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SOME REACTIONS OF A FURANOID 2-AMINOGLYCAL DERIVATIVE*

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ABSTRACT

Some reactions, catalyzed by *p*-toluenesulfonic acid, of 2-acetamido-1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol (**1**), a furanoid 2-aminoglycal derivative, were examined. Reaction with methyl and with benzyl alcohol gave the corresponding furanoid 2,3-unsaturated glycosides (**2** and **3**) in good yield. Similar reaction with water, followed by acetylation, gave 2-acetamido-1,4,6-tri-*O*-acetyl-2,3-dideoxy-D-*ribo*-hex-2-enopyranose, which was hydrogenated to 2-acetamido-1,4,6-tri-*O*-acetyl-2,3-dideoxy-D-*ribo*-hexopyranose (an *N*-acetyllividosamine derivative) and its *arabino* analog. Addition of a catalytic amount of *p*-toluenesulfonic acid to a solution of **1** in dry 1,4-dioxane afforded furanoid, (1→3)-disaccharides in high yield. Tosylation of **1** to yield a furan derivative was, however, unsuccessful. Hydrogenation of methyl 2-acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-D-*erythro*-hex-2-enofuranoside (**2**) was examined by use of palladium-on-carbon, as well as platinum oxide, as the catalyst.

INTRODUCTION

Our recent work[1–3] has shown that a furanoid 2-aminoglycal derivative (**1**) is readily obtainable from 2-acetamido-2-deoxy-D-glucose by a unique acetonation using 2,2-dialkoxypropane, *N*,*N*-dimethylformamide, and *p*-toluenesulfonic acid. Eiteman *et al.*[4] and Ireland *et al.*[5] recently reported an alternative route to furanoid glycals, for employment as useful precursors in synthetic carbohydrate chemistry. On the other hand, however, compounds in this series have been judged by Ferrier and Hurford[6] to be too reactive to constitute satisfactory glycosylating agents, in contrast to the fact that pyranoid glycals have often been used as useful intermediates in the synthesis of a variety of carbohydrate derivatives[7].

We now report some reactions of **1** catalyzed by *p*-toluenesulfonic acid, and a facile synthesis of 2-acetamido-2,3-dideoxy-D-*ribo*-hexopyranose (*N*-acetyllividosamine[8]) and its D-*arabino* analog *via* the 2,3-unsaturated intermediates (**2** and **6**) derived from **1**.

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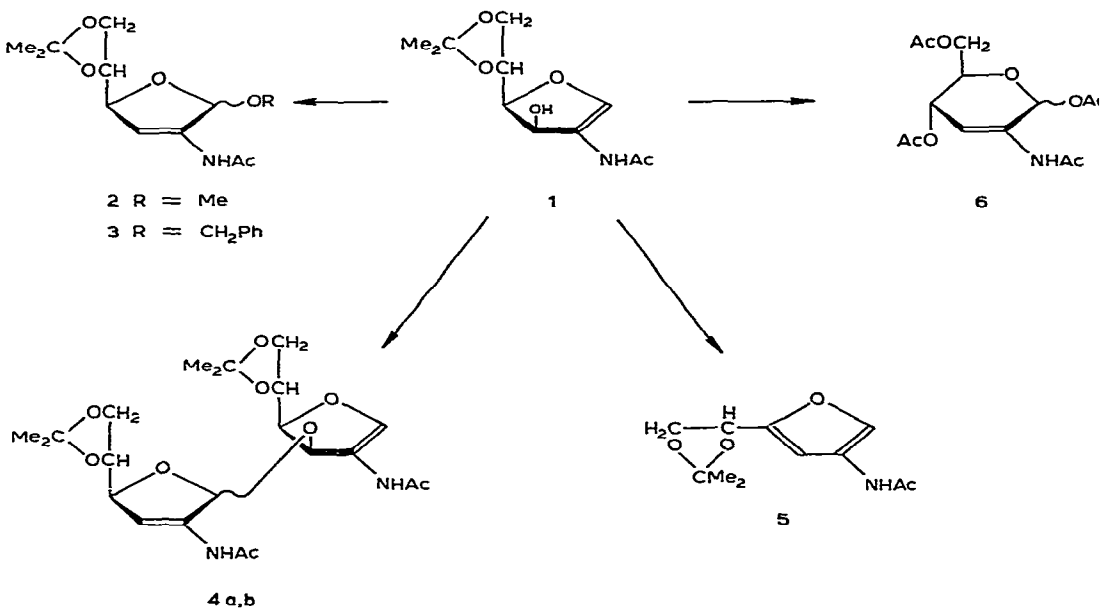
*The Behavior of Some Aldoses with 2,2-Dialkoxypropane–*N*,*N*-Dimethylformamide–*p*-Toluenesulfonic Acid, Part VIII. For Part VII, see ref. 1.

