Aminosugars. XXV. Synthesis of Benzyl 2-Acetamido-2-amino-2,3,4-trideoxy-α-D-*arabino*-hexopyranoside[1]

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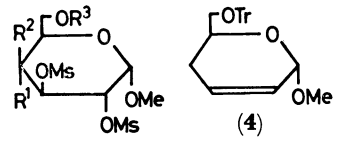
As the attempted substitution of methyl 4-deoxy-2,3-di-*O*-mesyl-6-*O*-trityl-α-D-*xylo*-hexopyranoside with sodium azide gave the unsaturated compound: methyl 2,3,4-trideoxy-6-*O*-trityl-α-D-*glycero*-hex-2-enopyranoside (**4**), benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-mannopyranoside was used as the starting material, which was converted into benzyl 2-acetamido-2-deoxy-3-*O*-mesyl-6-*O*-trityl-α-D-mannopyranoside (**10**). For the deoxygenation of C-4 position, chlorination of **10** with sulfuryl chloride gave unexpectedly benzyl 3′-*O*-mesyl-6′-*O*-trityl-α-D-talopyranosid [2′,3′,4′; 4,5,6]-2-methyl-4,5-dihydro-6*H*-oxazine, due to the anchimeric effect of the C_2-axial acetamido group. However, previous change of the conformation of **10** by the substitution of C_3-mesyl group with azido group gave successfully the corresponding chloro derivative (**13**). Reduction of **13** with tributyltin hydride gave the corresponding 3,4-epimino derivative (**14**), due to participation of initially hydrogenated azido group, but, catalytic hydrogenation of **14** gave the title compound as the main product.

L-Tuberactidine: α-(4-hydroxyl-2-imino-hexahydro-6(*R*)-pyrimidinyl)-(*S*)-glycine,[2] was found as the unique component of a peptide antibiotic, tuberactinomycin A.[3] In order to synthesize L-tuberactidine by utilization of sugars for the two asymmetric configurations, the title compound was synthesized as the key intermediate. This paper describes the synthesis and a few anchimeric effects of neighbouring groups in aminosugars found in the course of the study.

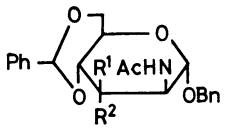
Results and Discussion

For the synthesis of a 2,3-diamino-2,3,4-trideoxy-hexose derivative from a neutral sugar, deoxygenation of *C*-4 position and introduction of amino groups into *C*-2 and *C*-3 positions are necessary. Concerning the title compound, Guthrie *et al.*[4] synthesized methyl 3-amino-2-azido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-altropyranoside by ring opening of the corresponding 2,3-epimino derivative with azide anion, which was obtained from D-glucose *via* ten-step conversions. This compound has the same configuration as the title compound, excepting the presence of C_4-hydroxyl group, but the C_4-deoxygenation after introduction of C_3-amino group was considered to be a rather difficult problem. On the other hand, it is known that some reagents such as potassium ethylxanthate,[5] sodium iodide and zinc dust,[6] trimethyl phosphite,[5] and others[7] apt to give unsaturated sugars from the corresponding vicinal disulfonates, while sodium azide gave mainly direct displacement products.[8] Consequently, we have firstly tried a one-step introduction of 2,3-diamino groups into a 4-deoxy sugar.

Partial hydrolysis of methyl 4,6-*O*-benzylidene-2,3-di-*O*-mesyl-α-D-glucopyranoside[5,9] with 70% acetic acid at 90—95 °C gave methyl 2,3-di-*O*-mesyl-α-D-glucopyranoside (**1**) in 98% yield. Tritylation of **1** gave the corresponding 6-*O*-trityl derivative, which was then chlorinated with sulfuryl chloride[10] to give the corresponding 4-chloro-4-deoxy derivative (**2**) in 88% yield. Hydrogenation of **2** with tributyltin hydride gave the desired 4-deoxy derivative (**3**) quantitatively. However, reaction of **3** with sodium azide in *N*,*N*-dimethylformamide for 20 h at refluxing temperature gave the corresponding 2,3-unsaturated compound (**4**) and starting material as main products in 15% and 38% yields, respectively. Although other three minor products were not examined and the reaction mechanism is also ambiguous, this fact indicates that the unsaturation is preferential in this reaction, and that the deoxygenation of *C*-4 position does not make any advantages for the vicinal diazide formation. The structure of **4** was supported by the long range couplings of the allylic system ($J_{1,3}$=2.0, $J_{2,4}$=1.0) in the PMR spectrum (Table 1).

