

峨眉雪胆的化学成分研究

华西医科大学药学院(成都 610041)

施亚琴* 杨培全 陈玲

彭州市药品检验所

张文锦

摘要 从峨眉雪胆 *Hemsleya emiensis* 块根中分得 7 个化合物。经理化性质和光谱分析分别鉴定为齐墩果酸-3-O- α -L-吡喃阿拉伯糖(1 \rightarrow 3)- β -D-吡喃葡萄糖醛酸甙(I)、竹节参甙 IVa(II)、雪胆皂甙 M_{a1} (III)、雪胆皂甙 G_1 (IV)、雪胆皂甙 H_1 (V)、雪胆甲素(VI)和雪胆乙素(VII)。这些化合物均系首次从该植物中分得,其中化合物 I 为首次从雪胆属植物中分得。

关键词 峨眉雪胆 雪胆属 三萜皂甙 葫芦素

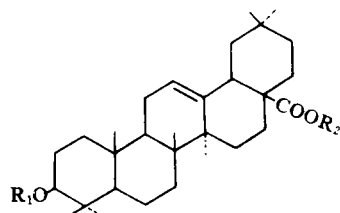
葫芦科雪胆属 *Hemsleya* Cogn. 植物现有 31 种,除 2 种产印度、越南外,中国均产。云贵川 3 省占 92%,是主要分布区。本属植物的块根在四川多作“金龟莲”药用。广泛用于治疗肝炎、菌痢、冠心病、气管炎、慢性宫颈炎等多种疾病。自 1982 年以来,雪胆属植物中一些典型品种的化学成分系统研究,包括马铜铃雪胆 *H. graciliflora* (Harms) Cogn.、曲莲 *H. amabilis* Diels、肉花雪胆 *H. carnosiflora* C. Y. Wu、中华雪胆 *H. chinensis* Cogn. 和长果雪胆 *H. dolichocarpa* W. J. Chang 等品种,已先后报道^[1]。本文报道 *H. emiensis* L. T. Shen et W. J. Chang 中化学成分 I~VII 的分离和鉴定。它们分别为齐墩果酸-3-O- α -L-吡喃阿拉伯糖(1 \rightarrow 3)- β -D-吡喃葡萄糖醛酸甙(oleanolic acid-3-O- α -L-arabinopyranosyl(1 \rightarrow 3)- β -D-glucopyranoside, I),竹节参甙 IVa(chikusetsusaponin IVa, II),雪胆皂甙 M_{a1} (hemsloside M_{a1} , III),雪胆皂甙 G_1 (hemsloside G_1 , IV),雪胆皂甙 H_1 (hemsloside H_1 , V),雪胆甲素(dihydrocucurbitacin F-25-O-acetate, VI)和雪胆乙素(dihydrocucurbitacin F₁, VII)。这些化合物均属首次从该植物中得到,其中化合物 I 为首次从该属植物中得到。化学结构式见图。

1 仪器和试剂

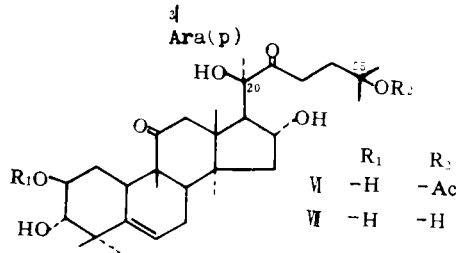
熔点用 Kofler 显微熔点仪测定,未校正;旋光用 Perkin-Elmer 241 型仪测定;红外光谱用 Nicolet FT-IR 205 \times B 型仪测定;质谱用 Finnigan-MAT 450 型仪测定;核磁共振谱用 Bruker Ac-E 200 型仪测定,TMS 为内标。柱层析用硅胶 H 为青岛海洋化工厂出品;反相填料 Lichroprep RP-8 由 MERCK 公司出品。

2 提取和分离

峨眉雪胆块根 1790g,用 95%乙醇回流提取,浓缩后加入适量水,依次用石油醚、乙酸乙酯及水饱和



R ₁	R ₂
I -GlcA- α -Ara(p)	-H
II -GlcA	-Glc
III -GlcA- α -Ara(p)	-Glc
IV -GlcA- α -Ara(p)	-Glc- β -Glc
V -GlcA- α -Glc	-Glc- β -Glc



R ₁	R ₂
VI -H	-Ac
VII -H	-H

图 化合物 I~VII 的化学结构式

* Address: Shi Yaqin, School of Pharmacy, West China University of Medical Sciences, Chengdu

