STUDIES ON NEW ANTIBIOTIC LIVIDOMYCINS. III
PARTIAL STRUCTURE OF LIVIDOMYCIN A

TAKESHI ODA, TOSHITO MORI and YOSHINORI KYŌTANI

Kowa Co., Ltd. Tokyo Research Laboratories,
Noguchi-cho, Higashimurayama, Tokyo, Japan

(Received for publication February 10, 1971)

The acid methanolysis of lividomycin A gave an amine, which was provisionally designated as C_{12}-amine*, and methyl lividotriosaminide. C_{12}-Amine was degraded to 2-deoxystreptamine and an amino sugar by acid hydrolysis of the N-acetyl derivative. The chemical structure of the amino sugar was determined to be 2-amino-2,3-dideoxy-D-glucopyranose or 3-deoxy-D-glucosamine from the NMR spectrum of peracetylated methyl glycoside of the amino sugar. An α-glycosidic linkage between 2-deoxystreptamine and 3-deoxy-D-glucosamine was shown by the NMR spectrum of N-acetyl C_{12}-amine, and N,N′-diacetyl-5,6-di-O-methyl-2-deoxystreptamine was obtained from permethylated N-acetyl C_{12}-amine. Therefore, C_{12}-amine is 4-O-(2-amino-2, 3-dideoxy-α-D-glucopyranosyl)-1, 3-diamino-1, 2, 3-trideoxy-*myo*-inositol or 3′-deoxy paromamine.

The physicochemical properties and biological activity of lividomycin A were reported previously[1]. This paper describes the structure of C_{12}-amine, which was obtained together with methyl lividotriosaminide by acid methanolysis of lividomycin A. The structures of methyl lividotriosaminide and lividomycin A are described in the next paper[2].

Lividomycin A sulfate (I) was easily solvolyzed by treatment with 0.4 N methanolic hydrogen chloride to give a crystalline amine, C_{12}-amine trihydrochloride (II), and a methyl glycoside, methyl lividotriosaminide dihydrochloride (III). Compound II was acetylated to give tri-N-acetyl C_{12}-amine (IV), which was further hydrolyzed with 2 N hydrochloric acid to yield 2-deoxystreptamine dihydrochloride (V) and an amino sugar, which was provisionally designated as C_6-amino sugar. Compound V was identical with an authentic sample obtained from neomycin in specific rotation, infrared absorption spectrum and melting point. The liberated C_6-amino sugar hydrochloride (VI) was acetylated to give N-acetyl C_6-amino sugar (VII). VII, when oxidized with sodium periodate, consumed 2.0 moles of periodate and yielded 0.74 mole of formaldehyde. This reaction mixture was further oxidized with bromine water and subsequently hydrolyzed with 1 N hydrochloric acid to give an amino acid (VIII), identical with D-aspartic acid in infrared absorption spectrum, melting point and specific rotation. When VI was reduced with sodium borohydride, acetylated and purified, N-acetyl dihydro-VII (IX) was obtained. Oxidation of IX with periodate and bromine water gave β-amino-γ-hydroxybutyric acid (X), which was identified by its

* C_{12}-Amine was reported as lividamine at the 174th meeting of Japan Antibiotic Research Association.

NMR spectrum. These results suggested that C_6-amino sugar was a 2-amino-2, 3-dideoxyhexose.

Thereafter, methyl N-acetyl-α-glycoside of C_6-amino sugar (**XI**) was obtained from the methylation of **VII** with BF_3-etherate in methanol and **XI** was further acetylated with acetic anhydride and pyridine, resulting in the formation of peracetyl-**XI** (**XII**). In the NMR spectrum of **XII** (Fig. 4), the coupling constants and chemical shifts indicated the proton at the C-2 position to be axial, the C-3 position to be unsubstituted and the configuration of the protons at C-4 and C-5 to be diaxial from which the structure of this compound, methyl triacetyl-3-deoxy-α-D-glucosaminide, was assigned as shown in Fig. 1 and the structure of C_6-amino sugar was determined to be 2-amino-2,3-dideoxy-D-glucopyranose or 3-deoxy-D-glucosamine.

In order to prove the structure of **VI**, it was synthesized by the method of modified MEYER ZU RECKENDORF and BONNER[3] as shown in Fig. 5. These authors stated that 2-amino-2, 3-dideoxy-D-glucopyranose hydrochloride was obtained as a powder with specific rotation $[\alpha]_D^{23}$ +13°. However, we have obtained **VI** as colorless crystals melting 132~135°C (d), and having specific rotation $[\alpha]_D^{25}$ +73.3° → +43.9° (*c* 1, H_2O). This synthetic compound was identical with **VI** obtained from lividomycin A in specific rotation, melting point and infrared absorption spectrum.

