

## Three New Isoflavonoids from the Aerial Parts of *Ammopiptanthus mongolicus*

by Xiao-Ming Tian<sup>a</sup>), Shi-Zhong Chen<sup>a</sup>), Li Tang<sup>b</sup>), and Peng-Fei Tu<sup>\*a</sup>)

<sup>a</sup>) Department of Natural Medicines, School of Pharmaceutical Sciences, Peking University Health Science Center, No. 38 Xueyuan Road, Beijing 100083, P. R. China  
(phone/fax: +86-10-82802750; e-mail: pengfeitu@vip.163.com)

<sup>b</sup>) Key Laboratory of China Minority Traditional Medicine Center, School of Life and Environment, Central University for Nationalities, No. 27 Zhongguancun South Street, Beijing 100081, P. R. China

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Three new isoflavonoids, namely ( $\pm$ )-ammopiptanine A (**1**), ammopiptanine B (**2**), ammopiptanoside A (**3**), together with 13 known compounds, were isolated from the aerial parts of *Ammopiptanthus mongolicus*. Their structures were elucidated on the basis of detailed spectroscopic analyses and by comparison with those of related model compounds. The isoflavonoids described, except formononetin, wistin, daidzein, and calycosin, were isolated from this plant for the first time.

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**Introduction.** – *Ammopiptanthus mongolicus* (MAXIM. ex KOM) CHENG f. is the only kind of evergreen shrubs in arid hungeriness area, belonging to the family Leguminosae, and it is a remnant plant of the ancient subtropical zone in the Tertiary Period and has been classified as the national tertiary protection species. Its branches and leaves can be used as rheumatism and petechia dispeller. The local inhabitants often use its leaves to treat frostbite and chronic rheumatoid arthritis externally [1]. Previous investigations reported that quinolizidine alkaloids, flavonoids, and resveratrol have been isolated from the title plant [2–11]. Herein, we report the isolation and characterization of three new isoflavonoids as ( $\pm$ )-5,7,4'-trihydroxy-8-(2'',3''-epoxyisopentyl)isoflavone<sup>1</sup>) (**1**), 5,4'-dihydroxyfuran[4'',5'':6,7]isoflavone<sup>1</sup>) (**2**), and 4'-methoxyisoflavone 7-O- $\beta$ -D-[6''-(*E*-but-2-enoyl)]glycoside<sup>1</sup>) (**3**). Furthermore, 13 known compounds were also isolated and identified by comparison with literature values as lupiwightone [12], formononetin [13], genistein [13], orobol [14], pratensein [15], pratensein 7-O- $\beta$ -D-glucoside [16], wistin [17], daidzein [13], glycitein [18], odoratin [19], ononin [13], 6''-acetylononin [20], and calycosin [21]. Except formononetin, wistin, daidzein, and calycosin, all isoflavonoids were isolated from this plant for the first time.

**Results and Discussion.** – Compound **1** was obtained as a white powder, with the molecular formula C<sub>20</sub>H<sub>18</sub>O<sub>6</sub>, based on the [*M* + H]<sup>+</sup> peak at *m/z* 355.1172 in the HR-ESI-MS, and confirmed by <sup>1</sup>H- and <sup>13</sup>C-NMR experiments (*Table 1*). The IR spectrum showed characteristic absorption bands of a OH group (3382 cm<sup>-1</sup>), an  $\alpha,\beta$ -unsaturated C=O group (1657 cm<sup>-1</sup>) and an aromatic ring (1613, 1583, 1516 cm<sup>-1</sup>). The UV spectrum exhibited maximum absorptions at 260 (band II) and 325 (sh) nm, which

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<sup>1</sup>) For systematic names, see *Exper. Part*.

