

Structure of Gitorin

The structure of gitorin was established as gitoxigenin monoglucoside by Tschesche.¹⁾ In Part IV²⁾ of Studies on Digitalis, the writer reported that gitorin, differing from other glycosides containing no 2-deoxysugar, was readily hydrolyzed by the Jensen's reagent for determining B-series glycosides of digitalis to give gitoxigenin. Since, however, the genin content of carefully purified gitorin (m.p. 122~124°) (Kofler block) did not agree with that of gitoxigenin monoglucoside, the writer, in fear of having mistaken other glycoside for gitorin, received samples of gitorin from Dr. Okada,³⁾ Mr. Hasegawa,⁴⁾ Mr. Uchibayashi,⁵⁾ and also from Prof. Tschesche through the courtesy of Prof. Takemoto of University of Osaka, and compared them with the gitorin obtained by the writer. As a result it was found that they all agree in Rf values in paper partition chromatography with various solvent systems, velocity of acid hydrolysis, and color in the Keller-Kiliani reaction.

The gitorin obtained by the writer was subjected to the action of a snail enzyme and then chromatographed (benzene•AcOEt•H₂O=8:5:4, ascending method), whereupon only one spot (Rf 0.485) appeared at a place different from those of gitorin (Rf 0.00) or gitoxigenin (Rf 0.68). From the reaction mixture, a product was isolated and was proved to be gitoroside. On the other hand, hydrolysis of gitorin under mild conditions (0.05N HCl in 50% EtOH, heated for 30 min.) afforded digilanidobiose as the sugar portion, and hence it is believed that gitorin is gitoxigenin digilanidobioside. When thus considered, it is well explained why gitorin is hydrolyzed so readily by the Jensen's reagent and is negative to the Keller-Kiliani reaction (since the sugar part is hydrolyzed as digilanidobiose).

Incidentally, gitoxigenin digilanidobioside corresponds to the glucogitoroside which was obtained by Okano⁶⁾ by partial hydrolysis with a snail enzyme of gitorocellobioside isolated from seeds of *Digitalis purpurea* L.

Research Laboratories,
Takeda Pharmaceutical Industries, Ltd.,
Juso-nishino-cho, Higashiyodogawa-ku,
Osaka.

Yoshio Sasakawa (笹川義郎)

December 27, 1958

- 1) R. Tschesche, G. Grimmer, F. Neuwald : Chem. Ber., **85**, 1103(1953).
- 2) Y. Sasakawa : Yakugaku Zasshi, **79**, (1959), in press.
- 3) M. Okada : Yakugaku Zasshi, **73**, 1123(1953).
- 4) H. Hasegawa, K. Inoue, J. Ishii, H. Iijima : This Bulletin, **4**, 319(1956).
- 5) R. Uchibayashi : *Ibid.*, **6**, 504(1958).
- 6) J. Okano : "Jikken Kagaku Koza" (Handbook of Experimental Chemistry), **22**, 169(1958), Maruzen, Tokyo.