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FURTHER APPLICATIONS OF SELECTIVE DISPLACEMENTS IN AN UNSYMMETRICAL DITRIFLATE. SYNTHESIS OF NEW TRIAMINO AND TETRAAMINO DISACCHARIDES OF THE TREHALOSE TYPE

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ABSTRACT

Although the known ring-opening with sodium azide in 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranosyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside gave mainly symmetrical 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranosyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside (**2**), the unsymmetrical 2,3′-diazido isomer **3** having the α-D-*altro*,α-D-*gluco* configuration was shown to be a second product that can be conveniently isolated on a preparative scale. The ditriflate **4** derived from **3** was subjected to regioselective displacement in the *altro* moiety with sodium azide, followed by displacement with sodium benzoate in the *gluco* moiety, to give a 2,3,3′-triazide having the α-D-*manno*,α-D-*manno* configuration. Alternatively, **4** was subjected to displacement first with benzoate and then with azide, thus providing the regioisomeric 2,3,2′-triazide of the same configuration. The ditriflate obtained from **2** furnished the corresponding 2,3,2′,3′-tetraazido derivative. Minor proportions of elimination products also arose in these reactions. The protected azido sugars were converted by standard methods into the 2,3,2′- and 2,3,3′-triamino derivatives and the 2,3,2′,3′-tetraamino derivative of α-D-mannopyranosyl α-D-mannopyranoside.

INTRODUCTION

In 1973, Hough and Richardson[1] synthesized 2-amino-2-deoxy-α-D-altropyranosyl 2-amino-2-deoxy-α-D-altropyranoside *via* the corresponding diazido derivative **2**, which they obtained in 71% yield from the readily available diepoxide **1** by reaction with sodium azide in *N*,*N*-dimethylformamide. They observed by t.l.c. the formation of two minor by-products which they did not isolate, but which they plausibly suggested to have arisen by anti Fürst–Plattner ring-openings in **1**. This observation kindled our interest in connection with a current project[2–5] of synthesis in the field of trehalose-type amino sugars, and we decided to examine the reaction of **1** with azide more closely, with a view to elaborating the preparation of some new, aminated disaccharides.

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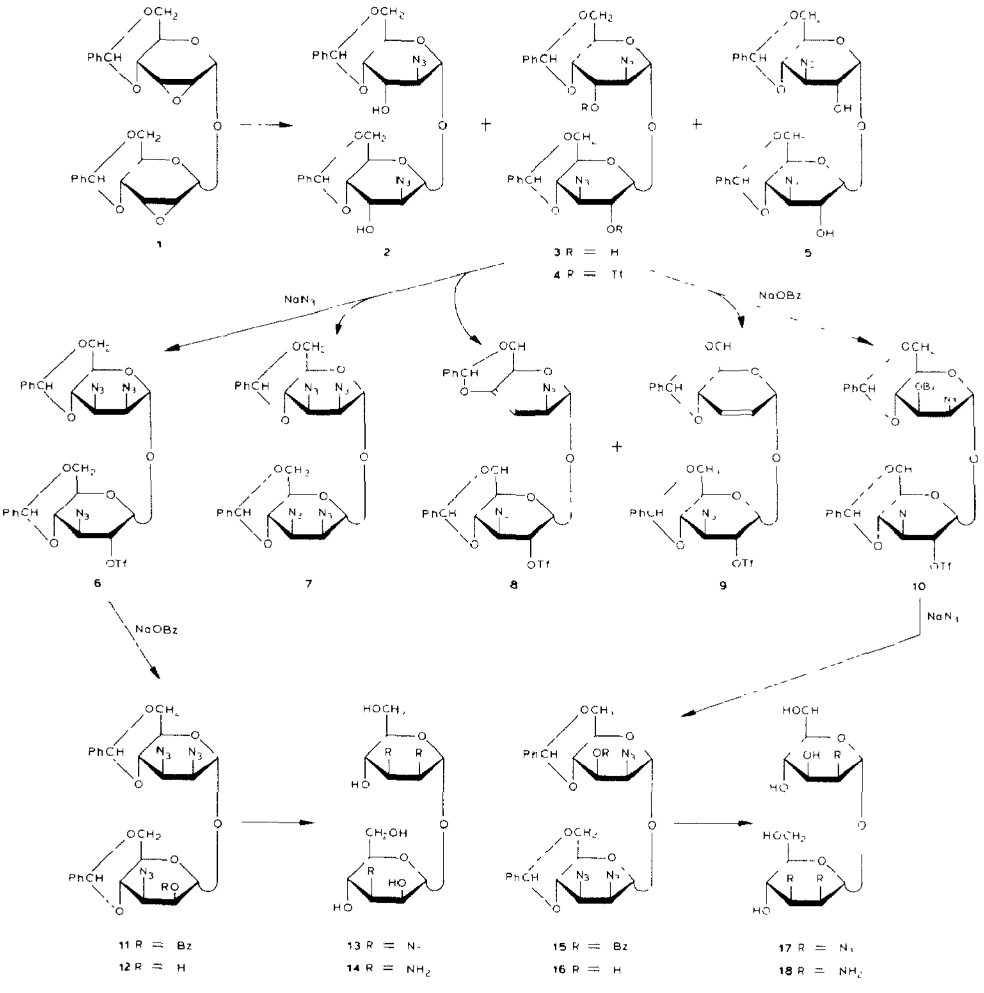
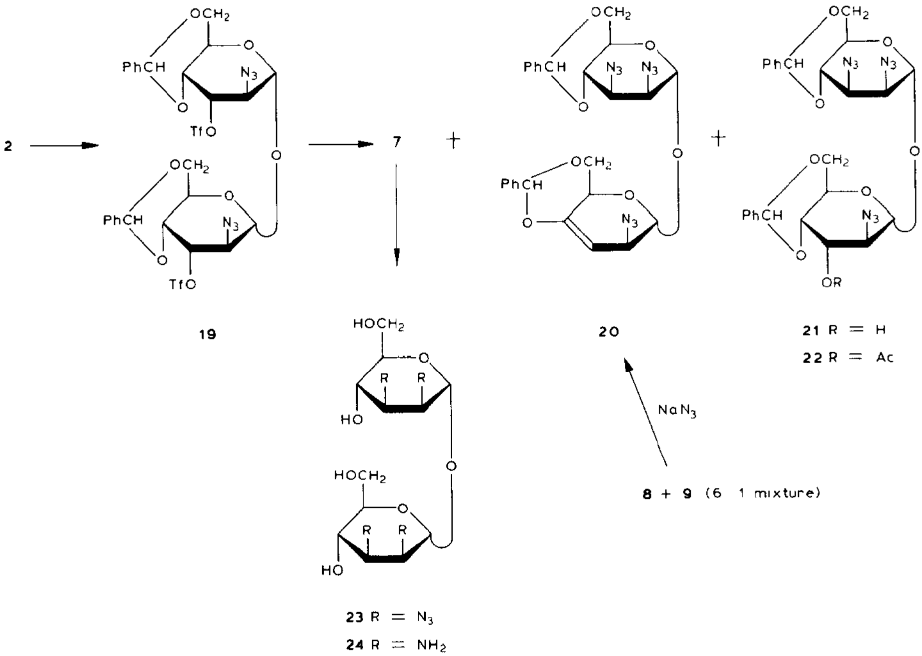
RESULTS AND DISCUSSION

