R_1=H, R_2=OCH_3, R_3=Ac
3β: R_1=OCH_3, R_2=H, R_3=Ac
4α: R_1=H, R_2=OCH_3, R_3=Ac
4β: R_1=OCH_3, R_2=H, R_3=Ac
5α: R_1=H, R_2=OCH_3, R_3=R_4=Ac
5β: R_1=OCH_3, R_2=H, R_3=R_4=Ac
6α: R_1=H, R_2=OCH_3, R_3=H
6β: R_1=OCH_3, R_2=H, R_3=H
7α: R_1=H, R_2=OCH_3, R_3=Ac, R_4=H
8α: R_1=H, R_2=OCH_3, R_3=R_4=Bz

Chart 2

TABLE III. ^{13}C-NMR Spectral Data for **1**—**5** (ppm Values)[a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	O<u>C</u>H$_3$	OCO<u>C</u>H$_3$	NHCO<u>C</u>H$_3$	<u>C</u>OCH$_3$		C$_3$–CH$_3$
1α	97.9	72.4	71.4	75.1	66.1	17.5	55.6	20.6	20.5	—	171.6 171.3	171.5	
1β	102.4	73.1	74.3	74.9	70.9	17.6	57.1	20.6		—	171.6 171.1	171.3	
2α	97.8	71.8	71.3	69.8	68.3	63.1	55.7	20.5		—	171.8 171.1	171.2 170.8	
2β	102.3	72.0	74.2	69.7	72.7	63.0	57.1	20.5		—	171.8 170.8	171.1 170.7	
3α	98.0	72.9	71.4	56.3	66.9	17.9	55.4	20.6	20.5	22.6	172.8	171.2	
3β	102.3	73.4	74.2	56.4	71.7	17.9	56.9	20.6		22.7	172.9 170.9	171.5	
4α	98.7	36.6	47.1	77.0	67.0	18.0	54.9	20.7		22.7	172.7	172.0	
4β	102.2	38.0	49.9	76.9	72.2	18.1	56.7	20.7		22.7	172.7	172.2	
5α	99.8	36.7	54.6	74.2	64.2	18.0	55.4	20.7		23.4[b]	172.3	171.8	24.0[b]
5β	100.4	39.1	55.8	73.2	69.7	17.8	56.6	20.6		22.2[c]	172.1	171.4	23.2[c]

a) Measured in CD_3OD at 25 MHz with TMS as an internal standard.
b, *c*) Assignments may be reversed.

properties, as well as the proton nuclear magnetic resonance (^{1}H-NMR) and carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectral data are summarized in Tables I—III, respectively.

Elemental analysis and chemical ionization (CI) mass spectral data for the two neutral monosaccharides, **1** and **2** indicate that their formulae are $C_{13}H_{20}O_8$ and $C_{15}H_{22}O_{10}$, respectively. The ^{1}H-NMR spectral data for **1** and **2** exhibit the presence of four consecutive and *trans*-diaxial protons (H-2—H-5) displaying large coupling constants. Therefore, compound **2α** is methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside and **2β** is its β-anomer. The signals at δ 1.28 (**1α**; 3H, d, J=6.0 Hz) and δ 1.23 (**1β**; 3H, d, J=6.0 Hz) are assignable to the 6-CH_3 group. Compound **1α** is methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-D-glucopyranoside and **1β** is its β-anomer. The two neutral sugars in SVD are thus 6-deoxy-D-glucose (D-quinovose) and D-glucose.

Compounds **3α** and **3β** are an anomeric pair of amino sugars, whose formula ($C_{13}H_{21}NO_7$) was determined from elemental analysis and CI mass spectral data. The ^{13}C-NMR chemical shifts of C-1 and the coupling constants of H-1 in the ^{1}H-NMR spectra of **3α** and **3β** indicate clearly that **3α** is the α-anomer and **3β** is the β-anomer. The signals at δ 1.23 (**3α**; 3H, d, J=6.0

Hz) and δ 1.30 (**3β**; 3H, d, J=6.0 Hz) are assigned to a 6-CH_3 group. The presence of four consecutive and *trans*-diaxial protons (H-2—H-5) shows that this amino sugar has the *gluco* configuration. The signals of H-4 are also coupled with the NH protons ($J_{4,NH}$=9.5 Hz) together with H-3 and H-5 . Since the optical rotation of the α-anomer, **3α** is more positive than that of the β-anomer, **3β**, these compounds are considered to have the D-configuration.[8] Therefore, **3α** is methyl 4-acetamido-2,3-di-*O*-acetyl-4,6-dideoxy-α-D-glucopyranoside and **3β** is its β-anomer.

