Carbohydrate Research, 46 (1976) 227–235

SYNTHESIS OF 3-AMINO-2,3,6-TRIDEOXY-D-*ribo*-HEXOSE HYDROCHLORIDE*†

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(Received October 11th, 1975; accepted for publication, October 25th, 1975)

ABSTRACT

The title sugar, the 5-epimer of daunosamine, was prepared in a sequence of high-yielding steps from methyl α-D-mannopyranoside (**1**). Conversion of **1** into methyl 3-acetamido-4-*O*-benzoyl-6-bromo-2,3,6-trideoxy-α-D-*ribo*-hexopyranoside (**2**), followed by reduction with hydrogen and Raney nickel, gave the 4-benzoate (**3**) of methyl 3-acetamido-2,3,6-trideoxy-α-D-*ribo*-hexopyranoside (**4**). Saponification of **3** gave **4** as an oil that gave a crystalline 4-acetate (**8**). *N*-Deacetylation of **4** was effected with barium hydroxide, and the resultant glycoside was hydrolyzed to give 3-amino-2,3,6-trideoxy-D-*ribo*-hexose hydrochloride (**7**). The 3-benzamido analogue (**5**) of **4** was prepared from **4** by *N*-deacetylation and subsequent benzoylation, and hydrolysis of **5** gave crystalline 3-benzamido-2,3,6-trideoxy-D-*ribo*-hexose (**6**). The crystalline 3-acetamido analogue (**9**) of **6** was obtained by acid hydrolysis of the glycoside **4**.

INTRODUCTION

A recent report from this laboratory[1,2] has described a simple sequence of reactions for converting methyl α-D-mannopyranoside (**1**) into 3-amino-2,3,6-trideoxy-L-*lyxo*-hexose (daunosamine) hydrochloride in 40% net yield. Key steps in the sequence involve C-2 deoxygenation, and amination at C-3 with the correct stereochemistry, with subsequent deoxygenation at C-6 and stereochemical inversion at C-5. The route has considerable potential for synthesis of stereochemical variants of the daunosamine structure by appropriate modification of steps from key intermediates. The present report describes such a variation to afford a high-yielding synthesis of 3-amino-2,3,6-trideoxy-D-*ribo*-hexose, which is the C-5 epimer of daunosamine and the enantiomorph of the naturally occurring amino sugar ristosamine.

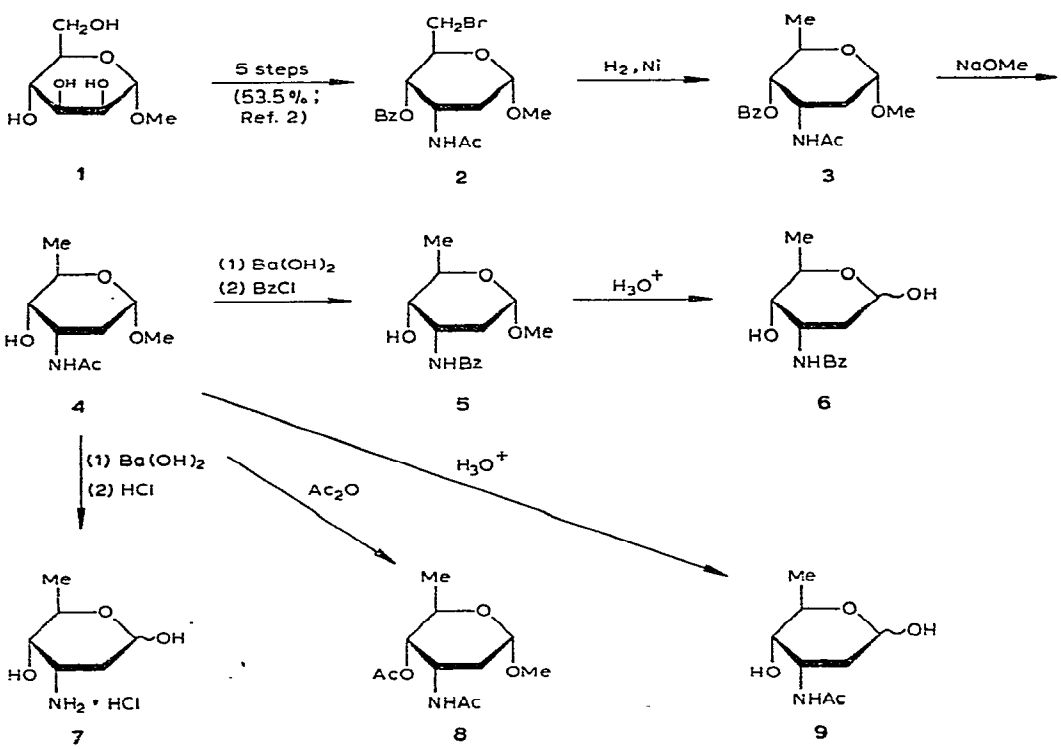
*Supported, in part, by Grant No. GM-11976 (The Ohio State University Research Foundation Project 1820) from the National Institute of General Medical Sciences, National Institutes of Health, U.S. Public Health Service, Bethesda, Md. 20014.
†For a preliminary report, see ref. 1.

