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SYNTHESIS OF 3-AMINO-3-DEOXY-α-D-MANNOPYRANOSYL α-D-MANNOPYRANOSIDE BY WAY OF A REGIOSELECTIVE SN2 DISPLACEMENT IN AN UNSYMMETRICAL, DISECONDARY DITRIFLATE OF A DISACCHARIDE

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ABSTRACT

3-Amino-3-deoxy-α-D-mannopyranosyl α-D-mannopyranoside was synthesized from known 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-altropyranosyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside, which is available in four steps from commercial α,α-trehalose. The 3,2′-ditriflate of the blocked disaccharide was first treated with sodium azide under phase-transfer conditions, which effected regioselective displacement of the 3-triflyloxy group, and subsequent reaction with sodium benzoate in *N,N*-dimethylformamide displaced the 2′-triflyloxy group. The blocked, 3-azido-2′-*O*-benzoyl derivative of α-D-mannopyranosyl α-D-mannopyranoside so obtained was conventionally debenzoylated and debenzylidenated, and subsequent, palladium-catalyzed transfer hydrogenation with formic acid effected reduction of the azido group and cleavage of the benzyl protecting groups, to give the title disaccharide in 13% over-all yield.

INTRODUCTION

In continuation of a program directed toward the synthesis of trehalose-type amino sugars[1–3], we have recently developed a procedure for the practical preparation of 3-amino-3-deoxy-α-D-mannopyranosyl 3-amino-3-deoxy-α-D-mannopyranoside, by which this disaccharide was obtained[4] in four steps starting from 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-altropyranosyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-altropyranoside. This symmetrical, 2,2′-dibenzyl ether had been obtained in 79% yield by oxirane ring opening, with sodium benzoxide, of the readily available 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranosyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside, and that reaction had also furnished, as a by-product isolated in 14% yield, the unsymmetrical isomer **1**, 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-altropyranosyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside[5]. Having performed the operations repeatedly and on fairly large scale, we eventually obtained a substantial quantity of crystalline **1** and it was utilized as the starting material for

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1 R = H
2 R = Tf
Phase transfer
3 (55 %)
4 (8 %)
5 (22 %)
HCONMe2
NaOBz
6
7
8
9 R = H, R' = NH2
10 R = Ac, R' = NHAc
Tf = SO2CF3

a synthesis of the title compound, 3-amino-3-deoxy-α-D-mannopyranosyl α-D-mannopyranoside (**9**), a hitherto unknown, monoaminated analog of α,α-trehalose. The potential biochemical interest of compounds of this kind has been reported previously[1-4].

RESULTS AND DISCUSSION

The synthesis of **9** was similar to that[4] of the aforementioned 3,3′-diamino analog. Trifluoromethylsulfonylation of **1** afforded the crystalline 3,2′-ditriflate **2** in 90% yield. The product was treated with sodium azide under phase-transfer conditions, employing tetrabutylammonium hydrogensulfate in a boiling mixture of toluene and water. This was the only procedure which, in the preceding work[4], had after many trials been found to yield an acceptable ratio of the desired displacement product to unwanted elimination products. In the present instance, the slow process affected predominantly the altrosyl moiety, giving after 7 days the 3-azido-2′-triflate **3** and the 3,4-unsaturated 2′-triflate **5** in 55 and 22% yields, respectively. The 3,2′-diazide **4** resulting from two-fold displacement was also obtained, but only in 8% yield. To our knowledge, this represents the first example of a rather selective monodisplacement in a carbohydrate disecondary ditriflate. The remarkable stability of the triflyloxy group at C-2 of the glucopyranosyl moiety, by virtue of which this pronounced regioselectivity occurred, was somewhat surprising; for although 2-sulfonate esters of aldosides are generally unreactive towards charged nucleophiles[6], it was not predictable to what extent that rule would hold even for the highly nucleofugal triflate group. In fact, several successful S_N2 displacements in aldoside 2-triflates have been recorded and reviewed[7]. Of special relevance to the present observation were reactions performed with 4,6:4′,6′-di-*O*-benzylidene-3,3′-di-*O*-tetrahydropyranyl-2,2′-di-*O*-triflyl-α,α-trehalose, which underwent two-fold displacement with benzenethiolate anion[8] (16 h at room temperature) and with benzoate anion[9] (72 h at 115°), both in *N,N′,N″*-hexamethylphosphoric triamide solution. It therefore stood to reason that **3** should, under appropriate conditions, be amenable to further displacement. Indeed, by treatment with sodium azide in *N,N*-dimethylformamide for 3 h at 80°, it was converted into **4** in 78% yield.

