The Chemical Constituents of *Polypodium niponicum*

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Three new steroids named as shuilongguine **I** (**1**), shuilongguine **II** (**2**) and shuilongguine **III** (**3**), together with eleven known compounds were isolated from *Polypodium niponicum* (Chinese name "Shuilonggu", Berberidaceae). Their structures were deduced by spectroscopic methods and 2D NMR experiments.

Keywords: *Polypodium niponicum*; Steroid; Elucidated.

INTRODUCTION

Polypodium niponicum Mett is a traditional Chinese folk medicine growing in many provinces of China (Chinese name "Shuilonggu"). Its root has been used in traditional medicine for the treatment of typhoid, fever, dysentery, rheumatism, and as an antipyretic, an antineoplastic and so on.[1] However, its chemical constituents have not been reported so far. We have carried out a detailed chemical examination of this species that has led to the isolation of three new steroids (**1**, **2** and **3**), together with eleven known compounds including three steroids, three flavonoids and five other compounds from the roots of *Polypodium niponicum*. Herein we report the isolation and structure elucidation of three new compounds.

RESULTS AND DISCUSSION

Fourteen compounds were isolated by repeated column chromatography on silica gel and preparative TLC from the ethanol extract of *Polypodium niponicum*. Their structures were identified as shuilongguine **I** (**1**), shuilongguine **II** (**2**), shuilongguine **III** (**3**), polyporusterone **I** (**4**)[2], β-sitosterol (**5**),[3] 3,6-dimethoxyl-5,7-dihydroxyflavone (**6**),[4] populnin (**7**),[5] 6,7-dihydrox-3′-methoxy-4′,5-methylenedioxyisoflavone (**8**),[6] hanliuin **I** (**9**),[6] 3,5,7-trimethoxyflavone (**10**),[7] salicin (**11**),[8] stigmast-5-en-3β-ol-7-one (**12**),[9] 6α,15β-epoxyeremophila-7(11)-en-8α,12-olide (**13**),[10] and gallic acid (**14**).[11] The known compounds were identified by comparison of their physical and spectroscopic data (MS, ^{1}H and ^{13}C NMR) with those reported in the literature.

Compound **1** was a white power, mp: 241-242 °C; $[\alpha]_D^{20}$ +55 (c, 0.5, MeOH). Its HR-EIMS gave a peak at *m/z* 498.3598 corresponding to the molecular formula $C_{31}H_{46}O_5$ (calc. 498.3604), indicating eight degrees of unsaturation, ascribed to one carbonyl group, two double bonds, four steroid rings and one acetyl carbonyl group. The usual colour test indicated **1** to be steroid. Meanwhile, the IR spectrum revealing absorption bands due to hydroxyl (3400 cm^{-1}), acetyl carbonyl (1734 cm^{-1} and 1659 cm^{-1}) suggested the presence of conjugated ketone. The ^{13}C NMR and DEPT spectra (Table 2) of **1** clearly exhibited 31 carbon signals (7 × CH_3, 7 × CH_2, 11 × CH, 6 × C). Meanwhile in the ^{13}C NMR, there were typical signals of three carbons bearing oxygen at δ 72.01, 68.33 and 82.30, a carbonyl carbon at δ 203.84 and an acetyl group carbon at δ 170.16. The ^{1}H NMR spectrum indicated the presence of seven methyl groups at δ 1.24 (s, 3H, 18-CH_3), 1.85 (s, 3H, 19-CH_3), 0.93 (d, 3H, 21-CH_3), 1.04 (d, 3H, 27-CH_3), 1.18 (d, 3H, 28-CH_3), 0.92 (t, 3H, 29-CH_3), and 2.02 (s, 3H, CH_3CO-). The signal at δ 6.25 (d, 1H, J = 2.5 Hz) revealed an olefine proton, at δ 5.90 (dd, 1H, J = 10.5, 3.8 Hz) and δ 6.22 (dd, 1H, J = 10.5, 3.8 Hz) indicating the presence of two other olefinc protons. The ^{13}C NMR chemical shifts in the moiety of C-20 to C-29 of compound **1** have a similar side-chain structure to those of polyhydroxydinostane **I**.[12] The signals at δ 157.14 and 133.11 are due to the double bond (C-22/C-23). The EIMS of compound **1** gave a significant frag-