Ristosamine is a component of the antibiotic ristomycin, a member of the vancomycin group[3]. Bognar and co-workers[4] determined its structure to be 3-amino-2,3,6-trideoxy-L-*ribo*-hexose by chemical degradation and by spectroscopy, and Bognar's group later reported[5] a synthesis of the sugar starting from L-rhamnose; a similar synthesis has also been reported by Lee and co-workers[6].

Although the D enantiomer of ristosamine has not yet been reported to occur naturally, current high interest in the antitumor antibiotics adriamycin and daunorubicin (see ref. 2 for detailed references) have prompted the quest for structural modifications in both the aglycon and the sugar (daunosamine) portions, to provide analogues of possible greater clinical utility; it is noteworthy that the 4'-epimer of adriamycin (inversion at C-4 in the daunosamine portion[7]) appears to lack the cardiotoxicity at high dose-levels that is an undesirable feature of adriamycin in cancer chemotherapy. Accordingly, the development of convenient, high-yielding routes to analogues of daunosamine epimeric at C-3, C-4 (acosamine[8]), and C-5 was considered a desirable objective, with the C-5 epimer being the subject of this article.

DISCUSSION

The starting point for the synthesis was methyl 3-acetamido-4-*O*-benzoyl-6-bromo-2,3,6-trideoxy-α-D-*ribo*-hexopyranoside (**2**), obtained[2] crystalline in 53.5% net yield in five steps from methyl α-D-mannopyranoside (**1**). Catalytic hydrogenation



of **2** in the presence of Raney nickel removed the bromine atom, to give the 6-deoxy derivative **3** in 91% yield as an analytically pure syrup. The n.m.r. spectrum of **3** (see Table I) resembled that[2] of **2**, except that the C-6 protons gave the anticipated *C*-methyl signal, a 3-proton doublet at high field ($\delta \sim 1.2$), instead of the 8-line, 2-proton pattern observed near δ 3.5 in the spectrum of the precursor **2**.

O-Debenzoylation of **3** by Zemplén catalytic transesterification gave syrupy methyl 3-acetamido-2,3,6-trideoxy-α-D-*ribo*-hexopyranoside (**4**) in 97% yield. The n.m.r. spectrum of **4** in methyl sulfoxide-d_6 showed the presence of one OH group; the spectrum was otherwise similar to that of **3**, except that the H-4 signal appeared, as expected, at higher field. The electron-impact mass spectrum of **4** showed a strong M^+ ion at *m/e* 203, together with fragment ions readily classified into the characteristic families proposed[9] for related glycosides and their derivatives.

N-Deacetylation of the glycoside **4** was readily achieved by the action of hot, aqueous barium hydroxide. Acid hydrolysis of the resultant amino glycoside could be effected under extremely mild conditions, as already observed[2] with the daunosamine analogue; this lability is, presumably, the consequence of the lack of an electronegative substituent at C-2. The resultant 3-amino-2,3,6-trideoxy-D-*ribo*-hexose was isolated as its solid hydrochloride salt (**7**), obtained in 81% yield; it melted at 123–125° and had $[\alpha]_D^{22}$ +85° in water. Although the product had the appearance of being crystalline, it failed to give the pattern of X-ray diffraction lines typical of a powdered, crystalline substance. Its extreme hygroscopicity necessitated careful precautions in weighing the sample for determination of its specific rotation.

