Aminocyclitols. 35. Synthesis of Deoxystreptamines[1]

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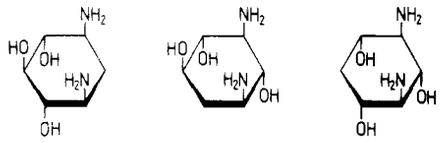
All three predicted positional isomers of deoxystreptamine have been synthesized. From the four disulfonates of cyclohexanepentols (**6**, **12a**, **14**, and **23a**) and the diepoxycyclohexanol (**24**), 2- (**1a**), 4- (**2a**), and 5-deoxystreptamine (**3a**) were obtained, together with the acetyl derivatives of four other diaminocyclohexanetriols (**9**, **15**, **28**, and **29**), by azidolysis or hydrazinolysis followed by catalytic reduction. Compounds **2a** and **3a** were also prepared starting from the suitably protected streptamine derivatives by deoxygenation via chlorination with sulfuryl chloride and successive hydrogenolysis. In addition, two triaminocyclohexanediols (**16** and **17**) were synthesized, which gave additional evidence on the structural elucidation of **15**.

In connection with the preceding paper,[2] synthesis of all the predicted deoxystreptamine isomers was carried out by azidolysis or hydrazinolysis and successive hydrogenation of dianhydro and disulfonate derivatives of cyclohexanepentols derived from *myo*-inositol, as well as by deoxygenation of the desired position of streptamine.



1a 2a 3a

2-Deoxystreptamine (**1a**), a common component of important aminocyclitol antibiotics,[3] has already been synthesized by several research groups.[4] (+)-4-Deoxystreptamine (**2a**) was first obtained from the antibiotic streptomycin in the course of the structural elucidation,[5] and, later, its optical antipode was synthesized from D-glucosamine.[6] On the other hand, synthesis of 5-deoxystreptamine (**3a**) has not been reported so far. The present synthetic procedure applied to labeled *myo*-inositol should lead to specifically labeled deoxystreptamines that are useful in studies on the biosynthesis of aminocyclitol antibiotics.

2-Deoxystreptamine (1a). On the basis of the previous results,[7] it was expected that hydrazinolysis of 1,5-di-*O*-tosyl-1,3,5/2,4-cyclohexanepentol, followed by hydrogenation, would give **1a** via the formation of the 1,3-hydrazino compound **7**. Therefore, the tri-*O*-acetyl derivative **6** was prepared by the following reaction sequence. Treatment of 4,5,6-tri-*O*-acetyl-1,3-di-*O*-tosyl-*myo*-inositol (**4**)[8] with sulfuryl chloride in pyridine gave tri-*O*-acetyl-5-chloro-5-deoxy-4,6-di-*O*-tosyl-*scyllo*-inositol (**5**) in 66% yield. Dechlorination of **5** was effected by treatment with tri-*n*-butyltin hydride in toluene in the presence of α,α'-azobis(isobutyronitrile),[9] and the corresponding deoxy compound **6** was obtained in 94% yield.[10]

Treatment of **6** with an excess of hydrazine in refluxing 2-methoxyethanol for 20 h, followed by catalytic hydrogenation with Raney nickel T-4[11] and conventional acetylation, gave a mixture of two penta-*N,O*-acetyl derivatives of diaminocyclohexanetriol that were resolved by chromatography on silica gel affording **1b** and **9** in 34 and 15% yields, respectively. Compound **1b** was identified with an authentic sample of tri-*O*-acetyl-(1,3/2,4,6)-4,6-diacetamido-1,2,3-cyclohexanetriol (penta-*N,O*-acetyl-2-deoxystreptamine)[12] by mixture melting point, IR, and ^{1}H NMR spectra. On the basis of ^{1}H NMR spectroscopy and the proposed reaction mechanism, **9** was assigned as tri-*O*-acetyl-(1,5/2,3,4)-2,4-diacetamido-1,3,5-cyclohexanetriol (penta-*N,O*-acetyl-5-deoxyepistreptamine). The ^{1}H NMR spectral data of the acetyl methyl protons listed in Table I[13] showed the presence of one axial acetoxy group and two magnetically equivalent equatorial acetoxy and two magnetically equivalent equatorial acetamido groups, indicating that **9** possessed the symmetrical structure. The signals due to ring methine protons were interpretable by a first-order method. Thus, 2-proton double triplets having 4.5-, 11-, and 11-Hz splittings at δ 4.96 were ascribed to H-1 and H-5, and a 1-proton triplet having 2.5-Hz splitting at δ 5.39 to H-3, establishing the 1,5/2*N*,3,4*N* stereochemistry. Formation of **1b** as the major product suggested that hydrazinolysis of **6** proceeded via initial cleavage of the acetate esters and intervention of an epoxide intermediate leading to the 1,3-hydrazino compounds such as **7** and **8**.

4-Deoxystreptamine (2a). This compound was first obtained by azidolysis of the dimesylate **12a** of cyclohexanepentol, followed by hydrogenation. Thus, readily available 3,4-*O*-cyclohexylidene-1,3,4/2,5-cyclohexanepentol (**10a**)[14] was converted into the corresponding trimesylate **10b** in the usual manner in 75% yield. Removal of the cyclohexylidene group of **10b** was accomplished by refluxing in 80% aqueous acetic acid for 20 min to give 1,2,5-tri-*O*-mesyl-1,3,4/2,5-cyclohexanepentol (**11**) in 73% yield. On the other hand, extension of the reaction time to 2.5 h resulted in partial displacement of the 5-mesyloxy function by an acetate ion giving the 1,2-dimesylate **12a** in 13% yield, along with **11** (53% yield). Compound **12a** was readily isolable as the triacetate **12b**[15] in 25% yield, after separation of **11** (52% yield) by crystallization.

Treatment of **12a** with an excess of sodium azide in refluxing 90% aqueous 2-methoxyethanol for 24 h gave a mixture of diazidocyclohexanetriols, which was not purified, but hydrogenated with Raney nickel followed by acetylation. The product thus obtained was separated by fractional crystallization to afford tri-*O*-acetyl-(1,3,5/2,4)-3,5-diacetamido-1,2,4-cyclohexanetriol (penta-*N,O*-acetyl-4-deoxystreptamine) (**2b**) and tri-*O*-acetyl-(1,4,5/2,3)-4,5-diacetamido-1,2,3-cyclohexanetriol (**15**) in 22 and 24% yields, respectively. Compound **2b** was shown to be identical with an optically active authentic sample[6] in all respects except optical activity. The assigned structure of **15** was confirmed on the basis of the following evidence. Compound **11** was treated under identical reaction conditions to give the known di-*O*-acetyl-(1,3/2,4,6)-2,4,6-triacetamido-1,3-cyclohexanediol (**16**)[16] and the hitherto unknown di-*O*-acetyltriacetamidocyclohexanediol (**17**) in 5 and 27% yields, and, when *N,N*-dimethylformamide was used instead as the reaction solvent, in 24 and 12% yields, respectively. The mechanism of azidolysis of **12a** might be considered as follows. The 1-mesyloxy group is initially replaced by an azide ion by an S_N2 mechanism, and then an intermediary epoxide formed on C-2 and C-3 is opened by an azide ion to give two azido compounds having 1,3*N*,5*N*/2,4 and 1,4*N*,5*N*/2,3 stereochemistries. A similar mechanism may be possible in the case of **11**, after replacement of the axially