Because C_{12}-amine is non-reducing, a glycosidic linkage must exist between 2-deoxystreptamine and 3-deoxy-D-glucosamine, and the NMR spectrum of **IV** exhibited a signal for the anomeric proton at $\delta_{DSS}^{D_2O}$ 5.26 ppm (1H, d, J=4 cps), establishing the

Fig. 1

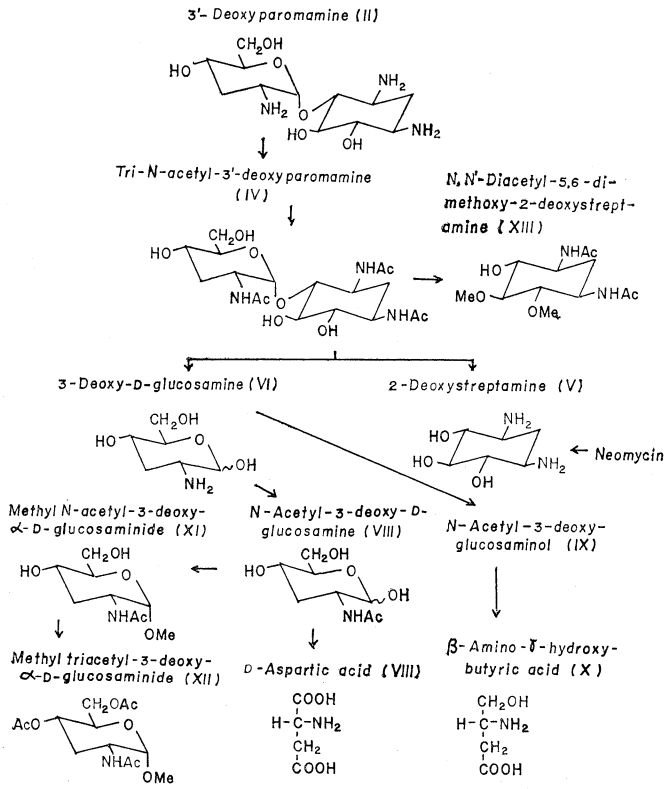
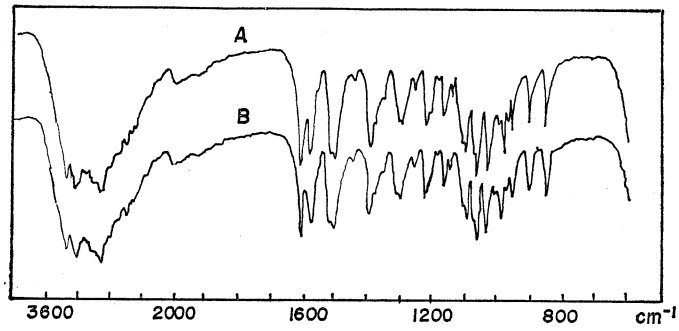


Fig. 2. Infrared absorption spectra of 2-deoxystreptamine dihydrochloride (KBr tablet)
A : from lividomycin A B : from neomycin



presence of an α-glycosidic linkage. Further, the signal for the methyl protons of the acetyl group at $\delta^{D_2O}_{DSS}$ 1.93 ppm (9H, s) indicated that the amino group of 3-deoxy glucosamine was equatorial[4]. The fact that oxidation with periodate and subsequent hydrolysis of **IV** resulted in the production of **VI**, also showed that 3-deoxy-D-glucosamine had a pyranose form in C_{12}-amine.

In order to determine the position where the 2-deoxystreptamine was linked, **IV** was methylated by the method of LEMIEUX and CUSHLEY[5], hydrolyzed and subsequently N-acetylated to give N, N'-diacetyl-5, 6-di-O-methyl-2-deoxystreptamine (**XIII**), which was identical with an authentic sample similarly obtained from N-acetylparomamine, which originated from paromomycin, in infrared absorption spectrum, melting point and optical rotatory dispersion.

These data show that C_{12}-amine is 4-O-(2-amino-2, 3-dideoxy-α-D-glucopyranosyl)-1, 3-diamino-1, 2, 3-trideoxy-*myo*-ionsitol or 3'-deoxy paromamine.

