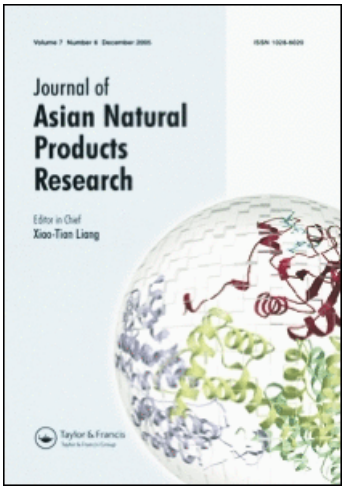

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Wei Wang[a]; Dong-Ge An[b]; Hu-Biao Chen[a]; Guang-Zhong Tu[b]; Yu-Ying Zhao[a]
[a] Department of Natural Medicines, School of Pharmaceutical Sciences, Peking University, Beijing, China [b] Beijing Institute of Microchemistry, Beijing, China

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TWO NEW PTEROCARPENES FROM *HEDYSARUM MULTIJUGUM*

WEI WANG[a], DONG-GE AN[b], HU-BIAO CHEN[a], GUANG-ZHONG TU[b] and YU-YING ZHAO[a,*]

[a]*Department of Natural Medicines, School of Pharmaceutical Sciences, Peking University, Beijing 100083, China;* [b]*Beijing Institute of Microchemistry, Beijing 100871, China*

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Two new pterocarpenes were isolated from the roots of *Hedysarum multijugum*, and their structures were elucidated as hedysarimpterocarpene B (**1**) and hedysarimpterocarpene C (**2**) on the basis of spectroscopic data.

Keywords: Leguminosae; *Hedysarum multijugum*; Pterocarpenes

INTRODUCTION

The roots of *Hedysarum multijugum* Linn. (Leguminosae) have been used as folk herbal drugs in China for the treatment of palpitation and chronic nephritis [1]. We have reported 11 compounds and a new pterocarpene from the roots of *H. multijugum* [2,3]. This paper deals with the isolation and structural elucidation of two new pterocarpenes, hedysarimpterocarpene B (**1**) and hedysarimpterocarpene C (**2**).

RESULTS AND DISCUSSION

Compound **1** was obtained as colorless needles, mp 143–148°C (dec.). EI-MS (*m/z*) showed 352[M]$^+$, 337[M − CH_3]$^+$. The negative HRFAB-MS exhibited a molecular formula $C_{21}H_{20}O_5$ (found *m/z* 351.1237[M − 1]$^-$; calcd *m/z* 351.1238).

The UV spectrum of this compound (λ_{max}^{MeOH} nm: 334, 224) was similar to that of 1,7-dihydroxy-3,9-dimethoxypterocarpene [3], suggesting a pterocarpene structure for **1**. The ^{1}H-NMR spectrum of **1** showed proton signals of the pterocarpene skeleton at δ 5.45 (2H, s, H-6), two *meta*-coupled aromatic proton signals at δ 6.07 (1H, d, $J = 2.0$ Hz) and δ 6.06 (1H, d, $J = 2.0$ Hz), two *ortho*-coupled proton signals at δ 7.07 (1H, d, $J = 8.0$ Hz) and δ 6.85 (1H, d, $J = 8.0$ Hz), a methoxyl signal at δ 3.88 (3H, s), and signals of a prenyl unit:

*Corresponding author. Tel.: +86-10-62091592. Fax: +86-10-62015584. E-mail: nmechem@mail.bjmu.edu.cn

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δ 5.30 (1H, t, $J = 7.0$ Hz, $-CH_2-CH{=}C<$), 3.58 (2H, d, $J = 7.0$ Hz, $-CH_2-CH{=}C<$), 1.84 (3H, s, $-CH_3$), 1.71 (3H, s, $-CH_3$). One and two dimensional NMR techniques (^{1}H-NMR, ^{13}C-NMR, HMQC and HMBC) permitted assignments of all ^{1}H and ^{13}C-NMR signals of **1** (Table I). The connection positions of the methoxy group and prenyl group were assigned on the basis of ^{1}H$-^{13}$C long-range correlations in the HMBC spectrum (Fig. 1). HMBC correlations from H-1′ (δ 3.58) of the prenyl group to the C-9 linked methoxy group and C-10a (δ 154.12) suggested that the methoxy and prenyl unit were in *ortho*-positions of the B ring. Compound **1** was therefore determined to be 1,3-dihydroxy-9-methoxy-10-prenylpterocarpane, which is a new compound named hedysarimpterocarpene B.