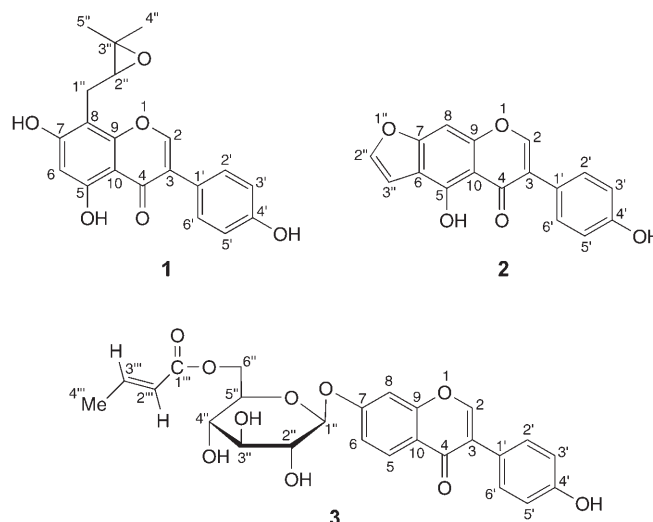
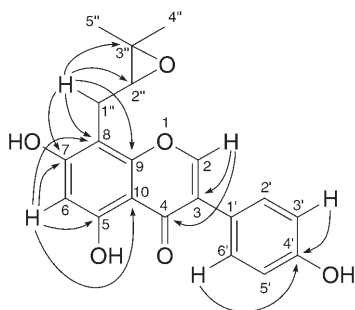
Table 1.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR Data<sup>2)</sup> of **1** and Genistein.  $\delta$  in ppm,  $J$  in Hz.

	<b>1</b> <sup>a)</sup>		Genistein <sup>b)</sup>	
	$\delta(\text{H})$	$\delta(\text{C})$	$\delta(\text{H})$	$\delta(\text{C})$
H–C(2)	8.27 (s)	154.2	8.27 (s)	153.9
C(3)		123.0		121.3
C(4)		181.7		180.1
C(5)		161.2		157.7
H–C(6)	6.17 (s)	100.2	6.34 (s)	99.2
C(7)		160.2		165.1
C(8) or H–C(8)		99.7	6.19 ( <i>d</i> , $J = 1.5$ )	93.8
C(9)		156.1		157.4
C(10)		106.7		104.2
C(1')		124.1		122.2
H–C(2'), H–C(6')	7.46 ( <i>dd</i> , $J = 6.5, 2.0$ )	131.1	7.36 ( <i>d</i> , $J = 8.4$ )	130.2
H–C(3'), H–C(5')	6.91 ( <i>dd</i> , $J = 6.5, 2.0$ )	115.9	6.81 ( <i>d</i> , $J = 8.4$ )	115.1
C(4')		158.4		161.9
CH <sub>2</sub> (1'')	3.06 ( <i>dd</i> , $J = 16.5, 5.1$ ), 2.73 ( <i>dd</i> , $J = 16.5, 6.9$ )	25.6		
H–C(2'')	3.90 (br. <i>s</i> )	68.6		
C(3'')		79.6		
Me(4'')	1.39 (s)	25.8		
Me(5'')	1.34 (s)	21.2		
OH	12.79 (br. <i>s</i> )		12.94 (br. <i>s</i> )	

<sup>a)</sup> Recorded in (D<sub>6</sub>)acetone, at 300 and 75 MHz, resp. <sup>b)</sup> Recorded in (D<sub>6</sub>)DMSO, at 300 and 75 MHz, resp.

indicated the absorptions of an isoflavone or flavanonoid. The signals of  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra further supported **1** to be an isoflavone. The  $^1\text{H}$ -NMR spectrum of **1** in (D<sub>6</sub>)acetone (Table 1) revealed H-atom signals at  $\delta(\text{H})$  8.27 (s, 1 H), a characteristic shift for H–C(2)<sup>2)</sup> of the isoflavone framework, 6.17 (s, 1 H) belonging to H–C(6), the only H-atom at the A-ring, 7.46 (*dd*,  $J = 6.5, 2.0$  Hz, 2 H) and 6.91 (*dd*,  $J = 6.5, 2.0$ , 2 H) belonging to the typical A<sub>2</sub>X<sub>2</sub> system of the B-ring, and 12.79 (br. *s*, 1 H) attributed to the H-atom of 5-OH, which was supported by the correlation in the HMBC (Fig. 2) from the H–C(6) ( $\delta(\text{H})$  6.17 (s)) to C(8) ( $\delta(\text{C})$  99.7). The  $^{13}\text{C}$ -NMR spectrum of **1** revealed five C-atom signals at  $\delta(\text{C})$  25.6, 68.6, 79.6, 25.8, 21.2, which indicated the presence of an isopentyl group substituted with an epoxide moiety [22–24]. Compared with the data of genistein [13], the chemical shift of C(8) in **1** was shifted downfield 5.9 ppm, which indicated that the epoxyisopentyl group should be attached to the C(8) position. The correlations in the HMBC (Fig. 2) from CH<sub>2</sub>(1'') ( $\delta(\text{H})$  3.06 (*dd*,  $J = 16.5, 5.1$ , 1 H), 2.73 (*dd*,  $J = 16.5, 6.9$ , 1 H)) to C(7) ( $\delta(\text{C})$  160.2), C(8) (99.7), C(9) (156.1), and C(2'') (68.6) supported this assumption. In addition, the remaining informations of a degree of unsaturation and two oxygenated C-atoms revealed the existence of the epoxide moiety between C(2'') and C(3''). The signal at  $m/z$  313 ( $[M - \text{C}_4\text{H}_7\text{O}]^+$ ) in the EI-MS also confirmed the above inference. The skeleton of **1** is consistent with its