Experimental

Lividomycin A sulfate (I):

Anal. Calcd. for $C_{29}H_{55}N_5O_{18}\cdot{}^5/_2H_2SO_4\cdot 2H_2O$: C 33.43, H 6.19, N 6.72, S 7.69.
Found : C 33.55, H 6.25, N 6.84, S 7.81.

Isolation of C_{12}-amine trihydrochloride (II) and methyl lividotriosaminide dihydrochloride (III):

A solution of **I** (10 g) in 900 ml of 0.4 N methanolic hydrogen chloride refluxed for 10 hours. After overnight refrigeration, the precipitate of **II** was collected by filtration and purified by recrystallization from H_2O-MeOH, yield 3.74 g, m. p. 206~208°C (d). $[\alpha]_D^{25}$ +67° (*c* 0.5, H_2O).

Anal. Calcd. for $C_{12}H_{25}N_3O_6\cdot 3HCl\cdot H_2O$: C 33.15, H 6.96, N 9.67, Cl 24.24.
Found : C 33.14, H 6.95, N 9.61, Cl 24.05.

The mother liquor from **II** was concentrated *in vacuo*. The residue was dissolved in water, neutralized with Dowex 3(OH^-), and adsorbed on a column of CM-Sephadex C-25(NH_4^+) (60×4 cm). Methyl lividotriosaminide was eluted with 0.028 N NH_4OH, and the effluent was concentrated *in vacuo*, dissolved in a small amount of 2 N HCl, and finally lyophilized after treating with active carbon, yield 3.18 g of a colorless powder (**III**), m. p. 168~173°C (d).

Anal. Calcd. for $C_{18}H_{34}N_2O_{13}\cdot 2HCl$: C 38.65, H 6.49, N 5.01, Cl 12.68.
Found : C 38.70, H 6.62, N 5.23, Cl 12.44.

Tri-N-acetyl C_{12}-amine (IV):

A solution of **II** (3.4 g) in water was adsorbed on a column of CM-Sephadex C-25 (NH_4^+) (60×4 cm), and eluted with 0.35 N NH_4OH. The ninhydrin-positive effluent was evaporated *in vacuo* to give C_{12}-amine free base. This was dissolved in 300 ml of absolute MeOH, and 5 ml of acetic anhydride was added. After stirring at room temperature for 15 minutes, white crystals (**IV**) were collected by filtration and recrystallized from acetic acid and acetone, yield 3 g, m. p. 274~276°C (d). $[\alpha]_D^{22}$ +92.2° (*c* 1.25, H_2O). NMR $\delta^{D_2O}_{DSS}$ 5.26 ppm (1H, d, J=4 cps), 1.93 ppm (3H×3, s).

Anal. Calcd. for $C_{18}H_{31}N_3O_9\cdot H_2O$: C 47.89, H 7.37, N 9.31.
Found : C 48.18, H 7.53, N 9.28.

Isolation of 2-deoxystreptamine dihydrochloride (V) and C_6-amino sugar hydrochloride (VI) from the acid hydrolysate of IV:

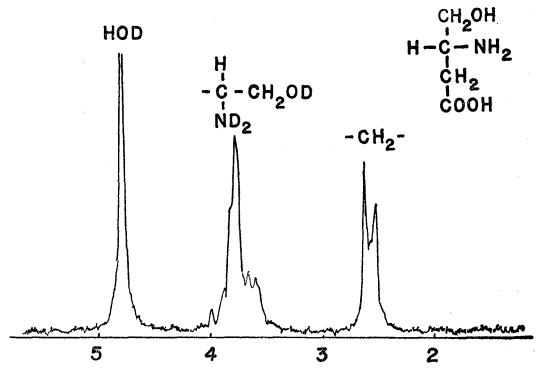
A solution of **IV** (3.55 g) in 2 N HCl (200 ml) was heated on a boiling water bath for 3 hours, then evaporated. The residue was dissolved in water, adsorbed on a column of

Dowex 50×2 (H^+) (24×2 cm). **VI** was eluted first with 0.07 N HCl. The effluent was collected, evaporated and recrystallized from MeOH and acetone, yield 1.03 g of crystals (**VI**).

Afterward, 2-deoxystreptamine dihydrochloride was eluted with 2 N or 3 N HCl. The ninhydrin-positive effluent was collected, concentrated and recrystallized from H_2O - EtOH, yield 1.2 g. m. p. 255~260°C (d). $[\alpha]_D^{25}$ 0° (*c* 1, H_2O).