The physical characterization of the L enantiomer of **7**, ristosamine, in the literature is somewhat ambiguous. It has been variously described as crystalline and anhydrous, having $[\alpha]_D$ +34.3° in water[4], and as a solid hemihydrate having $[\alpha]_D$ −42.2° or −26.9° in water[6]; neither report gives a melting point. It appears probable that low numerical values may have arisen because of the hygroscopicity of the compound, but the positive sign of rotation in one report[4] may also be in error.

The sequence **1**→**2**→**3**→**4**→**7** affords **7** in 38% overall yield from **1** without need for chromatographic purification at any of the steps, and all of the steps are readily amenable to scaled-up operation if large-scale preparation is required.

Methyl 3-benzamido-2,3,6-trideoxy-α-D-*ribo*-hexopyranoside (**5**) was readily prepared from the 3-acetamido analogue **4** by *N*-deacetylation with barium hydroxide, followed by *N*-benzoylation with benzoyl chloride. The product was obtained in high yield as an analytically pure oil, $[\alpha]_D$ +122.5° in benzene; the L enantiomer has been reported[4] to have $[\alpha]_D$ −104.3° in benzene. The n.m.r. spectrum of **5** was very similar to that of the 3-acetamido analogue **4**, except for absence of the acetyl-group signal and presence of a phenyl-group multiplet. The product showed a strong molecular-ion peak in its mass spectrum, together with characteristic fragment-ions (see Table II).

The benzamido glycoside **5** displayed high acid-lability, and underwent conversion into 3-benzamido-2,3,6-trideoxy-D-*ribo*-hexose (**6**) during 30 min at 100° in aqueous acetic acid. The benzamido sugar **6** was isolated crystalline in 92% yield,

TABLE I

100-MHz N.M.R. SPECTRAL DATA FOR COMPOUNDS 3, 4, 5, AND 8

Compound[a]	*Chemical shifts* (δ)[b] (*first-order couplings, Hz, in parentheses*)											
	H-1 ($J_{1,2a}$)	*H-2e* ($J_{1,2e}$)	*H-2a* ($J_{2a,3}$)	*H-3* ($J_{2e,3}$)	*H-4* ($J_{3,4}$)	*H-5* ($J_{4,5}$)	*H-6* ($J_{5,6}$)	*Aryl*	*NH*[c] ($J_{3,NH}$)	*OMe*	*Ac*	*OH*[c]
3[d]	4.89 dd (4.0)	1.89 m (1.5)	2.11 m (4.0)	← 4.85–4.74 m → (3.5)		4.08 m (9.5)	1.21 d (6.5)	7.65 m	6.85 d (8.5)	3.41 s	1.91 s	
4[e]	4.63 dd (3.5)	← 1.80 m → (3.5)		4.11 m ←(<1.0, 9.0)→	3.24 m (4.5)	3.74 m (8.0)	1.14 d (7.0)		7.18 d (9.0)	3.26 s	1.84 s	4.81
5	4.77 dd (2.8)	← 2.03 m → (1.8)		4.63 m ←(~1.0, 7.0)→	3.51 m (3.5)	3.78 m (9.0)	1.26 d (6.0)	7.55 m	7.90 d (~8.0)	3.43 s		4.11
8[f]	4.72 dd (3.5)	1.80 m (1.5)	2.05 m (3.5)	4.62 m (2.8)	4.53 dd (4.0)	3.92 m (9.5)	1.15 d (7.0)		6.82 d (8.0)	3.38 s	1.92 s 1.95 s	

[a] In chloroform-*d*, unless otherwise stated. [b] Signal multiplicities: d, doublet; m, multiplet; s, singlet. [c] Broadened signal. [d] $J_{2a,2e}$ 14.7 Hz. [e] In methyl sulfoxide-d_6. [f] $J_{2a,2e}$ 15 Hz; compare the data for the L enantiomer, methyl *N*-acetyl-*O*-acetylristosaminide, in refs. 4 and 6.

and its melting point was in good agreement with published values[4,5] for the L enantiomer, *N*-benzoylristosamine; the specific rotation in ethanol (+13.5°) also showed good correlation with the value (−11°) reported for *N*-benzoylristosamine. Mass-spectral data for **6** are recorded in Table II.

