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Chemical Transformation of Uronic Acids leading to Aminocyclitols. IV.[1] Synthesis of Hexaacetyl-streptamine from N-Acetyl-D-glucosamine by Means of Electrolytic Decarboxylation

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Through a short series of reactions (catalytic oxidation, electrolytic decarboxylation, cyclization with alkaline nitromethane, and reduction), a conversion of N-acetyl-D-glucosamine (1) into hexaacetyl-streptamine (6) has been accomplished without previous protection of the hydroxyl groups in the starting compound (1), although the overall yield was not fully satisfactory. The conversion may represent a new and widely applicable means for the synthesis of diaminocyclitols from amino-sugars. A β-methoxyethoxymethyl ether function was unaffected during the anodic oxidation.

Keywords——N-acetyl-D-glucosamine; hexaacetyl-streptamine; catalytic oxidation; anodic oxidation; nitromethane cyclization; amino-sugar; amino-uronic acid; diaminocyclitol; β-methoxyethoxymethyl ether

In preceding papers,[1,2] we reported short-step conversions from uronic acids to aminocyclitols and from glucuronide-saponins to aminocyclitol-oligoglycosides by making use of electrolytic decarboxylation[3] as the initial reaction. These conversion pathways are characteristic since the configurations and substituents, if any, at C-2, C-3, and C-4 of the uronic acid moiety in the strating substances are retained during the reaction. In the same reports, a neutral monosaccharide was also shown to be convertible to aminocyclitols *via* a corresponding uronic acid which is readily accessible by catalytic oxidation.[1,2] Therefore, that, if the conversion is started with an amino-sugar having an amino group at C-2, C-3, or C-4, it should be possible to synthesize *via* an amino-uronic acid without any protection of hydroxyl groups in the starting compound.

On the other hand, we have recently succeeded in a conversion of N-acetyl-D-glucosamine (1) to hexaacetyl-streptamine (6)[4] by means of the lead tetraacetate degradation method.[5] Reactions with lead tetraacetate are considered to resemble those that occur during electrolytic degradation.[1,2] We have therefore attempted a short-step conversion, initiated by anodic oxidation, from N-acetyl-D-glucosamine (1) to hexaacetyl-streptamine (6) in a similar fashion. This paper deals with the results in detail.

Methyl 2-acetamido-2-deoxy-α-D-glucopyranoside (2),[6] which was prepared in 55% yield from N-acetyl-D-glucosamine (1) by methanolysis, was subjected to catalytic oxidation over platinum, and an amino-uronic acid, *i.e.* methyl 2-acetamido-2-deoxy-α-D-glucopyranosiduronic acid (3), was obtained in 89% yield. The infrared (IR) spectrum of 3 shows absorption bands ascribable to a carboxylic group [3350 (br), 1734 cm^{-1}] and an amide group (1647, 1548 cm^{-1}). The proton nuclear magnetic resonance (^1H NMR) spectrum of 3 taken in pentadeutero(d_5-)pyridine shows signals due to an acetamide group (δ 2.13, 3H, s), a methoxyl group (δ 3.39, 3H, s), an α-anomeric proton (δ 5.23, 1H, d, J=3 Hz), and an amide proton (δ 8.78, 1H, d, J=8 Hz, disappeared on D_2O addition). Since 3 was extremely hygroscopic and could not be crystallized, it was quantitatively converted to a methyl ester (3a) for further confirmation of its structure. The crystalline methyl ester (3a) gave spectral data [IR, ^1H NMR, and mass spectrum (MS)] including an α-anomeric proton signal at δ 5.06 (d, J=3 Hz)

that were consistent with the proposed structure (see "Experimental"), so that a conversion from an N-acetylamino-sugar to an N-acetylamino-uronic acid had been effected without previous protection of hydroxyl groups.

When the amino-uronic acid (**3**) was subjected to electrolysis under constant current conditions in acetic acid containing triethylamine for 7 h, an acetoxylated product (**4**) was obtained in 43% yield. The IR spectrum of this product shows acetoxyl absorption bands (1734, 1239 cm^{-1}) together with amide bands (1646, 1541 cm^{-1}) while the ^1H NMR spectrum (in d_5-pyridine) shows signals due to an acetamide and an acetoxyl groups at δ 1.99, 2.04, 2.11, and 2.13 (each s, of 6H intensity altogether) and signals due to a methoxyl group at δ 3.39 and 3.53 (each s, of 3H intensity altogether), thus indicating the product (**4**) to be a mixture of epimeric C_5-acetoxylated compounds. Since these compounds were fairly unstable, they were immediately converted to their acetylated crystalline derivatives [5α-acetoxyl (**5a**), 12% from **3** and 5β-acetoxyl (**5b**), 21% from **3**] to confirm their structures.