When **1** was treated with sodium azide essentially as described[1], but in 2-methoxyethanol–water as the solvent, the α-D-*altro*,α-D-*altro* diazide **2** was obtained crystalline in 60% yield, and the aforementioned by-products were isolated by column chromatography. The preponderant by-product (25% yield) proved to be the unsymmetrical 2,3′-diazido isomer **3** having the α-D-*altro*,α-D-*gluco* configuration. Although it failed to crystallize, its structure was unambiguously assigned on the basis of its ^{1}H-n.m.r. spectrum (Table I) and was later on confirmed through consistent spectral evidence from the compounds derived from it. The third component was obtained crystalline in very small yield (1.4%) and was revealed by its ^{1}H-n.m.r. spectrum to be the symmetrical 3,3′-diazido



Tf = trifluoromethylsulfonyl



isomer **5** having the α-D-*gluco*,α-D-*gluco* configuration. The assumption previously made[1] concerning the nature of the minor products has thus been confirmed.

Compound **3** is a convenient stepping stone for entry into a series of unsymmetrically substituted trehalose-type sugars, for although its percentage yield is not high, it originates from the readily available **1** in a simple operation and can be prepared on a multigram scale without difficulty. We describe herein its use for the synthesis of two new, isomeric triamino sugars (**14** and **18**) that possess the α-D-*manno*,α-D-*manno* configuration and represent analogs of the previously-synthesized[2,3] 2,2′-, 2,3′-, and 3,3′-diamino sugars of that series.

Trifluoromethylsulfonylation of **3** readily furnished the ditriflate **4**. We have recently studied[4] nucleophilic displacements in an analogous, unsymmetrical ditriflate (**4**, but with benzyloxy in place of the azido groups) and discovered that the axial 3-triflate group in the *altro* unit could be regioselectively displaced by azide ion under phase-transfer conditions, and that the more-stable, equatorial 2′-triflate function in the *gluco* unit could subsequently be displaced under more-forcing conditions in *N*,*N*-dimethylformamide solution. Such differential reactivity proved to be present in **4** also, and was exploited as follows.

As one disadvantage of the phase-transfer reaction just mentioned[4] had been its slowness (7 days), it was examined whether selective monodisplacement is also achieved in a homogeneous-phase reaction, and this proved to be the case. Thus, treatment of **4** with tetramethylguanidinium azide in refluxing 4:1 benzene–dichloromethane for 45 min gave the 2,3,3′-triazido-2′-triflate **6**, isolated in

TABLE I

^{1}H-N M R DATA AT 300 MHz FOR COMPOUNDS **2–8** AND **10–24**

Compound[a]	*Residue*[b]	*Chemical shifts*[c] (δ)								
		H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6a*	*H-6e*	*Ph*-CH	*OH*
2	*altro*	5.08s	3.92dd	4.31m[d]	3.88dd	4 31m	3.82t	4.29dd	5.66	3.75d
3	*altro*	5.13s	3.92dd	4.23m[d]	3 94dd	[e]	3.79t	[e]	5.67	3.06d
	gluco	5.24d	3 66dt[f]	3.91t	3.53t	3.86m	3.75t	[e]	5.60	3.27d
4	*altro*	5 16s	4 18dd	5.14dd	4.09dd	[g]	3 74dd	[g]	5.59	
	gluco	5.41d	4.58dd	4.23t	3.59t	3.90td	3.77t	[g]	5.59	
5	*gluco*	5.19d	3 67m[f]	4.01t	3.58t	4.13td	3.75t	4.35dd	5.63	2.36d
6	*manno*	5.08d	3.91dd	4.19dd	4.11t	3 95td, 3.89td	3.80t, 3 77t	4 37dd, 4.26dd	5.61, 5.62	
	gluco	5.36d	4.55dd	4.17t	3.65t					
7	*manno*	5.04d	3.84m	←4.15–4.06m→		←3.88–3.70m→		4.26dd[h]	5.64	
8	*gluco*	5.38d	4.55dd	4.17t	3.62t	3.84td	3.75t	4.33dd	5.59, 5.57	
	threo	5.23s	3.63dd	5.37d		4.43dd	3.74t	4.52m[i]		
10	*manno*	5.14d	4.34dd	5.73dd	4.28t	4 08td	3.81t	4.36dd[i]	5.60, 5.58	
	gluco	5.40d	4.57dd	4.29t	3.64t	3.93td	3.76t	4.28dd		
11	*manno*[k]	5.27d	5.31dd	4.11dd	~3.9[j]	4.23td[i]	~3.9[j]	4.36m(2 H)	5 73, 5.66	
	manno[l]	5.09d	~3.9[j]	4.21dd	4.12t	3.95d[i]	3.81t			
12	*manno*[k]	5.12s[m]	3.97s[m]	←4.15–4.07m→		←3.90–3.70m(4 H)→		4 32dd[h], 4.26dd[h]	5.65	
	manno[l]	5.09	3 87m	3.99dd[i]	4.17t				5.65	
13[n]	*manno*[k]	5.17d, 5.07d	4 02m[f]	3.61dd	4.03m[d]	←3.91–3.61→				4.95d, 4.73d, 4 63d
	manno[l]		4.18dd	4.11dd	3.85m[d]					
14[o]	*manno*[p]	4.88d	3.73m	2.80dd	3.28~t(2 H)3.49–3.42m(2 H)		(3.55, 3.57; 3.68, 3 71)[q]			
	manno[r]	4.91d	2.94dd	2.89dd						
15	*manno*[k]	5.12d, 5.09d	4 26dd	5.73dd		←4 32–4.28m(3 H), 4.13m, 3 92–3.80m(4 H)→			5.65, 5.60	
	manno[l]		3.96dd	4.24dd						
16	*manno*[k]	5.06d	3.99dd	4 26m[j]	3 98t	3 81m[i], 3.70td	3.81t(2 H)	4.28dd, 4.26dd	5.66, 5.58	2.58br.s
	manno[l]	5 06d	3.88m	4 13m(2 H)						
17[n]	*manno*[k]	5.08d	4 13–4.07m(2 H)			←3.94–3.55m[s]→				3.42t, 4.99, 4 65, 4 36(3d)
	manno[l]	5.15d	4.18dd	4 05dd						
18[o]	*manno*[p]	4.90d	3 05dd	←3.8–3.4→		←3.8–3.4m→				
	manno[r]	4.85s	2.92m(2 H)		3.28t					

