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传统中药漆姑草(*Sagina japonica*)中的 C-27甾体成分

贾爱群[1,2], 谭宁华[1], 周 俊[1*]

[1]中国科学院昆明植物研究所, 昆明 650204; [2]南京理工大学化工学院, 南京 210014

摘 要: 利用 Diaion HP 20及硅胶柱层析进行化合物的分离,从乙酸乙酯萃取部位分离得到了 4个化合物,借助多种光谱技术进行结构鉴定分别鉴定为(25*R*)-螺甾-5-烯-1β, 3β-二醇 1-O-{O-α-*L*-鼠李吡喃糖苷-(1→2)-O-[β-*D*-木糖吡喃糖苷-(1→3)]-β-*D*-岩藻吡喃糖苷}(ophiopogonin D, **1**), (25*R*)-ruscogenin 1-O-[2-O-(乙酰基)-α-*L*-鼠李吡喃糖苷-(1→2)][β-*D*-木糖吡喃糖苷-(1→3)]-β-*D*-岩藻吡喃糖苷(**2**), (25*R*)-ruscogenin 1-O-[3-O-(乙酰基)-α-*L*-鼠李吡喃糖苷-(1→2)][β-*D*-木糖吡喃糖苷-(1→3)]-β-*D*-岩藻吡喃糖苷(**3**), 蜕皮甾酮(**4**)。所有化合物均为首次从该植物中分得。

关键词: 石竹科; 漆姑草; C-27甾体; 化学成分

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C-27 Steriods in *Sagina japonica* (Caryophyllaceae)

JIA Ai-qun[1,2], TAN Ning-hua[1], ZHOU Jun[1*]

[1]*Kunming Institute of Botany, CAS, Kunming 650204, China;*

[2]*School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210014, China*

Abstract C-27 steriods were isolated on Diaion HP-20 and silica gel column chromatography and the structures were identified by spectral technologies. Four compounds from ethyl acetate extracts were elucidated as (25-*R*-) ophiopogonin D, (25*R*)-spirost-5-ene-1β, 3β-diol[(25*R*)-ruscogenin] 1-O-{O-α-*L*-rhamnopyranosyl-(1→2)-O-[β-*D*-xyloptranosyl-(1→3)]-β-*D*-fucopyranoside} (**1**), (25*R*)-ruscogenin 1-O-[2-O-(acetyl)-α-*L*-rhamnopyranosyl-(1→2)][β-*D*-xylopyranosyl-(1→3)]-β-*D*-fucopyranoside (**2**), (25*R*)-ruscogenin 1-O-[3-O-(acetyl)-α-*L*-rhamnopyranosyl-(1→2)][β-*D*-xylopyranosyl-(1→3)]-β-*D*-fucopyranoside (**3**), ecdysterone(**4**). All of these compounds were first isolated from *Sagina japonica*.

Key words Caryophyllaceae; *Sagina japonica*; C-27 steroid; constituents

漆姑草(*Sagina japonica* (Sweet) Ohwi)又名瓜槌草,珍珠草,羊毛草,星宿草,日本漆姑草,腺漆姑草等,为石竹科漆姑草属植物。漆姑草属约 30种,分布于北温带。中国约 4种,南北均产。该种一年生小草本。分布于滇中、滇西北、滇东北和滇东南海拔 1300~3800 m 区域[1],我国长江流域和黄河流域各省区及东北、台湾、喜马拉雅地区(尼泊尔至阿萨姆),朝鲜、日本也有。全草味辛,性温,治面寒疼,可入药,退热解毒,秦岭南北用全草提脓拔毒,鲜叶揉汁可涂漆疮[2]。其化学成分研究不多,文献报道仅有黄酮类[3,4]成分。为寻找漆姑草中的活性成分,作者对该植物进行了系统的化学成分研究。现报道从云南产的漆姑草全草中分离鉴定了 4个 C-27甾体化合物,均为首次从该植物中分离得到。