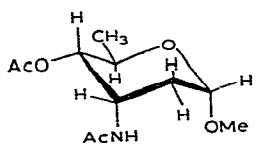
TABLE II

MASS-SPECTRAL DATA FOR COMPOUNDS **3–6**, **8**, AND **9**

m/e *of principal fragments* (% *of base peak*) *Compound*						*Assignment*[a]
3	**4**	**5**	**6**	**8**	**9**	
308 (0.02)	204 (0.6)	266 (0.5)	252 (0.3)	246 (0.2)	190 (0.07)	M+1
307 (0.03)	203 (6)	265 (3.5)	251 (2)	245 (0.04)	189 (0.5)	$M^{\ddagger}$
306 (0.09)	202 (0.05)			244 (0.15)	188 (2)	M−1
275 (0.18)	171 (2.7)	233 (2.5)	233 (4)	213 (0.3)	171 (7)	A_1
153 (34)	153 (9)	215 (3.5)	215 (1.5)	153 (48)	153 (5)	A_2
138 (7)	138 (2.3)	200 (1)	200 (1)	138 (18)	138 (3)	A_3
185 (11)	185 (0.6)	247 (0.6)	233 (4)	185 (7.5)	171 (7)	B_1
142 (24)	142 (3)	142 (2)	128 (3)	142 (39)	128 (6)	B_2
276 (2.2)	172 (6.5)	234 (2.5)	234 (1)	214 (6)	172 (2.1)	C_1
217 (0.3)	113 (7.5)	113 (4)	113 (0.2)	155 (1.5)	113 (1.5)	C_2
95 (9)	95 (3)	95 (2)	95 (0.6)	95 (20)	95 (2)	C_3
263 (0.5)	159 (5)	221 (0.5)	207 (3)	201 (0.7)	145 (12)	D_1
205 (2.4)	101 (100)	163 (34)	163 (10)	143 (14)	101 (43)	D_2
163 (2)	59 (60)			101 (30)	59 (45)	D_2-CH_2CO
105 (100)		105 (100)	105 (100)			$PhCO^+$
77 (17)		77 (33)	77 (32)			Ph^+
43 (17)	43 (49)			43 (100)	43 (90)	Ac^+
		122 (5)[b]	122 (23)[b]	288 (0.02)[c]	60 (100)[d]	other

[a]Fragment assignments according to the preceding paper[2]; see also ref. 9. [b]$PhCONH_2^{\ddagger}$. [c]M+43. [d]$H_3CCONH_3^{\ddagger}$.

Acetylation of the syrupy acetamido glycoside **4** gave crystalline methyl 3-acetamido-4-*O*-acetyl-2,3,6-trideoxy-α-D-*ribo*-hexopyranoside (**8**), whose specific rotation (+134.5° in chloroform) showed excellent correlation with values (−134°, −130.8° in chloroform) reported[4,6] for methyl *N*-acetyl-*O*-acetylristosaminide; the melting point of **8** (63–64°) was higher than literature values[4,6] (51–52°, 53–55°) for the ristosamine derivative. Compound **8** gave an excellent, first-order n.m.r. spectrum (see Table I), and the observed spin-couplings clearly demonstrated that the $^4C_1$(D) conformation is strongly favored, despite the *syn*-diaxial arrangement of the methoxyl



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group and the 3-acetamido group; this predisposition is, presumably, the result of the anomeric effect operating to favor the axial orientation of the methoxyl group[10].

The uniformly high values (8.0–9.5 Hz) observed for $J_{4,5}$ in compounds **3**, **4**, **5**, and **8** (see Table I) indicate that the $^4C_1$(D) conformation is favored in all of these derivatives.

Hydrolysis of the acetamido glycoside **4** with aqueous acetic acid gave an 80% yield of crystalline 3-acetamido-2,3,6-trideoxy-D-*ribo*-hexose (**9**); neither this compound nor its enantiomer appears to have been reported hitherto.

