

多穗金粟兰乌药烷型倍半萜二聚体类化学成分研究

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摘要: 目的 对金粟兰属植物多穗金粟兰 *Chloranthus multistachys* 根部乙醇提取物的化学成分进行研究。方法 利用多种色谱技术进行分离纯化, 通过理化性质和波谱数据鉴定化合物结构。结果 从多穗金粟兰的氯仿和醋酸乙酯提取物中分离得到 12 个乌药烷型倍半萜二聚体, 鉴定其结构为环银线草醇 A-9-O- β -葡萄糖苷 (1)、环银线草醇 A (2)、银线草醇 B (3)、银线草醇 C (4)、银线草醇 D (5)、银线草醇 F (6)、银线草醇 G (7)、多穗金粟兰醇 B (8)、草珊瑚内酯 B (9)、sarglabolide I (10)、8-O-methyltianshananol (11)、henriol B (12)。结论 化合物 1、7、9~12 为首次从该植物中分离得到, 化合物 9 和 10 为首次从金粟兰属植物中分离得到。

关键词: 多穗金粟兰; 乌药烷型; 倍半萜二聚体; 草珊瑚内酯 B; sarglabolide I; henriol B

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Chemical constituents in lindenane-type sesquiterpene dimers in roots of *Chloranthus multistachys*

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Abstract: Objective To study the chemical constituents contained in the ethanol extracts from the roots of *Chloranthus multistachys*.

Methods Twelve compounds were separated from the roots of *C. multistachys* and their structures were identified by using various chromatographic techniques. **Results** The structures of the 12 lindenane-type sesquiterpene dimers from the chloroform and ethyl acetate extract in the roots of *C. multistachys* were identified on the basis of physicochemical properties and spectral data as 9-O- β -glucopyranosylcycloshizukaol A (1), cycloshizukaol A (2), shizukaol B (3), shizukaol C (4), shizukaol D (5), shizukaol F (6), shizukaol G (7), chloramultiol B (8), sarcandrolide B (9), sarglabolide I (10), 8-O-methyltianshananol (11), and henriol B (12).

Conclusion Compounds 1, 7, and 9—12 are isolated from the roots *C. multistachys* for the first time and compounds 9 and 10 are obtained from the plants of *Chloranthus* Sw. for the first time.

Key words: *Chloranthus multistachys* Pei; lindenane-type; sesquiterpene dimers; sarcandrolide B; sarglabolide I; henriol B

多穗金粟兰 *Chloranthus multistachys* Pei 为金粟兰科 (Chloranthaceae) 金粟兰属 *Chloranthus* Sw. 植物, 俗称白四块瓦、四大天王、四眼牛膝^[1], 常以根及根状茎入药, 有祛湿散寒、理气活血、散瘀解毒等功效, 有小毒, 民间广泛用于治疗跌打骨折、腰腿痛、白带、疗肿、皮肤瘙痒等病症^[2]。多穗金粟兰的化学成分研究较少, 只有从多穗金粟兰中分离了少量萜类、香豆素、甾醇等化合物的报道^[3-4]。而多穗金粟兰的同属植物如宽叶金粟兰、及己等的化学成分研究较多, 尤其从宽叶金粟兰、及己中分离

得到了一系列倍半萜二聚体类, 该类化合物结构新颖且复杂, 通常是以 2 分子倍半萜通过分子内的 endo Diels-Alder 环加成反应形成复杂的结构, 另外结构中往往还具有 α , β -不饱和 γ -内酯或 α , β 不饱和酮的结构片段, 部分化合物形成独特的大环结构, 最大的为 18 元环^[5]。图 1 是一个乌药烷型倍半萜含 18 元大环内酯结构的二聚体, 目前已从金粟兰属植物中分离得到了 55 个乌药烷型倍半萜二聚体类化合物, 其中 21 个化合物含 18 元环结构。这类化合物大多数具有良好的生物活性^[6], 引起了国内外学

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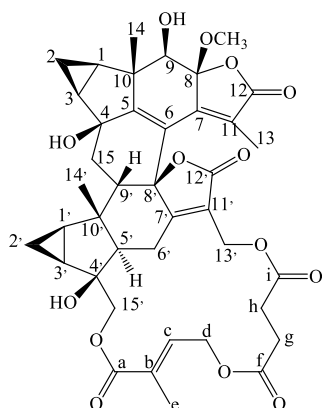


图1 化合物11的化学结构

Fig. 1 Structure of compound 11

者的广泛关注。

为了寻找多穗金粟兰中倍半萜二聚体类化合物,进一步开发利用该植物资源,本实验对多穗金粟兰根部氯仿和醋酸乙酯提取物进行了系统的分离研究,重点分离倍半萜二聚体类化合物。通过应用多种色谱技术从多穗金粟兰中分离得到12个乌药烷型倍半萜二聚体类化合物,分别鉴定为环银线草醇 A-9-O-β-葡萄糖苷(9-O-β-glucopyranosylcycloshizukaol A, **1**)、环银线草醇 A (cycloshizukaol A, **2**)、银线草醇 B (shizukaol B, **3**)、银线草醇 C (shizukaol C, **4**)、银线草醇 D (shizukaol D, **5**)、银线草醇 F (shizukaol F, **6**)、银线草醇 G (shizukaol G, **7**)、多穗金粟兰醇 B (chloramultiol B, **8**)、草珊瑚内酯 B (sarcandrolide B, **9**)、sarglabolide I (**10**)、8-O-methyltianmushanol (**11**)、henriol B (**12**)。化合物**1**、**7**、**9**~**12**为首次从该植物中分离得到,化合物**9**和**10**为首次从金粟兰属植物中分离得到。