1 仪器、材料和试剂

VG Auto Spec-3000型质谱仪; Bruker AM-400型核磁共振仪, TMS为内标; 200~300目和 100~200目柱层析硅胶及层析用 TLC硅胶板(青岛海洋化工厂); Sephadex LH-20(Pharmacia公司); Rp-18 (Fuji Silysia Chemical Ltd.); Diaion HP 20(日本); 其余试剂均为分析纯。

实验材料 2002年 9月采自云南嵩明县,经中国科学院昆明植物研究所周浙昆研究员鉴定该植物为漆姑草(*Sagina japonica* (Sweet) Ohwi)全草。

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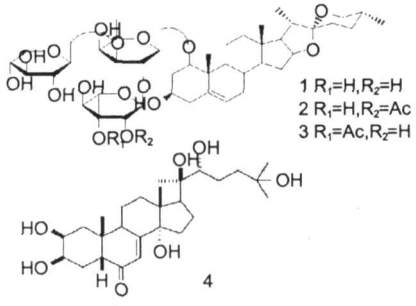
* 通讯作者 Tel: 86-871-5223264; E-mail: jzhou@mail.kib.ac.cn

2　提取与分离

漆姑草干重 21.0 kg, 粉碎后用 95% 工业乙醇分别回流提取三次 (3、1、1 h), 合并提取液, 浓缩, 后悬浮水中, 依次用石油醚 (60~90 ℃)、乙酸乙酯和正丁醇各萃取三次, 将乙酸乙酯萃取液合并, 减压蒸馏, 得膏状物约 430 g。取该部位 100 g 首先用 Diaion HP 20脱色, 后反复进行硅胶柱层析、Sephadex LH-20凝胶层析及 Rp-18柱层析, 分离得到化合物 **1** (58 mg), **2**(29 mg), **3**(11 mg), **4**(104 mg)。



3　结构鉴定

化合物 **1**　白色粉末, mp. 262~265 ℃, FAB$^-$-MS: 1008 (100, 855 + $C_7H_7NO_3$), 855 (30, M + 1), 737, 577, 255, 197; ^{13}C NMR (100 MHz, CD_3OD) δ 84.61 (d, C-1), 38.12 (t, C-2), 68.33 (d, C-3), 43.01 (t, C-4), 139.64 (s, C-5), 124.85 (d, C-6), 32.11 (t, C-7), 33.14 (d, C-8), 50.64 (d, C-9), 42.90 (s, C-10), 24.00 (t, C-11), 40.27 (t, C-12), 40.53 (s, C-13), 57.27 (d, C-14), 32.49 (t, C-15), 81.20 (d, C-16), 63.12 (d, C-17), 16.92 (q, C-18), 15.09 (q, C-19), 42.05 (d, C-20), 15.00 (q, C-21), 109.33 (s, C-22), 32.00 (t, C-23), 32.11 (t, C-24), 30.66 (d, C-25), 67.21 (t, C-26), 17.38 (q, C-27), 100.63 (d, fuc C-1), 73.50 (d, fuc C-2), 85.62 (d, fuc C-3), 72.76 (d, fuc C-4), 70.87 (d, fuc C-5), 17.19 (q, fuc C-6), 106.71 (d, xyl C-1), 74.75 (d, xyl C-2), 78.39 (d, xyl C-3), 71.07 (d, xyl C-4), 67.12 (t, xyl C-5), 101.80 (d, rha C-1), 72.61 (d, rha C-2), 72.76 (d, rha C-3), 74.34 (d, rha C-4), 69.40 (d, rha C-5), 19.21 (q, rha C-6); ^{1}H NMR (400 MHz, C_5D_5N) δ 6.34 (1H, *br* s, rha H-1), 5.58 (1H, *br* d, *J* = 5.38, H-6), 4.96 (1H, d, *J* = 7.58 Hz, xyl H-1), 4.61 (1H, d, *J* = 9.16 Hz, fuc H-1), 1.72 (3H, d, *J* = 6.10 Hz, rha Me-6), 1.50 (3H, d, *J* = 6.26 Hz, fuc Me-6), 1.40 (1H, s, Me-19), 1.06 (3H, d, *J* = 6.83 Hz, Me-21), 0.67 (3H, d, *J* = 5.02 Hz, Me-27), 0.85 (3H, s, Me-18)。以上数据与文献[5-7]报道的化合物 (25*R*)-螺甾-5-烯-1β, 3β-二醇 1-O-{O-α-*L*-鼠李吡喃糖苷-(1→2)-O-[β-*D*-木糖吡喃糖苷-(1→3)]-β-*D*-岩藻吡喃糖苷} (Ophiopogonin D) 基本一致。