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ment ion peak at *m/z* = 359 (M-$C_{10}H_{19}$). Based on the EIMS, the molecular formula of the side chain was established to be $C_{10}H_{19}$, indicating one degree of unsaturation. In the IR spectrum the signal of one ring was not observable, implying the presence of one double bond. The differences of the ^{1}H NMR data between polydroxydinostane **I** and **1** were that polydroxydinostane **I** was lacking the signal of methyl (at C-23) and the presence of one proton signal at δ 6.22. Several HMBC correlations (Fig. 1) provided additional unambiguous evidence for the side chain substructure.

The relative stereochemistry of **1** was determined by coupling constant analysis and the NOESY information of the small coupling constant between H-2 and H-3 (*J* = 3.8 Hz) indicated a cis arrangement of these protons, thus 3-OH and 2-OAc are cis-form. The relatively large coupling constant between H-2 and one of the H-1 protons (*J* = 8.9 Hz) indicated they are *trans*-form and have a chair conformation with H-2 in the α position, the same as for H-3; from the key NOESY, the 2-OAc and 3-OH were in β position. But a difference was found at C-2; the HMQC spectrum showed the nonequivalent methine proton at δ 4.60 (1H, ddd, *J* = 11.2, 8.9, 3.8 Hz, H-2), at 4.28 (1H, ddd, *J* = 11.2, 8.7, 3.8 Hz, H-3) correlated with C-2 (δ 72.01) and C-3 (δ 68.33). The HMBC spectrum showed there were cross peaks of an acetyl (δ 170.16) with H-2 (δ 4.60), thus the acetyl group must be attached to C-2. In the NOESY spectrum of **1**, the correlation between H-3, H-1 and H-4 also suggested that ring A has a chair conformation, H_3-21 did not give a correlation with H_3-18, and H_3-21 was found to exhibit a correlation with H-17. Thus, H-17 should be placed on the α phase. On detailed consideration of molecular models, structure **1** was established. This new natural product was named shuilongguine **I** (Fig. 2).

Compound **2** was obtained as white powder; the IR spectrum of **2** showed absorption bonds for hydroxyl (3468 cm^{-1}), aldehyde group (2720 cm^{-1}), ester carbonyl (1754 cm^{-1}), acetyl group carbonyl (1719 cm^{-1}), methyl group

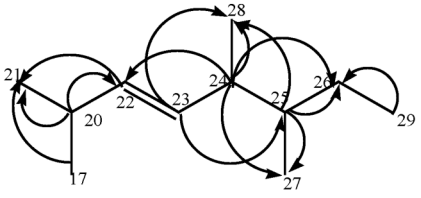

Fig. 1. HMBC correlation ($^{13}C \rightarrow {}^1H$) of the side chain of compound **1**.

