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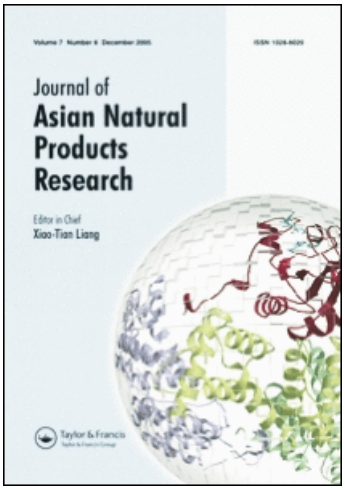

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
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To cite this Article Ruan, B. , Kong, L. -Y. , Takaya, Y. and Niwa, M.(2007) 'Studies on the chemical constituents of *Psoralea corylifolia* L.', Journal of Asian Natural Products Research, 9: 1, 41 — 44
To link to this Article: DOI: 10.1080/10286020500289618
URL: http://dx.doi.org/10.1080/10286020500289618

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Journal of Asian Natural Products Research, Vol. 9, No. 1, January–February 2007, 41–44

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Studies on the chemical constituents of *Psoralea corylifolia* L.

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(Received 8 March 2005; revised 21 June 2005; in final form 30 June 2005)

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A new isoflavone, corylinin (**1**), along with six known compounds, isopsoralen (**2**), psoralen (**3**), sophoracoumestan A (**4**), neobavaisoflavone (**5**), daidzin (**6**) and uracil (**7**), have been isolated from the dried fruits of *Psoralea corylifolia* L. The structure of **1** was established as 7,4′-dihydroxy-3′-[(*E*)-3,7-dimethyl-2,6-octadienyl]isoflavone on the basis of the spectroscopic methods. Structures of the known compounds were identified by comparison of the literature.

Keywords: *Psoralea corylifolia*; Isoflavone; Corylinin; 7,4′-Dihydroxy-3′-[(E)-3,7-dimethyl-2,6-octadienyl]isoflavone

1. Introduction

The dried fruit of *Psoralea corylifolia* L. (Leguminosae) as a well-known traditional Chinese medicine, "Buguzhi", has been widely used for thousands of years and recorded by Chinese Pharmacopoeia. There are 130 species of the plant genus *Psoralea* all over the world, whereas only the one species *Psoralea corylifolia* L. is distributed in China [1]. It is an effective invigorant against impotence, menstruation disorder and uterine haemorrhage [2]. It also shows skin photosensitivity activity [3], coronary vasodilatory activity, an inhibitory effect on HeLa cells and an estrogenic effect [4]. Clinically it is used for the treatment of vitiligo and psoriasis [5]. During our phytochemical studies on *P. corylifolia* L. we have isolated a new isoflavone, 7,4′-dihydroxy-3′-[(*E*)-3,7-dimethyl-2,6-octadienyl]isoflavone, named corylinin (**1**), together with six known compounds identified as isopsoralen (**2**) [6], psoralen (**3**) [6], sophoracoumestan A (**4**) [**7**], neobavaisoflavone (**5**) [8], daidzin (**6**) [9] and uracil (7) [10]. Compounds **6** and **7** were obtained from this genus for the first time. This paper is concerned with the isolation and structural elucidation of **1**.

2. Results and discussion

Compound **1** was obtained as an amorphous white powder. The quasi-molecular ion peak at *m/z* 391.1891 in the HRFAB-MS spectrum indicated the molecular formula to be $C_{25}H_{26}O_4$.

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Journal of Asian Natural Products Research
ISSN 1028-6020 print/ISSN 1477-2213 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/10286020500289618

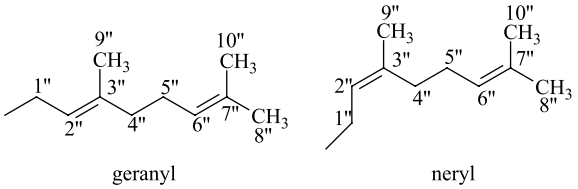

Figure 1. The two possible side chains of **1**.