Anal. Calcd. for $C_6H_{14}N_2O_3 \cdot 2HCl$:
C 30.65, H 6.86, N 11.92, Cl 30.16.
Found :
C 30.92, H 6.91, N 11.76, Cl 29.91.

Fig. 3. Nuclear magnetic resonance spectrum of β-amino-γ-hydroxy butyric acid.
(60 MHz in D_2O, DSS internal standard)



The **V** was identical with an authentic sample obtained from neomycin in specific rotation, melting point and infrared absorption spectrum.

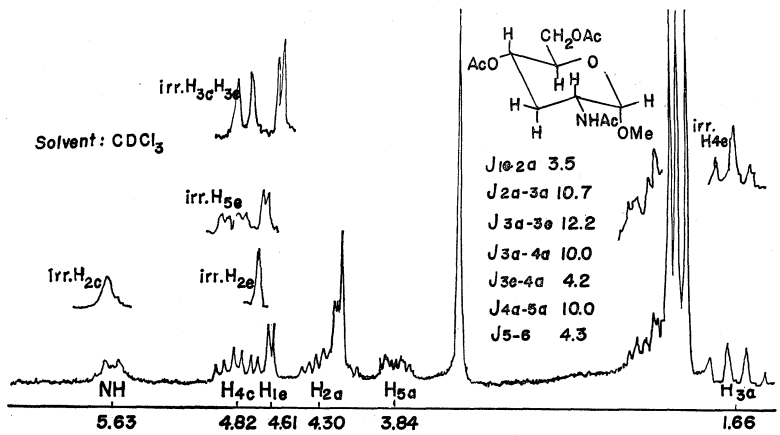
Isolation of **VI** from periodate oxidation of **IV**:

Two grams (0.00462 mole) of **IV** were added to a solution of 1.976 g (0.00924 mole) of $NaIO_4$ in 465 ml of water (1.99×10^{-5} mole/ml), the reaction mixture was stirred in the dark at room temperature for 18 hours, and 0.01 mole of ethylene glycol was added to terminate the oxidation reaction. The mixture then was stored for one hour, and concentrated *in vacuo*, the residue was dissolved in water and passed through a column of Dowex 50×2 (H^+) (20×2 cm). The effluent gave a syrup on concentration. A solution of the syrup in 4 N HCl (115 ml) was heated on a boiling water bath for 2 hours, concentrated to dryness, then dissolved in water. The solution was neutralized with Dowex 3 (OH^-) and adsorbed on a column of Dowex 50×2 (H^+) (50×2 cm) and the ninhydrin-positive effluent was eluted with 0.2 N HCl, collected and concentrated to dryness after treatment with active carbon. The residue was repeatedly extracted with EtOH, and the extract was concentrated to dryness and recrystallized from MeOH and acetone, yield 600 mg, m. p. 132~135°C (d). $[\alpha]_D^{25}$ +74° → +44.4° (*c* 1, H_2O). NMR $\delta_{DSS}^{D_2O}$ 5.30 ppm (d, J=4 cps), 4.85 ppm (d, J=9 cps).

Anal. Calcd. for $C_6H_{13}NO_4 \cdot HCl$: C 36.10, H 7.07, N 7.02, Cl 17.76.
Found : C 36.03, H 7.12, N 7.12, Cl 17.53.

The specific rotation of a synthetic sample (3-deoxy-D-glucosamine) was $[\alpha]_D^{25}$ +73.3° → +43.9° (*c* 1.05, H_2O).

Fig. 4. Nuclear magnetic resonance spectrum of methyl N-acetyl-4, 6-di-O-acetyl-3-deoxy-α-D-glucosaminide.
(100 MHz in $CDCl_3$, TMS external standard)



N-Acetyl C_6-amino sugar (**VII**):

According to the method of ROSEMAN and LUDOWIEG[6], 20 g of Dowex 1×2 (carbonate form) and 2 ml of acetic anhydride were added to a solution of 1.02 g of **VI** in 100 ml of MeOH, and the mixture was stirred in ice for 100 minutes, then the resin was removed from the mixture and the filtrate was concentrated to a colorless syrup. The syrup was crystallized from EtOH and ether, yield 1.17 g. m. p. 151~152°C (d). $[\alpha]_D^{25}$ +54.1°→+26.1° (*c* 1, H_2O). NMR $\delta_{DSS}^{D_2O}$ 1.98 ppm (3H, s).

Anal. Calcd. for $C_8H_{15}NO_5$: C 46.82, H 7.37, N 6.83.
Found : C 46.76, H 7.53, N 6.97.