化合物 **2**　白色粉末, FAB$^-$-MS: 1050 (100, M + $C_7H_7NO_{3+1}$) 896 (70, M$^+$), 722, 456, 131; ^{13}C NMR (100 MHz, CD_3OD) δ 84.98 (d, C-1), 38.13 (t, C-2), 68.35 (d, C-3), 43.90 (t, C-4), 139.65 (s, C-5), 124.90 (d, C-6), 32.13 (t, C-7), 33.17 (d, C-8), 50.68 (d, C-9), 42.92 (s, C-10), 24.07 (t, C-11), 40.30 (t, C-12), 40.56 (s, C-13), 57.29 (d, C-14), 31.86 (t, C-15), 81.23 (d, C-16), 63.14 (d, C-17), 16.96 (q, C-18), 15.11 (q, C-19), 42.08 (d, C-20), 14.36 (q, C-21), 109.37 (s, C-22), 32.51 (t, C-23), 29.34 (t, C-24), 30.68 (d, C-25), 66.90 (t, C-26), 17.40 (q, C-27), 100.48 (d, fuc C-1), 73.57 (d, fuc C-2), 84.98 (d, fuc C-3), 72.65 (d, fuc C-4), 71.02 (d, fuc C-5), 17.30 (q, fuc C-6), 106.79 (d, xyl C-1), 74.88 (d, xyl C-2), 78.09 (d, xyl C-3), 71.18 (d, xyl C-4), 67.14 (t, xyl C-5), 101.68 (d, rha C-1), 70.03 (d, rha C-2), 76.55 (d, rha C-3), 71.18 (d, rha C-4), 69.29 (d, rha C-5), 19.02 (q, rha C-6), OAc (→3 rhamnose) 21.38, 170.96; ^{1}H NMR (400 MHz, C_5D_5N) δ 6.45 (1H, *br* d, *J* = 7.29, rha H-1), 5.58 (1H, *br* d, *J* = 5.39 Hz, H-6), 5.01 (1H, d, *J* = 7.70 Hz, xyl H-1), 4.62 (1H, d, *J* = 4.12 Hz, fuc H-1), 1.73 (3H, d, *J* = 5.67 Hz, rha Me-6), 1.50 (3H, d, *J* = 5.43 Hz, fuc Me-6), 1.41 (1H, *br* s, Me-19), 1.06 (3H, d, *J* = 6.64 Hz, Me-21), 0.67 (3H, d, *J* = 4.63, Me-27), 0.85 (3H, s, Me-18)。以上数据与文献[5-7]报道的化合物为 (25R)-ruscogenin 1-O-[2-O-(乙酰基)-α-*L*-鼠李吡喃糖苷-(1→2)][β-*D*-木糖吡喃糖苷-(1→3)]-β-*D*-岩藻吡喃糖苷基本一致。

化合物 **3**　白色粉末, FAB$^-$-MS: 1050 (100, M + $C_7H_7NO_3$ + 1), 896 (70, M$^+$), 722, 456, 131; ^{13}C NMR (100 MHz, CD_3OD) δ 84.74 (d, C-1), 38.13 (t, C-2), 68.35 (d, C-3), 43.90 (t, C-4), 139.65 (s, C-5), 124.90 (d, C-6), 32.51 (t, C-7), 33.17 (d, C-8), 50.68 (d, C-9), 42.92 (s, C-10), 24.07 (t, C-11), 40.30 (t, C-12), 40.56 (s, C-13), 57.29 (d, C-14), 31.86 (t, C-15), 81.23 (d, C-16), 63.14 (d, C-17), 17.21 (q, C-18), 15.02 (q, C-19), 42.08 (d, C-20),