4-Amino-4,6-dideoxy-D-glucose has been isolated from cell extracts of *Chromobacterium violaceum*[9] and *E. coli* strain B[10] and was named viosamine. All properties of **3α** and **3β** are identical with those reported for synthetic methyl 2,3,4-triacetyl-α-D-viosaminide[11] and its β-anomer,[12] respectively. Accordingly, one of the amino sugars is D-viosamine.

While the isobutane CI mass spectra of the second amino sugar, **4α** and **4β**, show the protonated molecules (MH^+) at *m/z* 246, the ammonia CI spectra show the ammonium adduct ions $(M+NH_4)^+$ at *m/z* 263 as base peaks. The ^{13}C-NMR spectra of **4α** and **4β** allow differentiation of the α-anomer (**4α**; 98.7 ppm) from the β-anomer (**4β**; 102.2 ppm) on the basis of the chemical shifts of anomeric carbon atoms. Further, H-1 and H-2 give rise to an ABX signal system, which permits ready distinction of the α-anomer (**4α**; $J_{1,2ax}$=3.5, $J_{1,2eq}$=1.0 Hz) and the β-anomer (**4β**; $J_{1,2ax}$=9.5, $J_{1,2eq}$=2.0 Hz) from the ^1H-NMR spectra (Table II).[13] The signals at δ 1.15 (**4α**; 3H, d, J=6.5 Hz) and δ 1.24 (**4β**; 3H, d, J=6.5 Hz) are assigned to a 6-CH_3 group. Therefore, this amino sugar is considered to be a 2,6-dideoxyhexose derivative. The presence of four consecutive and *trans*-diaxial protons (H-2ax—H-5) displaying large coupling constants establishes that the substituents at C-3, 4 and 5 are equatorially disposed. The ^1H-NMR spectrum of **4α** in the presence of a lanthanide shift reagent, tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octadione)-europium (III) ($Eu(fod)_3$) shows four groups of signals, δ 1.44 (3H, d, J=6.5, –CH–C<u>H</u>$_3$), δ 4.33 (1H, dq, J_1=9.5, J_2=6.5 Hz, –CH–C<u>H</u>–CH_3), δ 5.30 (1H, t, J=9.5 Hz, –CH–C<u>H</u>–CH–) and δ 6.75 (1H, m, –C<u>H</u>–), due to the H-3—H-6 protons. Irradiation of the signal at δ 1.44, which is assigned to H-6, collapses the signal at δ 4.33 to a sharp doublet, assignable to H-5. Further, the signal at δ 5.30 changes to a doublet on irradiation of H-5, whereas the multiplet at the lowest field, δ 6.75, is unaffected. These data establish that NHAc and OAc groups are attached to C-3 and C-4, respcetively. Accordingly,

TABLE IV. Optical Rotations of Methyl *N*-acetyl-α-acosaminide and Methyl *N*,*O*-diacetyl-α-acosaminide

Absolute configuration	Author	Methyl *N*-acetyl-α-acosaminide		Methyl *N*,*O*-diacetyl-α-acosaminide	
		mp (°C)	$[\alpha]_D$(°)	mp (°C)	$[\alpha]_D$(°)
L	Lomakina[14]	160—162	−90[a] (c=0.1, MeOH)	158—163	−84[a] (c=0.5, MeOH)
	Gupta[15]	159—160	−148 (c=0.4, MeOH)	—	—
	Lee[16]	160—161	−146 (c=0.52, MeOH)	163—164	−191 (c=0.52, MeOH)
	Heyns[17]	—	—	153—154	−198 (c=2.3, EtOH)
D	Richardson[19]	157.5—158	+137 (c=1.55, MeOH)	—	—
	Baer[20]	—	—	162—163	+142 (c=1.0, $CHCl_3$)
	Horton[21]	155—156	+139 (c=1.0, MeOH)	161—162	+184 (c=0.9, MeOH)
	Monneret[22]	160—161	+137.5 (c=1.0, MeOH)	162—163	+194 (c=0.59, MeOH)

a) These compounds contained some of the β anomer.

