

· 论 文 ·

台湾狗牙花的生物碱类化学成分

谢 静^{1,2}, 范春林^{1,2}, 徐 杰^{1,2}, 张 建^{1,2}, 叶文才^{1,2,3}, 张晓琦^{1,2,3*}

(¹暨南大学药学院中药及天然药物研究所, 广州 510632; ²暨南大学广东省现代中药工程技术研究中心, 广州 510632;

³国家药品监督管理局中成药质量评价重点实验室, 广州 510632)

摘 要 采用硅胶、Sephadex LH-20、ODS、HPLC 等色谱方法进行分离纯化, 从夹竹桃科植物台湾狗牙花(*Ervatamia pandacaqui* Pichon)枝叶中分离得到 11 个生物碱类化合物, 根据其理化性质与波谱数据分别鉴定为 voacristine 7-hydroxyindolenine(**1**), iboxygaine (**2**), 19S-hydroxyibogamine (**3**), 3-oxotabersonine (**4**), 派利文碱(perivine, **5**), 佩西立文(pericyclivine, **6**), rhazinalinol (**7**), geissoschizol (**8**), 3, 14-dihydroolivacine (**9**), 瓦莱萨明碱(vallesamine, **10**), conolobine A(**11**)。化合物 **1**~**11** 均为首次从该植物中分离得到。

关键词 夹竹桃科; 台湾狗牙花; 生物碱; 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 1000-5048(2021)03-0287-06

doi: 10.11665/j.issn.1000-5048.20210304

引用本文 谢静, 范春林, 徐杰, 等. 台湾狗牙花的生物碱类化学成分[J]. 中国药科大学学报, 2021, 52(3): 287–292.

Cite this article as: XIE Jing, FAN Chunlin, XU Jie, et al. Alkaloids of *Ervatamia pandacaqui*[J]. J China Pharm Univ, 2021, 52(3): 287–292.

Alkaloids of *Ervatamia pandacaqui*

XIE Jing^{1,2}, FAN Chunlin^{1,2}, XU Jie^{1,2}, ZHANG Jian^{1,2}, YE Wencai^{1,2,3}, ZHANG Xiaoqi^{1,2,3*}

¹Institute of Traditional Chinese Medicine & Natural Products, College of Pharmacy, Ji'nan University, Guangzhou 510632;

²Guangdong Engineering Research Center for Modernization of TCM, Ji'nan University, Guangzhou 510632;

³NMPA Key Laboratory for Quality Evaluation of TCM(Traditional Chinese Patent Medicine), Guangzhou 510632, China

Abstract Eleven alkaloids were isolated from the twigs and leaves of *Ervatamia pandacaqui* using chromatographic methods of silica gel, Sephadex LH-20, ODS, and HPLC. Their structures were elucidated by physical, chemical and spectroscopic methods and determined as voacristine 7-hydroxyindolenine (**1**), iboxygaine (**2**), 19S-hydroxyibogamine (**3**), 3-oxotabersonine (**4**), perivine (**5**), pericyclivine (**6**), rhazinalinol (**7**), geissoschizol (**8**), 3, 14-dihydroolivacine (**9**), vallesamine (**10**), and conolobine A (**11**), respectively. All compounds were isolated from this plant for the first time.

Key words Apocynaceae; *Ervatamia pandacaqui*; alkaloids; chemical constituent; isolation and identification

This study was supported by the National Natural Science Foundation of China (No. U1801287, No. 82073712) and the Science and Technology Planning Project of Guangdong Province (No. 2018B020207008, No. 2020B1111110004)

台湾狗牙花(*Ervatamia pandacaqui* Pichon)为夹竹桃科(Apocynaceae)狗牙花属植物, 原产于菲律宾, 主要栽培于我国台湾省台南市及广东省南部岛屿; 具有清热降压和消肿解毒的作用, 常用于

收稿日期 2020-11-21 * 通信作者 Tel: 020-85223994 E-mail: tzhxq01@jnu.edu.cn

基金项目 国家自然科学基金资助项目(No. U1801287, No. 82073712); 广东省科技计划资助项目(No. 2018B020207008, No. 2020B1111110004)

治疗高血压、咽喉肿痛、痈疽疮毒、跌打损伤等;其化学成分研究较少^[1]。狗牙花属植物约有120种,主要分布于从印度起经中国西南部、越南、缅甸、泰国、马来西亚、印度尼西亚、菲律宾到澳大利亚地区;我国产狗牙花主要有15个种和5个变种,分布于西南到华南及台湾省等地区^[2]。狗牙花属植物中富含的生物碱结构复杂多变,生物活性显著,本课题组前期系统地对该属植物药用狗牙花、海南狗牙花和台湾狗牙花中的生物碱类成分进行研究,从中发现了一系列具有新颖骨架且生物活性好的化合物^[3-8]。本研究又从台湾狗牙花枝叶中分离得到11个生物碱类化合物,分别鉴定为:voacristine 7-hydroxyindolenine (**1**), iboxygaine (**2**), 19S-hydroxyibogamine (**3**), 3-oxotabersonine (**4**), 派利文碱(perivine, **5**), 佩西立文(pericyclivine, **6**), rhazinalinol (**7**), geissoschizol (**8**), 3, 14-dihydroolivacine (**9**), 瓦莱萨明碱(vallesamine, **10**), conolobine A (**11**)。所有化合物均为首次从该植物中分离得到。