Compound **2** was obtained as a colorless amorphous solid, mp 240°C (dec.). The UV spectrum of this compound (λ_{max}^{MeOH} nm: 333, 255, 217) was similar to that of hedysarimpterocarpene B, suggesting a pterocarpene structure for **2**. The ^{1}H-NMR and ^{13}C-NMR spectra of **2** gave characteristic proton and carbon signals of the pterocarpene at δ 5.50 (2H, s, H-6) and δ 65.00 (C-6). Two *meta*-coupled proton singals at δ 6.02 (1H, d, $J = 2.4$ Hz), 5.95 (1H, d, $J = 2.4$ Hz) and a proton signal at δ 6.49 (1H, s, H-8) were observed. The spectrum also showed the presence of two methoxyl signals at δ 3.73 (3H, s) and 3.77 (3H, s), and two hydroxyl signals at δ 9.97 (1H, s), 9.60 (1H, s). The carbon signals of **2** in the ^{13}C-NMR spectrum were in good agreement with those of hedysarimpterocarpene A (**3**) [3], except that the C-10 signal of **2** was shifted 9.29 ppm downfield, the C-8, C-9 and C-10a were shifted 2.89, 3.88, 2.73 ppm upfield, respectively, compared to **3**. The negative HRFAB-MS (*m/z*) of **2** gave 626[M]$^+$, the high resolution N-FAB-MS indicated the molecular formula $C_{34}H_{26}O_{12}$ (found *m/z* 625.1357[M $-$ 1]$^-$; calcd *m/z* 625.1351), The EI-MS (*m/z*) of **3** [3] showed 314[M]$^+$, suggesting **2** was a dimer of **3** linked at C-10. ^{1}H-NMR and ^{13}C-NMR spectral data were defined in Table I. Compound **2** is a new compound named hedysarimpterocarpene C (Fig. 1).

TABLE I The NMR data of compounds **1** and **2**

Compound **1** ($CDCl_3$)			Compound **2** (DMSO-d_6)		
No.	^{13}C	^{1}H	No.	^{13}C	^{1}H
1	151.96		1	153.02	
2	96.98	6.07 (1H, d, 2.0 Hz)	2	95.34	5.95 (1H, d, 2.4 Hz)
3	157.82		3	160.13	
4	96.96	6.06 (1H, d, 2.0 Hz)	4	94.08	6.02 (1H, d, 2.4 Hz)
4a	155.08		4a	155.13	
6	65.44	5.45 (2H, s)	6	64.98	5.50 (2H, s)
6a	104.70		6a	104.44	
6b	118.62		6b	108.33	
7	115.29	7.07 (1H, d, 8.0 Hz)	7	150.04	
8	108.27	6.85 (1H, d, 8.0 Hz)	8	95.34	6.49 (1H, s)
9	154.68		9	155.62	
10	114.17		10	98.15	
10a	154.12		10a	155.30	
11a	146.15		11a	144.63	
11b	97.34		11b	98.99	
9-OCH_3	56.72	3.88 (3H, s)	9-OCH_3	56.53	3.77 (3H, s)
1′	22.94	3.58 (2H, d, 7.0 Hz)	3-OCH_3	55.03	3.73 (3H, s)
2′	121.67	5.30 (1H, m, 7.0 Hz)	1-OH		9.60 (1H, s)
3′	132.20		7-OH		9.97 (1H, s)
4′	17.77	1.84 (3H, s)			
5′	25.68	1.71 (3H, s)			

