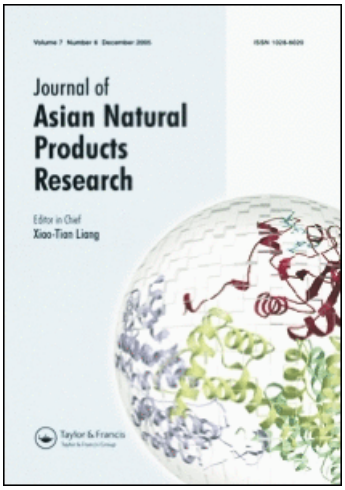

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A new geranyl flavanone from *Macaranga triloba*

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A new geranyl flavanone, 2′-hydroxy-macarangaflavnone A (**1**), and a known 4′,7-dihydroxy-8-methylflavan were isolated from the leaves of *Macaranga triloba* (Euphorbiceae). The structure of **1** was elucidated based on spectroscopic methods, including 1D and 2D NMR analysis.

Keywords: Geranyl flavanone; 2′-Hydroxy-macarangaflavanone A; *Macaranga triloba*; Euphorbiaceae

1. Introduction

Dried leaves of many *Macaranga* species (Euphorbiaceae) are used to heal fresh cuts, sores, swellings, bruises and boils [1,2]. Chemical investigation on various *Macranga* species has led to the structural elucidation of some geranyl flavanoids such as macarangaflavanone A, euchrestaflavanone A, and macarangin [1,3]. The plant *Macranga triloba* is a tree endemic to Southeast Asia at forest margins and its water extract is used as pain relief for stomach trouble in Java [3]. A literature search revealed that no phytochemical study on this species has been undertaken. In our study we isolated a new geranyl flavanone, 2′-hydroxy macarangaflavnone A (**1**), together with a known 4′,7-dihydroxy-8-methylflavan [3] from the chloroform fraction of EtOH extract of the title plant leaves. In this paper we describe the isolation and structural elucidation of a new geranyl flavanone **1**.

2. Results and discussion

Compound **1** was isolated as orange oil and exhibited a molecular formula of $C_{25}H_{28}O_6$, as deduced from its HREIMS and NMR data. It showed positive reaction with HCl/Mg and

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α-naphthol agents. The UV spectrum of **1** displayed maximum absorptions at 287 and 335 nm, indicating that **1** is a flavanone derivative [4]. The IR spectrum showed the presence of hydroxyl (3370 cm^{-1}), conjugated and 5-OH chelated ketone (1641 cm^{-1}), and aromatic rings (1500 cm^{-1}). The ^{1}H NMR spectrum (table 1) of **1** exhibited signals for three methyl singlets (δ 1.55, 1.58, 1.61), four low field methines (δ 5.02, 5.12, 5.53), and four aromatic protons, which were assignable to H-8, H-6 (δ 5.96, 6.00, each 1H, d, $J = 1.5$ Hz), H-5′ and H-6′ (δ 6.83. 6.97, each 1H, d, $J = 8.4$ Hz). The ^{13}C NMR (DEPT) data (table 1) showed clearly that **1** contains three methyls, four methylenes, seven methines (one oxygenated and six olefinic), and eleven quaternary carbons (one ketone and ten olefinic). Regarding the data mentioned above, **1** should be a tetrahydroxy-flavanone with a side chain contained five carbon atoms.

Further study showed that the ^{1}H and ^{13}C NMR data of **1** were very similar to those of a known geranyl flavanone macarangaflavanone A, **2** [3], which was isolated from another *Macaranga* species. Compared with **2**, the only difference was the absence of a H-2′ signal in ^{1}H NMR of **1** and presence of a downfield shift of C-2′ (δ 144.7 s in **1** and δ 128.6 d in **2**) in ^{13}C NMR. Thus, compound **1** was suggested to be a 2′-hydroxyl derivative of **2**. This suggestion was supported by HMBC correlations (table 1) between H-2/C-1′, C-2′, C-6′ and H-6′/C-2, C-2′, C-5′. The above deduction was also substantiated by its EIMS data as follows: the base peak at *m/z* 153 (fragment $[A1 + H]^{+}$), the peak at *m/z* 301 [fragment with loss of *m/z* 123 (side chain) from molecular ion], and the characteristic peak at *m/z* 149 (the ring B with two hydroxyl groups and a geranyl group) [5–7]. Therefore, the structure of **1** was elucidated as 2′-hydroxyl-macarangaflavanone A and the assignment of all the ^{1}H and

Table 1. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), and HMBC data of compound **1**[a].

