^{13}C-NMR (DMSO-d_6) δ: 156.8 (C-4), 129.2 (C-2, 6), 128.8 (C-1), 114.9 (C-3, 5), 71.6 (C-7), 64.5 (C-1′), 15.1 (C-2′). It was identified as 4-hydroxybenzyl ether by spectral analysis and comparison with data of literature[3].

Compound Ⅳ: Brown amorphous powder, FAB-MS; 307.0 $[M + Na]^+$, 284.0 $[M]^+$; ^{1}H-NMR (DMSO-d_6) δ: 9.37 (s, OH), 8.99 (1H, s, H-5), 7.59 and 7.53 (each 1H, d, J = 9.0 Hz, H-9, 10), 7.23 (1H, s, H-8), 7.00 and 6.80 (each 1H, d, J = 2.5 Hz, H-1, 3), 4.07, 3.95, 3.88 (each 3H, s, OCH_3); ^{13}C-NMR (DMSO-d_6) δ: 158.6 (C-2), 156.9 (C-4), 147.9 (C-7), 145.3 (C-6), 133.9 (C-10a), 127.0 (C-4b), 126.9 (C-8a), 124.7 (C-9), 123.6 (C-10), 114.8 (C-4a), 111.9 (C-5), 108.8 (C-1), 101.5 (C-8), 99.0 (C-3), 55.9, 55.2, 55.1 (OCH_3). It was identified as 6-hydroxy-2, 4, 7-trimethoxyphenanthrene by spectral analysis and comparison with data of literature[4, 5].

Compound Ⅴ: White powder; mp 108 ℃-109 ℃; FAB-MS: 749.3 $[M + Na]^+$, 765.3 $[M + K]^+$; ^{1}H-NMR (DMSO-d_6) δ: malic acid moiety: 2.83 and 2.60 (each 1H, d, J = 15.5 Hz, H-3), 1.54 (1H, m, H-5), 0.96 and 1.22 (each 1H, m, H-6), 0.74 (3H, t, J = 7.5 Hz, H-7), 0.80 (3H, d, J = 7 Hz, H-8), benzyl moiety: 7.00 and 7.25 (each 4H, d, J = 8.5 Hz, H-2′, 6′, 2″, 6″, 3′, 5′, 3″, 5″), 5.02 (2H, s, H-7′), 4.92 (2H, s, H-7″), glucose moiety: 4.83 (2H, d, J = 7.5 Hz, H-1×2), 3.12-3.32 (8H, m, H-2, 3, 4, 5×2), 3.66 and 3.45 (each 2H, m, H-6); ^{13}C-NMR (DMSO-d_6) δ malic acid moiety: 174.0 (C-1), 77.8 (C-2), 41.7 (C-3), 170.0 (C-4), 42.4 (C-5), 23.4 (C-6), 12.2 (C-7), 12.3 (C-8), benzyl moiety: 157.2 (C-1′, 1″), 116.1 (C-2′, 6′, 2″, 6″), 129.6 (C-3′, 5′, 3″, 5″), 129.1 (C-4′, 4″), 65.8 (C-7′), 65.3 (C-7″), glucose moiety: 100.3 (C-1×2), 73.1 and 73.2 (C-2), 76.5 and 76.0 (C-3), 69.6 and 69.7 (C-4), 77.0 (C-5×2), 60.7 and 60.5 (C-6). It was identified as *bis*[4-(*β*-*D*-glucopyranosyloxy)-benzyl] (*s*)-(-)-2-*sec*-butylmalate by spectral analysis and comparison with data of literature[6].

References:

[1] Wu Z Y. *Compendium of New China* (*Xinhua*) *Herbal* (新华本草纲要) [M]. Vol 3. Shanghai: Shanghai Scientific and Technical Publishers, 1991.

[2] Taguchi H, Yosioka I, Yamasaki K, *et al*. Studies on the constituents of *Gastrodia elata* Blume [J]. *Chem Pharm Bull*, 1981, 29(1): 55-62.

[3] Zhou J, Pu X Y, Yang Y B. Nine phenolic components from fresh *Gastrodia elata* [J]. *Chin Sci Bull* (科学通报), 1981, (18): 1118-1120.

