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三色马先蒿的化学成分研究*

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摘要: 从玄参科三色马先蒿 (*Pedicularis tricolor*) 全草的乙醇提取物中分离得到 17 个化合物, 采用波谱方法鉴定了它们的结构。其中化合物 **1** (2, 3, 5-tirmethoxy-4-hydroxy-xanthone) 是一个新的呫酮, 命名为三色马先蒿酮 A (pedicutricone A); **2** (8α-hydroxyl-4-carboxyl-5βH, 9βH-iridoid-1α-glycoside) 是一个新的环烯醚萜苷, 命名为三色马先蒿苷 A (pedicutricoside A); 化合物 **3~17** 为首次从该植物中分离得到。

关键词: 玄参科; 三色马先蒿; 三色马先蒿酮 A; 三色马先蒿苷 A
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Chemical Constituents of *Pedicularis tricolor* (Scrophulariaceae)*

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Abstract: To search for new bioactive constituents from *Pedicularis tricolor*, a new xanthone named pedicutricone A (**1**) and a new iridoid named pedicutricoside A (**2**), along with fifteen known compounds, were isolated from the ethanol extracts of the whole plants of *P. tricolor* for the first time. Their structures were elucidated based on spectroscopic methods, including two-dimensional nuclear magnetic resonance analysis.

Key words: Scrophulariaceae; *Pedicularis tricolor*; Pedicutricone A; Pedicutricoside A

Pedicularis L., as one of the largest genera of angiosperm, comprises about 329 species in China (Institute of Botany, 1979). Some species have been used as herbs to treat diseases for a long time (Jiangsu New Medical College, 1977). Many compounds were isolated from *Pedicularis* (Chu and Tan, 2006; Wu *et al*, 2002), and some of them showed biological activities of antioxidation and antitumour (Li *et al*, 1995; Yang *et al*, 2001). Phytochemical investigation of *Pedicularis tricolor* H.-M. has not been performed until now. In this paper, we report our study on the chemical constituents from the whole plants of *P. tricolor*. A new xanthone pedicutricone A (**1**) and a new iridoid pedicutricoside A (**2**), along with fifteen known compounds, namely viburtinal (**3**) (Godeau *et al*, 1977), 5, 7, 4′-trihydroxy-flavone (**4**) (Owen *et al*, 2003), 5, 7, 3′, 4′-tetrahydroxy-flavone (**5**) (Owen *et al*, 2003), 5, 7, 4′-trihydroxy-3′-methoxy-

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flavone (**6**) (Wagner and Chari, 1976), 5, 7, 4′-trihydroxy-3′, 5′-dimethoxy-flavone (**7**) (Chung *et al*, 2005), 3, 5, 4′-trihydroxy-3′, 5′-dimethoxy-flavone-7-O-β-D-glucopyranoside (**8**) (Wu *et al*, 1997), 3, 5, 4′, 5′-trtrahydroxy-3′-methoxy-flavone-7-O-β-D-glucopyranoside (**9**) (Cioffi *et al*, 2002), 3, 5, 3′, 4′-trtrahydroxy-flavone-7-O-β-D-glucopyranoside (**10**) (Flamini *et al*, 1997; Yu and Yang, 2002), 3β, 19α-dihydroxy-12-ursen-28-oic acid (**11**) (Huang *et al*, 1998), actoside (**12**) (ErsÖz *et al*, 2002), martynoside (**13**) (Wang and Jia, 1996), methyl 3, 4-dihydroxybenzoate (**14**) (Luo *et al*, 2001), benzyl 2-O-β-D-glucopyranosyl-β-D-glucopyranoside (**15**) (Okamura *et al*, 1981), daucosterol (**16**) (Yang *et al*, 1998) and β-sitosterol (**17**) (Zhang *et al*, 2002), were isolated using several chromatographic purification steps, including Si gel, Sephadex LH-20, MCI, Rp18 column chromatography and preparation HPLC on Rp18 from the ethanol extracts of whole plants of *P. tricolor* (Fig. 1).