1 仪器与材料

V-550型紫外-可见光谱仪, FT/IR-480 Plus Fourier Transform型红外光谱仪(日本Jasco公司); Advantage Max 质谱仪(美国Thermo Finnigan公司); 6210 ESI/TOF 质谱仪, 1200分析及制备型高效液相色谱仪(美国安捷伦公司); AV-400型超导核磁共振仪(美国Bruker公司)。

柱色谱用硅胶(100~200目、200~300目, 青岛海洋化工厂); RP₁₈柱色谱填料(C₁₈, 10~40 μm, 德国Merck公司); Sephadex LH-20(美国Pharmacia公司)。所用试剂均为分析纯或化学纯。

台湾狗牙花植物于2015年9月采集于台湾省台南市, 经香港科技大学董婷霞博士鉴定为台湾狗牙花(*Ervatamia pandacqui* Pichon)的干燥枝叶。标本(No. CP2015091001)存放于暨南大学药学院植物标本室。

2 提取与分离

台湾狗牙花枝叶5.0 kg, 粉碎成粗粉, 用95%乙醇渗滤提取3次, 减压浓缩后得到总浸膏450 g, 加水混悬后, 用10% HCl调pH至2~3后, 氯仿萃取, 酸水层用氨水调pH至9~10, 萃取液减压浓缩

得到粗总生物碱12.5 g。粗总生物碱部位通过硅胶柱色谱(石油醚-丙酮, 100:0→0:100)得到10个馏分(Fr. 1~10)。Fr. 5经Sephadex LH-20柱色谱(氯仿-甲醇, 1:1)得到Fr. 5A~5C; Fr. 5B经ODS反相柱色谱、Sephadex LH-20柱色谱(甲醇)以及制备型HPLC纯化得到化合物**1**[16 mg, 乙腈-水(30:70), t_R = 25.0 min]、化合物**2**[23 mg, 乙腈-水(32:68), t_R = 18.0 min]、化合物**3**[19 mg, 乙腈-水(35:70), t_R = 15.0 min]。Fr. 7经Sephadex LH-20柱色谱(氯仿-甲醇, 1:1)得到Fr. 7A~7C; Fr. 7B经ODS反相柱色谱、Sephadex LH-20柱色谱(甲醇)以及制备型HPLC纯化得到化合物**8**[21 mg, 乙腈-水(50:50), t_R = 27.0 min]、化合物**9**[27 mg, 乙腈-水(47:53), t_R = 23.0 min]、化合物**11**[18 mg, 乙腈-水(42:58), t_R = 28.0 min]。Fr. 9经Sephadex LH-20柱色谱(氯仿-甲醇, 1:1)得到Fr. 9A~9E; Fr. 9C经ODS反相柱色谱、Sephadex LH-20柱色谱(甲醇)以及制备型HPLC纯化得到化合物**4**[25 mg, 乙腈-水(35:65), t_R = 29.0 min]、化合物**5**[28 mg, 乙腈-水(30:70), t_R = 27.0 min]、化合物**6**[17 mg, 乙腈-水(28:70), t_R = 25.0 min]。Fr. 10经Sephadex LH-20柱色谱(氯仿-甲醇, 1:1)得到Fr. 10A~10C; Fr. 10B经ODS反相柱色谱、Sephadex LH-20柱色谱(甲醇)以及制备型HPLC纯化得到化合物**7**[23 mg, 乙腈-水(35:70), t_R = 20.0 min]、化合物**10**[18 mg, 乙腈-水(40:70), t_R = 16.0 min]。