Isolation of D-aspartic acid (**VIII**) from **VII**:

When a solution of **VII** (1.17 g) in 204 ml of $NaIO_4$ solution (10^{-4} mole) was stirred in the dark at room temperature for 11.5 hours, 2.0 moles of $NaIO_4$ were consumed and 0.74 mole of formaldehyde was formed as determined by the usual method[7]. After ethylene glycol was added to the reaction mixture, silica gel was added, the mixture was evaporated and the residue was added to the top of a column of silica gel (30×1.5 cm). A portion of aldehyde was eluted with $CHCl_3$ - 10 % MeOH and extracted with water. Without concentrating, this solution was neutralized with $BaCO_3$, and Br_2 (4.5 g) was added. The mixture was stirred for 38 hours at room temperature in the dark and concentrated to dryness after removal of excess bromine by aeration. The residue was dissolved in 1 N HCl and heated for 2 hours on a boiling water bath. The hydrolysate was concentrated to dryness, adsorbed on a column of Dowex 1×2 (OH^-) (20×5 cm), and eluted with 0.08 N acetic acid. The ninhydrin-positive effluent was collected, concentrated and recrystallized from water and acetone to yield 100 mg of white crystals (**VIII**), m.p. 270°C (d). $[\alpha]_D^{24}$ −23.6° (*c* 1.06, 6 N HCl).

Anal. Calcd. for $C_4H_7NO_4$: C 36.09, H 5.30, N 10.52.
Found : C 36.02, H 5.39, N 10.53.

The specific rotation of an authentic sample was $[\alpha]_D^{24}$ −23.7° (*c* 2.02, 6 N HCl).

N-Acetyl dihydro C_6-amino sugar (**IX**):

Sodium borohydride (200 mg) was added to an aqueous solution of **VI** (100 mg). After the reducing property of the mixture had been lost, the mixture was adsorbed on a column of CM-Sephadex C-25 (NH_4^+) (30×1 cm) and gradient eluted with 0.05 N to 0.2 N NH_4OH. The ninhydrin-positive and TTC*[8]-negative effluent was collected, concentrated to dryness, and acetylated with 5 ml of acetic anhydride in 10 ml of MeOH at room temperature. The residue from concentration of the solution was recrystallized from MeOH and acetone, yield 70 mg of needle crystals (**IX**), m.p. 87~88°C. $[\alpha]_D^{23}$ −14.3° (*c* 1.2, H_2O).

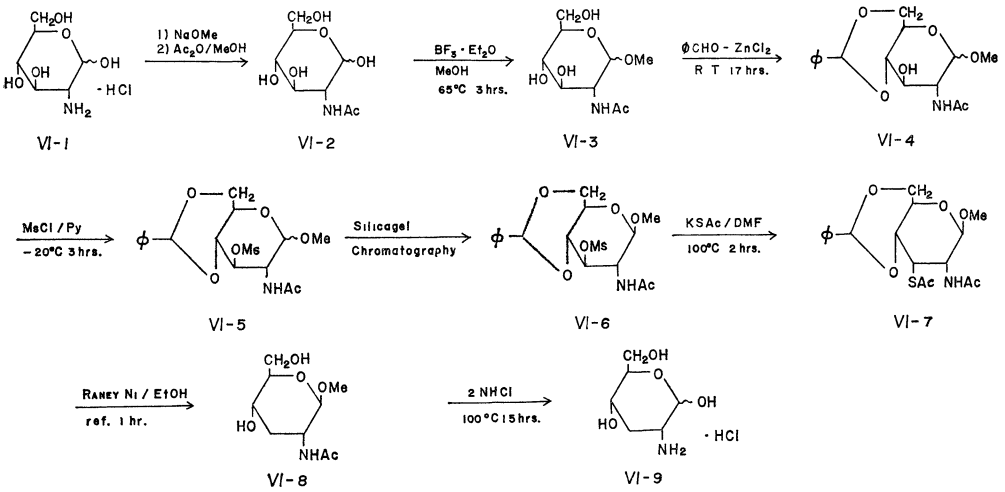
Anal. Calcd. for $C_8H_{15}NO_5$: C 46.37, H 8.27, N 6.76.
Found : C 46.22, H 8.20, N 6.53.