The diazide **4** represents a potential, preparative precursor for the corresponding 2,3′-diamino sugar, but as the latter had become available through a more convenient route[3], reduction and deblocking of **4** were not pursued. Instead, the differential triflate reactivities encountered in **2** were utilized to generate unequal functionality at C-3 and -2′, with a view to the synthesis of **9**. Thus, **3** was subjected to a similar displacement reaction with sodium benzoate in *N,N*-dimethylformamide (21 h at 98°), which afforded in 68% yield the blocked, 3-azido-2′-*O*-benzoyl derivative **6** of α-D-mannopyranosyl α-D-mannopyranoside. Debenzoylation of **6** with sodium methoxide followed by hydrolytic removal of the acetal groups with acetic acid sequentially gave the azidodi-*O*-benzyl derivatives **7** and **8** in high yields. The azido group in **8** was then reduced, and the benzyl ethers were simultaneously

TABLE I

^{1}H-N M R DATA (300 MHz) FOR COMPOUNDS **2–10**

Compound[a]	*Chemical shifts*[b] *(δ)*								
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*e	*H-6*a	*PhCH*[c]	*PhCH*$_2$[d]
2	4.96s	3.92dd	5.15t	4.17dd	4.3m (2H)		3.72~t		
								5.57, 5.49	4.77, 4.75, 4.70, 4.58
	5.32d	4.75dd	4.15t	3 61t	3.53sx	4.06dd	3.63t		
3	4.88d	3.69dd	3.80dd	4.22dd	3.89sx	4.24dd	3.78t		
								5.62, 5.50	4.84, 4.82, 4.72, 4.62
	5.25d	4.65dd	4.00t	3.61t	3.49sx	4.01dd	3.63t		
4	4.86d	3.63dd	3.96dd	4.05t		3.98dd	3.82t		
					[e]; 3.38sx			5.64, 5.56	4.85, 4.79, 4.67, 4.58
	4.91d	3.78dd	3.67dd	4.20dd		4.24dd	3.69t		
5	5.25s	4.00dd	5.45d[f]	—	4.47m	4.39dd	3.83t		
								5.62, 5.54	4.87, 4.74; 4.63s (2H)
	5.41d	4.76dd	4.10t	3.67t	[g]	4.24dd	[g]		
6	4.88d	3.66dd	3.72dd	4.20~t	~3.8m	4.29~d	~3.8m		
								5.64, 5.62	4.81, 4.60; (4.69, 4.66)[h]
	5.13d	5.40dd	3.94dd	4.11t	3.52sx	4.04dd	3.76t		
7	4.94d	3 69dd	3.76dd	4.22dd		4.04dd	3.85t		
					[i]; 3.49sx			5.65, 5.57	4.82, 4.79, 4.66, 4.61
	5.09d	3.95dd	3.80dd	4.06t					
8	4.99d	3.63dd							
			3.54dd;	4.09dt[j];	3.5m;	3.8–3.65m			4.71, 4.68, 4.59, 4.58
			3.44dd	3.89dt[j]	3.25sx				
	5.10d	3.85m							
9[k]	4.91d	3 71dd	2.76dd						
				[l]	[l]	[l]	[l]		
	4.96d	3.81dd	[l]						
10	5.15d	4.92dd	4.60ddd	5.00t					
					[m]	4.33–4.18[m]			*Other resonances*[n]
	5.09d	5.22dd	5.3m (2H)						

