

马比木根的化学成分研究

白永花^{1,2}, 宋启示^{1*}¹中国科学院西双版纳热带植物园 热带植物资源开放实验室, 昆明 650223;²中国科学院大学, 北京 100049

摘要: 通过硅胶、MCI 和 Sephadex LH-20 反复柱层析、纯化, 从马比木根的甲醇提取物中分离得到 14 个化合物, 运用现代波谱技术鉴定为 β -谷甾醇(1), β -胡萝卜苷(2), 7-酮基- β -谷甾醇(3), β -sitosteryl-3-O- β -D-glucopyranoside-2'-O-palmitate(4), 5 α , 6 β -二羟基胡萝卜苷(5), 羽扇豆醇(6), 3-乙酰氧基-12-齐墩果烯-28-醇(7), 喜树碱(8), 9-甲氧基喜树碱(9), 10-羟基喜树碱(10), 9-methoxy-mappicine-20-O- β -D-glucopyranoside(11), mappicine-20-O- β -D-glucopyranoside(12), (3S)-pumiloside(13), (1 $\rightarrow$ 3)-4, 2, 3, 4-tetrahydro- β -carboline-3-carboxylic acid(14)。化合物 1~7、9~14 为首次从该植物中分离得到。

关键词: 马比木; 根; 化学成分; 喜树碱

中图分类号: R284.2

文献标识码: A

Chemical Constituents from the Roots of *Nothapodytes pittosporoides*BAI Yong-hua^{1,2}, SONG Qi-shi^{1*}

¹Laboratory of Tropical Plant Resource Science, Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences, Kunming 650223, China; ²University of Chinese Academy of Sciences, Beijing 100049, China

Abstract: Fourteen compounds were isolated and purified from the roots of *Nothapodytes pittosporoides* by column chromatography on silica gel, MCI and Sephadex LH-20. Their structures were elucidated as β -sitosterol(1), β -daucosterol(2), 7-oxo- β -sitosterol(3), β -sitosteryl-3-O- β -D-glucopyranoside-2'-O-palmitate(4), 5 α , 6 β -dihydroxydaucosterol(5), lupeol(6), 3-acetoxy-12-oleanen-28-ol(7), camptothecin(8), 9-methoxy-camptothecin(9), 10-hydroxy-camptothecin(10), 9-methoxy-mappicine-20-O- β -D-glucopyranoside(11), mappicine-20-O- β -D-glucopyranoside(12), (3S)-pumiloside(13), (1 $\rightarrow$ 3)-4, 2, 3, 4-tetrahydro- β -carboline-3-carboxylic acid(14). Compounds 1-7, 9-14 were obtained from this plant for the first time.

Key words: *Nothapodytes pittosporoides*; root; chemical constituent; camptothecins

马比木(*Nothapodytes pittosporoides*)为茶茱萸科假柴龙树属(*Nothapodytes* sp.)植物, 又名海桐假柴龙树、公黄珠子、追风伞。马比木为灌木, 分布于贵州、湖南、湖北、四川等地。入药能祛风除湿、理气散寒, 主治风寒湿痹、浮肿、疝气。马比木植株中含有大量喜树碱及喜树碱的甲氧基衍生物^[1], 喜树碱具有较好的抗肿瘤活性, 已经成为了抗肿瘤药物的主要成分之一。马比木根中的喜树碱含量最高, 而细根中的喜树碱含量最高可达 0.53%, 主根次之, 茎、枝、叶、花序、果实和种子也含有喜树碱, 为极具价值的抗肿瘤药物资源^[2]。假柴龙树属有 7 个种, 该属

