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Iridoid glycosides from *Lonicera quinquelocularis*

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Abstract

A new iridoid glycoside 6′-*O*-β-apiofuranosylsweroside was isolated from the ethanolic extract of the roots of *Lonicera quinquelocularis* along with the known compounds loganin and sweroside. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Lonicera quinquelocularis; Caprifoliaceae; Iridoid glycoside; Loganin; Sweroside; 6′-*O*-β-apiofuranosyl sweroside

1. Introduction

Iridoid and secoiridoid glycosides possess hypotensive, sedative, antipyretic and anti-tussive activities (Basaran, Akdemir, Yuruker & Calis, 1988).

Lonicera quinquelocularis (Caprifoliaceae) is an evergreen shrub commonly found in Kumaon and Garhwal Himalayan region of U.P., India (The Wealth of India, 1962). A number of species of the genus Lonicera have been investigated, and different iridoids and bis-iridoids have been isolated (Machida, Asano & Kikuchi, 1995; Bailleal, Leaveau & Durand, 1981). From the aerial parts of *L. quinquelocularis* 1-inositol, hexacosanol, *n*-triacontanol, nonacosane and β-sitosterol have been isolated (Rastogi & Mehrotra, 1993). The present study deals with the isolation and structure elucidation of two known iridoids loganin **1**, sweroside **2** and new iridoid 6′-*O*-β-apiofuranosylsweroside **3**. Compounds **1** and **2** have been reported from the stem of *L. periclymenum* (Machida et al., 1995).

2. Results and discussion

Air-dried and powdered roots of *L. quinquelocularis* were extracted with aqueous hot EtOH. The EtOH extract on repeated CC over silica gel afforded **1**, **2** and **3**. Compounds **1** and **2** were identified as loganin and sweroside by comparison of the physical constants, ^{1}H and ^{13}C-NMR data with those of literature (Machida et al., 1995; Calis, Lahloub & Sticher, 1984).

Compound **3**, a crystalline colourless solid $[\alpha]_D^{19}$-206°(MeOH) showed molecular ion peak $(M + H)^+$ at *m/z* 491.17 and $(M + Na)^+$ at *m/z* 513.15 in the HR–FAB, and *m/z* 197 (M + H-162-132) corresponding to the loss of hexose and apiose moieties. FAB–MS was compatible with the molecular formula $C_{21}H_{30}O_{13}$. The UV spectrum showed absorption at 244 nm, indicating the iridoid nature of the compound. The ^{13}C-NMR spectrum of the **3** showed the presence of 21 carbon atoms. The assignment of all proton and carbon resonances of **3** were achieved by ^{1}H–^{1}H-homo (DQF-Cosy) and inverse ^{13}C–^{1}H heteronuclear correlated 2DNMR (HMQC) spectra. ^{13}C-NMR data showed presence of sweroside moiety (Machida et al., 1995). The ^{1}H-NMR spectrum of compound **3** exhibited doublet at δ4.66 ($J = 8$ Hz) for anomeric proton of β-linked D-glucose. A doublet ($J = 3.2$ Hz) at δ4.98 was assigned for ^{1}H proton of the β-linked apiofuranose. In the ^{13}C-NMR spectrum of compound **3** C-6 of the D-glucose moiety showed a downfield shift at δ68.54 while the slightly shielded C-5 resonance was at δ77.06. These shifts clearly indicated that C-6 of the

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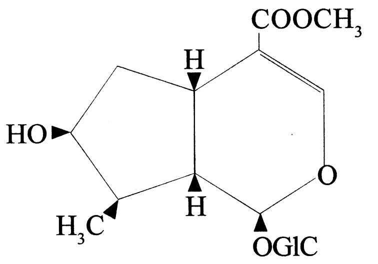

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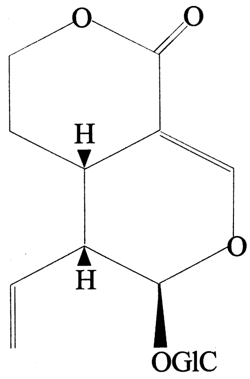

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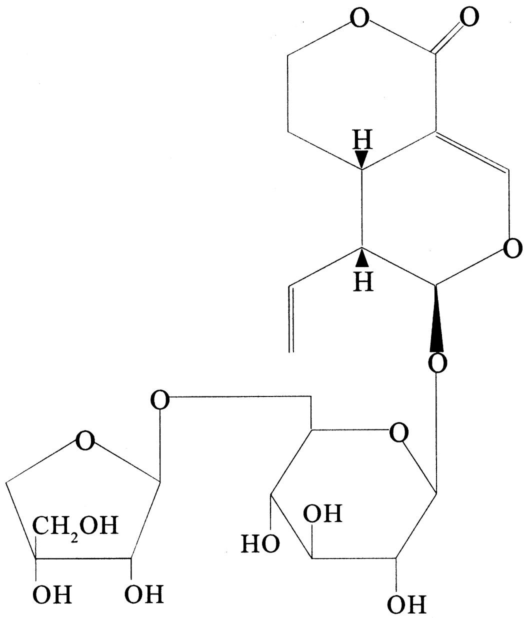

3

inner glucose moiety was glycosidated by an apiofuranosyl moiety.