Isolation of β-amino-γ-hydroxy butyric acid (**X**) from **IX**:

To a solution of **IX** (60.7 mg) in water, $NaIO_4$ (213.9 mg) was added and the mixture was stirred in the dark at room temperature overnight. After ethylene glycol was added, the mixture was oxidized with Br_2 (435 mg) and $BaCO_3$ (1.2 g) for 20 hours in the dark. The excess bromine was removed by aeration and the solution was passed through a column of Dowex 50×2 (H^+). The effluent was evaporated to dryness and the residue was dissolved in 2 N HCl and heated on a boiling water bath for 3 hours. The hydrolysate was concentrated to dryness and redissolved in water. This aqueous solution was adsorbed on a column of Dowex 1×2 (OH^-) (40×1 cm). The ninhydrin-positive fraction which was gradient eluted between water and 0.5 N acetic acid, was concentrated to dryness and recrystallized from water, yield 25 mg of white crystals (**X**), m.p. 208~210°C (d). $[\alpha]_D^{25}$ +18.1° (*c* 2.1, H_2O). IR ν^{KBr} 1055 cm^{-1} (primary hydroxy group). NMR $\delta_{DSS}^{D_2O}$ 2.5 ppm (2H, d).

* TTC : Triphenyltetrazolium chloride (200 mg)/0.5 N methanolic NaOH (10 ml).

Fig. 5. Synthesis of 2-amino-2, 3-dideoxy-D-glucose.

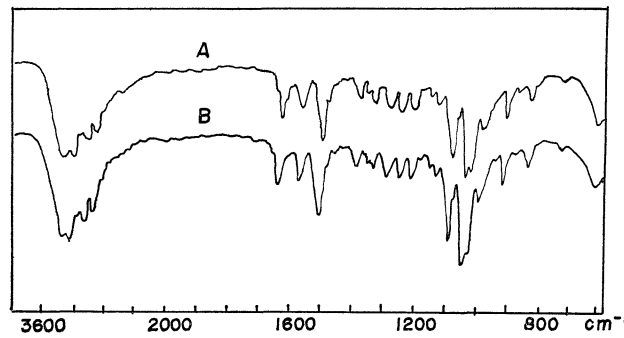


Anal. Calcd. for $C_4H_9NO_3$:
C 40.33, H 7.63, N 11.76.
Found :
C 40.13, H 7.65, N 11.84.

Methyl N-acetyl-α-glycoside of C_6-amino sugar (XI) :

To a solution of **VII** (5 g) in MeOH (50 ml), BF_3-etherate(1 ml) was added. The solution was heated at reflux for 3.5 hours, then concentrated to dryness and the residue was dissolved in water and desalted. The solution was evaporated to give white crystals (**XI**) and recrystallized from EtOH, yield 3 g, m. p. 206~209°C (d). $[\alpha]_D^{23}$ +112.2° (*c* 2.13, H_2O).

Fig. 6. Infrared absorption spectra of 3-deoxy-D-glucosamine hydrochloride (KBr tablet)
A : from lividomycin A B : synthethized sample



Anal. Calcd. for $C_9H_{17}NO_5$: C 49.31, H 7.82, N 6.39.
Found : C 49.16, H 7.69, N 6.40.

Methyl N-acetyl-4, 6-di-O-acetyl-3-deoxy-α-D-glucosaminide (XII) :

A mixture of **XI** (50 mg), pyridine (10 ml) and acetic anhydride (5 ml) was kept at room temperature overnight, then the mixture was evaporated to dryness and recrystallized from acetone and petroleum ether, yield 30 mg of white needles (**XII**), m. p. 134~135°C (d). $[\alpha]_D^{26}$ +90° (*c* 0.12, MeOH).

Anal. Calcd. for $C_{13}H_{21}NO_7$; C 51.45, H 6.93, N 4.43.
Found : C 51.48, H 6.98, N 4.62.

Methyl N-acetyl-4,6-O-benzylidene-3-O-methanesulphonyl-β-D-glucosominide (VI-6) :

Compound (**VI-6**) was obtained from methyl N-acetyl-4,6-O-benzylidene-D-glucosaminide (**VI-4**), m.p. 193~194°C (d), $[\alpha]_D^{25}$ −58° (*c* 0.77, DMSO), NMR $\delta_{TMS}^{CDCl_3}$ 2.05 ppm (3H, S), 2.96 ppm (3H, s), 3.55 ppm (3H, s), 5.05 ppm (1H, d, J=8 cps), 5.58 ppm (1H, s), 6.0 ppm (1H, broad), 7.44 ppm (5H).

Anal. Calcd. for $C_{17}H_{23}NO_8S$: C 50.86, H 5.78, N 3.49, S 7.99.
Found : C 50.54, H 5.76, N 3.61, S 7.81.

