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大花双参的环烯醚萜甙化学研究

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摘要 从云南民间药物大花双参(*Triplostegia grandiflora Gagnep.*)(川续断科)的根中分离到一个新的二聚环烯醚萜甙, 命名为大花双参甙 A (triplostoside A) (1), 通过化学降解,光谱分析以及核磁共振二维谱技术研究确定了其化学结构。同时, 还分离到已知的甲基马钱素(methyl loganin) (2), 马钱酸 (Leganic acid) (3) 和青叶胆苦甙 (sweroside) (4)。此外还分离到胡罗卜甙 (daucosterol).

关键词 大花双参; 川续断科; 环烯醚萜甙; 大花双参甙 A

IRIDOIDAL GLYCOSIDES FROM TRIPLOSTEGIA GRANDIFLORA

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Abstract A new bis-iridoidal glycoside, triplostoside A have been isolated from the roots of *Triplostegia grandiflora* Gagnep. (Dipsacaceae) along with the known iridoids, methyl loganin, loganic acid, sweroside and daucosterol. Its structure was elucidated on the basis of spectral data and chemical evidence.

Key words *Triplostegia grandiflora*; Dipsacaceae, Iridoidal glycosides; Triplostoside A

Triplostegia grandiflora Gagnep.(Dipsacaceae), Chinese name "Shuang-Sheng", which distributed in the southwest of China and has long been used in folk medicine as a tonic, an antidote and especially in the treatment of gynaecological diseases by nationalities [1] (Table 1). Up to now, there is no report concerning the chemical study for this plant. As a part of our ethnopharmaceutical studies of the minorities in Yunnan Province of China, we have investigated the chemical constituents of this plant. This paper reports the isolation and structure elucidation of triplostoside A(1), a new bis-iridoidal glycoside together with three known iridoids, methyl loganin (2), loganic acid (3), and sweroside (4), and daocosterol from the roots of this plant.

Triplostoside A(1) was obtained as a white amorphous powder. Its molecular formula $C_{38}H_{52}O_{20}$ was determined by the positive ion FAB-MS spectrum, in which the molecular ion peaks at

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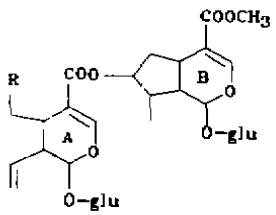
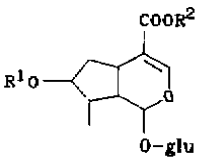
m / z 815[M+Na]$^+$ and 799[M+Li]$^+$ were exhibited. The UV absorption maximum at 235.5 nm indicated the presence of an α,β −unsaturated ester. The IR spectrum of 1 showed peaks at 3400(OH), 1695(C = 0), 1625(C = C), 1280(C−O−C) and 1070 (C−O−C) cm^{-1}, which is diagnostic of a typical IR absorption of the iridoidal glycoside [2] . On comparison of the ^{13}C NMR spectrum of **1** with those of known bis−iridoidal glycosides revealed that it possessed the same basic skeleton as sylvestroside− I **(5)** and cantleyoside **(6)** [3] . It also showed that the carbon signals due to part "b" of **1** are in good agreement with those of **5** and **6**. The difference between them only added two signals of methoxy groups in **1** than **5** and **6**, which let the signal of C−7 of part "a" shift to δ 103.4 in **1** from δ 60.8 (OH) in **5** and δ 206.7 (CHO) in **6**, It suggested that the two additional methoxy groups should be attached to C−7 of part "a" of **1**. This result was also supported by means of 2D−NMR analysis. In the ^{1}H−^{1}H COSY spectrum of **1**, the signal at δ 4.68 (1H, t, J = 4.0 Hz) was correlated to the signals at δ 1.86 (1H, m, H−6) and δ 2.30 (1H, m, H−6′), which was correlated with the carbon signal at δ 103.4 in ^{13}C−^{1}H COSY spectrum and was assigned to the H−7 of part "a". On alkaline hydrolysis, **1** provided **3** as one of main products by the direct comparison with an authentic sample. Based on the above evidence, the structure of **1** was established, which may be an artifact formed in the process of extraction and isolation with MeOH as solvent.

Table1. The medicinal uses of *T. grandiflora* by nationalities in Yunnan Province of China

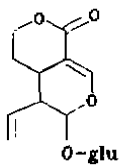
Nationalities	Local name(locality)	Uses
Yi	Ze−Fei, Bai−Du−La	tonic, impotence, cough
Na−Xi	Le−Ben−Ke	tonic, edema
Bai	Te−Shou−Ge	tonic, hemorrhagic trauma
Wa	Xi−Bi−Di	tonic
Han	Zi−Mu−Shen,Shuang−Shen	tonic, hepatitis, pregnancy



1 R=−CH(CH$_3$O)$_2$
5 R=−CH$_2$OH
6 R=−CHO



2 R^1=CH$_3$ R^2=CH$_3$
3 R^1=H R^2=H



4

glu=−β−D−glucopyranosyl

Methyl loganin **(2)** was obtained with the aid of prep. HPLC. On comparison of ^{13}C NMR spectrum of **2** with those of known loganin [3] , the carbon signals were most fully superimposiable. Only difference is that **2** showed an additional signal of methoxy group than loganin, which should be attached with C−7 position. Thus the structure of **2** was elucidated as methyl loganin. It is first time that **2**

was isolated from plant materials. But just as the situation of **1**, compound **2** perhaps was also an artifact. Other two known iridoidal glycosides were identified as loganic acid (**3**) and sweroside (**4**) respectively [4,5].