(2941 cm^{-1}) and C-O (1256 cm^{-1}) in the molecule of **2**. Its ^{13}C NMR and DEPT spectrum (Table 2) clearly exhibited 31 carbon signals (7 × CH_3, 9 × CH_2, 10 × CH, 5 × C); it was shown by HRMS to have the molecular formula $C_{31}H_{50}O_3$, based on the molecular ion peak at *m/z* 470.3924 (calcd 470.3932), indicating seven degrees of unsaturation, ascribed to two carbonyl groups, four steroid rings and one double bond. The usual colour test indicated **2** to be a steroid. Meanwhile, the ^{1}H-^{1}H COSY and HMQC spectra indicated the presence of an acetyl group (δc 170.81, 20.6, δ_H 1.98) at C-3 (δ_C 72.98), only one hydroxyl group (δ_H 4.00, 1H, interchangeable with D_2O) at C-5 (δ_C 79.78), one aldehyde group (δ_C 203.14, δ_H 9.72) at C-7 (δ_C 63.00) and one double bond (δ_C 154.20, 116.82) at C-24 (28). Close similarity in chemical shifts, coupling patterns and coupling constants led us to assume the similarity of the structures of zhonghualliaoine **II**.[10] A difference was found only at the side chain. The ^{1}H NMR spectrum showed that the signal proton on C-28 was clear evidence showing the expected quartet at δ 5.13; protons on the methyl group at C-29 gave a clearly defined doublet at δ 1.60 as expected for an ethylidene group. Therefore, compound **2** and fucosterol[15] have identical side chain structures. The signals of the ^{13}C NMR spectrum at δ 154.20 and 116.82 are due to the double bond (C-24/C-28) of the substituted propenyl group. The EIMS of compound **2** gave a significant fragment ion peak at *m/z* = 331 (21). Based on the EIMS, the formula of the side chain was established as $C_{10}H_{19}$, indicating one degree of unsaturation. In the IR spectrum, the signal of one ring was not observable, implying that compound **2** has one double bond. Furthermore, its ^{1}H NMR indicated the seven methyl group signals were at δ 1.22 (s, 3H, 18-CH_3), 1.83 (s, 3H, 19-CH_3), 0.93 (d, 3H, *J* = 6.5 Hz, 21-CH_3), 1.02 (d, 3H, *J* = 6.5 Hz, 26-CH_3), 1.00 (d, 3H, *J* = 6.5 Hz, 27-CH_3), 1.60 (d, 3H, *J* = 7.0 Hz, 29-CH_3), and 2.06 (s, 3H, CH_3-CO-). Its HMBC spectrum correlated to H_2-4 and H_2-2 confirmed that it has acetyl group functionality at C-3; besides, the HMBC spectrum showed that there were cross peaks of an acetyl with H-3 (δ 4.00) which also supported the above results.

The relative stereochemistry of compound **2** was determined on the basis of the NOESY information. Comparison of the NOESY spectrum with structurally related zhonghualiaoine **II** natural products showed their relative stereochemistry was the same. But the H_3-21 did not give a correlation with H_3-C_{18}, H_3-C_{19}, but H_3-C_{21} was found to exhibit a correlation with H-14, H-7. Thus, H-14 and H-7

