

cm^{-1} 峰。在酰胺III区域有明显的表征 α 螺旋的 $1\ 293\ \text{cm}^{-1}$ 峰。在表征C-C骨架伸缩振动的 $870\sim 960\ \text{cm}^{-1}$ 区域有 $924\ \text{cm}^{-1}$ 的强峰,表明 α 螺旋的存在。综上所述,火菇素蛋白的二级结构主要为 α 螺旋和 β 折叠,而无规则卷曲含量较少。

2.2.2 火菇素蛋白的侧链环境:酪氨酸在约 830 和 $850\ \text{cm}^{-1}$ 出现由环吸收振动和面弯曲振动产生的费米共振双峰。由这对谱带的强度比可以反映出蛋白质中酪氨酸所处的环境。当其强度比为 $0.3\sim 0.5$ 时,表示酪氨酸残基“埋藏”在疏水环境并在其OH基和负电荷受体之间形成强氢键,当强度比为 $1.25\sim 1.40$ 时,则表明酪氨酸残基全部暴露于溶剂中。对火菇素蛋白,测得 $I_{848}/I_{826}=1.01$ 。据这对谱带强度比值及Craig等确定的方程^[8],定量计算出“埋藏”和“暴露”的酪氨酸残基占酪氨酸残基总数的34%和66%。

2.2.3 S-S键的空间结构:在拉曼光谱中,S-S和C-C伸缩振动的谱带出现在 $500\sim 700\ \text{cm}^{-1}$;两个半胱氨酸侧链形成的二硫桥,其C-C-S-S-C-C键可能有3种构型,可由S-S键的振动频率进行判断: $510\ \text{cm}^{-1}$ 谱带属于扭曲-扭曲-扭曲式构型, $525\ \text{cm}^{-1}$ 谱带属于扭曲-扭曲-反式构型, $540\ \text{cm}^{-1}$ 谱带属于反式-扭曲-反式构型。在火菇素蛋白的拉曼图

谱中,S-S振动频率出现在 $537\ \text{cm}^{-1}$ 处,表明火菇素蛋白的C-C-S-S-C-C侧链为反式-扭曲-反式构型。

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Chemical constituents of *Rheum glaberrima* (I)

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Abstract: **Object** To study the chemical constituents in the root of *Rheum glaberrima*. **Methods** Compounds were isolated by various column chromatographies with silica gel. Their structures were elucidated by spectral analysis (MS, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$) and chemical evidence. **Results** Five compounds were isolated from the chloroform part, which were identified as chrysophanol (I), physcion (II), alo-emodin (III), emodin (IV), and β -sitosterol (V). **Conclusion** All above compounds are obtained from this plant for the first time.

Key words: Polygonaceae; *Rheum glaberrima* G. Sam; anthraquinones

光茎大黄的化学成分研究 (I)

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摘要: **目的** 对光茎大黄根部的化学成分进行研究。 **方法** 采用硅胶柱色谱分离、重结晶、MS、 $^1\text{H-NMR}$ 、 $^{13}\text{C-NMR}$ 等技术进行分离、鉴定结构。 **结果** 从该植物中分离并鉴定了5个化合物, 分别是大黄酚(chrysophanol,

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I)、大黄素甲醚(phycion, II)、芦荟大黄素(aloe-emodin, III)、大黄素(emodin, IV)、 β -谷甾醇(β -sitosterol, V)。结论 该 5 个化合物均为首次从该植物中分离得到。

关键词: 蓼科; 光茎大黄; 蒽醌类

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Rheum glabriculae G. Sam is distributed in Wudu, Wen and Ming County of Gansu Province in China. As a Chinese folk herb medicine, it was reported^[1] that it can clear away heat and toxic materials, starch and cool the blood. It is applied for purging and all kinds of haemorrhage. The research shows its purgative action is similar to that of *R. officinale* Baill. It was not reported about study on chemical constituents of *R. glabriculae*. The author studied chemical constituents of *R. glabriculae* in order to make sure the reliability in using drugs, comparing with that of *R. officinale*.

