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鞭打绣球中的苯丙素甙和环烯醚萜甙

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摘要 从鞭打绣球(*Hemiphragma heterophyllum* Wall.)(玄参科)的全草中分离到 2 个新的苯丙素甙, 命名为鞭打绣球甙 A 和 B(hemiphroside A and B), 2 个已知的苯丙素甙, plantamajoside 和 plantainoside D, 以及 3 个已知的环烯醚萜甙, globularicisin, globularin 和 iso-scrophularioside. 通过化学和光谱分析, 鞭打绣球甙 A 和 B 的结构分别鉴定为 2-(3-羟基-4-甲氧基苯基)乙基 O-β-D-葡萄吡喃糖基(1→3)-4-O-反式阿魏酰基-β-D-葡萄吡喃糖甙和 2-(3,4-二羟基苯基)乙基 O-[6-O-乙酰基-β-D-葡萄吡喃糖基(1→3)]-4-O-反式咖啡酰基-β-D-葡萄吡喃糖甙.

关键词 鞭打绣球, 玄参科, 苯丙素甙, 环烯醚萜甙, 鞭打绣球甙 A 和 B

PHENYLPROPANOID AND IRIDOID GLYCOSIDES FROM HEMIPHRAGMA HETEROPHYLLUM

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Abstract Two new phenylpropanoid glycosides, hemiphrosides A and B, were isolated from the whole plant of *Hemiphragma heterophyllum* togther with two known phenylpropanoid glycoside, plantamajoside and plantsinoside D and three known iridoid glycosides, globularicisin, globularin and iso-scrophularioside. The structures of hemiphrosides A and B were established by spectral and chemical analyses as 2-(3-hydroxy-4-methoxyphenyl) ethyl O-β-D-glucopyranosyl(1→3)-4-O-E-feruloyl-β-D-glucopyranoside and 2-(3,4-dihydroxyphenyl) ethyl O-[6-O-acetyl-β-D-glucopyranosyl(1→ 3)]-4-O-E-caffeoyl-β-D-glucopyrano-side, respectively.

Key words *Hemiphragma heterophyllum*, Scrophulariaceae, Phenylpropanoid glycosides, Iridoid glycosides, Hemiphrosides A and B

Hemiphragma heterophyllum Wall.(Scrophulariaceae) is a plant of monotype genus distributed from estern Himalayas to Yunnan province of China. The whole plant of this unique species is used in Chinese

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folk medicine for the treatment of cholecystitis, rheumatism, abnormal menstruation, toothache, etc [1]. As a continuation of our study on phenylpropanoid and iridoid glycosides from medicinal plants of Scrophulariaceae [2—7], we have investigated the methanol extracts of the whole plant of *H. heterophyllum*, which led to the isolation and structure elucidation of two new phenylpropanoid glycosides, named hemiphrosides A (**1**) and B(**2**), together with two known phenylpropanoid glycosides (**3** and **4**) and three known iridoid glycosides (5—7). On comparison with reported data (UV, ^1H and ^{13}C NMR spectra), compounds **3**— **7** were identified as plantamajoside [8], plantainoside D [9], globularicisin [10,11], globularin [11,12] and iso-scrophularioside [13], respectively.

Table 1 ^{13}C NMR spectral data of compounds 1—4 and 9 in CD_3OD_3OD (ppm)