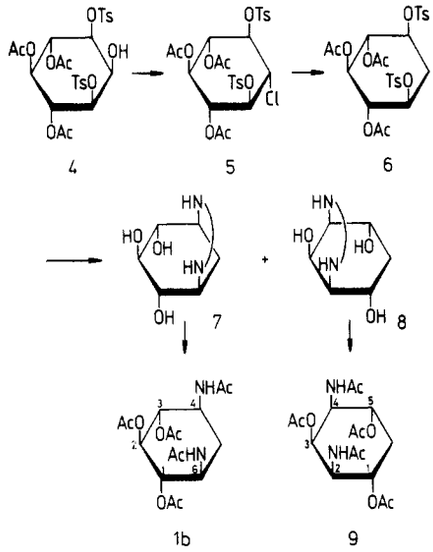


Figure 1. Synthesis of penta-*N,O*-acetyl-2-deoxystreptamine (**1b**) and -5-deoxyepistreptamine (**9**).

Table I. Chemical Shifts (δ) of Acetyl Methyl Protons of Penta-*N,O*-acetyldiaminocyclohexanetriols and -triaminocyclohexanediols in Dimethyl-d_6 Sulfoxide

Registry no.	Compd	Acetamido Ex	Acetamido Ax	Acetoxy Ex	Acetoxy Ax
62776-25-4	**2b**	1.73 1.75		1.88 1.93 1.97	
62708-18-3	**3b**	1.77[a]		1.92 1.98[a]	
62776-26-5	**9**	1.80[a]		2.04[a]	2.18
62776-27-6	**15**	1.78	1.94	1.94 2.02	2.10
62777-55-3	**16**	1.76 1.78[a]		1.92[a]	
62708-19-4	**17**	1.74 1.82	1.90	1.95	2.12
25850-50-4	**28**	1.78[a]		1.93[a]	2.13
62708-20-7	**29**	1.82	1.90	1.94 1.99	2.08

[a] Singlet for two methyl groups.

oriented 5-mesyloxy group by an azido group via an epoxide intermediate. The stereochemical assignments are supported by the ^{1}H NMR data which indicate that both **15** and **17** have one axial acetoxy group and one axial acetamido group in the favored conformations. Therefore, the stereochemistry of **17** is also assigned as 1,2/3*N*,4*N*,6*N*.

Alternatively, the selective synthesis of **2b** was developed by hydrazinolysis of the 2,5-dimesylate of 1,2,5/3,4-cyclohexanepentol. The dimesylate possessing the desired stereochemistry was available from **10b**. Thus, reaction of **10b** with sodium benzoate in *N,N*-dimethylformamide at 90 °C for 4 days resulted in preferential displacement of the 1-mesyloxy group by a benzoate group, affording 1-*O*-benzoyl-3,4-*O*-cyclohexylidene-2,5-di-*O*-mesyl-1,2,5/3,4-cyclohexanepentol (**13**) in 29% yield.[17] Treatment with aqueous acetic acid gave the corresponding de-*O*-cyclohexylidene derivative (**14**) in 84% yield. Hydrazinolysis of **14** in the usual manner, followed by hydrogenation and acetylation, gave **2b** as the sole crystalline product in 38% yield. This reaction seems to involve the selective formation of the 1,3-hydrazino compound **18**.

5-Deoxystreptamine (3a). Synthesis of the title compound was first attempted by hydrazinolysis of 1,5-di-*O*-tosyl-1,5/2,3,4-cyclohexanepentol derivative **23a**. Thus, chlorination

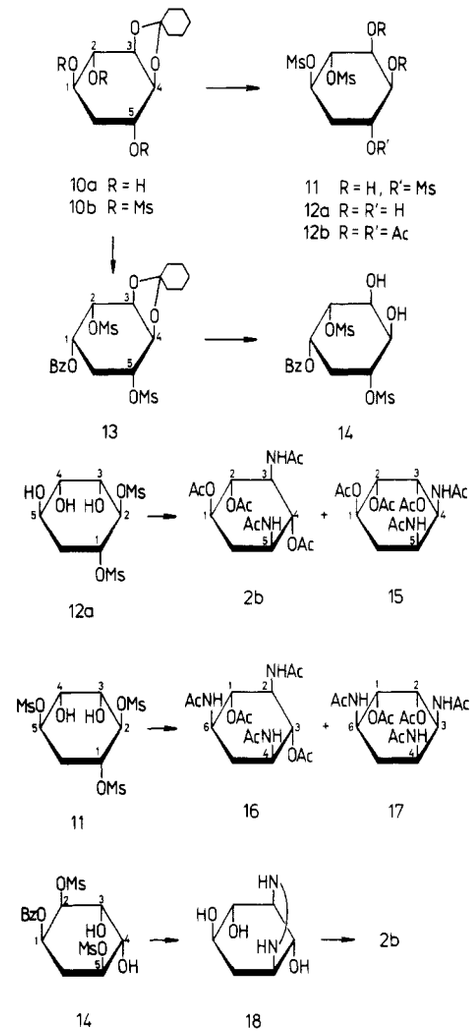


Figure 2. Synthesis of penta-*N,O*-acetyl-4-deoxystreptamine (**2b**) and the acetyl derivatives of diaminocyclohexanetriol (**15**) and two triaminocyclohexanediols (**16** and **17**).

of 1-*O*-benzoyl-2,3-*O*-cyclohexylidene-4,6-di-*O*-tosyl-*myo*-inositol (**19**)[18] with sulfuryl chloride in pyridine gave the chlorodeoxy compound **20**[18] in 91% yield, which was hydrogenated with tri-*n*-butyltin hydride, affording the corresponding deoxy compound **21** in 79% yield. De-O-cyclohexylidenation gave 2-*O*-benzoyl-1,5-di-*O*-tosyl-1,5/2,3,4-cyclohexanepentol (**23a**) in 48% yield. Alternatively, the di-*O*-acetyl derivative **23b** was obtained, in a yield of 94%, by dechlorination of 1,2-di-*O*-acetyl-3-*O*-benzoyl-5-chloro-5-deoxy-4,6-di-*O*-tosyl-*neo*-inositol (**22**)[18] in the usual way.

