

152. 6(C-3', C-5'), 137. 2(C-4'), 102. 8(C_G-1_X 2), 77. 2(C_G-5_X 2), 76. 5(C_G-3_X 2), 74. 2(C_G-2_X 2), 70. 0(C_G-4_X 2), 61. 0(C_G-6_X 2), 56. 4(4_X OCH₃), 数据与文献报道一致^[3]。

山奈酚-3-O-β-D-吡喃葡萄糖苷(III): ¹HNMR δ8. 03[H-2', H-6'(2H, d, J= 8. 8 Hz)], 6. 87[H-3', H-5'(2H, d, J= 8. 8 Hz)], 6. 42(H-8), 6. 19(H-6), 5. 44(1H, d, J= 7. 6 Hz); ¹³CNMR δ177. 4(C-4), 164. 3(C-7), 161. 2(C-5), 159. 9(C-4'), 156. 4(C-2), 156. 3(C-9), 133. 3(C-3), 130. 8(C-2', C-6'), 120. 9(C-1'), 115. 1(C-3', C-5'), 104. 0(C-10), 98. 7(C-6), 93. 7(C-8), 101. 1(C_G-1, 3-O-Glc), 77. 4(C_G-5), 76. 5(C_G-3), 74. 2(C_G-2), 70. 0(C_G-4), 60. 9(C_G-6), 数据与文献报道一致^[4]。

7-O-α-L-吡喃鼠李糖基-山奈酚-3-O-β-D-吡喃葡萄糖苷(IV): ¹HNMR δ8. 08[H-2', H-6'(2H, d, J= 8. 8 Hz)], 6. 90[H-3', H-5'(2H, d, J= 8. 7 Hz)], 6. 81(H-8), 6. 44(H-6), 5. 54(1H, br. s, Rha), 5. 47(1H, d, J= 7. 2 Hz), 1. 10(3H, d, J= 6. 4 Hz); ¹³CNMR δ177. 6(C-4), 161. 6(C-7), 160. 8(C-5), 160. 0(C-4'), 156. 7(C-2), 156. 0(C-9), 133. 5(C-3), 130. 9(C-2', C-6'), 120. 7(C-1'), 115. 1(C-3', C-5'), 105. 6(C-10), 98. 4(C-6), 94. 2(C-8), 100. 8(C_G-1, 3-O-Glc), 77. 4(C_G-5), 76. 4(C_G-3), 74. 2(C_G-2), 70. 2(C_G-4), 60. 8(C_G-6), 99. 3(C_R-1, 7-O-Rha), 71. 6(C_R-4), 70. 1(C_R-3), 70. 0(C_R-2), 69. 7(C_R-5), 17. 8(C_R-6), 数据与文献报道一致^[5]。

山奈苷(V): ¹HNMR δ7. 78[H-2', H-6'(2H, d, J= 8. 4 Hz)], 6. 90[H-3', H-5'(2H, d, J= 8. 5 Hz)], 6. 78(H-8), 6. 45(H-6), 5. 54(1H, br. s, Rha), 5. 29(1H, br. s, Rha), 1. 01(3H, d, J= 6. 4 Hz), 0. 79(3H, d, J= 6. 0 Hz); ¹³CNMR δ177. 8(C-4), 161. 6(C-7), 160. 9(C-5), 160. 0(C-4'), 157. 6(C-2), 156. 0(C-9), 134. 5(C-3), 130. 5(C-2', C-6'), 120. 3(C-1'), 115. 3(C-3', C-5'), 105. 7(C-10), 98. 4(C-6), 94. 5(C-8), 101. 8(C_R-1, 3-O-Rha), 71. 5(C_R-4), 70. 5(C_R-3), 70. 2(C_R-2), 69. 9(C_R-5), 17. 8(C_R-6), 99. 3(C_R-1, 7-O-Rha), 71. 1(C_R-4), 70. 3(C_R-3), 70. 2(C_R-2), 69. 7(C_R-5), 17. 3(C_R-6), 数据与文献报道一致^[5]。

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Chemical constituents from root of *Glycyrrhiza uralensis*

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Abstract Object To investigate the chemical constituents from the roots of *Glycyrrhiza uralensis* Fisch. **Methods** The constituents were isolated on normal and reversed silica gel column chromatography and their structures were identified by spectral evidence. **Results** A new oleanane-type triterpenoid saponin and twelve known compounds, including two triterpenoid saponins, two coumarins and eight flavonoids, were isolated. **Conclusion** The new compound was elucidated as 3-O-β-D-(6-methyl) glucuronopyranosyl (1→2)-D-glucuronopyranosyl]-24-hydroxy-glabrolide on the basis of ESI-MS, ¹HNMR, ¹³CNMR, HMQC and HMBC spectral evidence.