[4] Majumder P L, Banerjee S, Sen S. Three stilbenoids from the orchid *Agrostophyllum callosum* [J]. *Phytochemistry*, 1996, 42(3): 847-852.

[5] Coxon D T, Ogunadana S K, Dennis C. Antifungal phenanthrenes in yam tubers [J]. *Phytochemistry*, 1982, 21(6): 1389-1392.

[6] Li Y M, Zhou Z L, Hong Y F. Studies on the phenolic constituents of *Galeola faberic* [J]. *Acta Pharm Sin* (药学学报), 1993, 28(10): 766-771.

遍地金的化学成分研究

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遍地金 *Hypericum wightianum* Wall. ex Wight et Arn. 属藤黄科金丝桃属植物, 全草入药。分布于云南、四川、贵州、西藏等省。有收敛止血、清热解毒的功效。民间用于治疗小儿炎症、久痢、久泻、毒蛇咬伤等疾病[1]。近年来, 由于金丝桃属植物在抗抑郁和抗病毒方面的突出作用[2~5], 该属植物的研究受到普遍重视。我国金丝桃属植物有约 50 种, 多为特有种, 但大部分未做化学成分研究或研究不深入。遍地金的化学成分国内外尚未见报道, 为更好地开发和利用我国金丝桃属植物资源, 我们对遍地金

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的化学成分进行了研究, 从中分离得到 6 个化合物, 这些化合物均为首次从该植物中分离得到。

1 仪器和材料

XRC-1 型熔点仪(温度计未校正), VG Auto Spec 3000 型质谱仪, Brucker AC-300P 型核磁共振仪(TMS 内标), 薄层色谱硅胶 G60 和柱色谱硅胶均为青岛海洋化工厂产品, 药材采自云南西双版纳, 由中国科学院西双版纳热带植物园崔景云研究员鉴定。

2 提取分离

遍地金全草 1.6 kg, 粉碎, 90% 乙醇回流提取 3 次, 提取液浓缩得浸膏 200 g。浸膏用甲醇溶解, 石油醚萃取, 得萃取物 54 g。甲醇相蒸干, 用 1% 碳酸钠溶解, 氯仿萃取, 得萃取物 13 g。碳酸钠溶液再用稀盐酸调 pH 至 4～5, 用醋酸乙酯萃取, 得萃取物 55 g。各萃取物分别反复硅胶柱色谱分离, 石油醚-丙酮, 氯仿-甲醇梯度洗脱。从石油醚相得化合物 I (100 mg), 氯仿相得化合物III(45 mg), 醋酸乙酯相得化合物 II(50 mg), IV(76 mg), V(70 mg), VI (292 mg)。

3 结构鉴定

化合物 I: 无色针晶(丙酮), mp 141 ℃～142 ℃。与 β-谷甾醇标准品 TLC 的 Rf 值一致, 且混合熔点不下降, 故鉴定为 β-谷甾醇。

化合物II: 白色粉末, 272 ℃～274 ℃。与胡萝卜苷标准品 TLC 的 Rf 值一致, 且混合熔点不下降, 故鉴定为胡萝卜苷。

化合物III: 黄色粒状晶体(氯仿-甲醇), mp 193 ℃～195 ℃。ESI-MS m/z: 383$[M+H]^+$, 381$[M-H]^-$, 366$[M-H-CH_3]^-$。^{1}H-NMR(DMSO-d_6) δ 13.12(OH-5), 9.83 and 9.41 (each 1H, s, OH-3′ and OH-4′), 7.55(1H, d, J= 1.8 Hz, H-2′), 7.44 (1H, dd, J= 8.4, 1.8 Hz, H-6′), 6.90(1H, d, J= 8.4 Hz, H-5′), 6.60(1H, d, J= 9.9 Hz, H-4″), 6.46 (1H, s, H-6), 5.78(1H, d, J= 9.9 Hz, H-3″), 3.79 (3H, s, OCH_3-3), 1.43(6H, s, 2×CH_3-2″)。以上数据与文献报道的 7, 8-(2″, 2″-二甲基吡喃)-5, 3′, 4′-三羟基-3-甲氧基黄酮数据一致[6]。

