acterized as 2,3-acetonide (mp 222—224°, UV $\lambda_{\text{max}}^{\text{EtOH}}$ $m\mu$ (ϵ): 243 (11600), NMR (CDCl_3) δ : 0.81 (18- CH_3), 0.98 (19- CH_3), 1.36 (21- CH_3), 1.32, 1.49 (CH_3 groups in acetonide function), 4.99¹³) (23- H_A , d,d., $J=1.5$, 11 cps), 5.15¹³) (23- H_B , d,d., $J=1.5$, 17 cps), 5.81 (7-H, d., $J=2.5$ cps), 6.01¹³) (22- H_C , d,d., $J=11$, 17 cps)).

The ozonolysis of XX in dichloromethane-methanol mixture afforded the aldehyde XXII¹⁴) accompanied by a small amount of XIX. The selective Grignard reaction of XXI with 3-methyl-3-(tetrahydropyran-2-yloxy)butynyl magnesium bromide in tetrahydrofuran led to XXII with high stereospecificity. The catalytic hydrogenation of XXII with 10% palladium-charcoal in ethanol, followed by hydrolysis with 0.05N hydrochloric acid in 90% tetrahydrofuran gave the desired ecdysterone (mp 237—238°. UV $\lambda_{\text{max}}^{\text{EtOH}}$ $m\mu$ (ϵ): 243 (10300). NMR ($\text{C}_5\text{D}_5\text{N}$) δ : 1.06 (19- CH_3), 1.19 (18- CH_3), 1.36 (26- and 27- CH_3), 1.56 (21- CH_3), 6.20 (7-H), which was found to be identical with natural ecdysterone¹⁵) by direct comparison (mp, UV, IR, TLC and NMR).

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- 13) The protons of vinyl group was found as a typical ABC pattern: H_A , H_B and H_C were attributed as shown in Fig.
- 14) This aldehyde was unstable especially when impure, and accordingly, the characterization was not made.
- 15) Natural ecdysterone was kindly provided by Prof. T. Takemoto (Tohoku University).

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Isolation of Insect-Moulting Substances from *Blechnum amabile* and *Blechnum niponicum*

In a recent few years, we have clarified that a number of substances possessing insect-moulting hormone activity are distributed widely in ferns.¹⁾ In continuation of our work, we have further examined the methanol extracts of the whole plants of *Blechnum amabile* MAKINO and *B. niponicum* MAKINO²⁾ (Blechnaceae) grown in Japan which exhibit biological activity in the *Sarcophaga* assay. Thus, the polar fraction of each extract was subjected to chromatography over alumina and silica gel leading to the isolation of the following substances: ponasterone A, mp 268—269.5°, and ecdysterone, mp 245—246.5°, from B.

- 1) T. Takemoto, Y. Hikino, T. Arai, M. Kawahara, C. Konno, S. Arihara, and H. Hikino, *Chem. Pharm. Bull.* (Tokyo), **15**, 1816 (1967); T. Takemoto, Y. Hikino, T. Arai, C. Konno, S. Nabetani, and H. Hikino, *ibid.*, **16**, 759 (1968); T. Takemoto, S. Arihara, Y. Hikino, and H. Hikino, *ibid.*, **16**, 762 (1968); T. Takemoto, Y. Hikino, H. Jin, A. Arai, and H. Hikino, *ibid.*, **16**, 1636 (1968).
- 2) Japanese names: osashida and shishigashira, respectively.

amabile, and ponasterone A, mp 264—266°, ecdysterone, mp 243.5—244.5°, and a novel steroid with moulting hormone activity, mp 257—258°, which is named shidasterone,³⁾ from *B. niponicum*. It has been found that the contents of the three constituents of *B. niponicum* vary markedly depending upon the season and the location.

Of quite interest biogenetically is the co-existence of shidasterone and ecdysterone in the same plant, the former being a stereoisomer (most probably the 20-epimer) of the latter.³⁾ It is also worthy to note that, while 22-*epi*-ecdysterone shows no activity in the insect test,⁴⁾ shidasterone exhibits high activity.

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- 3) T. Takemoto, Y. Hikino, T. Okuyama, S. Arihara, and H. Hikino, *Tetrahedron Letters*, **1968**, 6095.
4) U. Kerb, R. Wicheert, A. Furlenmeier, and A. Fürst, *Tetrahedron Letters*, **1968**, 4277.

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Synthesis of 6,7-Dideoxy-6,7-epimino-1,2:3,4-di-O-isopropylidene- D (and L)-glycero- α -D-galacto-heptopyranose and Its Conversion into 6-Amino-6-deoxyheptose

Our recent papers¹⁾ described the preparation of some 5,6-epimino-hexofuranoses and the conversion of 5,6-epimino-D-glucofuranose derivative into a monosaccharide antibiotic, nojirimycin. Relative to these works, the present communication deals with synthesis of 6,7-(acetylepimino)-6,7-dideoxy-1,2:3,4-di-O-isopropylidene-D-glycero- α -D-galacto-heptopyranose (**1**) and its L-glycero epimer (**2**), and further transformation of these epimines into the corresponding 6-aminoheptoses (**3a** and **4a**). One of the aminoheptoses (**3a**) thereby obtained is assumed to be a promising intermediate for synthesizing lincosamine which constitutes a sugar component of an antibacterial antibiotic, lincomycin.

Treatment of 1,2:3,4-di-O-isopropylidene- α -D-galacto-hexodialdo-1,5-pyranose^{2,3)} with sodium cyanide in aqueous methanol afforded a mixture of 1,2:3,4-di-O-isopropylidene-L-glycero- α -D-galacto-heptopyranuronitrile (**5a**) and its D-glycero isomer (**6a**) in a good yield.³⁾ The relative ratio of epimers (**5a** and **6a**) in this mixture was determined as 1:1.8—2.5 by gas chromatographic analysis of the acetylated product. The cyanohydrin mixture was, without separation into each component, tosylated in pyridine to give a crystalline mass which was successfully separated into L-glycero-6-O-tosylate⁴⁾ (**5b**), needles, mp 152—154°, $[\alpha]_D^{20}$ —46.1° ($c=5.5$, CHCl₃), and the epimeric D-glycero-6-O-tosylate (**6b**), prisms or rods, mp 145—145.5°, $[\alpha]_D^{21}$ —110.4° ($c=2.3$, CHCl₃), by fractional recrystallization.

- 1) H. Saeki and E. Ohki, *Chem. Pharm. Bull.* (Tokyo), **16**, 2471, 2477 (1968); *idem, ibid.*, **17**, 1664 (1969).
2) D. Horton, J.B. Hughes, and J.M.J. Tronchet, *Chem. Commun.*, **1965**, 481; D. Horton, M. Nakadate, and J.M.J. Tronchet, *Carbohydr. Res.*, **7**, 56 (1968); G.B. Howarth, D.G. Lance, W.A. Szarek, and J.K.N. Jones, *Can. J. Chem.*, **47**, 75 (1969).
3) H. Saeki, T. Iwashige, E. Ohki, K. Furiyua, and M. Shirasaka, *Ann. Sankyo Res. Lab.*, **19**, 137 (1967).
4) All new compounds gave satisfactory elementary analyses.