	First-order coupling constants (Hz)						
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6e}$	$J_{5,6a}$	$J_{6a,6e}$
2	<1	3	3.1	9.4	*o*	*o*	*o*
	3.9	9.5	9.5	9	4.2	10	10.3
3	1.5	3.2	10.5	9.2	4.4	10.3	9.8
	3.8	9.5	9.5	10.5	3.7	9	10
4	1.4	3.8	9.6	9.4	4.8	10.3	10.3
	1.3	3.5	10	9.5	4.2	~10	10.4
5	<1	5.1[p]			6.3	10	10.3
	3.7	9.7	9.5	9.5	3.8		9.4
6	1.8	3.5	10	~10[o]	*o*	*o*	*o*
	1.8	3.5	10	10	5	10	10
7	1.5	3.4	9.2, 10.7		4.8	10.3	10.4
	1.5	3.6	9.5	9.5	4.6	10.3	10
8	1.5	~3.5	9.5, 10.5				
	1.5			10			
9	1.7	3.2	10	10			
	2	3.4					
10	1.5	4[q]	11	9.5			
	~2	4					

[a]In (^{2}H)chloroform unless indicated otherwise. [b]Values listed in the upper and lower lines refer, respectively, to the glycosyl moieties named first and second in the nomenclature for each compound (*cf.* Experimental); values not specifically assigned to either moiety appear centered between the lines. Multiplicities are indicated as d (doublet), m (multiplet), s (singlet), sx (dt or ddd appearing as a sextet), and t (triplet). [c]One-proton singlets. [d]Unless otherwise indicated, the values refer to midpoints of doublets (J_{gem} 11–12 Hz) that represent parts of AB-quartets. [e]Signal probably near δ 3.65, obscured by others. [f]Lines of doublet broadened due to long-range coupling. [g]Part of unresolved, 2-proton multiplet at δ 3.75. [h]Inner lines of AB-quartet. [i]Signal probably near δ 3.8, obscured by others. [j]Triplet after D_2O exchange. The OH protons gave five exchangeable signals in the δ 2.8–2.3 range. [k]In deuterium oxide. [l]Part of unresolved multiplets at δ 3.7–3.63 (3H) or 3.6–3.5 (5H); a clear t (*J* 10 Hz) occurred at δ 3.28. [m]Part of unresolved multiplet (4H) at δ 4.15–3.95. [n]5.60d (NH); 2.13, 2.11, 2.04, 2.04, 2.02, 2.01, 1.95, and 1.88 (8 H_3,·Ac). [o]Not first order. [p]$J_{2,5}$ 1.7 Hz, [q]$J_{3,NH}$ 9 Hz.

cleaved by palladium-catalyzed transfer hydrogenation with formic acid as the hydrogen donor[10]. This produced the title disaccharide **9**, which was isolated and characterized as its peracetyl derivative **10** (obtained in 58% yield), and regenerated from the latter in pure form by hydrolysis with barium hydroxide. The overall yield of **9** in the seven-step sequence from **1** via **10** was 13%. The ^{1}H-n.m.r. data (300 MHz) obtained for all new compounds unambiguously confirmed the assigned structures (Table I); signal attribution was aided by comparison with the spectra of close structural analogs[4] and, for **2**–**5**, by use of homonuclear-shift-correlated experiments.

The α-D-*gluco*,α-D-*gluco* stereoisomer of **9**, previously synthesized by us[2], has later been reported[11] to be a metabolite of *Norcardiopsis trehalosei* and to show antibiotic activity against some Gram-positive bacteria.