3 结构鉴定

化合物**1** 黄色粉末, 改良碘化铋钾反应呈阳性。UV $\lambda_{\text{MeOH}}^{\text{max}}$: 207, 228, 291 nm; IR (KBr): 3 423, 3 263, 1 734, 1 541, 1 474 cm⁻¹; ESI-MS m/z : 401.5 [M+H]⁺。¹H NMR (CD₃OD, 400 MHz) δ : 7.30 (1H, d, J = 8.4 Hz, H-12), 6.97 (1H, d, J = 2.4 Hz, H-9), 6.88 (1H, dd, J = 8.4, 2.4 Hz, H-11), 4.30 (1H, s, H-21), 4.03 (1H, m, H-19a), 3.83 (3H, s, OMe), 3.68 (3H, s, COOMe), 3.58 (1H, m, H-5 α), 2.96 (1H, m, H-5 β), 2.90 (1H, m, H-3a), 2.84 (1H, m, H-3b), 2.83 (1H, d, J = 13.8, H-17 α), 2.26 (1H, m, H-6 β), 2.00 (1H, m, H-17 β), 1.90 (1H, m, H-14), 1.65 (1H, m, H-6 α), 1.75 (1H, m, H-15 α), 1.50 (1H, m, H-15 β), 1.50 (1H, m, H-20), 1.12 (3H, d, J = 6.3, H-18); ¹³C NMR (CD₃OD, 100 MHz) δ :

189.5(C-2), 173.7(COOMe), 161.0(C-10), 145.6(C-8), 145.6(C-13), 121.7(C-12), 114.8(C-11), 109.5(C-9), 88.5(C-7), 72.7(C-19), 58.7(C-21), 58.2(C-16), 56.2(OMe), 53.4(COOMe), 49.9(C-

5), 48.9(C-3), 40.8(C-20), 38.2(C-6), 34.3(C-17), 28.1(C-14), 25.2(C-15), 20.7(C-18)。综上所述,化合物数据与文献[9]报道一致,故鉴定化合物 **1** 为 voacristine 7-hydroxyindolenine。

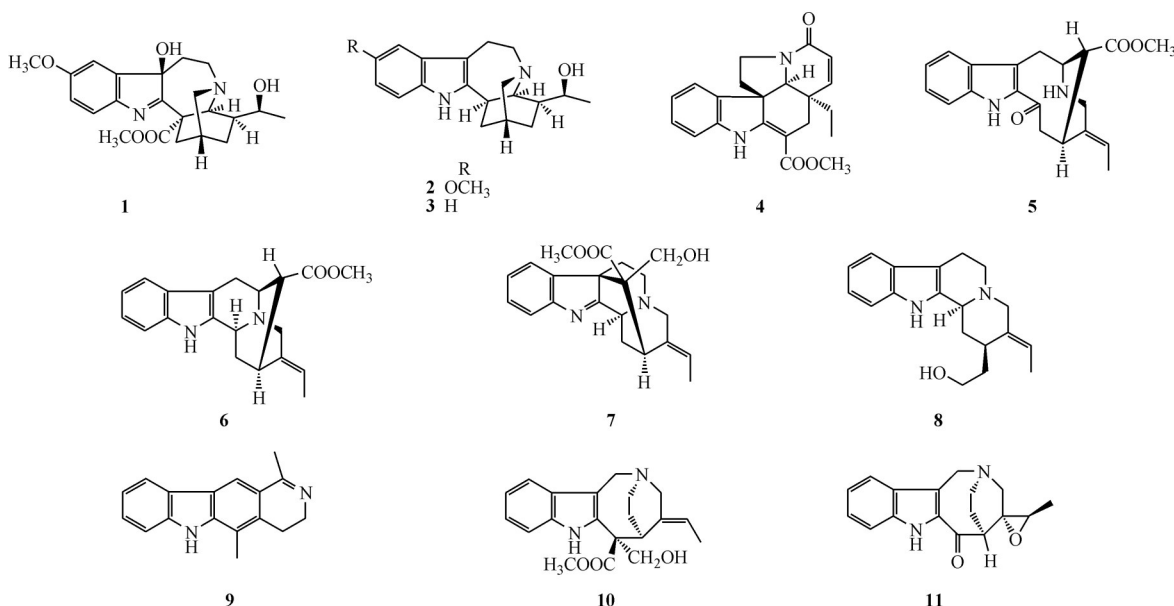


Figure 1 Chemical structures of compounds 1 - 11

化合物 **2** 白色粉末,改良碘化铋钾反应呈阳性。UV $\lambda_{\text{Max}}^{\text{MeOH}}$: 207, 227, 287 nm; IR (KBr): 3 399, 3 234, 2 922, 1 487, 1 455, 1 215, 823 cm^{-1} ; ESI-MS m/z 327. 3 $[\text{M}+\text{H}]^+$. ^1H NMR (CD_3OD , 400 MHz) δ : 7.11 (1H, d, $J = 8.4$ Hz, H-12), 6.90 (1H, d, $J = 2.4$ Hz, H-9), 6.69 (1H, dd, $J = 8.4, 2.4$ Hz, H-11), 4.15 (1H, m, H-19), 3.824 (3H, s, OMe), 3.35 (2H, m, H-5), 3.18 (1H, m, H-6 β), 3.17 (1H, m, H-16), 3.11 (1H, m, H-3a), 3.11 (1H, m, H-6 α), 3.11 (1H, s, H-21), 2.97 (1H, m, H-3b), 2.71 (1H, dd, $J = 14.6$ Hz, 3.6 Hz, H-17 α), 2.15 (1H, m, H-17 β), 1.98 (1H, m, H-14), 1.91 (1H, m, H-15 α), 1.74 (1H, m, H-15 β), 1.66 (1H, m, H-20), 1.14 (3H, d, $J = 6.4$ Hz, H-18); ^{13}C NMR (CD_3OD , 100 MHz) δ : 154.9(C-10), 143.5(C-2), 131.8(C-13), 131.1(C-8), 111.9(C-12), 111.4(C-11), 108.3(C-7), 101.1(C-9), 73.2(C-19), 61.9(C-21), 56.4(OMe), 54.2(C-5), 50.4(C-3), 43.6(C-20), 41.1(C-16), 35.4(C-17), 27.5(C-14), 24.6(C-15), 21.2(C-6), 20.3(C-18)。综上所述,化合物数据与文献[10]报道一致,故鉴定化合物 **2** 为 iboxygaine。