Position	δ_H	δ_C	*HMBC (H–C)*
2	5.53 (1H, dd, 2.7, 13.4)	76.4 (d)	C-1′, C-2′, C-C-4, C-6′
3	3.12 (1H, dd, 13.4, 17.0)	42.3 (t)	C-1′, C-2, C-4
	2.74 (1H, dd, 2.7, 17.0)		
4		196.6 (s)	
5		165.0 (s)	
6	6.00 (1H, d, 1.5)	96.7 (d)	C-8, C-10
7		163.4 (s)	
8	5.96 (1H, d, 1.5)	95.6 (d)	C-6, C-7, C-10
9		164.2 (s)	
10		102.9 (s)	
1′		128.2 (s)	
2′		144.7 (s)	
3′		126.4 (s)	
4′		142.5 (s)	
5′	6.83 (1H, d, 8.4)	113.0 (d)	C-1′, C-4′, C-6′
6′	6.97 (1H, d, 8.4)	118.9 (d)	C-2, C-2′, C-5′
1″	3.46 (2H, d, 6.6)	25.3 (t)	C-2″, C-3″, C-3′, C-4′
2″	5.12 (1H, t, 6.6)	121.2 (d)	C-1″, C-3′, C-4″, C-5″
3″		138.9 (s)	
4″	1.61 (3H, s)	16.2 (q)	C-2″, C-3″, C-5″
5″	2.05 (2H, m)	39.5 (t)	C-2″, C-4″, C-3″, C-6″, C-7″
6″	2.09 (2H, m)	26.2 (t)	C-3″, C-5″, C-7″, C-8″
7″	5.02 (1H, t, 5.5)	123.6 (d)	C-6″, C-9″
8″		123.6 (s)	
9″	1.55 (3H, s)	17.7 (q)	C-7″, C-8″, C-10
10″	1.58 (3H, s)	25.7 (q)	C-7″, C-8″, C-9″

[a] Measured in CDCl3. δ (ppm) relative to internal TMS. Multiplicities and splitting (Hz) was given in brackets.

^{13}C NMR signals were made unambiguously by its ^{1}H–^{1}H COSY, HMQC and HMBC experiments (table 1).

3. Experimental section

3.1 General experimental procedures

IR spectra were taken on a Nicolet Magna FTIR-750 instructment. Mass spectra were obtained on a MAT-95 spectrometer. All NMR spectra were recorded on a Bruker AM-600 NMR spectrometer with TMS as internal standard.

3.2 Plant material

The leaves of *Macranga triloba* (Blume) Muell–Arg. were collected in Binh Chau preserved forest, Southern Vietnam, March 2001. A voucher specimen (Eu-MT-010) has been identified by Dr. Truong Thi Dep, the head of Department of Botany of Faculty of Pharmacy, HCMC Univ. of Medicine and Pharmacy and deposited in this faculty.

3.3 Extraction and isolation

Air-dried leaves (5 kg) of *Macranga triloba* were percolated with 95% EtOH at room temperature for one week. Evaporation of EtOH extract *in vacuo* gave a concentrated liquid (2.5 L), which was dissolved in 2.5 L water and the suspension was extracted successively with $CHCl_3$ (each 1 L × 3) and EtOAc (each 3 L × 3). The $CHCl_3$ extract was concentrated *in vacuo* to give a residue (90 g), which was subjected to a silica gel column, eluting with a $CHCl_3$–EtOAc mixture containing increasing amounts of EtOAc to afford 5 fractions. Fraction 2 (27 g) was further purified on a silica gel column, eluted with petrol ether–Me_2CO (from 10:1 to 1:1), followed by $CHCl_3$–EtOAc (40:1), petrol ether–Me_2CO (3:1) to yield compound 1 (15 mg) and 4′,7-dihydroxy-8-methylflavan (14 mg).

3.3.1 2′-hydroxy-macarangaflavanone A (1). $[\alpha]_D^{25}$ 0.86 (*C* 0.055, $CHCl_3$). UV λ_{max}^{MeOH} nm (log ε): 287.5 (4.15), 335 (sh), IR ν_{max}^{film} (cm^{-1}): 3370 (OH), 2968, 2920 (C═CH), 1641 (conj. C═O), 1500, 1458, 827. ^{1}H and ^{13}C NMR data see Table 1. HREIMS *m/z*: 424.1861 $[M]^+$ (cald. for $C_{25}H_{28}O_6$, 424.1886). EIMS *m/z* (rel. int.): 424 $[M]^+$(36), 406 $[C_{25}H_{26}O_5]^+$(3.7), 301 $[C_{16}H_{13}O_6]^+$(6.1), 153 $[C_7H_5O_4]^+$(100), 149 $[C_7H_5O_4]^+$(1.2), 123 $[C_9H_{15}]^+$(8.9), 69 $[C_5H_9]^+$(13).

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