RESULTS AND DISCUSSION

2-Acetamido-1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol (**1**) was treated with methyl or benzyl alcohol in dry 1,4-dioxane containing a trace of *p*-toluenesulfonic acid for 30 min at 20–25°. The solution was made neutral with Amberlite IR-45 ion-exchange resin, and evaporated *in vacuo*. The residual syrup from the reaction with methanol gave an almost pure sample of methyl 2-acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-D-*erythro*-hex-2-enofuranoside (**2**, 98%) without further purification. The anomeric ratio (α:β) in **2** was estimated at ~7:5 on the basis of the n.m.r. intensity of H-1α and H-1β. Similarly, benzyl 2-acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-D-*erythro*-hex-2-enofuranoside (**3**, α:β ~2:1) was obtained in 70% yield, as a sample absolutely free from benzyl alcohol. When this reaction was conducted at −20°, the anomeric ratio changed to 5:1, strongly indicative of a favored α-glycosylation in this reaction system.



Addition of a trace of *p*-toluenesulfonic acid to a solution of **1** in dry 1,4-dioxane afforded a novel type of furanoid (1→3)-disaccharide, namely, 2-acetamido-3-*O*-(2-acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-D-*erythro*-hex-2-enofuranosyl)-1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol (**4a,b**) in high yield. One glycosidic isomer (**4b**, 26%) was crystallized pure as plates from ether–ethanol, whereas the other (**4a**) was isolated from the mother liquor as an amorphous solid in 71% yield.

N.m.r. data for the synthetic, furanoid, 2,3-unsaturated glycosides are shown in Table I. The anomeric configurations of compounds in this series were determined

TABLE I

N.M.R. DATA[a] FOR FURANOID, 2,3-UNSATURATED GLYCOSIDES

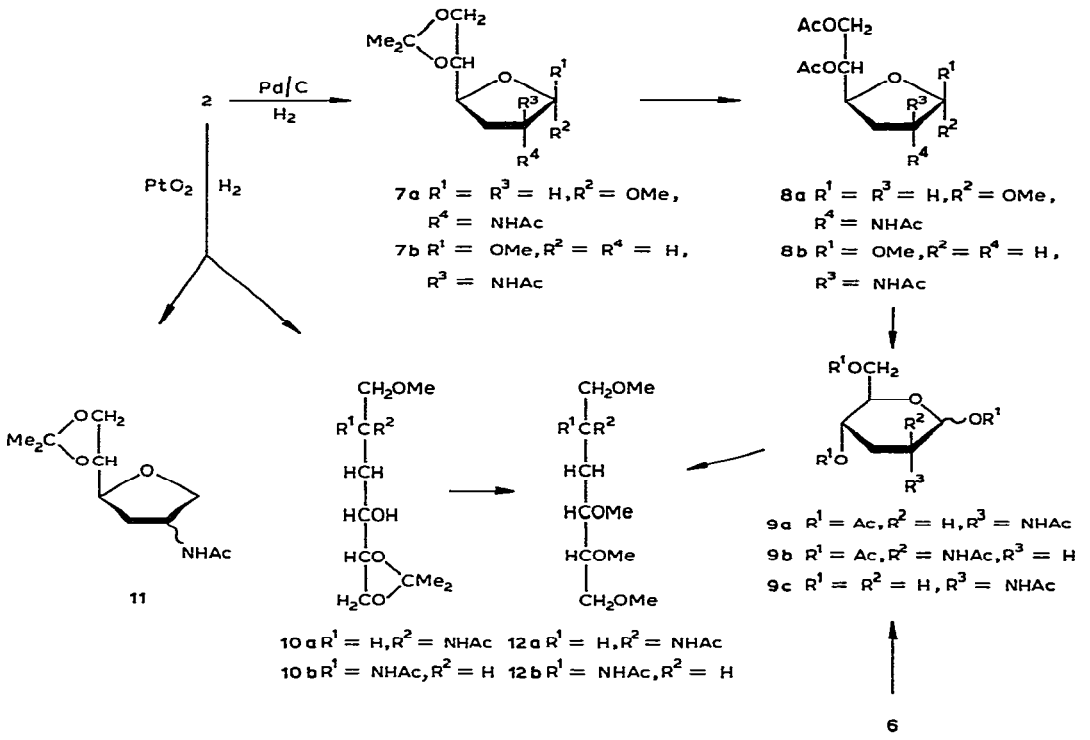
Compound[b]	*Chemical shifts (δ)*			*Coupling constants (Hz)*	
	H-1	*H-3*	*H-4*	$J_{1,3}$	$J_{1,4}$
2 (α)	5.69	6.42	4.88	<1.0	4.0
2 (β)	5.55	6.36	4.80	1.0	1.0
3 (α)	5.80	6.40	4.65–5.0	<1.0	4.0
3 (β)	5.70	6 35	4.65–5.0	1.0	1.0
	H-1'	*H-3'*	*H-4'*	$J_{1',3'}$	$J_{1',4'}$
4a	5.55	6.25	5.15	2.0	5.0
	5.83[c]	6.15[c]	4.82[c]	2.0[c]	5.0[c]
4b	5.50	6.25	4.90	2.0	3.6

