

This article was downloaded by:

On: 22 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Asian Natural Products Research

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713454007>

Two new phenanthrofurans from *Pleione bulbocodioides*

Xin-Qiao Liu^a; Yuan-Qiang Guo^b; Wen-Yuan Gao^a; Tie-Jun Zhang^c; Lu-Lu Yan^a

^a School of Pharmaceutical Science and Technology, Tianjin University, Tianjin, China ^b Department of Pharmaceutical Sciences, Nankai University, Tianjin, China ^c Tianjin Institute of Pharmaceutical Research, Tianjin, China

Online publication date: 27 July 2010

To cite this Article Liu, Xin-Qiao , Guo, Yuan-Qiang , Gao, Wen-Yuan , Zhang, Tie-Jun and Yan, Lu-Lu(2008) 'Two new phenanthrofurans from *Pleione bulbocodioides*', Journal of Asian Natural Products Research, 10: 5, 453 – 457

To link to this Article: DOI: 10.1080/10286020801892391

URL: <http://dx.doi.org/10.1080/10286020801892391>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Two new phenanthrofurans from *Pleione bulbocodioides*

Xin-Qiao Liu^{ab}, Yuan-Qiang Guo^c, Wen-Yuan Gao^{a*}, Tie-Jun Zhang^d and Lu-Lu Yan^a

^aSchool of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China; ^bSchool of Chemical and Environmental Engineering, Hubei University of Technology, Wuhan 430068, China;

^cDepartment of Pharmaceutical Sciences, Nankai University, Tianjin 300071, China; ^dTianjin Institute of Pharmaceutical Research, Tianjin 300193, China

(Received 28 August 2007; final version received 20 December 2007)

Two novel phenanthrofurans, shanciols G (**1**) and shanciols H (**2**), together with three known phenolic compounds were isolated from the tubers of *Pleione bulbocodioides* (Franch) Rolfe. Their structures were elucidated by spectroscopic methods.

Keywords: *Pleione bulbocodioides*; phenanthrofurans; shanciol G; shanciol H; phenolic compounds

1. Introduction

The tubers of *Pleione bulbocodioides* (Franch) Rolfe have been used in Chinese medicine as anticancer and antibacterial agents. A number of stilbenoids have been isolated from *P. bulbocodioides*,^{1,2} and various biological activities, such as anti-microbial and antiallergic activities have been reported.^{3,4} During our search for anticancer compounds from Chinese herbal medicine, we investigated the constituents of *P. bulbocodioides*, which led to the isolation of two new phenanthrofurans, shanciols G (**1**) and shanciols H (**2**), together with three known phenolic compounds **3–5**. Herein, we describe the structural determination of compounds **1** and **2**.

2. Results and discussion

An ethanolic extract of the tubers of *P. bulbocodioides* was partitioned with petroleum ether, EtOAc, and *n*-BuOH successively. The EtOAc part was repeatedly subjected to column chromatography to yield

two new phenanthrofurans **1**, **2** and three known phenolic compounds **3–5**.

Compound **1** was obtained as an amorphous powder. Its molecular formula C₂₇H₂₆O₇ was determined based on the quasimolecular ion peak [M + Na]⁺ at *m/z* 485.1574 in the HR-ESI-MS spectrum. The IR spectrum revealed the absorption bands of hydroxyl (3393 cm⁻¹), carbonyl (1733 cm⁻¹), and aromatic rings (1610 and 1456 cm⁻¹). The ¹H NMR spectrum of **1** (Table 1) showed signals characteristic of a dihydrophenanthrene skeleton with one multiplet at δ 2.67 (4H, m, H-9, H-10), three aromatic protons as an ABX system at δ 6.63 (1H, m, H-6), 6.65 (1H, d, *J* = 2.5 Hz, H-8), 8.09 (1H, d, *J* = 8.5 Hz, H-5), and a singlet at δ 6.58 (1H, s, H-3),⁵ a 4'-hydroxy-3'-methoxyphenyl group with three aromatic protons as an ABX system at δ 6.83 (1H, d, *J* = 8.5 Hz, H-5'), 6.92 (1H, dd, *J* = 8.5, 1.5 Hz, H-6'), 7.07 (d, 1H, *J* = 1.5 Hz, H-2'), two methines at δ 5.76 (d, 1H, *J* = 7.5 Hz, H-12), 3.79 (1H, m, H-11), an oxygenated methylene at δ 4.03 (1H, dd, *J* = 11.0, 7.5 Hz, H-13), 3.67 (1H, dd,

*Corresponding author. Email: pharmgao@tju.edu.cn

Table 1. ^1H and ^{13}C NMR data of compounds **1** and **2** (^1H , 500 MHz and ^{13}C , 125 MHz, in CD_3OD).