植物的化学成分研究目前报道的只有青脆枝和假柴龙树, 而对青脆枝的研究较多, 分离到的化合物主要为喜树碱及其衍生物^[3-4]。

本文对马比木根的化学成分进行了研究, 分离鉴定了 14 个化合物, 其中 5 个为甾体类成分, 2 个为三萜类成分, 7 个为生物碱类成分。分别为: β -谷甾醇(1), β -胡萝卜苷(2), 7-酮基- β -谷甾醇(3), β -sitosteryl-3-O- β -D-glucopyranoside-2'-O-palmitate(4), 5 α , 6 β -二羟基胡萝卜苷(5), 羽扇豆醇(6), 3-乙酰氧基-12-齐墩果烯-28-醇(7), 喜树碱(8), 9-甲氧基喜树碱(9), 10-羟基喜树碱(10), 9-methoxy-mappicine-20-O- β -D-glucopyranoside(11), mappicine-20-O- β -D-glucopyranoside(12), (3S)-pumiloside(13), (1 $\rightarrow$ 3)-4, 2, 3, 4-tetrahydro- β -carboline-3-carboxylic acid(14)。化合物 1~7、9~14 为首次从该植物

收稿日期: 2012-12-28 接受日期: 2013-04-10

基金项目: 中国科学院重要方向项目(KSCX2-EW-R-15)

* 通讯作者 E-mail: songqs@xtbg.ac.cn

中分离得到。

1 仪器与材料

熔点在 XTRC-1 显微熔点测定仪上测定; 核磁共振谱用 Bruker AV-400、DRX-500 及 Avance III-600 超导核磁共振仪测定, TMS 为内标; EI-MS 用 Waters AutoSpec Premier P776 双聚焦三扇形磁质谱仪测定; 柱层析硅胶(200~300 目)及薄板层析硅胶(GF₂₅₄)均为青岛海洋化工厂生产; MCI 为日本三菱化学株式会社生产; 凝胶材料使用 GE Healthcare 的 Sephadex LH-20。所有有机试剂均为分析纯。

马比木(*Nothapodytes pittosporoides*) 根于 2011 年 10 月采于湖南省凤凰县, 并由中国科学院西双版纳热带植物园宋启示研究员鉴定, 标本存放在中国科学院西双版纳热带植物园民族药研究组实验室。

2 提取与分离

将马比木根晾干, 粉碎, 称重得 84 kg。用 90% 甲醇加热回流提取 3 次(4, 3, 3 h)。合并提取液, 减压浓缩得甲醇浸膏 4752 g, 本实验取用 4252 g。将浸膏用水搅拌溶解稀释后依次用石油醚、氯仿、正丁醇萃取, 每种溶剂各萃取 3 次, 得到石油醚萃取物 107 g, 氯仿萃取物 145 g, 正丁醇萃取物 622 g。石油醚部分经硅胶柱(200~300 目)层析, 以石油醚-丙酮梯度洗脱(100:0, 90:10, 80:20, 60:40, 50:50, 0:100)得到六个粗组份(A1-A6); A2 经硅胶柱层析(石油醚-丙酮梯度洗脱)和 Sephadex LH-20(氯仿-甲醇洗脱)纯化, 得到化合物 6(52 mg), 7(46 mg); A4 经反复硅胶柱层析和 Sephadex LH-20(氯仿-甲醇洗脱)纯化, 得到化合物 5(56 mg)。氯仿部分经硅胶柱(200~300 目)层析, 以石油醚-丙酮(90:10, 70:30, 60:40, 50:50, 30:70, 10:90)梯度洗脱, 得到六个粗组份(B1-B6); B1 经硅胶柱层析(石油醚-丙酮梯度洗脱), 其中第一个组份(5% 丙酮-石油醚)经重结晶得化合物 1(800 mg); B2 经反复硅胶柱层析和 Sephadex LH-20 纯化, 得到化合物 2(75 mg), 3(52 mg), 4(33 mg); B3 和 B5 部分经反复硅胶柱层析、MCI、重结晶和 Sephadex LH-20 纯化, 从 B3 部分得到化合物 8(900 mg), 9(560 mg), B5 部分得到化合物 11(8 mg)。正丁醇部分上大孔树脂分段, 分别以 10%、30%、50%、80%、95% 比例的甲醇/水溶液和丙酮梯度洗脱得到六个组份(C1-C6); C3 部分经 MCI 柱层析和 Sephadex LH-20 纯化, 得到化合物 12