The IR spectrum of **5a** shows absorption bands ascribable to an amide group (3428, 1664, 1505 cm^{-1}) and an acetoxyl function (1742 cm^{-1}). The ^1H NMR spectrum shows four singlets at δ 1.96, 2.00, 2.03, and 2.13 (3H each) due to an acetamide group and three acetoxyl groups, a singlet at δ 3.40 (3H) due to a methoxyl group, a doublet at δ 4.80 (1H, J=4 Hz) due to an α-anomeric proton, and a doublet at δ 6.31 (1H, J=4 Hz) which is assignable to a 5β-proton, thus the 5α-acetoxyl configuration ($^4C_1$) is confirmed. The IR and ^1H NMR spectra of **5b** give similar structural information, except that the ^1H NMR spectrum of **5b** shows a doublet at δ 4.78 (1H, J=3 Hz) due to an α-anomeric proton and a doublet at δ 5.93 (1H, J=9 Hz) as cribable to a 5α-proton, substantiating the 5β-acetoxyl configuration ($^4C_1$) in **5b**.

Finally, treatment of **4** with nitromethane and methanolic sodium methoxide, and subsequent reduction over Raney Ni (T-4)[7] and acetylation with acetic anhydride and pyridine, furnished an acetate which was identical with hexaacetyl-streptamine (**6**).[4] Although the overall yield in the final conversion (6% from **4**) was unsatisfactory, a short-step conversion

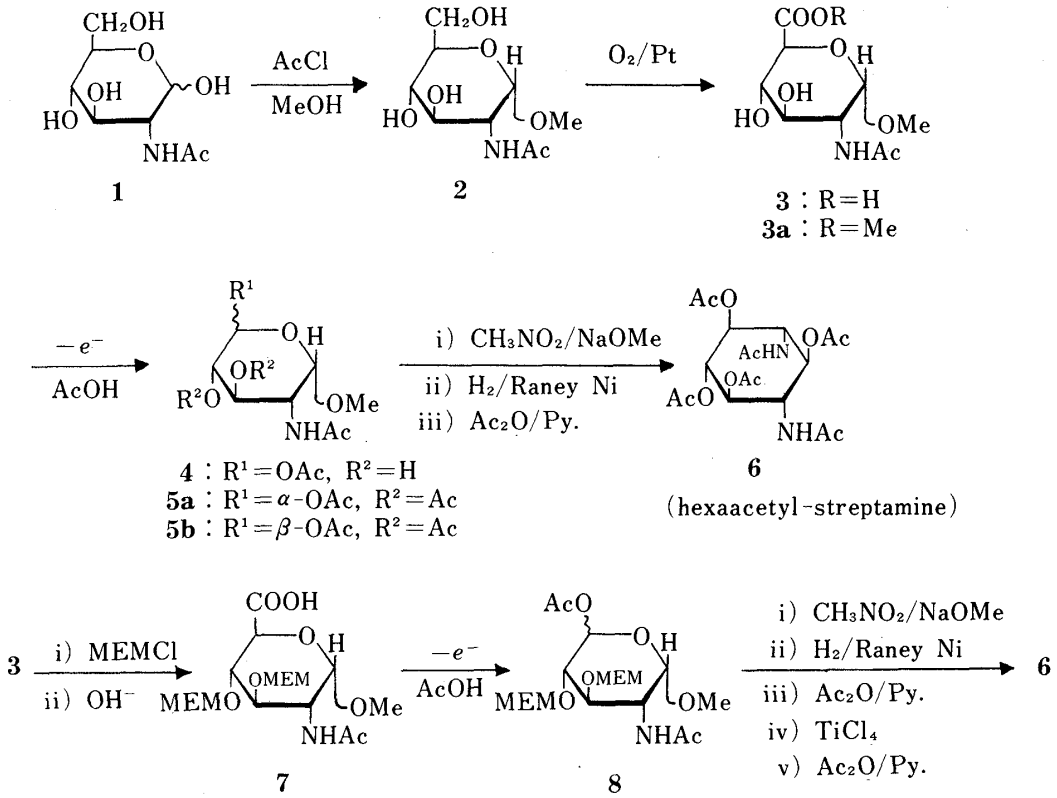

Chart 1

from N-acetyl-D-glucosamine to hexaacetyl-streptamine has been achieved without any protection of hydroxyl groups in the starting compound.

