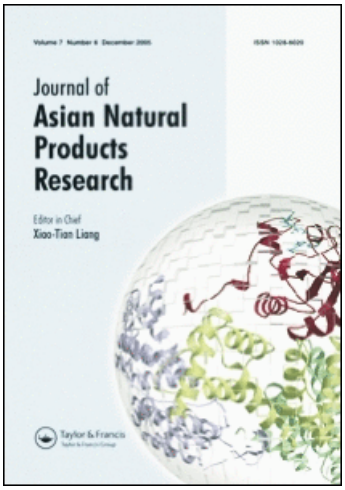

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A NEW STILBENE DIMER – SHEGANSU B FROM *BELAMCANDA CHINENSIS*

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A new dimeric stilbene, named shegansu B (**1**) was isolated from the ethanolic extract of the roots of *Belamcanda chinensis* (L.) DC., along with the known compounds isorhapontigenin, resveratol, *p*-hydroxybenzoic acid, iridin, tectoridin, tectorigenin and daucosterol. The structures were elucidated by means of spectroscopic evidence including 2D-NMR studies.

Keywords: *Belamcanda chinensis*; Shegansu B; Isorhapontigenin; Resveratol

INTRODUCTION

The rhizome of *Belamcanda chinensis* (L.) DC., a commonly used Chinese traditional medicine, has been used in China as an antiinfective, antitussive and expectorant agent. As part of our systematic studies on oligomer stilbene constituents, we obtained an isorhaportigenin dimer from *Belamcanda* of *Iridaceae* for the first time. It is another example [1,2] of the dehydrogenation oligomer derived from isorhapontigenin [(*E*)-3,5,4′-trihydroxy-3′-methoxystilbene] in some woody plant.

In previous papers [3–5], eleven compounds were isolated from *B. chinensis* (L.) DC., most of them were isoflavones and their glucosides. In continuation of our studies on the acetone soluble fraction, a new dimeric stilbene, named shegansu B was isolated. Its structure was elucidated as **1** by using 2D-NMR techniques (500 MHz). In addition, two other stilbene derivatives, isorhapontigenin and resveratol, were separated from this plant

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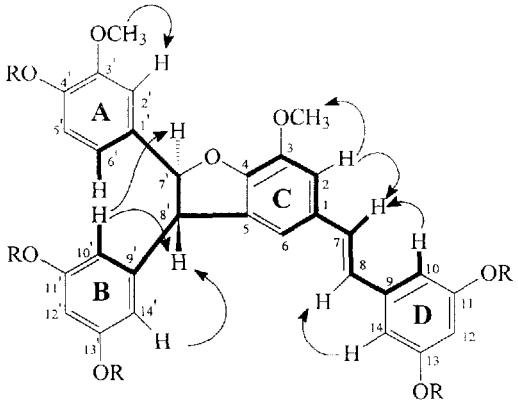

FIGURE 1 Important NOEs and HMBC correlation of shegansu B.

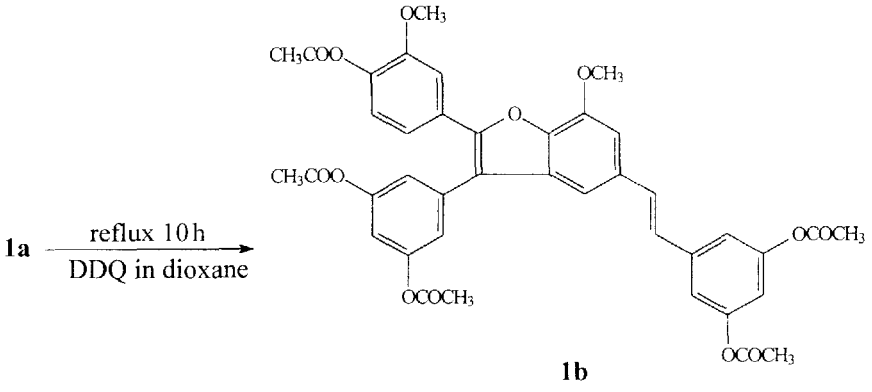

FIGURE 2 The structure of **1b**.

for the first time. Pharmacological test indicated that shegansu B has potent antagonism to lenukotriene D_4 receptor with an IC_{50} of 10^{-5} mol L^{-1} [6]. Further pharmacological activity is being investigated (Figs. 1 and 2).