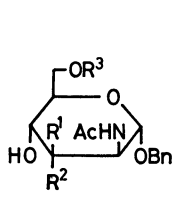


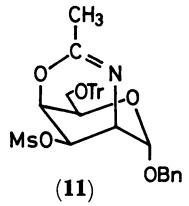
(**4**)



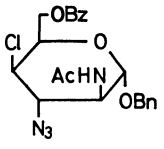
(**1**) R^1=OH, R^2=R^3=H
(**2**) R^1=H, R^2=Cl, R^3=Trityl
(**3**) R^1=R^2=H, R^3=Trityl

(**5**) R^1=OH, R^2=H
(**6**) R^1=OMs R^2=H
(**7**) R^1=H, R^2=N_3



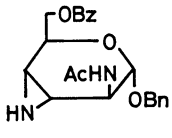


(**11**)

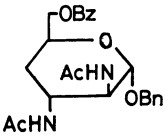


(**13**)

(**8**) R^1=R^3=H, R^2=NH_2
(**9**) R^1=R^3=H, R^2=NH-C(=NH)NH_2
(**10**) R^1=OMs, R^2=H, R^3=Trityl
(**12**) R^1=H, R^2=N_3, R^3=Bz



(**14**)



(**15**)

Because more simple and fewer steps are desired for synthesis of optically active none-carbohydrate compounds, benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-mannopyranoside (**5**)[11] was used as the starting

Table 1. PMR parameters of ring protons of compounds **4**, **7**, **11**, **12**, and **13**

Compound	H_1	H_2	H_3	H_4	H_5	H_6	$H_{6'}$	Other protons
4	4.89(broad s)	5.76(m)	5.97(m)	2.0—1.83(m)	4.12(sex)	3.25(q)	3.07(q)	7.6—7.18 (Ph)
	$J_{1,2}$=*ca.* 2.0	$J_{2,3}$=10.0	$J_{3,4}$=3.0	$J_{4,5}+J_{4',5}$=	$J_{5,6}$=6.0	$J_{5,6}$=4.2	$J_{6,6'}$=	3.47(OMe)
	$J_{1,3}$=*ca.* 1.5	$J_{2,4}$=1.0	$J_{3,4'}$=4.5	14.8			10.0	
7[a]	4.65(broad s)	4.35(q)	4.09(t)	3.88(q)	*ca.* 4.28(m)	4.24(q)	3.67(t)	7.55—7.22(Ph), 5.57 (methine), 1.97(NAc), 4.70 and4.55(ABq; J=12.0)
	$J_{1,2}$=<0.5	$J_{2,3}$=3.0	$J_{3,4}$=3.5	$J_{4,5}$=9.0	$J_{5,6}$=6.9	$J_{5,6}=J_{6,6}$=10.0		
11	4.84(d)	*ca.* 3.77(m)	5.15(t)	*ca.* 4.63(m)	3.86(broad t)	3.27(d)		7.55—7.18(Ph); 4.50 and 4.63(CH_2); ABq, J=12.0, 2.96(OMs), 1.87(CMe)
	$J_{1,2}$=2.0		$J_{2,3}=J_{3,4}$=2.1		$J_{4,5}$=2.1	$J_{5,6}$=7.2		
12[a]	4.72(d)	*ca.* 4.4(m)	4.10(t)	3.85(q)	*ca.* 4.22(m)	*ca.* 4.5(broad d)		8.10—7.20(Ph) 1.93(NAc)
	$J_{1,2}$=<1.0	$J_{2,3}=J_{3,4}$=*ca.* 3.3		$J_{4,5}$=11.0				
13	4.88(t)	4.30(m)	4.0(broad s)	4.14(t)	4.69(m)	4.52(q)	4.38(q)	8.10—7.25(Ph); 6.36 (NH; J=9.0), 1.98 (NAc), 4.75 and 4.54 (CH_2; ABq, J=12.0)
	$J_{1,2}=J_{1,3}$ =1.0	$J_{2,3}$=2.8	$J_{3,4}=J_{4,5}$=3.5		$J_{5,6}$=3.0	$J_{5,6'}$ =5.0	$J_{6,6'}$ =10.0	

a) NH proton was deuterated.