[a]Measured in chloroform-*d*. [b]α or β indicates glycosidic linkage. [c]Measured in dimethyl sulfoxide-d_6.

from the observed $J_{1',4'}$ values, as, in such systems, the coupling between H-1 and H-4 is large (~4 Hz) when the protons are *trans*-related, and small (~1 Hz) when the relationship is *cis*[9]. The data given in Table I are also comparable to those of the 3-deoxypent-2-enose derivatives reported by Ferrier and Hurford[6]. For compounds **4a** and **4b**, however, the foregoing rule cannot be simply applied, because of the quite similar values of $J_{1',4'}$, although the chemical shifts of H-1', as well as the ratio of yields isolated, suggest that **4a** and **4b** might correspond to α- and β-glycosides, respectively.

On standing in water containing a trace of *p*-toluenesulfonic acid for 3.5 h at 45–50°, compound **1** was readily transformed into 2-acetamido-2,3-dideoxy-D-*erythro*-hex-2-enopyranose, which was acetylated to give **6** in 80% yield. 2-Acetamido-1,4,6-tri-*O*-acetyl-2,3-dideoxy-D-*ribo*-hexopyranose (**9a**) and 2-acetamido-1,4,6-tri-*O*-acetyl-2,3-dideoxy-D-*arabino*-hexopyranose (**9b**) were prepared in 60 and 23% yields respectively, by the hydrogenation of **6**, using 10% palladium-on-carbon as the catalyst. Mild *O*-deacetylation of **9a** afforded *N*-acetyllividosamine[8] (**9c**).

Compound **2**, the 2,3-unsaturated, methyl furanoside, was hydrogenated in the presence of 10% palladium-on-carbon, to give an inseparable mixture of methyl 2-acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-D-*ribo*- and -*arabino*-hexofuranosides (**7a,b**), which was subsequently converted, *via* *O*-deisopropylidenation and *O*-acetylation, into methyl 2-acetamido-5,6-di-*O*-acetyl-2,3-dideoxy-α-D-*ribo*-hexofuranoside (**8a**, 53%) and methyl 2-acetamido-5,6-di-*O*-acetyl-2,3-dideoxy-β-D-*arabino*-hexofuranoside (**8b**, 36%). The structures of **8a** and **8b** were confirmed by the respective transformation, *via* the hydrolysis of the methyl glycoside, into **9a** or **9b**, identical with those prepared from **6**. Interestingly, in **8a** as well as in **8b**, the configurational relationship between the substituents at C-1 and C-2 is *cis*, indicating



that the hydrogenation occurred almost exclusively on the back side of the methoxyl group at C-1. In fact, the isolated yields of **8a** and **8b** correspond fairly well to the anomeric ratio of **2** as estimated by n.m.r. spectroscopy. Pure samples of **7a** and **7b** were prepared by introduction of a 5,6-*O*-isopropylidene group into the *O*-deacetylated derivatives from **8a** and **8b**, respectively.

On the other hand, when the hydrogenation of **2** was conducted in the presence of platinum oxide in ethanol, the new 2-acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-1-*O*-methyl-D-*ribo*-hexitol (**10a**, 31%), 2-acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-1-*O*-methyl-D-*arabino*-hexitol (**10b**, 17%), and 3-acetamido-5-(1,2-*O*-isopropylidene-D-*glycero*-1,2-dihydroxyethyl)tetrahydrofuran (**11**, 22%) were isolated, besides **7a,b** (28%). Compounds **10a** and **10b** were respectively transformed, *via* complete *O*-methylation, into 2-acetamido-2,3-dideoxy-1,4,5,6-tetra-*O*-methyl-D-*ribo*-hexitol (**12a**) or 2-acetamido-2,3-dideoxy-1,4,5,6-tetra-*O*-methyl-D-*arabino*-hexitol (**12b**), identical with those independently prepared from **9a** or **9b** *via* reduction with sodium borohydride.

Some reactions of the hydroxyl group at C-3 of **1** were also examined. Attempted tosylation of **1**, for example, gave the furan derivative **5** in 60% yield without isolation of any tosylation product.

EXPERIMENTAL

General methods. — Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Specific rotations were determined with a Yanagimoto OR-50 polarimeter, and i.r. spectra were recorded with a Jasco IRA-spectrophotometer. N.m.r. spectra were recorded at 60 and 90 MHz with Hitachi R-24 and R-22 spectrometers, for solutions in chloroform-*d*, unless otherwise noted. Evaporations were conducted *in vacuo*.

