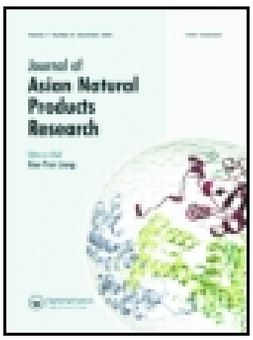


Journal of Asian Natural Products Research

ISSN: 1028-6020 (Print) 1477-2213 (Online) Journal homepage: http://www.tandfonline.com/loi/ganp20

New ecdysteroid and ecdysteroid glycosides from the roots of Serratula chinensis

Zi-Yue Zhang, Wei-Qun Yang, Chun-Lin Fan, Hui-Nan Zhao, Xiao-Jun Huang, Ying Wang & Wen-Cai Ye

To cite this article: Zi-Yue Zhang, Wei-Qun Yang, Chun-Lin Fan, Hui-Nan Zhao, Xiao-Jun Huang, Ying Wang & Wen-Cai Ye (2016): New ecdysteroid and ecdysteroid glycosides from the roots of Serratula chinensis, Journal of Asian Natural Products Research, DOI: 10.1080/10286020.2016.1209492

To link to this article: http://dx.doi.org/10.1080/10286020.2016.1209492

Published online: 18 Jul 2016.

JOURNAL OF ASIAN NATURAL PRODUCTS RESEARCH, 2016
http://dx.doi.org/10.1080/10286020.2016.1209492

Taylor & Francis
Taylor & Francis Group

New ecdysteroid and ecdysteroid glycosides from the roots of *Serratula chinensis*

Zi-Yue Zhang[a,b,c], Wei-Qun Yang[a,b,c], Chun-Lin Fan[b,c], Hui-Nan Zhao[b], Xiao-Jun Huang[b,c], Ying Wang[b,c] and Wen-Cai Ye[a,b,c]

[a]Department of Phytochemistry, China Pharmaceutical University, Nanjing 210009, China; [b]Institute of Traditional Chinese Medicine & Natural Products, College of Pharmacy, Jinan University, Guangzhou 510632, China; [c]JNU-HKUST Joint Laboratory for Neuroscience & Innovative Drug Research, College of Pharmacy, Jinan University, Guangzhou 510632, China

ABSTRACT

Three new ecdysteroid glycosides (**1–3**) and one new ecdysteroid (**4**), were isolated from the roots of *Serratula chinensis*. Their structures were established on the basis of extensive spectroscopic analysis and chemical methods.

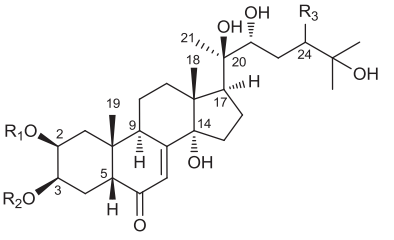
ARTICLE HISTORY
Received 22 April 2016
Accepted 1 July 2016

KEYWORDS
Compositae; *Serratula chinensis*; ecdysteroid; ecdysteroid glycoside

1. Introduction

The plant *Serratula chinensis* S. Mooe (Compositae) is a perennial herb widely distributed in southern China [1]. The roots of this plant, called "Guang Sheng Ma" in Chinese, are widely used as an alternative to the traditional Chinese medicine *Cimicifugae foetida* L. ("Sheng Ma") (Ranunculaceae) for the treatment of pharyngitis and morbilli in southern areas of China, such as Guangdong, Guangxi, and Fujian provinces [2]. Previous phytochemical investigations of this plant had led to the isolation of ecdysteroids, sphingolipids, and cerebrosides [3–5]. Among them, ecdysteroids are the major and characteristic components of the roots of *S. chinensis*, some of which have been reported to show potent antioxidant, hepatoprotective, immunomodulatory, antitumor, and erythropoietic activities [6–11]. During the course of our ongoing program to assess the chemical and biological diversities of medicinal plants growing in southern China [12–17], we carried out extensive phytochemical investigation on the roots of *S. chinensis* and had reported the isolation of several known ecdysteroids [18]. More recently, our further study of this plant led to the finding of three new ecdysteroid glycosides, 20-hydroxyecdysone-2-*O*-β-D-galactopyranoside (**1**), 3-*O*-acetyl-20-hydroxyecdysone-2-*O*-β-D-galactopyranoside (**2**), 3-*O*-acetyl-20-hydroxyecdysone-2-*O*-β-D-glucopyranoside (**3**) and a new ecdysteroid, 24-*O*-acetyl-*epi*-abutasterone (**4**) (Figure 1). To the best of our knowledge, there are only six ecdysteroid glycosides isolated from the genus *Serratula* [11,18], three of which were reported here. In this paper, we report the isolation and structural elucidation of these new compounds.