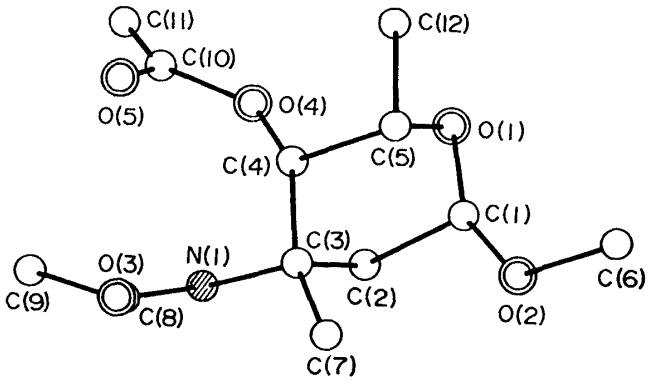
these results show that **4α** is methyl 3-acetamido-4-*O*-acetyl-2,3,6-trideoxy-α-*arabino*-hexopyranoside and **4β** is its β-anomer. Selective deacetylation of **4α** and **4β** with 5% methanolic barium methoxide afforded **6α** and **6β**, respectively.

A naturally occurring 3-amino-2,3,6-trideoxy-*arabino*-hexose was first isolated by Lomakina and co-workers in 1973 as a constituent of an antibiotic, actinoidin.[14] It was designated acosamine and has the L-configuration. Acosamine, its enantiomer and some derivatives have been synthesized by several groups.[15-22] The reported optical rotations for methyl *N*-acetyl-α-acosaminide and methyl *N*,*O*-diacetyl-α-acosaminide are shown in Table IV.

The foregoing results establish that the second amino sugar from SVD is 3-amino-2,3,6-trideoxy-D-*arabino*-hexose, namely, D-acosamine. The 3-amino-2,3,6-trideoxyhexoses, daunosamine (*lyxo*),[23] ristosamine (*ribo*)[13] and acosamine (*arabino*),[14] derived from various antibiotics all have the L-configuration. The present example is the second report of the natural occurrence of this type of amino sugar having the D-configuration;[24] D-angolosamine (*N*,*N*-dimethyl derivative of D-acosamine) was the first.[25]

The third amino sugar, **5α** and **5β** is also a 2,6-dideoxyhexose, whose formula is $C_{12}H_{21}NO_5$. That is, H-1 and H-2 appear as an ABX system which allows the structural assignment of the α-anomer (**5α**, $J_{1,2ax}=4.0$, $J_{1,2eq}=1.0$ Hz) and the β-anomer (**5β**, $J_{1,2ax}=10.0$, $J_{1,2eq}=2.0$ Hz), and the signals at δ 1.13 (**5α**, 3H, d, $J=6.0$ Hz) and δ 1.19 (**5β**, 3H, d, $J=6.0$ Hz) are assignable to a 6-CH_3 group. The presence of the methyl signals at δ 1.70 (**5α**, 3H, s) and δ 1.63 (**5β**, 3H, s) indicates that this amino sugar has a branched chain. Since H-2 protons are coupled with only H-1 and the hydroxy group of **7α** is readily acetylated under mild condition, it is evident that the NHAc and CH_3 groups, and OAc group are disposed at C-3 and C-4, respectively, in **5α** and **5β**, namely the compounds are methyl 3-acetamido-4-*O*-acetyl-2,3,6-trideoxy-3-*C*-methyl-α-hexopyranoside (**5α**) and its β-anomer (**5β**). The appearance of H-4 as a singlet shows that the relative configuration of **5α** and **5β** can be represented as *lyxo* or *xylo*.

Two naturally occurring 3-amino-2,3,6-trideoxy-3-*C*-methylhexopyranoses have been hitherto reported. One is L-vancosamine with the *lyxo* configuration derived from a glycopeptide antibiotic, vancomycin,[26,27] and the other is derived from a glycopeptide antibiotic A35512B as a C-3 epimer of L-vancosamine.[28] The X-ray crystallographic analysis of **5α** revealed the molecular structure I or its antipode shown in Fig. 1; the relative configuration is consistent with that of vancosamine.



I

Fig. 1. Molecular Structure and Atomic Numbering of **5α**

Finally, **5α** was subjected to exhaustive hydrolysis with barium hydroxide followed by benzoylation in pyridine to yield the *N*,*O*-dibenzoate, **8α**. The properties of **8α** were identical with those reported for methyl *N*,*O*-dibenzoyl-α-vancosaminide.[26] Accordingly, the last

amino sugar derived from SVD is determined to be L-vancosamine.

