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TWO HOMOISOFLAVONES FROM *OPHIOPOGON JAPONICUS*

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Key Word Index—*Ophiopogon japonicus*; Liliaceae; roots; homoisoflavones; 6-aldehydo-isoophiopogonone A; 6-aldehydo-isoophiopogonone B.

Abstract—Two novel homoisoflavones have been isolated from the roots of *Ophiopogon japonicus*.

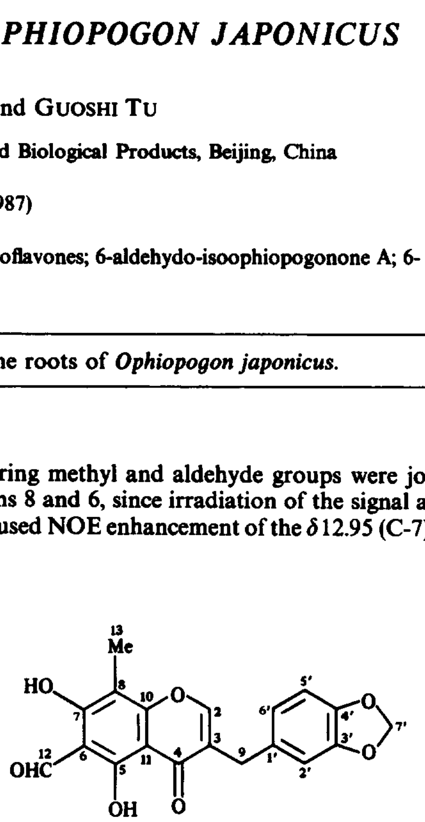
INTRODUCTION

The roots of *Ophiopogon japonicus* (Thunb) Ker-Gawl (known as Maidong in China) are widely used in traditional Chinese medicine. Homoisoflavonoids have been reported from *O. japonicus* Ker-Gawl var *genuinus* Maxim [1, 2] and *O. japonicus* (Thunb) Ker-Gawl [3]. But homoisoflavanones have been isolated only from the latter. We isolated two novel homoisoflavones, named 6-aldehydo-isoophiopogonone A (**1**) and 6-aldehydo-isoophiopogonone B (**2**) from *O. japonicus* (Thunb) Ker-Gawl.

RESULTS AND DISCUSSION

Compound **1** was found to have the molecular formula $C_{19}H_{14}O_7$ (high-resolution mass spectroscopy). In the ^1H NMR spectrum (Table 1), the signals of two hydroxyl groups and one aldehyde group were clearly seen, and were easily assigned by comparison to the reported chemical shift values for similar groupings in the literature [1–3]. The ^1H NMR signals of a benzylmethylene at $\delta 3.71$ (2H, *s*), a methylenedioxy group at $\delta 5.92$ (2H, *s*) and an aromatic ABC system at $\delta 6.72$ (3H, *s*, H-2′, 5′ and 6′) indicated the B-ring substitution pattern. This was also supported by the ^{13}C NMR spectral data (Table 2). One methyl group was found in the A-ring ($\delta 2.09$, 3H, *s*). The signal at $\delta 7.55$ (1H, *s*, H-2) indicated an olefinic proton. Bathochromic shifts of the UV absorption upon addition of $AlCl_3$ and NaOAc revealed the presence of hydroxyl groups at C-5 and C-7 [4]. The ^1H NMR signals at $\delta 13.75$ (1H, *s*) and $\delta 12.95$ (1H, *s*) indicated that the hydroxyl groups were chelated. Only the signal of the hydroxyl group at C-7 ($\delta 12.95$) was enhanced upon irradiation of the methyl signal at $\delta 2.09$. Therefore, it was considered that the methyl group was at C-8 and the aldehyde group ($\delta 10.19$, 1H, *s*) at C-6.