On hydrazinolysis followed by hydrogenation and acetylation, **23a** gave a complex mixture of tri-*O*-acetyldiacetamidocyclohexanetriols, from which **3b**, **28**, and **29** were isolated by chromatography on silica gel in 0.6, 42, and 8% yields, respectively. Under these conditions, substitution of the two tosyloxy groups was assumed to proceed via an epoxide intermediate, leading to the 1,3-hydrazino compounds **25** and **26** and the 1,4-hydrazino **27a** or the dihydrazino compound **27b**. Therefore, the three diaminocyclohexanetriols formed may possess 1,2,3/4*N*,6*N*, 1,3,5/2*N*,4*N*, and 1,3,4/2*N*,5*N* stereochemistries, and they can be differentiated from each other by comparing the spectral patterns of the signals due to acetyl methyl protons in the ^{1}H NMR spectra. The ^{1}H NMR data showed that both **3b** and **28** have symmetrical structures, and that the latter has one axial acetoxy group, whereas the ^{1}H NMR spectrum of **29** revealed five peaks due to acetyl methyl protons, indicating that **29** has an unsymmetrical structure. Furthermore, in the ^{1}H NMR spectrum

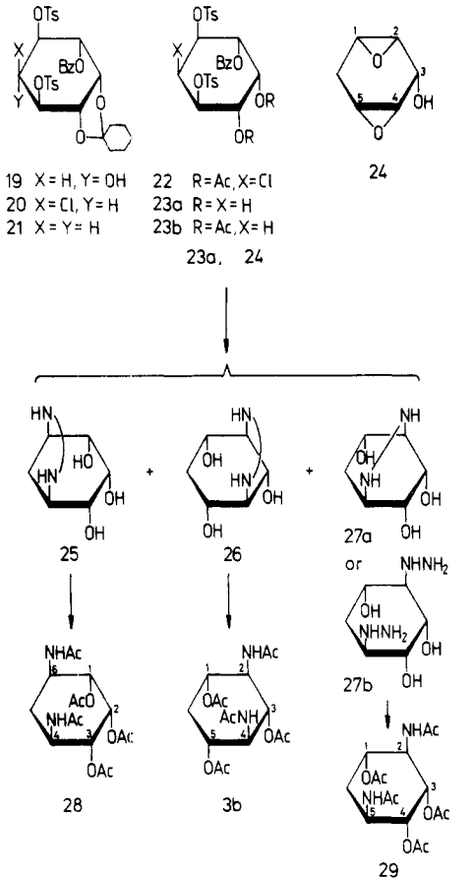


Figure 3. Synthesis of penta-*N,O*-acetyl-5-deoxystreptamine (**3b**) and the acetyl derivatives of two diaminocyclohexanetriols (**28** and **29**).

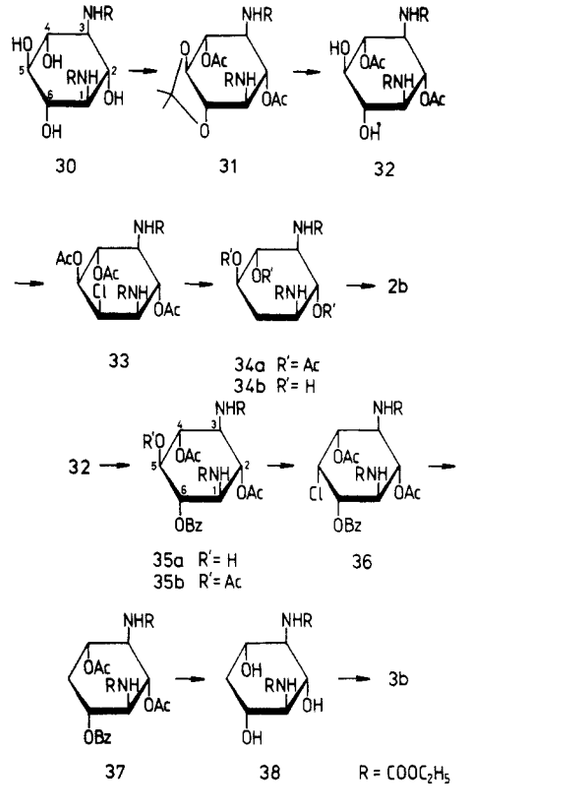


Figure 4. Deoxygenation of suitably protected streptamine derivatives.

of **28**, 2-proton double doublets having 2.5- and 11-Hz splittings at δ 4.91 are ascribed to H-1 and H-3, and a 1-proton narrow triplet at δ 5.69 ascribable to the equatorial methine proton was shown to be coupled with H-1 and H-3, being consistent with the proposed structure. Therefore, their structures were assigned as those formulated in Figure 3.

Under identical reaction conditions, **23b** was expected to give the same results as **23a** did. In order to avoid the complexity in the isolation of the reaction products, 1,2:4,5-dianhydro-1,2,3,4,5/0-cyclohexanepentol (**24**) derived by treating **23b** with methanolic sodium methoxide was subjected to the hydrazinolysis. After hydrogenation and acetylation, products were resolved by column chromatography giving **28** and **29** in 23 and 11% yields, respectively, along with a trace of **3b**.

Subsequently, for the purpose of obtaining **2a** as well as **3a** in large quantity, deoxygenation of the desired position of streptamine was studied using suitably protected derivatives. *N,N'*-Diethoxycarbonylstreptamine (**30**), obtainable by treating streptamine with ethyl chloroformate in basic solution, was allowed to react with 2,2-dimethoxypropane in *N,N*-dimethylformamide in the presence of *p*-toluenesulfonic acid, giving the *O*-isopropylidene derivative, which upon direct acetylation afforded di-*O*-acetyl-*N,N'*-diethoxycarbonyl-5,6-*O*-isopropylidenestreptamine (**31**) in 50% yield. Removal of the isopropylidene group gave 2,4-di-*O*-acetyl-*N,N'*-diethoxycarbonylstreptamine (**32**) in 81% yield.

Chlorination of **32** with sulfuryl chloride in pyridine proceeded selectively to give rise to a sole chlorodeoxy compound that was isolated as the triacetate **33** in 57% yield. The ^{1}H NMR spectrum of **33** revealed three peaks due to three acetoxy groups, indicating that **33** had the unsymmetrical structure, and that the chlorine atom was located on C-6. Hydrogenation of **33** with tri-*n*-butyltin hydride in the usual manner gave the tri-*O*-acetyl-*N,N'*-diethoxycarbonyl-4-deoxystreptamine (**34a**) in 82% yield, which was de-O-acylated with methanolic ammonia, affording the *N,N'*-diethoxycarbonyl derivative **34b** in 82% yield. The structure of **34b** was established by converting it into **2b** by hydrolysis with 6 M hydrochloric acid followed by acetylation.

Since the 6-hydroxyl group of **32** was found to be preferentially displaced by a chloride ion, protection of the 6 position was carried out by selective benzoylation, thus affording the 6-*O*-benzoyl derivative **35a** in 40% yield. The tri-*O*-acetyl derivative **35b** exhibited three peaks attributable to three acetoxy groups by ^{1}H NMR analysis, confirming the presence of the benzoyloxy group on C-6. Treatment of **35a** with sulfuryl chloride in pyridine gave a single chlorodeoxy compound **36** in 62% yield, which was subsequently dechlorinated with tri-*n*-butyltin hydride affording the corresponding deoxy compound **37** in 75% yield. De-O-acylation of **37** gave *N,N'*-diethoxycarbonyl-5-deoxystreptamine (**38**) in 73% yield, the structure of which was further established by converting it into **3b** in the usual manner.

Experimental Section[19]

1,2,3-Tri-*O*-acetyl-5-chloro-5-deoxy-4,6-di-*O*-tosyl-*scyllo*-inositol (5). To a stirred solution of 4,5,6-tri-*O*-acetyl-1,3-di-*O*-tosyl-*myo*-inositol (**4**)[8] (15 g) in dry pyridine (350 mL), sulfuryl chloride (7.9 mL, 4 equiv) was added dropwise at −10 to −20 °C for over 5 min. After having been stirred at −15 °C for 1 h, the solution was allowed to stand in a refrigerator overnight. The reaction mixture was evaporated to give a crystalline residue which was pulverized with ethanol and collected by filtration. The crude crystals were recrystallized from chloroform–ethanol to give 10.2 g (66%) of **5**: mp 222–224 °C; ^{1}H NMR ($CDCl_3$) δ 1.97 (s, 9, 3 OAc), 2.45 (s, 6, 2 tosyl CH_3).