material in the next experiments. Mesylation of **5** in pyridine gave the corresponding 3-*O*-mesylate (**6**) in a good yield, which was then transformed into 3-azido-3-deoxy derivative (**7**) of D-*altro* type. Hydrogenation of **7** gave the corresponding 3-amino-3-deoxy-derivative (**8**), which was then converted into 3-guanidino-3-deoxy derivative (**9**) by fusion with sodium cyanamide.[12]

For the deoxygenation of *C*-4 position, 4,6-*O*-benzylidene group of **6** was hydrolyzed and then tritylated to give benzyl 2-acetamido-2-deoxy-3-*O*-mesyl-6-*O*-trityl-α-D-mannopyranoside (**10**) in 62% yield. Chlorination of **10** in pyridine with sulfuryl chloride gave a product (**11**) in 80.5% yield, which contains no chlorine atom, and the analytical values consisted with that of monodehydrated product of **10**. Besides, the appearance of H_3 signal as a triplet (J=2.1 Hz) having no long range coupling and the absence of NH proton signal in the PMR spectrum of **11** indicates the normal *C1* conformation and the formation of intramolecular oxazin ring by the participation of axial 2-acetamido group. Consequently, **11** was characterized to be benzyl 3'-*O*-mesyl-6'-*O*-trityl-α-D-talopyranosid[2',3',4';4,5,6]-2-methyl-5,6-dihydro-4H-oxazine. Because the 4-*O*-chlorosulfonyl group formed in the initial step of the chlorination is a good leaving group, the participation of axial acetamido group to the β-carbon observed above will be very reasonable, and a similar participation was recently reported by Meyer zu Reckendorf *et al.*[13] Several attempts to open the oxazine-ring of **11** gave unsuccessful results.

To avoid the participation of the axial acetamido group, conformational change of the lactol ring is

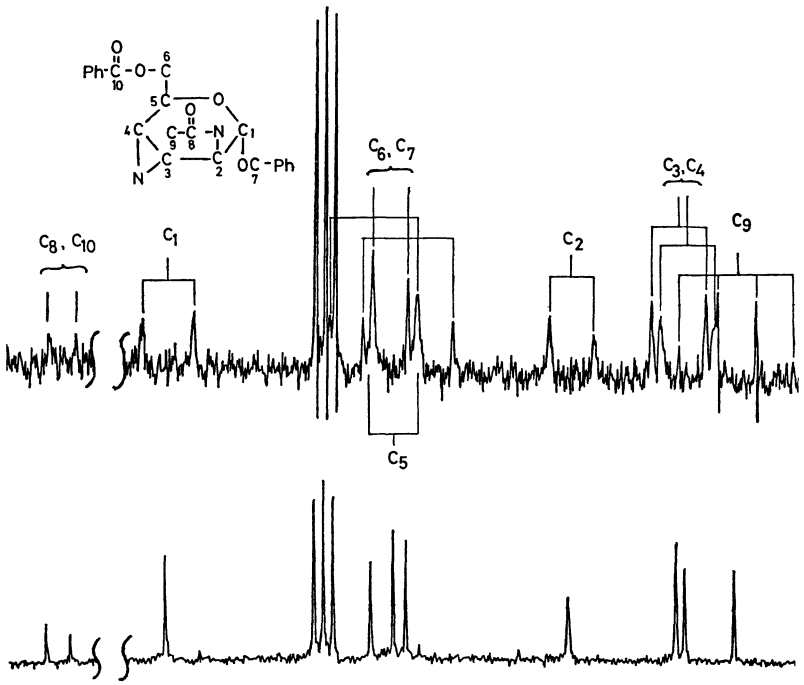


Fig. 1. CMR spectrum of compound **14**.

