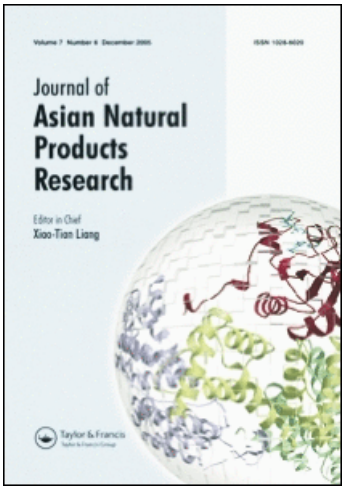

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Note

A NEW FLAVONE FROM *HYPERICUM WIGHTIANUM*

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A new flavone, wightianin (**1**), along with five known compounds, n-triacontanol (**2**), betulinic acid (**3**), oleanolic acid (**4**), 3,4-*O*-isopropylidene-shikimic acid (**5**), and isoquercitrin (**6**), were isolated from the whole plants of *Hypericum wightianum* Wall ex Wight et Arn. Their structures were elucidated on the basis of spectral data, including 2D NMR techniques.

Keywords: *Hypericum wightianum*; Wightianin; Flavone

INTRODUCTION

Hypericum is a large genus of herbs or shrubs that occurs widely in temperate regions of the world. Almost 55 species and 8 subspecies are distributed in China, and half of them have been used in Chinese herbal medicine, mainly for haemostatic and astringent purposes [1]. Recently, antifungal [2], antiviral, antidepressant [3] and antibacterial [4] compounds were isolated from this genus. *Hypericum wightianum* Wall ex Wight et Arn. has been used to treat inflammation in children, nausea, wounds and snake-bite in China [5]. Our previous paper reported the isolation of four flavonols along with β-sitosterol and β-daucosterol [6] from the ethanol extracts of this plant.

We report here the isolation and structural elucidation of a new flavone, wightianin (**1**), and five known compounds, n-triacontanol (**2**) [7], betulinic acid (**3**) [8], oleanolic acid (**4**) [9], 3,4-*O*-isopropylidene-shikimic acid (**5**) [10], and isoquercitrin (**6**) [11], from further investigation of this plant. These compounds were obtained from this plant for the first time. Their structures were determined by spectral data.

RESULTS AND DISCUSSION

Compound **1** was obtained as yellow needles. It gave a positive color reaction with HCl–Mg and showed strong yellow fluorescence under UV light (365 nm) in $AlCl_3$ solution.

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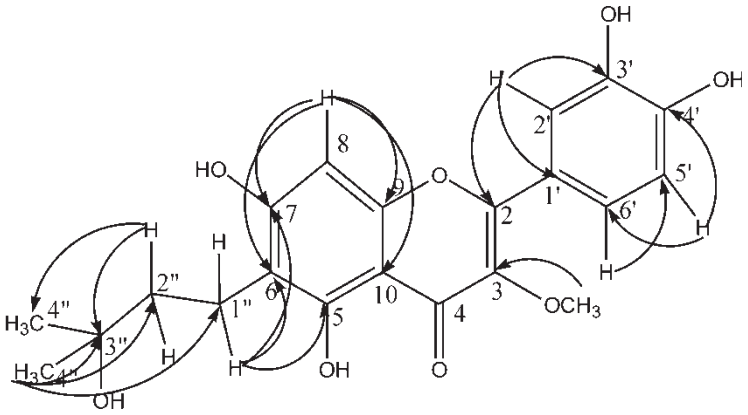

FIGURE 1 Selected HMBC correlations of compound **1**.

The chemical evidence suggested that **1** is a flavonoid. Its molecular formula $C_{21}H_{22}O_8$ was provided by positive APIESMS, negative ESIMS (at *m/z* 403 $[M + H]^+$ and 401 $[M - H]^-$) and HR-ESIMS (at *m/z* 425.1215 $[M + Na]^+$), and ^1H and ^{13}C NMR spectra. The IR spectrum suggested the presence of hydroxyl groups (3425, 3361 cm^{-1}), chelated carbonyl (1650 cm^{-1}) and aromatic rings (1605, 1567, 1519 cm^{-1}). From the ^1H NMR spectrum, a hydrogen-bonded hydroxyl group signal at δ 12.94 (1H, s), three aromatic hydroxyl groups signals at δ 10.84, 9.82, 9.46 (each 1H, s), three ABC-type aromatic proton signals at δ 7.54 (1H, d, $J = 1.8$ Hz), 7.44 (1H, dd, $J = 8.4$, 1.8 Hz) and 6.91 (1H, d, $J = 8.4$ Hz) due to H-2′, H-6′ and H-5′ of B-ring, an aromatic proton of A-ring at δ 6.47 (1H, s) and protons of a 3-hydroxy-3-methylbutyl group (δ 1.15 (6H, s), 1.51 (2H, m), 2.59 (2H, m), 4.26 (1H, s)) were recognized. From the HMBC correlations (Fig. 1) of the methoxyl protons (δ 3.78) with the C-3 (δ 138.2), the methoxyl group should be located at C-3. Correlations between the protons of H-1″ (δ 2.59) with C-2″ (δ 42.5), of H-2″ (δ 1.51) with the C-atoms at δ 17.8 (C-4″) and δ 69.6 (C-3″), and of H-4″ (δ 1.15) with the C-atoms at δ 29.7 (C-1″), 42.5 (C-2″) and 69.6 (C-3″) confirmed the structure of a 3-hydroxy-3-methylbutyl substituent group. In the HMBC spectrum (Fig. 1), the protons of H-1″ (δ 2.59) correlated with the C-atoms at δ 112.6 (C-6), 158.8 (C-5) and 162.6 (C-7), indicating that the 3-hydroxy-3-methylbutyl group was located at C-6 and the aromatic proton signal (δ 6.47) was due to H-8. Consequently, compound **1** was determined to be 5,7,3′,4′-tetrahydroxy-3-methoxy-6-(3-hydroxy-3-methylbutyl)-flavone, and was named wightianin.