化合物 **3** 黄色粉末,改良碘化铋钾反应呈阳性。[α] $_{\text{D}}^{25}$ -21.0° (c 0.16, CHCl_3); UV $\lambda_{\text{Max}}^{\text{MeOH}}$: 205, 226, 282 nm; IR (KBr): 3 399, 3 264, 2 926, 1 541, 1 456, 1 155, 742 cm^{-1} ; ESI-MS m/z 297. 4 $[\text{M}+\text{H}]^+$; ^1H NMR (CD_3OD , 400 MHz) δ : 7.39 (1H, d, $J = 7.7$ Hz, H-9), 7.22 (1H, d, $J = 7.7$ Hz, H-12), 7.02 (1H, t, $J = 7.7$ Hz, H-11), 6.96 (1H, t, $J = 7.7$ Hz, H-10), 4.16 (1H, m, H-19), 3.36 (1H, s, H-21), 3.33 (2H, m, H-5), 3.16 (1H, m, H-16), 3.15 (1H, m, H-6 β), 3.12 (1H, m, H-3a), 3.12 (1H, m, H-6 α), 2.96 (1H, m, H-3b), 2.75 (1H, m, H-17 α), 2.15 (1H, m, H-17 β), 1.98 (1H, m, H-14), 1.91 (1H, m, H-15 α), 1.76 (1H, m, H-15 β), 1.65 (1H, m, H-20), 1.14 (3H, d, $J = 6.4$ Hz, H-18); ^{13}C NMR (CD_3OD , 100 MHz) δ : 142.6(C-2), 136.7(C-13), 130.7(C-8), 121.6(C-11), 119.4(C-10), 118.5(C-9), 111.2(C-12), 108.4(C-7), 73.20(C-19), 61.9(C-21), 54.2(C-5), 50.4(C-3), 43.6(C-20), 41.0(C-16), 35.4(C-17), 27.5(C-14), 24.6(C-15), 21.2(C-6), 20.3(C-18)。综上所述,化合物数据与文献[11]报道一致,故鉴定化合物 **3** 为 19S-hydroxyibogaine。

mine。

化合物**4** 白色粉末,改良碘化铯钾反应呈阳性。 $[\alpha]_D^{25} -85.0^\circ (c\ 0.35, CH_3OH)$; UV λ_{Max}^{MeOH} : 207, 293, 329 nm; IR (KBr): 3 423, 2 947, 1 717, 1 661, 1 610, 1 461, 1 382, 751 cm^{-1} ; ESI-MS m/z 351.4 $[M+H]^+$; 1H NMR (CD_3OD , 400 MHz) δ : 4.22 (1H, m, H-5 β), 3.45 (1H, m, H-5 α), 1.98 (1H, m, H-6 β), 1.86 (1H, m, H-6 α), 7.38 (1H, d, $J = 7.8$ Hz, H-9), 7.23 (1H, t, $J = 7.8$ Hz, H-11), 7.06 (1H, d, $J = 7.8$ Hz, H-12), 6.96 (1H, t, $J = 7.8$ Hz, H-10), 6.65 (1H, d, $J = 9.9$ Hz, H-14), 5.92 (1H, d, $J = 9.9$ Hz, H-15), 4.10 (1H, m, H-21), 3.80 (3H, s, OMe), 2.68 (1H, d, $J = 15.1$ Hz, H-17 α), 2.51 (1H, d, $J = 15.1$ Hz, H-17 β), 1.07 (2H, m, H-19), 0.75 (3H, d, $J = 7.4$ Hz, H-18); ^{13}C NMR (CD_3OD , 100 MHz) δ : 169.4 (COOMe), 166.5 (C-3), 163.5 (C-2), 148.1 (C-15), 144.7 (C-13), 136.8 (C-8), 129.8 (C-11), 122.8 (C-14), 122.6 (C-9), 122.2 (C-10), 111.2 (C-12), 90.6 (C-16), 67.9 (C-21), 58.2 (C-7), 51.6 (COOMe), 44.9 (C-5), 44.4 (C-6), 41.7 (C-20), 27.9 (C-19), 27.2 (C-17), 7.6 (C-18)。综上所述,化合物数据与文献[12]报道一致,故鉴定化合物**4**为3-oxotabersonine。