In order to improve the yield through the electrolytic decarboxylation and nitromethane cyclization reactions, several protecting groups for hydroxyl functions have been examined. The following protecting groups have been tested: *tert*-butyldimethylsilyl (TBDMS) ether.[8] allyl ether,[9] tetrahydropyranyl (THP) ether, and β-methoxyethoxymethyl (MEM) ether.[10] However, the TBDMS and THP ethers of **3** could not be obtained, while an allyl ether of **3** was found to be unfavorable for electrolytic decarboxylation. It was found, however, that an MEM ether moiety was unaffected during anodic oxidation and subsequent alkaline treatment.

Treatment of **3** with MEM chloride and N,N-diisopropylethylamine furnished an oily product, which, on subsequent hydrolysis with potassium carbonate to remove an MEM group introduced at the carboxylic moiety, furnished a diMEM ether (**7**) in 58% yield. The IR spectrum of **7** shows absorption bands due to a carboxylic function [3250—3400 (br), 1743 cm^{-1}] and an acetamide group (1672, 1520 cm^{-1}), while the ^1H NMR spectrum corroborates the formation of two MEM linkages six-proton singlet at δ 3.40 and shows a broad singlet at δ 7.31 (1H, disappeared on D_2O addition) due to a carboxylic proton.

Next, the MEM ether (**7**) was subjected to constant current electrolysis in acetic acid containing triethylamine and an acetoxylated product (**8**) was obtained in 89% yield. The IR spectrum of **8** shows the presence of an acetoxyl function (1752 cm^{-1}) and retention of the acetamide moiety (3435, 1681, 1513 cm^{-1}). The ^1H NMR spectrum of **8** shows signals at δ 2.09 (2H, s) and 2.13 (1H, s), which are assignable to epimeric C_5-acetoxyl moieties, and signals due to an acetamide group (δ 1.96, 3H, s) and two methoxyl groups in the two MEM moieties (δ 3.35, 6H, s).

Finally, treatment of **8** with nitromethane and methanolic sodium methoxide and subsequent catalytic reduction over Raney Ni (T-4), acetylation, removal of MEM functions with titanium tetrachloride,[10] and reacetylation, furnished hexaacetyl-streptamine (**6**) which was identical with an authentic sample. It should be noted that although the yield in anodic oxidation has been improved as described, the cyclization reaction of the dialdehydic intermediate with alkaline nitromethane has become unsatisfactory and this has again resulted in an unsatisfactory overall yield. Further work on this subject seems to be necessary.

Experimental

The instruments used to obtain physical data and the experimental conditions for chromatography were the same as in our previous paper.[3] The electrolytic reactions were carried out in a beaker with stirring using a potentiostat/galvanostat apparatus (Hokuto Denko Co., model HA-105).

Methanolysis of N-Acetyl-D-glucosamine (1)——A suspension of **1** (10 g) in AcCl–MeOH (3: 40, 50 ml) was heated under reflux for 1.5 h. After neutralization with Amberlite IRA-400 (OH^- form), the solvent was removed from the filtrate under reduced pressure to give a product. Chromatographic purification of the product over SiO_2 (300 g) with $CHCl_3$–MeOH (4: 1) furnished an α-anomer (**2**, 5.9 g, 55%), a β-anomer (3.4 g, 31%), and a mixture of both (0.7 g). **2**, mp 195—196°C (colorless fine crystals from abs. EtOH), $[\alpha]_D^{25}$ +130° (c=1.33, H_2O) [lit.:[6] mp 188—189°C (EtOH, $[\alpha]_D$ +104° (H_2O)].