(67 mg), 14(46 mg); C4 经 MCI 柱层析、重结晶和 Sephadex LH-20 纯化, 得到化合物 10(45 mg), 13(75 mg)。

3 结构鉴定

化合物 1 无色针晶(氯仿), mp. 136~138 °C, 分子式为 C₂₉H₅₀O。其 ¹H NMR 图谱与 β-谷甾醇的标准图谱完全一致, TLC 上的斑点位置及显色均相同, 与 β-谷甾醇标准品混合熔点不下降, 所以化合物 1 鉴定为 β-谷甾醇。

化合物 2 白色粉末(甲醇), mp. 283~284 °C, 分子式为 C₃₅H₆₀O₆。其 ¹H NMR 图谱与 β-胡萝卜苷的标准图谱完全一致, TLC 上的斑点位置及显色均相同, 与 β-胡萝卜苷标准品混合熔点不下降, 所以化合物 2 鉴定为 β-胡萝卜苷。

化合物 3 白色粉末(甲醇), mp. 120~123 °C, 分子式为 C₂₉H₄₈O₂。¹H NMR(CDCl₃, 400 MHz) δ: 0.68(3H, s, H-18), 0.92(3H, d, J=6.3 Hz, H-21), 1.20(3H, s, H-19), 2.03(1H, d, J=12.6 Hz, H-12b), 2.24(1H, t, J=11.2 Hz, H-8), 2.51(1H, d, J=10.8 Hz, H-4a), 3.68(1H, t, J=11.0 Hz, H-3), 5.69(1H, s, H-6); ¹³C NMR(CDCl₃, 100 MHz) δ: 11.93(C-18, C-29), 17.27(C-19), 18.88(C-21), 18.98(C-26), 19.78(C-27), 21.17(C-11), 22.98(C-28), 25.97(C-23), 26.29(C-15), 28.53(C-16), 29.03(C-25), 31.13(C-2), 33.87(C-22), 36.05(C-20), 36.28(C-1), 38.24(C-10), 38.63(C-12), 41.75(C-4), 43.04(C-13), 45.36(C-8), 45.74(C-24), 49.85(C-9, C-14), 54.62(C-17), 70.48(C-3), 126.08(C-6), 165.11(C-5), 202.40(C-7)。以上数据与文献^[7]报道一致, 故鉴定化合物 3 为 7-酮基-β-谷甾醇。

化合物 4 白色无定形粉末, mp. 151~154 °C, 分子式为 C₅₁H₉₀O₇。EI-MS m/z: 414 [M-CH₃(CH₂)₁₄COOC₆H₁₀O₄]⁺, 256 [C₁₆H₃₂O₂]⁺, 239 [C₁₅H₃₁CO]⁺, 129, 73, 碎片峰中的系列峰与棕榈酸 EI-MS 图谱一致, 显示含有棕榈酸。¹H NMR(CDCl₃, 400 MHz) δ: 0.88(3H, m, H-21), 0.94(3H, s, H-19), 1.21(18H, br s, H-5''~13''), 3.27(1H, m, H-3), 5.29(1H, s, H-6); ¹³C NMR(CDCl₃, 100 MHz) δ: 11.71(C-18), 11.80(C-29), 18.65(C-21), 18.88(C-26), 19.22(C-19), 19.66(C-27), 20.97(C-11), 22.92(C-28), 24.19(C-15), 26.08(C-23), 28.13