<sup>2)</sup> Arbitrary atom numbering, see Fig. 1.

Fig. 1. Structures of compounds **1**, **2**, and **3**Fig. 2. HMBC Correlations (H → C) of **1**

signals in the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, HSQC and HMBC spectra. The optical rotation of **1** was measured to be 0. Therefore, compound **1** was elucidated as ( $\pm$ )-5,7,4'-trihydroxy-8-(2'',3''-epoxy)isopentylisoflavone<sup>1</sup>), and named as ammpiptanine A.

Compound **2** was obtained as a yellowish powder, with the molecular formula  $\text{C}_{17}\text{H}_{10}\text{O}_5$ , based on the  $[M + \text{H}]^+$  peak at  $m/z$  295.0586 in the HR-ESI-MS, and confirmed by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR experiments (Table 2). The IR spectrum showed characteristic absorption bands of a OH group ( $3366\text{ cm}^{-1}$ ), an  $\alpha,\beta$ -unsaturated  $\text{C}=\text{O}$  group ( $1658\text{ cm}^{-1}$ ), and an aromatic ring ( $1614, 1580, 1513\text{ cm}^{-1}$ ). The UV spectrum exhibited maximum absorptions at 265 (band II) and 349 (sh) nm, which also indicated the absorptions of an isoflavone or flavanoid. The signals in the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra further supported **2** to be an isoflavone. The  $^1\text{H}$ -NMR spectrum of **2** in ( $\text{D}_6$ )DMSO (Table 2) revealed the characteristic H-atom signal at  $\delta(\text{H})$  8.59 (s, 1 H) for H-C(2)<sup>2</sup> of the isoflavone framework, 7.09 (s, 1 H) belonging to the only H-atom of the A-ring, 7.42 (d,  $J = 8.4, 2\text{ H}$ ) and 6.84 (d,  $J = 8.4, 2\text{ H}$ ) belonging to a typical  $A_2X_2$  system of the B-ring. The *singlet* at  $\delta(\text{H})$  12.96 in the  $^1\text{H}$ -NMR spectrum suggested that

Table 2.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR Data<sup>a)</sup> of **2**.  $\delta$  in ppm,  $J$  in Hz.

	$\delta(\text{H})$	$\delta(\text{C})$
H–C(2)	8.59 (s)	154.1
C(3)		123.0
C(4)		181.3
C(5)		158.2
C(6)		108.1
C(7)		158.5
H–C(8)	7.09 (s)	94.9
C(9)		154.3
C(10)		107.5
C(1')		120.8
H–C(2'), H–C(6')	7.42 ( <i>d</i> , $J = 8.4$ )	130.3
H–C(3'), H–C(5')	6.84 ( <i>d</i> , $J = 8.4$ )	115.1
C(4')		157.6
H–C(2'')	8.04 ( <i>d</i> , $J = 2.1$ )	145.7
H–C(3'')	7.22 ( <i>d</i> , $J = 2.1$ )	103.7
OH	12.96 (br. s), 9.70 (br. s)	

<sup>a)</sup> Recorded in ( $\text{D}_6$ )DMSO- $d_6$ , at 300 and 75 MHz, resp.