CONTACT Ying Wang wangying_cpu@163.com; Wen-Cai Ye chywc@aliyun.com



	R_1	R_2	R_3
1	Gal	H	H
2	Gal	Ac	H
3	Glu	Ac	H
4	H	H	OAc

Figure 1. Chemical structures of **1**–**4**.

2. Results and discussion

Compound **1** was obtained as amorphous powder. The molecular formula of **1** was established as $C_{33}H_{54}O_{12}$ on the basis of the quasi-molecular ion at *m/z* 665.3532 $[M + Na]^+$ by its HR-ESI-MS. The IR spectrum showed the presence of hydroxyl (3406 cm^{-1}) and carbonyl (1660 cm^{-1}) groups. The ^1H NMR spectrum of **1** showed signals for five angular methyl groups (δ_H 0.91, 0.98, 1.20, 1.20, and 1.22, each 3H, s), three oxygenated methines [δ_H 3.34 (1H, m), 4.05 (1H, d*t*, *J* = 12.5, 3.5 Hz), and 4.16 (1H, d, *J* = 3.5 Hz)], as well as one olefinic proton [δ_H 5.82 (1H, d, *J* = 2.0 Hz)]. In the ^{13}C NMR spectrum of **1**, thirty-three carbon signals were observed. Among them, twenty-seven of which could be assigned to the aglycone moiety including five methyls (δ_C 18.0, 21.0, 24.2, 28.9, and 29.7), six oxygenated methines or quaternary carbons (δ_C 66.0, 71.3, 76.4, 77.9, 78.4, and 85.2), two olefinic carbons (δ_C 122.6 and 168.3), as well as a carbonyl (δ_C 206.5). Detailed interpretation of the 2D NMR (^1H-^1H COSY, HSQC and HMBC) spectra of **1** allowed the assignment of all proton and carbon resonances (Table 1). The aglycone of **1** was identified as 20-hydroxyecdysone by comparison of the NMR data of **1** with those published in literature [3]. In the NOESY spectrum of **1**, correlations between H-9 (δ_H 3.18) and H-2 (δ_H 4.05), as well as between H_3-19 (δ_H 0.98) and H-5 (δ_H 2.39) confirmed the presence of *cis* junction of rings A and B. Chemical shift values of C-12 (δ_C 32.5) and C-15 (δ_C 31.7) confirmed the *trans* junction of rings C and D [19]. The *α*-configurations of H-2 and H-3 could be confirmed by the large $^3J_{H1\beta\text{-}H2}$ coupling constant (12.5 Hz) and small $^3J_{H2\text{-}H3}$ coupling constant (3.5 Hz), as well as by the NOE correlation between H-2 (δ_H 4.05) and H-9 (δ_H 3.18). Furthermore, the NOE correlations between H-9 (δ_H 3.18) and H-12*α* (δ_H 1.76), between H-12*α* (δ_H 1.76) and H-17 (δ_H 2.41) suggested the presence of *α*-configuration of H-17 (Figure 2). The configurations of H-21 and H-22 were determined by comparison of the NMR data of C-17, C-20, C-21, C-22, and C-25 [3,20,21] among **1**, 20-hydroxyecdysone and 22-*epi*-20-hydroxyecdysone both in CD_3OD and C_5D_5N [3,20,21].

In addition, the ^1H and ^{13}C NMR spectra of **1** showed the presence of a sugar anomeric proton signal at δ_H 4.41 (1H, d, *J* = 7.5 Hz, H-1′) and the corresponding carbon signal at δ_C 103.3 (C-1′). Acid hydrolysis of **1** yielded the D-galactose, which was identified by HPLC analysis [22]. The relative anomeric configuration of the D-galactose was determined to be β based on the $^3J_{H1\text{-}H2}$ coupling constant of the anomeric proton (*J* = 7.5 Hz). The linkage position of the monosaccharide could be deduced by the HMBC correlation between the anomeric proton H-1′ (δ_H 4.41) and C-2 (δ_C 76.4) (Figure 2). Therefore, the structure of **1** was determined as 20-hydroxyecdysone-2-*O*-β-D-galactopyranoside.