Catalytic Oxidation of 2 giving 3——A solution of **2** (2 g) in H_2O (100 ml) and a platinum catalyst (prepared from 2 g of $PtO_2 \cdot 1$—3 H_2O) were put in a four-necked flask equipped with a stirrer, a gas-inlet, a reflux-condenser, and a dropping funnel, and the whole mixture was vigorously stirred at 70—80°C while a stream of oxygen was introduced. During this period, aq. $NaHCO_3$ was added to the reaction flask to maintain pH 7—8. After being stirred for 12 h, the reaction mixture was filtered and the filtrate was neutralized with Dowex 50W×8 (H^+ form). Removal of the solvent from the filtrate under reduced pressure furnished a fairly hygroscopic amino-uronic acid (**3**, 1.9 g, 89%). **3**, mp 165—167°C (colorless needles from MeOH–AcOEt), $[\alpha]_D^9$ +113° (c=1.27, MeOH), IR ν_{max}^{KBr} cm^{-1}: 3350 (br), 1734, 1647, 1548. ^1H NMR (d_5-pyridine, δ): 2.13 (3H, s, >NAc), 3.39 (3H, s, OMe), 5.23 (1H, d, J=3 Hz, 1-H), 8.78 (1H, d, J=8 Hz, disappeared on D_2O addition, >NH). MS (m/z, %): 231 (M^+-H_2O, 1), 114 (100).

Methylation of 3 giving 3a——Methylation of **3** (210 mg) with ethereal diazomethane in the usual manner furnished **3a** (220 mg), mp 207—209°C (colorless needles from acetone), $[\alpha]_D^{15}$ +104° (c=0.67, MeOH). *Anal.* Calcd for $C_{10}H_{17}NO_7$: C, 45.62; H, 6.51; N, 5.32. Found: C, 45.42; H, 6.50; N, 5.41. IR ν_{max}^{KBr} cm^{-1}: 3285, 1735, 1647, 1550, 1375. ^1H NMR (d_5-pyridine, δ): 2.03 (3H, s, >NAc), 3.29 (3H, s, OMe), 3.66 (3H, s, COOMe),

4.00—4.92 (6H, m), 5.06 (1H, d, J=3 Hz, 1-H), 8.57 (1H, d, J=7 Hz, disappeared on D_2O addition, >NH). MS (m/z, %): 264 (M^++1, 44), 114 (100).

Electrolysis of 3 giving 4——A solution of **3** (304 mg) in AcOH (20 ml) containing Et_3N (1 ml) was subjected to constant current electrolysis [Pt electrode; 100 mA (7.5 mA/cm²), 5—10°C] for 7 h. Removal of AcOH from the reaction mixture by freeze-drying gave a product which was purified by column chromatography (SiO_2 25 g, $CHCl_3$–MeOH=10: 1) to furnish **4** (140 mg, a mixture of C_5-acetoxyl epimers, 43%). **4**, IR ν_{max}^{KBr} cm^{-1}: 3240, 1734, 1646, 1541, 1239. ^1H NMR (d_5-pyridine, δ): 1.99, 2.04, 2.11, 2.13 (total 6H, each s, >NAc, OAc), 3.39, 3.53 (total 3H, each s, OMe), 8.84 (1H, d, J=9 Hz, disappeared on D_2O addition, >NH).