	1	9	2	3	4
Aglycone moiety					
C-1	132.89	132.97	131.42	131.52	131.35
2	117.09	117.14	116.58[a]	116.65[a]	116.55[a]
3	147.39[a]	147.53	144.60	144.70	144.61
4	147.27[a]	147.53	146.05	146.15	146.09
5	112.98	112.96	117.13	117.20	117.10
6	121.16	121.07	121.28	121.34	121.28
α	72.16	72 83	72.16	72.24	72.37
β	36.53	36 51	36.49	36.57	36.64
OMe	56.42[b]	56.54			
Sugar moiety					
inner Glc-1	104.02	103 94	103.87	104.02	104.02
2	75.08	74.40	75.08	75.09	74.41
3	84.21	88.21	84.27	84.31	87.68
4	70.89	70.08	70.53	70.96	70.33
5	75.92	77.61[a]	75.85	75.90[b]	75.03
6	62.52[c]	62.65[b]	62.24	62.48[c]	64.59
terminal Glc-1	105.74	105.31	105.58	105.80	105.23
2	75.92	75.52	75.20	76.04[b]	75.50
3	77 71	77.85[a]	77.51	77.72	78.13
4	71.32	71.58	71.18	71.27	71.54
5	78.00	78.20	75.71	77.91	77.77
6	62.33[c]	62.65[b]	64.42	62.35[c]	62.60
OAc			172.79		
			20.66		
Ester moiety					
1	127.72		127.64	127.76	127.66
2	111.79		115.41	115.35	115.09
3	150.72		149.43	149.74	149.60
4	149.42		146.77	146.86	146.74
5	116.52		116.32[a]	116.38[a]	116.37[a]
6	124.27		122 98	123.15	123.17
-C=O	168.51		168.28	168.56	169.08
α	115.62		115.13	115.26	114.82
β	147.58		147.25	147.46	1477.23
OMe	56.49[b]				

[a—c]: Signals in each vertical column can be interchangeable.

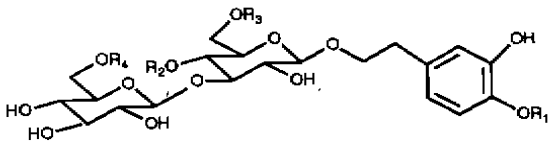
Table 2 ^{1}H NMR spectral data of compounds 1—4 and 9 in CD_3OD (ppm)*

	1	9	2	3	4
Aglycone moiety					
H-2	6.73(d,2.0)	6.75(d,1.6)	6.70(d,1.6)	6.70(br s)	6.68(d,2.0)
5	6.81(d, 8.2)	6.81(d,8.2)	6.68(d,8.1)	6.68(d,8.0)	6.64(d,8.0)
6	6.88(dd, 8 2,2.0)	6.68(ss,8.2,1.6)	6.57(dd,8.1,1.6)	6 57(dd,8.0,1.6)	6.54(dd,8.0,2.0)
α	3.7(m)	3.7(m)	3.7(m)	3.7(m)	3.7(m)
α'	4.0(m)	4.0(m)	4.0(m)	4.0(m)	4.0(m)
β	2.82(m)	2.81(m)	2.80(m)	2.80(m)	2.79(m)
OMe	3.80(s)	3.80(s)			
Sugar moiety					
inner Glc-1	4.41(d,7.9)	4.38(d,7.8)	4.41(d,7.9)	4.41(d,8.0)	4.39(d,8.0)
terminal Glc-1	4.53(d,7.7)	4.60(d,7.7)	4.55(d,7 8)	4.54(d,8.0)	4.58(d,7.8)
OAc			1.88(s)		
Ester moiety					
2	7.22(d,1.7)		7.06(d,1.8)	7.08(d,1.6)	7.04(d,2.0)
5	6.81(d,8.2)		6.79(d,8.3)	6.79(d,8.2)	6.77(d,8.2)
6	7.10(dd,8.2,1 7)		6.96(dd,8.3,1.8)	6.96(dd,8.2,1.6)	6.99(dd,8.2,2.0)
α	6.42(d,16.0)		6.27(d,16.0)	6.32(d,16.0)	6.28(d,16.0)
β	7.64(d,16.0)		7.56(d,16.0)	7.58(d,16.0)	7.55(d,16.0)
OMe	3.94(s)				

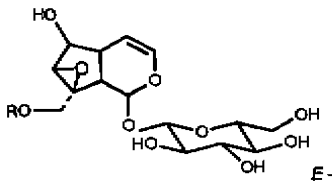
* The coupling patterns and coupling constants in Hz are expressed in parentheses.