The results mentioned above demonstrate that the constituent monosaccharides of SVD are D-quinovose, D-glucose, D-viosamine, D-acosamine and L-vancosamine.

Experimental

All melting points were determined on a micro-melting point apparatus (hot-stage type, Yanagimoto MP-S3) and are uncorrected. Optical rotations were measured with a JASCO DIP-SL polarimeter. Ultraviolet (UV) spectra were taken on a Hitachi 200-10 double beam spectrophotometer. Infrared (IR) spectra were determined with a Hitachi IR-215 spectrometer. ^{1}H-NMR spectra were recorded on Hitachi R-24B (60 MHz) and JEOL PS-100 (100 MHz) spectrometers and ^{13}C-NMR spectra were recorded on a JEOL FX-100 (25 MHz) spectrometer using tetramethylsilane as an internal standard. CI mass spectra were obtained using a Shimadzu LKB 9000B mass spectrometer. Operating conditions were as follows: ion source temperature 190°C; electron energy 140 or 300 eV; reagent gas pressure 0.3 Torr, accelerating voltage 3.5 kV. Thin layer chromatography (TLC) was performed on Merck pre-coated plates (Kieselgel 60 F_{254}). For column chromatography, Merck Kieselgel 60 (Art. 7729 or 7734) and Sephadex LH-20 (Pharmacia) were used.

Methanolysis of SVD-*N*-Ac——A solution of crude SVD (30 g) in MeOH (300 ml) was treated with acetic anhydride (30 ml) and the reaction mixture was stirred overnight at room temperature. The reaction mixture was concentrated to dryness to yield a pale yellow powder (30 g) of crude SVD-*N*-Ac. A solution of 7 g of crude SVD-*N*-Ac in 150 ml of 5% methanolic HCl was heated under reflux for 4 h. After cooling, the reaction mixture was neutralized with Ag_2CO_3 and filtered. The filtrate was concentrated under reduced pressure to a syrup. The residue was partitioned between H_2O and AcOEt. The H_2O layer was concentrated to dryness to give 3.54 g of a black-brown syrup. A solution of 2.86 g of the residue in pyridine (10 ml) was treated with acetic anhydride (6 ml) and the mixture was allowed to stand for 2 d at room temperature. The reaction mixture was concentrated to dryness to yield 5.03 g of a yellow oil. The residue was separated as shown in Chart 1 to give **1*α***, 964 mg; **1*β***, 281 mg; **2*α***, 374 mg; **2*β***, 89 mg; **3*α***, 126 mg; **3*β***, 54 mg; **4*α***, 594 mg; **4*β***, 90 mg; **5*α*** 79 mg; **5*β***, 20 mg. Physicochemical properties and ^{1}H-NMR and ^{13}C-NMR spectral data of these compounds are summarized in Table I—III, respectively.

Methyl 3-Acetamido-2,3,6-trideoxy-*α*-D-*arabino*-hexopyranoside (6*α*)——A solution of **4*α*** (40 mg) in MeOH (2 ml) was treated with 0.4 ml of 5% methanolic $Ba(OMe)_2$ and the reaction mixture was stirred for 30 min at room temperature. The reaction mixture was concentrated to dryness. The residue was subjected to column chromatography on Sephadex LH-20. Elution with MeOH afforded 31 mg of white powder, which was recrystallized from benzene–Et_2O to give colorless needles (22 mg), mp 162—163°C. [Physicochemical properties are given in Table I.] ^{1}H-NMR ($CDCl_3$) δ: 1.26 (3H, d, $J_{5,6}$=6.5 Hz, H-6), 1.63 (1H, dt, $J_{1,2ax}$=3.5, $J_{2ax,3}$=12.5, $J_{2ax,2eq}$=12.5 Hz, H-2ax), 2.00 (3H, s, NHCOC$\underline{H}_3$), 2.07 (1H, ddd, $J_{1,2eq}$=1.0, $J_{2eq,3}$=3.5, $J_{2ax,2eq}$=12.5 Hz, H-2eq), 3.07 (1H, t, $J_{3,4}$=$J_{4,5}$=9.5 Hz, H-4), 3.33 (3H, s, OCH_3), 3.71 (1H, dq, $J_{4,5}$=9.5, $J_{5,6}$=6.5 Hz, H-5), 4.13 (1H, m, H-3), 4.72 (1H, dd, $J_{1,2eq}$=1.0, $J_{1,2ax}$=3.5 Hz, H-1), 6.67 (1H, d, $J_{3,NH}$=8.0 Hz, NH), ^{13}C-NMR (CD_3OD) ppm: 18.3 (q, C-6), 22.8 (q, NCO$\underline{C}H_3$), 36.9 (t, C-2), 49.7 (d, C-3), 54.7 (q, OCH_3), 69.5 (d, C-5), 76.5 (d, C-4), 98.7 (d, C-1), 173.2 (s, NH$\underline{C}OCH_3$).

