



Pergamon

Tetrahedron Letters 41 (2000) 1069–1071

TETRAHEDRON
LETTERS

Two novel iridoids from *Scrophularia buergeriana*

Shuang-jun Lin, Shan-hao Jiang, Yi-ming Li, Jia-feng Zeng and Da-yuan Zhu *

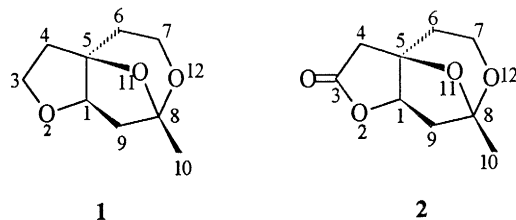
State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences,
294 Taiyuan Road, Shanghai 200031, PR China

Received 16 September 1999; accepted 29 November 1999

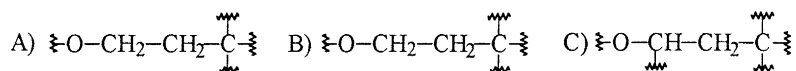
Abstract

Two new iridoid-related compounds with a new carbon skeleton, buergerinin F(**1**) and G(**2**) were isolated from the roots of *Scrophularia buergeriana* Miq., and their structures were determined by spectroscopic means as well as by X-ray crystallographic analysis. The ^1H , ^{13}C NMR and EI-MS data of **1** and **2** are given. © 2000 Elsevier Science Ltd. All rights reserved.

In an extension of a study of the chemical constituents of *Scrophularia buergeriana* Miq.,¹ two new-skeleton iridoids, buergerinin F(**1**) and G(**2**) were isolated and identified.^{5,6} The ^1H and ^{13}C NMR spectral data of compounds **1** and **2** and X-ray structure of **2** are given.



Compound **1**⁷ was obtained as an oil. The IR spectrum of **1** showed no absorption of any hydroxy group. The molecular formula was determined as $\text{C}_9\text{H}_{14}\text{O}_3$ by HRMS (M^+ :170.0941, calculated: 170.0943), along with ^1H and ^{13}C NMR spectral data (Table 1). The IR and ^{13}C NMR spectra of **1** showed that no unsaturated bond existed in **1**. In view of the degree of unsaturation, three rings were required. The ^1H NMR spectrum of **1** showed a tertiary methyl signal at δ 1.50 (3H, s) and a methine signal at δ 4.47 (1H, dd, $J=6.3, 1.5$ Hz) linked to oxygen. The ^{13}C NMR and DEPT spectra of **1** showed the existence of five methene carbons, a quaternary carbon linked to oxygen and an acetal carbon at δ 108.6(s). ^1H - ^1H COSY experiments indicated the presence of three segments as follows:



* Corresponding author.

Table 1
The ^1H and ^{13}C NMR spectral data of compounds **1** and **2** (400 MHz)

position	^1H NMR (CDCl ₃)		^{13}C NMR (CDCl ₃)	
	1	2	1	2
1	4.47 (1H, dd, 6.7, 2.0)	4.75 (1H, dd, 6.4, 1.3)	84.5	84.2
3	4.10 (td, 8.6, 6.4) 3.95 (td, 8.6, 3.2)		68.8	174.5
4	2.12 (ddd, 13.1, 6.4, 3.2) 1.85 (td, 13.1, 8.6)	2.75 (d, 18.0) 2.55 (d, 18.0)	36.2	39.2
5			91.6	85.9
6	2.25 (td, 12.9, 6.3) 1.40 (dd, 12.9, 3.8)	2.25 (td, 12.9, 6.4) 1.46 (dd, 12.9, 3.8)	30.7	29.7
7	4.00 (dd, 12.2, 6.3) 3.70 (td, 12.2, 3.8)	4.00 (dd, 12.3, 6.4) 3.70 (td, 12.3, 3.8)	61.4	59.9
8			108.6	107.7
9	2.42 (dd, 14.4, 6.7) 2.05 (dd, 14.4, 2.0)	2.49 (dd, 14.8, 6.4) 2.20 (dd, 14.8, 1.3)	44.8	42.7
10	1.50 (3H, s)	1.50 (3H, s)	24.3	23.9

Furthermore, the three segments A, B and C were connected by the $^2\text{J}_{\text{CH}}$, $^3\text{J}_{\text{CH}}$ correlations shown in HMBC spectrum. The most plausible structure of **1** is indicated in Fig. 1. The relative stereochemistry, with C-9 and O-11 in the *cis*-configuration² is the more stable and was confirmed by the NOESY spectrum (Fig. 1) in which cross peaks are shown between H-1 and H-7 α , H-9 β and H-10.