19	*altro*	5.12s	4.16dd	5.13m	4.09dd	4.20m	3.81t	4.36dd	5.65s	
20	*manno*	5.12d	3.90dd	4.18–4.08m		3.79m^i	3.82t	4.27dd^h	5.59, 5.65	
	threo	5.22s	3.56br.d	5.39br.d		4.30m^i	3.76t	4.47dd		
21	*manno*	5.06d	←4.33–4.16m(5 H), 4.08t^h, 3.91–3.79m(5 H), 3.76t→						5.64	
	altro	4.99s							5.64	2.30br.s
22	*manno*	5.12d	3.89dd	4.01dd	4.14dd	3.76m	3.84t	4.28dd	5.67, 5.61	
	altro	5.03s	3.98dd	5.27t	4.03dd	4.21m	3.78t	4.34dd		2.10(OAc)
23^t	*manno*	4.97d	4.11dd	4.01dd			←3.67–3.41m→			5.77d, 4.65t
24^o	*manno*	4.92s	3.00–2.93m(2 H)		3.33t	3.49m	←3.61dd, 3.77dd→			

Compound^a	*Residue*^{b}	*Coupling constants (Hz)*								
		$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6e}$	$J_{6a,6e}$	$J_{H,OH}$	$J_{2,5}$
2	*altro*	<0.5	3.2	2.8	9.6	9.6	4.8	9.6	6.3	1.2
3	*altro*	<0.5	3.0	2.7	10	10		10	4.0	1.0
	gluco	4.0	10	10	10	10	5.0	10	10	
4	*altro*	<0.5	3.2	2.6	9.6	10		12		1.0
	gluco	3.7	10.1	9.8	9.8	10.3	4.5	10.3		
5	*gluco*	4.0	10	10	10	10	5.0	10.5	7.0	
6	*manno*	1.6	3.3		10	10	4.4, 4.6	10, 10.3		
	gluco	3.8	10.1	9.8	9.6	10				
7	*manno*	1.2								
8	*gluco*	3.9	10	10	10	10	4.5	10		
	threo	<0.5	5.0			10.3	6.5	10.3		
10	*manno*	1.5	3.9	10	9.8	10.3	4.6	10.3		
	gluco	3.7	10.3	9.7	9.7	10.3	4.4	10.3		
11	*manno*^{k}	1.5	3.4	10.4	10	10	4.0			
	manno^l	1.2	3.5	9.9	10	10.2	5.0	10.2		
12	*manno*^{k}									
	manno^l	1.5	3.2	10	10					
13	*manno*^{k}	1.7	3.2	10.1	10					
	manno^l	1.7	3.7	9.8	9.7					
14	*manno*^{p}	1.0	3.2	10	10	5.5, 6.9; 1.8, 2.1; 12, 13				
	manno^q	1.5	4.0	10	10					
15	*manno*^{k}	1.5	3.9	10.4						
	manno^l	1.5	3.7	10						

TABLE I *(continued)*

Compound[a]	*Residue*[b]	Coupling constants (Hz)								
		$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6e}$	$J_{6a,6e}$	$J_{H,OH}$	$J_{2,5}$
16	*manno*[k]	1 5	4.2	10	10	9.7, 10	4.4, 5 6	9.8, 10		
	manno[l]	1.5	3.2							
17	*manno*[k]	1.0								
	manno[l]	1 7	3.4	9.5						
18	*manno*[p]	1.5	4.3							
	manno[r]	<0.5		9.6		9.6				
19	*altro*	0.5	2.9	2.8		10.5	4.7	10.5		0.7
20	*manno*	1.5	3.1			10		10		
	threo	<0 5	5.4			10.3	6.4	10.3		
21	*manno*	1.5				10.3		10.3		
	altro	<0.5								
22	*manno*	1.7	3.4	10.3	8.9	10.3	4.2	10.3		
	altro	0.5	3.1	3 1	9.6	10.3	5.1	10.3		
23	*manno*	1 5	3.7	9.5					5 7, 6.4	
24	*manno*	<0.5		10	10	6.0	2 2	12 5		

[a]For a solution in (^{2}H)chloroform unless indicated otherwise. [b]Where signal attribution to either residue in unsymmetrical compounds was not possible, data are centered between the two lines. [c]With reference to the $CHCl_3$ lock signal at δ 7.23. [d]Triplet after D_2O exchange. [e]Part of unresolved m (3 H) at δ 4.39–4.25. [f]Doublet of doublets after D_2O exchange. [g]Part of unresolved m (3 H) at δ 4 40–4 30. [h]Distorted because of second-order effect. [i]Partially obscured by overlapping signals. [j]Part of unresolved multiplet (3 H) [k]Monoazido residue. [l]Diazido residue. [m]Broad; sharpens on D_2O exchange. [n]For a solution in ($^2H_6$)acetone [o]For a solution in D_2O; acetone lock signal. [p]Monoamino residue. [q]Two sets of partially overlapping doublets of doublets. [r]Diamino residue. [s]Containing additionally one OH signal. [t]For a solution in di($^2H_3$)methyl sulfoxide; lock signal δ 2.49.

crystalline form in 68% yield. This monotriflate was treated with sodium benzoate in *N,N*-dimethylformamide at 100° for 1 h, to provide the *manno,manno* 2,3,3'-triazido-2'-benzoate **11**. For inverse substitution, **4** was treated first with sodium benzoate to give the 2,3'-diazido-3-*O*-benzoyl-2'-triflate **10**. In this case, phase transfer in a benzene–water system with tetrabutylammonium hydrogensulfate as the catalyst was employed and the reaction was not unduly sluggish, giving a 78% yield of **10** after 18 h at room temperature, followed by 2 h at reflux temperature. Sodium azide displacement in **10**, in *N,N*-dimethylformamide, then afforded the crystalline *manno,manno* 2,3,2'-triazido-3'-benzoate **15**.

It was to be expected from earlier experience[3,4] that monodisplacements in **4** would be accompanied by some two-fold displacement as well as elimination. In fact, the azide reaction produced, in addition to **6**, the crystalline tetraazide **7** (15% yield) and an inseparable mixture of elimination products (~8%) which appeared to consist of two components in a ratio of ~6:1, according to the ^{1}H-n.m.r. spectrum. To the preponderant component of this mixture was assigned the 3-enoside structure **8** since, by continued treatment with azide, it was converted into the same 2,2',3'-triazido-3-enoside **20** that was produced and structurally characterized in another sequence of experiments (see later). The minor elimination product present in the mixture gave ^{1}H-n.m.r. signals attributable to two, mutually coupled, alkenic protons as well as signals for an azidotriflate unit; on that basis, the 2-enoside structure **9** was tentatively assigned. Both by-products also arose, in nearly the same proportion and similar combined yield (~7%), in the reaction of **4** with sodium benzoate*.