**2** had a free OH group at the C(5) position. There were also two *doublets* at  $\delta(\text{H})$  8.04 (*d*,  $J = 2.1$ , 1 H) and 7.22 (*d*,  $J = 2.1$ , 1 H) assigned to the two H-atoms of the furano group fused to the aromatic ring [25], and confirmed by the  $^{13}\text{C}$ -NMR spectrum data at  $\delta(\text{C})$  145.7 (C(2'')) and 103.7 (C(3'')). In order to establish the exact orientation of the furano group on ring A, HMBC techniques were also used in **2**. In the HMBC spectrum (Fig. 3), correlations between H–C(2'') ( $\delta(\text{H})$  8.04 (*d*,  $J = 2.1$ , 1 H)) and C(6) ( $\delta(\text{C})$  108.1) and C(7) ( $\delta(\text{C})$  158.5), H–C(3'') ( $\delta(\text{H})$  7.22 (*d*,  $J = 2.1$ , 1 H)) and C(5) ( $\delta(\text{C})$  158.2) and C(7) ( $\delta(\text{C})$  158.5) confirmed that the furano group was fused at the 6,7-positions of the A-ring. From the above discussed conclusions, **2** was deduced to be 5,4'-dihydroxyfurano[4'',5'':6,7]isoflavone<sup>1</sup>, and named ammopiptanine B.

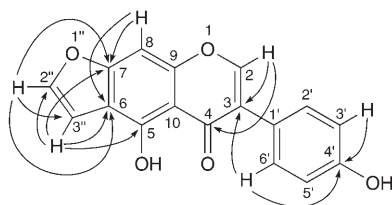


Fig. 3. HMBC Correlations (H → C) of **2**

Compound **3** was obtained as colorless crystalline needles, with the molecular formula of  $\text{C}_{26}\text{H}_{26}\text{O}_{10}$ , based on the  $[M + \text{Na}]^+$  peak at  $m/z$  521.1417 in the HR-ESI-MS, and confirmed by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR experiments (Table 3). The IR spectrum showed characteristic absorption bands of a OH group ( $3416\text{ cm}^{-1}$ ), an  $\alpha,\beta$ -unsaturated C=O group ( $1640\text{ cm}^{-1}$ ), and an aromatic ring ( $1610, 1570, 1510\text{ cm}^{-1}$ ). The UV spectrum

