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大苞蛇根草化学成分的研究

李 静[1,2], 宋启示[1], 项 伟[1*], 杨淑敏[1]

[1]中国科学院西双版纳热带植物园, 昆明 650223; [2]中国科学院研究生院, 北京 100039

摘 要: 利用柱色谱技术进行分离纯化, 通过理化性质及波谱方法对大苞蛇根草单体化合物进行了结构鉴定。从中共得到 6个单体化合物, 分别为豆甾醇 (**1**)、β-谷甾醇 (**2**)、胡萝卜甙 (**3**)、3β-乙酸基-20-羽扇豆烷 (**4**)、无羁萜 (**5**)、铁力木酸 (**6**)。均为首次从该植物中得到。

关键词: 蛇根草属; 大苞蛇根草; 化学成分

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Chemical Studies on *Ophiorrhiza grandibracteolata*

LI Jing[1,2], SONG Qi-shi[1], XIANG Wei[1*], YANG Shu-min[1]

[1]*Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences, Kunming 650223, China;*

[2]*The Graduate School of the Chinese Academy of Science, Beijing 100039, China*

Abstract To investigate the chemical constituents of *Ophiorrhiza grandibracteolata*, the compounds were separated with column chromatography and their chemical structures were identified by physiochemical and spectral method respectively. Six compounds were isolated from the plant. They were identified as α-ecdysone (**1**), β-daucosterol (**2**), vincosamide (**3**), 3β-acetoxy-20-lupanol (**4**), friedelin (**5**), myrtifolic acid (**6**). The six compounds were isolated from the plant for the first time.

Key words *Ophiorrhiza*; *Ophiorrhiza grandibracteolata*; chemical constituents

大苞蛇根草 (*Ophiorrhiza grandibracteolata*) 属茜草科蛇根草属多年生草本植物且为我国所特有, 生于海拔 1500米左右山区林间树阴间。主要分布于我国华东、华中及西南、华南等地。蛇根草 (日本蛇根草) 在《浙江民间草药》中则记述: 具有"治咳嗽, 肺痨, 吐血"的作用; 在《浙江民间常用草药》则称其有"活血化淤, 清肺发散"的作用。广泛的应用于治疗伤筋、扭伤脱臼、流火和月经及慢性气管炎的临床实验中[1]。目前对于蛇根草属植物的研究报道较少[2-5]。为了有效保护和合理开发蛇根草资源, 从中找寻有药用价值的生物活性成分, 我们对产自云南沧源县大苞蛇根草全草进行系统的研究, 从中分离到了 6种化合物, 均为首次从该种植物中得到。

1 仪器与材料

XTRC-1显微熔点仪上, 温度计未校正; Bruker AM-400, DRX-500 核磁共振仪, TMS 为内标; VG-AutoSpec-3000型质谱仪 (英国 VG公司); 柱层析硅胶 (200~300目)、薄层硅胶板 (50 mm × 100 mm, 青岛海洋化工厂); DM-130大孔树脂 (山东鲁抗医药股份有限公司); 大苞蛇根草样品采集于云南省沧源县南滚河自然保护区。采集的原料于背阴处晾干粉碎, 过 2号筛得粗粉, 备用。

2 提取与分离

大苞蛇根草全草 3.2 kg 粉碎后用工业甲醇冷凝回流提取 3次, 每次 24 h。合并提取液, 减压浓缩得到甲醇浸膏 (475.5 g), 浸膏用数倍量的水分散均匀后依次用石油醚、氯仿、正丁醇萃取, 得到石油醚萃取物 289.2 g 氯仿萃取物 148.4 g 正丁醇萃取物 114 g。石油醚和氯仿部分均以两倍量的硅胶 (100目) 拌样后以正相硅胶柱 (200~300目) 层析, 以石油醚-丙酮为洗脱剂梯度反复洗脱 (1:0~8:2, 梯度为 5%), 其中石油醚部分得化合物 **3** (483 mg), **4** (300 mg), **5** (40 mg), 氯仿部分得化合物 **1** (6 mg), **2** (13 mg), **5** (40 mg)。

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* 通讯作者 Tel: 86-871-5160902; E-mail: xiangwe@Xtbg.ac.cn

3 结构鉴定

化合物 **1** 白色针状结晶 (石油醚-丙酮), mp 142~144 ℃。TLC展开后紫外灯 (254 nm)下无荧光, 硫酸-乙醇显紫红色, 与豆甾醇标准品在多种溶剂体系作 TLC对照, R_f 值相同, 与豆甾醇标准品混合熔点不下降, 故确定为豆甾醇。

化合物 **2** $C_{29}H_{50}O$, M = 414, 无色片状结晶 (丙酮), mp 137~139 ℃, Liebermann-Burchard反应 (醋酐-浓硫酸反应)显紫红色后迅速变为绿色, Salkowski反应 (浓硫酸-氯仿反应)呈阳性, 该化合物与 β-谷甾醇对照品共进行薄层层析, 石油醚: 乙酸乙酯 (4∶1)和石油醚: 乙醚 (2∶1)展开, R_f 值一致; 以上信息及数据与参考文献报导一致[6,7], 确定该化合物为 β-谷甾醇。