*Methyl 2-acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-*D-erythro-*hex-2-enofuranoside* (**2**). — To a stirred solution of 2-acetamido-1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol[1] (**1**, 2.0 g) in methanol (4 mL) and dry 1,4-dioxane (100 mL) was added *p*-toluenesulfonic acid (20 mg), and stirring was continued for 30 min at 20–25°. The mixture was treated with Amberlite IR-45 (OH^-) ion-exchange resin to remove the acid, the suspension was filtered, and the filtrate was evaporated, to give **2** (2.1 g, 98%) as a syrup; ν_{max}^{film} 3280 (NH), 1680 (C=C), 1660 and 1530 (amide), and 850 cm^{-1} (Me_2C); n.m.r. data at 90 MHz: δ 1.32 and 1.42 (2 s, 6 H, Me_2C), 2.08 (s, 3 H, AcN), 3.30 and 3.40 (2 s, 3 H, OMe), 5.55 and 5.69 (dd, 1 H, H-1β and H-1α; see Table I for coupling constants), and 7.3 (s, 1 H NH).

Anal. Calc. for $C_{12}H_{19}NO_5$: C, 56.02; H, 7.44; N, 5.44. Found: C, 56.29; H, 7.40; N, 5.15.

*Benzyl 2-acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-*D-erythro-*hex-2-enofuranoside* (**3**). — To a stirred solution of **1** (0.5 g) and benzyl alcohol (2 mL) in dry 1,4-dioxane or chloroform (50 mL) was added *p*-toluenesulfonic acid (10 mg) at +20° or −20° and stirring was continued for 30 min at the respective temperature. The mixture was treated with Amberlite IR-45 (OH^-) ion-exchange resin to remove the acid, the suspension was filtered, and the resin was washed with 1,4-dioxane. The filtrate and washings were combined, and evaporated to a syrup which was chromatographed on a column of silicic acid (70 g) with benzene and then 50:1 benzene–methanol. The syrup (0.56 g) obtained on evaporation of the eluate (the latter solvent) was rechromatographed on a column of silica gel (30 g) with chloroform and then 100:1 chloroform–methanol. The chloroform–methanol eluate yielded **3** (0.48 g, 70% at 20°; 0.6 g, 88% at −20°); n.m.r. data at 60 MHz: δ 1.80 and 1.90 (2 s, 6 H, Me_2C), 1.95 (s, 3 H, AcN), 4.3–4.7 (m, 2 H, CH_2Ph), 5.70 and 5.80 (dd, 1 H, H-1β and H-1α; see Table I for coupling constants), 7.30 (s, 5 H, Ph), and 7.40 (s, 1 H, NH).

Anal. Calc. for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.55; H, 6.83; N, 3.97.

*2-Acetamido-3-*O*-(2-acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-*D-erythro-*hex-2-enofuranosyl)-1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-*D-arabino-*hex-1-enitol* (**4a,b**). — To a stirred solution of **1** (2.0 g) in dry 1,4-dioxane (80 mL) was added *p*-toluenesulfonic acid (10 mg), and stirring was continued for 30 min at 20–25°. The mixture was treated with Amberlite IR-45 (OH^-) ion-exchange resin to remove the acid, the suspension was filtered, and the resin was washed with 1,4-dioxane.

The filtrate and washings were combined, and evaporated to a syrup which was chromatographed on a column of silicic acid (40 g) with chloroform and then 50:1 chloroform–methanol. The chloroform–methanol eluate gave the title compound (mixture of the anomers) as a solid; **4b** was obtained as plates (0.47 g, 26%) from ether and ether–ethanol, and **4a** (1.4 g, 71%) as an amorphous solid from the mother liquor. Compound **4a** had $[\alpha]_D^{25}$ −81.7° (*c* 1.0, chloroform); ν_{max}^{Nujol} 3240 (NH), 1650 (C=C), 1660 and 1560 (amide), and 850 cm^{-1} (Me_2C); n.m.r. data at 60 MHz (in dimethyl sulfoxide-d_6): δ 1.26 and 1.34 (12 H, 2 Me_2C), 1.9 and 2.05 (2 s, 6 H, AcN), 5.83 (dd, 1 H, H-1′; see Table I for coupling constants), 6.70 (s, 1 H, H-1), and 9.59 and 9.76 (2 s, 2 H, NH).

Anal. Calc. for $C_{22}H_{32}N_2O_9$: C, 56.40; H, 6.89; N, 5.98. Found: C, 56.65; H, 6.86; N, 5.83.

Compound **4b** had m.p. 198–199°, $[\alpha]_D^{25}$ +7.6° (*c* 1.0, chloroform); n.m.r. data at 90 MHz (in dimethyl sulfoxide-d_6): δ 1.20 and 1.25 (12 H, 2 Me_2C), 1.86 and 1.98 (2 s, 6 H, AcN), 5.72 (m, 1 H, H-1′), 6.08 (m, 1 H, H-3′), 6.60 (s, 1 H, H-1), and 9.35 and 9.52 (2 s, 2 H, NH).

