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金线吊乌龟化学成分的研究

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摘要: 目的 研究金线吊乌龟 *Stephania cepharantha* Hayata 的化学成分。方法 金线吊乌龟 95% 乙醇提取物采用硅胶、Sephadex LH-20、大孔树脂、RP-C₁₈柱和制备液相进行分离纯化, 根据理化性质及波谱数据鉴定所得化合物的结构。结果 从中分离得到 15 个化合物, 分别鉴定为异粉防己碱 (1)、小檗碱 (2)、千金藤素 (3)、轮环藤宁 (4)、左旋四氢巴马汀 (5)、光千金藤啶碱 (6)、异紫堇定 (7)、腺嘌呤 (8)、腺嘌呤核苷 (9)、sinococuline (10)、cephamorphanine (11)、衡州乌药碱 (12)、coclaurine-12-O-β-D-glucopyranoside (13)、轮环藤酚碱 (14)、木兰花碱 (15)。结论 化合物 8~9、13 为首次从该植物中分离得到, 其中化合物 13 为新天然产物。

关键词: 金线吊乌龟; 化学成分; 分离鉴定

中图分类号: R284.1

文献标志码: A

文章编号: 1001-1528(2020)06-1498-06

doi:10.3969/j.issn.1001-1528.2020.06.020

Chemical constituents from *Stephania cepharantha*

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ABSTRACT: AIM To study the chemical constituents from *Stephania cepharantha* Hayata. **METHODS** The 95% ethanol extract of *S. cepharantha* was isolated and purified by silica, Sephadex LH-20, macroporous resin, RP-C₁₈ column and semi-preparative liquid chromatography, then the structures of obtained compounds were identi-

收稿日期: 2019-04-19

基金项目: 国家自然科学基金项目 (31100238)

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fied by physicochemical properties and spectral data. **RESULTS** Fifteen compounds were isolated and identified as isotetrandrine (1), berbamine (2), cepharanthine (3), cycleanine (4), (-) tetrahydropalmatine (5), stepholidine (6), isocorydine (7), adenine (8), adenosine (9), sinococuline (10), cepharamorphinanine (11), coclaurine (12), coclaurine-12-O- β -D-glucoside (13), cyclanoline (14), magnoflorine (15). **CONCLUSION** Compounds 8~9, 13 are isolated from this plant for the first time, and compound 13 is a new natural compound.

KEY WORDS: *Stephania cepharantha* Hayata; chemical constituents; isolation and identification

金线吊乌龟 *Stephania cepharantha* Hayata 为防己科千金藤属植物, 主要分布于我国西南、东南等地。民间常以其块根入药, 又名白药子、白大药、山乌龟等, 味苦、性寒, 具有清热解毒、散瘀止痛等功效, 常用于治疗咽喉肿痛、风湿痹痛、腮腺炎等疾病^[1~4]。该植物块根的甲醇提取物、氯仿可溶的生物碱部分具有抗病毒作用; 已从块根、茎叶和种子中分离得到多种类型的生物碱, 具有抗炎、抗癌细胞生长、抗骨肉瘤等多种临床药理活性^[3~13]。为进一步研究金线吊乌龟的化学成分, 本实验对其块根部分进行了提取与分离, 得到 15 个化合物, 其中化合物 13 为新天然产物, 化合物 8~9、13 为首次从该植物中分离得到。

1 材料

Waters Alliance 2695 高效液相色谱仪(美国 Waters 公司); LC-15C 高效液相色谱仪[岛津企业管理(中国)有限公司]; Mercury Plus 400 MHz 核磁共振仪(美国 Varian 公司); Bruker Ascend TM 600 MHz 超导核磁共振仪(德国 Bruker 公司); TripleTOF 5600+高分辨质谱仪(美国 Applied Bio-systems Sciex 公司); Rudolph Autopol IV-T 旋光仪(美国 Rudolph Research Analytical 公司); RP-C₁₈ (50 μ m, 日本 YMC 公司); Sephadex LH-20 (美国 GE Healthcare 公司); Kromasil C₁₈ 色谱柱(10 mm \times 250 mm, 5 μ m, 广州菲罗门科学仪器有限公司)。甲醇(HPLC 级, 上海百灵威科技有限公司); HZ818 大孔吸附树脂(上海华震科技有限公司); 薄层及柱色谱用硅胶(烟台江友硅胶开发有限公司)。其他试剂均为分析纯。