Compound **2** possessed the molecular formular $C_{19}H_{16}O_6$ (high resolution mass spectroscopy). The spectral data were very similar to those of compound **1**. ^1H NMR signals of a benzylmethylene at $\delta 3.72$ (2H, *s*), a methoxyl group at $\delta 3.78$ (3H, *s*) and an aromatic AA′BB′ system (6.85 and 7.17, $J = 8.5$) indicated the B-ring substitution pattern. Bathochromic shifts of UV absorption upon addition of $AlCl_3$ and NaOAc revealed the presence of hydroxyl groups at C-5 and C-7. Two hydroxyl protons appeared at $\delta 13.76$ and 12.95 (chelated). The A-ring methyl and aldehyde groups were joined at positions 8 and 6, since irradiation of the signal at $\delta 2.09$ only caused NOE enhancement of the $\delta 12.95$ (C-7) signal.



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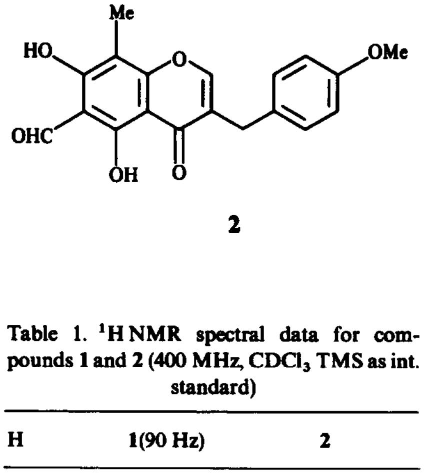

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Table 1. ^1H NMR spectral data for compounds **1** and **2** (400 MHz, $CDCl_3$ TMS as int. standard)

H	1(90 Hz)	2
2	7.55 *s*	7.52 *s*
5	13.75 *s*	13.76 *s*
7	12.95 *s*	12.95 *s*
9	3.71 *s*	3.72 *s*
12	10.19 *s*	10.20 *s*
13	2.09 *s*	2.08 *s*
2′, 5′, 6′	6.72 *s*	
2′, 6′		7.17 $J = 8.5$ Hz} AA′ BB′
3′, 5′		6.85
7′	5.92 *s*	3.78 *s*

Table 2. ^{13}C NMR (100 MHz) chemical shifts of homoisoflavones from Ophiopogon japonicus roots ($CDCl_3$)*

Carbon	1	2
2	152.6	152.5
3	124.9	125.2
4	180.7	180.8
5	167.3[a]	167.3[a]
6	104.4	104.4
7	165.7[a]	165.7[a]
8	102.4	102.3
9	30.5	29.9
10	158.2	158.2[b]
11	108.4	108.4
12	189.7	189.7
13	6.3	6.3
1′	131.0	129.2
2′	109.3[b]	130.0
3′	148.0[c]	114.3
4′	146.6[c]	158.6[b]
5′	108.5[b]	114.3
6′	122.0	130.0
7′	101.1	55.3

*Chemical shifts are given in δ (ppm) relative to TMS. The assignments are based on on- and off-resonance spectra and on comparision to data from ref. [1].

[a,b,c]: Assignments interchangeable.

EXPERIMENTAL

Isolation of homoisoflavones. Dried roots of *Ophiopogon japonicus* (Thunb) Ker-Gawl (collected in Zhejiang province, in China, authenticated by the Nanjing College of Pharmacy) were crushed and extracted with $CHCl_3$. The $CHCl_3$ extract was evapd (70 g) and chromatographed on a silica gel (2 kg) column with petrol–Et_2O (10:1–1:1). Three fractions were collected, A (100 mg), B (1.0 g) and C (40 mg). Prep. TLC (silica gel, C_6H_6) of fraction C gave **1** and **2**.

Compound **1**. Orange needles (from MeOH–$CHCl_3$), mp 170–172°. EIMS, 70 eV, m/z (rel. int.): 354.0768 $[M]^+$ (calc. for $C_{19}H_{14}O_7$ 354.0739) (100), 195 (50), 160 (8).

Compound **2**. White needles (from MeOH–$CHCl_3$), mp 144–145°. EIMS, 70 eV, m/z (rel. int.): 340.0965 $[M]^+$ (calc. for $C_{19}H_{16}O_6$ 340.0947) (100), 195 (78), 146 (11).

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