Table 1. ^{1}H and ^{13}C NMR spectral data of compounds **1-4** (*J* in Hz) [a][b].

No.	**1**[c]		**2**[d]		**3**[d]		**4**[c]	
	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	36.1	*a* 1.96; β 1.54 (*t*, 12.5)	37.7	*a* 2.44; *b* 1.83	37.5	*a* 2.46; β 1.87	37.4	β 1.80; *a* 1.44
2	76.4	4.05 (d*t*, 12.5, 3.5)	73.9	4.49	74.1	4.57	68.7	3.84
3	66.0	4.16 (d, 3.5)	68.6	5.65 (br s)	68.6	5.70 (br s)	68.5	3.96 (br s)
4	32.0	1.75	29.8	*a* 1.98; β 1.74	29.8	*a* 1.84; β 2.04	32.8	*a* 1.72; *b* 1.72
5	51.9	2.39	52.3	2.63 (dd, 14.0, 4.0)	52.1	2.66 (dd, 14.0, 4.0)	51.8	2.40 (dd, 13.0, 4.5)
6	206.5	–	202.3	–	202.6	–	206.2	–
7	122.6	5.82 (d, 2.0)	121.9	6.21 (d, 2.0)	122.2	6.24 (d, 2.0)	121.8	5.82 (d, 2.5)
8	168.3	–	167.0	–	167.3	–	167.9	–
9	35.0	3.18	34.6	3.60 (br s)	34.6	3.63 (br s)	35.1	3.17
10	39.5	–	39.2	–	39.0	–	39.3	–
11	21.3	*a* 1.88; β 1.68	21.3	*a* 2.08; *b* 1.70	21.2	*a* 2.07; *b* 1.73	21.5	*a* 1.81; β 1.70
12	32.5	β 2.15 (*t*d, 13.0, 4.5); *a* 1.76	32.0	β 2.15; *a* 1.85	32.0	*a* 2.54; *b* 1.91	32.5	*a* 2.14; β 1.77
13	48.5	–	48.3	–	48.2	–	48.5	–
14	85.2	–	84.4	–	84.5	–	85.2	–
15	31.7	*a* 1.99; β 1.63	32.2	*a* 2.51; *b* 1.96	32.1	*a* 2.13; *b* 1.92	31.8	β 1.96; *a*1.61
16	21.5	*a* 1.99; β 1.76	21.8	*a* 2.45; *b* 2.05	21.8	*a* 2.46; *b* 1.89	21.3	*a* 1.98; β 1.72
17	50.5	2.41	50.4	2.95 (*t*, 9.0)	50.3	2.97 (*t*, 9.0)	50.4	2.35 (*t*, 9.5)
18	18.0	0.91 (s)	18.1	1.20 (s)	18.1	1.21 (s)	18.1	0.90 (s)
19	24.2	0.98 (s)	24.4	1.03 (s)	24.3	1.04 (s)	24.4	0.98 (s)
20	77.9	–	77.2	–	77.1	–	77.6	–
21	21.0	1.20 (s)	22.0	1.55 (s)	22.0	1.57 (s)	21.0	1.20 (s)
22	78.4	3.34	77.8	3.87 (d, 9.5)	77.9	3.89 (d, 10.0)	73.8	3.31
23	27.4	*a* 1.67; *b* 1.30	27.7	*a* 2.15; *b* 1.85	27.7	β 2.18; *a* 1.87	33.1	*a* 1.76; *b* 1.57
24	42.3	*a* 1.81; *b* 1.45	42.9	*a* 2.30; *b* 1.81	42.9	*a* 2.33; *b* 1.83	78.7	5.09 (dd, 10.5, 1.5)
25	71.3	–	70.0	–	70.0	–	72.7	–
26	29.7	1.22 (s)	30.6	1.39 (s)	30.5	1.42 (s)	26.0	1.21 (s)
27	28.9	1.20 (s)	30.3	1.39 (s)	30.2	1.42 (s)	26.0	1.19 (s)
1′	103.3	4.41 (d, 7.5)	104.4	4.84 (d, 7.5)	104.1	4.95 (d, 7.5)	173.0	–
2′	72.7	3.56	72.8	4.40 (dd, 9.5, 7.5)	75.5	4.00 (*t*, 8.0)	21.0	2.11 (s)
3′	70.2	3.86 (d, 3.0)	75.6	4.10 (dd, 9.5, 3.0)	78.7	4.23		
4′	74.8	3.50 (dd, 9.7, 3.0)	70.4	4.55 (d, 3.0)	71.9	4.25		
5′	76.7	3.54	77.2	4.02 (*t*, 6.0)	78.6	3.94		
6′	62.4	3.77 (d, 8.0)	62.5	*a* 4.46; *b* 4.42	63.0	*a* 4.55 (dd, 11.0, 2.5)*b* 4.38 (dd, 11.0, 5.0)		
1′′			171.2	–	171.4	–		
2′′			21.5	1.96 (s)	21.4	2.01 (s)		