No.	1		2	
	δ_{H} (mult, J)	δ_{C}	δ_{H} (mult, J)	δ_{C}
1		118.2	6.68 (s)	109.2
2		160.1		158.7
3	6.58 (s)	94.3		125.0
4		159.4	8.06 (s)	125.2
5	8.09 (d, 8.5)	130.8		159.2
6	6.63 (m)	113.7	6.41 (d, 2.5)	99.4
7		156.3		157.7
8	6.65 (d, 2.5)	115.0	6.32 (d, 2.5)	108.3
9	2.67 (m)	30.9	2.65 (m)	31.8
10	2.67 (m)	28.0	2.65 (m)	31.5
11	3.79 (m)	45.9	5.39 (d, 7.0)	89.1
12	5.76 (d, 7.5)	86.6	3.71 (m)	51.7
4a		118.3		127.6
5a		126.1		116.8
8a		140.3		142.0
10a		137.8		140.7
13	4.03 (dd, 11.0, 7.5) 3.67 (dd, 11.0, 4.0)	64.1	4.33 (dd, 11.0, 8.0) 4.42 (dd, 11.0, 5.5)	67.1
1'		129.6		134.3
2'	7.07 (d, 1.5)	111.2	6.95 (d, 2.0)	110.5
3'		149.3		149.2
4'		148.1		147.1
5'	6.83 (d, 8.5)	116.0	6.79 (d, 8.0)	116.2
6'	6.92 (dd, 8.5, 1.5)	120.4	6.83 (dd, 8.0, 2.0)	120.0
CO		172.3		172.7
OCH ₃	3.86 (s)	56.1	3.82 (s)	56.4
	3.88 (s)	56.6	3.82 (s)	56.0
CH ₃	1.69 (s)	20.5	2.03 (s)	20.8

$J = 11.0, 4.0\text{ Hz}$, H-13), as well as two methoxyl groups at δ 3.88 (3H, s), 3.86 (3H, s), and a methyl group at δ 1.69 (3H, s). The ^{13}C NMR spectrum (Table 1) combined with HSQC spectrum exhibited signals for 27 carbons: one ester carbonyl, one methyl, one ethylene, one oxygenated methylene, two methoxyls, and two methines, one of which was oxygenated, along with 18 aromatic carbons (seven protonated carbons, six quaternary carbons and five oxygenated carbons). In the HMBC spectrum (Figure 1), the correlations of H-11 (δ 3.79) with C-1, C-2 and H-12 (δ 5.76) with C-1, C-2, C-1', C-13 revealed that C-1 and C-2 of the dihydrophenanthrene formed a furan ring with C-11, C-12, and an oxygen. The correlations of the methyl (δ 1.69) with the oxygenated carbonyl indicated the presence of an acetoxy group and

the correlations of H-13 (δ 4.03) with the carbonyl, C-12, C-1 indicated the acetoxy group was linked to C-13 and C-13 was linked to C-11. The correlations of H-12 (δ 5.76) with C-2', C-6'; H-6' (δ 6.92), H-2' (δ 7.07) with C-4' (δ 148.1); and the methoxyl (δ 3.88) with C-3' (δ 149.3) confirmed the presence of the 4'-hydroxy-3'-methoxyphenyl group and indicated that it was linked to C-12. Another methoxyl (δ 3.86) was linked to C-4 because of its HMBC correlation with C-4 of the dihydrophenanthrene skeleton. Therefore, shanciol G was elucidated to be structure **1**.

Compound **2** was obtained as an amorphous powder. Its molecular formula $\text{C}_{27}\text{H}_{26}\text{O}_7$ was determined based on the quasimolecular ion peak $[\text{M} - \text{H}]^-$ at m/z 461.1606 in HR-ESI-MS, which was the same as that of **1**. The ^1H and ^{13}C NMR spectra

