Pergamon

PII: S0031-9422(97)00243-4

Phytochemistry, Vol. 45, No. 8, pp. 1727–1728, 1997

0031-9422/97 $17.00+0.00

A FLAVONOL *C*-GLYCOSIDE FROM *MOGHANIA MACROPHYLLA*

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(*Received* 4 *December* 1996)

Key Word Index—*Moghania macrophylla*; Leguminosae; flavonol *C*-glycoside; 3,5,7,4′-tetrahydroxy-3′,5′-dimethoxyflavone 6-*C*-glucoside; syringetin 6-*C*-glucoside; Moghanin A.

Abstract—A novel flavonol *C*-glycoside was isolated from the roots of *Moghania macrophylla*. Its structure was established as syringetin 6-*C*-glucoside on the basis of IR, UV and NMR data. Six known flavonoids: genistein, eriosemaone A, fleminone, ourateacatechin, daidzin and genistin were also identified.

INTRODUCTION

Moghania macrophylla (Willd.) O. Kuntze (Leguminosae) has been used as an anti-rheumatic, anti-inflammatory and an anti-histamine in Taiwan and Southern China [1]. In a preliminary bioassay, ethyl acetate and *n*-butanol extracts of the roots showed antiplatelet aggregation and anti-inflammatory activity. Four compounds (**1**–**4**) were isolated from ethyl acetate extract and three flavonoid glycosides (**5**–**7**) from the *n*-butanol extract.

RESULTS AND DISCUSSION

Compounds **1**–**6** are known compounds and were assigned, respectively, by comparison with published spectral data as genistein (**1**) [2, 3], fleminone (**2**) [4], eriosemaone A (**3**) [5], ourateacatechin (**4**) [6, 7], genistin (**5**) and daidzin (**6**) [8]. Compounds **3**–**6** are reported for the first time from *M. macrophylla*. Compound **7** gave *m/z* 509 $[M+H]^+$ in the FABMS spectrum (positive mode) $C_{23}H_{24}O_{13}$, and responded to the Molish and Shinoda [Mg-HCl] tests. It gave a positive ferric chloride test suggesting the presence of a chelated hydroxyl group and its solubility in alkali indicated its phenolic nature. The IR spectrum showed a chelated hydroxyl group at 3418 cm^{-1} and a chelated carbonyl group at 1624 cm^{-1}. The UV spectrum of **7** in methanol showed absorptions at 255 (band II) and 376 (band I) nm, indicating a free hydroxyl group at C-3 of the flavonol skeleton [9]. The bathochromic shift of band I (61 nm) with aluminium chloride–hydrochloric acid is a characteristic feature of 3-hydroxy-4-carbonyl and/or 3,5-dihydroxy-4-carbonyl flavonols. The bathochromic shift of band II (24 nm) with sodium acetate revealed the presence of a free hydroxyl group at C-7 in the A ring. The UV absorption of band I was unchanged with sodium acetate–boric acid suggesting that there was no free *ortho*-dihydroxyl group in ring B. This was confirmed by the bathochromic shift of band I (61 nm) with aluminium chloride which was unchanged on addition of hydrochloric acid. From this UV spectral data, it is suggested that **7** had a 3,5,7,4′-tetrahydroxy flavonol skeleton.

The ^1H NMR spectrum (300 MHz, DMSO-d_6) of **7** indicated the presence of a methoxyl signal at δ 3.83 (6H, *s*, 3′-OMe or 5′-OMe), two aromatic proton signals at δ 6.53 (1H, *s*, H-8), 7.50 (2H, *s*, H-2′ or H-6′), four phenolic hydroxyl signals at δ 9.18 (1H, *s*, 4′-OH), 9.53 (1H, *s*, 3-OH), 10.56 (1H, *br*, *s*, 7-OH) and 13.02 (1H, *s*, 5-OH), and a glucosyl signal at δ 4.59 (1H, *d*, $J = 9.9$ Hz, H-1″) demonstrated the β-configuration of the glucosyl residues. The ^{13}C NMR spectrum (75.5 MHz, DMSO-d_6) showed a methoxyl carbon at δ 56.2 (3′,5′-OMe), one secondary glucosyl carbon at δ 61.3 (C-6″), two tertiary carbons at δ 93.3 (C-8), 106.0 (C-2′, 6′) and five tertiary glucosyl carbons at δ 70.3 (C-4″), 70.5 (C-2″), 73.1 (C-1″), 78.8 (C-3″) and 81.4 (C-5″), a carbonyl carbon at δ 176.0 (C-4) and the remains of quaternary carbons at δ 102.7 (C-10), 108.1 (C-6), 120.7 (C-1′), 135.8 (C-3), 138.2 (C-4′), 146.2 (C-2), 147.7 (C-3′, C-5′), 155.0 (C-9), 159.6 (C-5) and 163.0 (C-7). In the above ^{13}C NMR spectral data, C-6 was shifted downfield to δ 108.1, indicating that the glucosyl moiety was attached to C-6 of the aglycone. Therefore, **7** was characterized as

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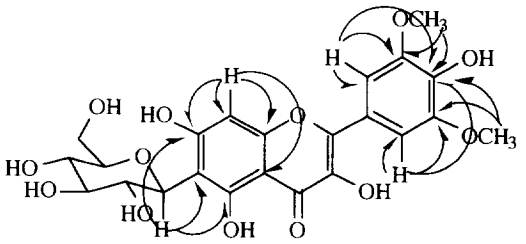

Fig. 1. HMBC Correlation of **7**.