化合物**5** 白色粉末,改良碘化铯钾反应呈阳性。UV λ_{Max}^{MeOH} : 206, 232, 315 nm; IR (KBr): 3 419, 2 949, 1 716, 1 643, 1 541, 1 456, 746 cm^{-1} ; HR-ESI-MS m/z 339.1708 $[M+H]^+$; 1H NMR (CD_3OD , 400 MHz) δ : 7.76 (1H, d, $J = 7.8$ Hz, H-9), 7.40 (1H, d, $J = 7.8$ Hz, H-12), 7.33 (1H, t, $J = 7.8$ Hz, H-11), 7.14 (1H, t, $J = 7.8$ Hz, H-10), 5.53 (1H, q, $J = 6.3$ Hz, H-19), 4.32 (1H, m, H-16), 4.21 (1H, d, $J = 14.6$ Hz, H-21 β), 4.10 (1H, m, H-5), 3.82 (1H, m, H-15), 3.73 (1H, m, H-6 β), 3.53 (1H, m, H-6 α), 3.53 (1H, m, H-14 β), 3.26 (1H, d, $J = 14.6$ Hz, H-21 α), 2.69 (1H, s, COOMe), 2.63 (1H, m, H-14 α), 1.73 (3H, d, $J = 6.3$ Hz, H-18); ^{13}C NMR (CD_3OD , 100 MHz) δ : 192.3 (C-3), 172.3 (COOMe), 138.4 (C-20), 138.1 (C-13), 135.4 (C-2), 129.5 (C-8), 127.6 (C-11), 121.8 (C-9), 121.5 (C-7), 121.4 (C-10), 121.2 (C-19), 113.2 (C-12), 51.80 (C-5), 51.1 (COOMe), 49.2 (C-16), 44.1 (C-21), 44.0 (C-14), 32.2 (C-15), 25.7 (C-6), 12.2 (C-18)。综上所述,

化合物数据与文献[13]报道一致,故鉴定化合物**5**为派利文碱(perivine)。

化合物**6** 黄色油状物,改良碘化铯钾反应呈阳性。UV λ_{Max}^{MeOH} : 205, 227, 280 nm; IR (KBr): 3 380, 2 940, 1 717, 1 541, 1 456, 732 cm^{-1} ; ESI-MS m/z 323.3 $[M+H]^+$; 1H NMR (CD_3OD , 400 MHz) δ : 7.7 (1H, d, $J = 7.8$ Hz, H-12), 7.36 (1H, d, $J = 7.8$ Hz, H-9), 7.04 (1H, t, $J = 7.8$ Hz, H-11), 6.96 (1H, t, $J = 7.8$ Hz, H-10), 5.33 (1H, q, $J = 6.7$ Hz, H-19), 4.24 (1H, m, H-5), 3.79 (1H, m, H-21 β), 3.69 (1H, m, H-3), 3.61 (1H, m, H-21 α), 3.04 (3H, s, COOMe), 2.99 (1H, m, H-15), 2.89 (2H, m, H-6), 2.62 (1H, m, H-14 β), 1.83 (1H, m, H-14 α), 1.64 (3H, d, $J = 6.7$ Hz, H-18); ^{13}C NMR (CD_3OD , 100 MHz) δ : 174.2 (COOMe), 139.7 (C-2), 138.6 (C-13), 138.5 (C-20), 128.1 (C-8), 122.0 (C-11), 119.7 (C-10), 118.4 (C-9), 116.0 (C-19), 112.0 (C-12), 105.3 (C-7), 56.5 (C-21), 54.2 (C-5), 51.6 (C-3), 51.4 (COOMe), 44.8 (C-16), 28.3 (C-15), 27.8 (C-14), 24.8 (C-6), 12.9 (C-18)。综上所述,化合物数据与文献[13]报道一致,故鉴定化合物**6**为佩西立文(pericyclivine)。