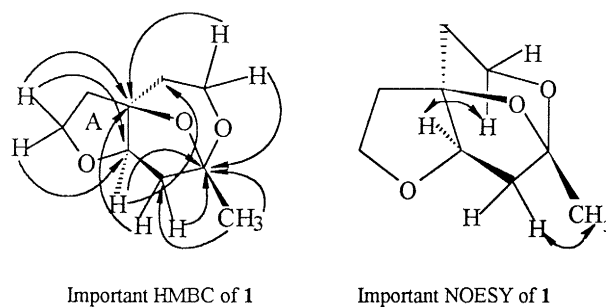


Fig. 1.

Compound **2**⁸ was obtained as colorless prismatic crystals. The HRMS of **2** showed an M^+ ion at m/z 184.0736 (calculated: 184.0735) indicating its molecular formula to be $\text{C}_9\text{H}_{12}\text{O}_4$, in agreement with ^1H and ^{13}C NMR spectral data. The NMR data for **2** showed it was similar in structure to **1**, but the left ring was a γ -lactone moiety confirmed by IR ν (KBr) cm^{-1} : 1765, ^1H and ^{13}C NMR spectral data (Table 1).³ Accordingly, compound **2** was identified as 3-one-buergerinin F.

In order to complete the structural elucidation of **2**, an X-ray crystallographic analysis⁴ was performed. The relative stereoscopic view of the molecule is shown in Fig. 2.

Acknowledgements

The National Science Foundation (No. 29632050) is acknowledged for financial support of this study.

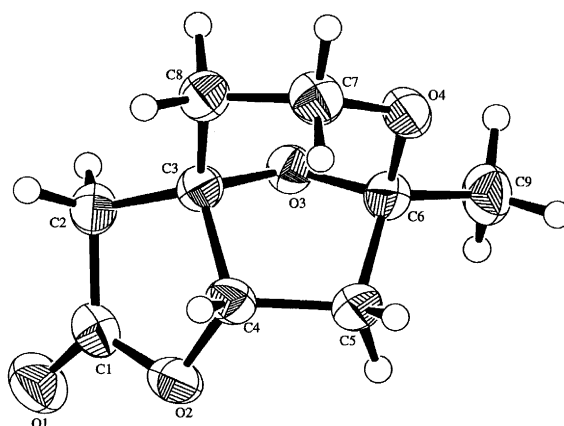


Fig. 2. X-Ray structure of **2**

References

1. Lin, S. J.; Jiang, S. H.; Li, Y. M.; Wang, H. Q.; Zeng, J. F.; Zhu, D. Y. submitted for publication in *Phytochemistry*.
2. Naf, R.; Velluz, A.; Decorzant, R.; Naf, F. *Tetrahedron Lett.* **1991**, *55*, 1873.
3. Yoshikawa, M.; Fukuda, Y.; Taniyama, T.; Kitagawa, I. *Chem. Pharm. Bull.* **1986**, *14*, 1403.
4. X-Ray analysis was performed on a Rigaku AFC7R diffractometer with graphite monochromated Mo-K α radiation and a 12 kW rotating anode generator.
5. *Plant material.* *Scrophularia buergeriana* Miq. was collected from Changbai mountains in Jilin province, China, in 1996.
6. *Extraction and isolation.* The air-dried roots were extracted with 60% EtOH at room temperature. A part of the petrol soluble fraction was chromatographed on a silica gel column with petrol:EtOAc (7:1) and then purified with CH₂Cl₂:acetone (3:1) to give compound **1**. Compound **2** was obtained by recrystallization from the mixed solvent (petrol and acetone) after column chromatography on silica gel with petrol:EtOAc (4:1).
7. Buergerinin F (**1**). Yellow oil. $[\alpha]_D^{18} +40.67$ (c 0.431 CHCl₃). IR ν (KBr) cm⁻¹: 1388, 1234. EI-MS: m/z 170 M⁺ (14), 110 (100), 84 (99). ¹H and ¹³C NMR (CDCl₃): see Table 1.
8. Buergerinin G (**2**). Colorless prismatic crystal. Mp:152–154°C. $[\alpha]_D^{18} +47.71$ (c 0.509 CHCl₃). IR ν (KBr) cm⁻¹: 1765, 1230. EI-MS: m/z 184 M⁺ (25), 80 (100). ¹H and ¹³C NMR (CDCl₃): see Table 1.