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FLAVONOL GLYCOSIDES FROM *HUMATA PECTINATA**

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Key Word Index—*Humata pectinata*; Davalliaceae; flavonols; 8-methoxyquercetin 3-glucoside; 8-methoxykaempferol 3-glucoside; ^{1}H NMR; ^{13}C NMR.

Abstract—A new flavonol glucoside, 8-methoxyquercetin 3-glucoside, and 8-methoxykaempferol 3-glucoside were characterized from the whole plant of *Humata pectinata*.

INTRODUCTION

In a previous paper [1], we have reported the isolation of some triterpenoids from the chloroform extract of the whole plant of *Humata pectinata* (J. Sm.) Desv. (Davalliaceae) collected in Taiwan. We now report the isolation and structural elucidation of a new flavonol glucoside (**1**) and 8-methoxykaempferol 3-*O*-glucoside (**3**) from the ethyl acetate extract of the same plant.

RESULTS AND DISCUSSION

1, $C_{22}H_{22}O_{13}\cdot H_2O$, showed a positive reaction with both magnesium–hydrochloric acid and ferric chloride and gave a negative response to zirconium hypochlorite–citric acid reagent. The aqueous ethanolic solution of **1** reduced Fehling's reagent after acid-hydrolysis. These properties suggested that **1** is a flavonol glucoside having no free hydroxyl group at C-3 [2]. In the UV spectrum of **1**, bathochromic shifts with sodium methoxide and sodium acetate indicated the presence of two free hydroxyl groups at C-7 and C-4′ [3]. Bathochromic shifts of 78, 47 and 21 nm in the absorption band at 368 nm in the spectrum of **1** were also observed with aluminium chloride, aluminium chloride–hydrochloric acid and sodium acetate–boric acid. Thus, **1** has no free hydroxyl group at C-3 and an *ortho*-dihydroxylated aromatic ring [4]. In the ^{1}H NMR spectrum of **1**, three aromatic proton signals which coupled with each other at δ 7.79 (*d*, J = 2 Hz), 7.66 (*dd*, J = 2 and 8 Hz) and 6.91 (*d*, J = 8 Hz) were due to H-2′, H-6′ and H-5′ of the B-ring, a singlet at δ 6.31 was due to H-6 [5] and a three-proton singlet at δ 3.88 indicated a methoxyl proton. In the ^{13}C NMR spectrum of **1**, the signal for C-3′ appeared as a singlet at δ 145.3 instead of a doublet at δ 116.4 in **3**, which was isolated from the same plant at this time and identified as 8-methoxykaempferol 3-*O*-glucoside. The chemical shifts of all carbons of **1** except for those on ring B were almost identical with those of **3** (Table 1). Acid hydrolysis of **1** afforded D-glucose and 8-methoxyquercetin (corniculatusin) **2**, which was identified by comparison of IR, ^{1}H NMR and mmp with the authentic sample. The β-linkage of the D-glucopyranose was inferred from the half band width of the anomeric proton signal at δ 5.36 (multiplet, $W_{1/2h}$ = 9 Hz) in the ^{1}H NMR spectrum of **1** [6]. On the basis of these results, **1** is identified as 8-methoxy-3,5,7,3′,4′-pentahydroxyflavone 3-*O*-β-D-glucoside (8-methoxyquercetin 3-glucoside).

Table 1. ^{13}C NMR spectra of 8-methoxyquercetin 3-glucoside (**1**) and 8-methoxykaempferol-3-glucoside (**3**)

C. No.	**1**	**3**	C. No.	**1**	**3**	C. No.	**1**	**3**
2	157.5 (*s*)	157.5 (*s*)	1′	122.6 (*s*)	122.3 (*s*)	1″	103.0 (*d*)	103.1 (*d*)
3	134.8 (*s*)	134.7 (*s*)	2′	116.7 (*d*)	132.1 (*d*)	2″	75.1 (*d*)	75.1 (*d*)
4	178.6 (*s*)	178.7 (*s*)	3′	145.3 (*s*)	116.4 (*s*)	3″	77.5 (*d*)	77.5 (*d*)
5	156.6 (*s*)	156.6 (*s*)	4′	149.2 (*s*)	160.4 (*s*)	4″	70.4 (*d*)	70.4 (*d*)
6	100.2 (*d*)	100.2 (*d*)	5′	117.5 (*d*)	116.4 (*d*)	5″	77.1 (*d*)	77.0 (*d*)
7	158.0 (*s*)	158.3 (*s*)	6′	123.3 (*d*)	132.1 (*d*)	6″	61.7 (*t*)	61.7 (*t*)
8	128.4 (*s*)	128.4 (*s*)						
9	149.5 (*s*)	149.6 (*s*)						
10	105.1 (*s*)	105.1 (*s*)						
OMe	62.4 (*q*)	62.3 (*q*)						

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*Part XVIII in the series "Constituents of Formosan Folk Medicine". For Part XVII, see *J. Nat. Prod.* (in press).