[a]Assignments were established by interpretation of the ^{1}H– ^{1}H COSY, HSQC, and HMBC spectra.
[b]Overlapped signals are reported without designating multiplicity.
[c]Measured in CD_3OD.
[d]Measured in C_5D_5N.

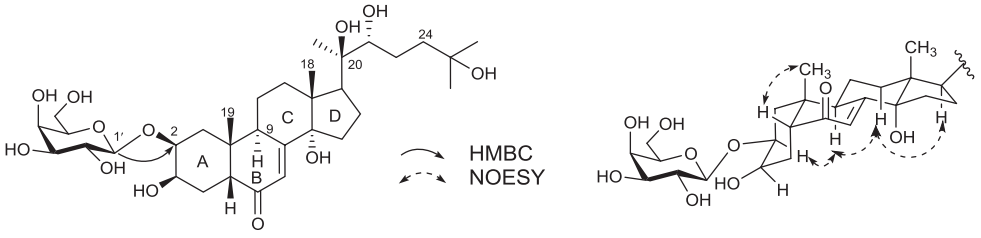


Figure 2. Key HMBC and NOESY correlations of **1**.

Compound **2** was isolated as amorphous powder. The molecular formula of **2** was assigned as $C_{35}H_{56}O_{13}$ by its HR-ESI-MS with a quasi-molecular ion peak at *m/z* 707.3609 $[M + Na]^+$. Comparison of the ^1H and ^{13}C NMR data of **2** with those of **1** (Table 1) revealed that they were very similar, except for the presence of signals assigned to an acetyl group [δ_H 1.96 (3H, s); δ_C 21.5 and 171.2] in **2**, and the significant downfield shift of C-3 and H-3 signals of **2**. In the HMBC spectrum, the correlation between H-3 (δ_H 5.65) and C-1″ (δ_C 171.4) indicated that the additional acetyl group was located at C-3 in **2**. Acid hydrolysis of **2** also afforded D-galactose, which was identified by HPLC analysis [22]. Furthermore, the $^3J_{H1\text{-}H2}$ coupling constant of the anomeric proton (J = 7.5 Hz) established the β-configuration of the sugar unit. The HMBC correlation between H-1′ (δ_H 4.84) and C-2 (δ_C 73.9) further confirmed that the C-2 position of the aglycone was glycosylated with D-galactose. Thus, compound **2** was deduced to be 3-*O*-acetyl-20-hydroxyecdysone-2-*O*-β-D-galactopyranoside.

Compound **3** showed the same molecular formula as **2** by its HR-ESI-MS at *m/z* 707.3609 $[M + Na]^+$. The ^1H and ^{13}C NMR spectral data of the aglycone part of **3** were in accordance with those of **2** (Table 1), suggesting that the aglycone of **3** was 20-hydroxyecdysone. Besides, the ^1H and ^{13}C NMR spectra displayed the signals due to one sugar moiety. Acid hydrolysis of **3** afforded D-glucose. The relative anomeric configuration of D-glucose was determined to be β based on the $^3J_{H1\text{-}H2}$ coupling constant (J = 7.5 Hz). In the HMBC spectrum, correlations between H-1′ (δ_H 4.95) and C-2 (δ_C 74.1), as well as between H-3 (δ_H 5.70) and C-1″ (δ_C 171.4) suggested that the D-glucose and acetyl group were attached to the C-2 and C-3 positions, respectively. Thus, the structure of **3** was determined as 3-*O*-acetyl-20-hydroxyecdysone-2-*O*-β-D-glucopyranoside.

