

扁担杆的化学成分 II

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[摘要] 目的:研究扁担杆 *Grewia biloba* 根皮的化学成分。方法:采用反复硅胶和凝胶柱等色谱分离纯化,根据多种波谱技术鉴定化合物结构。结果:分离鉴定了 4 个化合物,分别为 7-乙氧基槲皮素(1), $1\alpha, 3\beta, 23$ -trihydroxyolean-12-en-28-oic acid (2), 6 - C -glucosyl-quercetin(3), 6 - C -glucosyl-3', 4', 5', 7-pentahydroxyflavanone(4)。结论:化合物 1 为新的天然产物,其余化合物均为首次从该属植物中分离得到。

[关键词] 扁担杆;新天然产物;化学成分

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Studies on Chemical Constituents of *Grewia biloba* II

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[Abstract] **Objective:** To investigate the chemical constituents of *Grewia biloba*. **Method:** Individual constituents isolated and repeatedly purified on silica gel and Sephadex LH-20 column chromatography, were identified by physicochemical constants and structurally elucidated by spectral methods. **Result:** Four compounds were isolated and identified as: 3', 4', 5', 7-tetrahydroxy-7-ethoxyflavone (1), $1\alpha, 3\beta, 23$ -trihydroxyolean-12-en-28-oic acid (2), 6 - C -glucosyl-quercetin (3), 6 - C -glucosyl-3', 4', 5', 7-pentahydroxyflavanone (4). **Conclusion:** Compound 1 is a new natural product, others are isolated from the genus *Grewia* for the first time.

[Key words] *Grewia biloba*; new natural product; chemical constituent

扁担杆 *Grewia biloba* G. Don 为椴树科扁担杆属植物,在非洲和亚洲一些国家地区,部分扁担杆属植物被作为民间草药使用,多具有抗菌消炎作用^[1-3]。《新修本草》记载小花扁担杆枝叶煮汁可治小儿蛔虫病,《开宝本草》称其可“主三虫,下气消谷”,《中药大辞典》记载其全株和枝叶能祛风除湿,理气消痞,可治小儿因虫痞积,大人气痞,脾虚食少,妇女崩带,风湿^[4]。之前笔者发现扁担杆的根皮提取物具

有一定的抑菌和抗肿瘤作用^[5-6],并首次从中分离得到了 6 个化合物^[7]。本文继续报道从中分得的 4 个化合物,包括 1 个新的天然产物,首次从扁担杆属分得的 1 个三萜和 2 个黄酮碳苷类化合物。

1 材料

Bruker-500 型核磁共振波谱仪 (Bruker 公司); Agilent 1100LC/MSD Trap 液相色谱-质谱联用仪 (安捷伦公司); X-4 显微熔点仪 (未校正); 柱色谱硅胶 (200~300 目,青岛海洋化工厂); 柱色谱聚酰胺 (路桥四甲生化塑料厂); Sephadex LH-20 型葡聚糖凝胶 (日本三菱化工公司),所用试剂均为分析纯。

供试药材采自江西省萍乡市,原植物由安徽中医学院药学院刘守金博士鉴定为扁担杆 *G. biloba*,凭证标本 (No. 060801) 保存于江西中医学院现代中药制剂教育部重点实验室。

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2 提取与分离

扁担杆干燥根皮 5.5 kg 粉碎,用 90% 乙醇在室温下浸泡 12 h 后加热回流提取 3 次,滤过,合并滤液,减压浓缩得浸膏约 500 g。将其混悬于水中后,依次用石油醚、乙酸乙酯和正丁醇萃取。取乙酸乙酯部位浸膏共 150 g,经硅胶柱色谱分离,石油醚-丙酮系统梯度洗脱,得到石油醚-丙酮(1:0,20:1,10:1,1:1,0:1)共 6 个洗脱部分,将石油醚-丙酮(1:1)洗脱部分再经硅胶柱色谱分离,氯仿-甲醇洗脱,合并氯仿-甲醇(20:1)流份经凝胶柱色谱分离,甲醇洗脱,分别得到化合物 2(50 mg)和化合物 1(10 mg)。取正丁醇部位浸膏 80 g,经聚酰胺色谱柱分离,依次用水和甲醇洗脱,其中水洗脱部分再经反复凝胶柱色谱分离,甲醇洗脱,得到化合物 4(10 mg)。取水部位浸膏 100 g,用丙酮捏溶,得到丙酮部分 1.5 g,丙酮部分再经反复凝胶柱色谱分离,甲醇洗脱,得到化合物 3(20 mg)。