Though this is the first study on the chemistry of genus *Triplostegia*, it is noted that iridoidal glycosides especially bis-iridoidal glycosides were isolated from plants of Dipsacaceae as common constituents. This result not only could have provided some evidence to chemotaxonomy of this family, but also will be useful to evaluate and utilize these folk medicines.

EXPERIMENT

MPS are uncorrected. Optical rotations were on a J-20C polarimeter. UV and IR spectra were measured on shimadzu UV-210A and IR-450 spectrophotometer, in EtOH and KBr pellets respectivelly. ^1H and ^{13}C NMR spectra were measured on a Brucker spectrospin AM-400 spectrometer using TMS as internal standards. FAB-MS spectra were measured with ZAB-HS mass spectrometer.

Plant material The roots of *Triplostegia grandiflora* Gagnep. were collected in Luqai county, Yunnan province of China in May 1988. A voucher specimen of the examined plants is deposited in the herbarium of KIB.

Extraction and isolation Dried and powdered roots of *T. grandiflora* (2950 g) were refluxed three times with MeOH for 3 hours. After concentration of the combined extracts in vacuo, the residue (400 g) was afforded. 183 g of the MeOH extract were subjected to a dry column chromatography over silica gel developing with $CHCl_3$-MeOH-H_2O(70 : 30 : 5) to give eleven fractions A-K. Fr.B was crystallzed with MeOH-$CHCl_3$ after treated with acetone and MeOH to afforded daucosterol (100 mg). Fr.J (10 g) was repeatedly chromatographed on silica gel column by eluting with $CHCl_3$-MeOH-H_2O and then purified on a column of Diaion HP-20P(Mitsubishi Chemical Ind. Co.) and HPLC (Column: ULTRASPHERE ODS 5 μm, 1.0 —25 cm), eluting with MeOH-H_2O (55 : 45) to afforded **1** (30 mg) and **2** (30 mg). Fr. E (12.2 g) was chromatographed on a column of macroporous absorption resin D-101 eluting with MeOH-H_2O, and then on a silica gel column eluting with $CHCl_3$-MeOH(7 : 3) to provide **3** (600 mg). Fr.K (6.8 g) was chromatographed on a silica gel column eluting with $CHCl_3$-MeOH-H_2O (70 : 30 : 5) and again chromatographed on the combination of Sephadex LH-20 (eluting with MeOH) and Diaion HP-20P (eluting with MeOH-H_2O, 7 : 3) to afford **4** (60 mg).

Triplostoside A (1). White amorphous powder from MeOH, mp 127.5— 129℃ ; $[\alpha]_D^{24}$ -85.28 (C = 0.598, MeOH); UVλ_{max} nm (log ε): 235.5 (3.69). IR$\nu^{max}cm^{-1}$: 3400, 1659, 1625, 1435, 1280,1070; FAB-MS m / z: 815 [M ($C_{35}H_{52}O_{20}$)+Na]$^+$, 799[M+Li]$^+$; ^1H NMR (C_5D_5N), part "a" δ 5.89 (1H, d, J = 5.9 Hz, H-1),7.66 (1H, s, H-3), 3.27 (1H, m, H-5), 2.30 (1H, m, H-6), 1.86 (1H, m, H-6′), 4.68 (1H, t, J = 4.0 Hz, H-7), 5.85 (1H, m, H-8), 2.85 (1H, m, H-9), 5.16-5.21 (2H, m, H-10 × 2), 3.31 (6H, s, OCH_3 × 2), 5.36 (1H, d, J = 8.0 Hz, glu H-1); part "b" δ 5.65 (1H, d, J = 4.0 Hz, H-1), 7.63 (1H, brs, H-3), 3.27 (1H, m, H-5), 2.45 (1H, m, H-6), 1.86 (1H, m, H-6′), 5.25 (1H, m, H-7), 2.17 (1H, m, H-8), 2.31 (1H, m, H-9), 0.97 (3H, d, J = 6.7 Hz, CH_3-10), 3.58 (3H, s, OCH_3), 5.31 (1H, d, J = 8.0 Hz, glu H-1),^{13}C NMR data see Table 2.