Anal. Calcd for $C_{26}H_{29}ClO_{12}S_2$: C, 49.32; H, 4.62. Found: C, 49.32; H, 4.54.

Tri-*O*-acetyl-1,5-di-*O*-tosyl-1,3,5/2,4-cyclohexanepentol (6). To a solution of **5** (1 g) in dry toluene (60 mL) were added tri-*n*-butyltin hydride[20] (1 mL) and α,α'-azobis(isobutyronitrile) (10 mg), and the mixture was heated at 90 °C for 2 h under a nitrogen atmo-

sphere. The reaction mixture was evaporated to leave a crystalline residue, which was crystallized from chloroform–ethanol to give 0.89 g (94%) of **6**: mp 201–203 °C; ^{1}H NMR (Me_2SO-d_6) δ 1.70 (s, 6) and 1.90 (s, 3) (OAc), 2.48 (s, 6, 2 tosyl CH_3).

Anal. Calcd for $C_{26}H_{30}O_{12}S_2$: C, 52.17; H, 5.05; S, 10.71. Found: C, 52.39; H, 5.00; S, 10.47.

Tri-*O*-acetyl-(1,3/2,4,6)-4,6-diacetamido-1,2,3-cyclohexanetriol (Penta-*N,O*-acetyl-2-deoxystreptamine) (1b) and -(1,5/2,3,4)-2,4-diacetamido-1,3,5-cyclohexanetriol (Penta-*N,O*-acetyl-5-deoxyepistreptamine) (9). A mixture of **6** (2 g), anhydrous hydrazine (10 mL), and 2-methoxyethanol (20 mL) was heated under reflux for 20 h, and then evaporated to dryness. The residue was dissolved in water (20 mL) and treated with Amberlite IRA-400 (OH^-). The solution was then hydrogenated in a Parr shaker apparatus in the presence of Raney nickel T-4[11] under pressure (3.4 kg/cm^2) at room temperature overnight. The catalyst was removed by filtration and the filtrate was evaporated to dryness. The solid residue was treated with acetic anhydride (10 mL) and pyridine (10 mL) under stirring at room temperature for 2 days. The reaction mixture was evaporated to leave a partly crystalline residue that was chromatographed on silica gel (50 g) with chloroform–methanol (15:1, v/v). The fractions were combined according to the results of TLC in chloroform–methanol (10:1, v/v). The fractions (R_f 0.46) were evaporated and the residual crystals were recrystallized from ethanol to give 0.19 g (15%) of **9**: mp 246–247 °C; ^{1}H NMR (Me_2SO-d_6) δ 4.27 (br dt, 2, $J_{2,3} = J_{3,4} = 2.5$ Hz, $J_{1,2} = J_{4,5} = 11$ Hz, $J_{2,NH} = J_{4,NH} = 8.5$ Hz, H-2 and H-4), 4.96 (dt, 2, $J_{1,6ax} = J_{5,6ax} = 11$ Hz, $J_{1,6eq} = J_{5,6eq} = 4.5$ Hz, H-1 and H-5), 5.39 (t, 1, H-3), 8.12 (d, 2, 2 NHAc); other data, see Table I.

Anal. Calcd for $C_{16}H_{24}N_2O_8$: C, 51.60; H, 6.50; N, 7.52. Found: C, 51.32; H, 6.40; N, 7.37.

The fractions (R_f 0.40) were evaporated to give crystals that were recrystallized from ethanol affording 0.43 g (34%) of **1b**: mp 299–300 °C. This compound was identified with an authentic sample[12] by mixture melting point and by comparison of IR and ^{1}H NMR spectra.

3,4-*O*-Cyclohexylidene-1,2,5-tri-*O*-mesyl-1,3,4/2,5-cyclohexanepentol (10b). To a stirred solution of 3,4-*O*-cyclohexylidene-1,3,4/2,5-cyclohexanepentol (**10a**)[13] (1 g) in dry pyridine (20 mL) was added mesyl chloride (2 mL) under ice cooling, and the mixture was allowed to stand in a refrigerator for 2 days. The mixture was poured into ice water, and the resulting crystals were collected and recrystallized from chloroform to give 1.46 g (75%) of **10b**: mp 184.5–185.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.14 (s, 3) and 3.22 (s, 6) (mesyl CH_3).

Anal. Calcd for $C_{15}H_{26}O_{11}S_3$: C, 37.65; H, 5.48; S, 20.10. Found: C, 37.58; H, 5.25; S, 19.89.

1,2,5-Tri-*O*-mesyl-1,3,4/2,5-cyclohexanepentol (11). A mixture of **10b** (2 g) and 80% aqueous acetic acid (40 mL) was refluxed for 20 min, and the reaction mixture was then evaporated to give a syrup that was crystallized from ethanol affording 1.2 g (73%) of **11**: mp 162–163 °C.

Anal. Calcd for $C_9H_{18}O_{11}S_3$: C, 27.15; H, 4.55; S, 24.14. Found: C, 27.61; H, 4.55; S, 23.84.

1,2-Di-*O*-mesyl-1,3,4/2,5-cyclohexanepentol (12a). (a) A mixture of **10b** (2 g) and 80% aqueous acetic acid (40 mL) refluxed for 3 h and then was evaporated to leave a syrup. Crystallization from chloroform–ethanol gave 0.9 g (53%) of **11**. The mother liquor was concentrated to a syrup that crystallized spontaneously to give 0.17 g (13%) of **12a**: mp 136–137 °C.

Anal. Calcd for $C_8H_{16}O_9S_2$: C, 29.99; H, 5.05; S, 20.01. Found: C, 29.90; H, 5.24; S, 19.73.

Compound **12a** (0.1 g) was treated with acetic anhydride (1 mL) in pyridine (1 mL) at room temperature overnight, and the mixture was poured into ice–water giving crystals. Recrystallization from chloroform–ethanol gave 0.1 g (71%) of the triacetate (**12b**): mp 193–195 °C; ^{1}H NMR ($CDCl_3$) δ 2.07 (s, 3) and 2.15 (s, 6) (OAc), 3.10 (s, 3) and 3.12 (s, 3) (mesyl CH_3).

Anal. Calcd for $C_{14}H_{22}O_{12}S_2$: C, 37.66; H, 4.97; S, 14.36. Found: C, 37.43; H, 5.23; S, 14.66.

(b) Compound **10b** (3.6 g) was treated with refluxing 80% aqueous acetic acid (70 mL) for 2.5 h. After **11** (1.6 g, 52%) had been isolated by crystallization from chloroform–ethanol, the mother liquor was concentrated and the residue was acetylated in the usual manner to give 0.84 g (24%) of **12b**: mp 189–192 °C.