The IR spectrum of **1** indicated the presence of an aromatic ring (1574, 1508 cm^{-1}), hydroxyl (3348 cm^{-1}) and carbonyl (1626 cm^{-1}). The UV absorptions at 246 and 298 nm and a singlet at δ 8.22 for H-2 in ^{1}H NMR showed that **1** was an isoflavone, which was confirmed by the HMBC correlations between H-2 (δ 8.22) with C-1′ (δ 123.7) and H-2′ (δ 7.23) with C-3 (δ 126.9).

The ^{1}H NMR spectrum revealed a set of signals consisting of three methyl singlets (δ 1.53, 1.56, 1.68), three methylene multiplets (δ 1.98, 2.05, 3.25) and two olefinic protons (δ 5.06, 5.32) assignable to geranyl or neryl moieties (figure 1). This side chain was proved to be a geranyl group by chemical shift values of 9″-CH_3 and 4″-CH_2 at δ 15.8 and 40.0 in the ^{13}C NMR spectrum, comparing the ^{13}C NMR data of the same carbon atoms of nerol at δ 22.8 and 31.5, respectively [11]. The NOESY spectrum showed a correlation between 1″-CH_2 (δ 3.25) and 9″-CH_3 (δ 1.56), further proving the presence of a geranyl group. In addition, the ^{1}H NMR spectrum of **1** showed two typical ABX systems in the aromatic proton region: δ 7.95 (1H, d, $J = 8.8$ Hz), 6.93 (1H, dd, $J = 8.8$, 2.3 Hz), 6.84 (1H, d, $J = 2.3$ Hz) and δ 6.82 (1H, d, $J = 8.2$ Hz), 7.18 (1H, dd, $J = 8.2$, 2.2 Hz), 7.23 (1H, d, $J = 2.2$ Hz), indicating the presence of three substituents including one geranyl group and two hydroxyl groups in **1**. Because of the deshielding effect of the carbonyl group, the doublet at δ 7.95 (1H, d, $J = 8.8$ Hz) should be due to H-5, which showed a vicinal coupling effect with H-6 at δ 6.93 (1H, dd, $J = 8.8$, 2.3 Hz). The HMBC spectrum showed that H-2′ (δ 7.23, d, $J = 2.2$ Hz) correlated with C-1″ (δ 27.8), proving that the geranyl group was located at C-3′, so that two hydroxyl groups must be located at C-7 and C-4′, respectively. Thus the structure of **1** was established as 7,4′-dihydroxy-3′-[(*E*)-3,7-dimethyl-2,6-octadienyl]isoflavone (figure 2).

3. Experimental

3.1 General experimental procedures

The UV spectra were recorded on a Shimadzu UV-2051 PC spectrophotometer in MeOH. The IR spectra were recorded on an Impact-410 (Nicolet) spectrophotometer. The 1D NMR and 2D NMR spectra were recorded on a JEOL A-600 spectrometer using TMS as an internal standard. The ESI-MS spectra were measured on an Agilent 1100 Series LC/MSD.

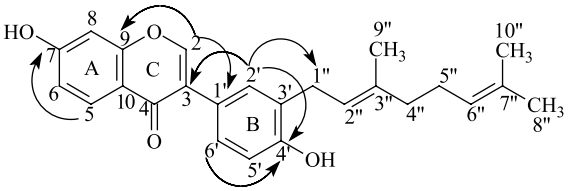

Figure 2. The key HMBC correlations of **1**.

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Table 1. ^{1}H NMR (600 MHz, DMSO-d_6) and ^{13}C NMR (150 MHz, DMSO-d_6) data of **1**.

