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Three new polyphenols from the rhizomes of *Arachniodes exilis*

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Three new polyphenols, araspidin BB (**1**), arachniodesin A (**2**) and arachniodesin B (**3**), together with two known compounds, epicatechin (**4**) and procyanidin B-2 (**5**), were isolated from the rhizomes of *Arachniodes exilis*. The structures of three new compounds were elucidated as 5-methyl-methylene-bis-phlorobutyrophenone (**1**), 4 β -ethoxycarbonylmethylepicatechin (**2**) and epicatechin-(4 β \rightarrow 8)-4 β -ethoxycarbonylmethylepicatechin (**3**), on the basis of their spectral analysis and by comparing them with the related model compounds. Compounds **4** and **5** were obtained from the title plant for the first time.

Keywords: *Arachniodes exilis*; polyphenols; araspidin BB; arachniodesin A; arachniodesin B

1. Introduction

Arachniodes exilis (Hance) Ching is widely distributed in the southern provinces of China. Its rhizomes have been used in folk medicine to treat dysentery, burn scald, and acute icterus hepatitis.¹ To our knowledge, little phytochemical investigations on the rhizomes of this plant have been reported. In our research, three new polyphenols, araspidin BB (**1**), arachniodesin A (**2**) and arachniodesin B (**3**), together with two known compounds, epicatechin (**4**)² and procyanidin B-2 (**5**),³ have been isolated from the methanolic extract of the rhizomes of the plant. Compounds **4** and **5** were obtained from the title plant for the first time.

2. Results and discussion

Compound **1** was isolated as pale yellow needles from acetone. The molecular formula was established by HR-ESI-MS (positive) at m/z 419.1719 [M + H]⁺ as C₂₂H₂₆O₈. The IR spectrum showed absorption bands at 3293 (OH), 1700 (C=O) and 1627, 1514 (C=C)

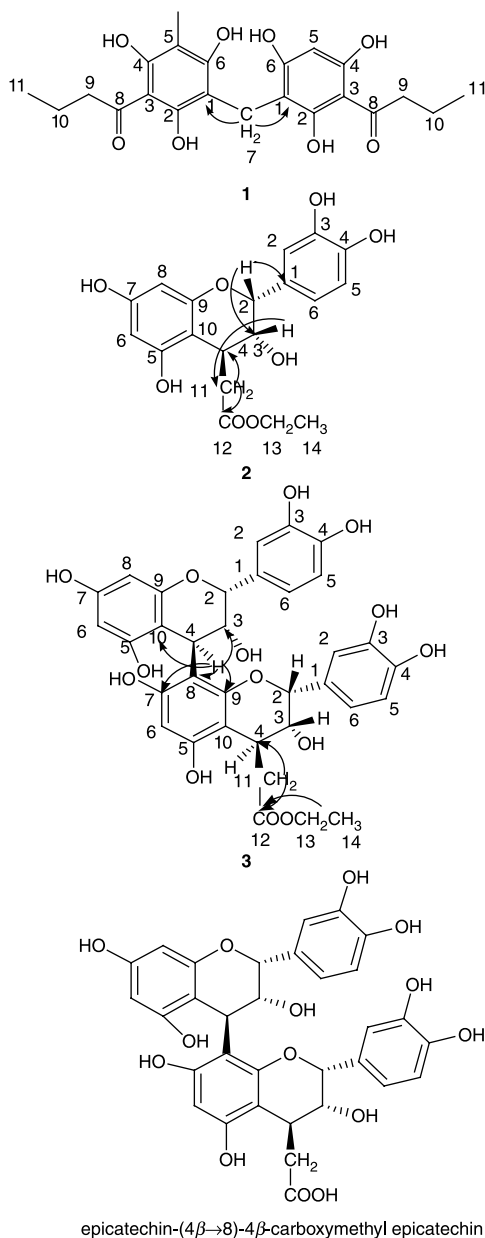
cm⁻¹. In the ¹³C NMR spectrum of **1** (see Table 1), the carbon signals at δ 161.6, 161.6, 161.2, 160.3, 157.5, 157.5, 105.8, 105.5, 105.5, 104.7, 104.2 and 95.6 indicated the presence of two aromatic rings. The carbon signals of a methyl at δ 7.7, a methylene at δ 16.4 and two butyryls at δ 13.8, 13.9 (–COCH₂CH₂CH₃), 18.2, 18.5 (–COCH₂CH₂CH₃), 45.9, 46.5 (–COCH₂CH₂CH₃) and 207.0, 207.4 (–COCH₂CH₂CH₃) were also observed, which were supported by the ¹H NMR spectral data at δ 0.92 (6H, t, $J = 7.8$ Hz, 2 \times –COCH₂CH₂CH₃), 1.66 (4H, m, 2 \times –COCH₂CH₂CH₃) and 3.07 (4H, t, $J = 7.3$ Hz, 2 \times –COCH₂CH₂CH₃). The HMBC correlations (Figure 1) between H-7 and C-1, C-1' indicated the presence of the methylene-bis-phloroglucinol moiety. Furthermore, the ¹H NMR and IR spectra of **1** were very similar to those of methylene-bis-methylphlorobutyrophenone.⁴ Based on the above data, **1** was assigned as 5-methyl-methylene-bis-phlorobutyrophenone, named araspidin BB.

