

紫毛香茶菜中的黄酮类化合物

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摘要: 从紫毛香茶菜 (*Isodon enanderianus*) 的茎叶提取物中分离到 7 个黄酮类化合物, 经波谱分析鉴定, 其中一个为新的黄酮甙, 即 5-羟基-6, 7, 4'-三甲氧基黄酮-8-O- β -D-葡萄糖甙(1); 其它 6 个已知的黄酮类化合物分别为 芫花素 (genkwanin, 2)、滨蓟素 (cirsimartin, 3)、胡麻素 (pedalitin, 4)、黧蒴花亭 (ladanetin, 5)、异牡荆素 (isothymusin-8-O- β -D-glucoside (6) 和槲皮素 (quercitrin, 7)。

关键词: 唇形科; 紫毛香茶菜; 黄酮类化合物

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Flavonoids from *Isodon enanderianus*

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Abstract: A new flavone glycoside, 5-hydroxy-6, 7, 4'-trimethoxyflavone-8-O- β -D-glucoside (1), together with six known flavonoids, genkwanin (2), cirsimartin (3), pedalitin (4), ladanetin (5), isothymusin-8-O- β -D-glucoside (6), and isoquercitrin (7), was isolated from the aerial parts of *Isodon enanderianus* (Labiatae). Their structures were elucidated on the basis of spectroscopic evidence.

Key words: Labiatae; *Isodon enanderianus*; Flavonoids

Isodon enanderianus (Hand. - Mazz.) H. W. Li, a perennial shrub plant in Labiatae family, is widely distributed in the southern part of Yunnan province. It has been used as folk medicine to diminish inflammation and detoxify (Kunming Institute of Botany, 1977) for a long history. The genus *Isodon* is known to be rich in *ent*-kaurane diterpenoids. A series of new *ent*-kaurane diterpenoids have been isolated from the dried leaves of *I. enanderianus* (Wang *et al.*, 1998). During the reinvestigation of chemical constituents of *I. enanderianus*, seven flavonoids including a new flavone glycoside were isolated from the 70% acetone extract of aerial parts from the whole plant. Their structures were elucidated by spectroscopic methods, especially by NMR experiments. The new compound was identified as 5-hydroxy-6, 7, 4'-trimethoxyflavone-8-O- β -D-glucoside (1) and the other compounds were genkwanin (2) (Wang *et al.*, 1998), cirsimartin (3) (Wang *et al.*, 1998), pedal-

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compounds were genkwanin (2) (Wang *et al*, 1998), cirsimartin (3) (Wang *et al*, 1998), pedalitin (4) (Zhang *et al*, 1994), ladanetin (5) (Agrawal *et al*, 1981), isothymusin-8-O- β -D-glucoside (6) (Wang *et al*, 1998) and quercitrin (7) (Markham *et al*, 1978).

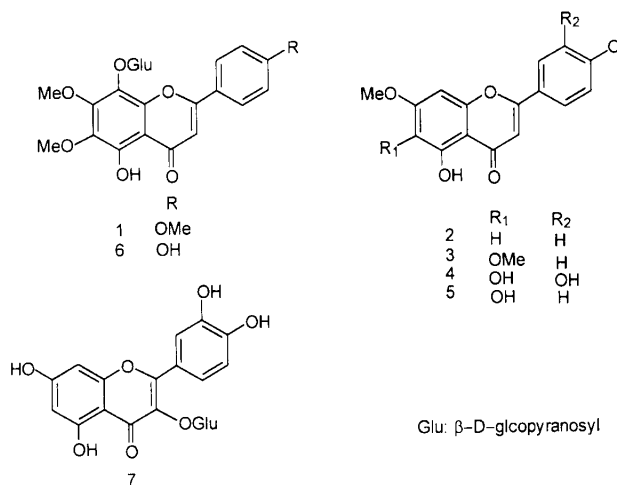


Fig.1 The structures of compounds 1-7

Results and Discussion

Compound **1** was obtained as pale yellow needles (MeOH). It was established to have a molecular formula of $C_{24}H_{26}O_{12}$, which was deduced by negative FABMS (base ion peak at m/z 505 [$M - H$] $^-$) and ^{13}C NMR data including DEPT technique. The IR spectrum had absorptions at 3422 and 1652 cm^{-1} corresponding to the hydroxy and hydrogen bonded unsaturated carbonyl groups. The UV spectrum showed bands at 326.5, 287.5, 205.5 nm. This information along with the analysis of 1H and ^{13}C NMR signals indicated that **1** was a flavone

