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景东山橙根中生物碱成分研究

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摘　要:本文对景东山橙 *Melodinus khasianus* 根部进行生物碱成分研究,从中分离并鉴定了 20 个化合物,分别为:*O*-甲基-长春醇(**1**)、*O*-甲基-表长春醇(**2**)、长春醇(**3**)、表长春醇(**4**)、(-)-象牙烯宁(**5**)、(-)-象牙酮宁(**6**)、leuconicine A(**7**)、alkaloid **376**(**8**)、leuconicine C(**9**)、(-)-rhazinilam(**10**)、16(*R*)-*E*-异西特斯日钦碱(**11**)、西特斯日钦碱(**12**)、花冠木碱 N^b-氧化物(**13**)、异长春花苷内酰胺(**14**)、9-β-*D*-吡喃葡萄糖基-四氢鸭脚木碱(**15**)、β-咔啉(**16**)、1-甲基-9*H*-吡啶并[3,4-*b*]吲哚(**17**)、喜树次碱(**18**)、坎特莱因碱(**19**)和 α-甲基-3-羟甲基吡啶(**20**)。生物碱 **6**、**12**、**15** 和 **16~20** 为首次从该属植物中分离得到。

关键词:夹竹桃科;景东山橙;生物碱

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Alkaloid Constituents from the Roots of *Melodinus khasianus*

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Abstract:Phytochemical investigation on the roots of *Melodinus khasianus* resulted in the isolation of 20 compounds. Their structures were identified as *O*-methyl-vincanol (**1**), *O*-methyl-epivincanol (**2**),vincanol (**3**),epivincanol (**4**),(-)-eburnamenine (**5**),(-)-eburnamonine (**6**),leuconicine A (**7**),alkaloid **376** (**8**),leuconicine C (**9**),(-)-rhazinilam (**10**),16(*R*)-*E*-isositsirikine (**11**),sitsirikine (**12**),stemmadenine N^b-oxide (**13**),strictosamide (**14**),9-β-*D*-glucopyranosyl-tetrahydroalstonine (**15**),β-carboline (**16**),harman (**17**),venoterpine (**18**),cantleyine (**19**) and α-methyl-3-pyridinemethanol (**20**) by comparison with the recorded literature. Alkaloids **6**,**2**,**15** and **16-20** were obtained from *Melodinus* species for the first time.

Key words:apocynaceae; *Melodinus khasianus*;alkaloids

景东山橙(*Melodinus khasianus*)为夹竹桃科(Apocynaceae)山橙属植物,系藤本类植物,主要分布在我国云南和贵州省[1]。山橙属植物在民间常用于治疗小儿疝气、腹痛、小儿疳疾、消化不良、睾丸炎、小儿脑膜炎、骨折和风湿性心脏病等[2]。课题组对山橙属的云南山橙(*M. yunnanensis*)[3,4]、思茅山橙(*M. henryi*)[5,6]、薄叶山橙(*M. tenuicaudatus*)[7,8]和山橙(*M. suaveolens*)[9,10]进行了系统研究,从中分离得到一些列新颖单萜吲哚生物碱类化合物。为了进一步研究该属植物中的生物碱成分,我们对采自云南西双版纳的景东山橙的根进行了化学成分研究,从中分离得到 20 个生物碱,分别鉴定为 *O*-甲基-长春醇(**1**)、*O*-甲基-表长春醇(**2**)、长春醇(**3**)、表长春醇(**4**)、(-)-象牙烯宁(**5**)、(-)-象牙酮宁(**6**)、leuconicine A(**7**)、alkaloid **376**(**8**)、leuconicine C(**9**)、(-)-rhazinilam(**10**)、16(*R*)-*E*-异西特斯日钦碱(**11**)、西特斯日钦碱(**12**)、花冠木碱 N^b-氧化物(**13**)、异长春花苷内酰胺(**14**)、9-β-*D*-吡喃葡萄糖基-四氢鸭脚木碱(**15**)、β-咔啉(**16**)、1-甲基-9*H*-吡啶并[3,4-*b*]吲哚(**17**)、喜树次碱(**18**)、坎特莱因碱(**19**)和 α-甲基-3-羟甲基吡啶(**20**)。

1　仪器与材料

ESI-MS 由 Waters Xevo TQ-S 三重四极杆质谱

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仪测定;拌样(80~100 目)、柱层析硅胶(200~300 目)及薄层层析硅胶板,均为青岛海洋化工厂生产;反相中压填充材料为 Lichroprep RP-18,粒径 40~63 μm,德国 Merck 公司生产;核磁谱图由 Bruker AM 400 兆和 AV600 兆超导核磁共振波谱仪上测定,TMS 作为内标,δ 表示化学位移(ppm),J 表示耦合常数(Hz);凝胶 Sephadex HL-20 为日本公司生产;Agilent 1200 高效液相色谱仪,半制备色谱柱 Agilent Zorbax SB-C_{18}(9.4 mm × 250 mm),流速:3 mL/min,二极管阵列检测器;显色剂为 Dragendorff 试剂或 10% 硫酸乙醇溶液(v/v),硅胶薄层板喷晒显色剂后适当加热显色;所有溶剂均重蒸后使用。