No.	δ_C	*HMQC*	*HMBC*
2	152.3	8.22 (1H, s)	C-4, C-9, C-1′
3	126.9		
4	174.5		
5	127.0	7.95 (1H, d, $J = 8.8$ Hz)	C-7, C-9
6	115.2	6.93 (1H, dd, $J = 8.8$, 2.3 Hz)	C-8
7	163.2		
8	114.4	6.84 (1H, d, $J = 2.3$ Hz)	C-10
9	157.6		
10	122.6		
1′	123.7		
2′	129.9	7.23 (1H, d, $J = 2.2$ Hz)	C-3, C-4′, C-1′, C-1″
3′	130.1		
4′	154.7		
5′	101.9	6.82 (1H, d, $J = 8.2$ Hz)	
6′	127.2	7.18 (1H, dd, $J = 8.2$, 2.2 Hz)	C-1′, C-2′, C-4′
1″	27.8	3.25 (2H, d, $J = 7.3$ Hz)	C-3″
2″	122.5	5.32 (1H, m, $J = 7.3$ Hz)	C-4″, C-9″
3″	134.9		
4″	40.0	1.98 (2H, m)	C-2″, C-3″, C-5″, C-9″
5″	26.1	2.05 (2H, m)	C-4″, C-6″, C-7″
6″	124.0	5.06 (1H, m)	
7″	130.6		
8″	25.3	1.68 (3H, s)	C-6″, C-7″, C-10″
9″	15.8	1.56 (3H, s)	C-2″, C-3″, C-4″
10″	17.5	1.53 (3H, s)	C-6″, C-7″, C-8″

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HRFAB-MS spectra were measured on a JEDL-HX-110 spectrometer using *m*-nitrobenzyl alcohol as a matrix. Column chromatography was carried out using Kieselgel 60 silica gel and Sephadex LH-20. TLC was conducted on Kieselgel 60 F_{254} plates.

3.2 Plant material

The fruits of *Psoralea corylifolia* L. were collected in the suburbs of Nanjing city, Jiangsu Province, China, and identified by Professor Min-Jian Qin, Department of Medicinal Plants, China Pharmaceutical University. A voucher specimen has been deposited in the Department of Natural Medicinal Chemistry, China Pharmaceutical University.

3.3 Extraction and isolation

The dried fruits (5.0 kg) of *P. corylifolia* L. were extracted with 95% EtOH (3 × 12 L) under reflux for 3 × 2 h. The extract (800 g) was suspended in H_2O (4 L) and extracted with petroleum ether, EtOAc and *n*-BuOH successively. The petroleum ether-soluble fraction (205 g) was subjected to silica gel chromatography and eluted by petroleum ether/EtOAc mixtures gradually increasing polarity to yield **2** (1.2 g) (petroleum ether/EtOAc = 97:3), **3** (800 mg) (petroleum ether/EtOAc = 96:4), **4** (50 mg) (petroleum ether/EtOAc = 90:10), and a white powder mixture containing compounds **1** and **5** (petroleum ether/EtOAc = 70:30), which was subjected to Sephadex LH-20 chromatography to yield **1** (5 mg) and **5** (10 mg). The *n*-BuOH-soluble fraction (39 g) was subjected to silica gel chromatography and eluted by chloroform/MeOH mixtures gradually increasing polarity to yield **6** (21 mg) (chloroform/MeOH = 100:12) and **7** (18 mg) (chloroform/MeOH = 100:8).

3.3.1 Corylinin (1). An amorphous white powder; UV λ_{max} (MeOH) (nm): 246, 298; IR ν_{max} (KBr) (cm^{-1}): 3348, 3109, 3038, 2930, 2559, 1626, 1574, 1508, 1456, 1379,1267,1055, 955, 858, 787; ESI-MS *m/z*: 391 $[M + H]^+$; HRFAB-MS *m/z*: 391.1891 $[M + H]^+$ (calcd for $C_{25}H_{27}O_4$, 391.1901); ^1H NMR (600 MHz, DMSO-d_6) and ^{13}C NMR (150 MHz, DMSO-d_6) data: see table 1.

Acknowledgements

The research work was supported by the Teaching and Research Award Program for Outstanding Young Teachers in Higher Education Institutions of MOE, China.

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