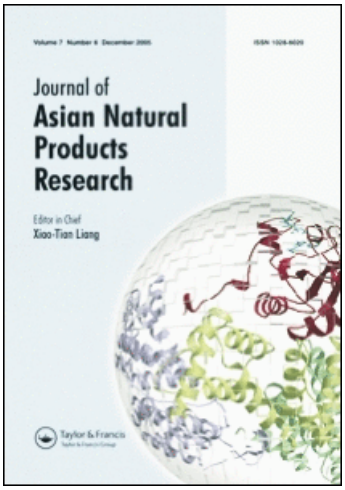

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Note

A new flavonoid from the whole plant of *Spiranthes australis* (R. Brown) Lindl

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A new flavonoid was isolated from the whole plant of *Spiranthes australis* (R. Brown) Lindl (Orchidacea). Its structure was characterized as 3,7-dimethoxy-5-hydroxy-2-{[4-(3-methyl-2-butenyl)oxy]phenyl}-4*H*-1-benzopyran-4-one on the basis of chemical and spectral evidence including 2D NMR analysis.

Keywords: Flavonoid; Orchidacea; *Spiranthes australis* (R. Brown) Lindl; 3,7-Dimethoxy-5-hydroxy-2-{[4-(3-methyl-2-butenyl)oxy]phenyl}-4*H*-1-benzopyran-4-one

1. INTRODUCTION

Spiranthes australis (R. Brown) Lindl is an Orchidacea plant distributed in the south of China. The whole herb of *Spiranthes australis* is used as a folk medicine to treat hemoptysis, headache, meningitis, coughs and so on [1,2]. According to the literature, the chemical constituents, such as hydrocarbons, fatty acids esters, sterols, orchinol, and dihydrophenathrenes, have been isolated from this plant [3]. Recently we also investigated its chemical constituents and isolated a new flavonoid from this herb.

2. Results and discussion

From the $CHCl_3$-soluble fraction of a 95% alcohol extract of the *Spiranthes australis* (R. Brown) Lindl compound **1** was isolated by repeated silica gel column chromatography.

1 was obtained as yellow needles, mp 122–123°C. HR-FABMS gave a quasi-molecular ion at *m/z* 383.1482 $[M + 1]^+$, corresponding to the molecular formula $C_{22}H_{22}O_6$. Compound **1**

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was positive to the Mg–HCl test. The IR spectrum showed hydroxyl (3427, 1226 cm^{-1}), aromatic ring (1597, 1496 cm^{-1}) and carbonyl (1658 cm^{-1}) absorptions, and its UV data showed maximum absorptions at 347 (band I) and 268 (band II) nm, which indicated that compound **1** was a flavone.

The ^{1}H NMR spectrum of **1** showed a doublet at δ6.36 (1H, d, $J = 2.0$ Hz) for H-6 and 6.45 (1H, d, $J = 2.0$ Hz) for H-8 of ring A, indicating 5,7-dioxygenation in this structure. In addition, protons of ring B showed an AA′BB′ coupling pattern, the signals at δ8.08 (2H, d, $J = 9.0$ Hz) and 7.04 (2H, d, $J = 9.0$ Hz) were assigned to H-2′, H-6′ and H-3′, H-5′ respectively; the characteristic H-3 signal was absent, which confirmed a 4′-substituent in ring B and a 3-substituent in ring C of **1**. The ^{13}C NMR data of **1** is in full agreement with the ^{1}H NMR data (table 1) [4]. The ^{1}H and ^{13}C NMR spectra indicated the presence of two methoxy groups [δ60.1, 3.87 (3H, s); 55.8, 3.88 (3H, s)] and an isopentenyloxy group [δ65.0, 4.61 (2H, d, $J = 6.7$); 119.1 (5.53, 1H, t, $J = 6.7$); 138.8; 25.8 (1.83, 3H, s); 18.2 (1.79, 3H, s)] [4], HR-FABMS showed a fragment ion at *m/z* 167.0521 $[M + 1 - OC_5H_8 - C_6H_4 - OC_3H_3]^+$ also confirming the presence of $-OC_5H_8$ and $-OCH_3$ groups in **1**. Furthermore, in the HMBC experiment, the proton signals at δ4.61, 7.04 showed correlations with the carbon signal at δ161.1, which suggest that the isopentenyloxy group is attached to the 4′ position of ring B. In addition, the methoxy proton signal (δ3.88) and the proton signals (δ6.36, 6.45) correlate with the carbon signal at δ165.4, indicating that the methoxy group is at C-7 of ring A; the proton signal of another $-OCH_3$ (δ3.87) correlated with the carbon signal at δ138.8, and it was determined that C-3 is connected with this methoxy. The remaining substituent, i.e. one hydroxyl group, has been placed at C-5. In the UV spectrum a bathochromic shift of 50 nm in band I with $AlCl_3$ (in MeOH) also confirmed the presence of a free hydroxyl group at C-5 [5].