景东山橙(*M. khasianus*)的根于 2008 年 11 月采自云南西双版纳勐腊县,由西双版纳热带植物园崔景云实验师鉴定。植物标本(Cui 20081128)存放于中国科学院昆明植物研究所。

2 提取与分离

景东山橙根部 7 kg 干燥样品,粉碎后用 MeOH 室温下浸提 3 次,每次 48 h,过滤并浓缩提取液得到总浸膏为 550 g。浸膏用 0.3% 稀盐酸溶解并过滤,酸溶液用 5% 氨水溶液调 pH 值至 9~10,边调节边用 EtOAc 萃取,总共萃取 3 次,得到总碱部分约 21 g。总碱部分用正相硅胶柱划段,用 $CHCl_3$-MeOH(1∶0→1∶1)洗脱得到六部分(Fr. A-E)。Fr. B(4 g)正相硅胶柱分离,用氯仿-丙酮(10∶1→6∶1)洗脱得到化合物 **5**(11 mg)、**6**(9 mg)和三个亚组分;Fr. A-II(1.1 g)经反复 RP-18 柱层析,用 MeOH-H_2O(6∶4→10∶0)洗脱得到化合物 **1**(23 mg)、**2**(18 mg)、**3**(35 mg)和 **4**(21 mg)。Fr. C(3.6 g)正相硅胶柱分离,用氯仿-丙酮(8∶1→4∶1)洗脱得到三个亚组分;Fr. C-II(1.1 g)经反复 RP-18 柱层析,用 MeOH-H_2O (5∶5→9∶1)洗脱得到化合物 **7**(31 mg)、**8**(12 mg)和 **9**(20 mg);通过结晶及重结晶的方法从 Fr. C-III(0.8 g)中得到化合物 **17**(38 mg),其母液通过半制备 HPLC(CH_3CN-H_2O,40%→60%)得到化合物 **10**(4 mg,t_R = 18.2 min)和 **16**(3 mg,t_R = 16.5 min)。Fr. D(3.2 g)正相硅胶柱分离,用氯仿-甲醇(12∶1→8∶1)洗脱得到三个亚组分;Fr. D-I(1.3 g)经反复 RP-18 柱层析,用 MeOH-H_2O(4∶6→8∶2)洗脱得到化合物 **11**(10 mg)、**12**(3 mg)、**13**(11 mg)和 **14**(16 mg);通过结晶及重结晶的方法从 Fr. D-III(0.8 g)中得到化合物 **15**(37 mg)。Fr. E(5 g)正相硅胶柱分离,用氯仿-甲醇(10∶1→5∶1)洗脱得到化合物 **20**(48 mg)和二个亚组分;Fr. E-II(1.8 g)经反复 RP-18 柱层析,用 MeOH-H_2O(4∶6→7∶3)洗脱得到化合物 **18**(223 mg)和 **19**(108 mg)。

3 结构鉴定

化合物 1 针状晶体($CHCl_3$-MeOH)。分子式为 $C_{20}H_{26}N_2O$,ESI-MS *m/z* 311 [M + H]$^+$。^{1}H NMR (600 MHz,$CDCl_3$) δ:7.58 (1H,d,J = 8.0 Hz,H-9),7.48 (1H,d,J = 8.0 Hz,H-12),7.18 (1H,t,J = 8.0 Hz,H-11),7.15 (1H,t,J = 8.0 Hz,H-10),5.53 (1H,dd,J = 9.6,5.4 Hz,H-16),3.94 (1H,s,H-21),3.34 (3H,s,OMe),0.93 (3H,t,J = 7.2 Hz,Me-18);^{13}C NMR (600 MHz,$CDCl_3$) δ:136.6 (s,C-13),128.6 (s,C-8),121.4 (d,C-11),120.1 (d,C-10),118.0 (d,C-9),111.9 (d,C-12),105.8 (s,C-7),82.3 (d,C-16),58.9 (d,C-21),50.9 (t,C-5),50.6 (q,OMe),44.3 (t,C-3),36.6 (t,C-17),36.5 (s,C-20),28.9 (t,C-19),25.2 (t,C-15),20.5 (t,C-14),16.8 (t,C-6),7.6 (q,Me-18)。以上数据与文献报道一致[11],故鉴定为 *O*-甲基-长春醇(*O*-Methyl-vincanol)。