正丁醇萃取,获乙酸乙酯萃取物 38g 及正丁醇萃取物 202g。

乙酸乙酯萃取物经硅胶柱层析,氯仿-丙酮-乙酸乙酯(7:2:1)洗脱,分为 A、B、C3 部分。由 A 中获化合物 VI 50mg。B 部分再经硅胶柱层析,氯仿-丙酮-乙酸乙酯(4:3:1)洗脱,分得化合物 VII 30mg。

正丁醇萃取物经 D₁₀₁ 大孔吸附树脂纯制后,获总皂甙 76g。取 26g 经硅胶柱层析,氯仿-甲醇-水(30:10:1)洗脱,分为 A、B、C、D4 部分。A 部分经硅胶柱层析,氯仿-甲醇-水(7:3:1)洗脱,以及 RP-8 反相柱层析,甲醇-水(3:1)洗脱,获化合物 I 50mg。B 部分经硅胶柱层析,氯仿-甲醇-水(7:3.5:1)洗脱,以及 RP-8 反相柱层析,甲醇-水(3:1)洗脱,获化合物 II 80mg。C 部分经硅胶柱层析,氯仿-甲醇-水(65:35:10)洗脱,以及 RP-8 反相柱层析,甲醇-水(2:1)洗脱,获化合物 III 150mg。D 部分经硅胶柱层析,氯仿-甲醇-水(6:3.5:1)洗脱,分为 D₁ 和 D₂ 部分。由 D₁ 部分获化合物 IV 150mg。D₂ 部分再经硅胶柱层析,氯仿-甲醇-水(6:3.5:1)洗脱,以及 RP-8 反相柱层析,甲醇-水(2:1)洗脱,获化合物 V 150mg。

化合物 I~V 经 AMBERLITE MB-3 离子交换树脂处理后测定 NMR。

3 鉴定

化合物 I:白色粉末, $[\alpha]_D^{25} + 17.6$ (c, 0.21, MeOH),不被 5mol/L NH₄OH 水解,薄层板上酸水解。检出齐墩果酸、葡萄糖醛酸和阿拉伯糖,¹³C-NMR 信号 δ ppm 105.8, 106.5 和 ¹H-NMR 信号 δ ppm 5.04(1H, d, J=7.8Hz), 5.40(1H, d, J=6.8Hz),说明化合物 I 为齐墩果酸的双糖甙。化合物 I 乙酰化物的 EI-MS 259m/z,示有末端阿拉伯糖。综合各数据分析结果,化合物 I 为齐墩果酸-3-O- α -L-吡喃阿拉伯糖(1 \rightarrow 3)- β -D-吡喃葡萄糖甙,其¹³C-NMR 数据与文献^[2]报道一致,见表。

化合物 II:无色针晶,mp 214-216 C(dc.), $[\alpha]_D^{25} + 5.3$ (c, 0.15, MeOH),5mol/L NH₄OH 水解检出葡萄糖,薄层板上酸水解检出齐墩果酸、葡萄糖和葡萄糖醛酸。¹³C-NMR 信号 δ ppm 107.1, 95.6 和 ¹H-NMR 信号 δ ppm 5.00(1H, d, J=7.5Hz), 6.30(1H, d, J=8Hz),示该化合物为齐墩果酸的双糖甙。数据分析表明化合物 II 为齐墩果酸-3-O- β -D-吡喃葡萄糖醛酸-28-O- β -D-吡喃葡萄糖甙(竹节参甙 IVa),其它¹³C-NMR 数据与文献^[2]报道一致,见表。

化合物 III:白色粉末, $[\alpha]_D^{25} + 11.2$ (c, 0.13, MeOH),5mol/L NH₄OH 水解检出葡萄糖,薄层板上酸水解检出齐墩果酸、阿拉伯糖、葡萄糖和葡萄糖醛酸。¹³C-NMR 信号 δ ppm 105.5, 106.5, 95.7 和 ¹H-NMR 信号 δ ppm 5.00(1H, d, J=7.6Hz), 5.40(1H, d, J=7.2Hz), 6.28(1H, d, J=8Hz),示化合物 III 为齐墩果酸的叁糖甙。化合物 III 乙酰化物的 EI-MS m/z 331, 259 示有末端葡萄糖和末端阿拉伯糖。各种数据分析表明,化合物 III 为齐墩果酸-3-O- α -L-吡喃阿拉伯糖(1 \rightarrow 3)- β -D-吡喃葡萄糖醛酸-28-O- β -D-吡喃葡萄糖酯甙(雪胆皂甙 M_{a1})。其¹³C-NMR 数据与文献^[2]报道一致,见表。

