Synthesis of Methyl 2,6-Di-*N*-acetyl-2,3,4,6,7-pentadeoxy-L-*lyxo*-heptopyranoside, a Derivative of 6-*epi*-D-Purpurosamine B[1]

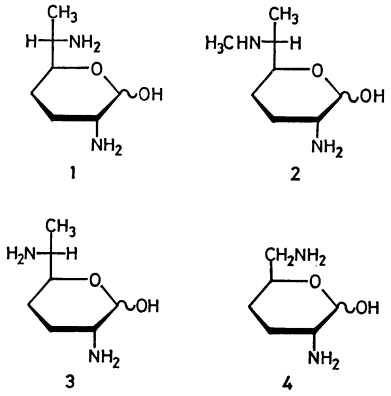
Tetsuo SUAMI,* Yutaka HONDA, Tsuguhiro KATO, Mikio MASU, and Kinya MATSUZAWA

Department of Applied Chemistry, Faculty of Engineering, Keio University, Hiyoshi, Yokohama 223

(Received August 16, 1979)

6-*epi*-D-Purpurosamine B, 2,6-diamino-2,3,4,6,7-pentadeoxy-L-*lyxo*-heptopyranose, was found to be a component of antibiotic fortimicins. Methyl 2,6-di-*N*-acetyl-6-*epi*-α-D-purpurosaminide B has been synthesized from methyl 2-acetamido-2-deoxy-6-*O*-trityl-α-D-glucopyranoside.

6-*epi*-D-Purpurosamine B (**1**) is a component of antibiotic fortimicins, together with an aminocyclitol moiety named fortamine.[2,3] The configuration of **1** has been established by spectroscopic study of its di-*N*-acetyl diethyl dithioacetal derivative, in relation to the corresponding D-purpurosamine B derivative,[4] as 2,6-diamino-2,3,4,6,7-pentadeoxy-L-*lyxo*-heptopyranose.[5]



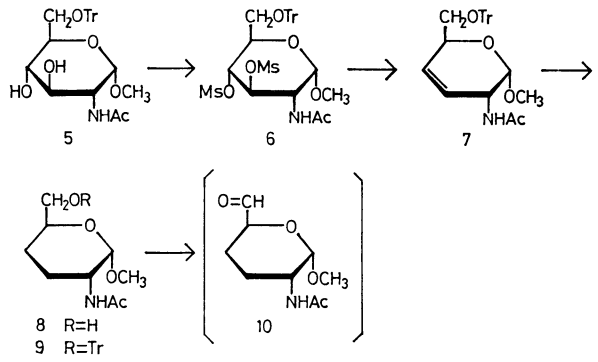
Scheme 1.

In purpurosamine families, D-purpurosamine A (**2**), B (**3**), and C (**4**) are known as components of antibiotic gentamicins C_1, C_2, and C_{1a}, respectively.[6,7] D-Purpurosamine C and its 2-epimer have been synthesized by several investigators,[8–13] but not D-purpurosamine A or B, except DL-form of **3**.[14]

In connection with studies on fortimicins, we attempted to synthesize D-purpurosamines. We wish to report the synthesis of 6-*epi*-D-purpurosamine B derivative.