化合物 2 针状晶体($CHCl_3$-MeOH)。分子式为 $C_{20}H_{26}N_2O$,ESI-MS *m/z* 311 [M + H]$^+$。^{1}H NMR (600 MHz,CD_3OD) δ:7.39 (1H,d,J = 7.7 Hz,H-9),7.27 (1H,d,J = 8.1 Hz,H-12),7.11 (1H,t,J = 7.5 Hz,H-11),7.05 (1H,t,J = 7.5 Hz,H-10),5.46 (1H,br d,J = 2.9 Hz,H-16),3.86 (1H,s,H-21),3.47 (3H,s,OMe),0.93 (3H,t,J = 7.6 Hz,Me-18);^{13}C NMR (600 MHz,CD_3OD) δ:137.2 (s,C-13),131.3 (s,C-2),129.9 (s,C-8),122.2 (d,C-11),121.0 (d,C-10),118.9 (d,C-9),111.9 (d,C-12),106.1 (s,C-7),84.2 (d,C-16),60.5 (d,C-21),55.9 (q,OMe),52.3 (t,C-5),45.7 (t,C-3),35.9 (s,C-20),35.7 (t,C-17),29.8 (t,C-19),26.6 (t,C-15),21.6 (t,C-14),17.6 (t,C-6),7.9 (q,Me-18)。以上数据与文献报道一致[11],故鉴定为 *O*-甲基-表长春醇 (*O*-Methyl-epivincanol)。

化合物 3 白色无定型粉末。分子式为 $C_{19}H_{24}N_2O$,ESI-MS *m/z* 297 [M + H]$^+$。^{1}H NMR (600 MHz,CD_3OD) δ:8.25 (1H,d,J = 7.6 Hz,H-9),7.34 (1H,d,J = 7.6 Hz,H-12),7.07 (1H,t,J = 7.6 Hz,H-11),7.02 (1H,t,J = 7.6 Hz,H-10),

5.43 (1H, m, H-16), 3.40 (1H, s, H-21), 0.82 (3H, t, J = 7.2 Hz, Me-18); ^{13}C NMR (150 MHz, CD_3OD) δ: 138.3 (s, C-13), 133.0 (s, C-2), 129.8 (s, C-8), 122.1 (d, C-11), 120.9 (d, C-10), 118.8 (d, C-9), 113.1 (d, C-12), 105.8 (s, C-7), 77.0 (d, C-16), 59.6 (d, C-21), 51.5 (t, C-5), 45.1 (t, C-3), 43.3 (t, C-17), 37.8 (s, C-20), 29.2 (t, C-19), 25.8 (t, C-15), 21.2 (t, C-14), 17.6 (t, C-6), 7.8 (q, Me-18)。以上数据与文献报道一致[11,12]，故鉴定为长春醇(Vincanol)。

化合物 4 白色无定型粉末。分子式为 $C_{19}H_{24}N_2O$, ESI-MS m/z 297 [M + H]$^+$。^{1}H NMR (600 MHz, CD_3OD) δ: 7.43 (1H, d, J = 7.6 Hz, H-9), 7.39 (1H, d, J = 7.6 Hz, H-12), 7.09 (1H, t, J = 7.6 Hz, H-11), 7.04 (1H, t, J = 7.6 Hz, H-10), 5.93 (1H, d, J = 3.6 Hz, H-16), 3.77 (1H, s, H-21), 0.91 (3H, t, J = 7.8 Hz, Me-18); ^{13}C NMR (150 MHz, CD_3OD) δ: 136.9 (s, C-13), 131.3 (s, C-2), 129.9 (s, C-8), 122.0 (d, C-11), 120.7 (d, C-10), 118.8 (d, C-9), 111.8 (d, C-12), 105.5 (s, C-7), 74.8 (d, C-16), 60.6 (d, C-21), 52.2 (t, C-5), 45.7 (t, C-3), 41.6 (t, C-17), 35.8 (s, C-20), 29.7 (t, C-19), 26.8 (t, C-15), 21.7 (t, C-14), 17.6 (t, C-6), 7.9 (q, Me-18)。以上数据与文献报道一致[11,12]，故鉴定为表长春醇(Epivincanol)。

化合物 5 无色油状物。分子式为 $C_{19}H_{22}N_2$, ESI-MS m/z 301 [M + Na]$^+$。^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (1H, d, J = 7.7 Hz, H-9), 7.34 (1H, d, J = 8.0 Hz, H-12), 7.19 (1H, t, J = 7.2 Hz, H-11), 7.12 (1H, t, J = 7.4 Hz, H-10), 6.92 (1H, br d, J = 7.9 Hz, H-16), 5.08 (1H, br d, J = 7.9 Hz, H-16), 4.28 (1H, s, H-21), 1.01 (3H, t, J = 7.5 Hz, Me-18); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.5 (s, C-13), 130.2 (s, C-2), 128.2 (s, C-8), 121.5 (d, C-11), 119.8 (d, C-10), 119.7 (d, C-16), 118.4 (d, C-9), 116.7 (d, C-17), 108.5 (d, C-12), 107.1 (s, C-7), 55.8 (d, C-21), 52.1 (t, C-5), 45.4 (t, C-3), 37.3 (s, C-20), 31.1 (t, C-19), 27.5 (t, C-15), 20.8 (t, C-14), 16.5 (t, C-6), 9.0 (q, Me-18)。以上数据与文献报道一致[13,14]，故鉴定为(-)-象牙烯宁[(-)-Eburnamenine)]。