(C-16), 29.00 (C-25), 29.61 (C-2), 31.73 (C-8), 31.83 (C-7), 33.80 (C-22), 36.08 (C-20), 36.53 (C-10), 37.19 (C-1), 38.75 (C-4), 39.68 (C-12), 42.20 (C-13), 45.65 (C-24), 50.05 (C-9), 56.10 (C-17), 56.67 (C-14), 79.72 (C-3), 121.81 (C-6), 140.30 (C-5), 63.83 (C-6'), 70.48 (C-4'), 73.15 (C-2'), 73.48 (C-5'), 76.26 (C-3'), 101.24 (C-1'), 13.98 (C-16''), 22.58 (C-15''), 24.98 (C-3''), 29.72 (C-4'' ~ C-13''), 29.77 (C-14''), 34.19 (C-2''), 173.94 (C-1''). 以上数据与文献^[8]报道一致,故鉴定化合物4为 β -sitosteryl-3-O- β -D-glucopyranoside-2'-O-palmitate。

化合物5 白色粉末(甲醇), mp. 296 ~ 298 °C, 分子式为 $C_{35}H_{62}O_8$ 。 1H NMR (C_5D_5N , 600 MHz) δ : 0.73 (3H, s, H-18), 0.83-0.90 (9H, m, H-26, 27, 29), 0.99 (3H, m, H-21), 2.51 (1H, dd, $J = 4.5, 12.7$ Hz, H-4b), 2.96 (1H, m, H-4a), 4.17 (1H, br s, H-6), 5.68 (1H, s, H-3), 3.76 (1H, m, H-5'), 4.08 (1H, m, H-2'), 4.22 (1H, t, $J = 9.0$ Hz, H-4'), 4.42 (1H, dd, $J = 5.1, 11.9$ Hz, H-6'b), 4.52 (1H, dd, $J = 2.2, 11.9$ Hz, H-6'a), 4.98 (1H, d, $J = 7.7$ Hz, H-1'); ^{13}C NMR (C_5D_5N , 150 MHz) δ : 12.61 (C-29), 12.83 (C-18), 17.49 (C-19), 19.45 (C-21), 19.67 (C-26), 20.47 (C-27), 22.16 (C-11), 23.80 (C-28), 25.13 (C-15), 26.84 (C-23), 29.15 (C-16), 29.85 (C-25), 30.31 (C-2), 31.66 (C-8), 33.54 (C-1), 34.64 (C-22), 36.11 (C-7), 37.02 (C-20), 39.09 (C-4), 39.63 (C-10), 41.06 (C-12), 43.49 (C-13), 46.26 (C-9), 46.47 (C-24), 56.98 (C-14), 57.03 (C-17), 75.40 (C-3), 75.99 (C-5), 76.80 (C-6), 63.16 (C-6'), 71.98 (C-4'), 75.80 (C-2'), 78.85 (C-5'), 79.08 (C-3'), 102.67 (C-1')。以上数据与文献^[8]报道一致,故鉴定化合物5为 $5\alpha, 6\beta$ -二羟基胡萝卜苷。

化合物6 白色针状结晶(丙酮), mp. 215 ~ 216 °C, 分子式为 $C_{30}H_{50}O$ 。 1H NMR ($CDCl_3$, 400 MHz) δ : 0.76 (3H, s, H-24), 0.78 (3H, s, H-28), 0.82 (3H, s, H-25), 0.94 (3H, s, H-27), 0.96 (3H, s, H-23), 1.02 (3H, s, H-26), 1.68 (3H, s, H-30), 3.19 (1H, dd, $J = 11.1, 4.8$ Hz, H-3), 4.56 (1H, s, H-29a), 4.68 (1H, s, H-29b); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 14.50 (C-27), 15.34 (C-24), 15.93 (C-26), 16.10 (C-25), 17.96 (C-28), 18.27 (C-6), 19.26 (C-30), 20.87 (C-11), 25.07 (C-12), 27.36 (C-15),

27.39 (C-2), 27.95 (C-23), 29.68 (C-21), 34.21 (C-7), 35.53 (C-16), 37.11 (C-10), 37.98 (C-13), 38.64 (C-1), 38.82 (C-4), 39.96 (C-22), 40.77 (C-8), 42.78 (C-14), 42.96 (C-17), 47.95 (C-19), 48.28 (C-18), 50.37 (C-9), 55.23 (C-5), 78.97 (C-3), 109.30 (C-29), 150.98 (C-20)。以上数据与文献^[10]报道一致,故鉴定化合物6为羽扇豆醇。