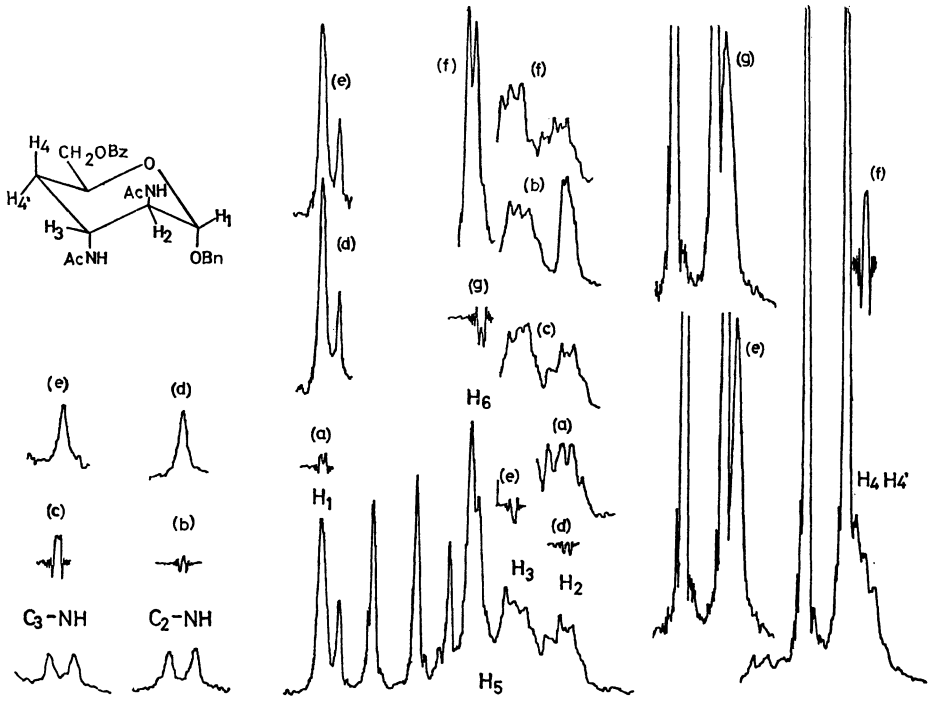


Fig. 2. The proof of the structure of **16** with the decoupling technique.

desirable. So, **7** was partially hydrolyzed, and then partially benzoylated to give benzyl 2-acetamido-3-azido-6-*O*-benzoyl-2-deoxy-α-D-altropyranoside (**12**) in 80% yield. The chlorination of **12** gave the corresponding 4-chloro-4-deoxy derivative (**13**) in 70.5% yield as expected. The coupling constants of ring protons of **12** are very similar to that of **7** (Table 1), indicating the *C1* conformation of **12**. However, it is characteristic that the $J_{1,2}$ values of them are smaller than that of **11** having a typical *C1* conformation, due to the flattening of the pyranose-ring. This tendency of D-*altro*-configuration of **7** and **12** is stronger than that of D-*manno*-configuration of **6** ($J_{1,2}$=1.5) and **10** ($J_{1,2}$=1.0). Consequently, it is deduced that a slight deformation of the conformation in **12** prevented the anchimeric contribution of C_2-acetamido group. It is also noteworthy that **13** has still *C1* conformation, nevertheless, the pyranose-ring has four axial substituents. It seems likely to be due to the dipolar repulsions between four electronegative substituents (Cl, N_3, NHAc, and OBn).

Hydrogenation of chlorine atom of **13** with tributyltin hydride proceeded smoothly together with that of the azido group. The structure of the product (**14**) could not be confirmed to be either the corresponding 3-amino or 3,4-epimino derivative by usual methods, but CMR spectrum (Fig. 1) indicated the presence of only two methylene carbons. Consequently, the structure was determined to be benzyl 2-acetamido-6-*O*-benzoyl-3,4-epimino-2,3,4-trideoxy-α-D-altropyranoside. This conclusion suggests that the hydrogenation of azido group was faster than that of the chlorine atom. Hydrogenation of **14** in the presence of Raney nickel gave fortunately the desired 3-amino-3,4-dideoxy derivative as main product, which was then converted into 3-acetamido derivative (**15**) in 60% yield. The configuration of **15** was completely proved by the double resonance technique in the PMR spectrum (Fig. 2). By irradiation of H_1 and two NH protons (a, b, c), multiplets at δ *ca.* 4.15 and 4.30 were assigned to H_2 and another ring proton (H_3) of the position of the acetamido group, respectively, and the reverse irradiation (d, e) indicated that only the latter is vicinal to the ring methylene protons at δ *ca.* 1.84, showing the sharpening of them. These facts indicate that the deoxygenated position should be *C*-4. Moreover, the conclusion was confirmed by the irradiation of ring-methylene protons (f) and a ring proton (H_5) other than two acetamido positions (g).