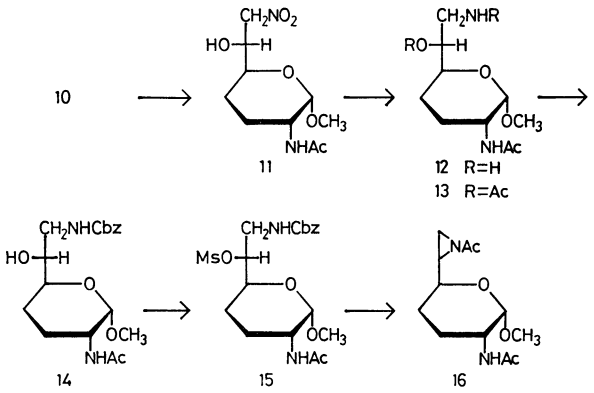
Results and Discussion

When methyl 2-acetamido-2-deoxy-6-*O*-trityl-α-D-glucopyranoside[15] (**5**) was treated with an excess amount of methanesulfonyl chloride in pyridine, the 3,4-di-*O*-mesyl derivative (**6**) was obtained in 95% yield. Treatment of **6** with sodium iodide and zinc powder in *N*,*N*-dimethylformamide (DMF) at 150 °C gave the corresponding 3,4-unsaturated derivative (**7**) in 64% yield. Catalytic hydrogenation of **7** in aqueous methanol in the presence of palladium black afforded methyl 2-acetamido-2,3,4-trideoxy-α-D-*erythro*-hexopyranoside (**8**) as a major product in 72% yield and methyl 2-acetamido-2,3,4-trideoxy-6-*O*-trityl-α-D-*erythro*-hexopyranoside (**9**) in 23% yield. Compound **9** was readily converted into **8** by mild acid hydrolysis.



Scheme 2.

Compound **8** was oxidized in a mixture of dimethyl sulfoxide (DMSO) and dicyclohexylcarbodiimide (DCC) in the presence of pyridinium trifluoroacetate.[16] The resulting aldehyde (**10**), without purification, was reacted with nitromethane in methanol under ice cooling in the presence of sodium methoxide to give methyl 2-acetamido-2,3,4,7-tetradeoxy-7-nitro-α-D-*ribo*-heptopyranoside (**11**) in 52% yield as crystals. The proposed configuration of **11** was deduced by chemical conversion into the 6-*epi*-D-purpurosamine B derivative.



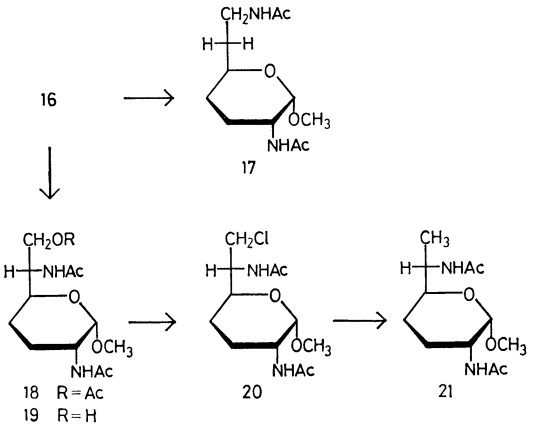
Scheme 3.

Catalytic hydrogenation of **11** in methanol in the presence of Raney nickel afforded methyl 2-acetamido-7-amino-2,3,4,7-tetradeoxy-α-D-*ribo*-heptopyranoside (**12**) as amorphous solid, which was converted into a crystalline 2,7-di-*N*-acetyl-6-*O*-acetyl derivative (**13**) which was characterized by ^{1}H NMR spectroscopy.

When **12** was treated with benzyloxycarbonyl chloride in an aqueous alkaline solution, its 7-*N*-benzyloxycarbonyl derivative (**14**) was obtained in 74% yield. *O*-Mesylation of **14** with methanesulfonyl chloride in

pyridine gave a crystalline 6-*O*-mesyl derivative (**15**) in 86% yield.

Treatment of **15** with sodium isopropoxide in isopropyl alcohol gave an epimino derivative, which was further converted into a crystalline *N*-acetylepimino derivative (**16**) in 84% yield. The presence of an aziridine ring was demonstrated by a characteristic IR absorption of an acylaziridine-carbonyl group at 1700 cm^{-1} [17] and by ^1H NMR spectroscopy. The configuration of **16** was proposed as 6,7-(*N*-acetylepimino)-6,7-dideoxy-L-*lyxo*-heptopyranoside, according to the stereochemistry of an aziridine ring formation which has been well studied by several investigators.[18–22]



Scheme 4.

Catalytic hydrogenation of **16** in ethanol in the presence of Raney nickel gave a crystalline product (**17**) in a quantitative yield, which was found to be analytically pure. ^1H NMR spectrum of **17** revealed the presence of two acetamido and one methoxyl groups, but not a terminal methyl group. Thus **17** was identified as methyl 2,7-di-*N*-acetyl-2,3,4,6,7-pentadeoxy-α-D-*erythro*-heptopyranoside.