金线吊乌龟药材购于浙江宁波德康生物制品有限公司, 产地为四川省, 经复旦大学药学院康云讲师鉴定为防己科千金藤属植物金线吊乌龟 *Stephania cepharantha* Hayata 的干燥块根, 标本保存于上海市复旦大学药学院。

2 提取与分离

金线吊乌龟块根粗粉 6 kg, 室温下以 95% 乙醇

浸泡、渗漉提取, 减压回收溶剂, 得浸膏约 800 g。浸膏以 2% 盐酸水溶液分散均匀, 用石油醚脱脂, 以氨水调节到 pH=10, 用二氯甲烷萃取 3 次, 减压浓缩萃取液, 得二氯甲烷萃取物 200 g, 水层再用正丁醇萃取, 减压浓缩得正丁醇萃取物 24 g。二氯甲烷萃取物经正相硅胶柱, 以二氯甲烷-甲醇溶剂系统(80:1、50:1、25:1、14:1、1:1、0:1)梯度洗脱, 再经反复 RP-C₁₈ 柱层析(甲醇-水)、制备型高效液相色谱(RP-C₁₈ 色谱柱, 甲醇-水或乙腈-水)以及制备 TLC 等方法分离, 得到化合物 1 (15 mg)、2 (5 mg)、3 (380 mg)、4 (150 mg)、5 (5 mg)、6 (4.5 mg)、7 (3 mg)。正丁醇部位萃取物进行大孔树脂 HZ818 柱层析, 用乙醇-水(3:7、5:5、7:3、95:5)梯度洗脱, 再经反复 Sephadex LH-20 柱层析(甲醇-水)、RP-C₁₈ 开放柱层析(甲醇-水)以及制备型高效液相色谱(RP-C₁₈ 色谱柱, 甲醇-0.02% 二乙胺-水溶液)等方法分离, 得到化合物 8 (2 mg)、9 (6 mg)、10 (27 mg)、11 (4 mg)、12 (5 mg)、13 (8 mg)、14 (7 mg)、15 (1.1 mg)。

3 结构鉴定

化合物 1: 淡黄色无定形粉末, 分子式 C₃₈H₄₂N₂O₆, $[\alpha]_D^{25} +146^\circ$ (c 0.10, CHCl₃)。ESI-MS *m/z*: 623.3 [M + H]⁺。¹H-NMR (600 MHz, CDCl₃) δ : 7.27 (1H, dd, *J* = 8.2, 1.7 Hz, H-10'), 7.10 (1H, d, *J* = 8.2 Hz, H-11'), 6.81 (1H, d, *J* = 8.2 Hz, H-13), 6.78 (1H, d, *J* = 8.2 Hz, H-14), 6.65 (1H, d, *J* = 8.2 Hz, H-13'), 6.53 (1H, s, H-5'), 6.50 (1H, s, H-10), 6.41 (1H, d, *J* = 8.2 Hz, H-14'), 6.27 (1H, s, H-5), 5.98 (1H, s, H-8'), 3.91 (3H, s, 12-OCH₃), 3.75 (3H, s, 6-OCH₃), 3.61 (3H, s, 6'-OCH₃), 3.50 (1H, s, H_a-3), 3.40 (1H, m, H_a-3'), 3.12 (3H, s, 7-OCH₃), 2.56, 2.25 (6H, s, 2 \times NCH₃); ¹³C-NMR (150 MHz, CDCl₃) δ : 62.0 (C-1), 46.0 (C-3), 22.7