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Key words *Glycyrrhiza uralensis* Fisch; triterpenoid saponins; 3-*O*-[β -*D*-(6-methyl) glucuronopyranosyl (1 \rightarrow 2)-*D*-glucuronopyranosyl]-24-hydroxy-glabrolide

乌拉尔甘草中的化学成分

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摘要: 目的 分析乌拉尔甘草 *Glycyrrhiza uralensis* 的化学成分。方法 采用正、反相硅胶柱层析分离, 应用波谱方法进行结构鉴定。结果 从甘草中共分离出 3 个三萜皂苷、2 个香豆素和 8 个黄酮类化合物, 其中一个三萜皂苷为新化合物。结论 通过 ESI-MS, $^1\text{H NMR}$, $^{13}\text{C NMR}$, HMQC 和 HMB C 分析, 将新三萜皂苷的结构鉴定为 3-*O*- β -*D*-葡萄糖醛酸甲酯-(1 \rightarrow 2)- β -*D*-葡萄糖醛酸]-24-羟基-甘草内酯。

关键词: 乌拉尔甘草; 三萜皂苷; 3-*O*- β -*D*-葡萄糖醛酸甲酯-(1 \rightarrow 2)- β -*D*-葡萄糖醛酸]-24-羟基-甘草内酯

中图分类号: R283.3 **文献标识码:** A **文章编号:** 0253-2670(2003)03-0198-04

As a part of investigation on glycyrrhiza, a famous Chinese herbal medicine, a new oleanane-type triterpenoid saponin was isolated from the roots of *Glycyrrhiza uralensis* Fisch. Twelve known compounds, including two triterpenoid saponins, two cumarins and eight flavonoids were also isolated. This paper deals with the isolation and structure elucidation of these compounds.

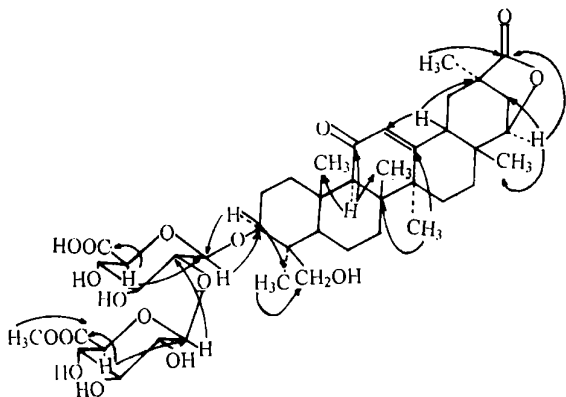


Fig. 1 Structure and key HMBC correlation of I

1 Results and discussion

Compound I was obtained as white powder, $[\alpha]_D^{25} + 3.5$. Its molecular formula was assigned as $\text{C}_{43}\text{H}_{62}\text{O}_{17}$ by HR-ESI-MS ($[M + H]^+$ m/z 851.4029, calc. 851.4065). The IR spectrum of I showed the presence of hydroxyl (3447 cm^{-1}) and carbonyl groups (1753 cm^{-1}). $^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectra (Table 1) of I suggested it was a 24-hydroxy-glabrolide 3-*O*-glycoside^[1,2]. Acidic hydrolysis of I on TLC indicated that sugar moiety was composed of glucuronic acid. $^{13}\text{C NMR}$ signals due to the sugar moiety suggested it was glucuronopyranosyl (1 \rightarrow 2)-glucuronopyranosyl^[2] and

the anomeric proton signals at δ 4.97 (d, $J = 7.6$ Hz), and 5.59 (d, $J = 7.2$ Hz) indicated that the two glucuronopyranosyls were in β -orientated. Signals at δ 52.1 and δ 3.82 showed one of the glucuronopyranosyl was methyl esterified and the fragment ion at m/z 659 $[M - 191]^+$ in negative ion ESI-MS/MS analysis revealed that the terminal glucuronopyranose was esterified. It was proved by the correlation in HMBC spectrum. Therefore, the structure of I was elucidated as 3-*O*- β -*D*-(6-methyl) glucuronopyranosyl (1 \rightarrow 2)-*D*-glucuronopyranosyl]-24-hydroxy-glabrolide shown in Fig. 1. Analysis of HMQC and HMB C spectra allows proton and carbon signals assigned in Table 1.