化合物 IV:白色粉末, $[\alpha]_D^{25} + 2.6$ (c, 0.23, C₅H₅N),薄层板上酸水解检出齐墩果酸、阿拉伯糖、葡萄糖和葡萄糖醛酸。¹³C-NMR 信号 δ ppm 106.6, 105.7, 105.1, 95.6 和 ¹H-NMR 信号 δ ppm 5.01(1H, d, J=7.7Hz), 5.06(1H, d, J=8.1Hz), 5.39(1H, d, J=7.1Hz), 6.27(1H, d, J=7.6Hz),示化合物 IV 为齐墩果酸的四糖甙。数据分析表明,化合物 IV 为齐墩果酸-3-O- α -L-吡喃阿拉伯糖(1 \rightarrow 3)- β -D-吡喃葡萄糖醛酸-28-O- β -D-吡喃葡萄糖(1 \rightarrow 6)- β -D-吡喃葡萄糖酯甙(雪胆皂甙 G₁),其¹³C-NMR 数据与文献^[3]报道一致,见表。

化合物 V:白色粉末, $[\alpha]_D^{25} + 3.9$ (c, 2.1, C₅N₅H),薄层板上酸水解检出齐墩果酸、阿拉伯

糖、葡萄糖和葡萄糖醛酸。¹³C-NMR 信号 δ ppm 103.5, 105.0, 105.1, 105.2, 95.5 和 ¹H-NMR 信号 δ ppm 5.01(1H, d, J=7.3Hz), 5.07(1H, d, J=7.4Hz), 5.38(1H, d, J=7.6Hz), 5.75(1H, d, J=7.6Hz), 6.30(1H, d, J=7.6Hz)。示化合物 V 为齐墩果酸的五糖甙, 化合物 V 乙酰化物的 EI-MS m/z 331 示有末端葡萄糖。数据分析表明化合物 V 为齐墩果酸-3-O- β -D-吡喃葡萄糖(1 \rightarrow 2)-[α -L-吡喃阿拉伯糖(1 \rightarrow 3)]- β -D-吡喃葡萄糖醛酸-28-O- β -D-吡喃葡萄糖(1 \rightarrow 6)- β -D-吡喃葡萄糖酯甙(雪胆皂甙 H₁), 其¹³C-NMR 数据与文献^[4]报道一致, 见表。

化合物 VI: 无色柱晶, 味苦, mp 226~228 C, Liebermann-Burchard 反应为正反应。其 R_f 值和 IR 与标准品一致, 与标准品的混合熔点不下降, 确证为雪胆甲素。

化合物 VII: 无色针晶, 味苦, mp 156~157 C, Liebermann-Burchard 反应为正反应。其 R_f 值和 IR 与标准品一致, 与标准品的混合熔点不下降, 确证为雪胆乙素。

表 化合物 I ~ V 的¹³C-NMR 数据(TMS 为内标, 吡啶为溶剂)

碳元 C	I	II	III	IV	V	糖基 C	I	II	III	IV	V
1	38.5	38.7	38.7	38.6	38.7	3-glcA	105.8	107.1	105.5	106.6	105.2
2	26.5	26.5	26.5	26.5	26.4		74.4	75.4	74.3	74.3	79.0
3	89.2	89.1	89.1	89.2	89.5		85.8	77.6	85.7	85.8	85.8
4	39.5	39.1	39.5	39.1	39.4		72.8	73.3	72.6	72.7	72.7
5	55.7	55.7	55.7	55.7	55.5		77.5	78.0	77.1	77.8	77.1
6	18.4	18.5	18.5	18.4	18.1		172.6	172.6	172.0	172.2	171.9
7	33.3	33.1	33.2	33.1	33.0	-ara	106.5		106.5	105.7	105.0
8	39.7	39.9	39.9	39.8	39.7	(1 \rightarrow 3)	71.3		71.5	71.5	71.2
9	47.9	48.0	48.0	47.9	47.8		74.3		74.6	74.6	74.5
10	36.9	36.9	37.0	36.9	36.7		69.0		69.2	69.3	69.5
11	23.7	23.6	23.8	23.6	23.5		67.0		67.1	67.0	67.6
12	122.5	122.6	122.7	122.4	122.4	-glc					103.5
13	144.8	144.1	144.1	141.1	141.0	(1 \rightarrow 2)					76.2
14	42.0	42.2	41.8	42.0	42.0						78.5
15	28.1	28.2	28.3	28.2	27.7						72.2
16	23.7	23.4	23.4	23.3	23.5						77.7
17	46.6	47.0	47.0	46.9	46.8						63.1
18	42.0	41.7	41.8	41.6	41.5	28-glc		95.6	95.7	95.6	95.5
19	46.6	46.2	46.3	46.2	46.1			74.0	74.1	75.0	74.9
20	30.9	30.7	30.8	30.7	30.6			78.7	78.9	78.3	78.2
21	34.2	34.0	34.1	34.0	33.9			71.1	71.2	71.4	71.2
22	33.2	32.5	32.6	32.4	32.3			79.2	79.2	77.4	78.2
23	28.2	28.2	28.2	28.0	28.1			62.2	62.3	69.2	69.2
24	16.9	16.9	16.7	16.8	16.5	-glc				105.1	105.1
25	15.4	15.5	15.5	15.5	15.4	(1 \rightarrow 6)				73.8	73.7
26	17.3	17.4	17.5	17.4	17.3					78.3	78.2
27	26.2	26.1	26.1	26.0	25.9					70.8	70.7
28	180.1	176.5	176.4	176.5	176.4					78.6	78.5
29	33.2	33.1	33.2	33.1	33.0					62.5	62.4
30	23.7	23.6	23.7	23.6	23.2						