exhibited maximum absorptions at 259 (band II) and 308 (sh) nm, which indicated that **3** was an isoflavone. The signals of the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra further supported this assumption. The  $^1\text{H}$ -NMR spectrum of **3** in  $(\text{D}_6)$ DMSO (Table 3) revealed the characteristic H-atom signal at  $\delta(\text{H})$  8.43 (*s*, 1 H) for H–C(2)<sup>2</sup> of an isoflavone framework, 8.03 (*d*,  $J = 8.5$ , 1 H), 7.20 (*d*,  $J = 2.5$ , 1 H), and 7.12 (*dd*,  $J = 2.5, 8.5$ , 1 H) belonging to an *ABX* system of the *A*-ring, 7.52 (*dd*,  $J = 6.5, 2.0$ , 2 H) and 6.99 (*dd*,  $J = 6.5, 2.0$ , 2 H) belonging to a typical  $A_2X_2$  system of the *B*-ring. The sugar in **3** was identified as  $\beta$ -D-glucose from the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, HSQC, and  $^1\text{H}, ^1\text{H}$ -COSY spectra (Table 3). In the HMBC spectrum (Fig. 4), the correlation from H–C(1'') ( $\delta(\text{H})$  5.16 (*d*,  $J = 8.0$ , 1 H)) to C(7) ( $\delta(\text{C})$  161.1) indicated that  $\beta$ -D-glucose was attached to C(7) of the aglycone. In comparison of the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of **3** with those of ononin [13] and 6''-acetylononin [20], similar data were obtained for the aglycone moiety. However, in the  $^{13}\text{C}$ -NMR spectrum of the  $\beta$ -glucose unit of **3**, a difference was observed with respect to ononin [13] and a resemblance to 6''-acetylononin [20]. A downfield shift of the C(6'') signal (2.6 ppm) and an upfield shift of the C(5'') signal (2.7 ppm) were observed in the  $\beta$ -glucose moiety of **3**, with similar signals for C(5'') and C(6'') in 6''-acetylononin [20], indicating acylation at the 6''-position. Comparison of the molecular formulae of **3** and ononin [13] showed that the acyl moiety in **3** contains four C-atoms. In the  $^{13}\text{C}$ -NMR spectrum of **3**, these extra four C-atoms appeared at  $\delta(\text{C})$  165.2, 122.1, 145.3, and 17.7. The signal at 165.2 could be assigned to an  $\alpha,\beta$ -unsaturated CO ester group. The two signals at 122.1 and 145.3 – substituted with one H-atom each – corresponded to the C(2'') and C(3''), respectively. In the  $^1\text{H}$ -NMR spectrum of **3**, one of these two H-atoms appeared as a signal at  $\delta(\text{H})$  5.87 (*dd*,  $J = 16.0, 1.5$ , 1 H), indicating the (*E*)-configuration of the C=C bond. The second H-atom appeared as a signal at 6.84–6.90 (*m*, 1 H). The fourth signal was assigned to a Me group, which was found in the  $^1\text{H}$ -NMR spectrum of **3** at 1.83 (*dd*,  $J = 6.0, 2.0$ , 3 H). Thus, the structure of the acyl moiety was established as a (2*E*)-but-2-enoxy group (MeCH=CHC=O). This was proved by inspection of the  $^{13}\text{C}$ -NMR spectrum of (*E*)-but-2-enoate, which showed signals at  $\delta(\text{C})$  165.2, 122.1, 145.3 and 17.7. In the HMBC spectrum (Fig. 4), the correlations between H–C(6'') ( $\delta(\text{H})$  4.39 (*dd*,  $J = 12.0, 2.0$ , 1 H), 4.10 (*dd*,  $J = 12.0, 2.0$ , 1 H)) and C(1''') ( $\delta(\text{C})$  165.2) confirmed that the (*E*)-but-2-enoate was linked to C(6''). From the above evidence, compound **3** was characterized as 4'-methoxyisoflavone 7-O- $\beta$ -D-{6''-[(*E*)-but-2-enoyl]}glycoside<sup>1</sup>), and named am-mopiptanoside A.

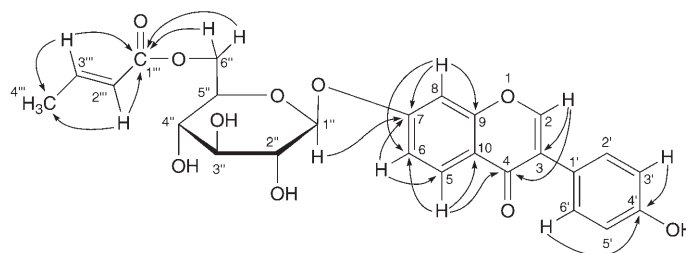


Fig. 4. HMBC Correlations (H  $\rightarrow$  C) of **3**

Table 3. <sup>1</sup>H- and <sup>13</sup>C-NMR Data<sup>2</sup>) of **3**, Ononin, and 6''-Acetylononin. δ in ppm, J in Hz.