Methyl 2,6-di-*N*-acetyl-7-*O*-acetyl-2,3,4,6-tetradeoxy-β-L-*lyxo*-heptopyranoside (**18**) was obtained in 88% yield by heating **16** in glacial acetic acid. In the reaction, nucleophilic attack by an acetate ion on the aziridine ring occurs exclusively at C-7 position. This is in line with the fact that acetolysis of 6,7-(*N*-acetylepimino)-dideoxy-L-*glycero*-α-D-*galacto*-heptopyranoside derivative yielded 6-acetamido-7-*O*-acetyl-L-*glycero*-α-D-*galacto*-heptopyranoside derivative.[17]

De-*O*-acetylation of **18** in methanolic ammonia gave methyl 2,6-di-*N*-acetyl-2,3,4,6-tetradeoxy-β-L-*lyxo*-heptopyranoside (**19**) in 92% yield as crystals. Chlorination of **19** was performed by the triphenylphosphine–carbon tetrachloride procedure[23,24] to give a 7-chloro-7-deoxy derivative (**20**). Dehalogenation of **20** was carried out with tributylstannane[25–27] in the presence of α,α′-azobisisobutyronitrile under nitrogen atmosphere, methyl 2,6-di-*N*-acetyl-6-*epi*-α-D-purpurosamineide B (**21**) being obtained in 56% yield. Compound **21** was identical with an authentic sample prepared by methanolysis of tetra-*N*-acetylfortimicin B.[5]

Experimental

General Methods. Melting points were determined in capillary tubes and are corrected. Solutions were concentrated under reduced pressure below 40 °C. Optical rotations were measured with a Japan Spectroscopic DIS-SL polarimeter. ^1H NMR spectra were recorded with a Varian EM360A spectrometer at 60 MHz or a Varian XL-100 spectrometer at 100 MHz, peak positions being given in δ values. IR spectra were recorded with a Hitachi 225 spectrophotometer in KBr disks. TLC was performed on Wakogel B-10 (Wako Pure Chemical Co. Ltd.) plates, silica gel (Wakogel C-300) being used for column chromatography.

*Methyl 2-Acetamido-2-deoxy-3,4-di-O-mesyl-6-O-trityl-α-D-glucopyranoside (**6**).* Methanesulfonyl chloride (4.9 ml) was added to a stirred solution of methyl 2-acetamido-2-deoxy-6-*O*-trityl-α-D-glucopyranoside[15] (**5**, 10.0 g) in pyridine (50 ml). After being stirred for 2 h at 50 °C, the solution was concentrated, the residue being repeatedly extracted with chloroform and the combined chloroform solution washed with cold water. The chloroform layer was dried over Na_2SO_4 and concentrated. The residue was recrystallized from ethyl acetate to give 12.4 g (95%) of **6**, mp 184—185 °C (dec), $[\alpha]_D^{20}$ +53° (*c* 1.0, chloroform). ^1H NMR: δ 2.01 (s, 3, NAc), 2.52 (s, 3, SCH_3), 3.06 (s, 3, SCH_3), 3.41 (s, 3, OCH_3), 5.89 (d, 1, $J_{2,NH}$=9 Hz, NH).

Found: C, 57.08; H, 5.77; N, 1.95; S, 9.92%. Calcd for $C_{30}H_{35}NO_{10}S$: C, 56.85; H, 5.57; N, 2.21; S, 10.12%.

*Methyl 2-Acetamido-2,3,4-trideoxy-6-O-trityl-α-D-erythro-hex-3-enopyranoside (**7**).* Compound **6** (5.0 g) was heated with sodium iodide (50 g) and zinc powder (25 g) in DMF (280 ml) at 150 °C for 18 h with mechanical agitation under reflux. The reaction mixture was filtered and the filtrate was concentrated. The residue was dissolved in chloroform, the chloroform solution being washed repeatedly with 20% sodium thiosulfate solution and water. The solution was dried over Na_2SO_4 and concentrated. The residue was recrystallized from ether to give 2.3 g (64%) of **7**, mp 151—152 °C, $[\alpha]_D^{21}$ −34° (*c* 3.0, chloroform). ^1H NMR: δ 1.97 (s, 3, NAc), 4.80 (s, 1, H-1), 5.87 (d, 1, $J_{2,NH}$=10 Hz, NH).

Found: C, 75.89; H, 6.77; N, 3.12%. Calcd for $C_{28}H_{29}NO_4$: C, 75.82; H, 6.59; N, 3.16%.