(C-4), 128.9 (C-4a), 128.9 (C-4a'), 105.5 (C-5), 151.8 (C-6), 137.0 (C-7), 148.3 (C-8), 120.7 (C-8a), 127.7 (C-8a'), 137.0 (C-9), 115.8 (C-10), 149.9 (C-11), 146.9 (C-12), 111.1 (C-13), 122.7 (C-14), 63.6 (C-1'), 46.0 (C-3'), 25.7 (C-4'), 111.1 (C-5'), 149.5 (C-6'), 143.5 (C-7'), 119.8 (C-8'), 135.3 (C-9'), 130.1 (C-10'), 121.6 (C-11'), 153.9 (C-12'), 122.0 (C-13'), 132.1 (C-14'), 38.7 (C-15), 37.7 (C-15'), 42.6 (2-NCH₃), 42.8 (2'-NCH₃), 55.7 (6-OCH₃), 55.5 (6'-OCH₃), 60.5 (7-OCH₃), 56.0 (12-OCH₃)。以上数据与文献[14]基本一致,故鉴定为异粉防己碱。

化合物2: 淡黄色无定形粉末,分子式C₃₇H₄₀N₂O₆,[α]_D²⁵+114°(c 0.10, CHCl₃)。ESI-MS m/z: 609.3 [M + H]⁺。¹H-NMR (600 MHz, CDCl₃) δ : 7.28 (1H, d, J = 8.0 Hz, H-10'), 7.10 (1H, d, J = 8.0 Hz, H-11'), 6.79 (1H, d, J = 8.0 Hz, H-13), 6.73 (1H, d, J = 8.0 Hz, H-14), 6.57 (1H, d, J = 8.0 Hz, H-13'), 6.51, 6.27 (2H, s, H-5, 5'), 6.50, 5.98 (2H, s, H-10, 8'), 6.43 (1H, brs, H-14'), 3.87 (1H, m, H-1'), 3.82 (1H, m, H-1), 3.75 (3H, s, 6-OCH₃), 3.58 (3H, s, 6'-OCH₃), 3.50 (1H, s, H_a-3), 3.40 (1H, m, H_a-3'), 3.11 (3H, s, 7-OCH₃), 2.57, 2.25 (6H, s, 2×NCH₃);¹³C-NMR (150 MHz, CDCl₃) δ : 62.3 (C-1), 45.9 (C-3), 25.5 (C-4), 128.8 (C-4a), 128.8 (C-4a'), 105.3 (C-5), 151.7 (C-6), 136.9 (C-7), 147.5 (C-8), 120.8 (C-8a), 127.9 (C-8a'), 136.9 (C-9), 115.2 (C-10), 143.6 (C-11), 148.2 (C-12), 114.6 (C-13), 123.4 (C-14), 63.7 (C-1'), 45.9 (C-3'), 25.5 (C-4'), 111.1 (C-5'), 149.8 (C-6'), 143.4 (C-7'), 119.8 (C-8'), 135.7 (C-9'), 132.8 (C-10'), 121.8 (C-11'), 153.7 (C-12'), 121.3 (C-13'), 130.3 (C-14'), 38.6 (C-15), 37.7 (C-15'), 42.7 (2-NCH₃), 42.8 (2'-NCH₃), 55.7 (6-OCH₃), 55.5 (6'-OCH₃), 60.5 (7-OCH₃)。以上数据与文献[15]基本一致,故鉴定为小檗碱。

化合物3: 淡黄色无定形粉末,分子式C₃₇H₃₈N₂O₆,[α]_D²⁵+274°(c 0.10, CHCl₃)。ESI-MS m/z: 607.3 [M + H]⁺。¹H-NMR (400 MHz, CD₃OD) δ : 7.41 (1H, brd, J = 8.2 Hz, H-14'),