14.89(q, C-21), 109.37(s, C-22), 32.13(t, C-23), 30.05(t, C-24), 30.68(d, C-25), 66.90(t, C-26), 17.21(q, C-27), 100.59(d, fuc C-1), 73.77(d, fuc C-2), 85.55(d, fuc C-3), 72.79(d, fuc C-4), 71.18(d, fuc C-5), 17.40(q, fuc C-6), 106.04(d, xyl C-1), 74.79(d, xyl C-2), 78.47(d, xyl C-3), 70.81(d, xyl C-4), 67.23(t, xyl C-5), 98.45(d, rha C-1), 74.87(d, rha C-2), 70.89(d, rha C-3), 74.69(d, rha C-4), 69.56(d, rha C-5), 19.16(q, rha C-6); ^{1}H NMR(400 MHz, C_5D_5N) δ 6.45(1H, *br* d, *J* = 7.29 Hz, rha H-1), 5.58(1H, *br* d, *J* = 5.39 Hz, H-6), 5.01(1H, d, *J* = 7.70, xyl H-1), 4.62(1H, d, *J* = 4.12 Hz, fuc H-1), 1.73(3H, d, *J* = 5.67 Hz, rha Me-6), 1.50(3H, d, *J* = 5.43 Hz, fuc Me-6), 1.41(1H, *br* s, Me-19), 1.06(3H, d, *J* = 6.64 Hz, Me-21), 0.67(3H, d, *J* = 4.63 Hz, Me-27), 0.85(3H, s, Me-18)。以上数据与文献[5-7]报道的化合物为(25R)-ruscogenin 1-O-[3-O-(乙酰基)-α-L-鼠李吡喃糖苷-(1→2)][β-D-木糖吡喃糖苷-(1→3)]-β-D-岩藻吡喃糖苷基本一致。

化合物 **4** 无色结晶, mp.246~248 ℃, FAB$^-$-MS: 479(100, M-1), 328, 295, 273, 183, 125; ^{13}C NMR(100 MHz, CD_3OD) δ 38.03(t, C-1), 68.21(d, C-2), 68.13(d, C-3), 32.48(t, C-4), 51.44(d, C-5), 203.57(s, C-6), 121.73(d, C-7), 166.16(s, C-8), 34.52(d, C-9), 38.72(s, C-10), 21.54(t, C-11), 31.81(t, C-12), 48.18(s, C-13), 84.28(s, C-14), 32.08(t, C-15), 21.54(t, C-16), 50.17(d, C-17), 17.94(q, C-18), 24.51(q, C-19), 77.64(s, C-20), 21.74(q, C-21), 76.96(d, C-22), 27.51(t, C-23), 42.66(t, C-24), 69.69(s, C-25), 30.05(q, C-26), 30.15(q, C-27); ^{1}H NMR(500 MHz, C_5D_5N) δ 2.16(1H, m, eq H-1), 1.95(1H, m, ax H-1), 3.94(1H, *br* s, H-2), 3.84(1H, m, H-3), 2.12(1H, m, ax H-4), 2.36(1H, m, eq H-4), 3.16(1H, dd, *J* = 2.52, 10.16, H-5), 5.80(1H, s, H-7), 3.34(1H, m, H-9), 1.88(1H, m, eq H-11), 1.71(1H, m, ax H-11), 2.36(2H, m, H-12), 1.78(2H, m, H-15), 1.95(2H, m, H-16), 2.36(1H, dd, *J* = 8.56, 8.28 Hz, H-17), 0.95(3H, s, H-18), 0.88(3H, s, H-19), 1.19(3H, s, H-21), 3.93(1H, m, H-22), 1.97(1H, m, H-23), 1.77(1H, m, H-23), 1.61(2H, m, H-24), 1.19(3H, s, H-26), 1.18(3H, s, H-27)。以上数据与文献[8]报道的化合物蜕皮甾酮基本一致。

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