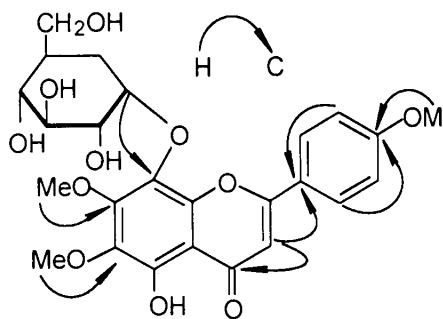


Fig.2 The key HMBC correlations of compound 1

glycoside. FABMS exhibited a fragmental ion peak at m/z 343 [aglycone- H] $^-$, which showed that the aglycone ($C_{18}H_{16}O_7$) was a flavone containing two hydroxyl groups and three methoxyl groups. The 1H NMR spectrum of this compound revealed a characteristic proton signal at δ 12.82, which showed the presence of a free hydroxyl group at C-5 position, an AX pair of aromatic doublets at δ 8.23 (2H, $J = 8.6\text{ Hz}$) and 7.06 (2H, $J = 8.6\text{ Hz}$), indicating a *para*-substituted aromatic ring. The NMR data and HMQC, HMBC spectra indicated that the sugar was glucose and its anomeric proton and carbon were at δ 4.83 (d, $J = 7.6\text{ Hz}$) and 102.2, respectively, suggesting the presence of a β -O-glycosidic bond. The chemical shifts of the carbons in ring A agreed well with glycosylation effect (Yao *et al*,

1995). In general, the carbon at the site of glycosylation is shifted to a higher field following glycosylation, whereas the *ortho*- and *para*-related carbons shifted downfield. By comparison of ^{13}C NMR spectrum of its aglycone (Tokunaru *et al.*, 1995), a downfield shift of C-5 (3.5 ppm), C-7 (4.3 ppm) and C-9 (3.3 ppm), and an upfield shift of C-8 (2.2 ppm) indicated that the sugar moiety was linked at C-8, which was confirmed by HMBC experiments. Therefore, compound **1** was elucidated as 5-hydroxy-6, 7, 4'-trimethoxyflavone-8-O- β -D-glucoside. The structures of other six known compounds were identified by comparison of the spectral data (MS, ^1H and ^{13}C NMR) with literature.

Table 1 ^1H (400 MHz) and ^{13}C (100.6 MHz) NMR data of compound **1** (in DMSO- d_6)

No	C	H (J in Hz)	No	C	H (J in Hz)
2	163.3		4'	161.8	
3	103.1	6.92 (s)	5'	113.7	7.06 (d, 8.6)
4	181.8		6'	128.2	8.23 (d, 8.6)
5	148.2	12.82 (s, OH-5)	6-OCH ₃	60.4	3.81 (s)
6	135.3		7-OCH ₃	60.8	4.01 (s)
7	152.3		4'-OCH ₃	54.8	3.84 (s)
8	128.3		1''	102.2	4.83 (d, 7.6)
9	144.6		2''	73.3	
10	105.4		3''	75.7	
1'	122.0		4''	69.4	
2'	128.2	8.23 (d, 8.6)	5''	76.5	3.10-3.63
3'	113.7	7.06 (d, 8.6)	6''	60.4	(6H, overlap)

Experimental

General Melting point was measured on an XRC-1 micro melting point apparatus and is uncorrected. IR spectra were obtained on a Bio-Rad FTS-135 spectrometer with KBr pellets. UV spectra were recorded on a UV 210A spectrometer. Optical rotation was taken on a SEPA-300 polarimeter. The EI and FAB MS were carried out on a VG Auto Spec-3000 spectrometer at 70 eV. 1D- and 2D-NMR spectra were run on Bruker AM-400 and DRX-500 instruments with TMS as internal standard.

Extraction and isolation The aerial parts of *Isodon enanderianus* were collected in Shiping county of Yunnan province in 1997. The air-dried powdered plant (7.8 kg) was extracted with 70% acetone (3 \times 20 L) at room temperature for 3 days each time. The extract was concentrated and partitioned with EtOAc. The EtOAc extract (391 g) was chromatography on a silica gel column (2.0 kg, 200-300 mesh) eluting with CHCl_3 by increasing Me_2CO to yield eight fractions (I-VIII). From fraction III (45 g), compounds **2** (13 mg) and **3** (25 mg) were isolated by CC on Si-gel (200-300 mesh) eluting with cyclohexane/2-propanol (10:1). Compounds **4** (55 mg) and **5** (46 mg) were obtained from fraction IV (24 g) by Si-gel CC (cyclohexane/2-propanol, 8:1). Fraction VII (24 g) was Si-gel CC with $\text{CHCl}_3/\text{CH}_3\text{OH}$ (25:1 \rightarrow 5:1) to yield compounds **1** (50 mg), **6** (70 mg) and **7** (1.2 g).

5-hydroxy-6, 7, 4'-trimethoxyflavone-8-O- β -D-glucoside (1), $\text{C}_{24}\text{H}_{26}\text{O}_{12}$ pale yellow needles (MeOH); mp 203-205 $^\circ\text{C}$; $[\alpha]_D^{25}$ -39.0 ($c=0.250$, $\text{C}_5\text{H}_5\text{N}$); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 326.5, 287.5, 205.5; IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3422, 1652, 1603, 1566, 1431, 1375, 1312, 1071, 1019, 828; EIMS m/z (%): 506 $[\text{M}]^+$ (5), 344 $[\text{aglycone}]^+$ (88), 329 (66), 211 (4), 197 (23), 169 (9), 133 (14), 69 (100); FABMS (neg.): 505 $[\text{M-H}]^-$ (100), 343 $[\text{343-H}]^-$ (65); ^1H and ^{13}C NMR data see Table 1.

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