EXPERIMENTAL

General methods. — Evaporations were performed under diminished pressure. Melting points were determined with a Thomas–Hoover apparatus and are uncorrected. A Perkin–Elmer Model 141 polarimeter and 1-dm tubes were used for measurement of specific rotations. I.r. spectra were recorded with a Perkin–Elmer Model 457 grating i.r. spectrophotometer, and n.m.r. spectra at 100 MHz with a Varian HA-100 spectrometer. Chemical shifts refer to an internal standard of tetramethylsilane ($\delta = 0.00$), and are recorded, together with spin-coupling values (Hz), in Table I. T.l.c. was performed with Silica Gel G (E. Merck, Darmstadt, Germany), activated at 120°, as the adsorbent, and 2:3 (v/v) benzene–acetone as the developing solvent; zones were detected by u.v. light, and with sulfuric acid and subsequent heating. Microanalyses were performed by W. N. Rond. Mass spectra were recorded by C. R. Weisenberger with an AEI MS-9 double-focusing, high-resolution spectrometer operating at an ionizing potential of 70 eV and an accelerating potential of 8 kV; the source temperature (direct-inlet system) was 150°. Data and probable assignments are recorded in Table II. X-Ray powder diffraction data give interplanar spacings, Å, for CuKα radiation. The camera diameter was 114.59 mm. Relative intensities were estimated visually: m, moderate; s, strong; v, very; w, weak. The strongest lines are numbered (1, strongest).

*Methyl 3-acetamido-4-O-benzoyl-2,3,6-trideoxy-α-*D-ribo-*hexopyranoside* (**3**). — A mixture of methyl 3-acetamido-4-*O*-benzoyl-6-bromo-2,3,6-trideoxy-α-D-*ribo*-hexopyranoside[2] (**2**, 5 g, 12.95 mmoles), Raney nickel (~10 g), and triethylamine (2 ml) in methanol (150 ml) was shaken under hydrogen at 50 lb.in.$^{-2}$ for 8 h, whereupon t.l.c. indicated the reaction to be complete. The catalyst was removed by filtration, the filtrate evaporated, and the semicrystalline residue (~6 g) dissolved in chloroform (100 ml). The solution was washed twice with water to remove triethylammonium bromide, dried (magnesium sulfate), and evaporated to give **3** as a syrup; yield 3.61 g (91%), $[\alpha]_D^{23}$ +126° (*c* 1.3, chloroform); ν_{max}^{film} 3420 (NH), 1725 (ester C=O), 1670 and 1520 (amide), 1600 and 1585 cm^{-1} (monosubstituted phenyl). For analytical purposes, a sample was kept over phosphorus pentaoxide, potassium hydroxide, and paraffin in a desiccator for several days.

Anal. Calc. for $C_{16}H_{21}NO_5$ (307.349): C, 62.53; H, 6.89; N, 4.56. Found: C, 62.48; H, 7.17; N, 4.74.

*Methyl 3-acetamido-2,3,6-trideoxy-α-*D-ribo-*hexopyranoside* (**4**). — To a solution of compound **3** (2.98 g, 9.72 mmoles) in abs. methanol (20 ml) was added M sodium methoxide (0.5 ml), and the mixture was kept for ~12 h at ~25°, whereupon t.l.c. indicated that saponification was complete. The solution was passed through a small column (250 × 20 mm) of silica gel (No. 7734, 63–200 μm, E. Merck, Darmstadt, Germany), and the resultant neutral effluent evaporated. The resulting syrup was dissolved in water (100 ml), treated with activated charcoal in order to remove methyl benzoate, and lyophilized to give pure **4** as a syrup; yield 1.92 g (97%), $[\alpha]^{23}$ +37° (*c* 1.8, chloroform); ν_{max}^{film} 3400, 3300 (OH, NH), 1650 and 1520 cm^{-1} (amide). For analytical purposes, a sample was distilled under diminished pressure (10 mtorr, bath temperature ~165°).

Anal. Calc. for $C_9H_{17}NO_4$ (203.24): C, 53.19; H, 8.43; N, 6.89. Found: C, 52.98; H, 8.27; N, 7.01.