1-*O*-Benzoyl-3,4-*O*-cyclohexylidene-2,5-di-*O*-mesyl-1,2,5/3,4-cyclohexanepentol (13). A mixture of **10b** (3.2 g) and sodium benzoate (5 g) in *N,N*-dimethylformamide (30 mL) was heated at 80–90 °C with stirring for 100 h. Insoluble material was removed by filtration and the filtrate was evaporated to dryness. The residue was extracted with hot 2-butanone (30 mL) and the extract was evaporated to leave a syrup that was chromatographed on silica gel (80 g) with benzene–2-butanone (15:1, v/v). The main fractions were combined and evaporated to give crystals that were recrystallized from ethanol giving 1 g (29%) of **13**: mp 157.5–159 °C; ^{1}H NMR ($CDCl_3$) δ 2.48 (t, 2, $J = 6$ Hz, H-6 and H-6′), 3.06 (s, 3) and 3.17 (s, 3) (mesyl CH_3), 4.54 (t, 1) and 4.71 (t, 1) ($J = 5.5$ Hz, H-3 and H-4), 5.02 (t, 1, H-5), 5.27 (dd, 1, $J_{1,2} = 3$ Hz, H-2), 5.65 (dt, 1, H-1).

Anal. Calcd for $C_{21}H_{28}O_{10}S_2$: C, 49.99; H, 5.59; S, 12.71. Found: C, 49.70; H, 5.56; S, 12.35.

1-*O*-Benzoyl-2,5-di-*O*-mesyl-1,2,5/3,4-cyclohexanepentol (14). Compound **13** (0.4 g) was treated with refluxing 80% aqueous acetic acid (10 mL) for 1 h and then the reaction mixture was evaporated to dryness. The crystalline residue was recrystallized from ethanol to give 0.28 g (84%) of **14**: mp 194–195 °C.

Anal. Calcd for $C_{15}H_{20}O_{10}S_2$: C, 42.45; H, 4.75; S, 15.11. Found: C, 42.53; H, 4.73; S, 15.28.

Tri-*O*-acetyl-(1,3,5/2,4)-3,5-diacetamido-1,2,4-cyclohexanetriol (Penta-*N,O*-acetyl-4-deoxystreptamine) (2b) and -(1,4,5/2,3)-4,5-diacetamido-1,2,3-cyclohexanetriol (Penta-*N,O*-acetyl-3-deoxy-*allo*-inosadiamine-1,2) (15). (a) A mixture of **12a** (0.57 g), sodium azide (0.5 g), and 90% aqueous 2-methoxyethanol (20 mL) refluxed for 24 h and then was evaporated to dryness. The residual solid was treated with acetic anhydride (10 mL) and pyridine (15 mL) at room temperature overnight. Insoluble material was removed by filtration and the filtrate was evaporated to leave a syrup that was dissolved in chloroform and passed through a short alumina column. The chloroform solution was evaporated to give a syrup that was hydrogenated in ethanol solution (20 mL) as described above for the preparation of **1b** and **9**. The products were acetylated in the usual way to give a mixture of the penta-*N,O*-acetyldiaminocyclohexanetriols. Fractional crystallization from both ethanol–ether and ethanol–ethyl acetate gave 0.11 g (22%) of **2b**, mp 310–311 °C (dec), and 0.12 g (24%) of **15**, mp 246 °C: ^{1}H NMR data, see Table I.

Anal. Calcd for $C_{16}H_{24}N_2O_8$: C, 51.60; H, 6.50; N, 7.52. Hemihydrate: C, 50.39; H, 6.61; N, 7.34. Found for **2b**: C, 51.78; H, 6.48; N, 7.39, and for **15**: C, 50.91; H, 6.47; N, 7.26.

(b) A mixture of **14** (0.55 g), anhydrous hydrazine (2 mL), and 2-methoxyethanol (20 mL) was refluxed for 18 h, and then processed as described above for the preparation of **1b** and **9**. The crude products were fractionally crystallized from ethanol to give 0.18 g (38%) of **2b**, mp 290–293 °C dec. It was identical with the compound obtained above, and both were identified with an authentic optically active sample[6] by comparison of IR and ^{1}H NMR spectra in all respects except optical activity.

Di-*O*-acetyl-(1,3/2,4,6)-2,4,6-triacetamido-1,3-cyclohexanediol (Penta-*N,O*-acetyl-5-amino-2,5-dideoxystreptamine) (16) and -(1,2/3,4,6)-3,4,6-triacetamido-1,2-cyclohexanediol (Penta-*N,O*-acetyl-3-deoxy-*allo*-inosatriamine-1,2,4) (17). (a) A mixture of **11** (1 g), sodium azide (1 g), and 90% aqueous 2-methoxyethanol (50 mL) refluxed for 24 h and then was processed as described for the preparation of **2b** and **15**. The products were fractionally crystallized from ethanol–ethyl acetate to give 0.043 g (5%) of **16**, mp 310 °C dec (lit.[16] 355–357 °C dec), and 0.25 g (27%) of **17**, mp 252–253 °C: ^{1}H NMR (Me_2SO-d_6) for **16**, δ 4.89 (t, 2, $J_{1,2(2,3)} = J_{1,6(3,4)} = 10.5$ Hz, H-1 and H-3), 7.88 (d, 3, $J = 8.5$ Hz, three amido protons); for other data, see Table I.

Anal. Calcd for $C_{16}H_{25}N_3O_7$: C, 51.74; H, 6.79; N, 11.31. Hemihydrate: C, 50.52; H, 6.89; N, 11.05. Found for **16**: C, 51.94; H, 6.76; N, 11.43. Found for **17**: C, 51.20; H, 7.10; N, 10.69.

(b) A mixture of **11** (2 g), sodium azide (2 g), and 90% aqueous *N,N*-dimethylformamide (80 mL) was refluxed for 24 h. The reaction mixture was processed as described for the preparation of **2b** and **15**, and the products were fractionally crystallized from ethanol–ethyl acetate to give 0.46 g (24%) of **16** and 0.23 g (12%) of **17**.

1-*O*-Benzoyl-5-chloro-2,3-*O*-cyclohexylidene-5-deoxy-4,6-di-*O*-tosyl-*neo*-inositol (20). To a solution of 1-*O*-benzoyl-2,3-*O*-cyclohexylidene-4,6-di-*O*-tosyl-*myo*-inositol (**19**)[18] (3 g) in dry pyridine (90 mL), sulfuryl chloride (1.45 mL, 4 molar equiv) was added dropwise at −15 °C. After having been kept in a refrigerator overnight, the reaction mixture was evaporated and the residue was crystallized from chloroform–ethanol to give 2.8 g (91%) of **20**, mp 184–185 °C (lit.[18] 180–181 °C). This compound was identical with an authentic sample[18] in all respects.