化合物7 白色结晶(丙酮), 分子式为 $C_{32}H_{52}O_3$ 。 1H NMR ($CDCl_3$, 400 Hz) δ : 0.94 (3H, s, H-27), 0.96 (3H, s, H-23), 1.16 (9H, s, 30), 2.05 (3H, s, CH_3COO), 3.21 (1H, d, $J = 10.9$ Hz, H-28a), 3.55 (1H, d, $J = 10.9$ Hz, H-28b), 4.49 (1H, m, H-3), 5.19 (1H, br s, H-12); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 15.55 (C-25), 16.66 (C-24), 16.66 (C-26), 18.18 (C-6), 21.32 ($CH_3C=O$), 21.90 (C-16), 23.48 (C-2, C-11, C-22), 23.54 (C-29), 25.46 (C-15), 25.86 (C-27), 27.98 (C-23), 30.92 (C-20), 32.43 (C-7), 33.16 (C-30), 34.01 (C-21), 36.89 (C-10), 37.66 (C-4), 38.20 (C-1), 39.73 (C-8), 41.65 (C-17), 42.28 (C-18), 46.34 (C-19), 47.43 (C-9), 51.07 (C-14), 55.17 (C-50), 69.70 (C-28), 80.86 (C-3), 122.23 (C-12), 144.16 (C-13), 171.06 (C=O)。以上数据与文献^[11]报道一致,故鉴定化合物7为3-乙酰氧基-12-齐墩果烯-28醇。

化合物8 浅黄色针晶(氯仿), mp. 265 ~ 270 °C, 分子式为 $C_{20}H_{16}N_2O_4$ 。 1H NMR (DMSO, 400 MHz) δ : 0.88 (3H, t, $J = 7.0$ Hz, H-18), 1.86 (2H, m, H-19), 5.27 (2H, s, H-5), 5.42 (2H, s, H-17), 7.34 (1H, s, H-14), 7.70 (1H, t, $J = 7.6$ Hz, H-10), 7.85 (1H, t, $J = 7.5$ Hz, H-11), 8.11 (1H, d, $J = 8.1$ Hz, H-9), 8.16 (1H, d, $J = 8.4$ Hz, H-12), 8.68 (1H, s, H-7); ^{13}C NMR (DMSO, 100 MHz) δ : 7.82 (C-18), 30.29 (C-19), 50.27 (C-5), 65.29 (C-17), 72.42 (C-20), 96.74 (C-14), 119.10 (C-16), 127.70 (C-10), 127.98 (C-8), 128.54 (C-9), 129.06 (C-12), 129.87 (C-6), 130.43 (C-11), 131.59 (C-7), 145.51 (C-3), 147.94 (C-13), 150.03 (C-15), 152.58 (C-2), 156.86 (C-16a), 172.54 (C-21)。以上数据与文献^[12]报道一致,故鉴定化合物8为喜树碱。

化合物9 浅黄色针晶(氯仿), mp. 255 ~ 260 °C 分子式为 $C_{21}H_{18}N_2O_5$ 。 1H NMR (DMSO, 500 MHz) δ : 0.87 (3H, t, $J = 7.3$ Hz, H-18), 1.86 (2H, m, H-19), 4.03 (3H, s, OCH_3), 5.24 (2H, s, H-5), 5.42

(2H, s, H-17), 6.54 (1H, s, OH), 7.15 (1H, d, $J = 7.6$ Hz, H-10), 7.31 (1H, s, H-14), 7.71 (1H, d, $J = 8.5$ Hz, H-12), 7.76 (1H, m, H-11), 8.84 (1H, s, H-7); ^{13}C NMR (DMSO, 125 MHz) δ : 7.70 (C-18), 30.38 (C-19), 50.44 (C-5), 56.14 (OCH₃), 65.25 (C-17), 72.34 (C-20), 96.72 (C-14), 105.95 (C-10), 119.03 (C-16), 120.09 (C-8), 121.02 (C-12), 126.02 (C-7), 129.07 (C-6), 130.58 (C-11), 145.47 (C-3), 148.78 (C-13), 149.95 (C-15), 152.64 (C-2), 154.90 (C-9), 156.84 (C-16a), 172.39 (C-21)。以上数据与文献报道^[1]一致,故鉴定化合物9为9-甲氧基喜树碱。