Hemiphroside A(1) was obtained as an amorphous powder, whose molecular formula was determined to be $C_{13}H_{40}O_{16}$ by the negative FAB mass spectrum in which a quasi-molecular ion peak exhibited at m / z 667 in combination with the ^{13}C NMR(DEPT) spectrum. Its IR spectrum showed absorption bands due to hydroxy groups(3390 cm^{-1}, br), an α,β-unsaturated ester($\nu_{C=O}$1698 and $\nu_{C=C}$1624 cm^{-1}) and aromatic rings(1595 and 1505 cm^{-1}). The presence of these functional groups were also supported by its UV spectrum which displayed strong absorbtion bands at 222, 245, 288 and 330 nm. The ^{1}H and ^{13}C NMR spectra of **1** (*vide* Table 1 and 2) exhibited typical signals arising from ferulic acid and 2-(3-hydroxy-4-methoxyphenyl) ethyl alchohol moieties [9,14] and almost same signals due sugar moiety as those of plantamajoside (3) and plantainoside D(4). On acid hydrolysis, 1 only yielded glucose as sugar residue. When hydrolysed with 0.5 mol / L NaOH, ferulic acid was tested out by TLC. The sequence and interglycosidic linkage positions were established as follows. Alkaline hydrolysis of 1 with 1 mol / L NaOH-MeOH(1 : 1) afforded compounds **8** and **9**. Compound **8** was readily identified as methyl ferulate by comparison of its ^{1}H and ^{13}C NMR signals with reported data [2,9,14]. In the ^{1}H and ^{13}C NMR spectra of **9**, only the signals due to a 3-hydroxy-4-methoxyphenylethyl alchohol moiety [9,14] were observed with two sets of signals corresponding to β-glucopyranosyl units[δ4.38(d, J = 7.8Hz), 4.60(d, J = 7.7 Hz)for anomeric proton signals and 103.94, 105.31 for anomeric carbon ones], suggesting that compound **9** was the desferuloyl product of **1**. In addition, the presence of the typical signals at δ88.21 due to sugar moiety in the ^{13}C NMR spectrum of **9** indicated that the terminal glucose was attached to the hydroxy group of C-3 of the inner glucose. Therefore, the structure of **9** was established to be 2-(3-hydroxy-4-methoxyphenyl) ethyl O-β-D-glucopyransyl(1→3)-β-D-glucopyranoside. Compared to **9**,**1** showed remarkable upfield shifts for the signals of C-3($\triangle\delta$-1.69ppm)of the inner glucose in the ^{13}C NMR spectrum (*vide* Table 1), indicating that the ferulic acid moiety should be linked to the hydroxy group of C-4 of the inner glucose. Based on the above evidence, the structure of **1** was shown to be

2-(3-hydroxy-4-methoxyphenyl)ethyl O-β-D-glucopyranosyl(1→ 3)-4-O-E-feruloyl-β-D-glucopyranoside.

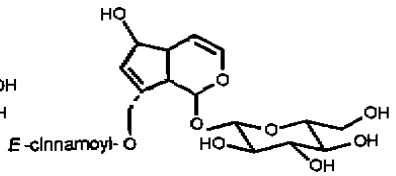


	R_1	R_2	R_3	R_4
1	Me	*E*-furuloyl	H	H
2	H	*E*-caffeoyl	H	Ac
3	H	*E*-caffeoyl	H	H
4	H	H	*E*-caffeoyl	H
9	Me	H	H	H



R

5 *Z*-cinnamoyl
6 *E*-cinnamoyl



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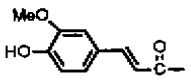
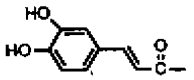
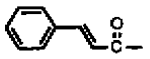


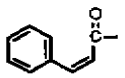
E-furuloyl (*m/z* 177)



E-caffeoyl (*m/z* 163)