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EXPERIMENTAL

Mps are uncorr. ^{1}H NMR (100 MHz) and ^{13}C NMR (25.0 MHz) were recorded in $CDCl_3 + 10\%$ DMSO-d_6 except when otherewise noted. Chemical shifts were shown in δ-values (ppm) with TMS as int. standard. MS were taken with a direct inlet system. UV spectra were determined in MeOH and IR recorded in KBr.

Plant material. Humata pectinata (J. Sm.) Desv. was collected on Orchid Island, Taiwan, and verified by Professor C.-S. Kouh. A herbarum specimen is deposited in the Herbarum of Chia-Nan Junior College of Pharmacy, Tainan, Taiwan, Republic of China.

Extraction and separation. The EtOH extract of the whole plant of *Humata pectinata* (1 kg) was treated with $CHCl_3$ and H_2O. The aq. layer was extracted with EtOAc and *n*-BuOH. The EtOAc extract was chromatographed on Si gel and eluted successively with $CHCl_3$, $CHCl_3$–MeOH (4:1) and MeOH to give **3** (0.6 g) and **1** (0.5 g).

8-*Methoxykaempferol* 3-*glucoside* (**3**). Yellow needles from MeOH, mp 264–265° (lit. mp 223–225° [7]). Found: C, 55.11; H, 4.71. $C_{22}H_{22}O_{12}$ requires C, 55.23; H, 4.64%. IR ν_{max} cm^{-1}: 3400, 3250, 1650, 1615, 1560 and 1510. MS *m/z*: 316 (aglycone ion), 301 (100%), 287, 286, 273, 147, 139 and 121. ^{1}H NMR: δ 2.80–4.10 and 4.70–5.32 (10H, *br*, glucosyl-H), 3.86(3H, *s*, OMe), 5.44(1H, *m*, $W_{1/2h} = 9$ Hz, anomeric-H), 6.32(1H, *s*, H-6), 6.94(2H, *d*, $J = 8$ Hz, H-3′ and H-5′), 8.12(2H, *d*, $J = 8$ Hz, H-2′ and H-6′) and 12.36(1H, *s*, OH-5). Compound **3** was identified by comparison of IR, mass and ^{1}H NMR spectra with lit. data [7] with an authentic sample of 8-methoxykaempferol 3-glucoside.

8-*Methoxyquercetin* 3-*glucoside* (**1**). Yellow needles from MeOH, mp 176–178°. Found: C, 51.16; H, 4.76. $C_{22}H_{22}O_{13} \cdot H_2O$ requires C, 51.56; H, 4.72%. UV λ_{max} nm: 268 and 368; + NaOAc: 280, 328 and 401; + $AlCl_3$: 281, 308, 345, and 446; + $AlCl_3$ + HCl: 279, 306, 364 and 415; + NaOMe: 278, 325 and 389; + NaOAc + H_3BO_4: 268 and 389. IR ν_{max} cm^{-1}: 3350, 1650, 1610, 1562 and 1510. MS *m/z*: 332 (aglycone ion), 317(100%), 303, 302, 301, 289, 167, 163, 139 and 137. ^{1}H NMR: δ 2.80–4.10(10H, glucosyl-H), 3.88(3H, *s*, OMe), 5.36(1H, *m*, $W_{1/2h} = 9$ Hz, anomeric-H), 6.31(1H, *s*, H-6), 6.91(1H, *d*, $J = 8$ Hz, H-5′), 7.66(1H, *dd*, $J = 8$ and 2 Hz, H-6′), 7.79(1H, *d*, $J = 2$ Hz, H-2′), 12.28(1H, *s*, OH-5).

Acid hydrolysis of **1**. 0.1 g **1** was refluxed with conc. HCl for 10 min to afford yellow needles from Me_2CO, mp 285–287°. IR ν_{max} cm^{-1}: 3340–3120, 1650, 1590, 1550 and 1510. MS *m/z*: 332[M]$^{+}$, 331, 317, 316, 301, 300, 288, 285, 272, 163, 139, 137 and 69. ^{1}H NMR (Me_2CO-d_6): δ 3.98 (3H, *s*, OMe), 6.33 (1H, *s*, H-6), 7.05(1H, *d*, $J = 8$ Hz, H-5′), 7.81(1H, *dd*, $J = 8$ and 2 Hz, H-6′), 7.92(1H, *d*, $J = 2$ Hz, H-2′), 8.70(4H, *br*, 4 × OH), 11.94(1H, *s*, OH-5). This compound was identified as 8-methoxyquercetin (**2**) by comparison of IR and ^{1}H NMR spectra and mmp with an authentic sample. The sugar residue was identified as glucose by PPC.

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