化合物**7** 黄色粉末,改良碘化铯钾反应呈阳性。UV λ_{Max}^{MeOH} : 207, 288, 335 nm; IR (KBr): 3 418, 3 216, 2 942, 1 733, 1 649, 1 541, 1 456, 752 cm^{-1} ; ESI-MS m/z 353.4 $[M+H]^+$; 1H NMR (CD_3OD , 400 MHz) δ : 7.82 (1H, d, $J = 7.5$ Hz, H-9), 7.47 (1H, d, $J = 7.5$ Hz, H-12), 7.26 (1H, t, $J = 7.5$ Hz, H-11), 7.14 (1H, t, $J = 7.5$ Hz, H-10), 5.64 (1H, q, $J = 6.8$ Hz, H-19), 4.47 (1H, m, H-3), 4.41 (1H, m, H-17a), 4.34 (1H, m, H-17b), 4.08 (1H, d, $J = 17.3$ Hz, H-21 α), 3.21 (1H, d, $J = 17.3$ Hz, H-21 β), 3.16 (3H, s, COOMe), 3.15 (1H, m, H-6 β), 2.66 (1H, m, H-5 α), 2.55 (1H, m, H-5 β), 2.45 (1H, m, H-14 α), 2.37 (1H, m, H-14 β), 3.28 (1H, m, H-15), 1.80 (1H, m, H-6 α), 1.75 (3H, d, $J = 6.8$ Hz, H-18); ^{13}C NMR (CD_3OD , 100 MHz) δ : 191.5 (C-2), 173.8 (COOMe), 156.1 (C-13), 148.3 (C-8), 139.2 (C-20), 128.5 (C-11), 127.0 (C-9), 126.6 (C-10), 122.9 (C-19), 120.7 (C-12), 65.0 (C-16), 64.2 (C-17), 58.9 (C-7), 55.7 (C-3), 53.6 (C-21), 52.0 (COOMe), 51.8 (C-5), 36.3 (C-6), 35.8 (C-15),

32.2(C-14), 14.7(C-18)。综上所述,化合物数据与文献[14]报道一致,故鉴定化合物 **7** 为 rhazin-alinol。

化合物 **8** 黄色粉末;改良碘化铋钾反应呈阳性。 $[\alpha]_D^{25} -18.5^\circ$ (c 0.72, CH₃OH); UV $\lambda_{\text{Max}}^{\text{MeOH}}$: 207, 223, 281 nm; HR-ESI-MS m/z 297.196 9 [M+H]⁺; ¹H NMR (CD₃OD, 400 MHz) δ : 7.41 (1H, d, $J = 7.8$ Hz, H-9), 7.33 (1H, d, $J = 7.8$ Hz, H-12), 7.07 (1H, t, $J = 7.8$ Hz, H-11), 6.99 (1H, t, $J = 7.8$ Hz, H-10), 5.59 (1H, q, $J = 6.8$ Hz, H-19), 4.29 (1H, s, H-3), 3.67 (1H, m, H-21 α), 3.43 (2H, m, H-17), 3.25 (1H, m, H-5 α), 3.12 (1H, m, H-5 β), 3.04 (1H, m, H-6 α), 3.04 (1H, m, H-21 β), 2.97 (1H, m, H-15), 2.68 (1H, m, H-6 β), 2.27 (2H, t, $J = 5.1$ Hz, H-14), 1.69 (3H, q, $J = 6.8$ Hz, H-18), 1.59 (1H, m, H-16a), 1.42 (1H, m, H-16b); ¹³C NMR (CD₃OD, 100 MHz) δ : 137.8 (C-13), 137.5 (C-20), 134.4 (C-2), 128.5 (C-8), 122.8 (C-19), 122.1 (C-11), 119.8 (C-10), 118.6 (C-9), 112.0 (C-12), 107.0 (C-7), 61.0 (C-17), 54.70 (C-3), 54.0 (C-21), 51.90 (C-5), 36.9 (C-16), 33.3 (C-14), 32.2 (C-15), 18.70 (C-6), 13.2 (C-18)。综上所述,化合物数据与文献[15]报道一致,故鉴定化合物 **8** 为 geissoschizol。

化合物 **9** 黄色粉末;改良碘化铋钾反应呈阳性; UV $\lambda_{\text{Max}}^{\text{MeOH}}$: 203, 241, 285, 306, 339 nm; ESI-MS m/z 249.3 [M+H]⁺; ¹H NMR (CD₃OD, 400 MHz) δ : 8.18 (1H, s, H-21), 8.11 (1H, d, $J = 7.8$ Hz, H-9), 7.52 (1H, d, $J = 7.8$ Hz, H-12), 7.41 (1H, t, $J = 7.8$ Hz, H-11), 7.22 (1H, t, $J = 7.8$ Hz, H-10), 4.11 (2H, m, H-3), 3.29 (2H, m, H-14), 2.65 (3H, s, H-18), 2.55 (3H, s, H-17); ¹³C NMR (CD₃OD, 100 MHz) δ : 150.0 (C-19), 142.5 (C-2), 142.0 (C-13), 129.2 (C-15), 127.1 (C-11), 124.7 (C-8), 122.8 (C-7), 121.7 (C-20), 121.2 (C-9), 120.7 (C-10), 118.5 (C-16), 117.6 (C-21), 112.2 (C-12), 57.5 (C-3), 25.7 (C-14), 13.9 (C-18), 13.0 (C-17)。综上所述,化合物数据与文献[16]报道一致,故鉴定化合物 **9** 为 3,14-dihydroolivacine。