致谢: 离子交换树脂(AMBERLITE MB·3)承中国科学院昆明植物所聂瑞麟研究员提供。

参 考 文 献

- 1 聂瑞麟. 云南植物研究, 1994, 16(2): 201
- 2 Nie R L, et al. Planta Medica, 1984(4): 322
- 3 Kasai R, et al. Chem Pharm Bull, 1990, 38(5): 1320
- 4 Morita T, et al. Chem Pharm Bull, 1986, 34(1): 101

(1994-08-22 收稿)

ABSTRACTS OF ORIGINAL ARTICLES

Studies on the Chemical Constituents of Emeixuedan (*Hemsleya emeiensis*)

Shi Yaqin, Zhang Wenjin, et al

Seven compounds were isolated from the tubers of *Hemsleya emeiensis* L. T. Shen et W. J. Chang and identified as oleanolic acid-3-O- α -L-arabinopyranosyl (I \rightarrow 3)- β -D-glucopyranoside (I), chikusetsusaponin Va (II), hemslosides Ma₁ (III), G₁(N), H₁(V), dihydrocucurbitacin F-25-O-acetate (VI) and dihydrocucurbitacin F(VII) on the basis of chemical and physical properties and spectral data. They all were isolated from this plant for the first time. Among them, I was obtained for the first time from the genus of *Hemsleya* Cogn.

(Original article on page 619)

Studies on the Chemical Constituents of Tubeflower Dutchmanspipe (*Aristolochia tubiflora*)

Peng Guoping, Lou Fengchang, Chen Yuanzhu, et al

Seven constituents were isolated from the stem and root of *Aristolochia tubiflora* Dunn. They were identified as palmitone (I), β -sitosterol (II), eupomatenoic acid (III), stigmastame-3,6-dione (IV), vanillic acid (V), stigmast-4-en-3,6-dione (VI), aurantiamide acetate (VII). VII showed cytotoxicity against A-549, MCF-7, HT-29 cells in culture.

(Original article on page 623)

Study on the Quality Standard of Shixiangzhitong Pill

Xu Renliu, Ning Tong

TLC was used for the qualitative identification of *Magnolia officinalis* Rehd. et wils, *Cyperus rotundus* L. and *Rheum palmatum* L. in Shixiangzhitong pill. The content of chrysophanol in Shixiangzhitong pill was assayed by TLC-scanning. The proposed method can be used to control the quality of Shixiangzhitong pill.

(Original article on page 629)

Spectrophotometric Determination of Trace of Mercury in Traditional Chinese Medicine with Iodine-Rhodamine B-Polyvinyl Alcohol

Cheng Guangxin, Wang Lihua, Ni Kunyi, et al

A spectrophotometric method for the determination of trace amounts of mercury (II) was described based on the formation of a complicated ion-association complex of Hg(II)-I⁻-Rhodamine B in the presence of polyvinyl alcohol. The maximum absorption of the ion-association complex was at 595nm. Beer's law was obeyed for mercury (II) in the range of 0~5 μ g/25ml. The apparent molar absorptivity was 7.36×10^5 L/mol \cdot cm. The recovery of mercury was 97.0%~103.0%, RSD <3%. The procedure was highly selective with good sensitivity and the result of determination was satisfactory.

(Original article on page 632)

Effects of Membranous Milkvetch (*Astragalus membranaceus*) on the Action of "Decoction of Invigorating Yang for Recuperation"

Lin Guitao, Li Wanzhong

Astragalus membranaceus (AM) plays an important role in the traditional Chinese recipe "Decoction of Invigorating Yang for Recuperation" (DIC) as the main ingredient which invigorates Qi and promotes blood circulation. But in clinics, doses of AM used in the recipe often varies. For the purpose to investigate the effect of different doses of AM on the action of DIC, animal experiments were designed and studied. Results showed that when the doses of AM were 15 and 30g, the resulting DIC showed a better antiirritability and enhancing immunity effects, as well as in vivo antithrombosis and vitro anticoagulation actions as compared to a dose of 120g AM in DIC ($P < 0.05$).

(Original article on page 639)