化合物 **3** 白色无定形粉末 (甲醇), mp 281~282 ℃, Liebermann-Burchard 反应 (醋酐-浓硫酸反应)阳性, Molish反应阳性, TLC展开后, 紫外灯 (254 nm)下无荧光, 硫酸-乙醇显紫红色, 在多种有机溶剂中不易溶解。^{1}H NMR (500 MHz, DMSO)有 δ 5.29 (1H, brs, 6-H)烯氢信号, δ 4.18 (1H, d, J = 7.2 Hz)糖基端上氢信号, 呈 β构型, 2.84~4.20范围内存在糖基上的多个质子。δ 0.99 (3H, s, 19-CH_3)和 0.63 (3H, s, 18-CH_3)为角甲基上的氢信号, 0.88 (3H, d, J = 6.3 Hz), 0.86 (3H, t, J = 6.0 Hz), 0.81 (3H, d, J = 5.4 Hz)和 0.79 (3H, d, J = 6.0 Hz)为甲基上的氢信号; 以上数据与文献报道[8]对照, 确定该化合物为胡萝卜苷。

化合物 **4** 白色针状结晶 (石油醚-丙酮), mp 253~254 ℃; 与发烟硫酸作用呈红色。^{1}H NMR (CDCl$_3$)显示有 9个甲基 [0.81 (s), 0.85 (s), 0.86 (s), 0.87 (s), 0.96 (s), 1.07 (s), 1.13 (s), 1.18 (s), 2.05 (s)]; 且^{13}C NMR (CDCl$_3$) δ 38.3 (C-1), 27.5 (C-2), 80.9 (C-3), 37.7 (C-4), 55.2 (C-5), 18.2 (C-6), 34.4 (C-7), 41.3 (C-8), 50.1 (C-9), 37.0 (C-10), 21.4 (C-11), 27.4 (C-12), 37.4 (C-13), 44.6 (C-14), 27.7 (C-15), 35.5 (C-16), 43.5 (C-17), 48.3 (C-18), 49.9 (C-19), 73.5 (C-20), 29.0 (C-21), 40.2 (C-22), 28.0 (C-23), 16.1 (C-24), 16.5 (C-25), 16.2 (C-26), 14.7 (C-27), 19.2 (C-28), 24.7 (C-29), 32.5 (C-30), 21.3 (C-1′), 177.0 (C-2′)与参考文献[9]一致, 故确定为 3β-乙酸基-20-羽扇豆烷。

化合物 **5** 白色针状结晶 (石油醚-丙酮), mp. 260~263 ℃, 与发烟硫酸作用呈红色。EI-MS m/z: 426 (36), 411 (32), 341 (16), 302 (36), 273 (72), 254 (40), 205 (80), 269 (100); IR ν_{max}^{KBr} cm^{-1}: 2926, 2971, 2868, 1714, ^{1}H NMR (CDCl$_3$) δ: 0.89 (3H, d, J = 6.8 Hz, 23-CH_3), 0.74 (3H, s, 24-CH_3), 0.88 (3H, s, 25-CH_3), 1.02 (3H, s, 26-CH_3), 1.06 (3H, s, 27-CH_3), 1.20 (3H, s, 28-CH_3), 1.01 (H, s, 29-CH_3), 0.97 (3H, s, 30-CH_3), 2.3~2.4 (2H, m, 2-H), 2.27 (1H, q, J = 6.8 Hz, 4-H); ^{13}C NMR (CDCl$_3$) δ: 22.3 (C-1), 41.5 (C-2), 213.2 (C-3), 58.2 (C-4), 42.1 (C-5), 41.2 (C-6), 18.2 (C-7), 51.5 (C-8), 37.5 (C-9), 59.5 (C-10), 35.3 (C-11), 23.7 (C-12), 39.0 (C-13), 38.8 (C-14), 30.1 (C-15), 36.1 (C-16), 32.5 (C-17), 43.5 (C-18), 36.0 (C-19), 28.3 (C-20), 32.9 (C-21), 39.1 (C-22), 16.8 (C-23), 14.7 (C-24), 18.2 (C-25), 17.7 (C-26), 19.3 (C-27), 31.7 (C-28), 34.4 (C-29), 31.9 (C-30)与文献值[10]一致, 确定为无羁萜。

化合物 **6** 白色粉末 (甲醇), mp. 259~260 ℃, 分子式为 $C_{30}H_{48}O_3$, Liebermann-Burchard反应成阳性。FAB-MS m/z (rel. int): 455 (100), 456 (30)。^{1}H NMR (400 MHz, C_5D_5N) δ 5.76 (1H, s, H-COOH), 5.49 (1H, s, H-7), 3.46 (1H, m, H-3OH), 七个甲基峰 [0.88 (s), 0.94 (d), 0.99 (d), 1.02 (s), 1.22 (s), 1.24 (s), 2.49 (s)]; 从^{13}C NMR (125 MHz, C_5D_5N)谱上可以看出 δ 178.3为 28位羧基碳, δ 138.2和 124.5为 7, 8位双键碳, δ 76.8为 3位与羟基相连的碳; 以上数据与文献报道[11]一致, 故确定为铁力木酸。

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