1 仪器与材料

AB SCIEX TripleTOF 5600+高分辨飞行时间质谱联用仪(美国Sciex公司); Bruker AVANCE III HD 600 MHz 核磁共振仪(瑞士Bruker公司);薄层色谱硅胶 GF₂₅₄和柱色谱用硅胶(100~200目, 200~300目)均为青岛海洋化工厂产品; D101型大孔吸附树脂为天津海光化工有限公司生产;葡聚糖凝胶 Sephadex LH-20 为 Amersham Pharmacia Biotech 公司产品; Buchi R-205 型旋转蒸发仪(瑞士Buchi公司); Waters 半制备型液相色谱仪(美国Waters公司),制备型反相色谱柱为 YMC-Pack ODS-A C₁₈, (250 mm×20 mm, 5 μm),分析型反相色谱柱为 Kromasil 100A C₁₈ (150 mm×4.6 mm, 5 μm);所用试剂均为分析纯或色谱纯。

药材于2014年11月采自江西井冈山市,由江西中医药大学赖学文教授鉴定为金粟兰科金粟兰属植物多穗金粟兰 *Chloranthus multistachys* Pei, 凭证标本保存于江西中医药大学标本馆(20141116)。

2 提取与分离

干燥的多穗金粟兰根部 10.5 kg, 粉碎后用 95%乙醇冷浸提取3次。提取液减压回收溶剂得到总浸膏 312 g。总浸膏经硅胶减压柱分离,用石油醚、氯仿、醋酸乙酯、丙酮、甲醇依次洗脱,减压回收溶剂后得到石油醚部位(13 g)、氯仿部位(25 g)、醋酸乙酯部位(48 g)、丙酮部位(52 g)和甲醇部位(163 g)。

氯仿部位(25 g)经硅胶减压柱分离,以石油醚-醋酸乙酯(40:1→0:1)梯度洗脱,得到8个组分(LA~LH)。LD(5.0 g)经 ODS 分别用甲醇-水(30%、50%、70%、100%)洗脱,得到4个组分(LD1~LD4),其中 LD2 经制备液相(70%甲醇-水)分离,得到化合物**2**(89.1 mg)。LE(6.1 g)经硅胶色谱柱分离,以石油醚-丙酮(40:1→1:1)梯度洗脱,得到7个组分(LE1~LE7),其中 E5 经制备液相(67%甲醇-水)分离,得到化合物**3**(95.3 mg)、**7**(15.6 mg)。

醋酸乙酯部位(48 g)经硅胶减压柱分离,以石油醚-丙酮(10:1→0:1)梯度洗脱,得到5个组分(YA~YE)。YB(14.4 g)经硅胶色谱柱分离,以石油醚-丙酮(20:1→0:1)梯度洗脱,得到7个组分(YB1~YB7),其中 YB4 经制备液相(67%甲醇-水)分离,得到化合物**4**(45.0 mg)、**5**(35.5 mg)、**6**(12.9 mg); YC(14.4 g)经反相树脂分别用乙醇-水(30%、50%、70%、95%)洗脱,得到4个组分(YC1~YC4),YC1(5.1 g)经硅胶色谱柱分离,以石油醚-丙酮(10:1→0:1)梯度洗脱,得到5个组分(YC1-1~YC1-5),其中 YC1-4 经制备液相(60%甲醇-水)分离,得到化合物**8**(19.1 mg); YC2(8.0 g)经硅胶色谱柱分离,以石油醚-丙酮(20:1→0:1)梯度洗脱,得到6个组分(YC2-1~YC2-6),其中 YC2-4 经制备液相(50%甲醇-水)分离,得到化合物**1**(29.8 mg)、**9**(15.9 mg)、**10**(8.0 mg)、**11**(13.5 mg)、**12**(14.8 mg)。

3 结构鉴定

化合物**1**: 白色粉末, ESI-MS m/z : 733 $[M+Na]^+$, C₃₈H₄₆O₁₃。¹H-NMR (600 MHz, CDCl₃) δ: 2.00 (1H, m, H-1), 0.95 (1H, m, H-2α), 0.29 (1H, d, J =3.4 Hz, H-2β), 2.18 (1H, m, H-3), 6.97 (1H, s, H-6), 3.99