Anal. Calc. for $C_{22}H_{32}N_2O_9$: C, 56.40; H, 6.89; N, 5.98. Found: C, 56.52; H, 6.89; N, 5.90.

*3-Acetamido-5-(1,2-O-isopropylidene-*D-glycero-*1,2-dihydroxyethyl)furan* (**5**). — A mixture of **1** (0.5 g) and *p*-toluenesulfonyl chloride (0.46 g) in dry pyridine (5 mL) was stirred for 9 h at 40°, and then extracted with chloroform. The extract was successively washed with 2M hydrochloric acid, 10% sodium carbonate, and water, dried (sodium sulfate), and evaporated. The residual syrup was chromatographed on a column of silicic acid with chloroform and then with 50:1 chloroform–methanol; the latter eluate yielded **5** (0.27 g, 58%) as a syrup, $[\alpha]_D^{23}$ −19.8° (*c* 0.5, chloroform); ν_{max}^{film} 3300 (NH), 1660 (C=C), 1650 and 1530 (amide), and 830 cm^{-1} (Me_2C); n.m.r. data at 60 MHz: δ 1.40 and 1.45 (6 H, Me_2C), 2.05 (s, 3 H, AcN), 3.85–4.35 (m, 2 H, H-2′), 4.98 (t, 1 H, $J_{1',2'}$ 7.0 Hz, H-1′), 6.27 (s, 1 H, H-2), 7.88 (s, 1 H, H-4), and 8.03 (s, 1 H, NH).

*2-Acetamido-1,4,6-tri-*O*-acetyl-2,3-dideoxy-*D-erythro-*hex-2-enopyranose* (**6**). — A solution of **1** (0.5 g) in water (15 mL) containing a catalytic amount of *p*-toluenesulfonic acid (10 mg) was stirred for 3.5 h at 45–50°. The mixture was treated with Amberlite IR-45 (OH^-) ion-exchange resin to remove the acid, the suspension was filtered, and the filtrate was evaporated to a syrup which was acetylated with acetic anhydride (3 mL) and pyridine (5 mL) under ice-cooling. The mixture was evaporated *in vacuo*, and the residue was chromatographed on a column of silicic acid (30 g) with chloroform and then 70:1 chloroform–methanol. The latter eluate yielded **6** (0.54 g, 80%) as a syrup; ν_{max}^{film} 3280 (NH), 1750 (ester), 1650 and 1530 (amide), and 1221 cm^{-1} (ester); n.m.r. data at 90 MHz: δ 2.05–2.13 (12 H, AcN and 3 AcO), 5.54 (near s, H-β), 5.70 (d, $J_{1,4}$ 4.0 Hz, H-1α), 6.30 (m, 1 H, H-3), and 7.40 (1 H, NH).

Anal. Calc. for $C_{14}H_{19}NO_8$: C, 51.06; H, 5.82; N, 4.25. Found: C, 51.24; H, 6.10; N, 4.03.

*Methyl 2-acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-α-*D-ribo-*hexofuranoside*

(**7a**) *and methyl 2-acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-β-*D-arabino-*hexofuranoside* (**7b**). — To a solution of **8a** (0.2 g) or **8b** (0.18 g) in methanol (5 mL) was added a catalytic amount of sodium metal. After being stirred for 15 min at room temperature, the respective mixture was treated with Amberlite IRC-50 (H^+) ion-exchange resin, the suspension was filtered, and the filtrate was evaporated to a syrup. To a solution of this syrup and 2,2-dimethoxypropane (1 mL) in *N*,*N*-dimethylformamide (5 mL) was added a trace of *p*-toluenesulfonic acid, and the mixture was stirred for 20 min at 40°. The mixture was treated with Amberlite IR-45 (OH^-) ion-exchange resin to remove the acid, the suspension was filtered, and the filtrate and washings were combined, and evaporated to a syrup which was chromatographed on a column of silicic acid (15 g) with chloroform and then with 70:1 chloroform–methanol. From the latter solvent, the title compound **7a**, or **7b**, was obtained as a syrup (0.17 g, 99%), or as needles (0.14 g, 91%), respectively.

Compound **7a** had $[\alpha]_D^{25}$ +9.7° (*c* 0.3, chloroform); ν_{max}^{Nujol} 3300 (NH), 1650 and 1540 (amide), and 840 cm^{-1} (Me_2C); n.m.r. data at 60 MHz: δ 1.3 and 1.4 (2 s, 6 H, Me_2C), 1.95 (s, 3 H, AcN), 3.35 (s, 3 H, OMe), 1.4–2.7 (m, 2 H, H-3), 4.80 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), and 6.18 (d, 1 H, NH).

Anal. Calc. for $C_{12}H_{21}NO_5$: C, 55.58; H, 8.16; N, 5.40. Found: C, 55.29; H, 7.98; N, 5.15.