The 2,3,3'-triazide **11** was converted by sequential Zemplén debenzoylation (giving the alcohol **12**), hydrolytic debenzylidenation (giving the triazidopentaol **13**), and catalytic transfer hydrogenation into 2,3-diamino-2,3-dideoxy-α-D-mannopyranosyl 3-amino-3-deoxy-α-D-mannopyranoside (**14**). The same sequence applied to the 2,3,2'-triazide **15** led, *via* **16** and **17**, to 2,3-diamino-2,3-dideoxy-α-D-mannopyranosyl 2-amino-2-deoxy-α-D-mannopyranoside (**18**).

Although the symmetrical tetraazido sugar **7** was formed, as a minor product, in one of the aforementioned operations, a more rational way of preparing it obviously starts from the symmetrical diazide **2**. Thus, trifluoromethanesulfonylation provided the 3,3'-ditriflate **19**, in 86% yield, and subsequent displacement using tetramethylguanidinium azide in *N,N*-dimethylformamide afforded a 75% yield of **7**. In addition the triazido-3-enoside **20** (13.5%) that arose by competing elimination, and a very small proportion (1.2%) of the triazido alcohol **21** that resulted from partial, sulfonic ester hydrolysis were obtained; compound **21** was

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*Only traces of the 2,3'-dibenzoate were detected. Guthrie and assoc.[6] have obtained high yields of 2-enosides by treatment of vicinal azido sulfonate esters (and of a *manno* 2,3-diazide) with hydrazine hydrate. Although the mechanism of these transformations has not been fully elucidated, it is apparent that an axial azido group can become a leaving group. However, the conversion implies a decrease in oxidation state of the sugar, and it is at present unclear how this might occur in the reactions **4**→**9** under the conditions described.

acetylated to give **22** for spectroscopic examination. The main product **7** was debenzylidenated hydrolytically to give the tetraazidotetraol **23**, which was finally reduced to the new tetraamino sugar, 2,3-diamino-2,3-dideoxy-α-D-mannopyranosyl 2,3-diamino-2,3-dideoxy-α-D-mannopyranoside (**24**).

EXPERIMENTAL

General methods. — For general, preparative, and instrumental techniques, see preceding articles from this laboratory[2–5]. The following solvent combinations (v/v) were employed for chromatography, unless specified otherwise: (*A*) 3:2, (*B*) 3:7, (*C*) 1:4, (*D*) 3:17, (*E*) 1:9, and (*F*) 1:19 ethyl acetate–hexane; (*G*) 1:9 and (*H*) 1:19 ethanol–ethyl acetate; (*I*) 12:5:3 and (*J*) 5:4:1 methanol–chloroform–conc. NH_3 (aq.).

2-Azido-4,6-O-benzylidene-2-deoxy-α-D-altropyranosyl 2-azido-4,6-O-benzylidene-2-deoxy-α-D-altropyranoside (**2**), *2-azido-4,6-O-benzylidene-2-deoxy-α-D-altropyranosyl 3-azido-4,6-O-benzylidene-3-deoxy-α-D-glucopyranoside* (**3**), *and 3-azido-4,6-O-benzylidene-3-deoxy-α-D-glucopyranosyl 3-azido-4,6-O-benzylidene-3-deoxy-α-D-glucopyranoside* (**5**). — A mixture of *allo,allo* diepoxide[7,8] **1** (19.4 g, 0.04 mol), NaN_3 (20 g), NH_4Cl (8 g), 2-methoxyethanol (200 mL), and water (54 mL) was stirred and gently boiled under reflux for 31 h. The cooled mixture was concentrated under reduced pressure to a small volume, and partitioned between dichloromethane and water. The aqueous phase was extracted once with fresh dichloromethane, and the combined organic solution was washed with water, diluted with ethanol (100 mL), and concentrated to a volume of ~10 mL of liquid containing some solid precipitate. The mixture was boiled briefly with added ethanol (20 mL) and filtered while hot; the filter residue washed with ethanol proved to be unreacted **1** (560 mg, 2.9%). From the cooled filtrate crystallized the main crop of **2** (13.03 g), R_F 0.35 (t.l.c., solvent *B*), m.p. 112–115°, unchanged on recrystallization, $[\alpha]_D^{25}$ +121.3° (*c* 1, chloroform); ν_{max}^{Nujol} 3560 (OH) and 2115 cm^{-1} (N_3); ^{1}H-n.m.r. (vacuum-dried material): no signals for ethanol, although **2** had been reported[1] as an ethanolate, m.p. 114–115°, $[\alpha]_D$ +120°. Additional **2** (745 mg) was obtained from the mother liquor following chromatography (see below), for a total yield of 60.6%.

Anal. Calc. for $C_{26}H_{28}N_6O_9$ (568.5): C, 54.92; H, 4.96; N, 14.78. Found: C, 54.84; H, 5.11; N, 14.77.

The mother liquors were evaporated and the residue, showing t.l.c. spots having R_F 0.42, 0.35, and 0.28 (solvent *B*), was chromatographed on silica gel with solvent *D*. Mixed fractions were rechromatographed, and a total of 5.69 g of **3** (25%), R_F 0.42, could be elaborated as a dry, colorless foam that failed to crystallize; ν_{max}^{Nujol} 3385 (OH) and 2115 cm^{-1} (N_3). Although traces of impurities were present (t.l.c.), the material was suitable for further use as judged by its ^{1}H-n.m.r. spectrum (see Table I).

The slow-moving component (R_F 0.28), eluted from the columns, crystallized from carbon tetrachloride to give **5** (312 mg, 1.4%), m.p. 217–218° (dec.), $[\alpha]_D^{25}$ +89° (*c* 0.8, chloroform); ν_{max}^{Nujol} 3600 (sharp) and 3480 (OH), and 2120 cm^{-1} (N_3).

Anal. Calc. for $C_{26}H_{28}N_6O_9$ (568.5): C, 54.93; H, 4.96; N, 14.78. Found: C, 55.18; H, 4.87; N, 14.63.