化合物 10 浅黄色粉末,分子式为 $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_5$ 。 ^1H NMR (DMSO, 400 MHz) δ : 0.86 (3H, t, $J = 7.1$ Hz, H-18), 1.84 (2H, m, H-19), 5.21 (2H, s, H-5), 5.39 (2H, s, H-17), 7.24 (1H, s, H-14), 7.26 (s, 1H, H-9), 7.40 (1H, d, $J = 9.0$ Hz, H-11), 8.00 (1H, d, $J = 9.1$ Hz, H-12), 8.43 (1H, s, H-7); ^{13}C NMR (DMSO, 100 MHz) δ : 7.85 (C-18), 30.27 (C-19), 50.22 (C-5), 65.30 (C-17), 72.49 (C-20), 95.95 (C-14), 108.86 (C-9), 118.19 (C-16), 123.12 (C-11), 129.35 (C-8), 129.75 (C-7), 130.00 (C-9), 130.72 (C-12), 143.27 (C-13), 145.97 (C-3), 149.48 (C-2), 150.16 (C-15), 156.73 (C-10), 156.95 (C-16a), 172.65 (C-21)。以上数据与文献^[13]报道一致,故鉴定化合物10为10-羟基喜树碱。

化合物 11 浅黄色粉末,分子式为 $\text{C}_{26}\text{H}_{30}\text{N}_2\text{O}_8$ 。EI-MS m/z : 521 $[\text{M} + \text{Na}]^+$ 。 ^1H NMR (DMSO, 600 MHz) δ : 0.85 (3H, t, $J = 7.3$ Hz, H-18), 1.70 ~ 1.87 (2H, m, H-19), 2.15 (3H, s, H-17), 3.90 (1H, d, $J = 7.5$ Hz, H-1'), 4.03 (3H, s, OCH₃), 5.21 (2H, s, H-5), 7.14 (1H, d, $J = 7.7$ Hz, H-10), 7.35 (1H, s, H-14), 8.81 (1H, s, H-7); ^{13}C NMR (DMSO, 150 MHz) δ : 9.77 (C-18), 11.95 (C-17), 28.45 (C-19), 50.49 (C-5), 56.22 (OCH₃), 74.07 (C-20), 98.84 (C-14), 105.77 (C-10), 119.82 (C-16), 121.00 (C-12), 125.97 (C-11), 127.02 (C-8), 129.06 (C-6), 130.58 (C-7), 142.57 (C-3), 148.84 (C-13), 149.33 (C-15), 153.51 (C-2), 155.01 (C-9), 160.49 (C-16a), 61.25 (C-6'), 70.40 (C-4'), 73.67 (C-2'), 76.82 (C-3'), 77.34 (C-5'), 99.62 (C-1')。根据文献^[13,14]报道,鉴定化合物11为9-methoxy-mappicine-20- O - β -D-glucopyranoside。