化合物 6 白色无定型粉末。分子式为 $C_{19}H_{22}N_2O$, ESI-MS m/z 295 [M + H]$^+$。^{1}H NMR (600 MHz, CD_3OD) δ: 8.25 (1H, m, H-9), 7.44 (1H, m, H-12), 7.28 (1H, m, H-11), 7.26 (1H, m, H-10), 4.23 (1H, s, H-21), 2.79 (1H, d, J = 16.7 Hz, H-17a), 2.49 (1H, d, J = 16.7 Hz, H-17b), 0.94 (3H, t, J = 7.6 Hz, Me-18); ^{13}C NMR (150 MHz, CD_3OD) δ: 169.5 (s, C-16), 135.6 (s, C-13), 132.7 (s, C-2), 131.4 (s, C-8), 125.4 (d, C-11), 125.1 (d, C-10), 119.3 (d, C-9), 116.9 (d, C-12), 114.0 (s, C-7), 58.5 (d, C-21), 51.5 (t, C-5), 45.3 (t, C-3), 44.8 (t, C-17), 39.7 (s, C-20), 29.0 (t, C-19), 27.9 (t, C-15), 21.4 (t, C-14), 17.2 (t, C-6), 7.8 (q, Me-18)。以上数据与文献报道一致[15]，故鉴定为(-)-象牙酮宁[(-)-Eburnamonine]。

化合物 7 淡黄色粉末。分子式为 $C_{22}H_{23}N_3O_2$, ESI-MS m/z 362 [M + H]$^+$。^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.42 (1H, d, J = 3.2 Hz, H-NH_2), 8.45 (1H, d, J = 8.0 Hz, H-12), 8.24 (1H, s, H-17), 7.35 (1H, d, J = 7.4 Hz, H-9), 7.32 (1H, t, J = 7.8 Hz, H-11), 7.25 (1H, t, J = 7.4 Hz, H-10), 6.21 (1H, d, J = 3.2 Hz, H-NH_2), 4.05 (1H, br s, H-3), 1.01 (3H, t, J = 7.4 Hz, Me-18); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 165.9 (s, $CONH_2$), 161.5 (s, C-2), 161.0 (s, C-22), 145.3 (d, C-17), 140.5 (s, C-13), 139.8 (s, C-8), 128.1 (d, C-11), 126.9 (d, C-10), 120.2 (s, C-23), 120.1 (d, C-9), 117.4 (d, C-12), 115.6 (s, C-16), 61.1 (d, C-3), 55.4 (s, C-7), 54.3 (t, C-5), 51.3 (t, C-21), 44.8 (t, C-6), 38.6 (d, C-20), 36.2 (d, C-15), 31.3 (t, C-14), 26.4 (t, C-19), 11.4 (q, Me-18); ^{1}H NMR (600 MHz, CD_3OD) δ: 8.45 (1H, d, J = 7.7 Hz, H-12), 8.22 (1H, s, H-17), 7.58 (1H, d, J = 7.4 Hz, H-9), 7.39 (1H, td, J = 7.7, 1.2 Hz, H-11), 7.35 (1H, td, J = 7.5, 0.9 Hz, H-10), 4.17 (1H, br s, H-3), 1.10 (3H, t, J = 7.5 Hz, Me-18); ^{13}C NMR (150 MHz, CD_3OD) δ: 168.2 (s, $CONH_2$), 162.8 (s, C-2), 162.7 (s, C-22), 146.5 (d, C-17), 141.8 (s, C-13), 141.3 (s, C-8), 129.3 (d, C-11), 128.5 (d, C-10), 122.0 (d, C-9), 121.1 (s, C-23), 118.4 (d, C-12), 117.0 (s, C-16), 63.0 (d, C-3), 56.7 (s, C-7), 54.8 (t, C-5), 52.2 (t, C-21), 45.5 (t, C-6), 39.9 (d, C-20), 37.1 (d, C-15), 32.0 (t, C-14), 27.4 (t, C-19), 11.8 (q, Me-18)。以上数据与文献报道一致[16]，故鉴定为 Leuconicine A。

