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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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.

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, *Carbohyd. 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. Furyua, and M. Shirasaka, *Ann. Sankyo Res. Lab.*, **19**, 137 (1967).
4) All new compounds gave satisfactory elementary analyses.

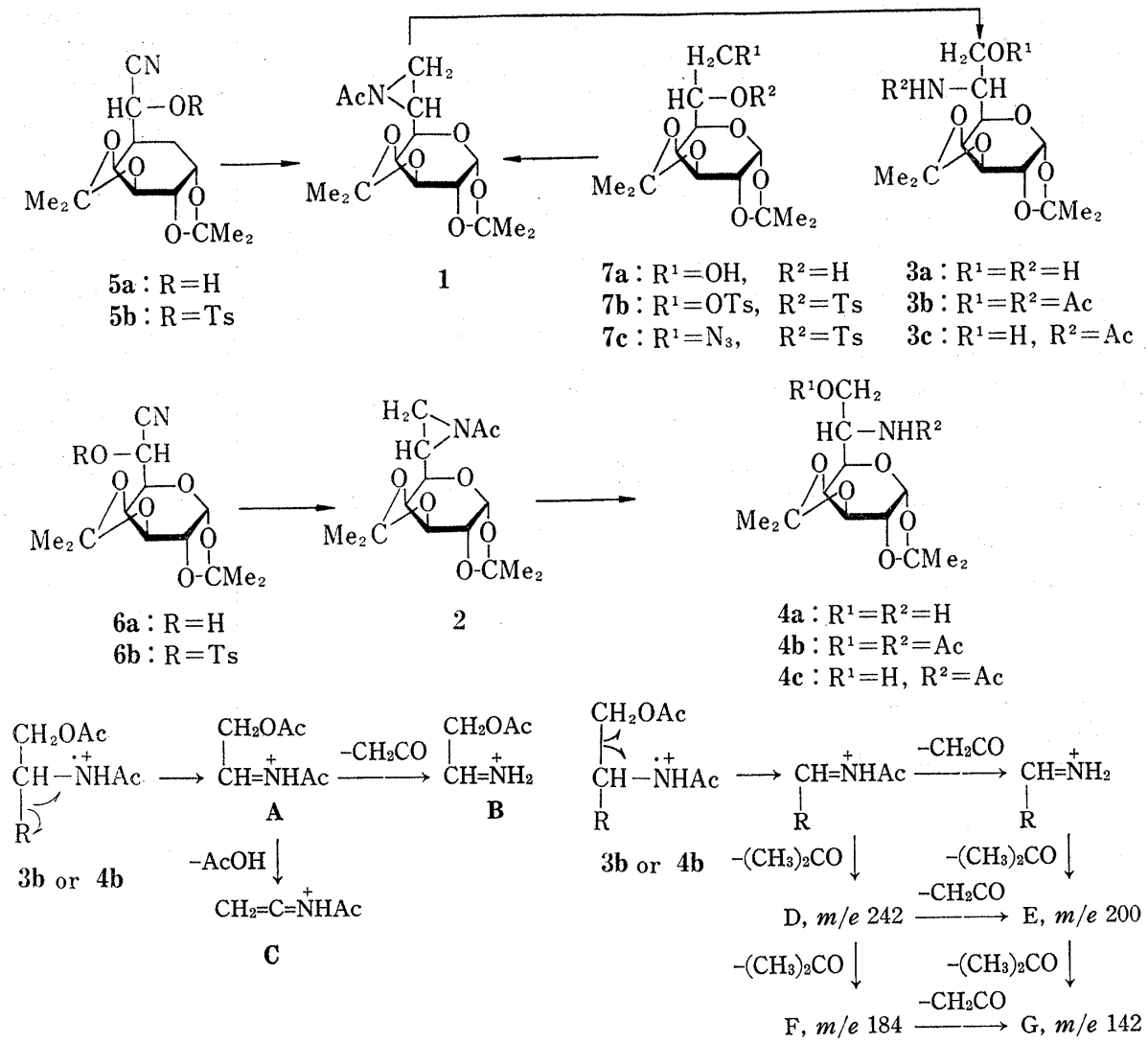

Chart 1

In 1967, Ichimura and Ohta[5] reported an ingenious method of preparing monosubstituted aziridine by treatment of α-chloronitrile with lithium aluminum hydride. Analogously, reduction of **5b** and **6b** with lithium aluminum hydride in ether, and successive N-acetylation gave 6,7-(acetylepimino)-6,7-dideoxy-1,2:3,4-di-O-isopropylidene-D-*glycero*-α-D-*galacto*-heptopyranose (**1**), syrup of $[\alpha]_D^{20}$ −50.9° (c=2.5, $CHCl_3$) and its L-*glycero* epimer (**2**), needles of mp 95—96°, $[\alpha]_D^{21}$ −121.0° (c=0.7, $CHCl_3$), respectively, in a fair yield. The presence of N-acetylepimino ring in the molecule of **1** and **2** was shown by a characteristic infrared absorption at 1710—1700 cm^{-1}. In order to ascertain the structure of these acetyl epimines, an unequivocal route to **1** was examined in the following way. Tosylation of 1,2:3,4-di-O-isopropylidene-L-*glycero*-α-D-*galacto*-heptopyranose[6] (**7a**) and successive treatmetn of the resultant syrupy ditosylate (**7b**), $[\alpha]_D^{21}$ −63.9° (c=2.4, $CHCl_3$), with sodium azide in dimetyhl sulfoxide gave 7-azido-7-deoxy-6-tosylate (**7c**), thick syrup of $[\alpha]_D^{21}$ −82.7° (c=1.7, $CHCl_3$). The azido-tosylate (**7c**) was reduced with lithium aluminum hydride in ether, as described in our previous papers,[1] to give 6,7-deoxy-6,7-epiminoheptose, whose N-acetyl derivative was identified with **1** by thin-layer chromatography, and infrared and nulcear magnetic resonance spectrometry.