2-Azido-4,6-O-benzylidene-2-deoxy-3-O-trifluoromethylsulfonyl-α-D-altropyranosyl 3-azido-4,6-O-benzylidene-3-deoxy-2-O-trifluoromethylsulfonyl-α-D-glucopyranoside (**4**). — Trifluoromethanesulfonic anhydride (1 mL) in dry dichloromethane (5 mL) was added dropwise, with magnetic stirring, to a chilled (0°) solution of **3** (1.42 g, 2.5 mmol) in dichloromethane (15 mL) containing pyridine (2 mL). Stirring was continued at 0° for 10 min and at ambient temperature for another 10 min, after which a single major spot, R_F 0.35, was seen in t.l.c. (solvent *C*). The mixture was shaken with an equal volume of water, and the aqueous phase was extracted once with dichloromethane. The combined organic phases were washed with dilute, aqueous $NaHCO_3$ solution, dried (Na_2SO_4), and evaporated to give a crystalline residue from which added portions of dichloromethane and toluene were evaporated to remove pyridine. The product was recrystallized twice by dissolution in the minimum amount of dichloromethane, addition of methanol (10 mL), and brief heating to remove most of the dichloromethane. Cooled, collected, washed with methanol, and dried, the chromatographically homogeneous **4** (1.684 g, 80.9%) had m.p. 149–150° (dec.), $[\alpha]_D^{25}$ +70.9° (*c* 0.6, chloroform); ν_{max}^{Nujol} 2120 cm^{-1} (N_3).

Anal. Calc. for $C_{28}H_{26}F_6N_6O_{13}S_2$ (832.7): C, 40.39; H, 3.15; N, 10.09. Found: C, 40.58; H, 3.39; N, 10.14.

Reaction of **4** *with sodium azide. — (a) 2,3-Diazido-4,6-O-benzylidene-2,3-dideoxy-α-D-mannopyranosyl 3-azido-4,6-O-benzylidene-3-deoxy-2-O-trifluoromethylsulfonyl-α-D-glucopyranoside* (**6**). A mixture of **4** (1.583 g), tetramethylguanidinium azide[9] (3.0 g), dichloromethane (20 mL), and benzene (80 mL) was efficiently stirred, and boiled under reflux for 45 min. In t.l.c. (solvent *C*), **4** was absent after 30 min and 3 spots were visible, R_F 0.52, 0.47, and 0.41. The cooled mixture was shaken with an equal volume of water, the aqueous phase was extracted once with fresh benzene, and the combined organic solution was washed four times with water, dried (Na_2SO_4), and evaporated. The residue crystallized from methanol, but in chromatographically non-homogeneous form, and the entire material was therefore chromatographed on a column of silica gel (27 × 2.5 cm) with solvent *F* as the eluant. Mixed fractions were rechromatographed together with mother liquors of **6** (R_F 0.4) which crystallized from methanol after its isolation from reasonably pure fractions. A total of 942 mg (68.3%) of pure **6** was obtained, m.p. 177–181° (dec.), $[\alpha]_D^{25}$ +93.3° (*c* 0.8, chloroform); ν_{max}^{Nujol} 2118 cm^{-1} (N_3).

Anal. Calc. for $C_{27}H_{26}F_3N_9O_{10}S$ (725.6): C, 44.69; H, 3.61; N, 17.37. Found: C, 44.91; H, 3.71; N, 17.30.

(b) By-product **7**. The major part (154 mg) of the product having R_F 0.52 was obtained, by crystallization from methanol, from mixed fractions (R_F 0.52 and 0.47)

of the chromatography just described. An additional 16 mg was obtained by chromatography of the remaining material in 1:1 benzene–hexane which allowed separation from compounds having R_F 0.47. The product proved to be the tetra-azide **7** (see a subsequent paragraph) by comparison of R_F values and ^{1}H-n.m.r. spectra.

*(c) 3-Azido-4,6-O-benzylidene-3-deoxy-2-O-trifluoromethylsulfonyl-α-D-glucopyranosyl 2-azido-4,6-O-benzylidene-2,3-dideoxy-α-D-*threo*-hex-3-enopyranoside* (**8**) *and presumed 2,3-dideoxyhex-2-enopyranoside* **9**. — The material showing R_F 0.47 was obtained as a syrup (105 mg; 8%, calc. as **8**); ν_{max}^{Nujol} 2115 (N_3) and 1690 cm^{-1} (vinyl ether). The 300-MHz, ^{1}H-n.m.r. spectrum revealed the presence of two components in a ratio of 6:1. The signals for the major component accorded with structure **8** (see Table I). The minor component, tentatively assigned structure **9**, was manifested by two doublets of narrow multiplets for the alkenic H-2 (δ 6.00) and H-3 (δ 6.31), with $J_{2,3}$ 10 Hz, characteristic[5,10] for α-D-*erythro*-hex-2-enopyranosides, and a doublet (δ 5.50, $J_{1,2}$ 3.9 Hz) for H-1 of the *gluco* residue, as well as two benzylic singlets (δ 6.06 and 5.60).

Treatment of the mixture (91 mg) with sodium azide (25 mg) in *N,N*-dimethylformamide (2 mL) at 80° for 1.5 h gave, after conventional processing, the unsaturated triazide **20** (55 mg, crystallized from ethanol). Its 300-MHz ^{1}H-n.m.r. spectrum was identical with that of **20** obtained from **19**, except for additional, weak signals due to the azide displacement product from **9**, which evidently cocrystallized.

Reaction of **4** *with sodium benzoate. — (a) 2-Azido-3-O-benzoyl-4,6-O-benzylidene-2-deoxy-α-D-mannopyranosyl 3-azido-4,6-O-benzylidene-3-deoxy-2-O-trifluoromethylsulfonyl-α-D-glucopyranoside* (**10**). A mixture of **4** (1.374 g, 1.65 mmol), sodium benzoate (2.16 g), tetrabutylammonium hydrogensulfate (1.0 g), water (15 mL), and benzene (50 mL) was stirred overnight at room temperature, and then heated under reflux for 2 h. T.l.c. (solvent *C*) showed a strong spot for the main product (R_F 0.33), a minor spot (R_F 0.4), and a trace of unreacted **4** (R_F 0.27). The cooled benzene phase was washed thrice with water, dried (Na_2SO_4), and evaporated to give a syrup which failed to crystallize. The material was chromatographed on a silica gel column (66 × 1.8 cm) by sequential elution with solvents *F*, *E*, and *C*. The following materials were obtained from appropriately pooled fractions: **A** (173 mg, R_F 0.4), **B** (15 mg, immediately following **A**), **C** (69 mg, mixture; discarded), **D** (1.157 g, R_F 0.3), and **E** (12 mg, R_F 0.28, identified as **4**).

Fraction **D** represented **10**, a solid foam that did not crystallize; yield, 87.2%, $[\alpha]_D^{25}$ +104.4° (*c* 0.4, chloroform); ν_{max}^{Nujol} 2110 (N_3) and 1725 cm^{-1} (PhCO).

Anal. Calc. for $C_{34}H_{31}F_3N_6O_{12}S$ (804.7): C, 50.75; H, 3.88; N, 10.44. Found: C, 50.40; H, 4.06; N, 10.00.