Experimental section spectrum

General experimental procedures. Melting points were determined on a X- 4 digital micro-melting point apparatus and are uncorrected. VG ZAB - HS mass spectrometer was used to record the EIMS. NMR spectra was measured on a Burker AM - 400 spectrometer, using TMS as internal standard. Coupling constants (*J* values) are given in Hz · Si gel (100- 200 mu) and Si gel G (both from Qingdao Marine Chemical Group Co., Qingdao, Shandong Province, China) were used for column chromatography and TLC, respectively.

Plant material. All roots of *R. glabriculae* were collected in Wudu County, Gansu Province in China, in August, 2001, and identified by Prof. Zhao Ru-neng, from Lanzhou Medical College. A voucher specimen is deposited in the Museum of Medicinal Plant, Lanzhou Medical College.

Extraction and isolation

The air-dried and pulverized roots of *R. glabriculae* (4.0 kg) were soaked and extracted ten times with 95% EtOH in normal temperature, 24 hours each time. After removal of solvent, obtained 488 g powder sample. The sample was subjected to column chromatography on silica gel and eluted with CHCl₃, EtOAc, and EtOH, respectively. The elutes were collected in 300 mL portions,

monitored by TLC. Five compounds in this dissertation were obtained from the part which had been eluted with CHCl₃. Compound I was obtained by purifying with CHCl₃ and EtOAc from fr2; fr18- fr22 eluted with petroleum ether-EtOAc (15 1, 10 1) and petroleum ether-acetone (5 1, 3 1) were subjected to repeated column chromatography to yield compound II, IV, and V; Compound III was obtained by purifying with EtOAc and acetone from fr24- fr37.

Structural identification

Compound I (chrysophanol): yellow piece (EtOAc), mp 204- 206 °C, Bornträger reaction showed red, (AcO)Mg reaction showed salmon pink, EIMS *m/z*: 254[M⁺], 239, 237, 226, 198. ¹H-NMR (CDCl₃) δ 12.08 (1H, s, C₁-OH), 11.96 (1H, s, C₈-OH), 7.78 (1H, dd, *J* = 8.0, 1.2 Hz, C₅-H), 7.64 (1H, t, *J* = 8.0 Hz, C₆-H), 7.60 (1H, d, *J* = 1.2 Hz, C₄-H), 7.26 (1H, dd, *J* = 8.0, 1.2 Hz, C₇-H), 7.05 (1H, d, *J* = 1.2 Hz, C₂-H), 2.44 (3H, s, Ar-CH₃). ¹³C-NMR are seen in Table 1. All above data are consistent with those of chrysophanol in reference^[2].

Table 1 Spectral data of compounds I - IV

C	I	II	III	IV
1	162.3	166.5	161.5	164.4
2	124.5	106.7	119.3	107.9
3	149.3	162.5	153.7	165.2
4	121.3	110.2	117.1	108.7
5	119.9	121.3	120.6	124.1
6	136.9	148.4	137.3	148.2
7	124.3	124.5	124.4	120.4
8	162.6	165.2	161.3	161.4
9	192.4	190.8	191.6	189.6
10	181.8	182.0	181.3	181.2
4 α	133.2	135.2	133.0	135.0
10 α	133.5	133.2	133.2	132.7
8 α	115.8	113.6	114.3	113.3
9 α	113.6	108.2	115.8	108.9
CH ₃	22.2	22.2		21.5
OCH ₃		56.1		
CH ₂ OH			62.0	

Compound II (phycion): salmon pink needles (EtOAc), mp 215- 217 °C, Bornträger reac-

tion showed red, (Aco)Mg reaction showed salmon pink, EIMS m/z : 284 [M^+], 269, 256. $^1\text{H-NMR}$ (CDCl_3) δ 12.31 (1H, s, $\text{C}_1\text{-OH}$), 12.11 (1H, s, $\text{C}_8\text{-OH}$), 7.61 (1H, brs, $\text{C}_4\text{-H}$), 7.35 (1H, d, $J = 2.4$ Hz, $\text{C}_5\text{-H}$), 7.07 (1H, brs, $\text{C}_2\text{-H}$), 6.68 (1H, d, $J = 2.4$ Hz, $\text{C}_7\text{-H}$), 3.94 (3H, s, OCH_3), 2.45 (3H, s, Ar-CH_3). $^{13}\text{C-NMR}$ are seen in Table 1. All above data are consistent with those of physcion in reference^[21].