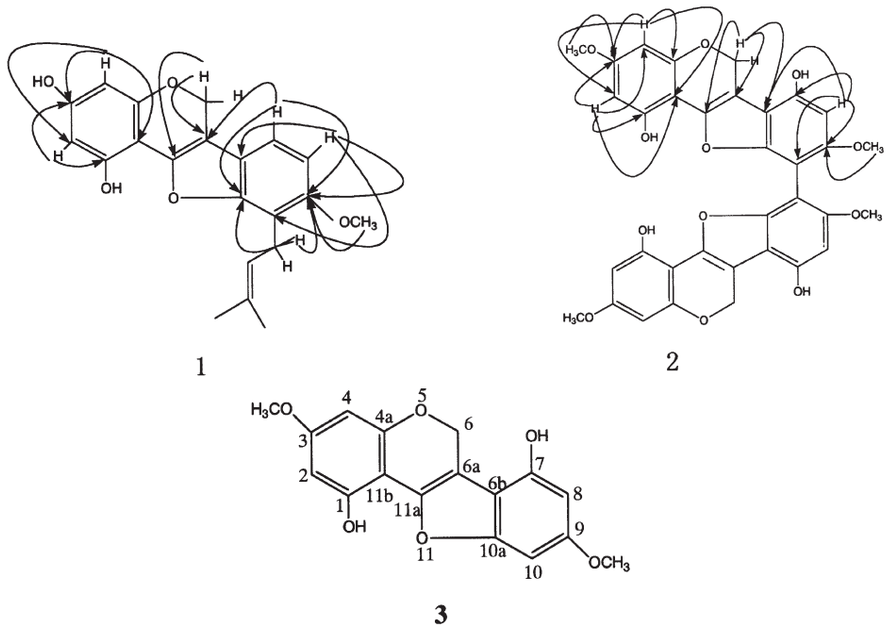

FIGURE 1 Important HMBC correlations of **1** and **2** and structures of **1**–**3**.

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were determined on XT-4A micromelting point apparatus. The UV spectra were measured on a Jingdao 260. HRFAB-MS were recorded on an APEXII. ^{1}H, ^{13}C-NMR, HMBC, HMQC spectra were taken on a Bruker DRX-500 and VXR-300. Column chromatography was carried out on silica gel from the Qingdao Haiyang Chemical Factory. Sephadex LH-20 was purchased from OUYA Company in Beijing.

Plant Material

The roots of *H. multijugum* were collected from the Gansu Province of China, and were identified by Professor Chen Hu-biao of the School of Pharmaceutical Science, Peking University. A voucher specimen is deposited at the Herbarium of the School of Pharmaceutical Science, Peking University.

Extraction and Isolation

The roots (8 kg) of *H. multijugum* were refluxed with 95% EtOH three times and the extract was concentrated to give a residue (600 g) under reduced pressure. The residue (300 g) was subjected to chromatographic separation on a silica gel column, and was eluted with $CHCl_3$–MeOH (9:1), Fractions I–VI were obtained. Fr. V was separated by Sephadex LH-20 (90% MeOH) to give compound **1** (30 mg). Fr. VI was separated by Sephadex LH-20 (80% MeOH), and compound **2** (10 mg) was obtained.

Compound 1

Hedysarimpterocarpane B was isolated as colorless needles, mp 143–148°C (dec.). UV λ_{max}^{MeOH} nm: 334, 224. EI-MS (*m/z*) 352$[M]^+$, 337$[M - CH_3]^+$, N-HRFAB-MS: 351.1237$[M - 1]^-$ (calcd for $C_{21}H_{20}0_5$: 351.1238). ^{1}H-NMR and ^{13}C-NMR see Table I.

Compound 2

Hedysarimpterocarpene C was obtained as a colorless amorphous solid, mp 240°C (dec.). UV λ_{max}^{MeOH} nm: 333, 255, 217, FAB-MS (*m/z*): 626$[M]^+$, N-HRFAB-MS: 625.1357$[M - 1]^-$ (calcd for $C_{34}H_{26}O_{12}$: 625.1351). ^{1}H-NMR and ^{13}C-NMR see Table I.

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