7.06 (1H, brd, J = 8.2 Hz, H-13'), 6.87 (1H, brd, J = 8.2 Hz, H-10'), 6.82 (2H, m, H-13, 14), 6.68 (1H, s, H-8), 6.36 (2H, s, H-5, 5'), 6.31 (1H, brd, J = 8.2 Hz, H-11'), 5.55 (2H, s, -OCH₂O-), 5.47 (1H, brs, H-10), 3.83 (3H, s, 12-OCH₃), 3.70 (3H, s, 6-OCH₃), 2.60, 2.55 (6H, s, 2×NCH₃);¹³C-NMR (150 MHz, CD₃OD) δ : 63.5 (C-1), 44.4 (C-3), 26.2 (C-4), 101.9 (C-5), 147.6 (C-6), 138.5 (C-7), 142.0 (C-8), 131.7 (C-9), 131.5 (C-10), 120.6 (C-11), 152.3 (C-12), 121.7 (C-13), 130.6 (C-14), 61.5 (C-1'), 49.7 (C-3'), 28.9 (C-4'), 111.1 (C-5'), 148.9 (C-6'), 149.0 (C-7'), 111.2 (C-8'), 129.6 (C-9'), 118.3 (C-10'), 138.5 (C-11'), 142.0 (C-12'), 101.9 (C-13'), 125.6 (C-14'), 133.1 (C-4a), 123.7 (C-8a), 129.5 (C-4a'), 127.8 (C-8a'), 39.8 (C-15), 37.1 (C-15'), 42.4 (2-NCH₃), 42.5 (2'-NCH₃), 54.2 (6-OCH₃), 101.9 (OCH₂O)。以上数据与文献[16]基本一致,故鉴定为千金藤素。

化合物4: 淡黄色无定形粉末,分子式C₃₈H₄₂N₂O₆,[α]_D²⁵-11°(c 1.0, CHCl₃)。ESI-MS m/z: 623.3 [M + H]⁺。¹H-NMR (400 MHz, CD₃OD) δ : 7.06 (2H, brd, J = 8.6 Hz, H-10, 10'), 6.88, 6.80 (2H, brd, J = 8.2 Hz, H-11, 11'), 6.66 (2H, brs, H-5, 5'), 6.54 (2H, m, H-14, 14'), 6.39 (2H, brs, H-13, 13'), 3.88, 3.72 (6H, s, 6, 6'-OCH₃), 3.56, 3.21 (6H, s, 7, 7'-OCH₃), 3.30 (2H, m, H-15'), 3.09, 2.55 (6H, s, 2×NCH₃), 2.64 (2H, m, H-15);¹³C-NMR (150 MHz, CD₃OD) δ : 61.1 (C-1), 43.7 (C-3), 23.8 (C-4), 108.4 (C-5), 151.4 (C-6), 137.9 (C-7), 148.7 (C-8), 136.1 (C-9), 115.0 (C-10), 151.2 (C-11), 149.0 (C-12), 111.2 (C-13), 122.2 (C-14), 62.0 (C-1'), 53.6 (C-3'), 34.9 (C-4'), 110.9 (C-5'), 147.0 (C-6'), 146.5 (C-7'), 148.7 (C-8'), 134.1 (C-9'), 131.2 (C-10'), 119.2 (C-11'), 153.6 (C-12'), 120.0 (C-13'), 129.3 (C-14'), 128.9 (C-4a), 120.6 (C-8a), 129.2 (C-4a'), 127.1 (C-8a'), 40.0 (C-15), 36.5 (C-15'), 40.8 (2-NCH₃), 43.0 (2'-NCH₃), 54.4 (6-OCH₃), 54.0 (6'-OCH₃), 58.5, 58.1 (7, 7'-OCH₃)。

