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STRUCTURES OF IRIDOIDS FROM LONICERA MORROWII A. GRAY II

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Recently we reported on the isolation and structures of morroniside (I) and kingiside (II) from the fruits of Lonicera Morrowii A. Gray (kingimboku) (1). From the young leaf* of L. morrowii A. Gray a new iridoid glycoside and sweroside were isolated. The former new iridoid was first isolated in nature and named loniceroside but the same substance was derived as a biological important precursor from menthiafolin by A.R. Battersby et. al. (2). It has been already known that the secologanin type iridoid is an intermediate between loganin and indol alkaloids. Now the typical secologanin iridoid, loniceroside, to be obtained in nature is very significant. Also the absence of morroniside and kingiside in the leaf of this plant on t. l. c. is interesting.

Fractionation of the ethanol extract of the fresh leaf on Celite-charcoal column afforded a glycoside mixture, which was further separated by silica gel chromatography into some glycosides. One of which is loniceroside (III) and another is sweroside (IV). Sweroside (IV) and tetraacetylsweroside (VI) were identified by the comparison with authentic samples.

III, $[\alpha]_D$-105° (c=1.1, MeOH) was noncrystalline substance and its spectroscopic data, λ_{max}^{EtOH} 236 mμ (ε=9,800) ν_{max}^{neat} 3400, 1700, 1623 cm^{-1}, seem to suggest the iridoid glycoside.

Acetylation of III using acetic anhydride and pyridine gave tetraacetylloniceroside (V). V, m.p. 115-116°, $[\alpha]_D$-102° (c=1.0, $CHCl_3$) has a formula, $C_{25}H_{32}O_{14}$ (requires: C, 53.95; H, 5.80%. Found: C, 54.24, H, 5.94%). The spectroscopic data of V indicated the presence of the group -O-CO-C=CH-O- [λ_{max}^{EtOH} 232 mμ (ε=10,700), ν_{max}^{Nujol} 1715, 1640, τ 2.62], a methoxy group [τ 6.34 (s, 3H)], -CHO [ν_{max}^{Nujol} 1730 cm^{-1}, τ 0.33 (t. 1H, J=1.5 Hz)] and the absence of methyl group (no signal at methyl region τ 8.8-10.0). With these data we thought of the structure III, which was supported by the conversion experiment of V into tetraacetylsweroside (VI).

V was hydrolyzed with 5% aqueous sodium hydroxide and reduced with sodium borohydride. The product isolated after acetylation was identified with tetraacetylsweroside (VI) by the i. r. spectrum and mixed melting point. Thus the structure and stereochemistry of loniceroside (III) was confirmed as shown.

*Collected at the beginning of June in Ishikari, Hokkaido.

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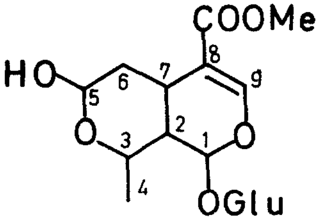
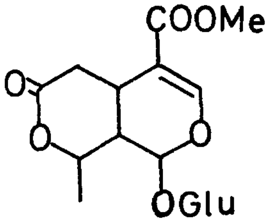


I



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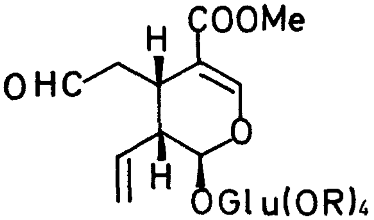
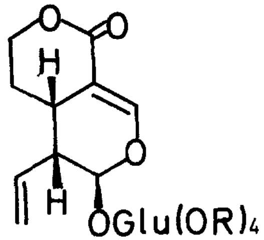


III R=H
V R=Ac



IV R=H
VI R=Ac

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1) I. Souzu and H. Mitsuhashi, Tetrahedron letter 1969, 2725.

2) A.R. Battersby, A.R. Burnett and P.G. Parsons, Chem. Comm., 1968, 1280.