By mild acid hydrolysis and subsequent acetylation, **7** was readily converted into methyl 2-acetamido-6-*O*-acetyl-2,3,4-trideoxy-α-D-*erythro*-hex-3-enopyranoside, mp 131—132 °C, $[\alpha]_D^{20}$ −37° (*c* 0.95, chloroform). ^1H NMR: δ 2.01 (s, 3, NAc), 2.10 (s, 3, OAc), 3.48 (s, 3, OCH_3).

Found: C, 54.37; H, 7.05; N, 5.86%. Calcd for $C_{11}H_{17}NO_5$: C, 54.31; H, 7.05; N, 5.76% .

*Methyl 2-Acetamido-2,3,4-tridoxy-α-D-erythro-hexopyranoside (**8**).* (*a*): Compound **7** (0.10 g) was hydrogenated in 80% aqueous methanol in the presence of palladium black at 50 °C overnight. After the catalyst had been filtered off, the filtrate was concentrated and the residue was fractionated on a silica gel column using 20:1 (v/v) benzene–ethanol as an eluant. Fractions moving fast on TLC in the same solvent system were combined and concentrated to give 10 mg (23%) of methyl 2-acetamido-2,3,4-trideoxy-6-*O*-trityl-α-D-*erythro*-hexopyranoside (**9**), mp 183—184 °C, $[\alpha]_D^{21}$ +38° (*c* 0.23, chloroform).

Found: C, 75.48; H, 7.03; N, 2.95%. Calcd for $C_{28}H_{31}NO_4$: C, 75.48; H, 7.01; N, 3.14%.

Fractions moving slowly on TLC were combined and concentrated to give 33 mg (72%) of **8** as a syrup, $[\alpha]_D^{21}$ +137° (*c* 1.76, methanol). ^1H NMR (CD_3OD): δ 1.91 (s, 3, NAc),

3.35 (s, 3, OCH_3), 4.54 (d, 1, $J_{1,2}$=3.2 Hz, H-1).

Found: C, 53.36; H, 8.37; N, 6.70%. Calcd for $C_9H_{17}NO_4$: C, 53.18; H, 8.43; N, 6.89%.

(*b*): Compound **7** (3.7 g) was catalytically hydrogenated as described in (a), and the residual mixture was hydrolyzed in 50% aqueous acetic acid (60 ml) at 60 °C for 1 h. The hydrolyzate was diluted with cold water (60 ml) and triphenylmethanol precipitated was removed by filtration. The filtrate was concentrated to give **8** in a quantitative yield as a crude syrup.

Compound **8** (83 mg) was acetylated and the product was recrystallized from ether–petroleum ether to give 70 mg (70%) of methyl 2-acetamido-6-*O*-acetyl-2,3,4-trideoxy-α-D-*erythro*-hexopyranoside, mp 106—107 °C, $[\alpha]_D^{20}$ +100° (*c* 1.0, chloroform). ^{1}H NMR: δ 1.97 (s, 3, NAc), 2.04 (s, 3, OAc), 3.38 (s, 3, OCH_3), 4.61 (d, 1, $J_{1,2}$=3.6 Hz, H-1), 5.67 (d, 1, $J_{2,NH}$=9.0 Hz, NH).

Found: C, 53.97; H, 7.70; N, 5.84%. Calcd for $C_{11}H_{19}NO_5$: C, 53.86; H, 7.81; N, 5.71%.

*Methyl 2-Acetamido-2,3,4-trideoxy-*α-erythro-*hexodialdo-1,5-pyranoside* (**10**). A solution of DCC (7.9 g) in DMSO (1 ml) was added under ice cooling to a stirred solution of **8** (2.6 g) in freshly distilled DMSO (4 ml) containing trifluoroacetic acid 0.5 ml) and pyridine (1 ml). Stirring was continued for 6 h at ambient temperature, and a solution of oxalic acid (2.3 g) in methanol (2 ml) was added to the reaction mixture. Dicyclohexylurea precipitated was filtered off and the filtrate containing **10** was used for the subsequent reaction.

A part of the filtrate was treated with 2,4-dinitrophenylhydrazine in phosphoric acid to give a hydrazone of **10**, mp 229—230 °C (dec).

Found: C, 47.27; H, 5.05; N, 18.32%. Calcd for $C_{15}H_{19}N_5O_7$: C, 47.24; H, 5.02; N, 18.37%.