化合物 12 黄色粉末,分子式为 $\text{C}_{25}\text{H}_{28}\text{N}_2\text{O}_7$ 。 ^1H NMR (DMSO, 600 MHz) δ : 0.86 (3H, t, $J = 7.1$ Hz, H-18), 1.73 (1H, m, H-19), 1.84 (1H, m, H-19), 2.17 (3H, s, H-17), 3.92 (1H, d, $J = 7.4$ Hz, H-1'), 5.20 (2H, d, $J = 10.7$ Hz, H-5), 7.34 (1H, s, H-14), 7.66 (1H, t, $J = 7.4$ Hz, H-10), 7.81 (1H, m, H-11), 8.07 (1H, d, $J = 8.1$ Hz, H-9), 8.12 (1H, d, $J = 8.4$ Hz, H-12), 8.62 (1H, s, H-7); ^{13}C NMR (DMSO, 150 MHz) δ : 9.80 (C-18), 11.97 (C-17), 28.48 (C-19), 50.22 (C-5), 74.13 (C-20), 98.88 (C-14), 127.04 (C-16), 127.43 (C-10), 127.83 (C-8), 128.63 (C-9), 128.94 (C-12), 129.73 (C-6), 130.37 (C-11), 131.50 (C-7), 142.56 (C-3), 147.97 (C-13), 149.40 (C-15), 153.36 (C-2), 160.50 (C-16a), 61.27 (C-6'), 70.42 (C-4'), 73.69 (C-2'), 76.85 (C-3'), 77.36 (C-5'), 99.66 (C-1')。以上数据与文献^[1]报道一致,故鉴定化合物12为mappicine-20- O - β -D-glucopyranoside。

化合物 13 白色粉末,分子式为 $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_8$ 。 ^1H NMR (DMSO, 400 MHz) δ : 2.01 (1H, m, H-14), 2.63 (1H, m, H-20), 2.99 (1H, m, H-2'), 3.16 (2H, m, H-3', 5'), 3.68 (1H, m, H-6'), 4.31 (1H, d, $J = 14.0$ Hz, H-5), 4.46 (1H, d, $J = 13.6$ Hz, H-5), 4.53 (1H, d, $J = 7.8$ Hz, H-1'), 4.74 (1H, d, $J = 10.9$ Hz, H-3), 5.33 (1H, d, $J = 11.6$ Hz, H-18), 5.44 (1H, m, H-18), 5.78 (1H, m, H-19), 7.04 (1H, d, $J = 2.4$ Hz, H-17), 7.33 (1H, t, $J = 7.4$ Hz, H-10), 7.59 (1H, d, $J = 8.1$ Hz, H-12), 7.66 (1H, m, H-11), 8.11 (1H, d, $J = 7.8$ Hz, H-9), 12.15 (1H, s, N-H); ^{13}C NMR (DMSO, 100 MHz) δ : 23.67 (C-15), 28.17 (C-14), 43.62 (C-20), 47.53 (C-5), 59.47 (C-3), 94.81 (C-21), 108.62 (C-16), 113.02 (C-6), 118.40 (C-12), 120.63 (C-18), 123.36 (C-10), 124.78 (C-9), 125.29 (C-8), 131.24 (C-11), 132.46 (C-19), 140.39 (C-13), 145.18 (C-17), 149.84 (C-2), 164.05 (C-16a), 173.07 (C-7), 61.10 (C-6'), 70.10 (C-4'), 73.19 (C-2'), 76.47 (C-3'), 77.32 (C-5'), 97.79 (C-1')。以上数据与文献^[14]报道一致,故鉴定化合物13为(3S)-pumiloside。

化合物 14 白色粉末,分子式为 $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$ 。 ^1H NMR ($\text{C}_5\text{D}_5\text{N}$, 400 MHz) δ : 3.71 (2H, m, H-4), 4.98 (1H, m, H-3), 5.42 (2H, m, H-1); ^{13}C NMR

(C_5D_5N , 100 MHz) δ : 24.03 (C-4), 41.92 (C-1), 56.95 (C-3), 106.84 (C-4a), 113.18 (C-8), 119.17 (C-5), 120.36 (C-7), 122.95 (C-6), 127.52 (C-4b), 128.27 (C-9a), 138.19 (C-8a), 173.71 (COOH)。以上数据与文献^[13]报道一致,故鉴定化合物 14 为 (→)-3S)-1,2,3,4-tetrahydro- β -carboline-3-carboxylic acid。