RESULTS AND DISCUSSION

Shegansu B (**1**) was isolated as a yellowish amorphous powder with an optical rotation $[\alpha]_D^{25}$ +21 (*c* 0.048 EtOH). The molecular formula $C_{30}H_{26}O_8$

was determined from a combination of FABMS (*m/z* 515 $[M+1]^+$) and elementary analysis (*Anal.* C 67.13%, H 5.24%, calcd. for $C_{30}H_{26}O_8 \cdot H_2O$, C 67.67%, H 5.26%) as well as the FABMS data of the acetylated derivative (**1a**), the fragment ion peak of **1a** at *m/z* 725 $[M+1]^+$ indicated the presence of five hydroxyl groups in the molecule. The UV maximum at 328 nm indicated characteristics of a hydroxystilbene, no shift was observed by adding sodium acetate–boric acid, suggesting the absence of ortho-dihydroxyl groups in the molecule. The IR spectrum showed the presence of hydroxyl groups (3400 cm^{-1}), aromatic and olefinic groups (1660, 1610, 1510, 1500 cm^{-1}). The ^{1}HNMR spectrum of **1** revealed two signals of aromatic methoxyl groups at δ 3.83 (3H, s, 3′-OCH_3), 3.92 (3H, s, 3-OCH_3); two methine groups at δ 4.48 (1H, d, $J=8.6$ Hz, H-8′), 5.54 (1H, d, $J=8.6$ Hz, H-7′); two *trans*-coupling olefinic protons at δ 6.89 (1H, d, $J=16.3$ Hz, H-7), δ 7.00 (1H, d, $J=16.3$ Hz, H-8) and eleven aromatic protons at δ 6.26–7.14, in which two signals of protons H-2 and H-6 (δ 7.14 and 6.79) were attributed to *meta* coupling ($J=1.1$ Hz) on ring C; the signals of protons H-5′, H-6′, H-2′ (δ 6.81, 6.83, 7.02) belonged to an ABX system on ring A. The remaining six protons [H-12, H-10, H-14 (δ 6.26, 6.51) and 12′, 10′, 14′ (δ 6.20, 6.23)] were attributed to two sets of AB2 system ($J=2.2$ Hz) on rings D and B, respectively. The ^{13}CNMR spectrum of **1** displayed 26 signals representing 30 carbons: 2 methoxyl carbons (δ 56.3, 56.5), 2 methine carbons (δ 58.1, 94.4), 2 olefinic carbons (δ 127.5, 129.3), 13 quaternary aromatic carbons and 11 protonated aromatic carbons (see Table I). The structure of **1** was further clarified by means of ^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY, HMBC and NOE analyses as well as comparison with the spectroscopic data in literature [7]. The location of the two methoxy groups, two *trans*-coupling olefinic protons and the relative configuration of the two methine groups were supported by DIFNOE spectrum of **1**. The signals of H-7 (δ 6.89) and 3-OCH_3 (δ 3.92) were enhanced after irradiation of the signal of H-2 (δ 7.14), and the signals of H-7 and H-8 (δ 7.00) were enhanced after irradiation of H-10 and H-14 (δ 6.51), indicating that rings C and D were connected by the *trans*-double bond. Irradiation of 3′-OCH_3 (δ 3.83) gave NOEs to H-2′ (δ 7.02), indicating H-2′ was adjacent to 3′-OCH_3. The signals of H-7′ (δ 5.54) and H-8′ (δ 4.48) were enhanced after irradiation of H-10 and H-14 (δ 6.02), indicating that H-7′ should be *trans* oriented to H-8′. Thus we suggested that the structure of **1** was an isorhapontigenin dimer. The connectivity of the two parts of isorhapontigenin was further confirmed by HMBC spectrum. The cross peaks were assigned as: H-2 (δ 7.14)/C-4 (δ 149.1), H-7 (δ 6.89)/C-2 (δ 111.6) and C-9 (δ 140.6), H-10 (δ 6.51)/C-8 (δ 129.3), H-8′ (δ 4.48)/C-5 (δ 133.0) and C-1′ (δ 132.7), H-10′ (δ 6.20)/C-8′

