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## Journal of Asian Natural Products Research

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/ganp20>

### Two new polyacetylenic compounds from *Atractylodes chinensis* (DC.) Koidz.

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Available online: 30 Mar 2011

To cite this article: He Meng, Guo-Yu Li, Rong-Hua Dai, Yue-Ping Ma, Ke Zhang, Cui Zhang, Xian Li & Jin-Hui Wang (2011): Two new polyacetylenic compounds from *Atractylodes chinensis* (DC.) Koidz., *Journal of Asian Natural Products Research*, 13:04, 346-349

To link to this article: <http://dx.doi.org/10.1080/10286020.2011.557662>

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## Two new polyacetylenic compounds from *Atractylodes chinensis* (DC.) Koidz.

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Xian Li<sup>a</sup> and Jin-Hui Wang<sup>abcd\*</sup>

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(Received 26 October 2010; final version received 21 January 2011)

Two new polyacetylenic compounds, (6*E*,12*Z*)-tetradecadiene-8,10-diyne-1,3-diol (**1**) and (6*Z*,12*Z*)-tetradecadiene-8,10-diyne-1,3-diol (**2**), were isolated from *Atractylodes chinensis* (DC.) Koidz. Their structures were established by analysis of spectroscopic data.

**Keywords:** *Atractylodes chinensis* (DC.) Koidz.; polyacetylenic compounds; (6*E*,12*Z*)-tetradecadiene-8,10-diyne-1,3-diol; (6*Z*,12*Z*)-tetradecadiene-8,10-diyne-1,3-diol

### 1. Introduction

The rhizome of *Atractylodes chinensis* (DC.) Koidz., an important Chinese traditional medicine, has been used to treat rheumatic diseases, digestive disorders, night blindness, and influenza [1]. Previous investigations showed that the polyacetylenic compounds were the characteristic and active constituents of *A. chinensis*, which had significant anti-ulcer activity toward some experimental gastric disorders [2], and strong anti-inflammatory activity [3]. The present study on the phytochemistry of *A. chinensis* led to the isolation of two new polyacetylenic compounds, which were the *Z* isomers of (6*E*,12*E*)-tetradecadiene-8,10-diyne-1,3-diol [4] (Figure 1).

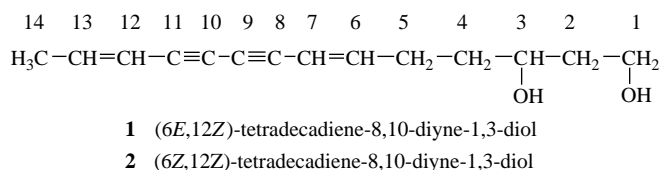
### 2. Results and discussion

Compound **1** was obtained as a pale yellow oil. The molecular formula was determined

to be C<sub>14</sub>H<sub>18</sub>O<sub>2</sub> by HR-TOF-MS at *m/z* 241.1204 [M + Na]<sup>+</sup>. The <sup>1</sup>H NMR spectrum of **1** showed the presence of olefinic protons assignable to a *trans* and a *cis* double bond at δ 5.65 (1H, d, *J* = 16.2 Hz), 6.33 (1H, dt, *J* = 4.8, 16.2 Hz), and δ 5.56 (1H, d, *J* = 10.2 Hz), 6.17 (1H, m), respectively, and a methyl proton at δ 1.88 (3H, dd, *J* = 1.8, 7.2 Hz). <sup>13</sup>C NMR spectrum showed 14 signals: one methyl, four methylenes, one methine, four olefinic carbons, and four acetylene carbons.

Analysis of the HMQC spectrum enabled us to allot the H-atoms to their bonded C-atoms (Table 1). The information concerning the location of these units was obtained from the HMBC experiment (Figure 2). The HMBC correlations from H-14 to C-12 and C-13, H-13 to C-11, and H-12 to C-10 suggested the presence of unit A (Figure 2). Another

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Figure 1. Structures of compounds **1** and **2**.

double bond H-7 correlated with C-5 and C-9, and H-6 correlated with C-8 and C-4, indicating the presence of unit B (Figure 2). The HMBC correlations from H-1 to C-2 and C-3, H-5 to C-3, and H-4 to C-2 established the unit C attached to C-4 (Figure 2). Finally, the acetylene carbon C-9 was connected to C-10. The structure could be further confirmed by COSY spectrum (Figure 3). Thus, compound **1** was characterized as (6*E*,12*Z*)-tetradecadiene-8,10-diyne-1,3-diol.