化合物 8 白色无定型粉末。分子式为 $C_{23}H_{24}N_2O_2$,ESI-MS *m/z* 377 [M + H]$^+$。^{1}H NMR (600 MHz,$CDCl_3$) δ:8.46 (1H,d,*J* = 7.9 Hz,H-12),7.81 (1H,s,H-17),7.26 (1H,d, *J* = 7.1 Hz,H-9),7.25 (1H,t,*J* = 8.0 Hz,H-11),7.16 (1H,t,*J* = 7.5 Hz,H-10),4.98 (1H,s,H-3),3.84 (3H,s,OMe),0.95 (3H,t,*J* = 7.4 Hz,Me-18);^{13}C NMR (150 MHz,$CDCl_3$) δ:165.8 (s,CO_2Me),162.1 (s,C-22),158.8 (s,C-2),145.9 (d,C-17),140.7 (s,C-13),139.4 (s,C-8),128.1 (d,C-11),126.6 (d,C-10),119.9 (d,C-9),119.9 (s,C-23),117.6 (d,C-12),114.0 (s,C-16),62.0 (d,C-3),55.5 (s,C-7),54.3 (t,C-5),52.3 (q,CO_2Me),51.3 (t,C-21),44.7 (t,C-6),38.6 (d,C-20),36.0 (d,C-15),31.2 (t,C-14),26.3 (t,C-19),11.4 (q,Me-18)。以上数据与文献报道一致[16,17],故鉴定为 Alkaloid 376。

化合物 9 白色无定型粉末。分子式为 $C_{22}H_{21}N_3O_2$,ESI-MS *m/z* 282 [M + Na]$^+$。^{1}H NMR (600 MHz,$CDCl_3$) δ:9.52 (1H,d,*J* = 3.0 Hz,*N*H),8.57 (1H,d,*J* = 7.8 Hz,H-12),8.47 (1H,s,H-17),7.48 (1H,d,*J* = 7.8 Hz,H-9),7.42 (1H,td,*J* = 7.8,1.2 Hz,H-11),7.34 (1H,td,*J* = 7.8,1.2 Hz,H-9),5.88 (1H,d,*J* = 3.0 Hz,*N*H),5.54 (1H,s,H-21),4.20 (1H,br s,H-3),2.14 (2H,q,*J* = 7.2 Hz,H-19),1.07 (3H,t,*J* = 7.2 Hz,Me-18);^{13}C NMR (150 MHz,$CDCl_3$) δ:166.1 (s,CO*N*H_2),161.3 (s,C-2),158.3 (s,C-22),143.1 (d,C-17),140.7 (s,C-13),139.9 (s,C-8),130.0 (d,C-21),128.5 (d,C-11),127.2 (d,C-10),122.9 (s,C-20),121.0 (s,C-23),120.6 (d,C-10),119.4 (s,C-16),118.0 (d,C-12),60.1 (d,C-3),56.7 (s,C-7),53.7 (t,C-5),46.2 (t,C-6),33.8 (d,C-15),31.0 (t,C-14),27.5 (t,C-19),12.9 (q,Me-18)。以上数据与文献报道一致[16],故鉴定为 Leuconicine C。

化合物 10 白色无定型粉末。分子式为 $C_{19}H_{22}N_2O$,ESI-MS *m/z* 317 [M + Na]$^+$。^{1}H NMR (600 MHz,CD_3OD) δ:7.38 (1H,d,*J* = 7.4 Hz,H-9),7.36 (1H,t,*J* = 7.7 Hz,H-11),7.30 (1H,t,*J* = 7.5 Hz,H-10),7.19 (1H,d,*J* = 7.9 Hz,H-12),6.51 (1H,d,*J* = 3.0 Hz,H-5),5.69 (1H,d,*J* = 3.0 Hz,H-6),4.00 (1H,dd,1H,d,*J* = 12.0,5.4 Hz,H-3b),3.77 (1H,dt,*J* = 12.0,4.8 Hz,H-3a),1.48 (1H,m,H-19b),1.21 (1H,m,H-19a),0.72 (3H,t,*J* = 7.3 Hz,Me-18);^{13}C NMR (150 MHz,CD_3OD) δ:180.0 (s,C-2),142.4 (s,C-13),139.6 (s,C-8),132.5 (d,C-5),131.2 (s,C-21),129.1 (d,C-11),128.1 (d,C-6),127.5 (d,C-10),120.0 (d,C-9),118.8 (s,C-7),110.8 (d,C-12),47.1 (t,C-3),40.2 (s,C-20),37.9 (t,C-16),34.4 (t,C-15),31.2 (t,C-19),29.2 (t,C-17),20.7 (t,C-14),8.5 (q,Me-18)。以上数据与文献报道一致[18],故鉴定为(-)-Rhazinilam。