	<b>3</b> <sup>a)</sup>		Ononin <sup>b)</sup>		6''-Acetylononin <sup>b)</sup>	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
H–C(2)	8.43 (s)	153.6	8.42 (s)	153.7	8.43 (s)	153.7
C(3)		123.4		123.4		123.4
C(4)		174.6		174.7		174.7
H–C(5)	8.03 (d, J=8.5)	126.9	8.04 (d, J=9.0)	127.0	8.05 (d, J=9.0)	127.0
H–C(6)	7.12 (dd, J=8.5, 2.5)	115.5	7.14 (dd, J=9.0, 2.1)	115.7	7.13 (dd, J=9.0, 2.1)	115.5
C(7)		161.1		161.5		161.2
H–C(8)	7.20 (d, J=2.5)	103.3	7.23 (d, J=2.1)	103.4	7.22 (d, J=2.1)	103.4
C(9)		156.9		157.0		157.0
C(10)		118.4		118.5		118.5
C(1')		123.9		124.0		124.0
H–C(2'), H–C(6')	7.52 (dd, J=6.5, 2.0)	130.0	7.52 (d, J=8.7)	130.1	7.52 (d, J=8.7)	130.1
H–C(3'), H–C(5')	6.99 (dd, J=6.5, 2.0)	113.6	6.98 (d, J=8.7)	113.6	6.98 (d, J=8.7)	113.6
C(4')		159.0		159.0		159.0
H–C(1'')	5.16 (d, J=8.0)	99.5	5.11 (d, J=7.2)	99.9	5.16 (d, J=7.2)	99.6
H–C(2'')	3.37–3.39 (m)	72.9	3.28–3.39 (overlapped)	73.2	3.31–3.40 (overlapped)	73.0
H–C(3'')	3.32–3.34 (m)	76.3	3.28–3.39 (overlapped)	77.2	3.31–3.40 (overlapped)	76.2
H–C(4'')	3.75–3.77 (m)	70.0	3.71–3.75 (overlapped)	69.6	3.73–3.77 (overlapped)	69.8
H–C(5'')	3.72–3.73 (m)	73.8	3.71–3.75 (overlapped)	76.5	3.73–3.77 (overlapped)	73.8
CH <sub>2</sub> (6'')	4.39 (dd, J=12.0, 2.0), 4.10 (dd, J=12.0, 2.0)	63.3	3.96 (dd, J=11.0, 2.0), 3.66 (dd, J=11.0, 4.0)	60.7	4.31 (d, J=11.5), 4.06 (dd, J=11.5, 6.6)	63.3
C(1''')		165.2				170.3
H–C(2''')	5.87 (dd, J=16.0, 1.5)	122.1			2.01 (s)	20.7
H–C(3''')	6.84–6.90 (m)	145.3				
Me(4''')	1.83 (dd, J=6.0, 2.0)	17.7				
MeO	3.78 (s)	55.1	3.77 (s)	55.1	3.77 (s)	55.2

<sup>a)</sup> Recorded in (D<sub>6</sub>)DMSO, at 500 and 125 MHz, resp. <sup>b)</sup> Recorded in (D<sub>6</sub>)DMSO, at 300 and 75 MHz, resp.

The thirteen known isoflavones were identified by comparison of their spectroscopic data with those reported in the literature.

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#### Experimental Part

*General.* Column chromatography (CC): SiO<sub>2</sub> H (200–300 mesh; *Qingdao Marine Chemical Industry*, China) and *Sephadex LH-20* gel (*Pharmacia*). Semi-prep. HPLC: *ODS* column (250 × 4.6 mm, 5 μm; *Kromasil*), with a *Waters 2487* photodiode-array detector (254 nm); flow rate, 2.0 ml min<sup>-1</sup>. Melting points: *X-4* micro-melting-point apparatus; uncorrected. Optical rotations: *Perkin-Elmer 243-B* digital polarimeter. UV Spectra: *Cary-300* spectrometer; λ<sub>max</sub> (log ε) in nm. IR Spectra: *NEXUS 470-FT-IR* spectrophotometer; KBr pellets; in cm<sup>-1</sup>. NMR Spectra: *JEOL JNM-A300* and *Varian UNITY-500* spectrometers, with TMS as an internal standard; δ in ppm, J in Hz. EI-MS *AEI-MS-50* spectrometer; in m/z (rel. %). HR-ESI-MS: *APEX II FT-ICRMS (Bruker Daltonics)* mass spectrometer.

*Plant Material.* The aerial parts (branches and leaves) of *Ammopiptanthus mongolicus* (MAXIM. ex KIM.) CHENG f. were collected in September 2003 from Inner Mongolia, P. R. China. The identification of the plant was performed by P.-F. T. A voucher specimen (CM200309) was deposited at the Herbarium of Peking University Modern Research Center for Traditional Chinese Medicine.