(1H, s, H-9), 1.53 (3H, s, H-13), 1.12 (3H, s, H-14), 3.31 (1H, d, $J = 13.5$ Hz, H-15 α), 2.20 (1H, d, $J = 13.5$ Hz, H-15 β), 3.69 (3H, s, 12-OMe), 1.88 (1H, m, H-1'), 0.90 (1H, m, H-2' α), 0.24 (1H, d, $J = 3.3$ Hz, H-2' β), 2.23 (1H, m, H-3'), 6.97 (1H, s, H-6'), 3.62 (1H, s, H-9'), 1.52 (3H, s, H-13'), 1.10 (3H, s, H-14'), 3.28 (1H, d, $J = 13.2$ Hz, H-15' α), 2.18 (1H, d, $J = 13.2$ Hz, H-15' β), 3.66 (3H, s, 12'-OMe), 4.62 (1H, d, $J = 8.4$ Hz, H-1''), 3.00 (1H, t, $J = 8.9$ Hz, H-2''), 3.59 (1H, t, $J = 9.7$ Hz, H-3''), 3.93 (1H, m, H-4''), 3.38 (1H, d, $J = 9.7$ Hz, H-5''), 3.74 (1H, m, H-6'' α), 3.83 (1H, m, H-6'' β); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ : 24.8 (C-1), 14.9 (C-2), 27.3 (C-3), 149.7 (C-4), 136.5 (C-5), 139.6 (C-6), 139.0 (C-7), 199.2 (C-8), 80.7 (C-9), 56.1 (C-10), 47.0 (C-11), 176.0 (C-12), 28.1 (C-13), 17.0 (C-14), 39.2 (C-15), 52.3 (12-OMe), 25.7 (C-1'), 14.4 (C-2'), 27.4 (C-3'), 148.7 (C-4'), 136.9 (C-5'), 139.3 (C-6'), 139.2 (C-7'), 198.7 (C-8'), 81.4 (C-9'), 55.8 (C-10'), 47.0 (C-11'), 176.1 (C-12'), 28.7 (C-13'), 16.4 (C-14'), 39.3 (C-15'), 52.4 (12'-OMe), 100.6 (C-1''), 72.5 (C-2''), 75.5 (C-3''), 67.7 (C-4''), 76.6 (C-5''), 60.8 (C-6''). 以上数据与文献报道基本一致^[7], 故鉴定化合物 **1** 为 A-9-O- β -葡萄糖苷。

化合物 **2**: 无色透明块状结晶 (甲醇), ESI-MS m/z : 571 $[\text{M} + \text{Na}]^+$, $\text{C}_{32}\text{H}_{36}\text{O}_8$ 。 $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 1.84 (2H, m, H-1, 1'), 0.88 (2H, m, H-2 α , 2 α'), 0.23 (2H, m, H-2 β , 2 β'), 1.98 (2H, m, H-3, 3'), 7.18 (2H, s, H-6, 6'), 3.81 (2H, s, H-9, 9'), 1.52 (6H, s, H-13, 13'), 1.01 (6H, s, H-14, 14'), 2.97 (2H, d, $J = 13.2$ Hz, H-15 α , 15 α'), 2.62 (2H, d, $J = 13.5$ Hz, H-15 β , 15 β'), 3.65 (3H, s, H-OCH₃); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ : 24.7 (C-1, 1'), 14.0 (C-2, 2'), 27.9 (C-3, 3'), 147.4 (C-4, 4'), 135.8 (C-5, 5'), 138.4 (C-6, 6'), 137.3 (C-7, 7'), 199.0 (C-8, 8'), 81.0 (C-9, 9'), 58.4 (C-10, 10'), 47.8 (C-11, 11'), 175.5 (C-12, 12'), 28.5 (C-13, 13'), 16.0 (C-14, 14'), 38.3 (C-15, 15'), 52.1 (12, 12'-OMe)。以上数据与文献报道基本一致^[8], 故鉴定化合物 **2** 为环银线草醇 A。

化合物 **3**: 白色粉末, ESI-MS m/z : 755 $[\text{M} + \text{Na}]^+$, $\text{C}_{40}\text{H}_{44}\text{O}_{13}$ 。 $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 2.06 (1H, m, H-1), 1.02 (1H, m, H-2 α), 0.33 (1H, m, H-2 β), 1.89 (1H, m, H-3), 3.96 (1H, s, H-6), 3.88 (1H, s, H-9), 1.95 (3H, s, H-13), 1.04 (3H, s, H-14), 2.81 (1H, m, H-15 α), 2.58 (1H, m, H-15 β), 1.61 (1H, m, H-1'),