化合物 11 白色无定型粉末。分子式为 $C_{21}H_{26}N_2O_3$,ESI-MS *m/z* 355 [M + H]$^+$。^{1}H NMR (600 MHz,CD_3OD) δ:7.39 (1H,d,*J* = 7.8 Hz,H-9),7.30 (1H,d,*J* = 7.8 Hz,H-12),7.06 (1H,t,*J* = 7.8 Hz,H-11),6.97 (1H,t,*J* = 7.8 Hz,H-10),5.67 (1H,q,*J* = 6.8 Hz,H-19),4.25 (1H,br s,H-3),3.75 (3H,s,CO_2Me),1.69 (3H,d,*J* = 6.8 Hz,Me-18);^{13}C NMR (150 MHz,CD_3OD) δ:176.5 (s,CO_2Me),137.9 (s,C-13),135.2 (s,C-2),134.1 (s,C-20),128.5 (s,C-8),125.3 (d,C-19),122.3 (d,C-11),119.9 (d,C-10),118.7 (d,C-9),112.1 (d,C-12),107.2 (s,C-7),63.2 (t,C-17),53.8 (d,C-3),52.3 (q,CO_2Me),51.8 (t,C-21),50.8 (t,C-5),50.9 (d,C-16),34.0 (d,C-15),31.4 (t,C-14),18.8 (t,C-6),13.5 (q,Me-18)。以上数据与文献报道一致[19],故鉴定为 16(*R*)-*E*-异西特斯日钦碱[16(*R*)-*E*-isositsirikine]。

化合物 12 白色无定型粉末。分子式为 $C_{21}H_{26}N_2O_3$,ESI-MS *m/z* 355 [M + H]$^+$。^{1}H NMR (600 MHz,CD_3OD) δ:7.37 (1H,d,*J* = 7.8 Hz,H-9),7.28 (1H,d,*J* = 8.1 Hz,H-12),7.04 (1H,t,*J* = 7.5 Hz,H-11),6.96 (1H,t,*J* = 7.5 Hz,H-10),5.66 (1H,dt,*J* = 9.5 Hz,H-19),5.27 (1H,dd,*J* = 17.2,1.4 Hz,H-18a),5.21 (1H,dd,*J* = 10.4,1.8 Hz,H-18b),4.00 (1H,dd,*J* = 10.9,8.3 Hz,H-17a),3.69 (1H,dd,*J* = 10.9,6.5 Hz,H-17b),3.65 (3H,s,CO_2Me),3.11 (1H,dd,*J* = 11.4,5.5 Hz,H-21a),2.73 (2H,dd,*J* = 15.5,4.4 Hz,H-6b),1.87 (1H,tt,*J* = 12.0,3.1 Hz,H-15),1.41 (1H,q,*J* = 12.4 Hz,H-14b);^{13}C NMR (150 MHz,CD_3OD) δ:174.8 (s,CO_2Me),139.8 (d,C-19),138.2 (s,C-13),128.2 (d,C-8),122.1 (d,C-11),

119.8 (d,C-10),118.7 (t,C-18),118.6 (d,C-9),112.0 (s,C-12),107.8 (s,C-7),62.4 (t,C-17),62.0 (t,C-5),61.4 (d,C-3),54.1 (t,C-21),51.8 (q,CO_2Me),50.2 (d,C-16),45.3 (d,C-20),40.8 (d,C-15),31.3 (t,C-14),22.2 (t,C-6)。以上数据与文献报道一致[20],故鉴定为西特斯日钦碱(Sitsirikine)。

化合物 13 白色无定型粉末。分子式为 $C_{21}H_{26}N_2O_4$,ESI-MS *m/z* 371 [M+H]$^+$。^{1}H NMR (600 MHz,CD_3OD) δ:7.51 (1H,d,*J* = 7.9 Hz,H-9),7.39 (1H,d,*J* = 8.1 Hz,H-12),7.13 (1H,t,*J* = 7.5 Hz,H-11),7.07 (1H,t,*J* = 7.5 Hz,H-10),5.59 (1H,q,*J* = 7.0 Hz,H-19),4.33 (1H,d,*J* = 10.5 Hz,H-22a),4.31 (1H,d,*J* = 10.5 Hz,H-22b),3.77 (3H,s,CO_2Me),1.77 (3H,dd,*J* = 7.0,1.9 Hz,Me-18);^{13}C NMR (150 MHz,CD_3OD) δ:174.2 (s,C-17),136.9 (s,C-13),135.3 (s,C-2),132.0 (d,C-19),129.7 (s,C-20),128.2 (s,C-8),123.2 (d,C-11),120.6 (d,C-10),118.6 (d,C-9),112.5 (d,C-12),109.6 (s,C-7),75.7 (t,C-21),74.4 (t,C-5),69.4 (t,C-22),64.9 (t,C-3),61.5 (s,C-16),53.1 (q,CO_2Me),34.9 (d,C-15),27.0 (t,C-14),25.1 (t,C-6),14.4 (q,Me-18)。以上数据与文献报道一致[21],故鉴定为花冠木碱 N^b-氧化物(Stemmadenine N^b-oxide)。

