acterized as 2,3-acetonide (mp 222—224°, UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (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), 4.99[13] (23-H$_A$, d.,d., J=1.5, 11 cps), 5.15[13] (23-H$_B$, d.,d., J=1.5, 17 cps), 5.81 (7-H, d., J=2.5 cps), 6.01[13] (22-H$_C$, d.,d., J=11, 17 cps)).

The ozonolysis of XX in dichloromethane–methanol mixture afforded the aldehyde XXI[14] 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 $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (ε): 243 (10300). NMR (C$_5$D$_5$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 ecdysterone[15] by direct comparison (mp, UV, IR, TLC and NMR).

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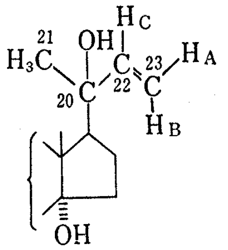
[13] The protons of vinyl group was found as a typical ABC pattern: H$_A$, H$_B$ and H$_C$ were attributed as shown in Fig.

[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* Makino[2] (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.

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[2] Japanese names: osashida and shishigashira, respectively.

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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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[Chem. Pharm. Bull. 17(9)1974—1976(1969)] *UDC 547.457.07*

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 papers[1] 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*-heptopyranurononitrile (**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-tosylate[4] (**5b**), needles, mp 152—154°, $[\alpha]_D^{20}$ −46.1° (c=5.5, $CHCl_3$), and the epimeric D-*glycero*-6-O-tosylate (**6b**), prisms or rods, mp 145—145.5°, $[\alpha]_D^{21}$ −110.4° (c=2.3, $CHCl_3$), by fractional recrystallization.

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[4] All new compounds gave satisfactory elementary analyses.

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