0.75 (1H, m, H-2' α), 1.35 (1H, m, H-2' β), 1.41 (1H, m, H-3'), 1.86 (1H, m, H-5'), 2.50 (1H, m, H-6' α), 2.70 (1H, m, H-6' β), 1.85 (1H, m, H-9'), 4.55 (1H, m, $J = 12.0$ Hz, H-13' α), 5.10 (1H, d, $J = 12.0$ Hz, H-13' β), 0.83 (3H, s, H-14'), 3.66 (1H, s, H-15' α), 4.62 (1H, d, $J = 12.0$ Hz, H-15' β), 6.62 (1H, t, $J = 6.9$ Hz, H-c), 4.64 (1H, m, H-d α), 5.08 (1H, m, H-d β), 1.92 (3H, s, H-e), 2.48 (1H, m, H-g α), 2.90 (1H, m, H-g β), 2.67 (1H, m, H-h α), 2.80 (1H, m, H-h β), 3.71 (3H, s, 12-OMe); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ : 26.0 (C-1), 16.0 (C-2), 24.8 (C-3), 142.4 (C-4), 132.1 (C-5), 41.0 (C-6), 131.5 (C-7), 200.8 (C-8), 79.9 (C-9), 50.9 (C-10), 147.3 (C-11), 170.2 (C-12), 20.1 (C-13), 15.3 (C-14), 25.4 (C-15), 25.6 (C-1'), 11.6 (C-2'), 27.7 (C-3'), 77.1 (C-4'), 61.3 (C-5'), 23.4 (C-6'), 174.7 (C-7'), 93.3 (C-8'), 55.5 (C-9'), 44.9 (C-10'), 123.3 (C-11'), 171.7 (C-12'), 54.3 (C-13'), 26.0 (C-14'), 72.2 (C-15'), 167.1 (C-a), 129.3 (C-b), 135.5 (C-c), 61.6 (C-d), 13.0 (C-e), 171.6 (C-f), 28.7 (C-g), 29.2 (C-h), 172.1 (C-i), 52.4 (12-OMe)。以上数据与文献报道基本一致^[9], 故鉴定化合物 **3** 为银线草醇 B。

化合物 **4**: 黄色油状物, ESI-MS m/z : 657 $[\text{M} + \text{Na}]^+$, $\text{C}_{36}\text{H}_{42}\text{O}_{10}$ 。 $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 2.06 (1H, m, H-1), 1.01 (1H, m, H-2 α), 0.32 (1H, m, H-2 β), 1.83 (1H, m, H-3), 3.90 (1H, d, $J = 3.5$ Hz, H-6), 3.93 (1H, s, H-9), 1.90 (3H, s, H-13), 1.00 (3H, s, H-14), 2.81 (1H, m, H-15 α), 2.57 (1H, m, H-15 β), 1.60 (1H, m, H-1'), 0.71 (1H, m, H-2' α), 1.26 (1H, m, H-2' β), 1.51 (1H, m, H-3'), 1.91 (1H, m, H-5'), 2.27 (1H, m, H-6' α), 2.72 (1H, m, H-6' β), 2.05 (1H, m, H-9'), 3.31 (1H, d, $J = 13.6$ Hz, H-13' α), 4.39 (1H, d, $J = 13.6$ Hz, H-13' β), 0.86 (3H, s, H-14'), 3.85 (1H, d, $J = 11.5$ Hz, H-15' α), 4.17 (1H, d, $J = 11.5$ Hz, H-15' β), 6.87 (1H, qq, $J = 7.7, 3.3$ Hz, H-c), 1.83 (1H, d, $J = 7.0$ Hz, H-d), 1.84 (1H, brs, H-e), 3.76 (3H, s, 12-OMe); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ : 26.2 (C-1), 16.0 (C-2), 24.8 (C-3), 142.5 (C-4), 132.2 (C-5), 41.0 (C-6), 131.3 (C-7), 200.3 (C-8), 79.9 (C-9), 51.0 (C-10), 147.0 (C-11), 171.2 (C-12), 20.3 (C-13), 15.5 (C-14), 25.3 (C-15), 25.4 (C-1'), 11.8 (C-2'), 28.3 (C-3'), 77.4 (C-4'), 60.0 (C-5'), 22.2 (C-6'), 168.5 (C-7'), 93.4 (C-8'), 54.7 (C-9'), 44.8 (C-10'), 127.4 (C-11'), 172.4 (C-12'), 55.0 (C-13'), 26.0 (C-14'), 71.0

(C-15'), 168.3 (C-a), 128.0 (C-b), 138.9 (C-c), 14.5 (C-d), 12.1 (C-e), 52.7 (12-OMe)。以上数据与文献报道基本一致^[9], 故鉴定化合物 **4** 为银线草醇 C。