Table 1. NMR data of compound **1** in $CDCl_3$.

Position	δ_C (*ppm*)	δ_H (*ppm*)	*HMBC*	*NOESY*
2	156.0			
3	138.8			
4	178.8			
5	162.1			
6	97.8	6.36 (1H, d, $J = 2.0$ Hz)	C_8, C_{10}, C_5, C_7	H-7″
7	165.4			
8	92.2	6.45 (1H, d, $J = 2.0$ Hz)	C_6, C_{10}, C_9, C_7	H-7″
9	156.8			
10	106.1			
1′	122.7			
2′	130.1	8.08 (1H, d, $J = 9.0$ Hz)	C_2	H-3′
3′	114.7	7.04 (1H, d, $J = 9.0$ Hz)	C_1′, C_4′	H-2′
4′	161.1			
5′	114.7	7.04 (1H, d, $J = 9.0$ Hz)	C_1′, C_4′	H-6′, H-1″
6′	130.1	8.08 (1H, d, $J = 9.0$ Hz)	C_2	H-6″, H-5′
1″	65.0	4.61 (2H, d, $J = 6.7$ Hz)	C_2″, C_3 ″, C_4′	H-5′, H-2″ H-5″
2″	119.1	5.53 (1H, t, $J = 6.7$ Hz)		H-1″, H-4″
3″	138.8			
4″	25.8	1.83 (3H, s)	C_2″, C_3″	H-2″
5″	18.2	1.79 (3H, s)	C_2″, C_3″ ″	H-1″
6″	60.1	3.87 (3H, s)	C_3	H-6′, H-1″
7″	55.8	3.88 (3H, s)	C_7	H-6, H-8

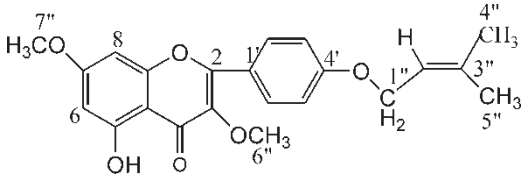

Figure 1. Structure of compound **1**.

Further determination was carried out by HMQC, HMBC and NOESY spectra (table 1).

On the basis of the above evidence, compound **1** was elucidated as 3,7-dimethoxy-5-hydroxy-2-{[4-(3-methyl-2-butenyl)oxy]phenyl}-4*H*-1-benzopyran-4-one (figure 1).

3. Experimental

3.1 General experimental procedures

Melting points were determined on a Kofler-hot stage instrument and are uncorrected. The UV spectrum was taken on a UV-1201 Shimadzu spectrometer, and the IR spectrum was recorded on a Bruker IFS-55 infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were run on a Bruker ARX-300 spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard. HR-FABMS spectra were obtained on a Bruker APEX II mass spectrometer. Separation and purification were performed by column chromatography on silica gel (200–300 mesh) (Qingdao Ocean Chemical Group Go. of China).

4. Plant material

Dried whole plants were purchased from the General Corporation of Medicinal Materials of Jiang-Su Province, China. A voucher specimen was identified by Professor Yun Zhen Guo and has been deposited in the Department of Chinese Traditional Medicine Analysis, Shenyang Pharmaceutical University, China.

5. Extraction and isolation

The plant material (10 kg) was cut into small pieces and extracted successively with 95% alcohol under reflux to give an alcohol extract. The extract was concentrated *in vacuo* then suspended in water and thoroughly partitioned with chloroform. The chloroform-soluble fraction (300 g) was roughly separated by silica gel column chromatography and eluted with petroleum–chloroform (100:5) to yield fraction A, which was further purified with petroleum–chloroform (5:1) to give compound **1** (6 mg).

Compound **1**, yellow needles (6 mg), mp 122–123°C, showed a yellow spot with 5% H_2SO_4. UV (MeOH) λ_{max} (nm): 268 [log ε (4.35)], 347, 208; λ_{max} ($AlCl_3$) (nm): 397 (sh), 347, 304 (sh), 276, 208 ($AlCl_3$ + HCl) 397 (sh), 347, 303 (sh), 277, 207; IR (KBr) ν_{max} (cm^{-1}): 3427, 1657, 1597, 1496, 1454, 1375, 1226, 1167, 1090, 947, 821; HR-FABMS *m/z* 383.1482 $[M + 1]^+$ (calcd for $C_{22}H_{23}O_6$ 383.1494), 315.0860 $[M + 1 - C_5H_8]^+$,

300.0624 $[M + 1 - C_5H_8 - CH_3]^+$, 285.0752 $[M + 1 - C_5H_8 - CH_3 - CH_3]^+$, 167.0521 $[M + 1 - C_5H_8O - C_6H_4 - C_3H_3O]^+$; ^1H NMR ($CDCl_3$, 300 MHz), ^{13}C NMR ($CDCl_3$, 75 MHz), HMBC, HMQC, NOESY data see table 1.

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