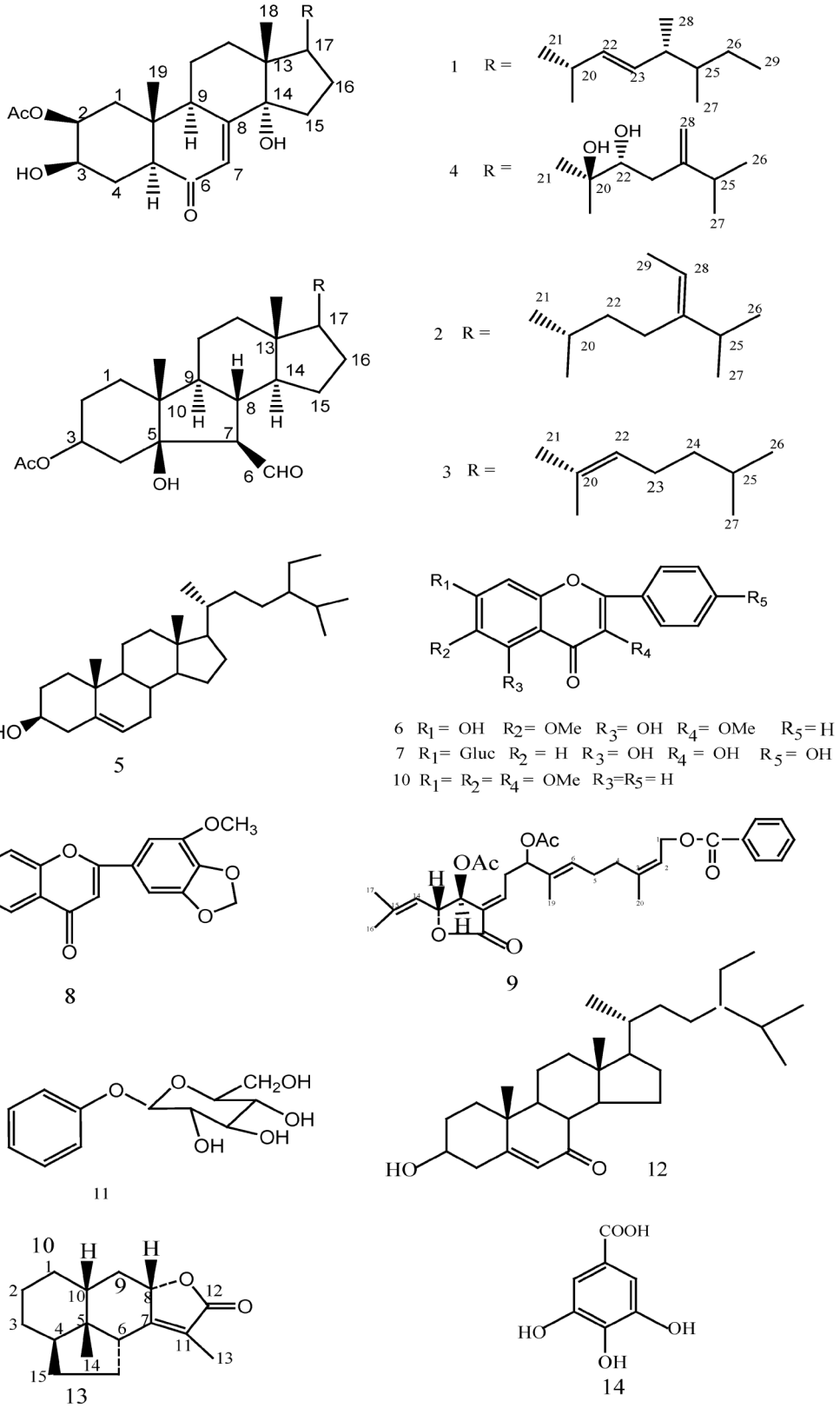

Fig. 2. The structures of compounds (**1-14**).

Table 1. ^{1}H NMR spectral data of compounds **1**, **2** and **3** (400 MHz, δ ppm, $CDCl_3$, TMS)*

Proton	**1**	**2**	**3**
NO	δ_H coupling (Hz)	δ_H coupling (Hz)	δ_H coupling (Hz)
1α	2.22 (dd, 9.0, 3.8)	1.54 (m)	1.53 (m)
1β	1.92 (dd, 9.0, 3.8)	1.34 (m)	1.32 (m)
2α, 2β	4.60 (ddd, 11.2, 8.9, 3.8)	1.51 (m), 1.60 (m)	1.50 (m), 1.61 (m)
3	4.28 (ddd, 11.2, 8.9, 3.8)	4.00 (quintet, 3.2)	3.98 (quintet, 3.2)
4α, 4β	1.64 (m), 1.78 (m)	1.64 (dd, 6.5, 3.2), 2.01 (Br)	1.62 (dd, 6.5, 3.2), 1.99 (Br)
5	2.49 (dd, 10.5, 4.5)		
6		9.72 (d, 11.2)	9.70 (d, 11.2)
7	6.25 (d, 10.5)	2.23 (dd, 6.5, 3.2)	2.21 (dd, 6.5, 3.2)
8		2.10 (m)	2.09 (m)
9	3.61 (m)	1.23 (m)	1.20 (m)
10			
11	1.76 (m)	1.29 (m)	1.28 (m)
12	1.38 (m), 1.63 (m)	1.02 (m), 2.03 (m)	1.05 (m), 2.01 (m)
13			
14		1.22 (m)	1.24 (m)
15	1.41 (m)	1.04 (m), 1.40 (m)	1.06 (m), 1.38 (m)
16	1.91 (m), 1.42 (m)	1.24 (m), 1.80 (m)	1.22 (m), 1.79 (m)
17	1.42 (m)	1.10 (m)	1.12 (m)
18	1.24 (s)	1.22 (s)	1.20 (s)
19	1.85 (s)	1.83 (s)	1.81 (s)
20	1.40 (m)	1.31 (m)	
21	0.93 (d, 6.5)	0.93 (d, 6.5)	1.61 (d, 1.2)
22	5.90 (dd, 10.5, 3.8)	1.10 (m), 1.55 (m)	5.40 (qt, 6.9, 1.3)
23	6.22 (dd, 10.5, 3.8)	2.03 (m), 1.78 (m)	2.24 (m)
24	2.27 (m)		1.62 (m)
25	2.29 (m)	2.80 (m)	1.23 (m)
26	1.04 (m)	1.09 (d, 6.5)	1.01 (d, 6.5)
27	1.04 (d, 6.5)	1.00 (d, 6.5)	1.00 (d, 6.5)
28	1.18 (d, 6.9)	5.14 (q, 6.5)	
29	0.92 (t, 6.5)	1.63 (d, 6.0)	
OAc	2.02 (s)	2.04 (s)	2.02 (s)