化合物 14 白色无定型粉末。分子式为 $C_{26}H_{30}N_2O_8$,ESI-MS *m/z* 499 [M+H]$^+$。^{1}H NMR (600 MHz,CD_3OD) δ:7.38 (1H,s,H-17),7.36 (1H,d,*J* = 7.8 Hz,H-9),7.33 (1H,d,*J* = 8.1 Hz,H-12),7.07 (1H,t,*J* = 7.5 Hz,H-11),6.99 (1H,t,*J* = 7.4 Hz,H-10),5.63 (1H,dt,*J* = 10.1 Hz,H-19),5.39 (1H,d,*J* = 1.5 Hz,H-21),5.35 (1H,dd,*J* = 16.9,1.1 Hz,H-18a),5.30 (1H,dd,*J* = 10.3,1.3 Hz,H-18b),4.56 (1H,d,*J* = 8.0 Hz,H-1′);^{13}C NMR (150 MHz,CD_3OD) δ:167.0 (s,C-22),149.1 (d,C-17),137.7 (s,C-2),134.7 (s,C-13),134.3 (d,C-19),128.6 (s,C-8),122.4 (d,C-10),120.6 (t,C-18),120.1 (d,C-11),118.7 (d,C-9),112.3 (d,C-12),110.2 (s,C-16),109.2 (s,C-9),100.4 (d,C-1′),98.0 (d,C-21),78.1 (d,C-5′),77.9 (d,C-3′),74.2 (d,C-2′),71.2 (d,C-4′),62.5 (t,C-6′),55.0 (d,C-3),44.7 (t,C-5),44.6 (d,C-20),27.2 (t,C-6),24.9 (d,C-15),22.1 (t,C-14)。以上数据与文献报道一致[22],故鉴定为异长春花苷内酰胺(Strictosamide)。

化合物 15 淡黄色无定型粉末。分子式为 $C_{27}H_{34}N_2O_9$,ESI-MS *m/z* 531 [M + H]$^+$。^{1}H NMR (600 MHz,CD_3OD) δ:7.55 (1H,s,H-17),6.95 (1H,d,*J* = 8.0 Hz,H-12),6.90 (1H,t,*J* = 7.9 Hz,H-11),6.67 (1H,d,*J* = 7.7 Hz,H-10),5.03 (1H,d,*J* = 7.7 Hz,H-1′),4.46 (1H,m,H-19),3.87 (1H,dd,*J* = 12.6,1.6 Hz,H-6′a),3.73 (3H,s,CO_2Me),3.69 (1H,dd,*J* = 12.2,5.1 Hz,H-6′b),3.51 (1H,t,*J* = 8.5 Hz,H-2′),3.47 (1H,t,*J* = 8.8 Hz,H-3′),3.24 (1H,br d,*J* = 11.7 Hz,H-3),3.10 (1H,br d,*J* = 12.5 Hz,H-21b),3.00 (1H,dd,*J* = 15.9,4.0 Hz,H-6b),2.94 (1H,dd,*J* = 11.4,6.0 Hz,H-5b),2.45 (1H,td,*J* = 11.7,4.4 Hz,H-5a),1.39 (1H,q,*J* = 12.4 Hz,H-14a),1.36 (3H,d,*J* = 6.2 Hz,Me-18);^{13}C NMR (150 MHz,CD_3OD) δ:169.6 (s,CO_2Me),156.9 (d,C-17),153.0 (s,C-9),139.7 (s,C-13),134.4 (s,C-2),122.4 (d,C-11),119.3 (s,C-8),110.9 (s,C-16),107.9 (s,C-7),107.0 (d,C-12),104.5 (d,C-10),102.3 (d,C-1′),78.5 (d,C-3′),78.1 (d,C-5′),75.3 (d,C-2′),73.6 (d,C-19),71.4 (d,C-4′),62.6 (t,C-6′),61.7 (d,C-3),57.1 (t,C-21),55.1 (t,C-5),51.7 (q,CO_2Me),39.8 (d,C-20),34.8 (t,C-14),32.6 (d,C-15),24.5 (t,C-6),18.9 (q,Me-18)。以上数据与文献报道一致[21],故鉴定为 9-*β*-*D*-吡喃葡萄糖基-四氢鸭脚木碱(9-*β*-*D*-glucopyranosyl-tetrahydroalstonine)。