EXPERIMENTAL

General methods. — For general, preparative, and instrumental techniques, see preceding papers[3,4]. The following solvent combinations (v/v) were used for t.l.c. and column chromatography on silica gel: *A*, 1:1 ethyl acetate–hexane; *B*, the same solvents, but 1:4; *C*, the same, but 1:9; and *D*, 5:3:1 methanol–chloroform–ammonia (conc., aqueous).

2-O-Benzyl-4,6-O-benzylidene-3-O-trifluoromethylsulfonyl-α-D-altropyranosyl 3-O-benzyl-4,6-O-benzylidene-2-O-trifluoromethylsulfonyl-α-D-glucopyranoside (**2**). — A solution of compound[5] **1** (7.00 g, 0.01 mol) in dry dichloromethane (70 mL) and pyridine (6 mL) was chilled (0°), and a solution of trifluoromethanesulfonic anhydride (7.5 mL) in dry dichloromethane (20 mL) was added dropwise, with stirring. After removal of the ice bath, the mixture was allowed to attain ambient temperature, and it was then shaken with added water. The aqueous phase was extracted once with dichloromethane, and the combined organic phases were washed once with dilute, aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated *in vacuo* at 35° (bath temp.) to a thin syrup. Several portions of added toluene were evaporated from the syrup in order to remove the residual pyridine. Trituration of the residue with lukewarm ethanol (15 mL) caused partial crystallization of **2** (weighing 5.462 g after collection and washing with cold ethanol), and an additional amount (1.347 g) crystallized from the filtrate. The mother liquor was concentrated by evaporation and the residue processed by dissolution in dichloromethane, washing (aq. $NaHCO_3$), drying (Na_2SO_4), evaporation of the solution, and crystallization with ethanol, to give a further 1.633 g of product. Chromatography of the remaining material on a short column of silica gel (solvent *C*) gave a final crop (0.252 g) of **2**, for a total of 8.697 g (90.3%). For analysis, a sample was redissolved in dichloromethane, the solvent evaporated, and the resulting syrup crystallized by trituration with ethanol; m.p. 103.5–107.5° (dec.), $[\alpha]_D^{25}$ +49.3° (*c* 0.5, chloroform).

Anal. Calc. for $C_{42}H_{40}F_6O_{15}S_2$ (962.9): C, 52.39; H, 4.19; S, 6.66. Found: C, 52.61; H, 4.33; S, 6.49.

Reaction of **2** *with sodium azide. — A. Formation and separation of products.* A solution of **2** (8.66 g) in toluene (400 mL) and a solution of NaN_3 (10 g) and tetrabutylammonium hydrogensulfate (3 g) in water (100 mL) were mixed with efficient stirring, and heated under reflux. The progress of reaction was monitored by t.l.c. with solvent *B*, and boiling was terminated after 7 days when **2** (R_F 0.36) was no longer visible. After cooling and phase separation, the aqueous layer was extracted once with benzene (100 mL), and the combined organic phase was washed three times with water, dried (Na_2SO_4), and evaporated to give a syrup that showed three prominent spots, R_F 0.49, 0.42, and 0.40, and a trace (R_F 0.37) in t.l.c. The syrup was chromatographed on a column (45 × 3.5 cm) of silica gel with solvent *C* as the eluant, whereby partial separation was achieved. The fractions that contained solely or chiefly the component having R_F 0.49 furnished upon concentration compound **5**, which crystallized from hot ethanol, and the fractions that contained mainly the component of R_F 0.40 similarly yielded crystalline **4**. Between these were eluted several mixture-fractions, as well as fractions containing almost-pure **3** (R_F 0.42) which was obtained as a solid foam. The mixture-fractions were combined with the mother liquors of crystallization from **4** and **5**, and evaporated, and the residue was chromatographed again on silica gel (37 × 2 cm) with solvent *C*, yielding additional amounts of **3**–**5**. Finally, 50 mg of material having R_F 0.37 was eluted and crystallized. The 300-MHz, ^{1}H-n.m.r. spectrum indicated that it was a ~1:1 mixture of **2** and an unidentified, but closely related, transformation product, possibly the product resulting from hydrolytic loss of the 3-triflate group.