Experimental

All melting points were determined with Yanaco micro melting point apparatus and not corrected. The solutions were evaporated under reduced pressure at a bath temperature not exceeding 50 °C. The IR spectra were measured in KBr discs with a Hitachi EPI-GS spectrometer. The PMR spectra were obtained at 100 MHz with a JEOL 4H-100 spectrometer in deuteriochloroform, using TMS as an internal reference. Specific rotations were measured in a 0.5-dm tube with a Carl Zeiss SEP-AL polarimeter in chloroform unless otherwise stated. Chemical shifts and coupling constants were recorded in δ and Hz units, and IR frequencies in cm^{-1}.

Methyl 2,3-Di-O-mesyl-α-D-glucopyranoside (*1*). A suspension of methyl 4,6-*O*-benzylidene-2,3-di-*O*-mesyl-α-D-glucopyranoside (7 g, 16 mmol) in 70% acetic acid (100 ml) was heated at 90—95 °C for 4 h under monitering with TLC until the starting material has disappeared, and then evaporated to give white powder which was crystallized from ethanol. Yield, 5.5 g (98%), mp 148—149 °C; $[\alpha]_D^{22}$+84.2° (*c* 1.0, acetone).

Found: C, 31.07; H, 5.15; S, 17.83%. Calcd for $C_9H_{18}O_{10}S_2$: C, 30.85; H, 5.18; S, 18.30%.

Methyl 4-Chloro-4-deoxy-2,3-di-O-mesyl-6-O-trityl-α-D-galactopyranoside (*2*). A solution of **1** (1 g, 2.9 mmol) and trityl chloride (1 g, 3.6 mmol) in pyridine (30 ml) was kept at room temperature, and then poured into ice–water to give the corresponding 6-*O*-trityl derivative in 86% (1.5 g) yield (mp 155—

156 °C after recrystallization from benzene). To an ice-cooled solution of 6-*O*-trityl derivative (1.5 g, 2.5 mmol) in pyridine was added dropwise sulfuryl chloride (0.27 ml, 3.3 mmol) with stirring, and then poured into ice–water after standing overnight at room temperature. The resulting solution was extracted with chloroform, and the extract was treated in a usual manner to give a sirup (1.36 g, 88%) which was crystallized and recrystallized from methanol. Mp 130—131 °C, $[\alpha]_D^{23}$ +53.0° (*c* 1.0).

Found: C, 55.04; H, 5.11; S, 10.21%. Calcd for $C_{28}H_{31}O_9S_2Cl$; C, 55.02; H, 5.11; S, 10.49%.

*Methyl 4-Deoxy-2,3-di-*O*-mesyl-6-*O*-trityl-α-*D*-xylo-hexopyranoside* (**3**). A solution of **2** (200 mg, 0.33 mmol), tributyltin hydride (0.5 ml) and a catalytic amount of 2,2′-azobisisobutyronitrile in toluene (8 ml) was heated at 80—90 °C for 20 h under argon atmosphere, and then evaporated to give crystals quantitatively, which were recrystallized from ethanol. Mp 187—188 °C; $[\alpha]_D^{23}$ +59.5° (*c* 1.0).

Found: C, 58.51; H, 5.90; S, 11.05%. Calcd for $C_{28}H_{32}O_9S_2$: C, 58.31; H, 5.59; S, 11.12%.

*Methyl 2,3,4-Trideoxy-6-*O*-trityl-α-*D*-glycero-hex-2-enopyranoside* (**4**). A suspension of **3** (1.0 g, 1.7 mmol) and sodium azide (680 mg, 10 mmol) in DMF (30 ml) was refluxed for 20 hr, poured into water, and the resulting solution was extracted with ether. The ether layer was washed with saturated sodium chloride, dried with sodium sulfate, and then evaporated to give a sirup which showed five spots on TLC (benzene:ethyl acetate=95:5). The starting material (R_f= 0.20; 380 mg, 38%) and 5 (R_f=0.58; 100 mg, 15%) were isolated as main products on a sillica gel column (benzene). $[\alpha]_D^{22}$ −22.6° (*c* 1.0); IR: 1660 (C=C).