*3-Amino-2,3,6-trideoxy-*D-ribo-*hexose hydrochloride* (**7**). — A solution of *N*-acetylated glycoside **4** (590 mg, 2.9 mmoles) and barium hydroxide octahydrate (1.9 g, 6 mmoles) in water (25 ml) was boiled under reflux for 12 h, after which time t.l.c. revealed only a trace of the starting material **4** (R_F 0.40) accompanying the *N*-deacetylated product (R_F 0.22). The pH was then adjusted to 3 by adding 0.5M sulfuric acid, and the mixture was kept for 2 h at 98°. Barium sulfate was removed by filtration with suction through Celite, and the excess of sulfuric acid was removed by treatment with Amberlite IRA-400 (OH^-). Hydrochloric acid (M, 3 ml) was added, and the solution was lyophilized to give a solid that proved to be extremely hygroscopic. Addition of dry acetone (5 ml) gave an apparently crystalline product that could be filtered off in an inert atmosphere (nitrogen) and dried; yield 430 mg (81%), m.p. 123–125° (dec.), $[\alpha]_D^{22}$ +85° (equil., *c* 2.7, water; mean of 3 determinations). The product did not give an X-ray powder diffraction pattern showing discrete lines, indicating that the compound was not actually crystalline.

Anal. Calc. for $C_6H_{14}ClNO_3$ (183.637): C, 39.24; H, 7.69; N, 7.63. Found: C, 37.93; H, 7.58; N, 6.97.

The analytical values observed, although not in full accord with the anhydrous compound, were in better accord with this formulation than with values calculated for the hemihydrate.

The enantiomer of **7**, ristosamine (3-amino-2,3,6-trideoxy-L-*ribo*-hexose) hydrochloride, has been described as crystalline[4] and as an extremely hygroscopic solid containing 0.5 mole of water[6] per mole, but no melting points were given. The optical rotations reported are $[\alpha]_D$ 34.3° in* water[4], and $[\alpha]_D$ −26.9 and −42.2° in water[6].

*Methyl 3-benzamido-2,3,6-trideoxy-α-*D-ribo-*hexopyranoside* (**5**). — A solution of compound **4** (815 mg, 4 mmoles) and barium hydroxide octahydrate (2.6 g, 8.25 mmoles) in water (30 ml) was boiled under reflux for 24 h, whereupon t.l.c. indicated saponification to be complete. Solid carbon dioxide was added, and the

*Omission of the negative sign in this report was presumably a typographical error.

resultant precipitate of barium carbonate was filtered off with suction. To the filtrate was added potassium hydrogen carbonate (5 g), and the solution was cooled to 0°. A cold solution of benzoyl chloride (2 ml, 17.4 mmoles) in acetone (20 ml) was added, and the mixture was stirred for 3 h at 0° and then for 18 h at ~25°. The inorganic material was removed by filtration with suction, the acetone distilled off, and the remaining aqueous solution extracted with chloroform (50-, 30-, and 30-ml portions). The extract was successively washed with aqueous sodium hydrogen carbonate and water, dried (magnesium sulfate), and evaporated to give **6** as a colorless oil that migrated as a single spot in t.l.c.; yield 930 mg (88%), $[\alpha]_D^{22}$ +87.5° (*c* 1.9, chloroform) and +122.5° (*c* 1.4, benzene); ν_{max}^{film} 3500–3300 (OH, NH), 1655 and 1535 (amide), 1605 and 1585 cm^{-1} (monosubstituted phenyl). For analytical purposes, a sample was kept over phosphorus pentaoxide, potassium hydroxide, and paraffin in a desiccator for several days.

Anal. Calc. for $C_{14}H_{19}NO_4$ (265.312): C, 63.38; H, 7.22; N, 5.28. Found: C, 63.49; H, 7.36; N, 5.46.

The L enantiomer, methyl *N*-benzoyl-α-D-ristosaminide, has been reported as an oil, $[\alpha]_D$ −104.3° in benzene[4].

3-Benzamido-2,3,6-trideoxy-D-ribo-*hexose* (**6**). — A solution of the glycoside **5** (380 mg, 1.43 mmoles) in water (15 ml) and acetic acid (3 ml) was boiled for 30 min under reflux, whereupon t.l.c. indicated that the hydrolysis was complete. Evaporation of the solvent gave a crystalline residue that was filtered off with the aid of 1:2 (v/v) ethyl acetate–ether, to give pure **6**; yield 329 mg (92%), m.p. 128–129°, $[\alpha]_D^{23}$ +39° (equil., *c* 0.6, water) and +13.5° (equil., *c* 1, ethanol); ν_{max}^{KBr} 3360, 3280 (OH, NH), 1630 and 1540 (amide), 1600 and 1578 cm^{-1} (monosubstituted phenyl); X-ray powder diffraction data: 14.84 w, 8.15 m, 7.64 s (2), 6.78 w, 5.17 m, 4.83 m, 4.28 vs (1), 4.06 s (3), 3.86 s, 3.64 m, 3.39 w, 3.18 s, 3.06 m, and 2.86 m.