*B. 3-Azido-2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-*D*-mannopyranosyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-trifluoromethylsulfonyl-α-*D*-glucopyranoside* (**3**). Isolated as a dry, solid foam (4.19 g, 55.1%) that resisted all attempts at crystallization, **3** showed a sharp i.r. band at 2115 cm^{-1} (azido group); $[\alpha]_D^{25}$ +60.3° (*c* 0.7, chloroform). Although traces of the other components were seen to be present (t.l.c.), the absence of significant extraneous signals in the well-resolved 300-MHz ^{1}H-n.m.r. spectrum (Table I) indicated for the compound a degree of purity sufficient for the intended purpose.

Anal. Calc. for $C_{41}H_{40}F_3N_3O_{12}S$ (855.8): C, 57.54; H, 4.71; N, 4.91. Found: C, 57.37; H, 4.75; N, 4.95.

*C. 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-*D*-*threo*-hex-3-enopyranosyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-trifluoromethylsulfonyl-α-*D*-glucopyranoside* (**5**). Crystallized from ethanol in several crops totaling 1.563 g (21.7%), compound **5** had m.p. 77–79°, $[\alpha]_D^{25}$ +99.3° (*c* 0.4, chloroform), ν_{max}^{Nujol} 1695 cm^{-1} (vinyl ether; no azido absorption present).

Anal. Calc. for $C_{41}H_{39}F_3O_{12}S$ (812.8): C, 60.58; H, 4.84; S, 3.94. Found: C, 60.60; H, 4.90; S, 3.98.

*D. 2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-*D*-mannopyranosyl 3-azido-2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-*D*-mannopyranoside* (**4**). Crystallized from ethanol in several crops totaling 515 mg (7.7%), compound **4** had m.p. 85–87.5°, $[\alpha]_D^{25}$ +55.6° (*c* 0.6, chloroform); ν_{max}^{Nujol} 2115, with shoulder at 2155 cm^{-1} (azido groups).

Anal. Calc. for $C_{40}H_{40}N_6O_9$ (748.8): C, 64.16; H, 5.38; N, 11.22. Found: C, 64.27; H, 5.52; N, 11.18.

E. Conversion of **3** *into* **4**. A magnetically stirred mixture of **3** (240 mg), NaN_3 (240 mg), and dry *N,N*-dimethylformamide (2 mL) was heated at 80° for 3 h, with exclusion of moisture. The cooled mixture was diluted with benzene, washed with water (5 times), dried (Na_2SO_4), and evaporated. The residue crystallized from ethanol to give **4** (163 mg, 78%), m.p. 85–87°, identical with the aforedescribed product according to the i.r. and n.m.r. spectra, and t.l.c.

*3-Azido-2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-*D*-mannopyranosyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-*D*-mannopyranoside* (**6**). — The monotriflate **3** (966 mg) and sodium benzoate (480 mg) dissolved in dry *N,N*-dimethylformamide (10 mL) were placed in the inner chamber of a jacketed reaction vessel together with a magnetic stirring-bar, and protected from atmospheric moisture. The mixture was heated for 21 h by water boiling under reflux in the outer chamber. The cooled mixture was thereafter diluted with water (50 mL) and shaken with benzene (50 mL), and the aqueous phase was extracted once more with benzene (25 mL). The combined organic solution was washed with water (4 × 50 mL), dried, and evaporated to give crude **6** (0.99 g). It had the same mobility as the starting material **3** (R_F 0.42 in t.l.c. with solvent *B*) but differed from it by the brown spot color (*vs.* black) produced on spraying the plate with 5% H_2SO_4 in ethanol, followed by heating. Fast- and slow-moving impurities were removed by passage of the product through a short column of silica gel in solvent *C*. Pure **6** (638 mg, 68%) was obtained as a solid foam which could not be crystallized; ν_{max}^{film} 2110 (azide) and 1721 cm^{-1} (benzoate); $[\alpha]_D^{25}$ +38.0° (*c* 0.5, chloroform).