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Table 1. ^1H (600 MHz, $\text{DMSO}-d_6$) and ^{13}C NMR (150 MHz) spectral data of **1** (J in Hz).

Position	δ_{H}	δ_{C}
1		106
2		158
3		106
4		162
5		105
6		160
5- CH_3	1.96 (s)	7.7
8		207
9	3.07 (t, 7.3)	46.5
10	1.66 (m)	18.5
11	0.92 (t, 7.8)	13.8
1'		106
2'		158
3'		104
4'		162
5'	6.23 (s)	95.6
6'		161
7	3.69 (s)	16.4
8'		207
9'	3.07 (t, 7.3)	45.9
10'	1.66 (m)	18.2
11'	0.92 (t, 7.8)	13.9

Compound **2** was obtained as a tan amorphous powder from EtOAc–MeOH (1:1). The molecular formula $\text{C}_{19}\text{H}_{20}\text{O}_8$ was established by HR-ESI-MS at m/z 377.1218 $[\text{M} + \text{H}]^+$. The IR spectrum showed absorption bands at 3324 (OH), 1729 (C=O), and 1627, 1520 ($\text{C}=\text{C}$) cm^{-1} . The ^1H and ^{13}C NMR spectra (see Table 2) of **2** closely resembled with those of 4 β -carboxymethyl epicatechin,⁵ and H-2 and H-3 demonstrated very small coupling constants (each s), indicating the 2,3-*cis* configuration of the flavan moiety. It was further supported by the EI-MS of **2**, which showed, together with a peak at m/z 376 due to $[\text{M}]^+$, peaks at m/z 224 and 152 formed by a retro-Diels–Alder-type fission of the flavan C-ring. The ^{13}C NMR spectrum also showed the presence of a methylene (δ 40.5) and a carbonyl (δ 174.7) group. In addition, the observation of a methylene at δ 62.1 and a methyl at δ 15.1 in the ^{13}C NMR spectrum, as well as the signals at δ 4.19 (2H, q, $J = 7.0$ Hz) and 1.28 (3H, t, $J = 7.0$ Hz) in the ^1H NMR spectrum, indicated the presence of an ethoxy group.



epicatechin-(4 β →8)-4 β -carboxymethyl epicatechin

Figure 1. Structure and key HMBC correlations of **1–3**, and epicatechin-(4 β →8)-4 β -carboxymethyl epicatechin.

The HMBC experiments demonstrated the long-range correlation between H-13 and C-12, suggesting that compound **2** was the ethyl ester of 4-carboxymethyl epicatechin. The NOESY spectrum of **2** showed a cross-peak between H-2 (δ 4.83, s) and one proton (δ 2.37)

Table 2. ^1H (600 MHz, $\text{DMSO}-d_6$) and ^{13}C NMR (150 MHz) spectral data of **2** and **3** (J in Hz).