Electrolysis followed by Acetylation of 3 giving 5a and 5b——A solution of **3** (502 mg) in AcOH (20 ml) containing Et_3N (1 ml) was subjected to constant current electrolysis as described above for 8.5 h. The product, obtained after work-up as described above, was acetylated with Ac_2O–pyridine (1: 1, 8 ml) at room temperature (20°C) with stirring for 12 h. The reaction mixture was poured into ice-water and extracted with AcOEt. Work-up of the AcOEt extract in the usual manner and removal of the solvent under reduced pressure furnished a syrupy product (0.7 g). Chromatography of the product over SiO_2 (70 g) with benzene–AcOEt (1: 1) furnished **5a** (62 mg, 12%), **5b** (114 mg, 21%), and a mixture of both (12 mg). **5a**, mp 137—139°C (colorless needles from ether), $[\alpha]_D^{18}$ +7.9° (c=0.94, $CHCl_3$). *Anal.* Calcd for $C_{14}H_{21}NO_9$: C, 48.41; H, 6.09; N, 4.03. Found: C, 48.10; H, 6.15; N, 4.07. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3428, 1742, 1664, 1505. ^1H NMR ($CDCl_3$, δ): 1.96, 2.00, 2.03, 2.13 (3H each, all s, >NAc, OAc×3), 3.40 (3H, s, OMe), 4.40 (1H, d.d.d, J= 4, 9, 10 Hz, 2-H), 4.80 (1H, d, J=4 Hz, 1-H), 5.14 (1H, d.d, J=4, 10 Hz, 4-H), 5.51 (1H, d.d, J=10, 10 Hz, 3-H), 6.09 (1H, d, J=9 Hz, disappeared on D_2O addition, >NH), 6.31 (1H, d, J=4 Hz, 5-H). MS (m/z, %): 316 (M^+−OMe, 4), 156 (100). **5b**, mp 150.5—152°C (colorless needles from ether), $[\alpha]_D^{15}$ +95° (c=0.21, $CHCl_3$). *Anal.* Calcd for $C_{14}H_{21}NO_9$: C, 48.41; H, 6.09; N, 4.03. Found: C, 48.28; H, 6.05; N, 4.17. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3435, 1759, 1682, 1513. ^1H NMR (δ): (in $CDCl_3$) 1.96 (3H, s), 2.01 (6H, s), 2.11 (3H, s) (>NAc, OAc×3), 3.54 (3H, s, OMe), 4.40 (1H, d.d.d, J=4, 10, 10 Hz, 2-H), 4.77 (1H, d, J=4 Hz, 1-H), 5.16—5.33 (2H, m, 3-H, 4-H), 5.77 (1H, d, J=10 Hz, disappeared on D_2O addition, >NH), 5.96 (1H, d, J=8 Hz, 5-H); (in d_6-acetone) 1.89, 1.92, 1.97, 2.04 (3H each, all s, >NAc, OAc×3), 3.50 (3H, s, OMe), 4.36 (1H, d.d.d, J=3, 8, 9 Hz, 2-H), 4.78 (1H, d, J=3 Hz, 1-H), 5.07, 5.26 (1H each, both d.d, J=9, 9 Hz, 3-H, 4-H), 5.96 (1H, d, J=9 Hz, 5-H), 6.92 (1H, d, J=8 Hz, disappeared on D_2O addition, >NH). MS (m/z, %): 347 (M^+, 1), 316 (M^+−OMe, 1), 288 (M^+−OAc, 8), 114 (100).

Conversion from 4 to Hexaacetyl-streptamine (6)——A solution of **4** (242 mg) in aqueous MeOH (MeOH–H_2O=2: 1, 6 ml) was treated with CH_3NO_2 (4 ml) and the mixture was stirred at room temperature (17°C) under an argon atmosphere for 10 min. After addition of 10% NaOMe–MeOH (2.1 ml), the reaction mixture was stirred for a further 48 h under the same conditions. The whole mixture was then neutralized with Dowex 50W×8 (H^+ form) and the solvent was removed under reduced pressure. The residue was dissolved in H_2O (10 ml) and the solution was shaken with a suspension of Raney Ni (T-4) in EtOH (10 ml) under a hydrogen atmosphere for 6 h. Removal of the solvent from the filtrate gave a product which was acetylated with Ac_2O–pyridine (1: 1, 8 ml) at room temperature (18°C) with stirring for 12 h. Concentration of the whole mixture by evaporation under reduced pressure yielded a product which was partitioned into an H_2O–AcOEt mixture. The AcOEt phase was dried over $MgSO_4$ and removal of the solvent under reduced pressure followed by crystallization from MeOH furnished **6** (25 mg, 6%) which was identical with an authentic sample[4] as judged by mixed mp determination and IR (KBr), TLC (benzene–MeOH=3: 1; $CHCl_3$–MeOH=15: 1), and ^1H NMR (d_6-DMSO) comparisons.