Found: C, 80.14; H, 6.90%. Calcd for $C_{26}H_{26}O_3$: C, 80.80; H, 6.78%.

*Benzyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-mesyl-α-*D*-mannopyranoside* (**6**). To an ice-cooled solution of benzyl 2-acetamido-4,6-*O*-benzylidene-D-deoxy-α-D-mannopyranoside (200 mg, 0.5 mmol) in pyridine (2 ml) was added dropwise methanesulfonyl chloride (150 mg, 1.3 mmol) with stirring. The resulting solution was kept at room temperature for 4 h, Poured into ice–water, and the crystals (230 mg, 96%) deposited were recrystallized from ethanol. Mp 167—168 °C; $[\alpha]_D^{23}$+114.5° (*c* 1.5); IR: 3280 (NH), 1650 and 1535 (amide), 1370 (sulfonate).

Found: C, 57.90; H, 5.74; N, 3.08%. Calcd for $C_{23}H_{27}O_8SN$: C, 57.85; H, 5.70; N, 2.93%.

*Benzyl 2-Acetamido-3-azido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-altropyranoside* (**7**). A solution of **6** (1.0 g, 2.1 mmol) and lithium azide (1.0 g, 143 mmol) in HMPA (50 ml) was heated at 150—157 °C overnight, poured into cold sodium chloride solution, and then extracted with ether. The extracts were washed with 5% sodium chloride, dried, and evaporated to give a sirup (740 mg, 83%) which was crystallized and recrystallized from ethanol. Mp 160 °C; $[\alpha]_D^{23}$ +70.8° (*c* 1.2); IR: 3280 (NH), 2100 (N_3), 1650 and 1535 (amide).

Found: C, 62.39; H, 5.75; N, 13.34%. Calcd for $C_{22}H_{24}N_4O_5$: C, 62.25; H, 5.70; N, 13.20%.

*Benzyl 2-Acetamido-3-amino-4,6-*O*-benzylidene-2,3-dideoxy-α-D-altropyranoside* (**8**). A suspension of **7** (740 mg 1.7 mmol) and Raney nickel (2.3 g) in ethanol (80 ml) was hydrogenated in an autoclave under a hydrogen pressure of 80—100 kg/cm² at room temperature overnight, and then filtered. Evaporation of the filtrate gave crystals (600 mg, 88%) which were recrystallized from ethanol. Mp 236—238 °C; $[\alpha]_D^{19}$ +82.0° (*c* 1.02); IR: 3160—3350 (NH), 1660 and 1560 (amide).

Found: C, 66.25; H, 6.69; N, 6.92%. Calcd for $C_{22}H_{26}N_2O_5$: C, 66.31; H, 6.58; N, 7.03%.

Benzyl 2-Acetamido-2,3-dideoxy-3-guanidino-α-D-altropyranoside (**9**). To a solution of **8** (0.45 g, 1.13 mmol) in aqueous ethanol containing equimolar hydrochloric acid was added cyanamide (72 mg, 1.7 mmol), then the temperature of the mixture was raised to 130 °C in an oil-bath during 1 h, and the mixture was kept at the temperature for 30 min. The glassy reaction mixture was dissolved in aqueous ethanol, treated with IRA-410 (OH form, 5 ml) overnight, and then filtered, The filtrate was heated at 90—100 °C for 6 h together with acetic acid (70%, 40 ml), evaporated, and then absorbed on an Amberlite CG-50 column (20 ml). The column was eluated. in turn with water (200 ml), aqueous ammonia (2.8%, 200 ml), water (200 ml) and then 0.5 M hydrochloric acid. The last effluent of pH 6—8 was evaporated, and the residue was extracted with ethanol. The ethanol extract was treated with IRA-410 (OH^- form, 20 ml) overnight, and the filtrate was evaporated to give a colourless glassy solid (200 mg, 50%) which is positive in the Sakaguchi reaction. $[\alpha]_D^{23}$ +58.7° (*c* 1.07, water).

Found: C, 49.63; H, 6.91; N, 14.85%. Calcd for $C_{16}H_{24}N_4O_5\cdot 2H_2O$; C, 49.47; H, 7.27; N, 14.43%.