Compound **4** gave a molecular formula $C_{29}H_{46}O_9$ by its HR-ESI-MS at *m/z* 561.3045 $[M + Na]^+$. The ^1H NMR spectrum of **4** indicated the presence of signals for five methyl groups (δ_H 0.90, 0.98, 1.19, 1.20 and 1.21, each 3H, s), four oxygenated methines [δ_H 3.31(1H, m), 3.84 (1H, m), 3.96 (1H, br s), and 5.09 (1H, dd, J = 10.5, 1.5 Hz)], as well as one olefinic proton [δ_H 5.82 (1H, d, J = 2.5 Hz)]. The ^{13}C NMR and DEPT spectra of **4** showed the signals for twenty-nine carbons, including five methyls (δ_C 18.1, 21.0, 24.4, and 26.0 × 2), seven oxygenated carbon signals (δ_C 68.5, 68.7, 72.7, 73.8, 77.6, 78.7, and 85.2), two olefinic carbons (δ_C 121.8 and 167.9), as well as a carbonyl (δ_C 206.2). The NMR spectral data of **4** were similar to those of 24-*epi*-abutasterone [23], except for the presence of signals assigned to an acetyl group [δ_H 2.11 (3H, s); δ_C 21.0 and 173.0] (Table 1). The HMBC correlations between H-24 (δ_H 5.09) and C-1′ (δ_C 173.0)/C-22 (δ_C 73.8)/C-23 (δ_C 33.1)/C-26, 27 (δ_C 26.0 × 2) suggested that the additional acetyl group was located at C-24 in **4**. The relative configuration of **4** could be further determined on the basis of NOESY experiment, which was identical to 24-*epi*-abutasterone. However, the stereochemistry of C-24 in the side-chain

could not be assigned based on current evidence. Thus, the structure of **4** was established as 24-*O*-acetyl-*epi*-abutasterone.

3. Experimental

3.1. General experimental procedures

Optical rotations were measured on Jasco P-1020 digital polarimeter at room temperature (Jasco, Tokyo, Japan). UV data were obtained on a JASCO V-550 UV/vis spectrophotometer (Jasco, Tokyo, Japan). Jasco FT/IR-480 plus Fourier Transform Spectrometer was used for scanning IR spectra with KBr pellets (Jasco, Tokyo, Japan). NMR spectra were acquired with Bruker AV-500 Spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR, Bruker, Fällanden, Switzerland). HR-ESI-MS analyses were recorded with Agilent 6210 ESI/TOF mass spectrometer (Agilent, Pala Alto, CA, USA). Silica gel (200–300 mesh or 300–400 mesh, Qingdao Haiyang Chemical Corporation, Qingdao, China) and Sephadex LH-20 (Pharmacia, Uppsala, Sweden) were used for column chromatography.

3.2. Plant material

The roots of *Serratula chinensis* were purchased from Qingping market of traditional Chinese medicine, Guangzhou city, Guangdong province of China, in October of 2012, and authenticated by Professor Guang-Xiong Zhou (College of Pharmacy, Jinan University). A voucher specimen (No. 20,121,015) was deposited in the Institute of Traditional Chinese Medicine & Natural Products, College of Pharmacy, Jinan University, Guangzhou, China.

3.3. Extraction and isolation

Air-dried and powdered roots (20.0 kg) of *S. chinensis* were extracted with 95% (v/v) ethanol for three times. The solvent was removed under vacuum to obtain a crude extract (370 g), which was then suspended in H_2O and successively extracted with petroleum ether, EtOAc and *n*-BuOH. The *n*-BuOH fraction (190 g) was subjected to silica gel column chromatography eluted gradually with $CHCl_3$-MeOH (100:0–0:100, v/v) to yield seven fractions (Fr. 1-Fr. 7). Fr. 4 (14 g) was further subjected to silica gel column chromatography eluted by $CHCl_3$-MeOH (100:0–0:100, v/v) to yield seven subfractions (Fr. 4a-Fr. 4 g). Fr. 4d (1.6 g) was further purified with Sephadex LH-20 column chromatography (MeOH:H_2O, 70:30, v/v) to yield **1** (10 mg), **2** (16 mg) and **4** (13 mg), respectively. Fr. 4e (0.8 g) was further separated by preparative HPLC using MeOH-H_2O (65:35, v/v, 6 ml/min) to afford **3** (RT: 25.2 min, 6 mg).