(b) By-products. The aforementioned fraction **A** (173 mg) was heated in an oil-pump vacuum at 100° to yield benzoic acid (32 mg) as a sublimate, identified by an undepressed mixture melting point and its n.m.r. spectrum. The residue was

rechromatographed on a small column, to give 75 mg (7%) of a syrupy, 6:1 mixture of **8** and **9**, having a 300-MHz, ^{1}H-n.m.r. spectrum virtually identical with that of the similar mixture obtained previously.

The 300-MHz, ^{1}H-n.m.r. spectrum of fraction **B** (for a solution in $CDCl_3$) suggested that it was the di-*O*-benzoyl derivative arising from twofold displacement in **4**, contaminated by some benzoic acid: δ 7.45 (m, arom.), 5.78 (dd, $J_{2,3}$ 3.9, $J_{3,4}$ 10.3 Hz, H-3), 5.39 (nm, H-2'), 5.31 (d, $J_{1',2'}$ 1.5 Hz, H-1'), 5.15 (d, $J_{1,2}$ 1.5 Hz, H-1), 4.41–4.18 (m, 5 H), 4.08 (dt, H-5 or -5'), and 4.00–3.78 (m, 4 H).

*3-Azido-2-O-benzoyl-4,6-O-benzylidene-3-deoxy-α-*D*-mannopyranosyl 2,3-diazido-4,6-O-benzylidene-2,3-dideoxy-α-*D*-mannopyranoside* (**11**). — A mixture of **6** (1.02 g), sodium benzoate (1.0 g), and dry *N,N*-dimethylformamide (20 mL) was stirred in a two-walled reaction vessel, and heated by refluxing toluene contained in the outer compartment. After 1 h, t.l.c. (solvent *C*) indicated that all of the triflate (R_F 0.4) had been replaced by a product having R_F 0.47. The mixture was cooled, diluted with benzene (100 mL), and shaken with water (100 mL). The aqueous layer was extracted with fresh benzene, and the combined organic phases were washed four times with water, dried, and evaporated to yield a syrup which crystallized from methanol, giving a first crop of **11** (727 mg), m.p. 158–161°. Additional crops were obtained from the mother liquor, increasing the yield to 884 mg (90.5%). Recrystallized from methanol, an analytical sample had m.p. 162–164°, $[\alpha]_D^{25}$ +41.4° (*c* 0.7, chloroform); ν_{max}^{Nujol} 2105 (N_3) and 1725–1745 cm^{-1} (PhCO).

Anal. Calc. for $C_{33}H_{31}N_9O_9$ (697.6): C, 56.81; H, 4.48; N, 18.08. Found: C, 56.83; H, 4.76; N, 18.15.

*2,3-Diazido-4,6-O-benzylidene-2,3-dideoxy-α-*D*-mannopyranosyl 3-azido-4,6-O-benzylidene-3-deoxy-α-*D*-mannopyranoside* (**12**). — A suspension of **11** (907 mg) in dry methanol (20 mL) containing sodium methoxide (150 mg) was heated on a steam bath for 5 min, after which t.l.c. (solvent *C*) indicated complete conversion of **11** into the less mobile **12**. The mixture was processed by partial evaporation and partition between dichloromethane and water. The syrup obtained from the organic phase crystallized from hot methanol (2 mL) to yield **12** (715 mg, 92%), m.p. 193–195°, $[\alpha]_D^{25}$ +69° (*c* 0.6, chloroform); ν_{max}^{Nujol} 3560 (OH) and 2110 cm^{-1} (N_3).

Anal. Calc. for $C_{26}H_{27}N_9O_8$ (593.5): C, 52.61; H, 4.59; N, 21.24. Found: C, 52.55; H, 4.81; N, 21.36.

*2,3-Diazido-2,3-dideoxy-α-*D*-mannopyranosyl 3-azido-3-deoxy-α-*D*-mannopyranoside* (**13**). — Compound **12** (653 mg) was heated in 80% acetic acid (10 mL) on a steam bath for 1 h. The acid was removed by coevaporation with added water and ethanol. The remaining syrup contained, besides **13** (R_F 0.57), small proportions of faster-moving products (t.l.c., solvent *G*) which presumably resulted from partial acetylation. They were mostly removed by treatment of the syrup with 12:5:3 methanol–water–triethylamine (5 mL) for 30 min at 98°. Evaporation of the solution, followed by chromatographic removal of remnant impurities on a silica gel column (30 × 1.6 cm) with solvent *H* yielded **13** (423 mg, 92%) as a colorless, amorphous solid, $[\alpha]_D^{25}$ +136.3° (*c* 0.8, methanol); ν_{max}^{Nujol} 3360 (OH) and 2110 cm^{-1} (N_3).

Anal. Calc. for $C_{12}H_{19}N_9O_8$ (417.3): C, 34.53; H, 4.59; N, 30.21. Found: C, 34.23; H, 4.82; N, 29.72.

*2,3-Diamino-2,3-dideoxy-α-*D*-mannopyranosyl 3-amino-3-deoxy-α-*D*-mannopyranoside* (**14**). — To triazide **13** (334 mg) in methanol (5 mL) was added 10% Pd–C (0.35 g, previously moistened with 10 drops of water, and suspended in 1 mL of methanol) and 1,4-cyclohexadiene (1 mL). The flask was purged with N_2 and inserted in an ultrasonic water-bath at room temperature. After 10 min, t.l.c. (solvent *I*) showed a strong spot (R_F 0.25) for the reduction product, accompanied by trace spots (R_F 0.45 and 0.07), and sonication was stopped after 35 min. The catalyst was filtered off and washed exhaustively with methanol, and the filtrate was concentrated, clarified with activated charcoal, and evaporated to give **14** (264 mg, 97%) as a glass. The compound apparently existed in part as a carbonate salt and was non-homogeneous in t.l.c. When the faster-moving, main component and the slower-moving component were separated by multiple, fractional precipitations from methanol solution by 2-propanol, they gave virtually identical i.r. and ^{1}H-n.m.r. spectra. Samples so prepared were white, microcrystalline powders that tended to retain solvent of crystallization (^{1}H-n.m.r.) and to show sintering and swelling at 100–120°. An analytical sample had $[\alpha]_D^{25}$ +107° (*c* 0.6, water); ν_{max}^{Nujol} 3350 and 3290 (broad, OH and NH_2), and 1590 cm^{-1} (NH_2) and, after prolonged drying *in vacuo* at 10°, gave combustion values corresponding to a carbonate.

Anal. Calc. for $C_{12}H_{25}N_3O_8 \cdot H_2CO_3$ (401.4): C, 38.90; H, 6.78; N, 10.45. Found: C, 38.84; H, 6.92; N, 10.42.