*Benzyl 2-Acetamido-2-deoxy-3-*O*-mesyl-6-*O*-trityl-α-*D*-mannopyranoside* (**10**). A suspension of **6** (3.07 g, 6.4 mmol) in 70 % acetic acid (100 ml) was heated at 60—70 °C for 6 h, and after evaporation of the solvent, the residue was washed with petroleum ether. A solution of the dried residue and trityl hloride (2.6 g, 9.3 mmol) in pyridine (50 ml) was kept at room temperature overnight, and evaporated. The residue was purified on a silica gel column (benzene: ethyl acetate=4: 1) to give crystals (2.52 g, 62%). Mp 179—180 °C; $[\alpha]_D^{22}$ +37.4° (*c* 1.0, acetone); IR: 3350 (NH), 1650 and 1520 (amide).

Found: C, 65.92; H, 5.93; N, 2.04; S. 5.12%. Calcd for $C_{35}H_{37}NO_8S$: C, 66.54; H, 5.90; N, 2.22; S, 5.08%.

*Benzyl 3′-*O*-Mesyl-6′-*O*-trityl-α-*D*-talopyranosid[2′,3′,4′; 4,5,6]-2-methyl-5,6-dihydro-4*H*-oxazine* (**11**). To an ice-cooled solution of **10** (1.0 g, 1.6 mmol) in pyridine (50 ml) was added dropwise sulfuryl chloride (0.16 ml, 2.0 mmol), and the mixture was evaporated, after standing overnight in a refrigerator. The residue was dissolved in chloroform, and the solution was washed in turn with cold 2 M hydrochloric acid, saturated sodium hydrogen carbonate and sodium chloride, dried, and then removal of the solvent gave a sirup (1.04 g, 80.5%) which was crystallized from ethanol. Mp 129—130 °C; $[\alpha]_D^{24}$ +18.1° (*c* 1.0); IR: 1660 (C=N), 1360 (sulfonic ester).

Found: C, 68.44; H, 5.72; N, 2.29; S, 5.29%. Calcd for $C_{35}H_{35}O_7S$: C, 68.49; H, 5.74; N, 2.28; S, 5.23%.

*Benzyl 2-Acetamido-3-azido-6-*O*-benzoyl-2,3-dideoxy-α-D-altropyranoside* (**12**). A suspension of **7** (3.5 g, 8.3 mmol) in 70% acetic acid (50 ml) was heated at 60—70 °C for 5 hr, the resulting solution was evaporated, and then the residue was washed with petroleum ether. To a chilled solution of the dried residue in pyridine (50 ml) was added dropwise benzoyl chloride (1.1 ml, 9.5 mmol), the mixture was kept at room temperature overnight, poured into cold saturated sodium hydrogen carbonate, and then extracted with chloroform. Treatment of the extract in a usual manner gave a sirup (3.0 g, 80%) which was purified on a silica gel column (ethyl acetate). $[\alpha]_D^{23}$ +51.7° (*c* 1.0); IR: 3300 (NH, OH), 2100 (N_3), 1720 (ester), 1650 and 1540 (amide).

Found: C, 59.43; H, 5.58; N, 12.30%. Calcd for $C_{22}H_{24}O_6N_4$: C, 59.99; H, 5.49; N, 12.72%.

*Benzyl 2-Acetamido-3-azido-6-*O*-benzoyl-4-chloro-2,3,4-trideoxy-α-D-idopyranoside* (**13**). To an ice-cooled solution of **12** (1.5 g, 3.4 mmol) in pyridine (30 ml) was added dropwise sulfuryl chloride (0.32 ml, 4.0 mmol), the mixture was kept overnight in a refrigerator, and the solvent was evaporated. The residue was dissolved in chloroform, and the solution was washed in turn with cold 2 M hydrochloric acid, saturated

sodium bicarbonate, saturated sodium chloride, dried, and evaporation of the solvent afforded crystals (1.1 g, 70.5%) which was recrystallized from ethanol. Mp 175 °C; $[\alpha]_D^{23}$ +79.8 °C (*c* 1.0); IR: 3250 (NH), 2100 (N_3); 1720 (ester), 1650 and 1550 (amide).