Position	2		3	
	δ_{H}	δ_{C}	δ_{H}	δ_{C}
2	4.83 (s)	76.1	4.90 (s)	76
2''			4.79 (s)	74.1
3	3.88 (s)	71.1	3.82 (s)	71.9
3''			3.62 (s)	68.1
4	3.39 (dd, 3.7, 11.0)	37.2	3.16 (d, 9.6)	36.1
4''			4.61 (s)	36.2
5		159		157
5''				155
6	5.91 (d, 2.2)	96.3	5.77 (s)	96.6
6''			5.68 (s)	94.3
7		159		157
7''				157
8	5.95 (d, 2.2)	97.1		108
8''			5.77 (s)	95.2
9		158		155
9''				154
10		103		103
10''				102
11	2.37 (dd, 11.0, 15.7) 3.04 (dd, 3.7, 15.7)	40.5	2.35 (dd, 9.6, 13.8) 2.83 (d, 13.8)	39.1
12		175		173
13	4.19 (q, 7.0)	62.1	4.10 (q, 5.0)	60.5
14	1.28 (t, 7.0)	15.1	1.19 (t, 5.0)	14.9
1'		133		132
1''				131
2'	6.97 (d, 1.5)	116	6.77 (s)	115
2''			6.92 (s)	115
3'		146		145
3''				145
4'		147		145
4''				145
5'	6.76 (d, 8.0)	116	6.65 (d, 6.0)	115
5''			6.58 (d, 6.0)	115
6'	6.79 (dd, 1.5, 8.0)	120	6.50 (d, 6.0)	119
6''			6.77 (d, 6.0)	118

of the methylene, indicating that the ethoxycarbonylmethyl group at C-4 and H-2 are located on the same side. On the basis of all these evidence, compound **2** was identified as 4 β -ethoxycarbonylmethylepicatechin, named arachniodesin A.

Compound **3** was isolated as a tan amorphous powder from MeOH. The molecular formula $\text{C}_{34}\text{H}_{32}\text{O}_{14}$ was established by HR-ESI-MS at m/z 687.1690 $[\text{M} + \text{Na}]^+$. The IR spectrum showed absorption bands at 3338 (OH), 1703 (C=O) and 1627, 1520

(C=C) cm^{-1} . The chemical shifts of C-2, C-3, C-4, C-2'', C-3'' and C-4'' (see Table 2) suggested that **3** was a dimer of two flavan-3-ol units. The signals of H-2 and H-2'', which appeared as broad singlets in both the flavan-3-ol units, indicated the presence of epicatechin moieties.⁶ The HMBC correlations of H-11 with C-4, C-12 and H-13 with C-12 suggested that the lower flavan-3-ol unit of **3** was 4-ethoxycarbonylmethylepicatechin. The correlations between H-4'' and C-7, C-8, C-9 in the HMBC spectrum indicated the inter-

flavonoid linkage of C-4'' → C-8. The ¹H and ¹³C NMR spectra of **3** were very similar to those of epicatechin-(4β → 8)-4β-carboxymethylepicatechin⁵ except for an additional ethoxy group; together with the HMBC spectrum it suggested that **3** was the ethyl ester of epicatechin-(4β → 8)-4β-carboxymethylepicatechin. Based on the above fact, **3** was identified as epicatechin-(4β → 8)-4β-ethoxycarbonylmethylepicatechin, named arachniodesin B.

3. Experimental

3.1 General experimental procedures

Optical rotations were measured using a JASCO P-1010 polarimeter in CH₃OH. The melting points were determined on an X-4 micro melting-point apparatus. IR spectra were recorded using a Nicolet Magna FT-IR 750 spectrometer. NMR spectra were recorded at 600 MHz for ¹H NMR and 150 MHz for ¹³C NMR on a Bruker AV600. The chemical shifts are relative to internal standard TMS and the coupling constants are in Hertz. The ¹H and ¹³C NMR assignments were supported by ¹H-¹H COSY, HSQC and HMBC experiments. EI-MS data were recorded on a JEOL JMS-SX 102A spectrometer. The HR-ESI-MS spectrum was recorded on a MAT-711 mass spectrometer. Silica gel (Qing Dao Hai Yang Chemical Group Co., Shandong Province, China) was used for column chromatography and Sephadex LH-20 (Pharmacia) was used for molecular exclusion chromatography.