*2-Azido-3-O-benzoyl-4,6-O-benzylidene-2-deoxy-α-*D*-mannopyranosyl 2,3-diazido-4,6-O-benzylidene-2,3-dideoxy-α-*D*-mannopyranoside* (**15**). — Compound **10** (1.00 g) and NaN_3 (1.00 g) in *N,N*-dimethylformamide (10 mL) were heated with magnetic stirring in a two-walled reaction vessel, the outer compartment of which contained boiling benzene. The reaction was virtually complete after 1 h and was stopped after 1.5 h; t.l.c. (solvent *C*) showed one major spot, R_F 0.52. The mixture was diluted with benzene (50 mL) and water (50 mL), and separated, and the aqueous phase was further extracted with benzene. The combined organic phases were washed four times with water, dried, and evaporated to give a yellowish solid. After decoloration with activated charcoal from dichloromethane solution, the recovered material crystallized from a small amount of hot ethanol, yielding **15** (785 mg, 90.3%), m.p. 120.5–124°, $[\alpha]_D^{25}$ +133.6° (*c* 0.6, chloroform); ν_{max}^{Nujol} 2110 (N_3) and 1727 cm^{-1} (BzO).

Anal. Calc. for $C_{33}H_{31}N_9O_9$ (697.7): C, 56.81; H, 4.48; N, 18.07. Found: C, 56.62; H, 4.64; N, 17.99.

*2,3-Diazido-4,6-O-benzylidene-2,3-dideoxy-α-*D*-mannopyranosyl 2-azido-4,6-O-benzylidene-2-deoxy-α-*D*-mannopyranoside* (**16**). — Compound **15** (698 mg) was treated with sodium methoxide (0.15 g) in methanol (20 mL) for 6 min at 98°.

The mixture was distributed between water and dichloromethane. The organic phase was washed with $NaHCO_3$ solution, dried, and evaporated to give crude **16**, R_F 0.43 in t.l.c. (solvent *C*), suitable for use in the next step. An analytical sample crystallized from hot 2-propanol, m.p. 112–122°, $[\alpha]_D^{25}$ +122.8° (*c* 0.5, chloroform); ν_{max}^{Nujol} 3480 (OH) and 2102 cm^{-1} (N_3).

Anal. Calc. for $C_{26}H_{27}N_9O_8$ (593.5): C, 52.51; H, 4.59; N, 21.24. Found: C, 52.86; H, 4.83; N, 21.06.

*2,3-Diazido-2,3-dideoxy-α-*D*-mannopyranosyl 2-azido-2-deoxy-α-*D*-mannopyranoside* (**17**). — Crude **16** produced from **15** (0.9 mmol) was treated with 80% acetic acid (5 mL) for 45 min on a steam bath. The acid was removed by coevaporation with water and methanol. Although the product crystallized, in part, from hot ethanol, the presence of partially acetylated material in the mother liquor required a brief treatment (15 min at 98°) with 12:5:3 methanol–water–triethylamine (5 mL). Conversion of the more-mobile acetates into **17** (R_F 0.4) was indicated by t.l.c. (ethyl acetate). Evaporation of the solution and crystallization of the residue from hot ethanol furnished pure **17** in several crops totaling 288 mg (71% from **15**) of white crystals, m.p. 148–151°, $[\alpha]_D^{25}$ +161.8° (*c* 0.5, methanol); ν_{max}^{Nujol} 3240 (very broad) and 2110 cm^{-1}. The crystals contained both ethanol and water.

Anal. Calc. for $C_{12}H_{19}N_9O_8 \cdot 0.5\ C_2H_6O \cdot 0.5\ H_2O$ (449.4): C, 34.74; H, 5.16; N, 28.05. Found: C, 34.91; H, 5.12; N, 27.77.

*2,3-Diamino-2,3-dideoxy-α-*D*-mannopyranosyl 2-amino-2-deoxy-α-*D*-mannopyranoside* (**18**). — Triazide **17** (180 mg) was reduced by transfer hydrogenation (with agitation by ultrasound) as described for the isomer **13**. The amino sugar **18** was obtained as a solid (140 mg, 87%) which showed two spots (R_F 0.26 and 0.08) in t.l.c. (solvent *I*). As for **14**, separation of the components by manipulation with ethanol and 2-propanol gave products that did not differ in their i.r. and ^{1}H-n.m.r. spectra. A chromatographically homogeneous (R_F 0.26) sample of the more-soluble component, obtained from 2-propanol solution as white powder in 51% yield, was dried *in vacuo* at 100° and then appeared to be hygroscopic; it showed m.p. 107° (sintering) and $[\alpha]_D^{25}$ +109.7° (*c* 0.6, water); ν_{max}^{Nujol} 3350 and 3290 (broad), and 1595 cm^{-1}. The analytical sample possibly had retained both 2-propanol and water of crystallization.

Anal. Calc. for $C_{12}H_{25}N_3O_8 \cdot 0.5\ C_3H_8O \cdot H_2O$ (387.4): C, 41.85; H, 8.06; N, 10.86. Calc. for $C_{12}H_{25}N_3O_8$ (339.3): C, 42.47; H, 7.43; N, 12.38. Found: C, 42.07; H, 7.50; N, 10.81.

*2-Azido-4,6-O-benzylidene-2-deoxy-3-O-trifluoromethylsulfonyl-α-*D*-altropyranosyl 2-azido-4,6-O-benzylidene-2-deoxy-3-O-trifluoromethylsulfonyl-α-*D*-altropyranoside* (**19**). — Trifluoromethanesulfonic anhydride (2 mL) in dry dichloromethane (10 mL) was added dropwise (5 min) to an ice-cooled solution of **2** (2.84 g, 5 mmol) in dichloromethane (30 mL) and pyridine (4 mL). After 15 min, the mixture was allowed to warm to ambient temperature and kept for another 30 min. Two products having R_F 0.38 and 0.42 were observed in t.l.c. (solvent *C*), with the slower one gradually disappearing during the reaction. The mixture was shaken with an equal volume of water, and the aqueous phase was extracted once with dichloromethane. The combined organic phase was washed with dilute, aqueous $NaHCO_3$ solution, dried (Na_2SO_4), and evaporated with several additions and evaporations of toluene. A solution of the syrupy residue in benzene was clarified with Celite, diluted with methanol (3 vol.), and partially evaporated to give a first crop of crystalline **19** (2.962 g), m.p. 106–108° (dec.). Further concentration of the mother liquor, and trituration of the residue with warm methanol, followed by cooling gave additional crops to a total of 3.58 g (86%). An analytical sample was recrystallized from dichloromethane–methanol, m.p. 108.5–111° (dec.), $[\alpha]_D^{25}$ +61.6° (c 0.7, chloroform); ν_{max}^{Nujol} 2115 cm^{-1} (N_3).