Anal. Calc. for $C_{47}H_{45}N_3O_{11}$ (827.9): C, 68.18; H, 5.48; N, 5.08. Found: C, 68.46; H, 5.57; N, 4.97.

*3-Azido-2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-*D*-mannopyranosyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-*D*-mannopyranoside* (**7**). — A solution of benzoate **6** (704 mg) in benzene (2 mL) was mixed with methanol (15 mL) containing sodium methoxide (150 mg), and the mixture heated under reflux. The debenzoylation was complete after 30 min (t.l.c. with solvent *B*). Most of the solvent was evaporated, and the moist residue was partitioned between water and dichloromethane. Customary processing gave crude **7** (R_F 0.08) which, after purification by passage through a bed (4.5 × 4.5 cm) of silica gel with 3:7 ethyl acetate–hexane, was obtained as a non-crystallizable, dry foam (535 mg, 87%); $[\alpha]_D^{25}$ +50.0° (*c* 0.5, chloroform); ν_{max}^{film} 3460 (OH) and 2115 cm^{-1} (N_3).

Anal. Calc. for $C_{40}H_{41}N_3O_{10}$ (723.8): C, 66.38; H, 5.71; N, 5.81. Found: C, 66.23; H, 5.90; N, 5.65.

*3-Azido-2-*O*-benzyl-3-deoxy-α-*D*-mannopyranosyl 3-*O*-benzyl-α-*D*-mannopyranoside* (**8**). — A suspension of the bisacetal **7** (2.043 g) in 80% acetic acid (20 mL) was heated with occasional swirling on a steam bath for 35 min. The mixture was then concentrated, and the acid and benzaldehyde were removed by co-evaporation with several, sequentially added portions of water, ethanol, and

toluene. The material was freed from fast-moving impurities by passage through silica gel (4.5 × 4.5 cm) with ethyl acetate as the solvent, from which it was obtained as a non-crystallizable, dry foam (1.333 g, 86.2%); $[\alpha]_D^{25}$ +81.6° (*c* 0.2, methanol); R_F 0.25 (ethyl acetate), ν_{max}^{film} 3400 (OH) and 2110 cm^{-1} (N_3).

Anal. Calc. for $C_{26}H_{33}N_3O_{10}$ (547.5): C, 57.03; H, 6.08; N, 7.67. Found: C, 57.18; H, 6.33; N, 7.57.

*3-Acetamido-2,4,6-tri-*O*-acetyl-3-deoxy-α-*D*-mannopyranosyl 2,3,4,6-tetra-*O*-acetyl-α-*D*-mannopyranoside* (**10**). — A solution of **8** (1.013 g) in methanol (40 mL) and formic acid (10 mL) was efficiently stirred with 10% Pd–C (2 g) for 2 days at room temperature. Formation of a product having R_F 0.1 was observed (t.l.c., solvent *D*). The catalyst was removed by filtration and washed exhaustively with methanol. The filtrate and washings were concentrated, and residual formic acid was removed by repeated coevaporations of added toluene. Attempts to crystallize the crude amino sugar (818 mg) obtained at this stage were unsuccessful. The material was therefore acetylated by shaking its suspension in pyridine (6 mL) and acetic anhydride (3 mL) for 2 days at room temperature. The reaction mixture was filtered through Celite, which was washed with toluene, and the filtrate evaporated to dryness with several coevaporations of toluene. Chromatographic purification of the product on silica gel with solvent *B*, followed by ethyl acetate as eluants, gave **10** (726 mg, 57.8%) as a glassy solid, m.p. 79–90°, $[\alpha]_D^{25}$ +54.2° (*c* 0.7, chloroform).