Compound III (abe-emodin): Salmon pink needles (acetone), mp 235- 236, Bornträger reaction showed red, (Aco)Mg reaction showed salmon pink, EIMS m/z : 270 [M^+], 254. $^1\text{H-NMR}$ (DMSO-d_6) δ 11.92 (1H, s, $\text{C}_1\text{-OH}$), 11.85 (1H, s, $\text{C}_8\text{-OH}$), 7.76 (1H, dd, $J = 2.0$, 8.0 Hz, $\text{C}_5\text{-H}$), 7.64 (1H, dd, $J = 8.0$, 8.0 Hz, $\text{C}_6\text{-H}$), 7.63 (1H, d, $J = 1.2$ Hz, $\text{C}_4\text{-H}$), 7.34 (1H, dd, $J = 2.0$, 8.0 Hz, $\text{C}_7\text{-H}$), 7.23 (1H, d, $J = 1.2$ Hz, $\text{C}_2\text{-H}$), 5.59 (1H, -OH), 4.60 (2H, s, $-\text{CH}_2\text{OH}$). $^{13}\text{C-NMR}$ are seen in Table 1. All above data are consistent with those of abe-emodin in reference^[31].

Compound IV (emodin): Red grain (EtOAc), mp 263- 264, Bornträger reaction showed red, (Aco)Mg reaction showed salmon pink, EIMS

m/z : 270 [M^+], 255. $^1\text{H-NMR}$ (DMSO-d_6) δ 12.03 (1H, s, $\text{C}_1\text{-OH}$), 11.95 (1H, s, $\text{C}_8\text{-OH}$), 11.35 (1H, s, $\text{C}_6\text{-OH}$), 7.39 (1H, d, $J = 1.2$ Hz, $\text{C}_4\text{-H}$), 7.08 (1H, d, $J = 1.2$ Hz, $\text{C}_2\text{-H}$), 7.05 (1H, d, $J = 2.4$ Hz, $\text{C}_5\text{-H}$), 6.53 (1H, d, $J = 2.4$ Hz, $\text{C}_7\text{-H}$), 2.36 (3H, s, Me). $^{13}\text{C-NMR}$ are seen in Table 1. All above data are consistent with those of emodin in reference^[41].

Compound V (β -sitosterol): White needles (EtOAc), mp 143- 144. $\text{H}_2\text{SO}_4\text{-EtOH}$, Liebermann reaction showed positive. The data of $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ are consistent with those of β -sitosterol.

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赶山鞭挥发油化学成分的 GC-MS 分析

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赶山鞭 *Hypericum attenuatum Choisy* 系藤黄科金丝桃属植物。该属植物约 400 种, 除了南北两极地或荒漠地及大部分热带地外世界广布。我国约有 55 种 8 亚种, 几乎产于全国各地, 主要集中在西南, 其中滇西北分布有近五分之二的种类, 甘肃产约 7 种^[1]。本属植物约三分之二的种类在民间被用于治疗多种疾病^[2]。国内外对金丝桃属植物展开了深入的有效成分研究, 已完成了本属多数植物的成分检

测。并对约 70 种植物进行了详细的研究, 共发现 90 多种成分, 主要有双蒽酮、黄烷酮醇、黄酮及黄酮醇、香豆素、酚酸、间苯三酚衍生物、胡萝卜素、挥发油类等^[3]。挥发油类有 α -蒎烯、月桂酸、柠檬烯等, 认为这些成分是抗真菌的有效成分^[4]。传统中医药学认为赶山鞭性平, 味辛苦涩, 能清热解毒, 利湿, 收敛止血。主要用于治疗心脏病、类风湿性关节炎、内脏出血、细菌感染、炎症等。对赶山鞭挥发油化学成分的

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