化合物 **10** 黄色粉末,改良碘化铋钾反应呈阳性。UV $\lambda_{\text{Max}}^{\text{MeOH}}$: 221, 283; IR (KBr): 3 396, 3 261, 2 945, 1 716, 1 646, 1 620, 1 541, 1 459, 744 cm⁻¹;

HR-ESI-MS m/z 341.186 6 [M+H]⁺; ¹H NMR (CD₃OD, 400 MHz) δ : 7.43 (1H, d, $J = 7.8$ Hz, H-9), 7.33 (1H, d, $J = 7.8$ Hz, H-12), 7.11 (1H, t, $J = 7.8$ Hz, H-11), 7.01 (1H, t, $J = 7.8$ Hz, H-10), 5.60 (1H, q, $J = 6.6$ Hz, H-19), 4.70 (1H, d, $J = 16.8$ Hz, H-17a), 4.18 (2H, m, H-5), 4.17 (1H, d, $J = 10.1$ Hz, H-21 α), 4.04 (1H, d, $J = 16.8$ Hz, H-17b), 3.81 (1H, d, $J = 10.1$ Hz, H-21 β), 3.77 (3H, s, COOMe), 3.59 (1H, m, H-3a), 3.50 (1H, m, H-3b), 2.86 (1H, d, $J = 8.7$ Hz, H-15), 2.28 (1H, m, H-14a), 1.93 (1H, m, H-14b), 1.77 (3H, d, $J = 6.6$ Hz, H-18); ¹³C NMR (CD₃OD, 100 MHz) δ : 176.1 (COOMe), 136.7 (C-13), 134.5 (C-2), 134.3 (C-20), 129.3 (C-8), 125.5 (C-19), 122.9 (C-11), 119.7 (C-10), 118.6 (C-9), 111.6 (C-12), 108.7 (C-7), 70.6 (C-17), 60.2 (C-16), 54.6 (C-21), 53.1 (COOMe), 51.3 (C-5), 48.4 (C-3), 37.2 (C-15), 24.9 (C-14), 14.2 (C-18)。综上所述,化合物数据与文献[17]报道一致,故鉴定化合物 **10** 为瓦莱萨明碱(vallesamine)。

化合物 **11** 黄色粉末,改良碘化铋钾反应呈阳性。 $[\alpha]_D^{25} +24.1^\circ$ (c 0.21, CHCl₃); UV $\lambda_{\text{Max}}^{\text{MeOH}}$: 209, 313 nm; IR (KBr): 3 420, 2 931, 1 672, 1 547, 1 457, 1 385, 748 cm⁻¹; HR-ESI-MS m/z 283.144 7 [M+H]⁺; ¹H NMR (CD₃OD, 400 MHz) δ : 7.60 (1H, d, $J = 7.8$ Hz, H-9), 7.42 (1H, d, $J = 7.8$ Hz, H-12), 7.32 (1H, t, $J = 7.8$ Hz, H-11), 7.09 (1H, t, $J = 7.8$ Hz, H-10), 4.84 (1H, m, H-6a), 4.51 (1H, m, H-6b), 3.71 (1H, d, $J = 15.3$ Hz, H-21 α), 3.36 (1H, m, H-3a), 3.24 (1H, d, $J = 6.6$ Hz, H-15), 3.20 (1H, m, H-3b); 2.98 (1H, q, $J = 5.4$ Hz, H-19), 2.66 (1H, d, $J = 15.3$ Hz, H-21 β), 2.23 (1H, m, H-14a), 2.12 (1H, m, H-14b), 1.29 (3H, d, $J = 5.4$ Hz, H-18); ¹³C NMR (CD₃OD, 100 MHz) δ : 193.3 (C-16), 138.5 (C-13), 132.5 (C-2), 128.9 (C-8), 127.3 (C-11), 121.4 (C-9), 121.0 (C-10), 113.2 (C-12), 119.3 (C-7), 60.9 (C-20), 57.9 (C-19), 55.7 (C-21), 54.4 (C-6), 47.4 (C-15), 44.5 (C-3), 23.6 (C-14), 13.3 (C-18)。综上所述,化合物数据与文献[10]报道一致,故鉴定化合物 **11** 为 conolobine A。