Acetylation of compound **3** yielded hexaacetate **3a**. In the FAB–MS of **3a** the molecular ion peak at *m*/*z* 743 $(M+H)^+$ and the fragment resulting from the sugar moiety at *m*/*z* 547 were observed supporting the structure of compound **3**. The ^{1}H-NMR of **3a** showed six singlet (each for 3H) at δ1.96, 2.01, 2.04, 2.05, 2.09 and 2.11 corroborated with the presence of β-glucose and apiofuranosyl moiety in the molecule. On the basis of above spectral data compound **3** was identified to be 6′-*O*-β-apiofuranosylsweroside.

3. Experimental

3.1. General

Melting points were incorr., UV were taken in MeOH. ^{1}H-NMR were obtained at (400 MHz), ^{13}C-NMR at (100 MHz), TMS as international standard, using $CDCl_3$ and CD_3OD as solvent. All the signals are expressed as δ values downfield from TMS. CC was carried out on silica gel 60–120 mesh (Merck). TLC was performed on precoated silica gel. The used solvent system were $CHCl_3$–MeOH (95:5), (90:10) and (85:15). Spots were visualized by 7% H_2SO_4 followed by heating.

3.2. Plant material

The roots of *L. quinquelocularis* were collected from Phata, Chamoli, U.P., India during August. The plant was identified by the Prof. R.D. Gaur, Department of Botany, H.N.B. Garhwal University, Srinagar. A Voucher specimen is deposited in Ethanobotanical Plant Identification Laboratory, Department of Botany, H.N.B. Garhwal University Srinagar, U.P., India.

3.3. Extraction and isolation

The air-dried roots of the plant (3 kg) were exhaustively extracted by boiling with 90% aqueos EtOH for 72 h. The ethanolic extract was concentrated to dryness. Repeated CC afforded compounds **1** (1.5 gm), **2** (0.92 gm) and **3** (0.37 gm). Compound **1** and **2** were identified as loganin and sweroside, respectively by comparison of their spectral data with those reported in the literature (Machida et al., 1995; Calis et al., 1984).

3.4. Compound 3

Colourless crystalline solid mp — 115–119, $[\alpha]_D^{19}$ — 206° (MeOH, $c = 1.21$) UV (MeOH) λ_{max} (log ε) 244 (1.01) nm; FAB–MS *m*/*z* 513 $(M + Na)^+$, 491 $(M+H)^+$, 197 $(M+H)^+$, ^{1}H-NMR (400 MHz, CD_3OD), (aglycone), δ5.45 (*d*, $J = 1.2$ Hz), 7.60 (*d*, $J = 2.4$ Hz) 3.13 (H, *m*), 1.74 (*m*) 4.40 (2H, *m*), 5.53 (*m*), 2.72 (*m*), 5.31 (2H, *m*), (glycone–hexose) δ4.66 (*d*, $J = 8$ Hz), 3.19 (*m*), 3.37 (*m*), 3.30 (*m*), 3.46 (*m*), 3.63 (*dd*, $J = 5.6$, 6H, 6-H), 4.01 (*dd*, $J = 6.4$, 1.6 H, 6-H) (apiose,) δ4.98 (*d*, $J = 3.2$ Hz), 3.90 (*d*, $J = 9.0$ Hz), 3.76 (*d*, $J = 10$ Hz), 3.97 (*d*, $J = 10$ Hz), 3.56 (2H, brs.) and ^{13}C-NMR — (100 MHz, CD_3OD) (aglycone) δ98.11 (C_1), 153.8 (C_3), 105. 96 (C_4), 28.36 (C_5), 25.85 (C_6), 69.65 (C_7), 133.21 (C_8), 43.78 (C_9), 120.99 (C_{10}), 168.41 (C_{11}) (glycone) δ99.74 (C_1), 74.56 (C_2), 77.68 ($C_3{'}$), 71.39 (C_4), 77.0 ($C_5{'}$), 68.54 ($C_6{'}$), 110.89 ($C_1{''}$), 77.8 ($C_2{''}$), 80.41 ($C_3{''}$), 74.92 ($C_4{''}$), 65.45 (C5$''$).

3.5. Hexaacetate of compound 3

Compound **3** 2.5 mg was dissolved in a mixture of C_5H_5N (0.1 ml) and Ac_2O (0.1 ml) and the solution was kept at 60°C for 18 h. After addition of excess MeOH the solvent was removed under reduced pressure to give the hexaacetate **3a** (3.2 mg) FAB — ion given *m/z* 743.23 $(M + H)^+$, 766 $(M + Na)^+$, ^{1}H-NMR — (400 MHz, $CDCl_3$) (aglycone) δ5.47 (*d*, $J = 2.8$ Hz), 7.57 (*d*, $J = 2.4$ Hz) 3.57 (*m*), 1.71 (*m*), 4.44 (*d*, $J = 3.2$ Hz), 5.50 (*m*), 2.69 (*m*), 5.31 (*m*), (glycone) (hexose) δ4.92 (*d*, $J = 8$ Hz), 3.60 (*m*), 5.33 (*m*), 4.96 (*d*, $J = 4.8$ Hz), 3.76 (*m*), 3.75 (*m*, 6-H) 4.32 (*m*, 6-H), (apiose) 4.98 (*d*, $J = 2.4$ Hz), 4.46 (*d*, $J = 3.2$ Hz), 4.23, (*dd*, $J = 10$, 10 Hz, 4-H), 4.14 (*dd*, $J = 10$, 10, Hz, 4-H), 4.73 (*dd*, $J = 12$, 12 Hz, 5-H), 4.59 (*dd*, $J = 12$, 12 Hz, 5-H) 1.96–2.11 (*m*, OAc).

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