E-cinnamoyl



Z-cinnamoyl

Hemiphroside B(2) was also obtained as an amorphous powder. Its UV and IR spectra were very similar to those of plantamajoside (3). On acid hydrolysis, only glucose was detected as sugar residue. The ^1H and ^{13}C NMR spectra of 2 (*vide* Tables 1 and 2) showed the presence of caffeic acid and 2-(3,4-dihydroxyphenyl)ethyl alcohol moietied [2—4,9,14], and acetyl group and two sets of signals corresponding to two β-glucopyranosyl units. This was in accordance with the molecular formula $C_{31}H_{38}O_{17}$ deduced from the negative FAB mass spectrum ($[M-H]^-$ at m/z 681). The sequence and interglycosidic linkage positions of 2 were established by comparison of the ^1H and ^{13}C NMR spectra with those of 3. The ^1H NMR signals of 2 were almost superimposable on those of 3 except for an acetyl group (δ1.88). In the ^{13}C NMR spectrum of 2, besides the additional acetyl signals at δ172.79 and 20.68, only two signals due to sugar moiety were significantly different from those of 3, i.e. δ64.42 and 75.71 compared to δ62.35 and 77.91. The presence of the signal at δ64.42 in 2 confirmed that the acetyl group was attached to the hydroxy group of C-6 of a glucose, but the linkage position at C-6 of the inner glucose was excluded by the presence to the singal at 75.71 and absence of a signal resonated at about δ 78 corresponding to C-5 of the normal terminal glucose. Thus, this acetyl group was linked to the hydroxy group of C-6 of the terminal glucose and the structure of 2 was elucidated to be 2-(3,4-dihydroxyphenyl) ethyl O-[6-O-acetyl-

β-D-glucopyranosyl(1→3)]-4-O-E-caffeoyl-β-D-glucopyranoside.

EXPERIMENT

^1H and ^{13}CNMR(DEPT) spectra were recorded in CD_3OD at 400 MHz and 100 MHz, respectively, using TMS as int. standards.

Plant material The whole plant of *Hemiphragma heterophyllum* Wall. was collected in Luqian county, Yunnan province of China. A voucher specimen is deposited in the Herbarium of Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and isolation Dried whole plants(8 kg) were cut into piecies and then extracted with EtOH under reflux. After removal of solvents by evapn, the combined extracts (450 g) were dissolved in H_2O, defatted with Et_2O and $CHCl_3$ successively and then extracted with n-BuOH(satd with H_2O). The combined n-BuOH layers were coned to dryness to give a yellow residue(430 g), which was subjected to macroporous adsorbtion resin D-101 eluting with aq. MeOH to give three frs., fr.1(270 g of the H_2O eluate), fr. 2(64 g of 30% MeOH eluate) and fr.3(90 g of 60% MeOH eluate). Fr. 2 was chromatographed on silica gel with $CHCl_3$-MeOH-H_2O(50 : 10 : 1 to 30 : 10 : 1) and then on reversed phase silica gel (RP-8) with 70% MeOH to give **3** (2.0 g). Fr. 3 was repeatedly chromatographed on silica gel with $CHCl_3$-MeOH-H_2O(70 : 10 : 1 to 20 : 10 : 1) and reversed phase silica gel (RP-18, ODS-Q-3) with 70% or 60% MeOH to yield **4**(1.0 g), **1**(2.0 g), **2**(0.7 g), **5**(0.2 g), **6**(7.0 g) and **7**(0.06 g).

Hemiphroside A(**1**). $[\alpha]_D^{26}$-47° (MeOH; c 0.34); UVλ_{max}^{EtOH}nm(lgε): 222(4.27), 245(3.95), 288(4.06), 330(4.22); IRν_{max}^{KBr}cm^{-1}: 3390(OH), 1698(C=O), 1623(C=C), 1595 and 1505 (aromatic ring); FAB-MS (neg.)m / z: 667[M^+-H]$^-$, 505[M-H-Glc]$^-$, 491[M-Fer]$^-$, 353[505-(3-hydroxy-4-methoxy-phenylethyl)-H]$^-$, 339[491-(3-hydroxy-4-methoxypheny-lethyl)-H]$^-$.