References

- [1] Editorial Board of the Flora of China. *Flora of China: Volume 63* (中国植物志: 第63卷) [M]. Beijing: Science Press, 1977: 114.
- [2] Li BT, Chen XM. Comparative review on apocynaceae in flora reipublicae popularis sinicae and flora of China [J]. *Guihaia* (广西植物), 1997, 17(4): 299-305.
- [3] Liu ZW, Yang TT, Wang WJ, et al. Ervahainine A, a new cyano-substituted oxindole alkaloid from *Ervatamia hainanensis* [J]. *Tetrahedron Lett*, 2013, 54(48): 6498-6500.
- [4] Tang BQ, Wang WJ, Huang XJ, et al. Iboga-type alkaloids from *Ervatamia officinalis* [J]. *J Nat Prod*, 2014, 77(8): 1839-1846.
- [5] Liu ZW, Huang XJ, Xiao HL, et al. New iboga-type alkaloids from *Ervatamia hainanensis* [J]. *RSC Adv*, 2016, 6(36): 30277-30284.
- [6] Liu ZW, Tang BQ, Zhang QH, et al. Ervaoffines E-G, three iboga-type alkaloids featuring ring C cleavage and rearrangement from *Ervatamia officinalis* [J]. *RSC Adv*, 2017, 7(35): 21883-21889.
- [7] Zhang QH, Ding Y, Bai WX, et al. Studies on alkaloids from *Ervatamia pandacaqui* [J]. *China J Chin Mater Med* (中国中药杂志), 2018, 43(7): 1471-1475.
- [8] Liu ZW, Zhang J, Li ST, et al. Ervadivamines A and B, two unusual trimeric monoterpene indole alkaloids from *Ervatamia divaricata* [J]. *J Org Chem*, 2018, 83(17): 10613-10618.
- [9] Kam TS, Loh KY, Wei C. Conophylline and conophyllidine: new dimeric alkaloids from *Tabernaemontana divaricata* [J]. *J Nat Prod*, 1993, 56(11): 1865-1871.
- [10] Kam TS, Pang HS, Choo YM, et al. Biologically active ibogan and vallesamine derivatives from *Tabernaemontana divaricata* [J]. *Chem Biodivers*, 2004, 1(4): 646-656.
- [11] Kam TS, Sim KM. Five new iboga alkaloids from *Tabernaemontana corymbosa* [J]. *J Nat Prod*, 2002, 65(5): 669-672.
- [12] Achenbach H, Benirschke M, Torrenegra R. Alkaloids and other compounds from seeds of *Tabernaemontana cymosa* [J]. *Phytochemistry*, 1997, 45(2): 325-335.
- [13] Clivio P, Richard B, Hadi HA, et al. Alkaloids from leaves and stem bark of *Ervatamia polyneura* [J]. *Phytochemistry*, 1990, 29(9): 3007-3011.
- [14] Kam TS, Yoganathan K, Mok SL. Aspidofractinine alkaloids from *Kopsia teoi* [J]. *Phytochemistry*, 1997, 46(4): 789-792.
- [15] He YL, Chen WM, Feng XZ. Studies on chemical constituents of Longzhou Shancheng (*Melodinus morsei*) [J]. *Chin Tradit Herbal Drugs* (中草药), 1993, 24(12): 623-625, 670.
- [16] Azoug M, Loukaci A, Richard B, et al. Alkaloids from stem bark and leaves of *Peschiera buchtienii* [J]. *Phytochemistry*, 1995, 39(5): 1223-1228.
- [17] Luo XG, Chen HS, Liang S, et al. Alkaloids from stems of *Ervatamia yunnanensis* [J]. *Chin Chem Lett*, 2007, 18(6): 697-699.

·本刊讯·

《中国药科大学学报》微信公众号荣获“十佳微信公众号”

2021年5月,江苏省高校学报研究会从江苏省内高校学报微信公众号中评选出“十佳微信公众号”,《中国药科大学学报》微信公众号位列其中,继2019年后再次获此殊荣。

在媒体融合的大时代背景下,学术期刊微信公众平台对学术运营与传播起着非常重要的促进作用。《中国药科大学学报》的微信公众号“中国药科大学学报”始建于2013年,迄今关注用户已超过5 000人。作为传统媒体的延伸,编辑部依托微信公众号平台,实现了以下功能:将高水平论文置封面位置主推,提高优秀论文和通信作者的显示度,使本刊的学术内容进一步广泛传播;同步最新的校园资讯,特别是科研动态以及本刊编委获奖信息;发布全球新药研发动态以及全球医药经济走向资讯;向研究生作者、读者介绍检索和写作技巧,提供学习途径的各类实用技术帖;此外,还有节假日的温馨祝福等。丰富的内容形成了本刊微信公众号的特色,从而作者关注度和黏度不断提升。

本刊编辑部将继续秉承服务至上的理念,充分利用纸质期刊与微信平台的优势互补,向微信服务号转型,进一步扩大期刊影响力,提供更加周到的知识服务,使《中国药科大学学报》在新媒体融合发展时代更好地传播学术成果、服务广大作者和读者。

(本刊编辑部)