Compound I can not be detected from the hot water extract of the roots of *G. uralensis* by HPLC-MS (ODS column, MeOH/H₂O). So it may be an artifact due to the use of methanol in column chromatography and the original naturally occurring compound should be 3-*O*- β -*D*-glucuronopyranosyl (1 \rightarrow 2)-*D*-glucuronopyranosyl]-24-hydroxy-glabrolide which was detected in crude saponin by HPLC-MS (ODS column, MeOH/H₂O).

Based on directed comparison with the published spectral data and authentic samples, the known compounds were identified as liquiritigenin, liquiritin^[3], pinocembrin^[4], isoliquiritigenin^[5], liquiritigenin-7, 4'-diglucoside^[6], ononin^[7], glycyrol, isoglycyrol^[8], licoflavonol^[9], licoicidin^[10], glycyrrhizic acid^[11] and licorice-saponin E₂^[12], respectively.

2 Experiment

Table 1 ^1H NMR and ^{13}C NMR data of compound I (pyridine- d_5)

C	δ_{C}	δ_{H}	C	δ_{C}	δ_{H}	C	δ_{C}	δ_{H}
1	39. 6	2. 95	16	25. 9	1. 06, 1. 44, 2H, br	1'	104. 5	4. 97, 1H, d, $J= 7. 6$
2	26. 6	1. 36	17	35. 7		2'	82. 3	4. 24, 1H
3	89. 8	3. 45, 1H, dd, $J= 11. 6, 4. 5$	18	44. 6	2. 26, 1H, br	3'	77. 7	4. 26, 1H
4	44. 4		19	40. 8	1. 71, 2H, br	4'	72. 9	4. 50, 1H
5	56. 1	0. 83, 1H	20	42. 1		5'	77. 9	4. 54, 1H
6	18. 5	1. 29, 2. 13, 2H, br	21	38. 1	1. 94, 2H, br	6'	172. 2	
7	33. 5	1. 21, 1. 36, 2H, br	22	83. 9	4. 16, 1H, d, $J= 5. 8$	1''	105. 8	5. 59, 1H
8	44. 9		23	23. 0	1. 44, 3H, s	2''	75. 7	4. 22, 1H
9	61. 9	2. 38, 1H, s	24	63. 3	3. 67, 4. 33, $J= 11. 6$	36''	77. 3	4. 46, 1H
10	37. 1		25	16. 5	1. 20, 3H, s	4''	72. 7	4. 36, 1H
11	198. 9		26	18. 5	0. 95, 3H, s	5''	77. 7	4. 47, 1H
12	130. 0	5. 66, 1H, s	27	22. 3	1. 32, 3H, s	6''	170. 2	
13	164. 3		28	24. 0	0. 88, 3H, s	OCH_3	52. 1	3. 82, 3H
14	45. 0		29	20. 3	1. 15, 3H, s			
15	25. 2	1. 54, 1. 63, 2H, br	30	179. 6				

2. 1 General experimental procedures: Optical rotation was measured with PE-241 polarimeter. Spectral data were obtained using the following apparatus: IR spectrum with a Nicolet MX-1 spectrometer; NMR spectra with a Varian Unity Inova-400 spectrometer with tetramethylsilane (TM S) as an internal standard; HR-ESI-MS spectrum with a Bruker Daltonics Apex II mass spectrometer and MS/MS and HPLC-MS analysis with a ThermoFinnigan LCQ^{DECA} mass spectrometer. Silica gel (170-200 mesh) and Lobar LiChroprep RP-18 column were used for column chromatography.

2. 2 Plant material: The roots of *G. uralensis* Fisch. (Gancao) were collected in 1999 from Chifeng, Neimeng, China.

2. 3 Extraction and isolation: The air-dried and powdered glycyrrhiza (2 kg) was on ultrasonic extraction with $\text{NH}_3\text{-EtOH-H}_2\text{O}$ (0. 5: 10: 89. 5) for three times. After removal of the solvent, the syrup was suspended in H_2O and extracted with ethyl acetate for three times. Then the H_2O fraction was adjusted to $\text{pH}= 2$ by adding 70% H_2SO_4 , and centrifugalized to separate the precipitate. By using silica gel (petroleum/acetone or $\text{CHCl}_3\text{-MeOH}$) and RP-18 ($\text{MeOH-H}_2\text{O}$) columns, liquiritigenin (300 mg), liquiritin (8 g), pinocembrin (12 mg), isoliquiritigenin (10 mg), liquiritigenin-7, 4'-diglucoside (100 mg), ononin (240 mg), glycyrol (350 mg), isoglycyrol (120 mg), licoflavonol (100 mg) and licoricidin (380 mg) were

isolated from ethyl acetate extract and I (10 mg), glycyrrhizic acid (2 g) and licorice-saponin E₂ (30 mg) from the precipitate, respectively.