This material was reported to have melting point 195~196°C and $[\alpha]_D^{23}$ −63° (*c* 1.1, DMSO) in literature[3].

Methyl N-acetyl-4,6-O-benzylidene-3-deoxy-3-thioacetyl-β-D-glucosaminide (**VI-7**):

The mesylate (**VI-6**, 1.5 g) was heated with potassium thioacetate (2.1 g) in dimethylformamide (24 ml) for 2 hours at 100°C, and the mixture was poured into water and extracted with chloroform. The chloroform layer was washed with water, dried and evaporated *in vacuo*, whereupon addition of a small amount of water caused crystallization of the residue. The solid was recrystallized from isopropanol, yield 1.05 g, m.p. 235.5~236.5°C (d), $[\alpha]_D^{25}$ −117° (*c* 1.14, $CHCl_3$). NMR $\delta_{TMS}^{CDCl_3}$ 1.96 ppm (3H, s), 2.40 ppm (3H, s), 3.48 ppm (3H, s), 5.56 ppm (1H, s), 5.7 ppm (1H, broad), 7.34 ppm (5H).

Anal. Calcd. for $C_{18}H_{23}NO_6S$: C 56.68, H 6.08, N 3.67, S 8.41.
Found : C 56.87, H 6.33, N 3.71, S 8.59.

This material was reported to have melting point 232~233°C and $[\alpha]_D^{23}$ −120° (*c* 1.3, $CHCl_3$) in literature[3].

Methyl N-acetyl-3-deoxy-β-D-glucosaminide (**VI-8**):

VI-7 (920 mg) was heated with RANEY nickel W_4 (7.8 g) in refluxing absolute ethanol (40 ml) for one hour, the catalyzer filtered off and was washed with MeOH - H_2O. The combined filtrate and wash were evaporated to give colorless syrup. The syrup was recrystallized from MeOH - $CHCl_3$, yield 520 mg, m.p. 150~151°C (d), $[\alpha]_D^{25}$ −49° (*c* 1, H_2O). NMR $\delta_{DSS}^{D_2O}$ 1.6 ppm (1H, m), 2.05 ppm (3H, s), 2.35 ppm (1H, m), 3.59 ppm (3H, s), 4.53 ppm (1H, d, J=8 cps).

2-Amino-2,3-dideoxy-D-glucose hydrochloride (**VI-9**):

VI-8 (430 mg) was dissolved in 2 N HCl and heated on a boiling water bath for 1.5 hour. The solution was neutralized with Dowex-3 (OH^-), adsorbed on a column of Dowex 50×2 (H^+) (30×1 cm). The ninhydrin-positive fraction which was eluted with 0.03 N HCl, was concentrated *in vacuo*, then the syrup was recrystallized from MeOH - acetone, yield 295 mg, $[\alpha]_D^{25}$ +73.3° → +43.9° (*c* 1.05, H_2O).

This synthetic sample was identical with authentic sample obtained from lividomycin A in specific rotation, melting point and infrared absorption spectrum.

N, N′-Diacetyl-5,6-di-O-methyl-2-deoxystreptamine (**XIII**):

A suspension of **IV** (500 mg) in dimethylformamide (21 ml) was stirred with MeI (10 ml) and Ag_2O (4 g) at room temperature in the dark for 2 hours, Ag_2O (2 g) was added again and stirring was continued for 15 hours, then the insoluble material was removed, and the filtrate was evaporated. The residue was extracted with hot MeOH, and the methanolic solution was evaporated and redissolved in 18 ml of

Fig. 7. Infrared absorption spectra of N, N′-diacetyl-5,6-di-O-methyl-2-deoxystreptamine (KBr tablet)
A : from lividomycin A. B : from paromomycin

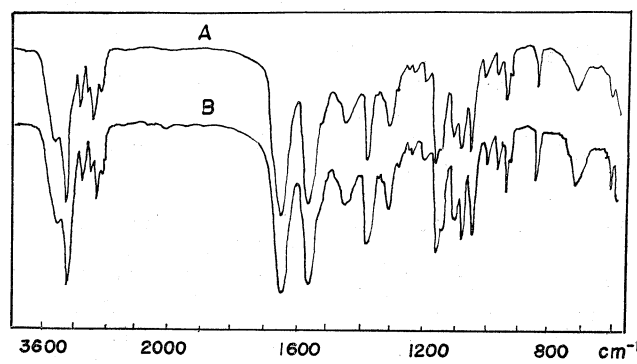
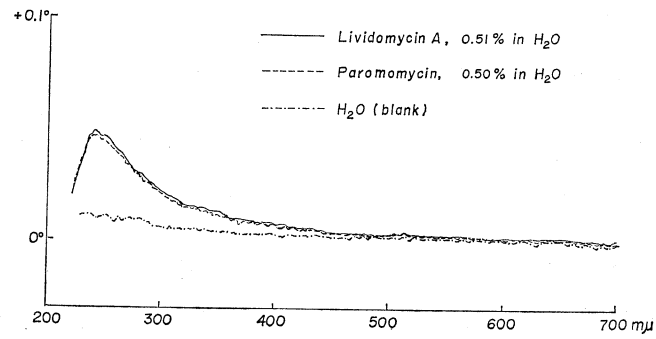


