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A COUMARIN GLYCOSIDE FROM *LONICERA GRACILIPES* VAR. *GLANDULOSA**

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Key Word Index—*Lonicera gracilipes* var. *glandulosa*; Caprifoliaceae; coumarin glycoside; aesculetin-6-*O*-β-D-apiofuranosyl-(1 → 6)-*O*-β-D-glucopyranoside.

Abstract—A new coumarin glycoside, aesculetin-6-*O*-β-D-apiofuranosyl-(1 → 6)-*O*-β-D-glucopyranoside, was isolated from the leaves of *Lonicera gracilipes* var. *glandulosa* and its structure determined by chemical and physicochemical evidence.

INTRODUCTION

As part of our phytochemical research on plants in the genus *Lonicera*, we have investigated *Lonicera gracilipes* var. *glandulosa*. This species, a deciduous shrub, is widely distributed in Japan. In this paper, we report on the characterization of a new coumarin glycoside from the leaves of this plant.

RESULTS AND DISCUSSION

Compound **1** was isolated as an amorphous powder, whose M_r was confirmed from $[M + Na]^+$ at *m/z* 495 in the positive ion FAB-mass spectrum. The UV spectrum showed characteristic coumarin absorption (described in the Experimental). Hydrolysis of **1** with 5% HCl yielded aesculetin, D-glucose and D-apiose. The ^1H and ^{13}C NMR spectra showed the presence of the coumarin skeleton [δ6.17 (1H, *d*, *J* = 9.5 Hz, H-3), 7.89 (1H, *d*, *J* = 9.5 Hz, H-4) and 112.0 (C-3), 146.4 (C-4)], glucosyl and apiosyl moieties. The two singlet proton signals, δ6.77 and 7.39, showed that two substituents were at C-6 and C-7 of the B-ring. Chemical shifts in the ^{13}C NMR spectrum of **1** were compared with aesculin (aesculetin-6-*O*-β-D-glucopyranoside) (**2**) and the apiosyl-(1 → 6)-glucosyl moiety of osmantolide (methoxyhydroquinone-4-*O*-β-D-apiofuranosyl-(1 → 6)-*O*-β-D-glucopyranoside, [2]) (Table 1). In the NOESY spectrum of **1**, cross-peaks were observed between H-4 and the δ7.39 signal, and between the glucosyl anomeric proton at δ4.81 and the same signal, indicating that the apiosyl-(1 → 6)-glucosyl moiety was attached to the C-6 hydroxyl group. Thus, the structure of **1** was determined to be aesculetin-6-*O*-β-D-apiofuranosyl-(1 → 6)-*O*-β-D-glucopyranoside.

*Part 4 in the series 'Studies on the constituents of *Lonicera* species'. For Part 3, see ref. [1].

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EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts are given on the δ (ppm) scale with TMS as int. standard. Prep. HPLC was carried out using a ODS-120A (7.8 mm i.d. × 30 cm) column with UV detector. GC was carried out using a 3% SE-52 Chromosorb W(AW) (60–80 mesh, 3 mm i.d. × 2 m) column with FID.

Extraction and isolation. Fr. leaves of *L. gracilipes* var. *glandulosa* (0.2 kg), collected in October 1990, in Sendai, Japan, were extracted with MeOH at room temp. for 1 month. The MeOH extract was concd under red. pres. and the residue suspended in a small excess of H_2O. This suspension was successively extracted with $CHCl_3$, Et_2O, EtOAc, *n*-BuOH and H_2O. The *n*-BuOH-soluble fr. was concd. under red. pres. to afford a residue (15.2 g) which was chromatographed on a silica gel column ($CHCl_3$–MeOH–H_2O, 30:10:1) and a Sephadex LH-20 column (MeOH–H_2O, 1:1), and then subjected to prep. HPLC (MeOH–H_2O, 3:7) to give **1** (3 mg).

Aesculetin-6-O-β-D-apiofuranosyl-(1 → 6)-O-β-D-glucopyranoside (**1**). Amorphous powder. $[\alpha]_D$ − 68.2° (MeOH; *c* 0.1). UV λ_{max}^{MeOH} nm (log ε): 221 sh (3.94), 250sh

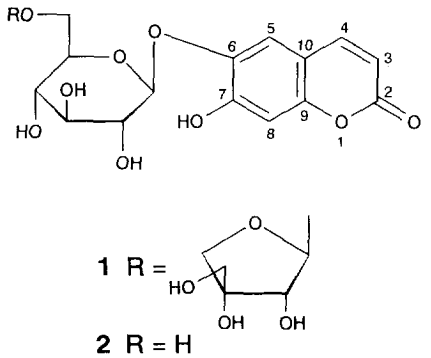

Table 1. ^{13}C NMR spectral data of **1** (in CD_3OD)

C	**1**	Aesculin	β-D-Apiosyl (1 → 6)-O-β-D-glucosyl*
2	164.1	163.7	—
3	112.0	113.1	—
4	146.4	145.9	—
5	116.4	116.9	—
6	153.0	153.4	—
7	145.1	144.4	—
8	104.7	104.6	—
9	153.0	152.6	—
10	112.0	112.8	—
Glc-1	104.2	104.4	103.8
Glc-2	74.9	74.8	75.0
Glc-3	78.0	78.5	78.1
Glc-4	71.6	71.4	71.7
Glc-5	77.3	77.7	77.0
Glc-6	68.8	62.6	68.8
Api-1	110.9	—	111.0
Api-2	77.5	—	78.0
Api-3	80.5	—	80.6
Api-4	74.8	—	75.0
Api-5	65.3	—	65.6

*Sugar moiety of osmantolide.

(3.64), 290sh (3.53), 330 (3.70), 386sh (3.15). IR ν_{max}^{KBr} cm^{-1}: 3388, 1700 sh, 1689, 1612, 1572, 1510. FAB-MS *m/z* 495 $[M + Na]^+$. ^1H NMR (CD_3OD): δ4.81 (1H, *d*, *J* = 7.7 Hz, Glc-H-1), δ5.01 (1H, *d*, *J* = 2.6 Hz, Api-H-1), δ6.17 (1H, *d*, *J* = 9.5 Hz, H-3), 6.77 (1H, *s*, H-8), 7.39 (1H, *s*, H-5), 7.89 (1H, *d*, *J* = 9.5 Hz, H-4). ^{13}C NMR: Table 1.

Acid hydrolysis. Hydrolysis of **1** with 5% HCl yielded aesculetin, D-glucose and D-apiose. Aesculetin was identified by TLC and the two sugars by GC after derivatization with TMS.

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