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马比木根的化学成分研究

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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**),5α,6β-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**),(3*S*)-pumiloside(**13**),(-)-(3*S*)-1,2,3,4- 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

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Chemical Constituents from the Roots of *Nothapodytes pittosporoides*

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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**),5α,6β-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**),(3*S*)-pumiloside(**13**),(-)-(3*S*)-1,2,3,4- 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[3-6]。

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**),5α,6β-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-羟基基喜树碱(**10**),9-methoxy-mappicine-20-*O*-β-*D*-glucopyranoside(**11**),mappicine-20-*O*-β-*D*-glucopyranoside(**12**),(3*S*)-pumiloside(**13**),(-)-(3*S*)-1,2,3,4- tetrahydro-β-carboline-3-carboxylic acid(**14**)。化合物 **1** ~ **7**、**9** ~ **14** 为首次从该植物

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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(GF_{254})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。所用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 ℃,分子式为 $C_{29}H_{50}O$。其 ^{1}H 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 ℃,分子式为 $C_{35}H_{60}O_6$。其 ^{1}H 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 ℃,分子式为 $C_{29}H_{48}O_2$。^{1}H NMR($CDCl_3$, 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);^{13}C NMR($CDCl_3$, 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 ℃,分子式为 $C_{51}H_{90}O_7$。EI-MS m/z: 414 [M-$CH_3(CH_2)_{14}COOC_6H_{10}O_4$]$^+$, 256[$C_{16}H_{32}O_2$]$^+$, 239[$C_{15}H_{31}CO$]$^+$, 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。^{1}H NMR($CDCl_3$, 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);^{13}C NMR($CDCl_3$, 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 ℃, 分子式为 $C_{35}H_{62}O_8$。^{1}H 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[9]报道一致,故鉴定化合物 **5** 为 5*α*,6*β*-二羟基胡萝卜苷。

化合物 6 白色针状结晶(丙酮), mp. 215 ~ 216 ℃, 分子式为 $C_{30}H_{50}O$。^{1}H 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 $C_{32}H_{52}O_3$。^{1}H 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 ℃, 分子式为 $C_{20}H_{16}N_2O_4$。^{1}H 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 ℃分子式为 $C_{21}H_{18}N_2O_5$。^{1}H 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(OCH_3),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[3]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$C_{20}H_{16}N_2O_5$。^{1}H 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$C_{26}H_{30}N_2O_8$。EI-MS m/z:521$[M+Na]^+$。^{1}H 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,OCH_3),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(OCH_3),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[3,6]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$C_{25}H_{28}N_2O_7$。^{1}H 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[3]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$C_{26}H_{28}N_2O_8$。^{1}H 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$C_{12}H_{12}N_2O_2$。^{1}H NMR(C_5D_5N,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[15]报道一致,故鉴定化合物 **14** 为 (-)-(3S)-1,2,3,4- tetrahydro-β-carboline-3-carboxylic acid。

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