

Communication to the editor

CHEMICAL CONVERSION OF
LIVIDOMYCIN A INTO
LIVIDOMYCIN B

Sir:

Lividomycin B was isolated from the fermentation broth of *Streptomyces lividus* nov. sp. in addition to lividomycin A^{1,2}. The structure of lividomycin A was determined³, the structure of lividomycin B was presumed to be demannosyllividomycin A as shown in Fig. 1. Therefore, it should be possible to convert lividomycin A into lividomycin B by the elimination of the mannose moiety.

This communication describes the chemical conversion of lividomycin A into lividomycin B by elimination of the mannose moiety using the method of the BARRY degradation⁴ and provides the structural confirmation of lividomycin B.

An aqueous solution (400 ml) of penta-N-acetyllividomycin A (4.0 g), prepared with acetic anhydride and methanol from lividomycin A³, was treated with sodium periodate (2.12 g), with stirring, in the dark at room temperature for 20 hours. The reac-

tion mixture was treated with ethylene glycol (1 ml) and freed from iodate by precipitation with lead diacetate (2.0 g), the excess lead ions being removed with 3 N sulfuric acid (1.2 ml). The filtrate was heated with 10% acetic acid (10 ml) and phenylhydrazine (10 ml) on a boiling water bath for 3 hours. After the reaction mixture was extracted with chloroform, the aqueous layer was passed through columns of Am-

Fig. 1. Structure of lividomycins A and B.

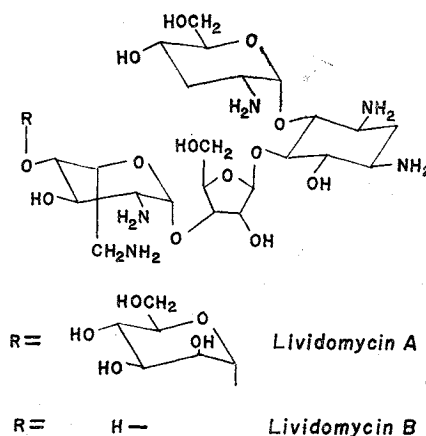


Table 1. Comparison of natural and chemically converted lividomycin B in physicochemical properties

	Natural	Converted
Melting point (dec. p.)	178~184°C	178~180°C
Specific rotation $[\alpha]_D^{25}$ (c 1, H ₂ O)	+62°	+63°
Elemental analyses. Calcd. for C ₂₃ H ₄₅ N ₅ O ₁₃ : C 46.07, H 7.56, N 11.68		
Found		
	C :	46.07
	H :	7.59
	N :	11.33
TLC using Silica Gel D-5 (Camag)*	A (Rf)	0.57
"	B (Rf)	0.26
"	C (Rf)	0.54
TLC using Aluminum oxide G (type E) (Merck)*	A (Rf)	0.79
Descending paper chromatography using No. 51 (Toyo)*	D (cm)	11.2
High-voltage electrophoresis 3000 V (1 mA/1 cm)*	E (Rm)	2.14
Retention time on isothermal gas chromatogram*	F (min.)	5.5

* A : Solvent system; upper layer of CHCl₃-MeOH-17% NH₄OH (2:1:1)

B : " ; n-BuOH-CH₃COOH-H₂O (1:1:1)

C : " ; MeOH-10% CH₃COONH₄ (1:1)

D : " ; n-BuOH saturated with H₂O - p-TsOH - t-BuOH (88:2:10), 20°C, 40 hours

E : Electrolyte solution: HCOOH-CH₃COOH-H₂O (22:75:900), pH 1.8

Toyo No. 51 filter paper. Rm; Relative mobility to alanine as 1.0

Detection: ninhydrin and bioassay

F : The column was a 0.3×100 cm glass tube, packed with 1.0% OV-1 on Gas-Chrom Q (100~120 mesh). The carrier was nitrogen at a flow rate of 30 ml/min. GLC was carried out at an oven temperature of 265°C.

berlite IR-120(H⁺) (80 ml) and Amberlite IRA-410(OH⁻) (80 ml). The effluent was lyophilized to obtain a pale yellow powder (2.6 g). This crude powder was confirmed to be penta-N-acetyllividomycin B by thin-layer chromatography of Silica Gel D-5 (Camag) using chloroform-methanol (1:1) (Rf 0.79).

The crude powder (2.0 g) in 4 N sodium hydroxide (60 ml) was heated on a boiling water bath for 5 hours. The reaction mixture was neutralized with 4 N hydrochloric acid, diluted with water and passed through a column (3.3×22 cm) of Amberlite IRC-50 (NH₄⁺). After it had been washed with water, the column was treated with 0.3 N ammonium hydroxide (500 ml) to elute a ninhydrin-positive effluent, which was rechromatographed on a column (2×70 cm) of CM-Sephadex C-25 (NH₄⁺) using gradient elution between 0.05 N (1,000 ml) and 0.12 N ammonium hydroxide (1,000 ml). The ninhydrin-positive and biologically active effluent was lyophilized and 1.1 g of a white powder was obtained in 60% yield from penta-N-acetyllividomycin A. The powder was identical with natural lividomycin B in infrared spectrum, other physicochemical properties (Table 1) and biological activities.

From this result, the structure of lividomycin B was proved to be 4-O-(2-amino-2,3-dideoxy- α -D-glucopyranosyl)-5-O-{3-O-(2,6-diamino-2,6-dideoxy- α -L-idopyranosyl)- β -D-ribofuranosyl}-1,3-diamino-1,2,3-trideoxy-*myo*-inositol.

Acknowledgement

The authors wish to acknowledge Dr. H. UMEZAWA, Institute of Microbial Chemistry, and Dr. K. MUNAKATA, Department of Agricultural Chemistry, Nagoya University, for their encouragement in the performance of this work.

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(Received October 9, 1971)

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