Compound **7b** had m.p. 75°, $[\alpha]_D^{25}$ −49° (*c* 0.4, chloroform); ν_{max}^{Nujol} 3300 (NH), 1640 and 1530 (amide), and 830 cm^{-1} (Me_2C); n.m.r. data at 60 MHz: δ 1.3 and 1.36 (2 s, 6 H, Me_2C), 1.95 (s, 3 H, AcN), 3.32 (s, 3 H, OMe), 1.4–2.7 (m, 2 H, H-3), 4.74 (d, 1 H, $J_{1,2}$ 4.3 Hz, H-1), and 6.05 (d, 1 H, NH).

Anal. Calc. for $C_{12}H_{21}NO_5$: C, 55.58; H, 8.16; N, 5.40. Found: C, 55.51; H, 8.06; N, 5.43.

*Methyl 2-acetamido-5,6-di-*O*-acetyl-2,3-dideoxy-α-*D-ribo-*hexofuranoside* (**8a**) *and methyl 2-acetamido-5,6-di-*O*-acetyl-2,3-dideoxy-β-*D-arabino-*hexofuranoside* (**8b**). — Compound **2** (2.2 g) was hydrogenated in ethanol (100 mL) in the presence of 10% palladium-on-carbon (0.5 g). The suspension was filtered, and the filtrate was evaporated to a syrup which was dissolved in 60% aqueous acetic acid and the solution kept for 2 h at 40°. Evaporation gave a syrup (1.96 g) which was acetylated with acetic anhydride and pyridine. The products were chromatographed on a column of silicic acid (40 g) with chloroform and then 100:1 chloroform–methanol. Crystallization from ethanol–ether of the syrup obtained from the latter eluate, followed by fractional recrystallization, gave **8a** (1.25 g, 53%) and **8b** (0.87 g, 36%).

Compound **8a** had m.p. 142–143°, $[\alpha]_D^{20}$ +10.5° (*c* 0.4, chloroform); ν_{max}^{Nujol} 3300 (NH), 1740 (ester), 1640 and 1530 (amide), and 1240 and 1220 cm^{-1} (ester); n.m.r. data at 60 MHz: δ 1.95 (s, 3 H, AcN), 2.04 and 2.07 (2 s, 6 H, 2 AcO), 3.38 (s, 3 H, OMe), 1.5–2.56 (m, 2 H, H-3), 4.86 (d, 1 H, $J_{1,2}$ 4.8 Hz, H-1), and 6.00 (d, 1 H, NH).

Anal. Calc. for $C_{13}H_{21}NO_7$: C, 51.48; H, 6.98; N, 4.62. Found: C, 51.45; H, 6.91; N, 4.48.

Compound **8b** had m.p. 141°, $[\alpha]_D^{20}$ −4.0° (*c* 0.5, chloroform); ν_{max}^{Nujol} 3320 (NH),

1740 (ester), 1640 and 1550 (amide), and 1250 cm^{-1} (ester); n.m.r. data at 60 MHz: δ 1.95 (s, 3 H, AcN), 2.04 and 2.07 (2 s, 6 H, 2 AcO), 3.37 (s, 3 H, OMe), 1.30–2.15 (m, 2 H, H-3), 4.77 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 5.05 (m, 1 H, H-5), and 6.0 (d, 1 H, NH).

Anal. Calc. for $C_{13}H_{21}NO_7$: C, 51.48; H, 6.98; N, 4.62. Found: C, 51.45; H, 6.88; N, 4.60.

*2-Acetamido-1,4,6-tri-*O*-acetyl-2,3-dideoxy-*D-ribo*-hexopyranose* (**9a**) *and 2-acetamido-1,4,6-tri-*O*-acetyl-2,3-dideoxy-*D-arabino*-hexopyranose* (**9b**). — (*A*) *From* **1** *or* **6**. A solution of **1** (0.5 g) in water (15 mL) containing a catalytic amount of *p*-toluenesulfonic acid (10 mg) was stirred for 3.5 h at 45–50°. The acid was neutralized with Amberlite IR-45 (OH^-) ion-exchange resin, the suspension was filtered, and the filtrate was evaporated to a syrup which was hydrogenated in water (30 mL) and ethanol (20 mL) in the presence of 10% palladium-on-carbon (0.3 g). The suspension was filtered, and the filtrate was evaporated to a syrup which was treated with acetic anhydride (3 mL) and pyridine (5 mL). Extraction with chloroform, and evaporation of the extract, gave a syrup that was chromatographed on a column of silicic acid (20 g) with chloroform and then 70:1 chloroform–methanol. The latter eluate yielded **9a** (0.41 g, 60%) and **9b** (0.16 g, 23%) as syrups.

Hydrogenation of **6** in ethanol with the palladium catalyst gave the title compounds in almost the same yields as just described.