3.3.1. Compound 1

Amorphous powder; $[\alpha]_D^{25}$ + 13.1 (*c* 0.01, MeOH); UV (MeOH) λ_{max}: 242 nm; IR (KBr) ν_{max}: 3406, 2954, 2928, 1660, 1384 cm^{-1}; ^{1}H and ^{13}C NMR spectral data see Table 1; HR-ESI-MS *m/z*: 665.3532 $[M + Na]^+$ (calcd for $C_{33}H_{54}O_{12}Na$, 665.3507).

3.3.2. Compound 2

Amorphous powder; $[\alpha]_D^{25}$ + 21.0 (*c* 0.01, MeOH); UV (MeOH) λ_{max}: 242 nm; IR (KBr) ν_{max}: 3420, 2925, 2857, 1647, 1382, 1057 cm^{-1}; ^1H and ^{13}C NMR spectral data see Table 1; HR-ESI-MS *m/z*: 707.3609 $[M + Na]^+$ (calcd for $C_{35}H_{56}O_{13}Na$, 707.3613).

3.3.3. Compound 3

Amorphous powder; $[\alpha]_D^{25}$ + 13.4 (*c* 0.01, MeOH); UV (MeOH) λ_{max}: 242 nm; IR (KBr) ν_{max}: 3423, 2962, 2923, 1728, 1660, 1382, 1051 cm^{-1}; ^1H and ^{13}C NMR spectral data see Table 1; HR-ESI-MS *m/z*: 707.3609 $[M + Na]^+$ (calcd for $C_{35}H_{56}O_{13}Na$, 707.3613).

3.3.4. Compound 4

Amorphous powder; $[\alpha]_D^{25}$ + 46.4 (*c* 0.01, MeOH); UV (MeOH) λ_{max}: 242 nm; IR (KBr) ν_{max}: 3420, 2964, 2929, 1713, 1648, 1383, 1054 cm^{-1}; ^1H and ^{13}C NMR spectral data see Table 1; HR-ESI-MS *m/z*: 561.3045 $[M + Na]^+$ (calcd for $C_{29}H_{46}O_9Na$, 561.3034).

3.4. Acid hydrolysis and sugar analysis

Compounds **1–3** (each 2 mg) were dissolved in 2 M HCl (10 ml) and stirred at 80 °C for 3 h, respectively [22]. The solution was extracted with chloroform to yield an aglycone fraction and an aqueous fraction. The aqueous layer was evaporated to give a residue, followed by adding with anhydrous pyridine (0.5 ml) and L-cysteine methyl ester (1 mg). The reaction mixture was heated at 60 °C for 1 h. After that, *O*-aryl isocyanate ester (5 μl) was added to the solution, which was then heated at 60 °C for another 1 h. Filtered with membrane (0.45 μm) after reaction, the solution was analyzed with HPLC under the following conditions: Cosmosil $5C_{18}$-MS-II (4.6 × 250 mm, i.d. 5.0 μm), mobile phase: acetonitrile-0.05% formic acid (25:75), detector wavelength: 250 nm, flow rate: 0.8 ml/min, acquisition time: 40 min. The derivatives of authentic D-glucose, L-glucose, D-galactose and L-galactose were prepared by the same method, and showed the retention times of 20.65, 18.69, 16.78 and 17.71 min. As a result, D-galactose [t_R (min): 16.72, 16.77] from the hydrolyzates of **1** and **2**, and D-glucose [t_R (min): 20.53] from the hydrolyzate of **3** were detected.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the National Natural Science Foundation of China [grant number 81473117], [grant number 81503210], [grant number 81502939]; the Joint Fund of NSFC-Guangdong Province [grant number U1401225].