Hemiphroside B(**2**). $[\alpha]_D^{26}$-60° (MeOH; c 0.30); UVλ_{max}^{EtOH}nm(lgε): 219(4.41), 229(4.33), 288(4.22), 329(4.40); IRν_{max}^{KBr}cm^{-1}: 3389(OH), 1700(C=O), 1623(C=C), 1595 and 1505 (aromatic ring); FAB-MS (neg.)m / z: 681[M^+-H]$^-$, 519[M-Caf]$^-$, 477[Glc—Aac]$^-$, 339[477-(3,4-dihydroxyphenyethyl)-H]$^-$.

Plantainoside (**3**)[8]. An amorphous powder, UVλ_{max}^{EtOH}nm(lgε): 220(4.17), 230(4.09), 285(3.95), 329(4.16); IRν_{max}^{KBr}cm^{-1}: 3350(OH), 1698(C=O), 1620(C=C), 1595 and 1515 (aromatic ring).

Plantamajoside (**4**)[9]. An amorphous powder, UVλ_{max}^{EtOH}nm(lgε): 220(4.88), 230(4.28), 247(4.17), 291(4.29); 334(4.46); IRν_{max}^{KBr}cm^{-1}: 3390(OH), 1698(C=O), 1624(C=C), 1595 and 1520 (aromatic ring).

Globularicisin (**5**)[10,11]. An amorphous powder, UVλ_{max}^{EtOH}nm(lgε): 216(4.16), 220(4.10), 279(4.17), 322(3.38); IRν_{max}^{KBr}cm^{-1}: 3400(OH), 1705(C=O), 1647 and 1625(C=C), 1580 and 1495 (aromatic ring); ^1H NMR δ: aglycone 5.03(1H, d, J=9.7 Hz, H-1), 6.35(1H, dd, J=6.0, 1.7 Hz, H-3), 5.06(1H, m, H-4), 2.23(1H, m, H-5), 3.91(1H, m, H-6), 3.32(1H, br s, H-7), 2.52(1H, dd, J=9.7, 7.6 Hz, H-9), 4.22 and 4.95(2H, ABq, J=12.7 Hz, H-10), Glc 4.74(1H, d, J=7.8 Hz, H-1), *cis*-Cinn. 7.60(2H, m, H-2′,6′), 7.37(3H, m, H-3′,4′,5′), 6.01(1H, d, J=12.6 Hz, H-α), 7.03(1H, d, J=12.6 Hz, H-β); ^{13}C NMR δ: aglycone (C-1→C-10) 95.61, 141.83, 103.73, 38.98, 79.45, 62.73, 63.34, 43.62, 64.37, Glc(C-1→C-6) 100.31, 74.85, 77.66, 71.56, 78.54, 63.06, *cis*-Cinn. 136.26(C-1′), 130.09(C-2′,6′), 129.19(C-3′,5′), 129.40(C-4′), 167.55(C=O), 120.08(C-α), 144.86(C-β).

Globularicisin (**6**)[11,12]. An amorphous powder, UVλ_{max}^{EtOH}nm(lgε): 217(4.11), 222(4.03), 280(4.31); IRν_{max}^{KBr}cm^{-1}: 3400(OH), 1695(C=O), 1645 and 1635(C=C), 1570 and 1495 (aromatic ring); ^1H NMR δ:

aglycone 5.08(1H, d, J=9.7 Hz, H-1), 6.36(1H, dd, J=6.0 Hz, H-3), 5.09(1H, m, H-4), 2.30(1H, m, H-5), 3.92(1H, m, H-6), 3.35(1H, br s, H-7), 2.67(1H, dd, J=9.7, 9.8 Hz, H-9), 4.27 and 5.04(2H, ABq, J=12.6 Hz, H-10), Glc 4.75(1H, d, J=7.9 Hz, H-1), *Trans*-Cinn. 7.61(2H, m, H-2′,6′), 7.40(3H, m, H-3′, 4′, 5′), 6.65(1H, d, J=16.0 Hz, H-α), 7.71(1H, d, J=16.0 Hz, H-β); ^{13}C NMR δ: aglycone (C-1→C-10) 95.59, 141.79, 103.71, 38.99, 79.43, 62.78, 63.53, 43.59, 64.45, Glc(C-1→C-6) 100.27, 74.78, 77.80, 71.43, 78.41, 62.99, *trans*-Cinn. 135.70(C-1′), 129.98(C-2′,6′), 129.33(C-3′,5′), 131.54(C-4′), 168.36(C=O), 118.60(C-α), 146.66(C-β).