2-*O*-Benzoyl-3,4-*O*-cyclohexylidene-1,5-di-*O*-tosyl-1,5/2,3,4-cyclohexanepentol (21). A mixture of **20** (0.5 g), tri-*n*-butyltin hydride (1 mL), and α,α′-azobis(isobutyronitrile) (10 mg) in dry toluene (25 mL) was heated at 90 °C under a nitrogen atmosphere for 2 h. The reaction mixture was evaporated to dryness and the crude product was crystallized from chloroform–ethanol to give 0.38 g (79%) of **21**: 174–177 °C; ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 3) and 2.48 (s, 3) (tosyl CH_3), 5.12 (td, 1, $J_{1,6eq} = 4$ Hz, $J_{1,2} = J_{1,6ax} = 8$ Hz, H-1), 5.56 (dd, 1, $J_{2,3} =$

3 Hz, H-3).

Anal. Calcd for $C_{33}H_{36}O_{10}S_2$: C, 60.35; H, 5.53; S, 9.76. Found: C, 59.93; H, 5.53; S, 10.00.

2-*O*-Benzoyl-1,5-di-*O*-tosyl-1,5/2,3,4-cyclohexanepentol (23a). A mixture of **21** (2.72 g) and 80% aqueous acetic acid (140 mL) refluxed for 3 h. The reaction mixture was evaporated to dryness and the residue was crystallized from methanol to give 1.13 g (48%) of **23a**: mp 156–157 °C.

Anal. Calcd for $C_{27}H_{28}O_{10}S_2$: C, 56.24; H, 4.89; S, 11.12. Found: C, 56.15; H, 5.11; S, 10.87.

2,3-Di-*O*-acetyl-4-*O*-benzoyl-1,5-di-*O*-tosyl-1,5/2,3,4-cyclohexanepentol (23b). 1,2-Di-*O*-acetyl-3-*O*-benzoyl-5-chloro-5-deoxy-4,6-di-*O*-tosyl-*neo*-inositol (**22**)[18] (1.5 g) was treated with tri-*n*-butyltin hydride in dry toluene as described above for **20**. The product was crystallized from chloroform–ethanol to give 1.3 g (94%) of **23b**: mp 158–161 °C; ^{1}H NMR ($CDCl_3$) δ 1.83 (s, 3) and 2.16 (s, 3) (OAc), 2.32 (s, 3) and 2.49 (s, 3) (tosyl CH_3). This compound was identical with the diacetate derived from **23a**.

Anal. Calcd for $C_{31}H_{32}O_{12}S_2$: C, 56.35; H, 4.88; S, 9.71. Found: C, 56.50; H, 5.03; S, 9.57.

1,2:4,5-Dianhydro-1,2,3,4,5/0-cyclohexanepentol (24). To a solution of **23b** (3 g) in chloroform (20 mL) and methanol (15 mL) was added 1 M methanolic sodium methoxide (14 mL, 3 molar equiv), and the mixture was allowed to stand at room temperature overnight. The mixture was evaporated to dryness and the residue was extracted with ethyl acetate (50 mL). The extract was evaporated and the product was recrystallized from ethanol–ether to give 0.41 g (70%) of **24**: mp 121–122 °C; ^{1}H NMR ($CDCl_3$) δ 2.11 (m, 1, H-6), 2.76 (br d, 1, J_{gem} = 17 Hz, H-6'), 3.02 (m, 1, OH), 3.37 (m, 4, H-1, -2, -4, and -5), 4.38 (br d, 1, $J_{3,OH}$ = 11 Hz, H-3).

Anal. Calcd for $C_6H_8O_3$: C, 56.24; H, 6.29. Found: C, 56.06; H, 6.22.

Tri-*O*-acetyl-(1,3,5/2,4)-2,4-diacetamido-1,3,5-cyclohexanetriol (Penta-*N,O*-acetyl-5-deoxystreptamine) (3b), -(1,2,3/4,6)-4,6-diacetamido-1,2,3-cyclohexanetriol (Penta-*N,O*-acetyl-2-deoxy-*neo*-inosadiamine-1,3) (28), and -(1,3,4/2,5)-2,5-diacetamido-1,3,4-cyclohexanetriol (Penta-*N,O*-acetyl-2-deoxy-*chiro*-inosadiamine-1,4) (29). (a) A mixture of **23a** (2.6 g), hydrazine hydrate (3.3 mL), and 2-methoxyethanol (30 mL) refluxed for 4.5 h and then was evaporated to dryness. After treatment with Amberlite IRA-400 (OH^-) in an aqueous solution (30 mL), the residual product was hydrogenated as described for the preparation of **1b** and **9**. The reduction product was treated with acetic anhydride (20 mL) and pyridine (20 mL) at room temperature under stirring for 2 days, and the resulting precipitates were collected by filtration to give 0.7 g (42%) of **28** as homogeneous crystals. Recrystallization from methanol gave a pure sample: mp 293–294 °C (lit.[16] 250–255 °C dec); for ^{1}H NMR data, see Table I.

Anal. Calcd for $C_{16}H_{24}N_2O_8$: C, 51.60; H, 6.50; N, 7.52. Found: C, 51.71; H, 6.52; N, 7.55.

The reaction mixture obtained by filtration of **28** was evaporated to dryness and the residual syrup was chromatographed on silica gel (30 g) with chloroform–methanol (20:1, v/v). The main fractions were further fractionally crystallized from ethanol–ether to give 10 mg (0.6%) of **3b**, mp 305–306 °C dec, and 0.14 g (8.4%) of **29**, mp 219–220 °C: ^{1}H NMR (Me_2SO-d_6) for **3b** δ 4.05 (q, 2, $J_{1,2(4,5)} = J_{2,3(3,4)} = 10.5$ Hz, $J_{2(4),NH}$ = 9 Hz, H-2 and H-4), 4.83 (m, 2, H-1 and H-5), 7.80 (d, 2, two amido protons); for other data, see Table I.

Anal. Calcd for $C_{16}H_{24}N_2O_8$: C, 51.60; H, 6.50; N, 7.52. Found for **3b**: C, 51.34; H, 6.49; N, 7.39. Found for **29**: C, 51.39; H, 6.52; N, 7.34.

(b) A mixture of **24** (0.36 g), anhydrous hydrazine (2 mL), and 2-methoxyethanol (20 mL) refluxed for 4.5 h. At this time, TLC indicated the formation of two new components [R_f 0.18 and 0.29 in 1-butanol–ethanol–water–28% aqueous ammonia (8:10:7:5, v/v)]. The reaction mixture was evaporated to dryness and the residual product was hydrogenated in water (20 mL) in the presence of Raney nickel catalyst in the usual manner. The reduction product was treated with acetic anhydride (20 mL) and pyridine (20 mL) at room temperature with stirring for 3 days. The resulting precipitates were collected by filtration and recrystallized from methanol to give 0.31 g (23%) of **28**: mp 293–294 °C. The filtrate was concentrated to a syrup which was crystallized from ethyl acetate to give an additional crop of **28** (0.02 g, total yield 25%). The remaining syrup was chromatographed on silica gel (10 g) with chloroform–methanol (10:1, v/v). The main fractions were evaporated and the product was crystallized from isopropyl alcohol–petroleum ether to give 0.12 g (11%) of **29**: mp 219–220 °C. The presence of a trace of **3b** was observed by TLC, but further separation was not attempted.

***N,N'*-Diethoxycarbonylstreptamine (30).** A solution of streptamine sulfate[21] (1.24 g) in water (150 mL) was treated with Amberlite IRA-400 (OH^-) (30 mL) and then evaporated to give the free base as a white powder. It was treated with ethyl chloroformate (1.7 mL) in water (30 mL) under vigorous agitation, the pH of the reaction mixture being adjusted to 7–8 by addition of 1 M aqueous sodium hydroxide. After standing overnight, the mixture was evaporated to dryness and the residue was extracted with hot dioxane (3 × 30 mL). The extracts were evaporated to give a white powder that was crystallized from methanol to give 0.59 g (44%) of **30**: mp 244–246 °C.