OCH₃)。以上数据与文献[17]基本一致,故鉴定为轮环藤宁。

化合物5: 淡黄色无定形粉末,分子式C₂₁H₂₅NO₄,[α]_D²⁵-248°(c 1.0, CHCl₃)。ESI-MS m/z: 356.8 [M+H]⁺。¹H-NMR (400 MHz, CDCl₃) δ : 6.89 (1H, d, J =8.4 Hz, H-11), 6.79 (1H, d, J =8.4 Hz, H-12), 6.74 (1H, s, H-1), 6.62 (1H, s, H-4), 4.25 (1H, d, J =15.8 Hz, H_a-8), 3.89 (3H, s, 9-OCH₃), 3.87 (3H, s, 10-OCH₃), 3.86 (3H, s, 3-OCH₃), 3.85 (3H, s, 2-OCH₃), 3.55 (2H, m, H_b-8, 13a);¹³C-NMR (150 MHz, CDCl₃) δ : 108.5 (C-1), 147.5 (C-2), 147.5 (C-3), 111.0 (C-4), 126.6 (C-4a), 129.4 (C-4b), 28.9 (C-5), 51.5 (C-6), 53.9 (C-8), 127.5 (C-8a), 150.3 (C-9), 145.1 (C-10), 111.3 (C-11), 123.9 (C-12), 128.3 (C-12a), 36.2 (C-13), 60.2 (C-13a), 55.9 (2-OCH₃), 56.1 (3-OCH₃), 59.3 (9-OCH₃), 55.9 (10-OCH₃)。以上数据与文献[18-19]基本一致,故鉴定为左旋四氢巴马汀。

化合物6: 淡黄色无定形粉末,分子式C₁₉H₂₁NO₄,[α]_D²⁵-44°(c 0.10, CHCl₃)。ESI-MS m/z: 328.8 [M+H]⁺。¹H-NMR (400 MHz, DMSO-d₆) δ : 6.73 (1H, s, H-1), 6.72 (1H, d, J =8.3 Hz, H-11), 6.68 (1H, d, J =8.3 Hz, H-12), 6.63 (1H, s, H-4), 4.40 (1H, d, J =16.5 Hz, H_a-8), 3.74 (3H, s, 3-OCH₃), 3.72 (3H, s, 9-OCH₃), 3.17 (1H, m, H_b-8), 3.12~2.55 (4H, m, H-5, 6), 2.87 (1H, m, H-13a), 2.54 (2H, m, H-13);¹³C-NMR (150 MHz, DMSO-d₆) δ : 112.3 (C-1), 147.8 (C-2), 145.1 (C-3), 112.9 (C-4), 125.1 (C-4b), 130.4 (C-4a), 29.0 (C-5), 51.6 (C-6), 54.0 (C-8), 129.2 (C-8a), 143.8 (C-9), 146.5 (C-10), 112.3 (C-11), 124.2 (C-12), 126.2 (C-12a), 36.3 (C-13), 59.7 (C-13a), 59.2 (3-OCH₃), 56.0 (9-OCH₃)。以上数据与文献[18-20]基本一致,故鉴定为光千金藤啶碱。

化合物7: 淡黄色无定形粉末,分子式C₂₀H₂₃NO₄,[α]_D²⁵-184°(c 1.0, CHCl₃)。ESI-MS m/z: 342.8 [M+H]⁺。¹H-NMR (400 MHz, CDCl₃) δ : 8.83 (1H, s, 11-OH), 6.86 (1H, m, H-8), 6.84 (1H, m, H-9), 6.71 (1H, s, H-3), 3.92 (6H, brs, 2, 10-OCH₃), 3.71 (3H, s, 1-

OCH₃), 2.60 (3H, s, NCH₃);¹³C-NMR (150 MHz, CDCl₃) δ : 143.2 (C-1), 153.1 (C-2), 111.5 (C-3), 127.1 (C-3a), 26.2 (C-4), 52.5 (C-5), 63.1 (C-6a), 122.1 (C-6b), 33.3 (C-7), 127.1 (C-7a), 119.6 (C-8), 111.0 (C-9), 150.3 (C-10), 144.3 (C-11), 119.6 (C-11a), 126.5 (C-11b), 42.4 (NCH₃), 62.3 (1-OCH₃), 56.0 (2-OCH₃), 56.2 (10-OCH₃)。以上数据与文献[20]基本一致,故鉴定为异紫堇定。