TABLE 1. ^{1}HNMR, ^{13}CNMR and HMBC data for compound **1** in DSMO-d_6[a]

H	ppm (Hz)	*C*	ppm	*HMBC*
1		1	132.6	
2	7.14 (d, 1.1)	2	111.6	H-7
3		3	145.4	H-2
4		4	149.1	H-2
5		5	133.0	H-8′, H-7′
6	6.79 (d, 1.1)	6	115.7	H-2
7	6.89 (d, 16.3)	7	127.5	H-2
8	7.00 (d, 16.3)	8	129.3	H-7, 10 or 14
9		9	140.6	H-7
10	6.51 (d, 2.2)	10	105.6	H-14
11		11	159.5	H-10 or 14
12	6.26 (t, 2.2)	12	102.1	H-10, 14
13		13	159.5	H-10 or 14
14	6.51 (d, 2.2)	14	105.6	H-10
		1′	132.7	H-8′
2′	7.02 (d, 2)	2′	110.9	H-7′
		3′	148.4[b]	
		4′	147.6[b]	H-2′
5′	6.81 (d, 8)	5′	120.1	H-2′
6′	6.83 (dd, 8, 2)	6′	116.6	H-7′, 2′
7′	5.54 (d, 8.6)	7′	94.4	H-8′, 2′
8′	4.48 (d, 8.6)	8′	58.1	H-14′, 10′
		9′	144.9	H-7′, 8′
10′	6.20 (d, 2.2)	10′	107.5	H-8′, 14′, 12′
		11′	159.7	H-14′, 12′
12′	6.23 (t, 2.2)	12′	102.6	H-14′ or 10′
		13′	159.7	H-14′, 12′
14′	6.20 (d, 2.2)	14′	107.5	H-8′, 12′
OCH_3	3.83, s	OCH_3	56.3	
OCH_3	3.92, s	OCH_3	56.5	

[a]Assignments were confirmed by DEPT, ^{1}H-^{1}H COSY and ^{1}H-^{13}C COSY experiments. [b]Interchangeable assignments.

(δ 58.1), H-6′ (δ 6.83)/C-7′ (δ 94.4), H-7′ (δ 5.54)/C-5 (δ 133.0), respectively (Fig. 1). Thus the fundamental structure of **1** was assigned to have a head to head and tail to tail connectivity of two isorhapontigenin molecules.

In order to verify the structure of shegansu B, the acetate (**1a**) was successfully converted into dehydrogenated benzofuran acetate as follows: (i) shegansu B was acetylated with acetic anhydride and pyridine to give (ii) shegansu B pentaacetylate. The acetate (**1a**) was dehydrogenated by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in dry dioxane to afford a dehydrogenated benzofuran acetate (**1b**). The ^{1}HNMR spectral data of **1b** resembled very closely to that of **1a**, except for the signals of H-7′ and H-8′. Thus the structure of **1** was unambiguously substantiated to be a dimeric isorhapontigenin.

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were determined on a XT4-100X micromelting point apparatus and are uncorrected. Optical rotation was measured on a Perkin-Elmer 241 polarimeter, and IR spectra were obtained on Perkin Elmer 683 infrared spectrophotometer. NMR spectra were determined on Bruker AM 500 spectrometer using TMS as internal standard. EIMS were obtained on a ZAB-2F mass spectrometer. FABMS were obtained on a JMS-DX 300 mass spectrometer. Elemental analysis was carried out on a MOD 1106 elemental analyzer. Column chromatography was performed using Si gel (Qing Dao Hai Yang Chemical Group Co., Qing Dao, People's Republic of China), TLC was conducted on Si gel GF_{254} (Qing Dao Hai Yang Chemical Group Co.) and monitored at 254 nm.