3.2 Plant material

Dried rhizomes of *Arachniodes exilis* (Hance) Ching were collected in October 2004 from Jiujiang county, Jiangxi province of China. The original plants were identified by the curator Ce-Ming Tan, Jiujiang Forest Plants Specimen Mansion. A specimen (No. AEC0601) has been deposited with the College of Pharmacy, Huazhong University of Science and Technology.

3.3 Extraction and isolation

Air-dried rhizomes of *A. exilis* (10 kg) were extracted with methanol at room temperature, and the solvent was evaporated under reduced pressure to give the methanolic extract (1500 g). The extract was suspended in water and then partitioned with petroleum, EtOAc and *n*-BuOH, successively. The EtOAc extract (76 g) was subjected to silica gel column chromatography eluting with a gradient eluent of CHCl₃-CH₃OH to yield four fractions. Fraction 1 was chromatographed over a silica gel column using CHCl₃-CH₃OH (8:1) as the eluent and then purified on a Sephadex LH-20 column using methanol as the eluent to afford **4** (89 mg). Fraction 2 was subjected to silica gel column chromatography using cyclohexane-acetone (6:1) as the eluent and then chromatographed over Sephadex LH-20 column using CHCl₃-CH₃OH (1:1) as the eluent to yield **1** (73 mg). Fraction 3 was chromatographed over a silica gel column using CHCl₃-CH₃OH-H₂O (4:1:0.1) as the eluent, repeatedly to produce **2** (69 mg). Fraction 4 was subjected to ODS reverse-phase silica gel column chromatography and eluted with MeOH-H₂O (1:1) repeatedly to give **3** (23 mg) and **5** (31 mg).

3.3.1 Compound 1

Pale yellow needles; mp 195–196°C; IR (KBr) ν_{\max} 3293 (OH), 2963 (CH), 1700 (C=O), 1627, 1514 (C=C), 1444, 1369, 1313, 1228, 1124 cm⁻¹; ¹H and ¹³C NMR spectral data, see Table 1; EI-MS *m/z* 166 (100), 209 (83), 152 (48), 223 (37), 196 (37), 417 (56); HR-ESI-MS *m/z* 419.1719 [M + H]⁺ (calcd for C₂₂H₂₇O₈, 419.1706).

3.3.2 Compound 2

Tan amorphous powder; mp 63–64°C, [α]_D²⁰ -31 (c 0.36, MeOH); IR (KBr) ν_{\max} 3324 (OH), 1729 (C=O), 1627, 1520 (C=C), 1467, 1373, 1283, 1148, 1101 cm⁻¹. ¹H and ¹³C NMR spectral data, see Table 2. EI-MS *m/z* 177 (100), 122 (69), 151 (66), 287 (12), 224 (6), 376 (3) [M]⁺;

HR-ESI-MS m/z 377.1218 $[M + H]^+$ (calcd for $C_{19}H_{21}O_8$, 377.1236).

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3.3.3 Compound 3

Tan amorphous powder; $[\alpha]_D^{20} + 50$ (c 0.27, MeOH); CD (c 0.0015, MeOH) (nm): $\Delta\epsilon_{237} = -2.52$, $\Delta\epsilon_{248} = 1.97$, $\Delta\epsilon_{269} = -1.66$, $\Delta\epsilon_{275} = -0.26$, $\Delta\epsilon_{280} = -0.82$, $\Delta\epsilon_{283} = -0.21$, $\Delta\epsilon_{288} = -1.16$; IR (KBr) ν_{\max} 3338 (OH), 2940, 2865, 1703 (C=O), 1627, 1520 (C=C), 1364, 893 cm^{-1} ; ^1H and ^{13}C NMR spectral data, see Table 2; HR-ESI-MS m/z 687.1960 $[M + \text{Na}]^+$ (calcd for $C_{34}H_{32}O_{14}\text{Na}$, 687.1960).

Acknowledgements

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