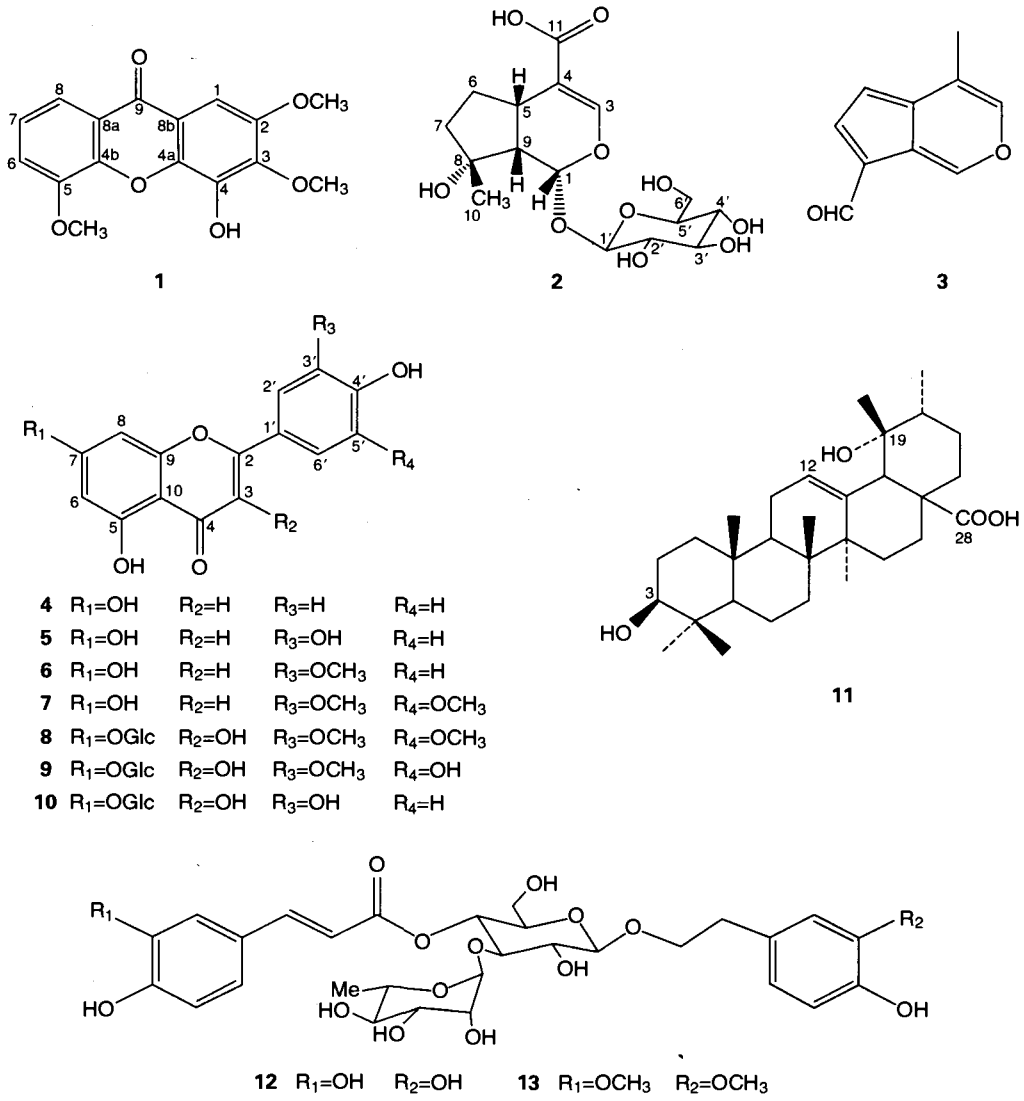

Fig. 1 Structure of compounds **1–13**

Result and Discussion

Compound **1** was isolated as a yellow powder. The molecular formula was established as $C_{16}H_{14}O_6$ by HR + TOF-MS (*m/z* 303.0871 $[M+H]^+$, calcd.

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303.0868), and which could be supported by evidences from the DEPT experiment. The ^{1}H-NMR spectrum showed existence of one hydroxyl group (δ 12.77, 1H, s), one 1, 2, 3-trisubstitution benzene ring (δ 7.83, 1H, d, J = 8.1 Hz; 7.32, 1H, t, J = 8.0 Hz; δ 7.25, 1H, d, J = 7.8 Hz), one isolated aromatic proton (δ 6.64, 1H, s), and three methoxyl groups (δ 4.04, 3.98, 3.94). Deducting three methoxyl groups in the ^{13}C-NMR spectrum, one carbonyl group (δ 181.1) and 12 carbon atoms were left, which indicated that **1** was possessed of the characteristic structure of C_6-C_1-C_6 of xanthone (Kijjoa *et al*, 2000). In the HMBC spectrum, the correlations of H-1 (δ 6.64, 1H, s) and H-8 (δ 7.83, 1H, d, 8.0) with the carbonyl group (δ 181.1) indicated that both of C-1 (δ 90.9) and C-8 (δ 116.5) were unsubstituted. C-2, 3, 4, 5 must be substituted by OMe or OH. Locations of these substituents were confirmed by the HMBC and ROESY experiments. The cross-peaks of H-1 (δ_H 6.64) with C-2 (δ_C 160.0) and C-3 (δ_C 132.0), 2-OCH_3 (δ_H 3.98) with C-2, 3-OCH_3 (δ_H 3.94) with C-3, 5-OCH_3 (δ_H 4.04) with C-5 (δ_C 148.2) in the HMBC spectrum, and H-1 with 2-OCH_3, H-6 (δ_H 7.25) with 5-OCH_3 in the ROESY spectrum revealed that δ_C 56.3, 60.8 and 56.3 must be located at C-2, C-3 and C-5, respectively. Therefore, hydroxyl group must be at C-4. Based on above spectral analysis, structure of **1** was assigned as 2, 3, 5-tirmethoxy-4-hydroxy-xanthone, named pedicutricone A, which is a new compound.

