

DERIVATION OF GENTIANIN FROM SWERTIAMARIN

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(Received 9 June 1961; in revised form 24 July 1961)

SWERTIA japonica Makino was found to contain, besides swertiamarin (Ia or Ib),<sup>1</sup> an alkaloid gentianin,<sup>2</sup> the biogenesis of which was recently discussed by Govindachari, Nagarajan and Rajappa<sup>3</sup>, and Wenkert and Bringi<sup>4</sup> respectively.

This paper describes the derivation of gentianin from swertiamarin under mild conditions.

Swertiamarin acetate (Ic or Id),  $C_{24}H_{30}O_{14}$ , m.p. 190-191° (300 mg) was dissolved in methanol (20 cc), concentrated aqueous ammonia (20 cc) was added and the solution allowed to stand until the bitterness was lost. Three days later, the solvent was removed under reduced pressure, and 5% hydrochloride acid was added to the amorphous residue, which shows properties of a glucoside, and the solution was refluxed for 30 min. After cooling, the neutral and acidic parts were removed with ether, the acidic solution made alkaline with ammonia and extracted with chloroform. The extract washed with water, dried and evaporated to dryness gave a pale yellow crystalline residue. Recrystall-

<sup>1</sup> T. Kubota and Y. Tomita, Tetrahedron Letters No. 5, 176 (1961).

<sup>2</sup> S. Shibata, M. Fujita and H. Igeta, J.Pharm.Soc.Japan 77, 116 (1957).

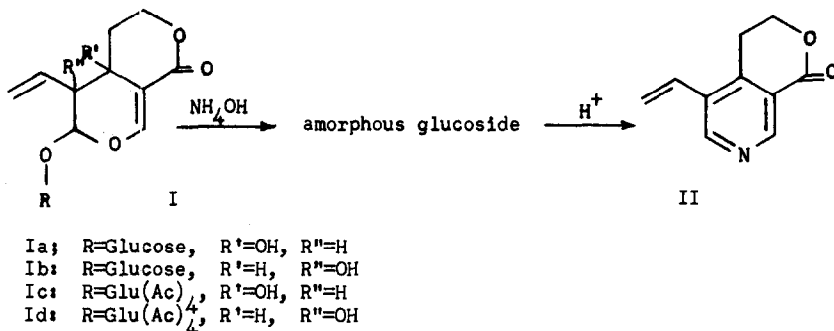
<sup>3</sup> T.R. Govindachari, K. Nagarajan and S. Rajappa, Experientia 14, 5 (1958).

<sup>4</sup> E. Wenkert, and N.V. Bringi, J.Amer.Chem.Soc. 81, 1474 (1959).

ization from petroleum ether gave colourless long needles, m.p. 82-83° (38 mg).

By mixed melting point and comparison of the infra-red absorption spectrum, this substance was found to be identical with gentianin (II), m.p. 82-84°, isolated from Swertia japonica Makino.

Therefore, the carbon skeleton of the formula I for swertiamarin may be positively established although the position of the tertiary hydroxyl group remains to be established.



Since the reaction described above proceeds under mild conditions, it is possible that gentianin can be produced in substantially the same manner in the plant.