Anal. Calcd for $C_{13}H_{22}N_2O_6$: C, 44.72; H, 6.88; N, 8.69. Found: C, 44.74; H, 6.73; N, 8.52.

2,4-Di-*O*-acetyl-*N,N'*-diethoxycarbonyl-5,6-*O*-isopropylidenestreptamine (31). A mixture of **30** (2 g), 2,2-dimethoxypropane (12 mL), and *N,N*-dimethylformamide (48 mL) was heated in the presence of *p*-toluenesulfonic acid (0.15 g) at 80 °C for 4 h. After cooling, the reaction mixture was treated with Amberlite IRA-400 (OH^-), and then evaporated to give the crude *O*-isopropylidene derivative (1.25 g). Without further purification, it was treated with acetic anhydride (10 mL) in pyridine (20 ml) at room temperature overnight. The mixture was poured into ice–water, and the resulting crystals were collected and recrystallized from ethanol to give 1.4 g (50%) of **31**: mp 240–242 °C; ^{1}H NMR ($CDCl_3$) δ 1.24 (t, 6, J = 8 Hz, two ethoxycarbonyl CH_3), 1.45 (s, 3) and 1.48 (s, 3) (isopropylidene CH_3), 2.08 (s, 3) and 2.12 (s, 3) (OAc), 4.15 (q, 4, two ethoxycarbonyl CH_2).

Anal. Calcd for $C_{19}H_{30}N_2O_{10}$: C, 51.12; H, 6.77; N, 6.27. Found: C, 50.86; H, 6.66; N, 6.20.

2,4-Di-*O*-acetyl-*N,N'*-diethoxycarbonylstreptamine (32). A mixture of **31** (1.4 g) and 50% aqueous acetic acid (100 mL) was heated at 70 °C for 2 h. The reaction mixture was evaporated to dryness and the residue was crystallized from ethanol–ethyl acetate to give 1 g (81%) of **32**: mp 180–181 °C; ^{1}H NMR (Me_2SO-d_6) δ 1.13 (t, 3) and 1.15 (t, 3) (J = 7 Hz, ethoxycarbonyl CH_3), 1.88 (s, 3) and 1.97 (s, 3) (OAc), 4.00 (q, 4, two ethoxycarbonyl CH_2).

Anal. Calcd for $C_{16}H_{26}N_2O_{10}$: C, 47.29; H, 6.45; N, 6.89. Found: C, 47.06; H, 6.33; N, 6.90.

Tri-*O*-acetyl-(1,2,3,5/4,6)-2-chloro-3,5-diethoxycarbonylamino-1,4,6-cyclohexanetriol (33). To a stirred solution of **32** (1.5 g) in dry pyridine (50 mL), sulfuryl chloride (1.8 mL, 6 molar equiv) was added dropwise at −18 °C, and the reaction mixture was then allowed to stand in a refrigerator for 6 h. The mixture was poured into ice-cooled saturated aqueous sodium hydrogen carbonate and extracted with chloroform (3 × 30 mL). The extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated to give a syrupy product. It was treated with acetic anhydride (10 mL) in pyridine (20 mL) at room temperature overnight. The reaction mixture was evaporated and the residual syrup was taken up in chloroform. After passage through a short alumina column, the solution was evaporated and crystallized from chloroform–ethanol to give 1 g (57%) of **33**: mp 180–182 °C; ^{1}H NMR ($CDCl_3$) δ 1.22 (t, 3) and 1.25 (t, 3) (J = 7 Hz, ethoxycarbonyl CH_3), 2.05 (s, 3), 2.07 (s, 3), and 2.10 (s, 3) (OAc), 4.13 (q, 2) and 4.17 (q, 2) (ethoxycarbonyl CH_2).

Anal. Calcd for $C_{18}H_{24}ClN_2O_{10}$: C, 46.61; H, 5.22; N, 6.04; Cl, 7.64. Found: C, 46.43; H, 5.48; N, 5.76; Cl, 7.92.

Tri-*O*-acetyl-(1,3,5/2,4)-3,5-diethoxycarbonylamino-1,3,5-cyclohexanetriol (Tri-*O*-acetyl-*N,N'*-diethoxycarbonyl-4-deoxystreptamine) (34a). A solution of **33** (0.3 g) in dry toluene (20 mL) was treated with tri-*n*-butyltin hydride (0.5 mL) in the presence of α,α'-azobis(isobutyronitrile) at 90 °C under a nitrogen atmosphere for 2 h. The reaction mixture was evaporated and the residue was recrystallized from chloroform–ether to give 0.23 g (82%) of **34a**: mp 214–215 °C; ^{1}H NMR ($CDCl_3$) δ 1.23 (t, 6, J = 7 Hz, two ethoxycarbonyl CH_3), 2.03 (s, 3), 2.05 (s, 3), and 2.09 (s, 3) (OAc), 4.14 (q, 4, two ethoxycarbonyl CH_2).

Anal. Calcd for $C_{18}H_{25}N_2O_{10}$: C, 50.35; H, 5.87; N, 6.52. Found: C, 50.06; H, 6.24; N, 6.61.

(1,3,5/2,4)-3,5-Diethoxycarbonylamino-1,3,5-cyclohexanetriol (*N,N'*-Diethoxycarbonyl-4-deoxystreptamine) (34b). Compound **34a** (0.47 g) was treated with methanolic ammonia (30 mL) at room temperature overnight. The mixture was evaporated to dryness and the product was crystallized from ethanol–ethyl acetate to give 0.3 g (88%) of **34b**: mp 178–180 °C.

Anal. Calcd for $C_{12}H_{22}N_2O_7$: C, 47.05; H, 7.24; N, 9.14. Found: C, 46.34; H, 6.90; N, 8.90.

Compound **34b** (0.27 g) was heated in refluxing 6 M hydrochloric acid (20 mL) overnight. The mixture was evaporated to give a crude dihydrochloride which was treated with Amberlite IRA-400 (OH^-) in an aqueous solution. The solution was evaporated and the crude free base obtained was directly treated with acetic anhydride and pyridine in the usual manner. The product was crystallized from methanol to give 0.14 g (42%) of **2b**: mp 310–311 °C dec. This compound was found to be identical with **2b** obtained before.

2,4-Di-*O*-acetyl-6-*O*-benzoyl-*N,N'*-diethoxycarbonylstreptamine (35a). To a solution of **32** (3 g) in dry pyridine (120 mL) was added benzoyl chloride (1.3 mL, 3 molar equiv) at −10 °C in two portions in 1-day intervals, and then the reaction mixture was kept in a refrigerator for 2 days. At this time, TLC in benzene–ethanol (7:1, v/v) showed that **32** was almost consumed and two new components (R_f 0.49 and 0.63) formed. The reaction mixture was poured into ice–water and the resulting crystals (1.2 g), consisting of two components, were collected by filtration. The filtrate (300 mL) was evaporated to give a partly crystalline residue. It was dissolved in chloroform (50 mL) and the solution was washed with aqueous sodium hydrogen carbonate and water, dried over anhydrous sodium sulfate, and evaporated to give crystals. Recrystallization from ethyl acetate–methanol gave 1.28 g (40%) of **35a** as homogeneous crystals: mp 176–180 °C. Further crystallization of the crystals from chloroform–ether raised its melting point to 184–185 °C; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3) and 1.15 (t, 3) (J = 7 Hz, ethoxycarbonyl CH_3), 1.91 (s, 3) and 1.98 (s, 3) (OAc), 3.86 (q, 2) and 4.03 (q, 2) (ethoxycarbonyl CH_2).