2. 4 Identification

Compound I : white powder, $[\alpha]_{\text{D}}^{25} + 3. 5$ ($\text{CHCl}_3\text{-CH}_3\text{OH}= 1: 5$, $c= 0. 002$). $\text{IR } \nu_{\text{max}}^{\text{KBr}} \text{ cm}^{-1}$: 3 447, 2 949, 1 753, 1 658, 1 085, 1 048; ESI-MS-MS(-) m/z : 659 $[\text{M}-\text{gluCH}_3]^-$ (849 \rightarrow 659); HR-ESI-MS(+) m/z 851. 402 9 ($[\text{M}+\text{H}]^+$, $\text{C}_{43}\text{H}_{63}\text{O}_{17}$, calc 851. 406 5), 467. 312 7 ($[\text{M}-(\text{gluCH}_3-\text{gluO})]^+$, $\text{C}_{30}\text{H}_{43}\text{O}_4$, calc 467. 316). ^1H NMR and ^{13}C NMR data were shown in Table 1.

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木芙蓉叶化学成分研究

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摘要: 目的 研究木芙蓉叶 *Hibiscus mutabilis* 的化学成分。方法 采用硅胶柱、 C_{18} 反相柱、聚酰胺柱色谱分离纯化, 通过理化常数测定和光谱分析鉴定化合物的结构。结果 从木芙蓉叶中分离得到 10 个化合物。根据波谱分析和理化数据, 鉴定出其中 9 个化合物分别为: 二十四烷酸 (tetracosanoic acid, I)、 β -谷甾醇 (β -sitosterol, II)、胡萝卜苷 (daucosterol, III)、水杨酸 (salicylic acid, IV)、大黄素 (emodin, V)、芸香苷 (rutin, VI)、山奈酚-3- O - β -芸香糖苷 (kaempferol-3- O - β -rutinoside, VII)、山奈酚-3- O - β -刺槐双糖苷 (kaempferol-3- O - β -robinobinoside, VIII) 及山奈酚-3- O - D -(6-*E* 对羟基桂皮酰基)-葡萄糖苷 [kaempferol-3- O - D -(6-*E*-*p*-hydroxycinnamoyl)-glucopyranoside, IX]。结论 除 II 和 VI 外, 其他化合物均为首次从该植物中分离得到。

关键词: 木芙蓉叶; 黄酮苷; 甾醇

中图分类号: R283.3 文献标识码: A 文章编号: 0253-2670(2003)03-0201-03

Studies on chemical constituents of *Hibiscus mutabilis*

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Abstract **Object** To study the chemical constituents of *Hibiscus mutabilis* L. **Methods** Isolation and purification were carried out on silica gel, or polyamide column chromatography *etc.* Constituents were identified and structurally elucidated by physicochemical properties and spectral analysis. **Results** Ten compounds were obtained, nine of them were determined as tetracosanoic acid (I), β -sitosterol (II), daucosterol (III), salicylic acid (IV), emodin (V), rutin (VI), kaempferol-3- O - β -rutinoside (VII), kaempferol-3- O - β -robinobinoside (VIII) and kaempferol-3- O - D -(6-*E*-*p*-hydroxycinnamoyl)-glucopyranoside (IX). **Conclusion** All compounds are isolated from the plant for the first time except II and VI.

Key words *Hibiscus mutabilis* L.; flavonoid glycosides; sterol

木芙蓉 *Hibiscus mutabilis* L. 属锦葵科木槿属植物, 其花、叶和根均可入药。具有清热解毒、消肿排脓、凉血止血之功用, 在民间广泛用于治疗痈肿疮疖。文献记载该药外用和口服有很好的抗炎、消肿作用, 可以治疗阑尾炎、腮腺炎, 也可以治疗痛风性关节炎、丹毒和灼伤^[1]。我校附属瑞金医院魏指薪老中医的经验方“消肿散”应用于临床 40 多年, 对丹毒、急性软组织损伤、痛风、滑膜炎等引起的红肿热

痛有非常好的疗效, 其中主要药物就是木芙蓉叶。药理实验已证实, 木芙蓉叶水提取物有较强的抗炎、镇痛作用, 且无明显胃肠道刺激作用^[2]。已报道木芙蓉叶的化学成分只有芦丁 (芸香苷)^[3]和 β -谷甾醇^[4]。我们对木芙蓉叶的化学成分进行了系统分离, 从中分离到 10 个化合物 (I ~ X), 鉴定了其中 9 个化合物, 分别为 4 个黄酮苷化合物: 芸香苷 (rutin, VI)、山奈酚-3- O - β -芸香糖苷 (kaempferol-3- O - β -ruti-

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