化合物 **5**: 黄色油状物, ESI-MS m/z : 589 $[M+Na]^+$, $C_{33}H_{38}O_9$ 。 1H -NMR (600 MHz, $CDCl_3$) δ : 2.06 (1H, m, H-1), 1.00 (1H, m, H-2 α), 0.30 (1H, m, H-2 β), 1.86 (1H, m, H-3), 3.91 (1H, d, J = 3.8 Hz, H-6), 4.06 (1H, s, H-9), 1.90 (3H, s, H-13), 1.02 (3H, s, H-14), 2.76 (1H, m, H-15 α), 2.60 (1H, m, H-15 β), 1.45 (1H, m, H-1'), 0.77 (1H, m, H-2' α), 0.84 (1H, m, H-2' β), 1.10 (1H, m, H-3' α), 1.58 (1H, m, H-3' β), 1.81 (1H, dt, H-5'), 2.47 (1H, d, J = 10.1 Hz, H-6' α), 2.47 (1H, d, J = 10.1 Hz, H-6' β), 1.92 (1H, m, H-9'), 4.33 (1H, d, J = 13.6 Hz, H-13' α), 4.39 (1H, d, J = 13.6 Hz, H-13' β), 0.66 (3H, s, H-14'), 3.77 (1H, m, H-15' α), 3.98 (1H, m, H-15' β), 2.09 (3H, s, H-b), 3.79 (3H, s, 12-OMe); ^{13}C -NMR (150 MHz, $CDCl_3$) δ : 25.7 (C-1), 15.9 (C-2), 24.8 (C-3), 142.4 (C-4), 131.7 (C-5), 40.6 (C-6), 131.5 (C-7), 200.7 (C-8), 79.9 (C-9), 51.1 (C-10), 147.0 (C-11), 171.1 (C-12), 20.5 (C-13), 15.3 (C-14), 25.6 (C-15), 24.3 (C-1'), 16.6 (C-2'), 21.8 (C-3'), 43.0 (C-4'), 59.2 (C-5'), 25.1 (C-6'), 168.7 (C-7'), 93.3 (C-8'), 54.5 (C-9'), 44.1 (C-10'), 126.7 (C-11'), 172.5 (C-12'), 54.9 (C-13'), 24.1 (C-14'), 66.2 (C-15'), 171.2 (C-a), 20.9 (C-b), 52.8 (12-OMe)。以上数据与文献报道基本一致^[9], 故鉴定化合物 **5** 为银线草醇 D。

化合物 **6**: 黄色油状物, ESI-MS m/z : 755 $[M+Na]^+$, $C_{40}H_{44}O_{13}$ 。 1H -NMR (600 MHz, $CDCl_3$) δ : 2.09 (1H, m, H-1), 1.04 (1H, m, H-2 α), 0.38 (1H, m, H-2 β), 1.88 (1H, m, H-3), 3.96 (1H, d, J = 3.2 Hz, H-6), 3.96 (1H, s, H-9), 1.94 (3H, s, H-13), 1.02 (3H, s, H-14), 2.82 (1H, m, H-15 α), 2.58 (1H, m, H-15 β), 1.65 (1H, m, H-1'), 0.73 (1H, m, H-2' α), 1.32 (1H, m, H-2' β), 1.40 (1H, m, H-3'), 1.96 (1H, m, H-5'), 2.66 (1H, m, H-6' α), 2.79 (1H, m, H-6' β), 1.95 (1H, m, H-9'), 4.72 (1H, d, J = 12.7 Hz, H-13' α), 4.93 (1H, m, H-13' β), 0.81 (3H, s, H-14'), 3.52 (1H, d, J = 11.8 Hz, H-15' α), 4.79 (1H, d, J = 11.8 Hz, H-15' β), 5.98 (1H, m, H-b), 4.38 (1H, m, H-d α), 5.05 (1H, m, H-d β), 2.15 (3H, s, H-e), 2.62 (1H, m, H-g α), 2.94 (1H, m, H-g β), 2.77 (1H, m, H-h α), 2.87 (1H, m, H-h β), 3.77 (3H, s, 12-OMe); ^{13}C -NMR (150 MHz, $CDCl_3$) δ : 26.4 (C-1), 16.1 (C-2), 24.9 (C-3), 142.7 (C-4), 132.8 (C-5), 41.7

(C-6), 130.6 (C-7), 200.2 (C-8), 79.7 (C-9), 51.0 (C-10), 147.4 (C-11), 170.4 (C-12), 19.9 (C-13), 15.7 (C-14), 25.4 (C-15), 26.2 (C-1'), 11.7 (C-2'), 27.5 (C-3'), 77.8 (C-4'), 61.0 (C-5'), 24.7 (C-6'), 174.2 (C-7'), 93.5 (C-8'), 54.8 (C-9'), 44.8 (C-10'), 123.5 (C-11'), 171.5 (C-12'), 55.2 (C-13'), 25.8 (C-14'), 71.2 (C-15'), 166.2 (C-a), 112.8 (C-b), 154.0 (C-c), 65.7 (C-d), 15.6 (C-e), 171.8 (C-f), 29.1 (C-g), 29.0 (C-h), 172.0 (C-i), 52.5 (12-OMe)。以上数据与文献报道基本一致^[10], 故鉴定化合物 **6** 为银线草醇 F。