Compound **2** was isolated as a pale yellow oil. The molecular formula was analyzed for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub> by HR-TOF-MS at *m/z* 241.1197 [M + Na]<sup>+</sup>. The <sup>1</sup>H and <sup>13</sup>C NMR spectral data of **2** indicated its structure to be closely related to that of **1**, with the difference in chemical shift and coupling constants of the four olefinic protons. The protons at δ 5.58 (1H, d,

*J* = 9.0 Hz, H-7) and 5.58 (1H, d, *J* = 9.0 Hz, H-12) indicated *Z* configuration for C-6-C-7 and C-12-C-13 double bonds. Thus, compound **2** was determined as (6*Z*,12*Z*)-tetradecadiene-8,10-diyne-1,3-diol.

### 3. Experimental

#### 3.1 General experimental procedures

UV spectra were obtained on a Shimadzu UV-2201 spectrophotometer. IR spectra were recorded on an IFS-55 spectrophotometer. Optical rotations were determined on a Perkin-Elmer 241 MC polarimeter. The NMR spectra were run on a Bruker AV-600 spectrometer (600 MHz for <sup>1</sup>H and 150 MHz for <sup>13</sup>C) in CD<sub>3</sub>OD with TMS as an internal standard. The HR-TOF-MS data were obtained on a Waters LCT Premier XE time-of-flying mass

Table 1. <sup>1</sup>H and <sup>13</sup>C NMR spectral data of compound **1** in CD<sub>3</sub>OD and key HMBC correlations (600 MHz for <sup>1</sup>H NMR and 150 MHz for <sup>13</sup>C NMR).

Position	δ <sub>C</sub>	δ <sub>H</sub>	HMBC
1	60.1	3.68 (2H, br s)	C-2, C-3
2	40.8	1.62 (1H, m)	C-1, C-3, C-4
		1.68 (1H, m)	C-1, C-3, C-4
3	69.1	3.72 (1H, br s)	C-2
4	37.5	1.55 (2H, m)	C-2, C-3, C-5, C-6
5	30.5	2.24 (1H, m)	C-3, C-4, C-6, C-7
		2.31 (1H, m)	C-3, C-4, C-6, C-7
6	149.3	6.33 (1H, dt, <i>J</i> = 4.8, 16.2 Hz)	C-4, C-5, C-8
7	109.9	5.65 (1H, d, <i>J</i> = 16.2 Hz)	C-5, C-6, C-9
8	81.7		
9	73.1		
10	79.1		
11	78.2		
12	110.0	5.56 (1H, d, <i>J</i> = 10.2 Hz)	C-10
13	143.4	6.17 (1H, m)	C-11, C-14
14	16.4	1.88 (3H, dd, <i>J</i> = 1.8, 7.2 Hz)	C-12, C-13

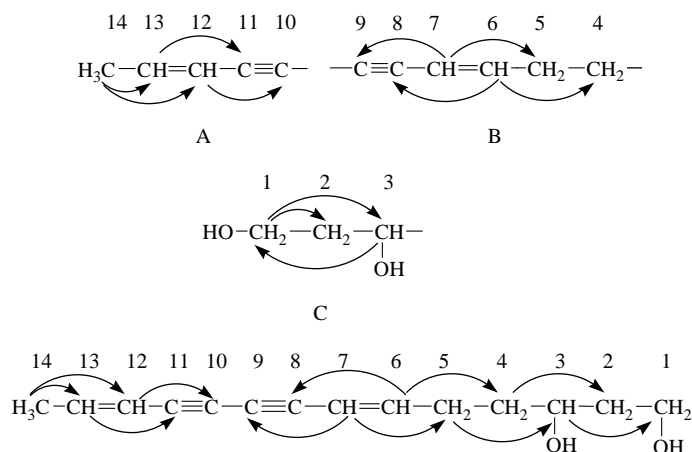


Figure 2. The key HMBC correlations of units A, B, C, and compound 1.

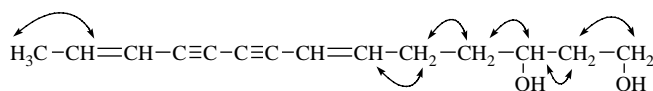


Figure 3. The key  $^1\text{H}$ - $^1\text{H}$  COSY correlations of compound 1.

spectrometer, and CD spectra on a Jasco CD-2095-plus spectrometer. Chromatography was performed on silica gel (200–300 mesh; Qingdao Marine Chemical Group Co., Qingdao, China), Sephadex LH-20 (Pharmacia, Piscataway, NJ, USA), ODS (30–50  $\mu\text{m}$ ; Tianjin Chemical Reagent Co., Tianjin, China), and preparative HPLC (Waters 600E pump, Waters 2489 UV spectrophotometric detector at 293 nm, Waters Sunfire Prep ODS reversed-phase column).