Compound **2** was isolated as a brown sticky solid. The molecular formula was established as $C_{16}H_{24}O_{10}$ by HR-TOF-MS (m/z 375.1292 [M-H]$^+$, calcd. 375.1291). The ^{1}H-NMR and ^{13}C-NMR spectrum data for **2** were typical for iridoid glycosides, and very similar to those reported for mussaenosidic acid (Kobayashi *et al*, 1985). The ROESY experiment displayed different relative configuration from mussaenosidic acid. The correlations of H-1 (δ 5.44, 1H, d, J = 3.6 Hz) with H-9 (δ 2.21, 1H, m) and H-10 (δ 1.31, 3H, s), and H-9 with H-5 (δ 3.13-3.39, 1H, m), suggested that H-1, H-5, H-9 and H-10 were in the same orientation (Fig. 1). According to the literature (Chu and Tan, 2006), the chemical shift of C-1 will be less than 100 if H-5 is in β-orientation; but if H-5 is in α-orientation, the chemical shift of C-1 will be over 100. Hence, H-1, H-5, H-9 and H-10 are in β-orientation because the chemical shift of C-1 in **2** is 95.2. Thus, **2** was determined to be 8α-hydroxyl-4-carboxyl-5βH, 9βH-iridoid-1α-glycoside, named pedicutricoside A, which is a new compound.

Experimental

General Experimental Procedures Optical rotations were determined on a Horbia SEAP-300 polarimeter. IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer with KBr pellets. UV spectra were obtained on a Shimadzu 2401PC spectrophotometer. NMR experiments were performed on a Bruker AM-400 and a DRX-500 spectrometer. TMS was used as the internal standard. MS was recorded on a VG Auto Spec-3000 spectrometer. Silica plate for TLC and silica gel (200-300 mesh) for column chromatography were obtained from Qingdao Marine Chemical Corporation (Qingdao, China) and Sepheadaex LH-20 (25-100 μm) from Pharmacia Fine Chemical Co., Ltd., Sweden).

Plant materials *Pedicularis tricolor* H.-M. was collected in Zhong Dian, Yunnan Province of China in August 2003 and identified by Professor Wang Hong (Kunming Institute of Botany, Chinese Academy of Sciences). The voucher specimen was deposited in the herbarium of Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation The dried whole plants (7.4 kg) of *P. tricolor* were powdered and extracted with 95% EtOH for four times (each one week) at room temperature. After evaporation to dryness under reduced pressure, 1.8 kg residue was obtained, which was suspended in water and then extracted successively with petroleum ether (60-90℃, 18 L) and EtOAc (25 L). The EtOAc-soluble part (1.0 kg) was chromatographed on silica gel (5.0 kg), eluted with a gradient $CHCl_3$-MeOH (20:1; 15:1; 9:1; 7:3; 1:1; each 8 L) mixture to obtain 20 fractions (2 L each). These fractions were combined into nine major fractions (A1-A9) based on TLC behaviors. Each fraction was chromatographed repeadly over a silica gel (200-300 mesh) column, Sephedax Sephadex LH-20 to yield **1** (6 mg), **2** (13 mg), **3** (17 mg), **4** (13 mg), **5** (12 mg), **6** (9 mg), **7** (25

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mg), **8** (5 mg), **9** (6 mg), **10** (9 mg), **11** (11 mg), **12** (317 mg), **13** (417 mg), **14** (18 mg), **15** (88 mg), **16** (21 mg). The petroleum ether-soluble part (164 g) was chromatographed on silica gel (1.5 kg), eluting with a petroleum ether-acetone (100:0; 7:3; 1:1; 3:7; 0:100; each 8 L) mixture to obtain 5 fractions (B1-B5). B2 and B3 were separated further by CC on silica gel to yield **17** (407 mg).