化合物 **7**: 白色粉末, ESI-MS m/z : 771 $[M+Na]^+$, $C_{40}H_{44}O_{14}$ 。 1H -NMR (600 MHz, $CDCl_3$) δ : 2.08 (1H, m, H-1), 1.04 (1H, m, H-2 α), 0.34 (1H, m, H-2 β), 1.87 (1H, m, H-3), 3.97 (1H, d, H-6), 3.91 (1H, s, H-9), 1.89 (3H, s, H-13), 1.05 (3H, s, H-14), 2.78 (1H, m, H-15 α), 2.61 (1H, m, H-15 β), 1.62 (1H, m, H-1'), 0.76 (1H, m, H-2' α), 1.36 (1H, m, H-2' β), 1.42 (1H, m, H-3'), 1.87 (1H, m, H-5'), 2.62 (1H, m, H-6' α), 2.82 (1H, m, H-6' β), 1.83 (1H, m, H-9'), 4.45 (1H, d, J = 11.9 Hz, H-13' α), 5.14 (1H, m, H-13' β), 0.83 (3H, s, H-14'), 3.62 (1H, d, J = 11.9 Hz, H-15' α), 4.68 (1H, d, J = 11.9 Hz, H-15' β), 6.76 (1H, m, H-b), 4.90 (1H, m, H-d α), 5.23 (1H, m, H-d β), 1.95 (3H, s, H-e), 4.64 (1H, m, H-g), 2.92 (1H, m, H-h α), 2.99 (1H, m, H-h β), 3.72 (3H, s, 12-OMe), 3.82 (1H, d, J = 6.8 Hz, g-OH); ^{13}C -NMR (150 MHz, $CDCl_3$) δ : 25.9 (C-1), 16.0 (C-2), 24.8 (C-3), 142.5 (C-4), 132.0 (C-5), 40.9 (C-6), 131.5 (C-7), 200.9 (C-8), 80.0 (C-9), 51.0 (C-10), 147.5 (C-11), 170.5 (C-12), 19.8 (C-13), 15.2 (C-14), 25.4 (C-15), 25.6 (C-1'), 11.7 (C-2'), 27.8 (C-3'), 77.3 (C-4'), 61.4 (C-5'), 24.1 (C-6'), 175.2 (C-7'), 93.4 (C-8'), 56.0 (C-9'), 45.0 (C-10'), 122.9 (C-11'), 171.8 (C-12'), 54.9 (C-13'), 26.1 (C-14'), 72.1 (C-15'), 167.3 (C-a), 129.0 (C-b), 135.8 (C-c), 62.2 (C-d), 13.1 (C-e), 173.4 (C-f), 67.2 (C-g), 38.9 (C-h), 170.7 (C-i), 52.8 (12-OMe)。以上数据与文献报道基本一致^[10], 故鉴定化合物 **7** 为银线草醇 G。

化合物 **8**: 黄色颗粒, ESI-MS m/z : 577 $[M+Na]^+$, $C_{30}H_{34}O_{10}$ 。 1H -NMR (600 MHz, Methanol- d_4) δ : 1.83 (1H, m, H-1), 0.83 (1H, m, H-2 α), 1.03 (1H, m, H-2 β), 1.82 (1H, m, H-3), 3.70 (1H, s, H-9), 1.58 (3H, s, H-13), 0.86 (3H, s, H-14), 1.87 (1H, m, H-15 α), 2.65 (1H, m, H-15 β), 1.61 (1H, m, H-1'), 0.59 (1H, m,

H-2'α), 1.17 (1H, m, H-2'β), 1.71 (1H, m, H-3'), 2.36 (1H, m, H-6'α), 2.89 (1H, m, H-6'β), 2.70 (1H, m, H-9'), 4.34 (1H, d, $J = 13.2$ Hz, H-13'α), 4.28 (1H, m, H-13'β), 1.01 (3H, s, H-14'), 3.48 (2H, brs, H-15'); ^{13}C -NMR (150 MHz, Methanol- d_4) δ : 28.2 (C-1), 8.1 (C-2), 30.1 (C-3), 78.5 (C-4), 163.2 (C-5), 123.3 (C-6), 153.9 (C-7), 103.6 (C-8), 77.3 (C-9), 49.6 (C-10), 123.5 (C-11), 171.9 (C-12), 9.3 (C-13), 12.7 (C-14), 40.4 (C-15), 26.3 (C-1'), 9.6 (C-2'), 28.7 (C-3'), 77.6 (C-4'), 51.1 (C-5'), 20.8 (C-6'), 169.7 (C-7'), 85.6 (C-8'), 51.0 (C-9'), 44.3 (C-10'), 127.0 (C-11'), 173.3 (C-12'), 53.2 (C-13'), 23.2 (C-14'), 66.9 (C-15')。以上数据与文献报道基本一致^[11], 故鉴定化合物 **8** 为多穗金粟兰醇 B。