Anal. Calc. for $C_{28}H_{26}F_6N_6O_{13}S_2$ (832.7): C, 40.39; H, 3.15; N, 10.09; S, 7.70. Found: C, 39.98; H, 3.46; N, 9.92; S, 7.59.

*2,3-Diazido-4,6-O-benzylidene-2,3-dideoxy-α-*D*-mannopyranosyl 2,3-diazido-4,6-O-benzylidene-2,3-dideoxy-α-*D*-mannopyranoside* (**7**), *2,3-diazido-4,6-O-benzylidene-2,3-dideoxy-α-*D*-mannopyranosyl 2-azido-4,6-O-benzylidene-2,3-dideoxy-α-*D-threo*-hex-3-enopyranoside* (**20**), *and 2,3-diazido-4,6-O-benzylidene-2,3-dideoxy-α-*D*-mannopyranosyl 2-azido-4,6-O-benzylidene-2-deoxy-α-*D*-altropyranoside* (**21**). — A suspension of tetramethylguanidinium azide[9] (5.5 g) in dry benzene (100 mL) was partially evaporated *in vacuo* to 60 mL, the supernatant solution decanted, and the residual azide dissolved in dry dichloromethane (20 mL). The two solutions were combined (whereby some azide precipitated), compound **19** (2.92 g) was added, and the mixture was stirred for 18 h at room temperature and, subsequently, for 2 h at reflux temperature. Monitoring by t.l.c. (solvent *C*) revealed no further change at that point, with spots having R_F 0.60 (**20**), 0.53 (**7**), and 0.40 (**21**) being visible. The mixture was shaken with an equal volume of water, the aqueous phase was extracted with fresh benzene, and the combined organic phase was washed three times with water, dried (Na_2SO_4), and evaporated. The residue crystallized, in part, upon concentration of its solution in dichloromethane (5 mL) and methanol (15 mL) on a steam bath. The crude crystals were **7**, contaminated by the other products. Four similar recrystallizations led to chromatographically pure **7** (1.236 g), and processing of the combined mother liquors by multiple recrystallizations gave additional crops, to a total of 1.60 g (73.7%), m.p. 226.5–228° (dec.), $[\alpha]_D^{25}$ +113° (c 0.7, chloroform); ν_{max}^{Nujol} 2125, with shoulder at 2150 cm^{-1} (N_3).

Anal. Calc. for $C_{26}H_{26}N_{12}O_7$ (618.6): C, 50.48; H, 4.24; N, 27.17. Found: C, 50.27; H, 4.24; N, 27.33.

The material obtained after evaporation of the combined mother liquors was chromatographed on a column of silica gel (32 × 1.8 cm) with solvent *F* as the eluant. The fast-moving **20** eluted first crystallized from ethanol in three crops totaling 272 mg (13.5%), m.p. 131–133°, $[\alpha]_D^{25}$ +207° (c 0.6, chloroform); ν_{max}^{Nujol} 2122 (N_3) and 1687 cm^{-1} (vinyl ether).

Anal. Calc. for $C_{26}H_{25}N_9O_7$ (575.5): C, 54.26; H, 4.38; N, 21.91. Found: C, 54.11; H, 4.34; N, 21.96.

The slow-moving compound **21** eluted from the column gave crystals (24 mg, 1.2%) from ethanol, m.p. 167–170°, $[\alpha]_D^{25}$ +120° (*c* 0.6, chloroform), ν_{max}^{Nujol} 3518 (OH) and 2120 cm^{-1} (N_3).

Anal. Calc. for $C_{26}H_{27}N_9O_8$ (593.5): C, 52.61; H, 4.59; N, 21.24. Found: C, 52.48; H, 4.53; N, 21.42.

A sample of **21** was acetylated with acetic anhydride and pyridine to give **22** for ^{1}H-n.m.r. spectroscopy (see Table I).

*2,3-Diazido-2,3-dideoxy-α-*D*-mannopyranosyl 2,3-diazido-2,3-dideoxy-α-*D*-mannopyranoside* (**23**). — A suspension of **7** (1.546 g) in 80% acetic acid (20 mL) was heated on a steam bath until all **7** had dissolved (1.75 h), and then for another 0.5 h. The slightly yellow solution was evaporated *in vacuo* with sequential additions of three portions of 1:1 ethanol–water (20 mL each). The resultant syrup showed in t.l.c. (solvent *A*) a major spot for **23** (R_F 0.33) accompanied by a weaker spot (R_F 0.55) and a trace spot (R_F 0.8). These by-products, which apparently arose by partial acetylation, were removed by treatment of the material with 12:5:3 methanol–water–triethylamine (20 mL) during 30 min on a steam bath. The brown solution was evaporated with added ethanol, and the crude product was applied (with a small amount of ethyl acetate) to a short, wide column (4 × 4.5 cm) of silica gel. Elution with ethyl acetate–hexane mixtures of gradually increasing polarity (from 3:7 to 7:3) furnished **23** that crystallized and was recrystallized from 2-propanol to give several crops of pure **23** (total 1.046 g, 94.5%), m.p. 170–172° (dec.), $[\alpha]_D^{25}$ +177.7° (*c* 0.9, methanol); ν_{max}^{Nujol} 3430 and 3250 (OH), and 2115 with shoulders at 2240 and 2190 cm^{-1} (N_3).

Anal. Calc. for $C_{12}H_{18}N_{12}O_7$ (442.4): C, 32.58; H, 4.10; N, 38.00. Found: C, 32.77; H, 4.24; N, 37.87.

*2,3-Diamino-2,3-dideoxy-α-*D*-mannopyranosyl 2,3-diamino-2,3-dideoxy-α-*D*-mannopyranoside* (**24**). — Pd–C (10%; 0.5 g), moistened with a little methanol–water, was added to a solution of **23** (442 mg) in methanol (20 mL) which was then efficiently stirred under H_2, at ambient temperature and pressure, for 4 h. The catalyst was removed and washed exhaustively with methanol, and the filtrate evaporated to give a yellowish syrup showing one main spot (R_F 0.15) accompanied by trace spots (R_F 0.20 and 0.0) in t.l.c. (solvent *J*). The contaminants were virtually completely removed by passage of an aqueous solution of the product through a bed of activated charcoal. The colorless solution was evaporated to give syrupy **24** (268 mg, 74%). By precipitation from a concentrated methanolic solution with excess ethanol, **24** was obtained as a white powder, apparently a hydrate, m.p. 114–150°, $[\alpha]_D^{25}$ +110° (*c* 0.8, water); ν_{max}^{Nujol} 3300 (broad; OH, NH_2) and 1590 cm^{-1} (NH_2).

Anal. Calc. for $C_{12}H_{26}N_4O_7 \cdot H_2O$ (356.4): C, 40.44; H, 7.92; N, 15.72. Found: C, 40.44; H, 7.99; N, 15.45.

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