Anal. Calc. for $C_{13}H_{17}NO_4$ (251.285): C, 62.14; H, 6.82; N, 5.57. Found: C, 62.26; H, 6.96; N, 5.77.

The L enantiomer, *N*-benzoylristosamine, has been reported to have m.p. 131–133°, $[\alpha]_D$ −14 → −11° (10 min) in ethanol[4], and m.p. 126–128°, $[\alpha]_D$ −10° (10 min) in ethanol[5].

Methyl 3-acetamido-4-O-*acetyl-2,3,6-trideoxy-α*-D-ribo-*hexopyranoside* (**8**). — Compound **4** (800 mg, 3.94 mmoles) was treated with 1:2 (v/v) acetic anhydride–pyridine (9 ml) for 18 h at ~25°. The excess of acetic anhydride was then decomposed by adding water (2 ml) while keeping the mixture cool in an ice–water bath. The solution was evaporated, and the residue recrystallized from hexane to give pure **8**; yield 778 mg (80.5%), m.p. 63–64°, $[\alpha]_D^{23}$ +134.5° (*c* 0.92, chloroform); ν_{max}^{KBr} 3400 (NH), 1740 (ester CO), 1660 and 1525 cm^{-1} (amide); X-ray powder diffraction data: 12.27 w, 7.10 w, 6.73 vs (1), 6.25 m, 5.68 m, 5.18 vw, 4.70 s (2), 4.27 w, 4.11 m, 3.93 m, 3.79 w, 3.56 s (3), 3.44 vw, 3.23 w, and 3.11 w.

Compound **8** could not be dried *in vacuo* without its being converted into a syrup; this fact might account for a broad range of values for elemental analysis obtained for different batches. This result contrasts with a recent report[6] on the L

enantiomer, for which repeated analysis was stated to indicate the presence of 0.5 mole of water per mole. For analytical purposes, therefore, a sample of **8** was distilled under diminished pressure (25 mtorr, bath temperature ~120°).

Anal. Calc. for $C_{11}H_{19}NO_5$ (245.278): C, 53.87; H, 7.81; N, 5.71. Found: C, 53.84; H, 8.27; N, 5.49.

For the L enantiomer, methyl *N*-acetyl-*O*-acetylristosaminide, the following constants have been reported: m.p. 53–55°, $[\alpha]_D$ −130.8 ±1.8° in chloroform[6]; m.p. 51–52°, $[\alpha]_D$ −134° in chloroform[4].

3-Acetamido-2,3,6-trideoxy-D-ribo-*hexose* (**9**). — A solution of the *N*-acetylated glycoside **4** (280 mg, 1.38 mmoles) in water (5 ml) and acetic acid (2 ml) was boiled for 30 min under reflux, whereupon t.l.c. indicated that hydrolysis was complete. The solution was evaporated, and the residue recrystallized from ethyl acetate to give compound **9**; yield 210 mg (80%), m.p. 134°, $[\alpha]_D^{23}$ +39° (equil., *c* 0.5, water); ν_{max}^{KBr} 3400, 3290 (OH, NH), and 1635 and 1570 cm^{-1} (amide); X-ray powder diffraction data: 7.49 m, 5.94 m, 5.18 m, 4.88 s (1), 4.43 s (2), 4.28 m, 3.96 w, 3.79 w, 3.62 m (3), 3.50 m, 2.97 w, 2.87 w, 2.71 m, and 2.58 m.

Anal. Calc. for $C_8H_{15}NO_4$ (189.214): C, 50.78; H, 7.99; N, 7.40. Found: C, 51.03; H, 8.19; N, 7.60.

ACKNOWLEDGMENT

The authors thank Mr. S. Eitelman for recording n.m.r. spectra.

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