### 3.2 Plant material

The rhizomes of *A. chinensis* (DC.) Koidz., collected from Heilongjiang Province of China, were bought from the Cooperation of Traditional Chinese Medicine of Shenyang, China, in June 2006, and were identified by Prof. Jincai Lu (Shenyang Pharmaceutical University). A voucher specimen (20061005) has been deposited in the School of Traditional

Chinese Medicine of Shenyang Pharmaceutical University, China.

### 3.3 Extraction and isolation

Dry rhizomes of *A. chinensis* (20.0 kg) were refluxed two times with 95% EtOH. The combined EtOH extracts were concentrated, suspended in  $\text{H}_2\text{O}$ , and then partitioned with petroleum ether (280.9 g),  $\text{CHCl}_3$  (300.5 g), and EtOAc (42.0 g) successively to give three different polar parts. The  $\text{CHCl}_3$  layer was subjected to silica gel column chromatography (CC) with a gradient of petroleum ether–acetone (100:1–100:100). The fraction eluted with a solvent of petroleum ether–acetone (100:10) (2.4 g) was further purified by Sephadex LH-20 CC eluted with  $\text{CHCl}_3$ –MeOH (1:1) to yield a fraction (1.4 g), which was further subjected to ODS CC eluted with MeOH– $\text{H}_2\text{O}$ . A fraction eluted with MeOH– $\text{H}_2\text{O}$  (65:35) (22.1 mg) was further separated by preparative HPLC (60% MeOH, flow rate

Table 2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of compound **2** in  $\text{CD}_3\text{OD}$  and key HMBC correlations (600 MHz for  $^1\text{H}$  NMR and 150 MHz for  $^{13}\text{C}$  NMR).

Position	$\delta_{\text{C}}$	$\delta_{\text{H}}$	HMBC
1	60.2	3.69 (2H, br s)	C-2, C-3
2	40.7	1.62 (1H, m)	C-1, C-3, C-4
		1.68 (1H, m)	C-1, C-3, C-4
3	69.5	3.72 (1H, m)	C-2
4	37.7	1.55 (2H, m)	C-2, C-3, C-5, C-6
5	28.2	2.39 (1H, m)	C-3, C-4, C-6, C-7
		2.45 (1H, m)	C-3, C-4, C-6, C-7
6	148.7	6.16 (1H, m)	C-4, C-5, C-7, C-8
7	109.1	5.58 (1H, d, $J = 9.0\text{ Hz}$ )	C-5, C-6, C-9
8	79.7		
9	78.7		
10	79.7		
11	78.9		
12	110.0	5.58 (1H, d, $J = 9.0\text{ Hz}$ )	C-10
13	143.5	6.16 (1H, m)	C-11, C-14
14	16.5	1.88 (3H, dd, $J = 1.8, 7.2\text{ Hz}$ )	C-12, C-13

2.5 ml/min, wavelength 230 nm) to obtain compounds **1** (4.7 mg) and **2** (6.5 mg).

### 3.3.1 (6E,12Z)-Tetradecadiene-8,10-diyne-1,3-diol (**1**)

Pale yellow oil,  $[\alpha]_{\text{D}}^{20} -24.0$  ( $c = 0.10$ , MeOH). IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 3376, 2940, 1661, 1384, 1054, 1031; UV (MeOH)  $\lambda_{\text{max}}$  (nm): 229, 266, 276, 293, 312; CD (MeOH)  $\Delta\epsilon_{286.6\text{ nm}} +2.139$ ,  $\Delta\epsilon_{338.0\text{ nm}} -3.484$ ;  $^1\text{H}$  and  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ ) spectral data, see Table 1; HR-TOF-MS  $m/z$ : 241.1204  $[\text{M} + \text{Na}]^+$  (calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_2\text{Na}$ , 241.1204).

### 3.3.2 (6Z,12Z)-Tetradecadiene-8,10-diyne-1,3-diol (**2**)

Pale yellow oil,  $[\alpha]_{\text{D}}^{20} -16.0$  ( $c = 0.15$ , MeOH). IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 3386, 2938, 1714, 1384, 1055, 1019; UV (MeOH)  $\lambda_{\text{max}}$  (nm): 236, 266, 276, 293, 312; CD (MeOH)  $\Delta\epsilon_{286.6\text{ nm}} +4.267$ ,

$\Delta\epsilon_{338.1\text{ nm}} -5.942$ ;  $^1\text{H}$  and  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ ) spectral data, see Table 2; HR-TOF-MS  $m/z$ : 241.1197  $[\text{M} + \text{Na}]^+$  (calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_2\text{Na}$ , 241.1204).

### Acknowledgements

This work was supported by the National Key Technologies R&D Program of China during the 11th Five-Year Plan Period (2006BAI09B06-01) and the National Major Special Science and Technology Project (2010ZX09401-304-104A).

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