References

[1] Chinese Academy of Sciences "Flora of China" editorial, *Flora Reipublicae Popularis Sinicae* (Science Press, Beijing, 1987), pp. 166–167.
[2] Jiangsu New Medical College, *Dictionary of Chinese Crude Drugs* (Shanghai Science and Technology Press, Shanghai, 1977), pp. 234–235.

[3] T.J. Ling, W.Z. Ma, and X.Y. Wei, *J. Trop. Subtrop. Bot*. **11**, 143 (2003).
[4] T.J. Ling, P. Wu, M.F. Liu, and X.Y. Wei, *J. Trop. Subtrop. Bot*. **13**, 403 (2005).
[5] T.J. Ling, T. Xia, X.C. Wan, D.X. Li, and X.Y. Wei, *Molecules* **11**, 677 (2006).
[6] J.Q. Dai, Y.J. Cai, Y.P. Shi, Y.H. Zhang, Z.L. Liu, L. Yang, and Y. Li, *Chin. J. Chem*. **20**, 497 (2002).
[7] Y.J. Cai, J.Q. Dai, J.G. Fang, L.P. Ma, L.F. Hou, L. Yang, and Z.L. Liu, *Can. J. Physiol. Pharmacol*. **80**, 1187 (2002).
[8] T.I. Shirshova, N.K. Politova, S.A. Burtseva, I.V. Beshlei, and V.V. Volodin, *Pharm. Chem. J*. **40**, 268 (2006).
[9] P.J. Lupien, C.M. Hinse, and K.D. Chaudhary, *Arch. Int. Physiol. Biochim*. **77**, 206 (1969).
[10] V.N. Syrov, A.G. Kurmukov, and M.B. Sultanov, *Dokl. Akad. Nauk. Uzssr*. **38**, 31 (1981).
[11] A. Ványolós, Z. Béni, M. Dékány, A. Simon, and M. Báthori, *Sci. World J*. **2012**, 651275 (2012).
[12] Y.Q. Jian, X.J. Huang, D.M. Zhang, R.W. Jiang, M.F. Chen, B.X. Zhao, Y. Wang, and W.C. Ye, *Chem. Eur. J*. **21**, 9022 (2015).
[13] L. Fan, Y. Wang, N. Liang, X.J. Huang, C.L. Fan, Z.L. Wu, Z. He, Y.L. Li, and W.C. Ye, *Phytochem. Lett*. **14**, 185 (2015).
[14] S.G. Li, M.M. Li, B.X. Zhao, Y. Wang, and W.C. Ye, *J. Asian Nat. Prod. Res*. **17**, 1153 (2015).
[15] X.L. Li, B.X. Zhao, X.J. Huang, D.M. Zhang, R.W. Jiang, Y.J. Li, Y.Q. Jian, Y. Wang, Y.L. Li, and W.C. Ye, *Org. Lett*. **16**, 224 (2014).
[16] S.G. Li, L.L. Chen, X.J. Huang, B.X. Zhao, Y. Wang, and W.C. Ye, *J. Asian Nat. Prod. Res*. **15**, 1145 (2013).
[17] Y.Q. Jian, Y. Wang, X.J. Huang, S.G. Li, B.X. Zhao, Q.Y. Guo, and W.C. Ye, *J. Asian Nat. Prod. Res*. **14**, 831 (2012).
[18] H.J. Tang, C.L. Fan, G.Y. Wang, W. Wei, Y. Wang, and W.C. Ye, *Chin. Tradit. Herb. Drugs*. **45**, 906 (2014).
[19] M. Takács, A. Simon, E. Liktor-Busa, M. Báthori, F. Zsila, Z. Bikádi, P. Horváth, G. Veress, A. Gergely, and G. Tóth, *Magn. Reson. Chem*. **48**, 386 (2010).
[20] J.P. Girault and R. Lafont, *J. Insect Physiol*. **34**, 701 (1988).
[21] A. Suksamrarn, S. Kumpun, and B. Yingyongnarongkul, *J. Nat. Prod*. **65**, 1690 (2002).
[22] T. Miyase and A. Mimatsu, *J. Nat. Prod*. **62**, 1079 (1999).
[23] A. Suksamrarn, N. Promrangsan, B. Chitkul, S. Homvisasevongsa, and A. Sirikate, *Phytochemistry* **45**, 1149 (1997).