Compound **1**, $C_{16}H_{14}O_6$, yellow powder, $[\alpha]_D^{26}$ + 1.25° (*c* 0.59, $CHCl_3$); UV λ_{max} ($CHCl_3$) nm: 204, 254, 273, 307, 363; IR (KBr) ν_{max} cm^{-1}: 3425, 2941, 1659, 1612, 1585, 1497, 1452, 1433, 1361, 1318, 1278, 1232, 1198, 1147, 1107, 993, 901, 792; ^{1}H-NMR and ^{13}C-NMR spectral data see Table 1; HR+TOF-MS *m/z*: 303.0871 $[M+H]^+$, calcd. 303.0868; EI-MS *m/z* (%): 302 $[M]^+$ (81), 287 (100), 273 (17), 259 (83), 244 (17), 216 (32), 188 (16), 122 (24), 107 (16).

Table 1 ^{13}C and ^{1}H-NMR spectral data of compound **1**

Carbon No.	HMQC		^{1}H-^{1}H COSY	HMBC	ROESY
	δ_C	δ_H			
1	90.9d	6.64 (s)			2-OMe
2	160.0s			H-1, 2-OMe	
3	132.0s			H-1, 3-OMe	
4	153.9s				
4a	153.2s			H-1	
4b	146.0s			H-6, 8	
5	148.2s			H-7, 5-OMe	
6	115.6d	7.25 (d, 7.8)	H-7	H-8	5-OMe
7	123.6d	7.32 (t, 8.0)	H-6, 8		
8	116.5d	7.83 (d, 8.0)	H-7	H-6	
8a	121.0s			H-7	
8b	104.2s			H-1	
9	181.1s			H-1, 8	
5-OMe	56.3q	4.04 (s)			
2-OMe	56.3q	3.98 (s)			
3-OMe	60.8q	3.94 (s)			
4-OH		12.77 (s)			

Note: in $CDCl_3$, 500 MHz for δ_H & 125 MHz for δ_C; δ in ppm, *J* in Hz; TMS

Table 2 ^{13}C and ^{1}H-NMR spectral data of compound **2**

Carbon No.	HMQC		^{1}H-^{1}H COSY	HMBC	ROESY
	δ_C	δ_H			
1	95.2d	5.44 (1H, d, 3.6)	H-9	H-3, 5, 9, 1′	H-6b, 7, 9, 10, 1′
3	151.8d	7.39 (1H, s)		H-1, 5	
4	113.8s			H-3, 5, 6a, 6b, 9	
5	32.0d	3.13-3.39 (1H, m)	H-6a, 6b, 9	H-1, 3, 6, 7, 9	H-6a, 9
6	30.7t	a: 2.27 (1H, m)	H-5, 6b, 7	H-5	H-6b, 7
		b: 1.47 (1H, m)	H-5, 6a, 7		H-6a
7	40.7t	1.71 (2H, t, 6.8)	H-6a, 6b	H-5, 6, 9, 10	H-1, 6a, 9, 10
8	80.5s			H-1, 5, 6a, 6b, 7, 9, 10	
9	52.3d	2.21 (1H, m)	H-1, 5	H-5, 6a, 6b, 7, 10	H-1, 5
10	24.6q	1.31 (3H, s)		H-7, 9	H-1, 7
11	171.0s			H-3, 5	
1′	99.6d	4.67 (1H, d, 7.8)		H-1	
2′	74.7d	3.13-3.39 (1H, m)			
3′	78.2d	3.13-3.39 (1H, m)			
4′	71.6d	3.13-3.39 (1H, m)			
5′	77.9d	3.13-3.39 (1H, m)			
6′	62.9t	a: 3.89 (1H, d, 11.4)			
		b: 3.64 (1H, dd, 6.1, 11.7)			

Note: in CD_3OD, 400 MHz for δ_H & 100 MHz for δ_C; δ in ppm, *J* in Hz; TMS

Compound **2**, $C_{16}H_{24}O_{10}$, brown sticky solid; $[\alpha]_D^{26}$ −69.9° (*c* 0.29, MeOH); UV λ_{max} (MeOH) nm: 201, 230; IR (KBr) ν_{max} cm^{-1}: 3425, 1680, 1640, 1384, 1075; ^{1}H-NMR and ^{13}C-NMR spectral data see Table 2; HR-TOF-MS *m/*

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z: 375.1292 [M-H]$^+$, calcd. 375.1291; FAB-MS (negative) *m/z* (%): 375 [M-H]$^+$ (100), 311 (12), 219 (24), 154 (18), 127 (42).

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