Anal. Calcd for $C_{23}H_{30}N_2O_{11}$: C, 54.11; H, 5.92; N, 5.49. Found: C, 54.02; H, 5.88; N, 5.46.

Treatment of **35a** (0.05 g) with acetic anhydride (3 mL) and pyridine (3 mL) at room temperature overnight. The product was crystallized from chloroform–ether to give 0.045 g (83%) of the triacetate (**35b**): mp 218–220 °C; ^{1}H NMR ($CDCl_3$) δ 1.02 (t, 3) and 1.23 (t, 3) (J = 7 Hz, ethoxycarbonyl CH_3), 1.91 (s, 3), 2.07 (s, 3), and 2.12 (s, 3) (OAc), 3.98 (q, 2) and 4.04 (q, 2) (ethoxycarbonyl CH_2).

Anal. Calcd for $C_{25}H_{32}N_2O_{12}$: C, 54,34; H, 5.84; N, 5.07. Found: C, 54.07; H, 5.81; N, 4.94.

1,5-Di-*O*-acetyl-3-*O*-benzoyl-(1,2,3,5/4,6)-4,6-diethoxycarbonylamino-2-chloro-1,3,5-cyclohexanetriol (36). To a solution of **35a** (1 g) in dry pyridine (30 mL) was added sulfuryl chloride (0.65 mL, 4 molar equiv) at −16 °C and the mixture was kept in a refrigerator for 7 h. The reaction mixture was processed as described for **33**. The crude syrupy product was chromatographed on silica gel with ethyl acetate–petroleum ether, giving a crystalline product. Recrystallization from ether gave 0.64 g (62%) of **36**: mp 192–193 °C; ^{1}H NMR ($CDCl_3$) δ 1.20 (t, 3) and 1.23 (t, 3) (J = 7 Hz, ethoxycarbonyl CH_3), 2.10 (s, 3) and 2.12 (s, 3) (OAc), 4.02 (q, 2) and 4.03 (q, 2) (ethoxycarbonyl CH_2), 4.58 (ddd, 2, J = 9, 10, and 10 Hz, H-4 and H-6), 5.00 (dd, 1, $J_{1,2}$ = 3 Hz, H-1).

Anal. Calcd for $C_{23}H_{29}ClN_2O_{10}$: C, 52.23; H, 5.53; N, 5.30; Cl, 6.70. Found: C, 52.28; H, 5.59; N, 5.23; Cl, 6.84.

1,3-Di-*O*-acetyl-5-*O*-benzoyl-(1,3,5/2,4)-2,4-diethoxycarbonylamino-1,3,5-cyclohexanetriol (37). A mixture of **36** (0.41 g), tri-*n*-butyltin hydride (0.5 mL), dry toluene (20 mL), and a catalytic amount of α,α'-azobis(isobutyronitrile) was heated at 90 °C under a nitrogen atmosphere for 2 h. The mixture was evaporated to give a crystalline residue that was recrystallized from chloroform–ethanol to give 0.29 g (75%) of **37**: mp 221–222 °C; ^{1}H NMR ($CDCl_3$) δ 1.07 (t, 3) and 1.23 (t, 3) (J = 7 Hz, ethoxycarbonyl CH_3), 2.07 (s, 3) and 2.12 (s, 3) (OAc), 4.02 (q, 2) and 4.13 (q, 2) (ethoxycarbonyl CH_2).

Anal. Calcd for $C_{23}H_{30}N_2O_{10}$: C, 55.86; H, 6.12; N, 5.66. Found: C, 55.67; H, 6.04; N, 5.76.

(1,3,5/2,4)-2,4-Diethoxycarbonylamino-1,3,5-cyclohexanetriol (*N,N'*-Diethoxycarbonyl-5-deoxystreptamine) (38). Compound **37** (0.22 g) was treated with methanolic ammonia (10 mL) at room temperature for 2 days. The reaction mixture was evaporated to give a syrup that was crystallized from ethyl acetate giving 0.1 g (73%) of **38**: mp 187–188 °C.

Anal. Calcd for $C_{12}H_{22}N_2O_7$: C, 47.05; H, 7.24; N, 9.14. Found: C, 46.65; H, 7.00; N, 8.88.

Compound **38** (0.08 g) was hydrolyzed with refluxing 6 M hydrochloric acid (15 mL), followed by acetylation, as described for the preparation of **2b** from **34b**. The product was crystallized from ethanol to give 0.06 g (61%) of **3b**: mp 305–306 °C (dec). This compound was identical with the sample obtained before.

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Registry No.—**1a,** 2037-48-1; **1b,** 6216-31-5; **2a,** 62708-21-8; **3a,** 62708-22-9; **4,** 34405-77-1; **5,** 62708-23-0; **6,** 62708-24-1; **10a,** 38836-67-8; **10b,** 62742-93-2; **11,** 62742-94-3; **12a,** 62708-25-2; **12b,** 62776-28-7; **13,** 62742-95-4; **14,** 62708-26-3; **19,** 39726-11-9; **20,** 62776-29-8; **21,** 62708-27-4; **22,** 62777-56-4; **23a,** 62708-28-5; **23b,** 62708-29-6; **24,** 62776-30-1; **30,** 62708-30-9; **31,** 62742-96-5; **32,** 62708-31-0; **33,** 62708-32-1; **34a,** 62708-33-2; **34b,** 627-08-34-3; **35a,** 62708-35-4; **35b,** 62708-36-5; **36,** 62708-37-6; **37,** 62708-38-7; **38,** 62708-39-8; sulfuryl chloride, 7791-25-5; mesyl chloride, 124-63-0; sodium benzoate, 532-32-1; sodium azide, 26628-22-8; streptamine sulfate, 62776-31-2; benzoyl chloride, 98-88-4.

References and Notes

(1) For paper 34 of this series, see K. Tadano, T. Shiratori, and T. Suami, *Bull. Chem. Soc. Jpn.*, **49**, 3193 (1976). Presented in part at the 28th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1, 1973 (abstracts of papers of the meeting, Vol. III, p 1315). The nomenclature and numbering of cyclitols used in this paper follow IUPAC and IUB tentative rules for cyclitol nomenclature [*J. Biol. Chem.*, **243**, 5809 (1968)]. For convenience, since the stereoisomers of diaminocyclohexanetriol and triaminocyclohexanediol could be regarded as the deoxy derivatives of streptamine or inosadiamine and -triamine, these generic names are also used retaining their original numbering. In this paper, all the compounds except for meso compounds are racemic. All the formulas depict only one enantiomer of the respective racemates.
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