5) K. Ichimura and M. Ohta, *Bull. Chem. Soc. Japan*, **40**, 432, (1967).
6) S. David and M.O. Popot, *Carbohyd. Res.*, **8**, 350 (1968).

These acetylepimines were also extremely sensitive to acetic acid as reported[1] earlier for 5,6-acetylepimino-hexofuranoses. Thus, treatment of **1** and **2** in warm acetic acid easily gave 6-acetamido-7-O-acetyl-6-deoxy-1,2:3,4-di-O-isopropylidene-D-*glycero*-α-D-*galacto*-heptopyranose (**3b**), amorphous powder of $[\alpha]_D^{21}$ −47.9° (c=3.4, $CHCl_3$), and its L-*glycero* epimer (**4b**), prisms of mp 137—140°, $[\alpha]_D^{21}$ −46.4° (c=3.8, $CHCl_3$), respectively. The mass spectra of **3b** and **4b** exhibit peaks, which would be originated from 1,2:3,4-di-O-isopropylidenegalactose moiety,[7] and, further, show common characteristic strong peaks at m/e 144, 102, and 84, which would be due to fragments A, B, and C, and at m/e 242, 200, 184, and 142, due to D, E, F, and G, as illustrated in the chart. This fact suggests that the acetamido group in **3b** and **4b** is not in the terminal position, but in the 6-position. On the other hand, deacetylation of **3b** and **4b** with catalytic amount of sodium methoxide gave the corresponding de-O-acetylated derivative (**3c**) as amorphous powder of $[\alpha]_D^{21}$ −41.5° (c=2.3, $CHCl_3$), and **4c**, mp 130—131.5°, $[\alpha]_D^{21}$ −43.5° (c=3.6, $CHCl_3$). Oxidation of both acetamido-alcohols (**3c** and **4c**) with the Pfitzner–Moffatt reagent[8] afforded the corresponding 7-oxo derivatives[9] with an aldehyed function, which reduced Fehling's solution. This fact also indicates the presence of hydroxyl group at the terimnal position in these acetamido-alcohols (**3c** and **4c**).

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8) K.E. Pfitzner and J.G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963); *idem, ibid.*, **87**, 5661 (1965).
9) Details on these materials and extension of carbon chain from them will be described in a forthcoming paper.