化合物8: 白色无定形粉末,分子式C₅H₅N₅。ESI-MS m/z: 136.0 [M+H]⁺。¹H-NMR (400 MHz, CD₃OD) δ : 8.18 (1H, s, H-2), 8.12 (1H, s, H-8);¹³C-NMR (150 MHz, CD₃OD) δ : 153.8 (C-3), 152.1 (C-4), 119.9 (C-5), 156.9 (C-6), 141.3 (C-8)。以上数据与文献[21]基本一致,故鉴定为腺嘌呤。

化合物9: 白色无定形粉末,分子式C₁₀H₁₃N₅O₄,[α]_D²⁵-132°(c 0.075, CH₃OH)。ESI-MS m/z: 268.0 [M+H]⁺。¹H-NMR (400 MHz, C₅D₅N) δ : 8.71 (1H, s, H-8), 8.62 (1H, s, H-2), 6.71 (1H, d, J =5.9 Hz, H-1'), 5.50 (1H, brs, H-4'), 5.06 (1H, brs, 5'-OH), 4.76 (1H, dd, J =5.9, 2.7 Hz, H-2'), 4.32 (1H, brd, J =12.3 Hz, H-3'), 4.17~4.11 (1H, m, H-5');¹³C-NMR (150 MHz, C₅D₅N) δ : 153.3 (C-2), 150.3 (C-4), 121.6 (C-5), 157.7 (C-6), 140.6 (C-8), 90.9 (C-1'), 75.5 (C-2'), 72.4 (C-3'), 87.9 (C-4'), 63.1 (C-5')。以上数据与文献[22]基本一致,故鉴定为腺嘌呤核苷。

化合物10: 淡黄色无定形粉末,分子式C₁₈H₂₃NO₅,[α]_D²⁵-113°(c 0.1, CH₃OH)。ESI-MS m/z: 334.2 [M+H]⁺。¹H-NMR (400 MHz, CD₃OD) δ : 6.75 (1H, d, J =8.2 Hz, H-2), 6.53 (1H, d, J =8.2 Hz, H-1), 4.40 (1H, d, J =5.6 Hz, H-9), 4.29 (1H, d, J =2.4 Hz, H-7), 3.84 (1H, m, H-6), 3.81 (3H, s, 3-OCH₃), 3.69 (3H, s, 8-OCH₃), 3.16 (1H, dd, J =17.5, 5.6 Hz, H_a-10), 2.96~2.87 (2H, m, H_a-5, H_b-10), 2.73 (1H, td, J =12.2, 4.8 Hz, H_a-16), 2.68~2.58 (1H, m, H_b-16), 2.17 (1H, d, J =13.4 Hz, H_b-5), 1.95 (1H, d, J =12.2 Hz, H_a-15), 1.87 (1H, td, J =12.2, 4.8 Hz, H_b-15);¹³C-NMR (150 MHz, CD₃OD) δ :

119.3 (C-1), 110.7 (C-2), 147.5 (C-3), 145.6 (C-4), 37.0 (C-5), 68.7 (C-6), 66.8 (C-7), 146.5 (C-8), 46.9 (C-9), 36.9 (C-10), 131.0 (C-11), 123.8 (C-12), 39.9 (C-13), 130.2 (C-14), 38.1 (C-15), 41.2 (C-16), 57.3 (3-OCH₃), 56.8 (8-OCH₃)。以上数据与文献[23]基本一致,故鉴定为sinococuline。