化合物IV: 黄色针晶(氯仿-甲醇), mp 282 ℃～284 ℃。ESI-MS m/z: 317$[M+H]^+$, 315$[M-H]^-$, 300$[M-H-CH_3]^-$。^{1}H-NMR(DMSO-d_6) δ 12.71 (OH-5), 10.86(OH-7), 9.78 and 9.42(each 1H, s, OH-3′ and OH-4′), 7.55(1H, d, J= 2.1 Hz, H-2′), 7.45(1H, dd, J= 8.0, 2.1 Hz, H-6′), 6.91(1H, d, J= 8.0 Hz, H-5′), 6.41(1H, d, J= 2.1 Hz, H-8), 6.20(1H, d, J= 2.1 Hz, H-6), 3.77(3H, s, OCH_3-3)。以上数据与文献报道的槲皮素-3-甲醚数据一致[7]。

化合物V: 黄色针晶(氯仿-甲醇), mp 300 ℃～302 ℃。^{1}H-NMR数据与文献报道的槲皮素数据一致[8]。

化合物VI: 黄色粉末, mp 266 ℃～268 ℃。^{1}H-NMR(DMSO-d_6) δ 12.48(OH-5), 9.60(each 1H, br. s, OH-3, OH-3′ and OH-4′), 7.72(1H, d, J= 1.5 Hz, H-2′), 7.58(1H, dd, J= 8.4, 1.5 Hz, H-6′), 6.90(1H, d, J= 8.1 Hz, H-5′), 6.79(1H, d, J= 1.5 Hz, H-8), 6.41(1H, d, J= 1.5 Hz, H-6), 5.54(1H, s, H-1 of rhamnose), 1.14(3H, d, J= 6.0 Hz, CH_3 of rhamnose)。2 mol/L HCl 50 ℃～60 ℃水解 24 h, 水解产物在 TLC 上检测出鼠李糖, 故确定为鼠李糖苷。以上数据与文献报道的槲皮素-7-*O*-α-*L*-鼠李糖苷数据一致[9]。

References:

[1] Wu Z Y. *Compendium of New China* (*Xinhua*) *Herbal* (新华本草纲要) [M]. Vol I. Shanghai: Shanghai Scientific and Technical Publishers, 1988.

[2] Dewilde A, Pellieux C, Hajjam S, *et al*. Virucidal activity of pure singlet oxygen generated by thermolysis of a water-soluble naphthalene endoperoxide [J]. *J Phytochem Phytobiol B*, 1996, 36(1): 23-29.

[3] Bennett D A Jr, Phun L, Polk J F, *et al*. Neuropharmacology of St. John's wort (*Hypericum*) [J]. *Ann Pharmacother*, 1998, 32(11): 1201-1208.

[4] Lenoir S, Degenring F H, Saller R. A double-blind randomized trial to investigate three different concentration of a standardized fresh plant extract obtained from the shoot tips of *Hypericum perforatum* L. [J]. *Phytomedicine*, 1999, 6 (3): 141-146.

[5] Calapai G, Crupi A, Firenzuoli F, *et al*. Effects of *Hypericum perforatum* on levels of 5-hydroxytryptamine, noradrenaline and dopamine in the cortex, diencephalon and brainstem of the rat [J]. *J Pharm Pharmacol*, 1999, 51(6): 723-728.

[6] Wu Q L, Wang S P, Du L J, *et al*. Chromone glycosides and flavonoids from *Hypericum japonicum* [J]. *Phytochemistry*, 1998, 49(5): 1417-1420.

[7] Herz W, Gibaja S, Bhat S V, *et al*. Dihydroflavonols and other flavonoids of *Eupatorium* species [J]. *Phytochemistry*, 1972, 11: 2859-2863.

[8] Qiu S X, Zhang Z X, Zhou J. The flavonol constituents of *Cynanchum thesioides* var. *australe* [J]. *Acta Bot Yunnan* (云南植物研究), 1990, 12(2): 227-228.

[9] Liao X, Chen Y Z, Ding L S, *et al*. Chemical constituents from *Anemone rupestris* ssp. *gelida* [J]. *Nat Prod Res Dev* (天然产物研究与开发), 1999, 11(4): 1-6.