化合物 **9**: 黄色油状物, ESI-MS m/z : 673 $[\text{M} + \text{Na}]^+$, $\text{C}_{36}\text{H}_{42}\text{O}_{11}$ 。 ^1H -NMR (600 MHz, CDCl_3) δ : 2.08 (1H, m, H-1), 0.34 (1H, m, H-2α), 0.99 (1H, m, H-2β), 1.87 (1H, m, H-3), 3.92 (1H, brs, H-6), 3.92 (1H, s, H-9), 1.91 (3H, s, H-13), 1.02 (3H, s, H-14), 2.58 (1H, m, H-15α), 2.83 (1H, m, H-15β), 1.65 (1H, m, H-1'), 0.73 (1H, m, H-2'α), 1.33 (1H, m, H-2'β), 1.45 (1H, m, H-3'), 1.90 (1H, m, H-5'), 2.41 (1H, m, H-6'α), 2.83 (1H, m, H-6'β), 1.95 (1H, m, H-9'), 4.34 (1H, d, $J = 15.3$ Hz, H-13'α), 4.42 (1H, m, H-13'β), 0.88 (3H, s, H-14'), 3.82 (1H, d, $J = 11.6$ Hz, H-15'α), 4.40 (1H, d, $J = 11.6$ Hz, H-15'β), 6.79 (1H, m, H-c), 4.27 (1H, m, H-dα), 4.46 (1H, m, H-dβ), 1.89 (3H, s, H-e), 3.75 (3H, s, 12-OMe); ^{13}C -NMR (150 MHz, CDCl_3) δ : 26.1 (C-1), 16.0 (C-2), 24.8 (C-3), 142.5 (C-4), 132.2 (C-5), 41.2 (C-6), 146.3 (C-7), 200.9 (C-8), 79.8 (C-9), 50.8 (C-10), 132.1 (C-11), 171.8 (C-12), 20.1 (C-13), 15.5 (C-14), 25.3 (C-15), 25.6 (C-1'), 11.6 (C-2'), 27.8 (C-3'), 77.4 (C-4'), 60.9 (C-5'), 23.1 (C-6'), 168.4 (C-7'), 93.1 (C-8'), 54.7 (C-9'), 44.8 (C-10'), 127.3 (C-11'), 172.3 (C-12'), 55.0 (C-13'), 26.1 (C-14'), 72.4 (C-15'), 167.7 (C-a), 127.4 (C-b), 141.9 (C-c), 59.6 (C-d), 12.6 (C-e), 53.2 (12-OMe)。以上数据与文献报道基本一致^[12], 故鉴定化合物 **9** 为草珊瑚内酯 B。

化合物 **10**: 黄色油状物, ESI-MS m/z : 575 $[\text{M} + \text{Na}]^+$, $\text{C}_{31}\text{H}_{36}\text{O}_9$ 。 ^1H -NMR (600 MHz, Methanol- d_4) δ : 2.01 (1H, m, H-1), 0.30 (1H, m, H-2α), 1.00 (1H, m, H-2β), 1.73 (1H, m, H-3), 3.95 (1H, d, $J = 3.8$ Hz, H-6), 4.05 (1H, s, H-9), 1.86 (3H, s, H-13), 1.05 (3H,

s, H-14), 2.55 (1H, m, H-15α), 2.84 (1H, m, H-15β), 1.63 (1H, m, H-1'), 0.70 (1H, m, H-2'), 1.55 (1H, m, H-3'), 1.71 (1H, m, H-5'), 2.26 (1H, m, H-6'α), 2.79 (1H, m, H-6'β), 1.83 (1H, m, H-9'), 4.25 (1H, d, H-13'α), 4.27 (1H, d, H-13'β), 0.93 (3H, s, H-14'), 3.33 (1H, d, H-15'α), 3.38 (1H, d, $J = 10.9$ Hz, H-15'β), 3.78 (3H, s, 12-OMe); ^{13}C -NMR (150 MHz, Methanol- d_4) δ : 25.1 (C-1), 14.7 (C-2), 24.0 (C-3), 141.8 (C-4), 132.3 (C-5), 40.5 (C-6), 133.0 (C-7), 200.8 (C-8), 79.8 (C-9), 51.2 (C-10), 145.7 (C-11), 171.7 (C-12), 19.1 (C-13), 14.4 (C-14), 24.6 (C-15), 24.9 (C-1'), 11.3 (C-2'), 27.7 (C-3'), 78.1 (C-4'), 59.2 (C-5'), 21.6 (C-6'), 172.9 (C-7'), 93.3 (C-8'), 55.9 (C-9'), 44.4 (C-10'), 127.1 (C-11'), 170.2 (C-12'), 52.9 (C-13'), 25.8 (C-14'), 67.9 (C-15'), 51.7 (12-OMe)。以上数据与文献报道基本一致^[13], 故鉴定化合物 **10** 为 sarglabolide I。