Plant Material

Rhizomes of *B. chinensis* were collected from Hebei province of the People's Republic of China in September 1992 and identified by Professor W.Z. Song of our Institute, where a voucher specimen (92025) of the plant has been deposited.

Extraction and Isolation

Powdered rhizomes (32 kg of B. *chinensis*) were extracted and isolated into A–F fractions according to Ref. [3]. Fraction F (4.14 g) was chromatographed on silica gel and eluted with $CHCl_3$–MeOH–Me_2CO (5 : 0.1 : 0.1) to yield tectorigenin (80 mg) and isorhapontigenin (61 mg). Fraction E (3.8 g) was rechromatographed on a silica gel column with $CHCl_3$–MeOH–EtOAc (9 : 0.5 : 0.5) as eluent and 7 portions were collected. Portion 2 was further purified on a silica gel column using cyclohexane–$CHCl_3$–MeOH–EtOAc–H_2O (1 : 7.5 : 1 : 0.5 : 0.1) as eluent and afforded shegansu B (100 mg). The fraction III (23 g) was carried out on a silica gel column and eluted with hexane–$CHCl_3$–EtOAc–MeOH–H_2O (1 : 7.5 : 0.5 : 1 : 0.1) and 7 portions were collected. Portion 3 was further separated on a silica gel column using cyclohexane–Me_2CO–EtOAc (3 : 2 : 0.1) as eluent to afford resveratrol (400 mg) and *p*-hydroxybenzoic acid (55 mg), respectively.

Shegansu B (1)

This was obtained as yellowish amorphous, $[\alpha]_D^{25}$ +21 (*c* 0.048, EtOH); UV (EtOH) λ_{max}(log ε) 285(sh) (4.21), 328(4.48) nm; UV (EtOH + NaOAc) λ_{max} 285(sh), 328 nm; IR (KBr) ν_{max} 3400, 1660, 1520, 1500, 960, 870 cm^{-1}; ^{1}HNMR, ^{13}CNMR, HMBC spectrum data see Table 1, FABMS *m/z* 515 $[M+1]^+$ (70%); *Anal.* C 67.13%, H 5.24%, calcd. for $C_{30}H_{26}O_8 \cdot H_2O$. C 67.67%, H 5.26%. The observed difference of NOE spectrum are summarized in structure **1**.

Acetylation of 1 (1a)

Ac_2O (1 mL) was added to pyridine (1 mL) solution of **1** (50 mg) by the usual method giving an amorphous powder (50 mg), m.p. 94 98°C: FABMS *m/z* 725 $[M+1]^+$ (100%).

Dehydrogenation of 1a (1b)

A solution of **1a** (40 mg, 0.055 mmol) in dry dioxane was added to DDQ (40 mg, 0.18 mmol) in dry dioxane (10 mL). Then the mixed solution was stirred under reflux for 10 h. The reaction mixture was evaporated to dryness, which was purified by column chromatography on silica gel using ($CHCl_3$–MeOH 200 : 1) as eluent and recrystallized from MeOH to afford **1b** (14 mg) as colorless needles. ^{1}HNMR ($CDCl_3$, 500 MHz) δ 2.28–2.31 (15H, m, 5 × OAc), 3.68 (3H, s, OCH_3), 4.10 (3H, s, OCH_3), 6.80 (1H, t, J = 2.1, H-12), 6.98 (1H, d, J = 16.4 Hz, H-7), 7.00 (1H, d, J = 2.1 Hz H-2′), 7.01 (1H, d, J = 2.1 Hz, H-6), 7.02 (1H, br, H-12′), 7.04 (1H, d, J = 8.3 Hz, H-5′), 7.12 (1H, d, J = 16.4 Hz, H-8), 7.13 (2H, d, J = 2.1 Hz, H-10,14), 7.14 (2H, J = 2.0 Hz, H-10′,14′), 7.18 (1H, d, J = 2.1 Hz, H-2), 7.36 (1H, dd, J = 2.1, 8.3 Hz, H-6′). EIMS *m/z* 722 $[M]^+$ (30%).

Acknowledgments

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