Table 2. ^{13}C NMR data of compounds 1—6

	1 (C_5D_5N)	5[3] (D_2O)	6[3] (D_2O)	2 (C_5D_5N)	3 (CD_3OD)	4 (C_5D_5N)
aglycones						
part "a"						
C-1	97.4	98.3	97.7			
3	152.2	153.6	154.2			
4	112.6	111.5	109.8			
5	29.3	30.7	28 2			
6	32.9	33.3	44.5*			
7	103 4	60.8	206 7			
8	135.9	134.7	133.9			
9	44.7	44.5	45 1*			
10	119.1	120.4	121.6			
C=0	167.4	169.5	168.9			
OMe	52.3					
OMe	53.1					
part "b"						
C-1	96.5	97.4	97.4	97.6	97.7	97.5
3	151.4	152.2	152.2	151.4	152.0	152.6
4	112.9	113 2	113.1	113.4	114.3	105.4
5	31.4	31.3	31.3	31.9	32.1	27.9
6	39.7	40.2	40.1	43.0	42.7	25.1
7	76.9	78.8	78.8	74.8	75.1	66.0
8	39.9	39.3	39.3	41.8	42.1	132.7
9	46.7	46 4	46.3	46.1	46.7	34.0
10	13.2	13.3	13.2	13.8	13.4	120.2
C=0	166.6	170.5	170.3	167.8	171.0	165.3
OMe	50.9	52.7	52.7	50.9		
sugar moieties						
part "a"						
C-1	100.7	99.6	99.6			
2	74.8	73.5	73.5			
3	78.9	76.6	76.6			
4	71.5	70.5	70 5			
5	78.8	77.2	77.2			
6	62.7	61.6	61.8			
part "b"						
C-1	100.8	99.6	99.6	100.9	100.1	100.6
2	74.6	73.5	73.5	73.6	74.8	74 9
3	78.9	76.6	76.6	78.9	78.3	78.7
4	71.6	70.5	70.5	71.9	71.7	71.5
5	78.5	77.2	77.2	78.6	78.1	78.4
6	62.7	61.6	61.8	62.8	62.8	62 6

* Assignments may be interchangeable.

Methyl loganin (2). White amorphous powder from MeOH mp 216–226℃; $[\alpha]_D^{18}$ −69.12 (C=0.068, MeOH); UVλ_{max}nm (logε): 233.1 (2.37); IRν_{max}cm^{-1}: 3400, 1705, 1645, 1445, 1300, 1270, 1100, 1070, 1030, 900; ^{1}H NMR(C_5D_5N) δ : 5.86 (1H, d, J=4.5 Hz, H–1), 7.87 (1H, d, J=0.8 Hz H–3), 3.72 (1H, m, H–5), 2.63 (1H, m, H–6), 1.75 (1H, m, H–6′), 3.35 (1H, m, H–7), 2.03 (1H, m, H–8), 2.44 (1H, m, H–9), 1.21 (3H, d, J=6.9 Hz, CH_3–10), 3.59 (6H, s, OCH_3×2), 5.35 (1H, d, J=7.9 Hz, glu H–1), ^{13}C NMR data see Table 2.

Loganic acid (3). White amorphous powder, mp 164–168℃; $[\alpha]_D^{24}$ −71.43 (C=0.518, MeOH); UVλ_{max}nm(logε): 232 (3.48); IR ν_{max}cm^{-1}: 3400, 1685, 1630, 1410, 1280, 1080; ^{1}H NMR (CD_3OD) δ : 5.27 (1H, d, J=4.4 Hz, H–1), 7.36 (1H, d, J=0.8 Hz, H–3), 3.09 (1H, dd,J=0.8, 5.4 Hz, H–5), 2.23 (1H, m, H–6), 1.67 (1H, m, H–6′), 3.66 (1H, dd, J=8.0, 5.6 Hz, H–7), 1.87 (1H, m, H–8), 2.03 (1H, m, H–9), 1.09 (3H, d, J=8.0 Hz, CH_3–10), 4.66 (1H, d, J=8.0 Hz, glu H–1); ^{13}C NMR data see Table 2.

Sweroside (4). Yellowish amorphous powder from MeOH, mp 102–105℃; $[\alpha]_D^{24}$ −187.2 (C=0.573, MeOH). UVλ_{max}nm(logε): 243 (3.92). IRν_{max}cm^{-1}: 3400, 1685, 1610, 1400, 1315, 1280, 1200, 1070, ^{1}H NMR(C_5D_5N) δ : 5.78 (1H, brs, H–1), 7.93 (1H, s, H–3), 5.01 and 5.09 (each 1H, brd, H–10 × 2), 5.30 (1H, d, glu H–1), 5.35 (1H, m, H–8); ^{13}C NMR data see Table 2.

Daucostero. White crystals, mp 293℃, IR, ^{1}H and ^{13}C NMR data were identified with authentic sample.

Alkaline hydrolysis of 1. A solution of 1 (4 mg) in 0.125 mol / l NaOH (1 ml) was heated at 100℃ for 15min. After neutralization with dilt. AcOH, the reaction mixture was evaporated to a syrup in vacuo, which was treated with TLC to give a degraded product. It was identical with 3 by direct comparison.

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