Anal. Calc. for $C_{28}H_{39}NO_{18}$ (677.6): C, 49.63; H, 5.80; N, 2.07. Found: C, 49.45; H, 5.75; N, 2.03.

*3-Amino-3-deoxy-α-*D*-mannopyranosyl α-*D*-mannopyranoside* (**9**). — The peracetyl derivative **10** was saponified with aqueous $Ba(OH)_2$ essentially under the conditions specified[12] for the *N*-deacetylation of methyl 2-acetamido-2-deoxy-α-D-glucopyranoside. For example, a solution of **10** (288 mg) in a small amount of methanol was introduced into water (4 mL), $Ba(OH_2) \cdot 8\ H_2O$ (0.5 g) was added, and the mixture heated briefly on a steam bath to evaporate the methanol. The mixture was then boiled under reflux, with stirring, until the hydrolysis was complete (overnight; a longer reaction-time than for the monosaccharide example described[12] was found necessary). The mixture was processed by sequential treatment with CO_2, H_2SO_4, and an anion-exchange resin (Dowex 1-X8, OH^-), as described[12], and **9** was obtained as a white, microcrystalline solid (after decolorization of its solution with activated charcoal, if necessary) by evaporation of its aqueous–methanolic solution and final coevaporation of added portions of ethanol. Yields in several runs ranged from 64–88% depending on the effectiveness of the washing operations performed with the inorganic precipitates and the resin during processing. Solid **9** apparently was a monohydrate; m.p. 200–210° (with softening from 150°), $[\alpha]_D^{25}$ +67.5° (*c* 2.4, water).

Anal. Calc. for $C_{12}H_{23}NO_{10} \cdot H_2O$ (359.3): C, 40.11; H, 7.01; N, 3.90. Found: C, 40.18; H, 6.97; N, 3.43.

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REFERENCES

1 H. H. BAER AND A. J. BELL, *Can. J. Chem.*, 56 (1978) 2872–2878.
2 H. H. BAER AND A J. BELL, *Carbohydr Res* , 75 (1979) 175–184; see also a corrigendum, *ibid.*, 78 (1980) c19.
3 H. H. BAER, L. SIEMSEN, J. DEFAYE, AND K. BURAK, *Carbohydr. Res.*, 134 (1984) 49–61
4 H H. BAER, B. RADATUS, AND J. DEFAYE, *Can. J. Chem.*, 63 (1985) 440–444
5 H. H. BAER AND B. RADATUS, *Carbohydr. Res* , 128 (1984) 165–174.
6 A. C. RICHARDSON, *Carbohydr. Res.*, 10 (1969) 395–402; D. H. BALL AND F. W. PARRISH, *Adv. Carbohydr. Chem. Biochem.*, 24 (1969) 139–197.
7 R. W. BINKLEY AND M. G. AMBROSE, *J. Carbohydr. Chem.*, 3 (1984) 1–49.
8 J. DEFAYE, H. DRIQUEZ, B. HENRISSAT, AND E. BAR-GUILLOUX, *Nouv. J. Chim.*, 4 (1980) 59–68.
9 A. LIAV AND M. B. GOREN, *Carbohydr. Res.*, 123 (1983) c22–c24.
10 B. EL AMIN, G. M. ANANTHARAMAIAH, G. P. ROYER, AND G. E. MEANS, *J. Org. Chem.*, 44 (1979) 3442–3444; V. S. RAO AND A. S. PERLIN, *Carbohydr. Res.*, 83 (1980) 175–177.
11 L. A. DOLAK, T. M. CASTLE, AND A. L. LABORDE, *J. Antibiot.*, 33 (1980) 690–694.
12 S HANESSIAN, *Methods Carbohydr. Chem.*, 6 (1972) 208–214.