化合物 **11**: 白色颗粒, ESI-MS m/z : 771 $[\text{M} + \text{Na}]^+$, $\text{C}_{40}\text{H}_{44}\text{O}_{14}$ 。 ^1H -NMR (600 MHz, $\text{DMSO}-d_4$) δ : 1.68 (1H, m, H-1), 0.66 (1H, m, H-2α), 1.00 (1H, m, H-2β), 1.70 (1H, m, H-3), 3.71 (1H, s, H-9), 1.48 (3H, s, H-13), 0.72 (3H, s, H-14), 1.68 (1H, m, H-15α), 2.57 (1H, m, H-15β), 1.55 (1H, m, H-1'), 0.51 (1H, m, H-2'α), 1.08 (1H, m, H-2'β), 1.46 (1H, m, H-3'), 2.11 (1H, m, H-5'), 2.51 (1H, m, H-6'α), 2.77 (1H, m, H-6'β), 2.51 (1H, m, H-9'), 4.45 (1H, d, $J = 11.9$ Hz, H-13'α), 4.86 (1H, d, $J = 11.9$ Hz, H-13'β), 0.81 (3H, s, H-14'), 3.71 (1H, d, $J = 6.9$ Hz, H-15'α), 4.60 (1H, d, $J = 6.9$ Hz, H-15'β), 6.52 (1H, t, H-c), 1.77 (3H, s, H-d), 4.52 (1H, m, H-eα), 4.95 (1H, m, H-eβ), 2.41 (1H, m, H-gα), 2.54 (1H, m, H-gβ), 2.54 (1H, m, H-hα), 2.56 (1H, m, H-hβ), 3.18 (3H, s, 8-OMe); ^{13}C -NMR (150 MHz, $\text{DMSO}-d_4$) δ : 28.8 (C-1), 9.0 (C-2), 31.0 (C-3), 78.1 (C-4), 164.0 (C-5), 122.6 (C-6), 153.8 (C-7), 104.1 (C-8), 76.3 (C-9), 49.1 (C-10), 122.0 (C-11), 172.7 (C-12), 10.5 (C-13), 14.7 (C-14), 40.5 (C-15), 26.8 (C-1'), 10.7 (C-2'), 29.2 (C-3'), 76.6 (C-4'), 54.9 (C-5'), 23.4 (C-6'), 176.7 (C-7'), 86.0 (C-8'), 49.8 (C-9'), 45.1 (C-10'), 122.0 (C-11'), 171.7 (C-12'), 54.4 (C-13'), 24.2 (C-14'), 73.5 (C-15'), 167.1 (C-a), 128.3 (C-b), 137.0 (C-c), 13.1 (C-d), 61.6 (C-e), 172.2 (C-f), 29.0 (C-g), 29.6 (C-h), 172.1 (C-i), 50.8 (8-OMe)。以上数据与文献报道基本一致^[14], 故鉴定化合物 **11** 为 8-*O*-methyltianshananol。

化合物 **12**: 黄色片状结晶 (甲醇), ESI-MS m/z : 659 $[M+Na]^+$, $C_{35}H_{40}O_{11}$ 。 1H -NMR (600 MHz, Methanol- d_4) δ : 1.84 (1H, m, H-1), 0.82 (1H, m, H-2 α), 1.05 (1H, m, H-2 β), 1.83 (1H, m, H-3), 3.70 (1H, s, H-9), 1.57 (3H, s, H-13), 0.85 (3H, s, H-14), 1.85 (1H, m, H-15 α), 2.70 (1H, m, H-15 β), 1.68 (1H, m, H-1'), 0.62 (1H, m, H-2' α), 1.21 (1H, m, H-2' β), 1.74 (1H, m, H-3'), 2.35 (1H, m, H-5'), 2.45 (1H, m, H-6' α), 2.92 (1H, m, H-6' β), 2.71 (1H, m, H-9'), 4.33 (1H, m, H-13'), 1.03 (3H, s, H-14'), 4.01 (1H, d, J = 11.0 Hz, H-15' α), 4.06 (1H, d, J = 11.0 Hz, H-15' β), 6.97 (1H, m, H-c), 1.94 (3H, d, J = 7.0 Hz, H-d), 1.84 (3H, s, H-e); ^{13}C -NMR (150 MHz, Methanol- d_4) δ : 28.5 (C-1), 8.3 (C-2), 30.1 (C-3), 77.0 (C-4), 163.2 (C-5), 123.1 (C-6), 153.8 (C-7), 103.8 (C-8), 77.6 (C-9), 49.4 (C-10), 123.2 (C-11), 172.2 (C-12), 9.3 (C-13), 12.9 (C-14), 40.2 (C-15), 26.5 (C-1'), 9.6 (C-2'), 28.8 (C-3'), 76.9 (C-4'), 51.9 (C-5'), 20.8 (C-6'), 169.8 (C-7'), 85.7 (C-8'), 50.7 (C-9'), 44.4 (C-10'), 127.1 (C-11'), 173.4 (C-12'), 53.2 (C-13'), 23.2 (C-14'), 68.6 (C-15'), 168.1 (C-a), 128.6 (C-b), 137.3 (C-c), 11.0 (C-d), 13.1 (C-e)。以上数据与文献报道基本一致^[15], 故鉴定化合物 **12** 为 henriol B。

4 讨论

乌药烷型倍半萜二聚体类化合物结构新颖且复杂, 大多数具有良好的生物活性, 如抗真菌、对 B 细胞有毒性介导的免疫抑制及对延迟整流钾电流有选择性的抑制作用等^[5]。另有研究显示, 化合物 **2**、**3**、**6** 呈剂量依赖性抑制 ICAM/LFA-1, TCAM/LFA-1 的表达, 有望成为有效的抗动脉粥样硬化和抗炎药物^[16], 化合物 **11** 有抑制络氨酸活性的作用^[14]。

研究表明, α 、 β -不饱和 γ -内酯和 α 、 β 不饱和酮均为细胞毒作用的有效基团^[17]。本实验分离得到的 12 个乌药烷型倍半萜二聚体 (其中化合物 **3**、**6**、**7**、**11** 含 18 元大环结构) 均含有该基团, 因此很有可能从中筛选出抗肿瘤的活性成分或先导化合物, 为创新药物的开发奠定基础。本课题组将重点研究这些化合物的药理作用, 包括 18 元大环结构在药理活性中的作用。

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