EXPERIMENTAL

General Experimental Procedures

Melting points were determined on an XRC-1 micro-melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker Avance 600 spectrometer; the chemical shifts (δ) are given in ppm (TMS as internal standard). HR-ESIMS, ESIMS and APIESMS were obtained on Bruker Dalonics ApexII, Finnigan LCQ-DECA, and AGILENT LC/MS/ESI mass spectrometers, respectively. IR and UV spectra were recorded on NICOLET 200SXV FT-IR and Perkin Elmer Lambda 35 UV/Vis spectrometers, respectively. TLC was performed on plates precoated with silica gel G. Separation and purification was performed by column chromatography on silica gel (100–200 and 200–300 mesh).

Plant Material

Dried whole plants of *H. wightianum* Wall ex Wight et Arn. were collected from Xishuang Banna of Yunnan province, China in April, 2001, and identified by Professor Jinyun Cui at the Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences. A voucher specimen has been deposited in the corresponding author's laboratory, Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu, China.

Extraction and Isolation

Powdered plant material (1.6 kg) was extracted with refluxing EtOH (3 × 1 L). After evaporation of EtOH under reduced pressure, 200 g of viscous residue was obtained. This residue was suspended in MeOH and partitioned with light petroleum to give a light petroleum extract (54 g). After evaporating MeOH under reduced pressure, the residue was partitioned between 1% Na_2CO_3 and $CHCl_3$, which yielded a $CHCl_3$ extract (13 g). The Na_2CO_3 solution was acidified with dilute HCl solution to pH 4–5 and partitioned with EtOAc to give a 55 g extract. The light petroleum extract (54 g) was chromatographed over silica gel gradiently eluted with light petroleum–acetone (1:0 to 1:1) to give compound **2** (25 mg), fractions A (13 g) and B (23 g). Fraction A (13 g) was subjected to silica gel column chromatography using light petroleum–acetone (6:1) as eluent to yield compounds **3** (20 mg) and **4** (47 mg). The $CHCl_3$ extract (13 g) was chromatographed over silica gel gradiently eluted with light petroleum–acetone (50:1 to 0:1) to give fractions A′ (1 g), B′ (5.2 g) and C′ (6.5 g). Fraction A′ (1 g) was chromatographed over silica gel gradiently eluted with light petroleum–acetone (3:1 to 1:1) to afford compound **1** (13 mg). The EtOAc extract (55 g) was chromatographed over silica gel gradiently eluted with light petroleum–acetone (6:1 to 0:1) to give fractions A″ (4.3 g), B″ (10 g), C″ (23.2 g) and D″ (10.8 g). Fraction A″ (4.3 g) was

TABLE I NMR data of compound **1** in DMSO-d_6 (600 MHz for ^{1}H, 125 MHz for ^{13}C, δ in ppm)

Position	*C* atom*	δ_H *(J in Hz)*	δ_C	*HMBC*
2	C		156.0	
3	C		138.3	
4	C		178.6	
5	C		158.8	
6	C		112.6	
7	C		162.6	
8	CH	6.47 (s)	93.4	C-10, C-6, C-9, C-7
9	C		154.6	
10	C		104.6	
1′	C		121.2	
2′	CH	7.54 (d, $J = 1.8$)	116.0	C-1′, C-4′, C-3′, C-2
3′	C		149.3	
4′	C		145.9	
5′	CH	6.91 (d, $J = 8.4$)	116.4	C-6′, C-4′
6′	CH	7.44 (dd, $J = 1.8, 8.4$)	121.6	C-5′
1″	CH_2	2.59 (m)	29.7	C-6, C-5, C-7
2″	CH_2	1.51 (m)	42.5	C-4″, C-3″
3″	C		69.6	
4″	CH_3	1.15 (s)	17.8	C-1″, 2″, 3″
3-OCH_3	CH_3	3.78 (s)	60.3	C-3
5-OH		12.94 (s)		C-10, C-6, C-5
7-OH		10.84 (s)		C-6, C-7
3′-OH		9.46 (s)		C-2′, C-4′, C-3′
4′-OH		9.82 (s)		C-5′, C-4′, C-3′

* Assignments based on HSQC experiments.

subjected to silica gel column chromatography using light petroleum–acetone (2:1) to yield compound **5** (36 mg). Fraction C″ (23.2 g) was chromatographed over silica gel gradient-eluted with $CHCl_3$–MeOH (10:1 to 1:1) to afford compound **6** (543 mg).

Compound **1** Yellow needles (acetone); mp 209-210°C; IR ν_{max} (cm^{-1}): (KBr): 3425, 3361, 3221, 2972, 2939, 2753, 1650, 1605, 1566, 1519, 1472, 1361, 1294, 1214, 1163, 1121, 1090, 1047, 889, 821, 785, 634, 601; UV (MeOH) λ_{max} (nm) ($\log \varepsilon$): 259 (4.36), 268 (4.34), 295 (4.07), 354 (4.36); APIESMS (*m/z*): 403 ($[M + H]^+$, 100), 385 (35), 304 (19), 274 (18); ESIMS (*m/z*): 401($[M - H]^-$, 100), 386 (39); HR-ESIMS (*m/z*): 425.1215 ($[M + Na]^+$, calcd 425.1207); for ^1H and ^{13}C NMR data see Table I.

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