Iso-scrophularioside (7)[13]. An amorphous powder, UVλ_{max}^{EtOH}nm(lgε): 215(3.93), 276(3.97); IRν_{max}^{KBr}cm^{-1}: 3400(OH), 1695(C=O), 1650 and 1625(C=C), 1595 and 1505 (aromatic ring); ^{1}H NMR δ: aglycone 4.97(1H, d, J=7.4 Hz, H-1), 6.34(1H, dd, J=5.9, 1.6Hz, H-3), 5.12(1H, dd, J=5.9, 3.9, H-4), 2.70(1H, m, H-5), 4.47(1H, m, H-6), 5.83(1H, br s, H-7), 2.97(1H, dd, J=7.2, 7.1 Hz, H-9), 5.00(2H, br s, H-10), Glc 4.71(1H, d, J=7.8 Hz, H-1), *trans*-Cinn. 7.60(2H, m, H-2′,6′), 7.40(3H, m, H-3′,4′,5′), 6.56(1H, d, J=16.0 Hz, H-α), 7.73(1H, d, J=16.0 Hz, H-β); ^{13}C NMR δ: aglycone (C-1→C-10) 98.01, 141.75, 105.57, 46.31, 82.86, 132.72, 142.58, 48.40, 63.63, Glc ((C-1→C-6) 100.22, 74.90, 77.94, 71.50, 78.23, 62.79, *trans*-Cinn. 135.67(C-1′), 130.05(C-2′,6′), 129.32(C-3′,5′), 131.62(C-4′), 168.29(C=O), 118.62(C-α), 146.73(C-β).

Acid hydrolysis of **1** and **2** on TLC plate and identification of the resulting monosaccharide were described in the previous paper[15].

Alkaline hydrolysis of **1** with 0.5 mol/L NaOH. A soln of **1** (ca. 4 mg) in 0.5 NaOH(1 mL) was keept at 60℃ for 10 min. The reaction mixture was examined with TLC using $CHCl_3$-MeOH-H_2O(7∶3∶1, lower layer) as development and UV lamp as detection. Ferulic acie was identified by compared with an authentic sample.

Alkaline hydrolysis of **1** with 1 mol/L NaOH-MeOH(1∶1). A soln of **1** (200 mg) in 1 mol/L NaOH-MeOH(1∶1; 8 mL) was allowed standing at room temp. for 24 h. The reaction mixture was neutralized with Amberlite MB-3(H^+, OH^-form), filtered, and then extracted with Et_2O and n-BuOH. The Et_2O layer was evaparated to dryness to give **8**(30 mg): ^{1}H NMR δ: 7.15(1H, d, J=1.4 Hz, H-2), 6.80(1H, d, J=8.0 Hz, H-5), 7.05(1H, dd, J=8.0, 1.4 Hz, H-6), 6.33(1H, d, J=16 Hz, H-α), 7.59(1H, d, J=16 Hz, H-β); ^{13}C NMR δ: 127.64(C-1), 111.81(C-2), 150.54(C-3), 149.43(C-4), 116.46(C-5), 123.99(C-6), 169.65(C=O), 115.21(C-α), 146.72(C-β), 51.95(OCH_3), 56.46($COO\underline{CH_3}$). The n-BuOH layer was evaparated to dryness to give a residue, which was purified on silica gel with $CHCl_3$-MeOH-H_2O(40∶10∶1) to furnish **9**: ^{1}H and ^{13}C NMR spectral data see Tables 1 and 2.

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