* Assignment from ^{1}H-^{1}H COSY, HMQC, HMBC and NOESY

should be placed on the α-phase. A NOE cross peak between H-8, H_3-C_{18} and H_3-C_{19} were also observed in the NOESY spectrum which indicated that they are cis to each other and thus all oriented β. Therefore, the structure of compound **2** was deduced as shuilongguine **II**.

Compound **3** was a colorless powder, mp: 192 °C; the IR spectrum of **3** showed absorption bands for hydroxyl (3460 cm^{-1}), acetyl group carbonyl (1741 cm^{-1}), methyl group (2939 cm^{-1}), and aldehyde group (2720 cm^{-1}) in the molecular of **3**. Its ^{13}C NMR and DEPT spectrum (Table 2) clearly exhibited 29 carbon signals (6 × CH_3, 8 × CH_2, 8 × CH, 5 × C, 2 × CO). It was shown by HRMS to have the molecular formula $C_{29}H_{42}O_5$, based on the HRMS of the molecular ion peak at *m/z* 458.3603 (calcd. 458.3610) indicating seven degrees of unsaturation, ascribed to two carbonyl groups, four steroid rings, and one double bond. The usual color test indicated this compound to be a steroid. Analysis of the ^{1}H, ^{13}C NMR and DEPT of **3**, meanwhile, by comparing the ^{1}H NMR and ^{13}C NMR spectral data with compound **2**, in compound **3** showed the presence of one acetyl group (δ_C 171.20, 21.81, δ_H 2.02) at C-3 (δ_C 73.21), only one hydroxyl group (δ_H 4.30, 1H, interchangeable with D_2O) at C-5 (δ 81.00), one aldehyde group at C-7 (δ_C 204.11, δ_H 9.68), and one double bond (δ 141.82, 129.76) at C-20 (22). The ^{1}H and ^{13}C NMR spectrum of **3** was very similar to that of compound **2**. This suggested that **3** and **2** have similar skeletons. Comparing the ^{13}C NMR and ^{1}H NMR spectra of **3** with those of **2** led to the conclusion that the main difference was a side chain. Based on the HR EIMS, the molecular formula was established as C_8H_{15} (*m/z* 111.1185), indicating one degree of unsaturation. Moreover, a broad triplet with J values of 1.3 Hz indicated a

Table 2. ^{13}C NMR spectral data of compounds **1**, **2** and **3** (100 MHz, δ ppm $CDCl_3$, TMS)*