*Methyl 2-Acetamido-2,3,4,7-tetradeoxy-7-nitro-*α-D-ribo-*heptopyranoside* (**11**). The filtrate containing **10** described above was diluted with methanol (10 ml). To the solution were added nitromethane (1.2 ml) and methanolic sodium methoxide (0.6 g Na in 5 ml of methanol) under ice cooling. After being settled overnight in a refrigerator, the pH of the solution was adjusted to 4 with Amberlite IR-120 (H^+) resin and concentrated. A solution of the residue in ethyl acetate was washed with cold water, dried over Na_2SO_4 and concentrated. The residue was recrystallized from ethyl acetate to give 1.52 g (45%) of **11**, mp 193—194 °C (dec), $[\alpha]_D^{21}$ +150° (*c* 1.0, methanol). The product showed a single spot at R_f 0.29 on TLC in 7:1 (v/v) benzene–ethanol. ^{1}H NMR (DMSO-d_6): δ 1.78 (s, 3, NAc), 3.24 (s, 3, OCH_3), 4.46 (d, 1, $J_{1,2}$=3.6 Hz, H-1).

Found: C, 45.94; H, 6.84; N, 10.71%. Calcd for $C_{10}H_{18}N_2O_6$: C, 45.79; H, 6.92; N, 10.68%.

From the mother liquor, a second crop of **11** (0.23 g, 7%) was obtained by column chromatography using 10:1 (v/v) benzene–ethanol as an eluant, followed by recrystallization from ethyl acetate.

*Methyl 2-Acetamido-7-amino-2,3,4,7-tetradeoxy-*α-D-ribo-*heptopyranoside* (**12**). Compound **11** (186 mg) was hydrogenated in methanol (6 ml) in the presence of Raney nickel overnight. After the catalyst had been filtered off, the filtrate was concentrated to give **12** as an amorphous solid in a quantitative yield, $[\alpha]_D^{21}$ +114° (*c* 2.28, methanol).

*Methyl 2,7-*N*-Acetyl-6-*O*-acetyl-2,3,4,7-tetradeoxy-*α-D-ribo-*heptopyranoside* (**13**). Compound **12** (89 mg) was acetylated and the product was recrystallized from ether–methanol to give 85 mg (70%) of **13**, mp 202—203 °C, $[\alpha]_D^{21}$ +101° (*c* 1.0, chloroform). ^{1}H NMR: δ 1.95 (s, 6, 2×NAc), 2.07 (s, 3, OAc), 3.33 (s, 3, OCH_3), 4.57 (d, 1, $J_{1,2}$=4 Hz, H-1), 4.83 (ddd, 1, $J_{6,7}$=6 Hz, $J_{6,7'}$=7 Hz, $J_{5,6}$=4 Hz, H-6), 5.86 (d, 1, $J_{2,NH}$=9.5 Hz, NH-2), 6.16 (t, 1, $J_{7,NH}$=5.5 Hz, NH-7).

Found: C, 52.89; H, 7.62; N, 8.82%. Calcd for $C_{14}H_{24}N_2O_6$: C, 53.15; H, 7.65; N, 8.86%.

^{1}H NMR spectrum of the corresponding 6-*O*-trideuterioacetyl derivative gave signals at δ 1.95 (s, 1, 6, 2×NAc) and 3.33 (s, 3, OCH_3).

*Methyl 2-Acetamido-7-*N*-benzyloxycarbonyl-2,3,4,7-tetradeoxy-*α-D-ribo-*heptopyranoside* (**14**). Benzyloxycarbonyl chloride (2.1 ml of 30% toluene solution) was added under ice cooling to a stirred solution of **12** (429 mg) in 94% aqueous ethanol (16 ml) containing sodium hydroxide (180 mg). After being settled in a refrigerator overnight, the reaction mixture was neutralized with 1 M hydrochloric acid and concentrated. The residue was purified on a silica gel column using 10:1 (v/v) benzene–ethanol as an eluant to give 498 mg (74%) of **14** as an amorphous solid, $[\alpha]_D^{21}$ +100° (*c* 1.0, methanol). ^{1}H NMR: δ 1.94 (s, 3, NAc), 3.32 (s, 3, OCH_3), 4.57 (d, 1, $J_{1,2}$=3.6 Hz, H-1), 5.09 (s, 2, benzyl CH_2), 5.48 (broad t, 1, NH-7), 5.81 (d, 1, $J_{2,NH}$=8.8 Hz, NH-2), 7.34 (s, 5, phenyl).