Fig. 8. Optical rotatory dispersion curves of N, N′-diacetyl-5,6-di-O-methyl-2-deoxystreptamine.



2 N HCl. This solution was heated on a boiling water bath for 3 hours and concentrated to dryness. The residue was dissolved in water and passed through a column of Dowex 1×2 (OH^-). The effluent was evaporated and acetylated with acetic anhydride (2 ml) in MeOH (20 ml). Then the solvent was removed and the residue was redissolved in water, desalted and yielded 300 mg of syrup after evaporation. This product was separated by preparative thin-layer chromatography on silica gel using as solvent $CHCl_3$ - MeOH (6 : 1). The portion showing Rf 0.17 on the thin-layer chromatography was extracted and recrystallized from EtOH, yield 74 mg of white crystals (**XIII**), m.p. 306~309°C (d). $[\alpha]_D^{20}$ +2° (*c* 1.1, H_2O). NMR $\delta_{DSS}^{D_2O}$ 3.52 ppm (3H, s), 3.62 ppm (3H, s), 2.00 ppm (6H, s).

Anal. Calcd. for $C_{12}H_{22}N_2O_5$: C 52.54, H 8.08, N 10.21.
Found : C 52.20, H 8.06, N 10.04.

Acknowledgements

The authors wish to acknowledge Dr. H. UMEZAWA, Dr. S. KONDO, Institute of Microbial Chemistry, and Dr. K. MUNAKATA, Department of Agricultural Chemistry, Nagoya University, for their helpful advices and encouragement in the performance of this work, and to thank Dr. T. TAKITA and Dr. H. NAGANAWA, Institute of Microbial Chemistry, for NMR (100 MHz) measurement and their kind advices in this work.

References

1) MORI, T.; T. ICHIYANAGI, H. KONDO, K. TOKUNAGA, T. ODA & K. MUNAKATA : Studies on new antibiotic lividomycins. II. Isolation and characterization of lividomycins A, B and other aminoglycosidic antibiotics produced by *Streptomyces lividus*. J. Antibiotics 24 : 339~346, 1971
2) ODA, T.; T. MORI, Y. KYOTANI & M. NAKAYAMA : Studies on new antibiotic lividomycins. IV. Structure of lividomycin A. J. Antibiotics 24 : 511~518, 1971
3) MEYER ZU RECKENDORF, W. & W. A. BONNER : Sulphur substitution compounds of aminosugars. V. The synthesis of 2-amino-2, 3-dideoxy-3-mercapto-D-allose and -D-glucose derivatives by displacement reactions. Tetrahedron 19 : 1711~1720, 1963
4) LICHTENTHALER, F. W. & H. LEINERT : NMR Studien an Zucker und Cyclanolen, II. Ber. Dtsch. Chem. Ges. 99 : 903~907, 1966
ONODERA, K. & S. HIRANO : The conformation of some pyranose moieties in the molecules of α-D-hexopyranose-1-phosphates, purine and pyrimidine 5′-(α-D-pyranosyl pyrophosphates), and mucopolysaccharides. Biochem. & Biophys. Res. Comm. 25 : 239~245, 1966
5) LEMIEUX, R. U. & R. J. CUSHLEY : The configuration of deoxystreptamine. Canad. J. Chem. 41 : 858~862, 1963
6) ROSEMAN, S. & J. LUDOWIEG : N-Acetylation of the hexosamines. J. Am. Chem. Soc. 76 : 301~302, 1954
7) DYER, J. R. : Use of periodate oxidations in biochemical analysis. Methods of Biochemical Analysis. Vol. 3, pp. 111~152, Interscience Publishers, Inc., 1956
8) MATTSON, A. N. & C. O. JENSEN : Colorimetric determination of reducing sugars with triphenyltetrazolium chloride. Anal. Chem. 22 : 351~355, 1950