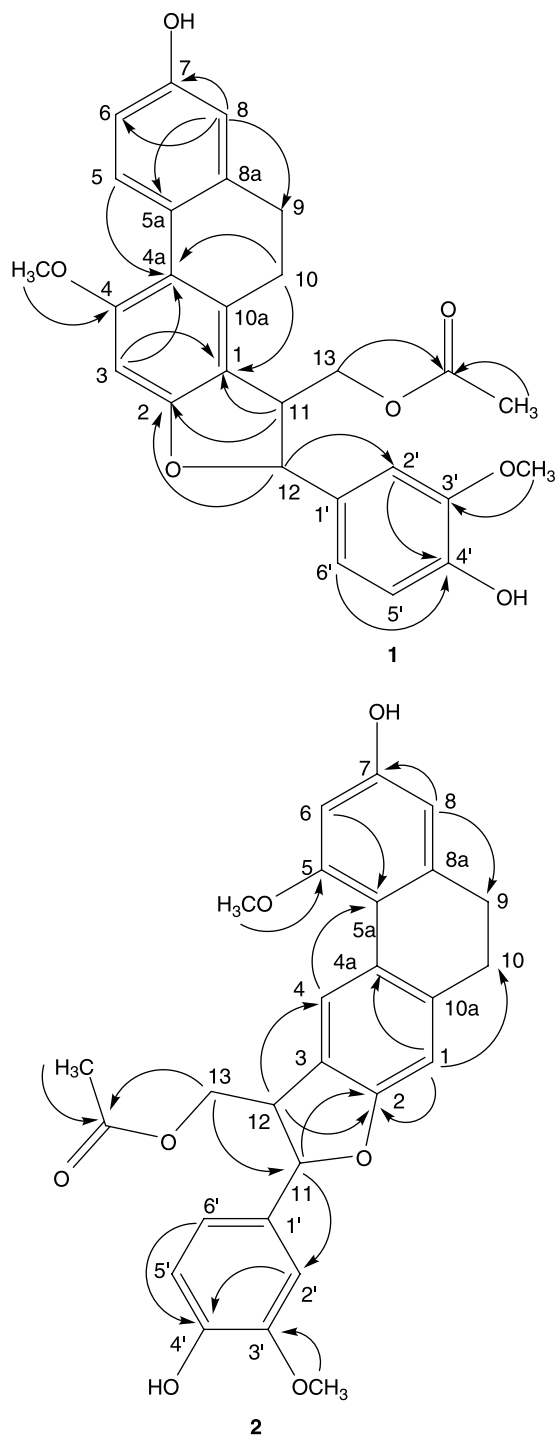


Figure 1. Key HMBC correlations of compounds 1 and 2.

showed that the structure of **2** is closely related to that of **1**, except for the substitution pattern of the functional groups in the dihydrophenanthrene moiety. The four aromatic protons at δ 6.32 (d, 1H, $J = 2.5$ Hz, H-8), 6.41 (d, 1H, $J = 2.5$ Hz, H-6), 6.68 (s, 1H, H-1), and 8.06 (s, 1H, H-4) suggested that the substitution position of the groups may be at 2, 3, 5, and 7, respectively.⁶ The HMBC correlation of the methoxyl (δ 3.82) with C-5 and its NOESY correlations with H-6 and H-4 indicated that the methoxyl group on the dihydrophenanthrene should be at C-5. The HMBC correlations of H-12 (δ 3.71) with C-2, C-4 and H-11 (δ 5.39) with C-2, C-3, C-1', and C-13 revealed that the furan ring was formed by C-2 and C-3 of the dihydrophenanthrene instead of C-1 and C-2 in **1**. And, the other ¹H and ¹³C signals could be attributed by analysis of the HMBC and HSQC spectra (Table 1 and Figure 1). Therefore, shanciol H was elucidated to be structure **2**.

In order to compare the spectral data with other phenanthrenes, we have used the phenanthrene numbering system instead of the systematic nomenclature. Thus, shanciol G and H should be called (7-hydroxy-2-(4-hydroxy-3-methoxyphenyl)-10-methoxy-2,3,4,5-tetrahydro-phenanthro[2,1-*b*] furan-3-yl)methyl acetate and (3-hydroxy-9-(4-hydroxy-3-methoxyphenyl)-1-methoxy-5,6,9,10-tetrahydrophenanthro[2,3-*b*] furan-10-yl)methyl acetate.

Compounds **3–5** were elucidated as *p*-dihydroxy benzene, 3-hydroxybenzoic acid, and methyl (4-OH) phenylacetate, respectively, by comparison of spectroscopic data with those reported in the literature.^{7–9} It should be noted that compounds **3–5** were isolated from this plant for the first time.

3. Experimental

3.1 General experimental procedures

Optical rotations were recorded on a PE 241 MC polarimeter. The IR spectra were recorded on a Bio-Rad FTS 6000 infrared spectrometer. UV spectra were measured on a Shimadzu UV-2450 spectrophotometer.