Found: C, 58.89; H, 7.08; N, 7.50%. Calcd for $C_{18}H_{29}N_2O_6$: C, 59.00: H, 7.15; N, 7.65%.

*Methyl 2-Acetamido-7-*N*-benzyloxycarbonyl-2,3,4,7-tetradeoxy-6-*O*-mesyl-*α-D-ribo-*heptopyranoside* (**15**). Methanesulfonyl chloride (0.08 ml) was added to a solution of **14** (336 mg) in pyridine (2 ml). After 3 h, the solution was concentrated and the residue was dissolved in chloroform. The chloroform solution was washed with water, dried over Na_2SO_4 and evaporated. The residue was recrystallized from ethyl acetate–petroleum ether to give 35 mg (86%) of **15**, mp 126—127 °C, $[\alpha]_D^{21}$ +75° (*c* 2.3, chloroform). ^{1}H NMR: δ 1.96 (s, 3, NAc), 2.99 (s, 3, SCH_3), 3.36 (s, 3, OCH_3), 4.61 (d, 1, $J_{1,2}$=3.6 Hz, H-1), 5.11 (s, 2, benzyl CH_2), 5.41 (broad t, 1, $J_{7,NH}$=6.0 Hz, NH-7), 5.71 (d, 1, $J_{2,NH}$=9.6 Hz, NH-2), 7.33 (s, 5, phenyl).

Found: C, 51.47; H, 6.24; N, 6.29; S, 6.99%. Calcd for $C_{19}H_{28}N_2O_8S$: C, 51.34; H, 6.35; N, 6.30; S, 7.21%.

*Methyl 2-Acetamido-6,7-(*N*-acetylepimino)-2,3,4,6,7-pentadeoxy-*β-L-lyxo-*heptopyranoside* (**16**). To a solution of **15** (323 mg) in dioxane (5 ml) was added a solution of sodium isopropoxide (40 mg of sodium) in isopropyl alcohol (2 ml). The solution was heated under reflux for 18 h, the progress of the reaction being monitored on TLC in 5:1 (v/v) benzene–ethanol. The starting material **15** (R_f 0.52) finally disappeared, three new spots appearing at R_f 0.10 (major), 0.16 (minor), and 0.64 (minor). The reaction mixture was filtered and the filtrate concentrated. The residue was acetylated with acetic anhydride in methanol, and after 10 min, pH of the solution was adjusted to 8. The solution was concentrated and the residue was extracted with ethyl acetate. The ethyl acetate solution was dried over Na_2SO_4 and concentrated. The residue was triturated in ether to give 156 mg (84%) of **16**, mp 174—175 °C, $[\alpha]_D^{21}$ +12° (*c* 1.0, chloroform). ^{1}H NMR: δ 1.95 (s, 3, NAc), 2.06 (d, 1, $J_{6,7}$=3.2 Hz, H-7), 2.16 (s, 3, AcN=), 2.24—2.59 (m, 2, H-6 and 7′), 3.36 (s, 3, OCH_3), 4.60 (d, 1, $J_{1,2}$=3.6 Hz, H-1), 5.77 (d, 1, $J_{2,NH}$=8.4 Hz, NH).

Found: C, 56.22; H, 7.66; N, 10.78%. Calcd for $C_{12}H_{20}N_2O_4$: C, 56.23; H, 7.87; N, 10.93%.

*Methyl 2,7-Di-*N*-acetyl-2,3,4,6,7-pentadeoxy-*α-D-erythro-*heptopyranoside* (**17**). Compound **16** (20 mg) was hydrogenated in ethanol (10 ml) in the presence of Raney nickel under hydrogen atmosphere (3.4 kg/cm^2) overnight. The catalyst was filtered off and the solution was concentrated. The residue was recrystallized from ether–methanol to give

19.5 mg (97%) of **17**, mp 207—208 °C, $[\alpha]_D^{20}$ +122.6° (*c* 0.47, methanol). ^{1}H NMR: δ 2.03 (s, 6, 2×NAc), 3.54 (s, 3, OCH_3), 4.79 (d, 1, $J_{1,2}$=3.2 Hz, H-1).