Found: C, 57.39; H, 5.07; N, 12.18%. Calcd for $C_{22}H_{23}O_5N_4Cl$: C, 57.39; H, 5.05; N, 12.21%.

Benzyl 2-Acetamido-6-O-benzoyl-2,3,4-trideoxy-3,4-epimino-α-D-altropyranoside (**14**). A solution of **13** (250 mg, 5.4 mmol) tributyltinhydride (3.0 ml) and catalytic amount of 2,2′-azobisisobutylonitrile in toluene was heated at 80—90 °C for 3 days under argon atmosphere, and crystals deposited at room temperature were filtered and recrystallized from toluene. Mp 142—143 °C; $[\alpha]_D^{22}$ +32.2° (*c* 1.0); IR: 3200—3300 (NH), 1710 (ester); 1660 and 1530 (amide and epimino); CNR (ppm): Ac (22.96), C_3 and C_4 (29.39, 30.53), C_2 (44.70), CH_2 (66.09, 70.71), C_5 (67.78), C_1 (97.78), C=O (165.89, 169.06).

Found: C, 66.09; H, 6.21; N, 6.93%. Calcd for $C_{22}H_{26}O_5N_2$: C, 66.31; H, 6.58; N, 7.03%.

Benzyl 2,3-Diacetamido-6-O-benzoyl-2,3,4-trideoxy-α-D-arabino-hexopyranoside (**15**). A suspension of **14** (200 mg, 0.5 mmol) and Raney nickel (2 g) in ethanol (10 ml) was hydrogenated in an autoclave at room temperature for 2 days, filtered, and the filterate was evaporated to give a sirup. The sirup in pyridine was acetylated with acetic anhydride at room temperature overnight, and the reaction mixture was poured into ice-water to give crystals which were recrystallized from ethanol–hexane. Yield, 130 mg (60%); Mp 214—215 °C; $[\alpha]_D^{22}$ −4.0° (*c* 0.5); IR: 3200—3300 (NH), 1720 (ester), 1660, 1640, 1560, and 1550 (amide).

Found: C, 64.12; H, 6.50; N, 6.09%. Calcd for $C_{23}H_{28}O_6N_2$: C, 64.47; H, 6.59; N, 6.54%.

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References

1) Part XXIV, *Nippon Kagaku Kaishi*, **1975**, 1958.
2) T. Wakamiya, T. Shiba, T. Kaneko, H. Sakakibara, T. Noda, and T. Take, *Bull. Chem. Soc. Jpn.*, **46**, 949 (1973).
3) A. Nagata, T. Ando, R. Izumi, H. Sakakibara, T. Take, K. Hayano, and J. Abe, *J. Antibiot.*, **21**, 681 (1968); R. Izumi, T. Noda, T. Ando, T. Take, and A. Nagata, *ibid.*, **25**, 201 (1972). cf. T. Wakamiya and T. Shiba, *Bull. Chem. Soc. Jpn.*, **48**, 2502 (1975).
4) R. D. Guthrie and D. Murphy, *J. Chem. Soc.*, **1965**, 3828.
5) E. Albano, D. Horton, and T. Tsuchiya, *Carbohyd. Res.*, **2**, 349 (1966).
6) R. S. Tipson and A. Cohen, *Carbohyd. Res.*, **1**, 338 (1965).
7) R. J. Ferrier., *Adv. Carbohyd. Res.*, **24**, 199 (1969).
8) J. Kovar, V. Dienstbierova, and J. Jary, *Collect. Czech. Chem. Commun.*, **32**, 2498 (1967).
9) J. Honeyman and J. W. W. Morgan, *J. Chem. Soc.*, **1955**, 3660.
10) H. Arita, N. Ueda, and Y. Matsushima, *Bull. Chem. Soc. Jpn.*, **45**, 567 (1972).
11) J. Yoshimura, H. Sakai, N. Oda, and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, **45**, 2027 (1972).
12) J. Yoshimura, T. Sekiya, and Y. Ogura, *Bull. Chem. Soc. Jpn.*, **47**, 1219 (1974).
13) W. Meyer zu Reckendorf, U. Kamprath-Scholz, E. Bischof, and N. Wassiliadou-Micheli, *Chem. Ber.*, **108**, 3397 (1975).