Carbon	1			2			3		
NO	δ_C	DEPT	HMBC	δ_C	DEPT	HMBC	δ_C	DEPT	HMBC
1	37.22	CH_2	19	26.52	CH_2	19	26.60	CH_2	19
2	72.01	CH	1, 3, 4	38.40	CH_2	1, 3, 4	38.41	CH_2	1, 3, 4
3	68.33	CH	1, 4, 5	72.98	CH	1, 4	73.21	CH	1, 4
4	32.34	CH_2	3, 5	44.57	CH_2	2, 3	44.46	CH_2	2, 3
5	50.90	CH	1, 4	79.78	C	1, 4	81.00	C	1, 4
6	203.84	C	4, 5	203.14	CH	7	204.11	CH	7
7	121.66	CH	9	63.00	CH	8, 9, 14	63.13	CH	8, 9, 14
8	166.42	C	9, 11	40.04	CH	7, 9, 11	39.86	CH	7, 9, 11
9	34.17	CH	5, 11, 19	49.92	CH	8, 11	49.76	CH	8, 11
10	38.82	C	1, 5, 9	44.96	C	1, 9, 11	44.92	C	1, 9, 11
11	21.05	CH_2	9, 12	22.10	CH_2	9, 12	22.07	CH_2	9, 12
12	32.11	CH_2	9, 11	39.14	CH_2	9, 11	39.22	CH2	9, 11
13	47.93	C	12, 17, 18	44.56	C	12, 17, 18	44.50	C	12, 17, 18
14	82.30	C	7, 9, 15	55.68	CH	7, 8, 15	55.62	CH	7, 8, 15
15	31.91	CH_2	16, 17	24.00	CH_2	14, 16, 17	23.98	CH_2	14, 16, 17
16	21.62	CH_2	15, 17, 20	28.46	CH_2	15, 17, 20	28.46	CH_2	15, 17
17	50.06	CH	16, 21	55.27	CH	16, 21	55.30	CH	16, 21
18	18.03	CH_3	12, 17	12.36	CH_3	12, 17	12.41	CH_3	12, 17
19	24.07	CH_3	1, 5, 9	17.98	CH_3	1, 9		CH_3	1, 9
20	36.13	CH	17, 21, 22	33.47	CH	17, 21, 22	141.82	C	17, 21, 22
21	18.24	CH_3	20, 22	17.95	CH_3	20, 22	17.99	CH_3	20, 22
22	157.14	CH	21, 23	34.72	CH_2	21, 23	141.82	CH	21, 23
23	133.11	CH	25, 28	30.14	CH_2	22, 24	129.76	CH_2	22, 24
24	30.34	CH	22, 26, 28	154.20	C	22, 23, 25, 28	18.02	CH_2	22, 23, 25, 28
25	27.62	CH	26, 27	27.44	CH	26, 27	39.94	CH	26, 27
26	21.58	CH_2	25, 27, 29	22.18	CH_3	25	27.40	CH_3	25
27	21.29	CH_3	25, 26	22.09	CH_3	25, 26	22.19	CH_3	25, 26
28	18.55	CH_3	24, 25	116.82	CH	23, 25	22.03		
29	20.81	CH_3	26	15.24	CH_3	28			
OAc	170.16	CO		170.81	CO		171.20	CO	
	20.92	CH_3		20.63	CH_3		21.81	CH_3	

*Assignments from ^1H-^1H COSY, HMQC and HMBC (from ^{13}C to ^1H).

vinylic methyl (δ_C 22.68) and favored a $\Delta^{20(22)}$ double bond justifying the quartet of triplets at δ 5.40 for H-22. The ^{13}C NMR spectrum clearly exhibited a trisubstituted double bond (C20/C22, δ_C 141.82, 129.76). Furthermore, in the HMBC spectrum the correlation peak between H-17 and C-20 of the side chain was clearly observed, so this side chain must be attached to C-17. From the above information, shuilongguine **III** was determined to have the structure as shown in **3** (Fig. 2).

EXPERIMENTAL SECTION

General Methods

Melting Points were determined using a Kofler melting point apparatus and optical rotations were made on a DIP-181 instrument. IR and UV spectra were taken on a Perkin-Elmer 599B and Shimadzu UV-300 spectrometers. ^1H NMR, ^{13}C NMR and 2D NMR spectra were recorded on a Bruker AM-400 FT NMR with TMS as internal standard and HR-EIMS and EIMS data were obtained on a MAT-12 (70 eV). Silica gel (100-200, 200-300 mesh) was used for column chromatography and silica gel GF_{254} for TLC.