Found: C, 55.52; H, 8.43; N, 10.94%. Calcd for $C_{12}H_{22}N_2O_4$: C, 55.79; H, 8.59; N, 10.85%.

*Methyl 2,6-Di-*N*-acetyl-7-*O*-acetyl-2,3,4,6-tetradeoxy-β-*L*-lyxo-heptopyranoside (**18**).* A solution of **16** (109 mg) in glacial acetic acid (3 ml) was heated at 50 °C for 1 h and concentrated. The residue was neutralized with a $NaHCO_3$ solution and extracted with ethyl acetate. After being dried over Na_2SO_4, the ethyl acetate layer was concentrated. The residue was triturated in ether to give 119 mg (88%) of an amorphous product. A portion of the product was recrystallized from ether–methanol to give analytically pure **18** as needles, mp 195—196 °C, $[\alpha]_D^{21}$ +73.2° (*c* 1.0, chloroform). ^{1}H NMR: δ 1.97 (s, 3, NAc), 2.03 (s, 6, NAc and OAc), 3.32 (s, 3, OCH_3).

Found: C, 52.93; H, 7.46; N, 8.95%. Calcd for $C_{14}H_{24}N_2O_6$: C, 53.15; H, 7.65; N, 8.86%.

*Methyl 2,6-Di-*N*-acetyl-2,3,4,6-tetradeoxy-β-*L*-lyxo-heptopyranoside (**19**).* A solution of **18** (89 mg) in methanolic ammonia (5 ml) was settled overnight in a refrigerator and concentrated. The residue was purified on a silica-gel column using 4 : 1 (v/v) benzene–ethanol as an eluant. Fractions homogeneous on TLC (R_f 0.13) in the same solvent system were combined and concentrated. The residue was recrystallized from ether–methanol to give 71 mg (92%) of **19**, mp 181—182 °C, $[\alpha]_D^{20}$ +70° (*c* 1.0, chloroform). ^{1}H NMR: δ 1.97 (s, 3, NAc), 2.04 (s, 3, NAc), 3.37 (s, 3, OCH_3), 4.58 (d, 1, $J_{1,2}$=3.2 Hz, H-1), 5.83 (d, 1, $J_{2,NH}$=8.9 Hz, NH), 6.23 (d, 1, $J_{6,NH}$=8.5 Hz, NH).

Found: C, 52.58; H, 7.98; N, 10.15%. Calcd for $C_{12}H_{22}N_2O_5$: C, 52.54; H, 8.09; N, 10.21%.

*Methyl 2,6-Di-*N*-acetyl-7-chloro-2,3,4,6,7-pentadeoxy-β-*L*-lyxo-heptopyranoside (**20**).* To a solution of **19** (198 mg) in acetonitrile (4 ml) was added a solution of triphenylphosphine (247 mg) in carbon tetrachloride (8 ml). The reaction mixture was heated for 2 h and concentrated. The residue was purified on a silica gel column using 5:1 (v/v) benzene–ethanol as an eluant. Fractions homogeneous on TLC (R_f 0.38) in 4 : 1 (v/v) benzene–ethanol were combined and concentrated to give 129 mg (61%) of **20** as a syrup.

*Methyl 2,6-Di-*N*-acetyl-2,3,4,6,7-pentadeoxy-β-*L*-lyxo-heptopyranoside (Methyl 2,6-Di-*N*-acetyl-6-epi-α-*D*-purpurosaminide B) (**21**).* Tributylstannane (0.8 ml) and a small amount of α,α′-azobisisobutyronitrile were added to a solution of **20** (129 mg) in dry dioxane (20 ml). The mixture was heated at 80—90 °C for 2 h under nitrogen atmosphere and then concentrated. The residue was washed with hexane and purified on a silica-gel column using 5:1 (v/v) benzene–ethanol. Fractions homogeneous on TLC (R_f 0.32) in 4:1 (v/v) benzene–ethanol were combined and concentrated to give 64 mg (56%) of **21**, mp 212—213 °C, $[\alpha]_D^{20}$ +63.3° (*c* 1.0, methanol). (Found: C, 55.58; H, 8.46; N, 10.66%). The ^{1}H NMR and IR spectra were superimposable with those of an authentic sample prepared by methanolysis of tetra-*N*-acetylfortimicin B,[5] mp 212—213 °C, $[\alpha]_D^{20}$ +62.9° (*c* 0.98, methanol). The mixed melting point determination of **21** with the authentic sample showed no depression of melting point.