3 结构鉴定

化合物 1 黄色粉末(甲醇),mp 265 ~ 267 °C。UV (MeOH) $\lambda_{\max}$ 258 nm。ESI-MS (-) m/z : 329 [M-H]⁻, 分子式 C₁₇H₁₄O₇。¹H-NMR (500 MHz, CD₃OD) δ : 6.19 (1H, d, J = 2.0 Hz, H-6), 6.39 (1H, d, J = 2.0 Hz, H-8), 7.73 (1H, d, J = 2.2 Hz, H-2'), 6.89 (1H, d, J = 8.5 Hz, H-5'), 7.63 (1H, dd, J = 8.5, 2.2 Hz, H-6'), 3.61 (2H, q, J = 7.0 Hz, OCH₂), 1.18 (3H, t, J = 7.0 Hz, Me); ¹³C-NMR (125 MHz, CD₃OD) δ : 148.1 (C-2), 137.2 (C-3), 177.4 (C-4), 158.3 (C-5), 99.3 (C-6), 165.6 (C-7), 94.4 (C-8), 162.5 (C-9), 104.6 (C-10), 124.2 (C-1'), 116.0 (C-2'), 146.2 (C-3'), 148.8 (C-4'), 116.2 (C-5'), 121.7 (C-6'), 58.3 (OCH₂), 18.4 (CH₃)。根据波谱数据及与文献[8]报道的合成 7-乙氧基槲皮素数据比较,鉴定化合物 1 为 7-乙氧基槲皮素。经检索,该化合物为新的天然产物。

化合物 2 白色粉末(甲醇),mp 244 ~ 246 °C。ESI-MS (-) m/z : 487 [M-H]⁻, 分子式 C₃₀H₄₈O₅。¹H-NMR (500 MHz, DMSO-d₆) δ : 3.48 (1H, t, H-1), 3.18 (1H, dd, J = 9.4, 3.6 Hz, H-3), 1.74 (1H, dd, J = 12.4, 4.3 Hz, H-5), 5.17 (1H, s, H-12), 3.04 (1H, dd, J = 10.5, 4.6 Hz, H-23), 3.30 (1H, dd, J = 10.5, 4.6 Hz, H-23), 0.54 (3H, s, Me-24), 0.71 (3H, s, Me-25), 0.92 (3H, s, Me-26), 1.10 (3H, s, Me-27), 0.88

(3H, s, Me-29), 0.88 (3H, s, Me-30), 4.18 (H, s, OH-1), 4.11 (H, s, OH-3), 4.37 (H, s, OH-23); ¹³C-NMR (125 MHz, DMSO-d₆) δ (HSQC): 67.4 (CH-1), 23.4 (CH₂-2), 75.5 (CH-3), 42.4 (C-4), 46.6 (CH-5), 17.4 (C-H₂-6), 32.0 (C-H₂-7), 39.3 (C-8), 47.0 (CH-9), 37.3 (C-10), 23.0 (CH₂-11), 121.4 (CH-12), 143.9 (C-13), 40.8 (C-14), 27.1 (CH₂-15), 23.3 (CH₂-16), 46.0 (C-17), 41.3 (CH-18), 45.4 (CH₂-19), 30.3 (C-20), 33.3 (CH₂-21), 32.0 (CH₂-22), 63.9 (CH₂-23), 13.6 (C-H₃-24), 16.8 (CH₃-25), 16.7 (CH₃-26), 25.6 (CH₃-27), 178.5 (C-28), 32.8 (CH₃-29), 23.3 (CH₃-30)。OH-1, H-3, H-5, H-25 与 C-1; H-5, H-23, H-24 与 C-3; H-23 与 C-3, C-4, C-5 之间的 HMBC 相关信号表明 3 个 OH 分别为 1, 3, 23 位取代。以上数据与文献[9]报道的 1 α , 3 β , 23-trihydroxyolean-12-en-28-oic acid 数据基本一致,故鉴定化合物 2 为 1 α , 3 β , 23-trihydroxyolean-12-en-28-oic acid。