Methyl 3-Acetamido-2,3,6-trideoxy-*β*-D-*arabino*-hexopyranoside (6*β*)——A solution of **4*β*** (27 mg) in MeOH (1 ml) was treated with 0.3 ml of 5% methanolic $Ba(OMe)_2$ and the mixture was stirred for 30 min at room temperature. The reaction mixture was concentrated to dryness and the residue was subjected to column chromatography on Sephadex LH-20. Elution with MeOH afforded 22 mg of white powder, which was recrystallized from AcOEt–MeOH to give colorless needles (15 mg), mp 224—225.5°C. [Physicochemical properties are given in Table I.] ^{1}H-NMR (CD_3OD) δ: 1.27 (3H, d, $J_{5,6}$=6.0 Hz, H-6), 1.94 (3H, s, NHCOC$\underline{H}_3$), 3.34 (3H, s, OCH_3), 3.85 (1H, m, H-5), 4.47 (1H, dd, $J_{1,2eq}$=2.5, $J_{1,2ax}$=10.0 Hz, H-1). ^{13}C-NMR (CD_3OD) ppm: 18.3 (q, C-6), 22.7 (q, NHCO$\underline{C}H_3$), 38.1 (t, C-2), 52.4 (d, C-3), 56.6 (q, OCH_3), 74.6 (d, C-5), 75.9 (d, C-4), 102.0 (d, C-1), 173.2 (s, NH$\underline{C}OCH_3$).

Methyl 3-Acetamido-2,3,6-trideoxy-3-*C*-methyl-*α*-L-*lyxo*-hexopyranoside (7*α*)——A solution of **5*α*** (100 mg) in MeOH was treated with 2 ml of 5% methanolic NaOMe and the mixture was stirred for 10 min at room temperature. The reaction mixture was concentrated to dryness, and the residue was subjected to column chromatography on Sephadex LH-20. Elution with MeOH afforded 74 mg of white powder, which was recrystallized from benzene–cyclohexane to give colorless prisms, mp 122—124°C. [Physicochemical properties are given in Table I.] ^{1}H-NMR ($CDCl_3$) δ: 1.25 (3H, d, J=6.0 Hz, H-6), 1.62 (3H, s, C_3–CH_3), 1.92 (3H, s, NHCOC$\underline{H}_3$), 3.29 (3H, s, OCH_3), 3.40 (1H, s, H-4), 4.08 (1H, q, J=6.0 Hz, H-5), 4.70 (1H, dd, $J_{1,2eq}$=1.0, $J_{1,2ax}$=4.1 Hz, H-1), 6.20 (1H, br s, NH). ^{13}C-NMR (CD_3OD) ppm: 17.6 (q, C-6), 23.6 (q, C_3–$\underline{C}H_3$ or NHCO$\underline{C}H_3$), 23.8 (q, NHCO$\underline{C}H_3$ or C_3–$\underline{C}H_3$), 35.7 (t, C-2), 55.1 (q, OCH_3), 55.7 (s, C-3), 64.6 (d, C-5), 72.6 (d, C-4), 99.4 (d, C-1), 172.2 (s, NH$\underline{C}OCH_3$).

Methyl 3-Benzamido-4-*O*-benzoyl-2,3,6-trideoxy-3-*C*-methyl-*α*-L-*lyxo*-hexopyranoside (8*α*)——A solution of **5*α*** (50 mg) in MeOH (2 ml) was treated with 2 ml of 8% $Ba(OH)_2$ (aq.) and the mixture was boiled under reflux for 3 h. After cooling, the reaction mixture was concentrated to dryness. The residue was subjected