Plant Material

The plant materials were collected from the west of Sichuan Province of P. R. China, in July 2007, and identified by Prof Yong-shan Lian of Northwest Normal University. A voucher specimen (NO. 36079) was deposited at the Herbarium of the College of Life Science, Northwest Normal University, Lanzhou 730070, P. R. China.

Extraction and Isolation

The dried and powdered roots of the *Polypodium niponicum* (6.5 kg) were extracted with 95% EtOH three times at room temperature (each process lasting 7 days).

The extract was concentrated under reduced pressure; the residue was extracted with petroleum ether (60-90 °C) -Et_2O (1:1, v/v), EtOAc and $CHCl_3$-MeOH (1:2, v/v) three times, respectively, successively. The petroleum ether-Et_2O extract (48 g) was chromatographed on silica gel (450 g, 100-200 mesh), using petroleum ether-$(CH_3)_2CO$ (50:1-1:1, v/v) gradient and purified by preparative TLC, to afford **5** (24 mg), **12** (15 mg) and **13** (17 mg). The EtOAc extract (64 g) was chromatographed on silica gel (200 g, 100-200 mesh), with a mixture of $CHCl_3$-EtOAc (10:1-1:1, v/v), EtOAc-MeOH (1:2, v/v) as eluted and purified by preparative TLC, to yield **6** (18 mg), **7** (25 mg), **8** (13 mg), **9** (20 mg), **10** (11 mg). The $CHCl_3$-MeOH extraction was concentrated to a syrup (56.2 g), which was chromatographed on silica gel (500 g, 100-160 mesh), using $CHCl_3$-MeOH (10:1, 5:1, 2:1, 1:1, v/v, each) gradient; three fractions were obtained (A 13 g, B 11 g, C 16 g). From fraction B by rechromatography on silica gel (300 g, 200-300 mesh), with $CHCl_3$-$(CH_3)_2CO$ (1:10, v/v) and $CHCl_3$-MeOH (5:1, v/v) as eluted and purified by preparative TLC, **4** (21 mg), **3** (16 mg), **2** (27 mg) and **1** (14 mg) were yielded. Then from fraction C, rechromatography on silica gel (100 g, 200-300 mesh) with $CHCl_3$-MeOH (3:2, v/v) as eluted, yielded **11** (26 mg) and **14** (20 mg).

Shuilongguine I: $C_{31}H_{46}O_5$, white powder, mp 241-242 °C, $[\alpha]_D^{20}$ +55° (c, 0.5, MeOH), UV λ_{max}^{MeOH} = 243 nm. IR (KBr): 3400, 2940, 2872, 1734, 1659, 1456, 1382, 804 cm^{-1}; HR-EIMS *m/z* 498.3598 (calc. 498.3604); EIMS *m/z* 498, 442, 414, 371, 359. ^1H and ^{13}C NMR, DEPT, HMBC data are listed in Tables 1 and 2.

Shuilongguine II: $C_{31}H_{50}O_3$, White powder, mp 184-185 °C, $[\alpha]_D^{20}$ +49° (c, 0.32, $CHCl_3$), UV λ_{max}^{MeOH} = 252 nm. IR (KBr): 3468, 2941, 2870, 2721, 1754, 1719, 1457, 1378, 1250, 892 cm^{-1}; HR-EIMS *m/z* 470.3924 (calc. 470.3932); EIMS *m/z* 470, 410, 373, 331, 300, 285. ^1H and ^{13}C NMR, DEPT, HMBC data are listed in Tables 1 and 2.

Shuilongguine III: $C_{29}H_{42}O_5$, colorless powder, mp 192 °C, $[\alpha]_D^{20}$ +48° (c, 0.32, $CHCl_3$), UV λ_{max}^{MeOH} = 254 nm, IR (KBr): 3460, 2939, 2720, 1743, 1719, 1458, 1377, 890 cm^{-1}; HR-EIMS *m/z* found 458.3603 (calc. 458.3610); EIMS *m/z* 458, 398, 361, 319, 300, 285. ^1H and ^{13}C NMR, DEPT, HMBC data are listed in Tables 1 and 2.

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