化合物 3 黄色粉末(甲醇),ESI-MS (-) m/z : 463 [M-H]⁻, 分子式 C₂₁H₂₀O₁₂。¹H-NMR (500 MHz, DMSO-d₆) δ : 6.50 (1H, s, H-8), 7.73 (1H, d, J = 2.2 Hz, H-2'), 6.94 (1H, d, J = 8.5 Hz, H-5'), 7.61 (1H, dd, J = 8.5, 2.2 Hz, H-6'), 4.67 (1H, d, J = 9.8 Hz, H-1''), 4.11 (1H, t, J = 9.0 Hz, H-2''); ¹³C-NMR (125 MHz, DMSO-d₆) δ (HSQC): 146.5 (C-2), 135.6 (C-3), 176.0 (C-4), 159.8 (C-5), 108.1 (CH-6), 163.1 (C-7), 93.0 (CH-8), 155.0 (C-9), 102.7 (C-10), 121.9 (C-1'), 114.9 (CH-2'), 145.0 (C-3'), 147.6 (C-4'), 115.6 (CH-5'), 119.9 (CH-6'), 73.1 (CH-1''), 70.2 (CH-2''), 78.9 (CH-3''), 70.6 (CH-4''), 81.5 (CH-5''), 61.4 (CH₂-6'')。H-1'' 与 C-5, C-6, C-7 之间的 HMBC 相关信号表明为 6 位碳苷。以上数据与文献[10]报道的 6-C-glucosyl-quercetin 数据基本一致,故鉴定化合物 3 为 6-C-glucosyl-quercetin。

化合物 4 白色粉末(甲醇),ESI-MS (-) m/z : 465 [M-H]⁻, 分子式 C₂₁H₂₂O₁₂。¹H-NMR (500 MHz, DMSO-d₆) δ : 4.96 (1H, d, J = 10.8 Hz, H-2), 4.48 (1H, dd, J = 10.8, 6.0 Hz, H-3), 5.91 (1H, s, H-8), 6.74 (1H, d, J = 1.0 Hz, H-2'), 6.87 (1H, d, J = 1.0 Hz, H-5'), 6.74 (1H, d, J = 1.0 Hz, H-6'), 4.80 (1H, d, J = 7.2 Hz, H-1''), 3.14 (1H, m, H-2''),

3.40 (1H, m, H-3''), 3.67 (1H, m, H-4''), 4.81 (1H, m, H-5''), 4.47 (2H, m, H-6''), 12.45, 10.55, 9.00, 8.94 (4H, s, OH-5, 7, 3', 4'), 5.78 (1H, d, $J = 6$ Hz, OH-3); $^{13}\text{C-NMR}$ (125 MHz, DMSO- d_6) δ : 82.8 (C-2), 71.5 (C-3), 197.8 (C-4), 162.5 (C-5), 106.0 (C-6), 165.9 (C-7), 94.7 (C-8), 161.2 (C-9), 100.1 (C-10), 127.9 (C-1'), 115.1 (C-2'), 144.9 (C-3'), 145.7 (C-4'), 115.2 (C-5'), 119.3 (C-6'), 72.9 (C-1''), 70.2 (C-2''), 79.0 (C-3''), 70.6 (C-4''), 81.4 (C-5''), 61.5 (C-6''). 以上数据与文献[11]报道的 6-*C*-glucosyl-3, 3', 4', 5, 7-pentahydroxyflavanone 数据基本一致, 故鉴定化合物 4 为 6-*C*-glucosyl-3, 3', 4', 5, 7-pentahydroxyflavanone。

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