MEM-ether Formation followed by Alkaline Hydrolysis of 3 giving 7——A solution of **3** (2 g) in DMF (20 ml) and CH_2Cl_2 (10 ml) was treated with N,N-diisopropylethylamine (5.2 ml) under a nitrogen atmosphere. MEM chloride (6.9 ml) was added dropwise to the stirred mixture over a period of 20 min and the whole was stirred at room temperature (20°C) for a further 5 days. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt extract was successively washed with aq. 5% HCl, aq. sat. $NaHCO_3$, and brine, and dried over $MgSO_4$. Removal of the solvent from the filtrate under reduced pressure yielded an oily product (4.4 g). A solution of the product in MeOH (30 ml) was treated with aq. 5% K_2CO_3 (9 ml) and the mixture was heated under reflux for 2.5 h. Removal of MeOH under reduced pressure gave an aqueous phase which was washed with AcOEt. After acidification (to pH *ca.* 1) of the aqueous phase with aq. 5% HCl, the aqueous phase was extracted with AcOEt. Washing of the AcOEt extract with brine followed by usual work-up furnished **7** (1.97 g, 58%), colorless oil, $[\alpha]_D^9$ +138.6° (c=2.80, $CHCl_3$). *Anal.* Calcd for $C_{17}H_{31}NO_{11}$: C, 48.00; H, 7.34; N, 3.29. Found: C, 48.12; H, 7.65; N, 2.91. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3435, 1743, 1672, 1520. ^1H NMR ($CDCl_3$, δ): 2.03 (3H, s, >NAc), 3.40 (6H, s), 3.43 (3H, s) (OMe× 3), 3.47—4.24 (10H, m), 4.61—5.14 (6H, m), 6.21 (1H, d, J=3 Hz, 1-H), 6.74 (1H, d, J=7 Hz, disappeared on D_2O addition, >NH), 7.31 (1H, br. s, $W_{h/2}$=22 Hz, disappeared on D_2O addition, COOH). MS (m/z, %): 424 (M^+−1, 4), 89 (100).

Electrolysis of 7 giving 8——A solution of **7** (131 mg) in AcOH (30 ml) containing Et_3N (2 ml) was subjected to constant current electrolysis [Pt electrode; 200 mA (10 mA/cm²), 5—10°C] for 15 h. After neutralization with $NaHCO_3$ (powder), the whole mixture was extracted with AcOEt. The AcOEt phase was then washed with aq. sat. $NaHCO_3$ and brine, and dried over $MgSO_4$. Removal of the solvent gave an

oily product (129 mg) which was purified by column chromatography (SiO_2 20 g, *n*-hexane–acetone=3: 1) to furnish **8** (a mixture of C_5-acetoxyl epimers, 121 mg, 89%). **8**, colorless oil. High resolution MS (*m/z*): Calcd for $C_{18}H_{34}NO_{11}$ (M^++1) 440.213, $C_{18}H_{33}NO_{11}$ (M^+) 439.205. Found: 440.211, 439.206. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3435, 1752, 1681, 1513, 1226, 1220. ^1H NMR ($CDCl_3$, δ): 1.96 (3H, s, >NAc), 2.09, 2.13 (total 3H (2: 1), both s, OAc), 3.35 (6H, s), 3.40 (3H, s) (OMe×3), 5.77 (d, J=8 Hz), 6.27 (d, J=3 Hz) (total 1H (2: 1), 5α-H, 5β-H), 6.45 (1H, d, J=6 Hz, disappeared on D_2O addition, >NH). MS (*m/z*, %): **440** (M^++1, 60), 439 (M^+, 5), 89 (100).

Conversion of 8 to Hexaacetyl-streptamine (6)——A solution of **8** (328 mg) in MeOH (5 ml) was mixed with CH_3NO_2 (5 ml) and 10% NaOMe–MeOH (4 ml), and the whole was stirred at room temperature (18°C) under a nitrogen atmosphere for 67 h. After neutralization with Dowex 50W×8 (H^+ form), the solvent was removed from the filtrate under reduced pressure. The residue was dissolved in EtOH (6 ml) and the solution was shaken with a suspension of Raney Ni (T-4) in EtOH (6 ml) at room temperature under a hydrogen atmosphere for 6 h. Removal of the solvent from the filtrate under reduced pressure gave a product which was acetylated with Ac_2O–pyridine (1: 1, 1 ml). A solution of the acetylated product in dry CH_2Cl_2 (1.5 ml) was treated with $TiCl_4$ (0.05 ml) and the mixture was stirred at room temperature (19°C) under a nitrogen atmosphere for 16 h. After neutralization with aq. conc. NH_3, the solvent was removed under reduced pressure and the residue was again acetylated with Ac_2O–pyridine (1: 1, 2 ml). Preparative TLC ($CHCl_3$–MeOH=15: 1) of the final acetate furnished hexaacetyl-streptamine (**6**, 20 mg), which was identical with an authentic sample[4] as judged by TLC (benzene–MeOH=3: 1, $CHCl_3$–MeOH=15: 1) and IR (KBr) comparisons.

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