致谢: 所用光谱数据均由中国科学院昆明植物研究所植物化学与西部植物资源持续利用国家重点实验室分析测试中心测定。

参考文献

- Zhang XD(张宪德), Ke MM(柯珉珉), Zhang WY(张文毅). Extract the camptothecin from Hippocrateaceae *Nothapodytes obtusifolia* (从假柴龙树中提取喜树碱). CN1045266A. 1990-09-12.
- Lv JM(吕江明), Liu SB(刘世彪), Cai QH(蔡其辉), et al. Microscopic fluorescence histological localization and variation of camptothecin in *Nothapodytes pittedporoides*. *Chin Tradit Herb Drugs*(中草药), 2010, 41: 1530-1534.
- Angela P, Luisella V, Pierluigi G, et al. Constituents of *Nothapodytes foetida*. *Chem Soc, Perkin Trans1*, 1995, 1181-1185.
- Wu TS, Leu YL, Hsu HC, et al. Constituents and cytotoxic principles of *Nothapodytes foetida*. *Phytochemistry*, 1995, 39: 383-385.
- Wu SF, Hesien PW, Wu CC, et al. Camptothecinoids from the seeds of Taiwanese *Nothapodytes foetida*. *Molecules*, 2008, 13: 1361-1371.
- Ramesha BT, Amna T, Ravikanth G, et al. Prospecting for camptothecines from *Nothapodytes nimmoniana* in the western Ghats, South India: identification of high-yielding sources of camptothecin and new families of camptothecines. *J Chromatogr Sci*, 2008, 46: 362-368.
- Pettit GR, Numata A, Cragg GM, et al. Isolation and structures of Schleicherastatins 1-7 and Schleicheols 1 and 2 from the teak forest medicinal tree *Schleichera oleosa*. *J Nat Prod*, 2000, 63: 72-78.
- Radwan MM, ElSohly MA, Slade D, et al. Non-cannabinoid constituents from a highpotency *Cannabis sativa* variety. *Phytochemistry*, 2008, 69: 2627-2633.
- Li SH, Zhang HJ, Yon P, et al. Non-taxane Compounds from the bark of *Taxus Yunnanensis*. *J Asian Nat Prod Res*, 2002, 4: 147-154.
- Zhang BY(张本印), Wang H(王环), Luo XD(罗晓东), et al. Chemical constituents from roots of *Euphorbia yinshanica*. *Chin Tradit Herb Drugs*(中草药), 2011, 42: 2193-2196.
- Yang SM(杨淑敏), Liu XK(刘锡葵), Qing C(卿晨), et al. Chemical constituents from the roots of *Homonoia riparia*. *Acta Pharm Sin*(药学学报), 2007, 42: 292-296.
- Ezell EL, Smith LL. 1H and ^{13}C NMR spectra of camptothecin and derivatives. *J Nat Prod*, 1991, 54: 1645-1650.
- Lin LZ, Cordell GA. ^{13}C NMR assignments of camptothecin and 10-hydroxycamptothecin. *J Nat Prod*, 1990, 53: 186-189.
- Kitajima M, Yoshida S, Yamagata K, et al. Camptothecin-related alkaloids from hairy roots of *Ophiorrhiza pumila*. *Tetrahedron*, 2002, 58: 9169-9178.
- Brossi A, Focella A, Teitel S. Alkaloids in mammalian tissues. 3. condensation of L-tryptophan and L-5-hydroxytryptophan with formaldehyde and acetaldehyde. *J Med Chem*, 1973, 16: 418-420.
- Li LH(李利华). Potato tuber thick polyphenols in vitro antioxidant activity. *Food Ferment Ind*(食品与发酵工业), 2011, 37: 176-179.
- Chen LH(陈莉华), Zuo LY(左林艳), Tang YJ(唐玉坚). Microwave auxiliary ethanol extracting gingerol and oil oxidation stability study. *Food Sci*(食品科学), 2011, 32(4): 69-73.
- Zhang JS(张俊生), Chen LH(陈莉华), Zhang WL(张文龙). Xiangxi successively grass flavonoids of ultrasonic extraction and oxidation research. *Food Sci*(食品科学), 2011, 32(16): 71-75.

(上接第 177 页)