*Extraction and Isolation.* The dried branches and leaves (7.3 kg) of *A. mongolicus* were extracted with 95% (v/v) aq. EtOH soln. for three times. After removal of the solvent under reduced pressure at 60°, the residue (1.3 kg) was suspended in H<sub>2</sub>O, and defatted with petroleum ether (PE). The aq. layer was acidified with 1M HCl, and then extracted with CHCl<sub>3</sub> successively. The CHCl<sub>3</sub> extract (30 g) was subjected to CC (SiO<sub>2</sub>; PE (b.p. 60–90°)/AcOEt 100:1 → 1:1 → CHCl<sub>3</sub>/MeOH 50:1 → 1:1) to give *Frs. A–O*. *Fr. C* (2 g) was subjected to CC (SiO<sub>2</sub>, PE/Me<sub>2</sub>CO 10:1 → 1:1 → CHCl<sub>3</sub>/MeOH 5:1 → 1:1; *Sephadex LH-20*, MeOH) to afford two subfractions. *Fr. C1* was recrystallized from MeOH to yield **1** (30 mg). *Fr. C2* was subjected to semiprep. HPLC (MeOH/H<sub>2</sub>O 60:40) to yield **2** (5 mg) and *lupiwightone* (12 mg). *Fr. D* (1.2 g) was subjected to CC (SiO<sub>2</sub>; CHCl<sub>3</sub>/MeOH 7:1) to yield *formononetin* (20 mg) and *genistein* (16 mg). *Fr. E* (0.9 g) was subjected to semiprep. HPLC (MeOH/H<sub>2</sub>O 50:50) to yield *orobol* (7 mg), *pratensein* (9 mg) and *pratensein 7-O-β-D-glucoside* (8 mg). *Fr. F* (2.1 g) was subjected to CC (*Sephadex LH-20*; MeOH/H<sub>2</sub>O 50:50) to afford two subfractions. *Fr. F1* was recrystallized by MeOH to yield *calycosin* (40 mg). *Fr. F2* was subjected to semiprep. HPLC (MeOH/H<sub>2</sub>O 35:65) to yield *daidzein* (14 mg). *Fr. G* (1.1 g) was subjected to CC (*Sephadex LH-20*; MeOH) to yield *glycitein* (9 mg) and *odoratin* (7 mg). *Fr. J* (0.8 g) was subjected to semiprep. HPLC (MeOH/1% AcOH in H<sub>2</sub>O 55:45) to yield *ononin* (8 mg), *6''-acetylononin* (22 mg) and **3** (5 mg). *Fr. K* (0.5 g) was subjected to semiprep. HPLC (MeOH/H<sub>2</sub>O 20:80) to yield *wistin* (40 mg).

*Ammopiptanine A* (= (±)-8-[(3,3-Dimethyloxiranyl)methyl]-5,7-dihydroxy-3-(4-hydroxyphenyl)-4H-1-benzopyran-4-one; **1**). White powder. M.p. 154–155°. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = 0 (c = 0.020, MeOH). UV (MeOH): 214 (3.11), 260 (3.81), 325 (sh). IR (KBr): 3382, 1657, 1613, 1583, 1516. <sup>1</sup>H- and <sup>13</sup>C-NMR: *Table 1*. HR-ESI-MS: 355.1172 ([*M* + H]<sup>+</sup>, C<sub>20</sub>H<sub>19</sub>O<sub>5</sub><sup>+</sup>; calc. 355.1176).

*Ammopiptanine B* (= 4-Hydroxy-6-(4-hydroxyphenyl)-5H-furo[3,2-g][1]benzopyran-5-one; **2**). Yellowish powder. M.p. 133–135°. UV (MeOH): 204 (3.31), 265 (2.57), 349 (0.31). IR (KBr): 3366, 1658, 1614, 1580, 1513. <sup>1</sup>H- and <sup>13</sup>C-NMR: *Table 2*. HR-ESI-MS: 295.0586 ([*M* + H]<sup>+</sup>, C<sub>17</sub>H<sub>11</sub>O<sub>5</sub><sup>+</sup>; calc. 295.0601).

*Ammopiptanoside A* (= 3-(4-Hydroxyphenyl)-7-((6-O-[(*E*)-1-oxobut-2-en-1-yl]-β-D-glucopyranosyl)oxy)-4H-1-benzopyran-4-one; **3**). Colorless crystalline needles. M.p. 187–189°. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = –26.7 (c = 0.020, MeOH). UV (MeOH): 204 (3.00), 259 (1.92), 308 (sh). IR (KBr): 3416, 1640, 1610, 1570, 1510. <sup>1</sup>H- and <sup>13</sup>C-NMR: *Table 3*. HR-ESI-MS: 521.1417 ([*M* + Na]<sup>+</sup>, C<sub>26</sub>H<sub>26</sub>NaO<sub>10</sub><sup>+</sup>; calc. 521.1418).

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