to column chromatography on Sephadex LH-20 to yield 28 mg of methyl α-vancosaminide as a colorless oil. A solution of the oily compound (22 mg) in pyridine (0.5 ml) was treated with benzoyl chloride (0.1 ml) under ice-cooling and the reaction mixture was stirred overnight at room temperature, then poured into H_2O and extracted three times with Et_2O. The extract was washed with 5% $NaHCO_3$, $CuSO_4$ (satd.) and H_2O and dried over K_2CO_3. Evaporation of the solvent gave a yellow oil (100 mg). The residue was purified by preparative TLC (toluene–AcOEt–EtOH=15: 5: 1.5) to afford 22 mg of the dibenzoyl derivative (**8α**), which was recrystallized from isopropyl ether–hexane to give colorless needles, mp 168—170°C. [Physicochemical properties are given in Table I.] ^{1}H-NMR ($CDCl_3$) δ: 1.25 (3H, d, $J_{5,6}$=6.0 Hz, H-6), 1.91 (3H, s, C_3–CH_3), 2.21 (1H, dd, $J_{1,2ax}$=4.5, $J_{2ax,2eq}$=13.5 Hz, H-2ax), 2.86 (1H, dd, $J_{1,2eq}$=1.0, $J_{2ax,2eq}$=13.5 Hz, H-2eq), 3.40 (3H, s, OCH_3), 4.35 (1H, q, $J_{5,6}$=6.0 Hz, H-5), 4.94 (1H, dd, $J_{1,2eq}$=1.0, $J_{1,2ax}$=4.5 Hz, H-1), 5.18 (1H, s, H-4), 6.70 (1H, s, NH), 7.36—7.70 (m, aromatic H), 8.09—8.26 (m, aromatic H). UV λ_{max}^{MeOH} nm (log ε): 227 (4.22), 270 (3.01).

X-Ray Analysis of 5α——Intensity measurements were performed with a Rigaku Denki automatic 4-circle diffractometer using monochromated Mo-*Kα* radiation. Colorless single crystals of **5α** for X-ray study were obtained from benzene–cyclohexane. The crystal data for **5α** are listed in Table V. The intramolecular bond distances (Å) and valence angles (°) are given in Table VI.

Table V. Crystal Data for **5α**

Molecular formula		$C_{12}H_{21}NO_5$
Molecular weight		259.30
Crystal system		Orthorhombic
Space group		$P2_12_12_1$
Cell dimensions		
	a	9.493(1) Å
	b	19.521(3)
	c	7.819(1)
	u	1449.0(3) Å^3
	z	4
	dx	1.188 gcm^{-3}
Final *R* value		9.7%

Table VI. Bond Lengths (Å) and Bond Angles (°)

C (1)—O (1)	1.42(1)	C (5)—O (1)	1.45(1)
C (1)—O (2)	1.42(1)	C (5)—C (12)	1.54(2)
C (1)—C (2)	1.54(1)	O (2)—C (6)	1.43(1)
C (2)—C (3)	1.58(1)	N (1)—C (8)	1.34(1)
C (3)—N (1)	1.48(1)	C (8)—O (3)	1.25(1)
C (3)—C (4)	1.56(1)	C (8)—C (9)	1.53(1)
C (3)—C (7)	1.52(1)	O (4)—C (10)	1.34(1)
C (4)—O (4)	1.45(1)	C (10)—O (5)	1.20(1)
C (4)—C (5)	1.53(1)	C (10)—C (11)	1.50(2)
C (5)—O (1)—C (1)	115.3(7)	O (4)—C (4)—C (5)	106.7(7)
O (1)—C (1)—O (2)	112.6(7)	C (4)—C (5)—O (1)	110.6(7)
O (1)—C (1)—O (2)	109.5(2)	C (4)—C (5)—C (12)	113.5(8)
O (2)—C (1)—C (2)	108.6(8)	O (1)—C (5)—C (12)	105.7(8)
C (1)—C (2)—C (3)	113.1(7)	C (1)—O (2)—C (6)	109.5(8)
C (2)—C (3)—C (4)	109.0(7)	C (3)—N (1)—C (8)	125.1(7)
C (2)—C (3)—N (1)	104.4(6)	N (1)—C (8)—O (3)	124.2(8)
N (1)—C (3)—C (4)	108.4(7)	N (1)—C (8)—C (9)	115.5(7)
N (1)—C (3)—C (7)	112.0(7)	O (3)—C (8)—C (9)	120.3(8)
C (2)—C (3)—C (7)	112.5(7)	C (4)—O (4)—C (10)	119.7(7)
C (4)—C (3)—C (7)	110.4(7)	O (4)—C (10)—O (5)	120.7(10)
C (3)—C (4)—C (5)	110.4(7)	O (4)—C (10)—C (11)	112.4(9)
C (3)—C (4)—O (4)	107.2(6)	O (5)—C (10)—C (11)	126.9(11)

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