化合物11:淡黄色无定形粉末,分子式C₁₈H₂₁NO₅,[α]_D²⁵-52°(c 0.1, CH₃OH)。ESI-MS m/z: 349.2 [M+NH₄]⁺、289.0 [M- (CH₂C≡N+H)]⁺。¹H-NMR (400 MHz, CD₃OD) δ : 7.19 (1H, brs, H-16), 6.80 (1H, d, J=8.5 Hz, H-2), 6.56 (1H, d, J=8.5 Hz, H-1), 5.09 (1H, brs, H-9), 4.37 (1H, d, J=2.8 Hz, H-7), 3.83 (1H, m, H-6), 3.81 (3H, s, 3-OCH₃), 3.76 (3H, s, 8-OCH₃), 3.40 (1H, brd, J=16.3 Hz, H_a-10), 3.20~3.12 (2H, m, H_a-5, H_b-10), 3.03 (1H, dd, J=20.5, 5.6 Hz, H_a-15), 2.78 (1H, brd, J=20.5 Hz, H_b-15), 2.17 (1H, d, J=13.6 Hz, H_b-5);¹³C-NMR (150 MHz, CD₃OD) δ : 120.6 (C-1), 111.6 (C-2), 148.7 (C-3), 148.0 (C-4), 35.8 (C-5), 68.0 (C-6), 65.3 (C-7), 145.8 (C-8), 64.5 (C-9), 34.1 (C-10), 129.9 (C-11), 126.0 (C-12), 37.0 (C-13), 114.6 (C-14), 38.9 (C-15), 144.0 (C-16), 56.7 (3-OCH₃), 56.1 (8-OCH₃)。以上数据与文献[24]基本一致,故鉴定为cephamorphinanine。

化合物12:白色粒状晶体(甲醇),分子式C₁₇H₁₉NO₃,[α]_D²⁵+21°(c 0.1, CH₃OH)。ESI-MS m/z: 286.0 [M + H]⁺。¹H-NMR (400 MHz, CD₃OD) δ : 7.09 (2H, d, J=8.2 Hz, H-10), 7.09 (1H, d, J=8.2 Hz, H-12), 6.76 (2H, d, J=8.2 Hz, H-9), 6.76 (1H, d, J=8.2 Hz, H-13), 6.67 (1H, s, H-6), 6.66 (1H, s, H-8), 4.14 (1H, m, H-1), 3.82 (3H, s, 6-OCH₃), 3.23 (1H, m, H_a-3), 3.18 (1H, m, H_a-15), 2.92 (1H, m, H_b-3), 2.84 (1H, m, H_b-15), 2.79 (2H, m, H-4);¹³C-NMR (150 MHz, CD₃OD) δ : 56.0 (C-1), 41.9 (C-3), 28.9 (C-4), 126.4 (C-4a), 131.5 (C-4b), 113.0 (C-5), 148.2 (C-6), 145.9 (C-7), 114.2 (C-8), 129.9 (C-9), 130.2 (C-10), 116.6 (C-11), 157.4 (C-12), 116.6 (C-13), 130.2 (C-14), 41.4 (C-1502

15), 57.4 (6-OCH₃)。以上数据与文献[23-25]基本一致,故鉴定为衡州乌药碱。

化合物13:淡黄色无定形粉末,分子式C₂₃H₂₉NO₈,[α]_D²⁵-19°(c 0.1, CH₃OH)。ESI-MS m/z: 447.0 [M]⁺。¹H-NMR (400 MHz, CD₃OD) δ : 7.19 (2H, d, J=8.1 Hz, H-11, 13), 7.07 (2H, d, J=8.1 Hz, H-10, 14), 6.67 (1H, s, H-5), 6.60 (1H, s, H-5), 4.89 (1H, d, J=7.5 Hz, H-1'), 4.11 (1H, brs, H-1), 3.92~3.35 (6H, m, H-2'~6'), 3.82 (3H, s, 12'-OCH₃), 3.20~2.75 (6H, m, H-3, 4, 15);¹³C-NMR (150 MHz, CD₃OD) δ : 57.9 (C-1), 41.5 (C-3), 29.3 (C-4), 126.7 (C-4a), 130.8 (C-4b), 114.2 (C-5), 148.7 (C-6), 145.9 (C-7), 113.0 (C-8), 133.5 (C-9), 131.5 (C-10), 118.1 (C-11), 158.1 (C-12), 118.1 (C-13), 131.5 (C-14), 42.2 (C-15), 102.5 (C-1'), 75.0 (C-2'), 78.2 (C-3'), 71.5 (C-4'), 78.1 (C-5'), 62.6 (C-6'), 56.4 (12-OCH₃)。以上数据与文献[26]基本一致,故鉴定为coclaurine 3-O- β -D-glucoside。