化合物 16 白色无定型粉末。分子式为 $C_{11}H_8N_2$,ESI-MS *m/z* 169 [M + H]$^+$。^{1}H NMR (600 MHz,CD_3OD) δ:8.80 (1H,s,H-1),8.29 (1H,d,*J* = 5.4 Hz,H-3),8.20 (1H,d,*J* = 7.9 Hz,H-5),8.12 (1H,d,*J* = 5.4 Hz,H-4),7.57 (2H,m,H-7,H-8),7.27 (1H,m,H-6);^{13}C NMR (150 MHz,CD_3OD) δ:142.9 (s,C-8a),138.0 (d,C-3),137.7 (s,C-9a),133.7 (d,C-1),130.7 (s,C-4a),130.0 (d,C-7),122.8 (d,C-5),122.1 (s,C-4b),121.0 (d,C-6),116.2 (d,C-4),112.9 (d,C-8)。以上数据与文献报道一致[23],故鉴定为 *β*-咔啉(*β*-Carboline)。

化合物 17 白色无定型粉末。分子式为 $C_{12}H_{10}N_2$,ESI-MS *m/z* 183 [M + H]$^+$。^{1}H NMR (600

MHz,$CDCl_3$) δ:8.71 (1H,br s,H-9),8.37 (1H,d,J = 4.8 Hz,H-3),8.12 (1H,d,J = 7.8 Hz,H-5),7.83 (1H,d,J = 5.4 Hz,H-4),7.54 (2H,m,H-7,H-8),7.29 (1H,td,J = 6.9,2.2 Hz,H-6),2.84 (3H,s,Me-1′);^{13}C NMR (150 MHz,$CDCl_3$) δ:141.7 (s,C-1),140.1 (s,C-8a),138.6 (d,C-3),134.6 (s,C-9a),128.4 (s,C-4a),128.2 (d,C-7),122.0 (d,C-4b),121.8 (d,C-5),120.1 (d,C-6),112.9 (d,C-4),111.6 (d,C-8),20.3 (q,Me-1′)。以上数据与文献报道一致[24],故鉴定为1-甲基-9*H*-吡啶并[3,4-*b*]吲哚(Harman)。

化合物18 针状晶体($CHCl_3$-MeOH)。分子式为$C_9H_{11}N_1O$,ESI-MS *m/z* 172 [M+Na]$^+$。^{1}H NMR (400 MHz,CD_3OD) δ:8.32 (1H,s,H-1),8.29 (1H,d,J = 4.9 Hz,H-9),7.32 (1H,d,J = 4.9 Hz,H-8),4.51 (1H,m,H-5),4.24 (1H,m,H-3),3.13 (1H,dd,J = 17.0,5.4 Hz,H-6a),2.90 (1H,dd,J = 17.0,1.8 Hz,H-6b),1.35 (3H,d,J = 7.1 Hz,Me-4);^{13}C NMR (100 MHz,CD_3OD) δ:153.7 (s,C-2),147.8 (d,C-1),145.2 (d,C-9),144.3 (s,C-7),122.0 (d,C-8),75.9 (d,C-5),44.0 (d,C-3),41.6 (t,C-6),12.4 (q,Me-4)。以上数据与文献报道一致[25],故鉴定为喜树次碱(Venoterpine)。

化合物19 针状晶体($CHCl_3$-MeOH)。分子式为$C_{11}H_{13}NO_3$,ESI-MS *m/z* 230 [M+Na]$^+$。^{1}H NMR (600 MHz,CD_3OD) δ:8.87 (1H,s,H-9),8.48 (1H,s,H-1),4.53 (1H,m,H-5),3.92 (3H,s,CO_2Me),1.38 (3H,d,J = 7.2 Hz,Me-4);^{13}C NMR (150 MHz,CD_3OD) δ:167.2 (s,CO_2Me),155.8 (s,C-7),149.3 (d,C-1),148.5 (d,C-9),145.3 (s,C-2),124.7 (s,C-8),75.6 (d,C-5),52.6 (q,CO_2Me),43.8 (d,C-3),42.9 (t,C-6),12.3 (q,Me-4)。以上数据与文献报道一致[25],故鉴定为坎特莱因碱(Cantleyine)。

化合物20 无色油状物。分子式为C_7H_9NO,ESI-MS *m/z* 145 [M+Na]$^+$。^{1}H NMR (400 MHz,CD_3OD) δ:8.54 (1H,s,H-2),8.42 (1H,d,J = 4.5 Hz,H-6),7.86 (1H,d,J = 7.9 Hz,H-4),7.41 (1H,dd,J = 7.7,4.9 Hz,H-5),4.90 (1H,q,J = 6.5 Hz,H-7),1.47 (3H,d,J = 6.5 Hz,Me-8);^{13}C NMR (100 MHz,CD_3OD) δ:148.7 (d,C-6),147.7 (d,C-2),143.9 (s,C-1),135.5 (d,C-4),125.2 (d,C-5),68.4 (d,C-7),25.4 (q,Me-8)。以上数据与文献报道一致[26],故鉴定为α-甲基-3-羟甲基吡啶(α-Methyl-3-pyridinemethanol)。

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