NMR spectra were run on Bruker AVANCE-400 and Varian unity INOVA-500 spectrometers, using TMS as the internal standard. Mass spectra were obtained using a IonSpec 7.0T FTMS instrument. Preparative HPLC was carried out on an ODS column (250 × 20 mm i.d., YMC) with a JASCO RI-1530 intelligent refractive index detector. Silica gel (200–300 mesh, Qingdao Ocean Chemical Group Co., Qingdao, China) and Sephadex LH-20 (Merck Co., Darmstadt, Germany) for column chromatography as well as silica gel GF254 (Qingdao Ocean Chemical Group Co.) for TLC were used.

3.2 Plant material

The tubers of *P. bulbocodioides* were purchased from Anguo Meiwei Maternal Medica Corporation in Hebei Province, China, in August 2005. The plant was identified by Professor Wen-Yuan Gao, School of Pharmaceutical Science and Technology, Tianjin University. The voucher specimen (No. 20050801) has been deposited at the School of Pharmaceutical Science and Technology, Tianjin University.

3.3 Extraction and isolation

The tubers of *P. bulbocodioides* (30 kg) were extracted three times with 95% EtOH under reflux for 3 h. After removal of solvent under reduced pressure, the extract was suspended in water and partitioned with petroleum ether, EtOAc, and *n*-BuOH successively. The EtOAc-soluble part (500 g) was subjected to column chromatography over silica gel eluting with petroleum ether–EtOAc to EtOAc–MeOH gradient system with increasing amounts of EtOAc and MeOH, respectively, to give seven fractions. Fraction 5 was rechromatographed over a silica gel column eluting with CHCl₃–MeOH (95:5, 9:1 and 85:15) to yield three subfractions. The second subfraction was further fractionated on a Sephadex LH-20 column (CHCl₃–MeOH, 1:1), and then purified by preparative HPLC

to afford compounds **1** (10 mg), **2** (8 mg), **3** (21 mg), **4** (11 mg), and **5** (15 mg).

3.3.1 *Shanciol G (1)*

Amorphous powder, C₂₇H₂₆O₇; $[\alpha]_D^{25} - 5.32$ (c 0.1, MeOH). UV (MeOH): λ_{\max} (log ϵ) = 216 (4.57), 283 (4.41), 306 (4.19); IR (KBr) ν_{\max} (cm⁻¹): 3393, 1733, 1610, 1456; ¹H NMR (CD₃OD, 500 MHz) and ¹³C NMR (CD₃OD, 125 MHz) spectral data, see Table 1; HR-ESI-MS (positive) m/z : 485.1574 [M + Na]⁺ (calcd for C₂₇H₂₆O₇Na, 485.1571).

3.3.2 *Shanciol H (2)*

Amorphous powder, C₂₇H₂₆O₇; $[\alpha]_D^{25} - 6.83$ (c 0.1, MeOH). UV (MeOH): λ_{\max} (log ϵ) = 223 (4.63), 282 (4.51), 307 (4.32); IR (KBr) ν_{\max} (cm⁻¹): 3369, 1734, 1610, 1459; ¹H NMR (CD₃OD, 500 MHz) and ¹³C NMR

(CD₃OD, 125 MHz) spectral data, see Table 1; HR-ESI-MS (negative) m/z : 461.1606 [M - H]⁻ (calcd for C₂₇H₂₅O₇, 461.1600).

References

- ¹L. Bai, N. Maxukawa, M. Yamaki, and S. Takagi, *Phytochemistry* **47**, 1637 (1998).
- ²L. Bai, N. Maxukawa, M. Yamaki, and S. Takagi, *Phytochemistry* **48**, 327 (1998).
- ³S. Takagi, M. Yamaki, and K. Inoue, *Phytochemistry* **22**, 1011 (1983).
- ⁴M. Hisashi, M. Toshio, H.H. Xie, and Y. Masayuki, *Planta Med.* **70**, 847 (2004).
- ⁵R.M. Letcher and L.R.M. Nhamao, *J. Chem. Soc. Perkin Trans. 1*, 2941 (1972).
- ⁶L. Bai, M. Yamaki, and S. Takagi, *Phytochemistry* **47**, 1125 (1998).
- ⁷J.R. Scheffer, Y.F. Wong, A.O. Patil, D.Y. Curtin and I.C. Paul, *J. Am. Chem. Soc.* **107**, 4898 (1985).
- ⁸R. Bernini, A. Coratti, and G. Provenzano, *Tetrahedron* **61**, 1821 (2005).
- ⁹A.C.P. Luc and J.V. Arnold, *Magn. Reson. Chem.* **27**, 754 (1989).