(*B*) *From* **8a** *or* **8b**. To a solution of **8a** (1.0 g) or **8b** (0.7 g) in methanol (50 mL) was added a catalytic amount of sodium metal. The respective mixture was stirred for 15 min at room temperature, and then treated with Amberlite IR-120 (H^+) resin. The suspension was filtered, and the filtrate was evaporated to a syrup which was treated with 90% aq. acetic acid (20 mL) plus 2M hydrochloric acid (5 mL) for 5 h at 55° with stirring. The mixture was evaporated *in vacuo*, and the residual syrup was co-evaporated with benzene, and then acetylated with acetic anhydride (3 mL) and pyridine (5 mL). The syrup obtained by evaporation was chromatographed on a column of silicic acid with the same solvent system as was used in (*A*). The 70:1 chloroform–methanol eluate yielded **9a** (0.97 g, 89%) or **9b** (0.49 g, 64%), respectively, as a syrup.

The α anomer of **9a** was crystallized from ether–hexane, to give needles, m.p. 151–152°, $[\alpha]_D^{23}$ +107.4° (*c* 0.5, chloroform); ν_{max}^{Nujol} 3300 (NH), 1740 (ester), 1638 and 1520 (amide), and 1240 cm^{-1} (ester); n.m.r. data at 90 MHz: δ 1.95 (s, 3 H, AcN), 2.02 and 2.14 (2 s, 9 H, 3 AcO), 1.54–2.45 (m, 2 H, H-3), 3.90 (m, 1 H, H-5), 4.15 (m, 2 H, 2 H-6), 4.40 (m, 1 H, H-2), 4.90 (m, 1 H, $J_{4,5} = J_{4,3a} = 10$ Hz, $J_{4,3e}$ 4.4 Hz, H-4), 5.60 (d, 1 H, NH), and 6.07 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1).

Anal. Calc. for $C_{14}H_{21}NO_8$: C, 50.75; H, 6.39; N, 4.23. Found: C, 50.51; H, 6.29; N, 4.22.

The β anomer of **9b** was also crystallized from ether–hexane, m.p. 174°, $[\alpha]_D^{20}$ −19.5° (*c* 0.22, chloroform); ν_{max}^{Nujol} 3300 (NH), 1740 (ester), 1640 and 1525 (amide), and 1230 and 1130 cm^{-1} (ester); n.m.r. data at 90 MHz: δ 2.20 (s, 3 H, AcN), 2.07 and 2.10 (2 s, 9 H, 3 AcO), 1.75–2.50 (m, 2 H, H-3), 3.94 (m, 1 H, H-5),

4.20 (m, 1 H, H-6), 4.48 (m, 1 H, H-2), 4.95 (m, 1 H, H-4), 5.82 (d, 1 H, NH), and 5.90 (d, 1 H, $J_{1,2}$ 3 Hz, H-1).

Anal. Calc. for $C_{14}H_{21}NO_8$: C, 50.75; H, 6.39; N, 4.23. Found: C, 50.62; H, 6.34; N, 4.07.

Compound **9a** was treated with dilute, methanolic sodium methoxide, to give an amorphous solid from which 2-acetamido-2,3-dideoxy-D-*ribo*-hexopyranose (**9c**; *N*-acetyllividosamine[8]) was crystallized from ethanol–ether, m.p. 145–147°, $[\alpha]_D^{25}$ +34° (equil.; *c* 0.4, water); lit.[8a] m.p. 151–152°, $[\alpha]_D$ +26.1° (*c* 1, water); lit.[8b] m.p. 150–152°, $[\alpha]_D$ +30° (equil.; *c* 0.6, water).

*2-Acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-1-*O*-methyl-*D-ribo-*hexitol* (**10a**), *2-acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-1-*O*-methyl-*D-arabino-*hexitol* (**10b**), *and 3-acetamido-5-(1,2-*O*-isopropylidene-*D*-glycero-1,2-dihydroxyethyl)tetrahydrofuran* (**11**). — Compound **2** was dissolved in ethanol (130 mL) and hydrogenated in the presence of platinum oxide (0.75 g) for 2.5 h at 40°. The suspension was filtered, and the filtrate was evaporated to a syrup which was chromatographed on a column of silicic acid (80 g) with suitable mixtures of chloroform and methanol. A 150:1 chloroform–methanol eluate yielded **8a,b** (0.86 g, 28%); 100:1, 50:1, and 30:1 eluates gave **11** (0.6 g, 22%), **10a** (0.52 g, 17%), and **10b** (0.98 g, 31%), respectively.

Compound **10a** had m.p. 70–71°, $[\alpha]_D^{20}$ −10.9° (*c* 1, chloroform); ν_{max}^{Nujol} 3250 (NH), 1640 and 1560 (amide), and 850 cm^{-1} (Me_2C); n.m.r. data at 60 MHz: δ 1.30 and 1.36 (2 s, 6 H, Me_2C), 1.95 (s, 3 H, AcN), 3.33 (s, 3 H, OMe), 1.05–2.20 (m, 2 H, H-3), and 6.72 (d, 1 H, NH).