化合物14:淡黄色无定形粉末,分子式C₂₀H₂₄NO₄⁺,[α]_D²⁵-112°(c 0.1, CH₃OH)。ESI-MS m/z: 342.2 [M]⁺。¹H-NMR (400 MHz, CD₃OD) δ : 6.81 (1H, d, J=8.2 Hz, H-11), 6.73 (1H, s, H-4), 6.62 (1H, s, H-1), 6.43 (1H, d, J=8.2 Hz, H-12), 4.80 (1H, brd, J=15.7 Hz, H_b-8), 4.59 (1H, dd, J=10.0, 5.8 Hz, H-13a), 4.53 (1H, brd, J=15.7 Hz, H_a-8), 3.81 (3H, s, 10-OCH₃), 3.79 (3H, s, 3-OCH₃), 3.21 (3H, s, -NCH₃);¹³C-NMR (150 MHz, CD₃OD) δ : 113.0 (C-1), 121.9 (C-1a), 149.8 (C-2), 152.3 (C-3), 115.2 (C-4), 123.3 (C-4a), 24.1 (C-5), 53.5 (C-6), 62.5 (C-8), 115.4 (C-8a), 151.4 (C-9), 150.0 (C-10), 110.7 (C-11), 117.5 (C-12), 121.7 (C-12a), 35.6 (C-13), 67.8 (C-13a), 51.0 (NCH₃), 56.5 (3-OCH₃), 56.5 (10-OCH₃)。以上数据与文献[27]基本一致,故鉴定为轮环藤酚碱。

化合物15:淡黄色无定形粉末,分子式C₂₀H₂₄NO₄⁺,[α]_D²⁵+59°(c 0.1, CH₃OH)。ESI-MS m/z: 342.0 [M]⁺。¹H-NMR (400 MHz, CD₃OD) δ : 6.76 (1H, d, J=7.8 Hz, H-8), 6.65 (1H, s, H-3), 6.64 (1H, d, J=7.8 Hz,

H-9), 3.81 (6H, s, 2-OCH₃, 10-OCH₃), 3.70~3.50 (3H, m, H-5, 6a), 3.36 (3H, s, -NCH₃), 3.16 (1H, brd, J =14.3 Hz, H-4 α), 2.99 (3H, s, NCH₃), 2.95~2.70 (3H, m, H-7, 4 β);¹³C-NMR (150 MHz, CD₃OD) δ : 150.9 (C-1), 152.1 (C-2), 109.7 (C-3), 116.0 (C-3a), 121.12 (C-3b), 24.8 (C-4), 62.8 (C-5), 71.8 (C-6a), 32.1 (C-7), 126.1 (C-7a), 117.2 (C-8), 109.7 (C-9), 150.9 (C-10), 150.0 (C-11), 123.9 (C-11a), 123.9 (C-11b), 56.1 (2-OCH₃), 56.4 (10-OCH₃), 49.6 (-NCH₃), 43.6 (-NCH₃)。以上数据与文献[28]基本一致,故鉴定为木兰花碱。

4 讨论

不同产地植物的次生代谢产物常有差异,本实验选择鲜有报道的四川产金线吊乌龟进行研究,以期丰富该种类的化学成分。金线吊乌龟的多种生物碱具有抗肿瘤、抗炎等作用^[7-13],本研究所得化合物可用于相关活性的筛选,以期有助于研究类似结构生物碱的构效关系,进一步阐明该植物的药效物质基础。

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