References

1) A preliminary communication presented at the American Chemical Society/Chemical Society of Japan Chemical Congress, Honolulu, Hawaii, April 5, 1979. Abstract CARB 9; T. Suami, Y. Honda, and T. Kato, *Chem. Lett.*, **1978**, 1125.

2) T. Nara, M. Yamamoto, I. Kawamoto, K. Takayama, R. Okachi, S. Takasawa, T. Sato, and S. Sato, *J. Antibiot.*, **30**, 533 (1977).

3) R. Okachi, S. Takasawa, T. Sato, S. Sato, M. Yamamoto, I. Kawamoto, and T. Nara, *J. Antibiot.*, **30**, 541 (1977).

4) P. J. L. Daniels, "Aminoglycoside antibiotics," ed by S. Mitsuhashi, Univ. of Tokyo Press. Tokyo (1975) pp 77—106.

5) R. S. Egan, R. S. Stanaszek, M. Cirovic, S. L. Mueller, J. Tadanier, J. R. Martin, P. Collum, A. W. Goldstein, R. L. De Vault, A. C. Sinclair, E. E. Fager, and L. A. Mitscher, *J. Antibiot.*, **30**, 552 (1977).

6) D. J. Cooper, M. D. Yudis, H. M. Marigliano, and T. Traubel, *J. Chem. Soc., C*, **1971**, 2876.

7) D. J. Cooper, P. J. L. Daniels, M. D. Yudis, H. M. Marigliano, R. D. Guthrie, and S. T. K. Bukhari, *J. Chem. Soc., C*, **1971**, 3126.

8) R. D. Guthrie and G. J. Williams, *J. Chem. Soc., Chem. Commun.*, **1971**, 923.

9) R. D. Guthrie and G. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, **1972**, 2619.

10) S. Umezawa, T. Tsuchiya, and Y. Okazaki, *Bull. Chem. Soc. Jpn.*, **44**, 3494 (1971).

11) J. Cleophax, J. Leboul, A. Olesker, and S. D. Gero, *Tetrahedron Lett.*, **1973**, 4911.

12) J. S. Brimacombe, I. Da'aboul, and L. C. N. Tucker, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 263.

13) J. S. Brimacombe, I. Da'aboul, and L. C. N. Tucker, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 979.

14) M. Chmielewski, A. Konowal, and A. Zamojski, *Carbohydr. Res.*, **70**, 275 (1979).

15) R. W. Jeanloz, *J. Am. Chem. Soc.*, **74**, 4597 (1952).

16) G. H. Jones and J. G. Moffatt, "Methods in Carbohydrate Chemistry," Academic Press, New York (1972), Vol. 6, p. 315.

17) H. Saeki and E. Ohki, *Chem. Pharm. Bull.*, **18**, 789 (1970).

18) W. D. Rhoads and P. H. Gross, *Carbohydr. Res.*, **11**, 561 (1969).

19) J. S. Brimacombe, J. A. Miller, and U. Zakir, *Carbohydr. Res.*, **41**, C3 (1975).

20) D. H. Buss, L. Hough, and A. C. Richardson, *J. Chem. Soc.*, **1963**, 5295.

21) H. L. Spell, *Anal. Chem.*, **39**, 185 (1967).

22) C. F. Gibbs, L. Hough, and A. C. Richardson, *Carbohydr. Res.*, **1**, 290 (1965).

23) J. B. Lee and T. J. Nolan, *Can. J. Chem.*, **44**, 1331 (1966).

24) C. R. Haylock, L. D. Melton, K. N. Slessor, and A. S. Tracey, *Carbohydr. Res.*, **16**, 375 (1971).

25) G. J. M. Van der Kerk, J. G. Noltes, and J. G. A. Lujiten, *J. Appl. Chem.*, **7**, 366 (1957).

26) H. Arita and Y. Matsushima, *J. Biochem. (Tokyo)*, **70**, 795 (1971).

27) T. Suami, S. Nishiyama, Y. Ishikawa, and S. Katsura, *Carbohydr. Res.*, **53**, 239 (1977).