Anal. Calc. for $C_{12}H_{23}NO_5$: C, 55.15; H, 8.87; N, 5.36. Found: C, 55.09; H, 8.84; N, 5.32.

Compound **10b** had m.p. 78–79°, $[\alpha]_D^{20}$ −13.6° (*c* 0.74, chloroform); ν_{max}^{Nujol} 3400–3250 (NH, OH), 1640 and 1530 (amide), and 850 cm^{-1} (Me_2C); n.m.r. data at 60 MHz: δ 1.30 and 1.35 (2 s, 6 H, Me_2C), 1.97 (s, 3 H, AcN), 3.32 (s, 3 H, OMe), 1.05–2.04 (m, 2 H, 2 H-3), and 6.25 (d, 1 H, NH).

Anal. Calc. for $C_{12}H_{23}NO_5$: C, 55.15; H, 8.87; N, 5.36. Found: C, 55.10; H, 8.79; N, 5.40.

Compound **11** was a syrup; ν_{max}^{film} 3260 (NH), 1650 and 1540 (amide), and 840 cm^{-1} (Me_2C); n.m.r. data at 60 MHz: δ 1.36 and 1.46 (2 s, 6 H, Me_2C), 1.93 (s, 3 H, AcN), 1.5–2.56 (m, 2 H, H-3), 3.49–4.53 (m, 6 H), 4.56 (m, 2 H, H-2), and 6.96 (d, 1 H, NH).

Compounds **10a** and **10b** were acetylated in the usual way, to give **10a′** and **10b′**, respectively, as syrups. Compound **10a′** had $[\alpha]_D^{20}$ ~0° (*c* 0.7, chloroform); ν_{max}^{film} 3250 (NH), 1740 (ester), 1650 and 1540 (amide), 1230 (ester), and 850 cm^{-1} (Me_2C); n.m.r. data at 60 MHz: δ 2.06 (s, 3 H, AcO) and 5.94 (m, 1 H, H-4) were observed (evidence of the presence of one hydroxyl group in **10a**).

Compound **10b′** had $[\alpha]_D^{23}$ −27° (*c* 0.3, chloroform); ν_{max}^{film} 3260 (NH), 1740 (ester), 1650 and 1540 (amide), 1230 (ester), and 850 cm^{-1} (Me_2C); n.m.r. data at 60 MHz: δ 2.00 (s, 3 H, AcO) and 4.95 (m, 1 H, H-4); otherwise, almost the same as **10b**.

*2-Acetamido-2,3-dideoxy-1,4,5,6-tetra-*O*-methyl-*D-ribo*-hexitol* (**12a**) *and 2-acetamido-2,3-dideoxy-1,4,5,6-tetra-*O*-methyl-*D-arabino*-hexitol* (**12b**). — A solution of **10a** (0.4 g) in 60% aq. acetic acid (10 mL) was stirred for 2 h at 45°. The mixture was evaporated *in vacuo*, and co-evaporated with benzene, to give a syrup which was stirred overnight with silver oxide (5 g) and methyl iodide (4 g) in *N,N*-dimethylformamide (5 mL) at room temperature. The suspension was filtered, and the filtrate was evaporated to a syrup which was chromatographed on a column of silicic acid (20 g) with chloroform and then 80:1 chloroform–methanol. The latter eluate yielded **12a** (0.4 g, 98%) as a syrup, $[\alpha]_D^{23}$ +4.1° (*c* 1, chloroform); ν_{max}^{film} 3280 (NH), 1650 and 1540 (amide), and 1120 cm^{-1} (ether); n.m.r. data at 90 MHz: δ 1.93 (s, 3 H, AcN), 3.29–3.40 (4 s, 12 H, 4 OMe), 6.02 (d, 1 H, NH), and 1.72 (m, 2 H, H-3).

Compound **10b** (0.2 g) was treated in the same way as for **10a**, to give **12b** (0.12 g, 59%) as a syrup, $[\alpha]_D^{23}$ −11.2° (*c* 0.5, chloroform); ν_{max}^{film} 3280 (NH), 1650 and 1540 (amide), and 1120 cm^{-1} (ether); n.m.r. data at 90 MHz: δ 1.93 (s, 3 H, AcN), 3.29, 3.31, 3.36, and 3.40 (4 s, 12 H, 4 OMe), and 5.96 (d, 1 H, NH).

N-Acetyllividosamine (**9c**), or its *arabino* analog prepared from **9a**, or **9b**, respectively, was reduced with sodium borohydride, and then per-*O*-methylated as just described, to give **12a**, or **12b**, respectively. The $[\alpha]_D$ value, and i.r. and n.m.r. data were identical with those given for **12a** or **12b** prepared from **10a** or **10b**, respectively.

Anal. Calc. for $C_{12}H_{25}NO_5$: C, 54.73; H, 9.57; N, 5.32. Found: For **12a**, C, 54.87; H, 9.50; N, 5.44. For **12b**, C, 54.91; H, 9.43; N, 5.00.

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