3,5,7,4′-tetrahydroxy-3′,5′-dimethoxyflavone 6-*C*-*β*-glucopyranoside (syringetin 6-*C*-glucoside, Moghanin A) and confirmed by DEPT, ^{1}H-^{1}H COSY, HMQC and HMBC (Fig. 1). It is a new natural product.

EXPERIMENTAL

Plant material. Moghania macrophylla (Willd.) O. Kuntze was collected on 5 October 1993 in Taichung, Taiwan and identified by Mr Nien-Yung Chiu, Graduate Institute of Chinese Pharmaceutical Science, China Medical College, Taichung, Taiwan. A voucher specimen has been deposited in the Graduate Institute of Pharmaceutical Chemistry, China Medical College, Taichung, Taiwan.

Extraction and isolation. Chopped fresh roots (5 kg) were exhaustively extracted with MeOH. The concd extracts (425 g) were suspended in H_2O and successively partitioned with EtOAc (236 g) and *n*-BuOH (129 g), respectively. The EtOAc extract (10 g) was chromatographed on a silica gel column (70–230 mesh) using $CHCl_3$–MeOH (25:1) as solvent to give six frs (Frs A–F). Fr. A (1420 mg) was rechromatographed on a silica gel column with $CHCl_3$–EtOAc (10:1) as eluent to obtain four subfractions (Frs A1–A4). Fr. A1 (124.5 mg) was subjected to silica gel CC with *n*-hexane–EtOAc (5:1) as eluent to yield **1** (5 mg) and Fr. A2 (191.4 mg) rechromatographed on a silica gel column with $CHCl_3$–EtOAc (95:5) as eluent to yield **2** (18 mg). Fr. A3 (916.7 mg) was subjected to a silica gel CC with $CHCl_3$–Me_2CO (6:1) as eluent to yield **3** (15 mg). Silica gel CC of Fr. E (437.9 mg) with $CHCl_3$–EtOAc (19:1) gave four subfrs (Frs E1–E4). Fr. E3 (137.4 mg) was subjected to a silica gel CC with EtOAc–MeOH (8:1) as eluent to yield **4** (16 mg).

The *n*-BuOH extract (50 g) was chromatographed on a silica gel column (70–230 mesh) using $CHCl_3$–MeOH (22:5) as solvent to give five frs (Frs A–E). Fr. B (2272 mg) was rechromatographed on a silica gel column with $CHCl_3$–MeOH–H_2O (40:3:1) as eluent to obtain four subfrs (Frs B1–B4). Fr. B3 (1371 mg) was recrystallized with $CHCl_3$–MeOH to afford **5** (400 mg). Fr. C (3168 mg) was subjected to a Sephadex LH-20 column (25–100 μm) with benzene–MeOH (1:4) as eluent to obtain eight subfrs (Frs C1–C8). Fr. C7 was subjected to a Sephadex LH-20 column with benzene–MeOH (4:1) as eluent to yield **6** (20.4 mg) and **7** (8.1 mg).

Compounds **1**–**6**. Properties and spectra were identical to those reported earlier [2–8].

Compound **7**. (3,5,7,4′-tetrahydroxy-3′,5′-dimethoxyflavone 6-*C*-*β*-glucopyranoside, syringetin 6-*C*-glucoside, Moghanin A). Amorphous, yellow powder; mp 248–249°; TLC: R_f 0.40 ($CHCl_3$–MeOH, 7:2), $[\alpha]_D$ −35.5 (MeOH, *c* 0.2); FABMS (positive), *m/z*: 507 $[M+H]^+$. IR ν_{max}^{KBr} cm^{-1}: 3418, 1651, 1624, 1609, 1489, 1458; UV λ_{max}^{MeOH} nm (log ε): 255 (4.83), 376 (4.87); ($AlCl_3$) 266, 437; ($AlCl_3$/HCl) 264, 437; (NaOAc) 279, 388; (NaOAc/H_3BO_3) 255, 376; ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 13.02 (1H, *s*, 5-OH), 10.56 (1H, *s*, 7-OH), 9.51 (1H, *s*, 3-OH), 9.18 (1H, *s*, 4′-OH), 7.48 (2H, *s*, H-2′, H-6′), 6.53 (1H, *s*, H-8), 4.59 (1H, *d*, J = 9.9 Hz, H-1″), 3.83 (6H, *s*, 3′,5′-OMe); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ ppm: 176.0 (*s*, C-4), 163.0 (*s*, C-7), 159.6 (*s*, C-5), 155.0 (*s*, C-9), 147.7 (*s*, C-3′,5′), 146.2 (*s*, C-2), 138.2 (*s*, C-4′), 135.8 (*s*, C-3), 120.7 (*s*, C-1′), 108.1 (*s*, C-6), 102.7 (*s*, C-10), 106.0 (*d*, C-2′,C-6′), 93.3 (*d*, C-8), 81.4 (*d*, C-5″), 78.8 (*d*, C-3″), 73.1 (*d*, C-1″), 70.5 (*d*, C-2″), 70.3 (*d*, C-4″), 61.3 (*t*, C-6″), 56.2 (*q*, 3′,5′-OMe).

Acknowledgements—We thank the National Science Council of the Republic of China for financial support (NSC-83-0420-B039-001 and NSC-84-0420-B039-001).

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