described in the literature [9].

Compound **6** $C_{35}H_{60}O_6$, white crystal, mp > 300 ℃. Both Liebermann-Burchard and Molish reactions were positive. It showed single spot at co-TLC plate with daucosterol. Its IR spectrum was identical with that of daucosterol.

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温郁金地上部分的化学成分

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[摘要] **目的**:研究中药莪术来源植物之一温郁金地上部分的化学成分。**方法**:利用反复硅胶色谱柱进行分离纯化,通过理化性质和波谱数据分析鉴定化合物结构。**结果**:分离并鉴定出 6种化合物: codonolactone (**1**), voleneol (**2**), octacosanoic acid (**3**), β谷甾醇 (**4**), mangdesisterol (**5**)和胡萝卜苷 (**6**)。**结论**:两个倍半萜化合物 **1**, **2** 和一个甾醇 **5**为首次从该植物中分得。

[关键词] *Curcuma wenyujin*; Zingiberaceae; codonolactone; voleneol

[责任编辑 王亚君]

滇丁香萜苷类化合物研究

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[摘要] **目的**:对滇丁香乙醇提取物的正丁醇部位进行研究。**方法**:色谱技术进行分离, MS, NMR, 2D NMR等波谱方法进行结构鉴定。**结果**:分离得到 7个化合物 Vogeloside (**1**), *epi*-Vogeloside (**2**), Loganoside (**3**), Loganin (**4**),

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Cincholic acid 28-O-β-D-glucopyranosyl ester(5), Cincholic acid-3-O-β-D-glucopyranoside, 28-O-β-D-glucopyranosyl ester (6), Cincholic acid-3-O-β-D-glucopyranoside(7)。**结论**:化合物 1～7为首次从该属植物中分离鉴定。

[**关键词**] 滇丁香;三萜苷;萜苷
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滇丁香 *Luculia pinceana* Hook.为茜草科滇丁香属植物,分布在喜马拉雅山至我国云南和广西[1]。《西藏植物志》记载滇丁香的根、花、果入药,可治疗百日咳、慢性支气管炎、肺结核、月经不调、痛经、风湿疼痛、偏头疼、尿路结石、病后头昏、心慌;外用可以治疗毒蛇咬伤[2]。

周法兴等人曾报道从滇丁香中分离出 2%的丹皮酚成分[3],而未见其他化学成分及活性的研究。作者在前期研究的基础上[4-7],从乙醇提取物的正丁醇部位又分离得到 4个环烯醚萜苷和 3个 cincholic acid类型三萜苷类: vogeloside (**1**), epi-vogeloside (**2**), loganoside (**3**), loganin (**4**), cincholic acid 28-O-β-D-glucopyranosyl ester (**5**), cincholic acid-3-O-β-D-glucopyranoside, 28-O-β-D-glucopyranosyl ester (**6**), cincholic acid-3-O-β-D-glucopyranoside (**7**)。

1 仪器和材料

XRC-1型显微熔点测定仪(温度未校正), Bio-Rad FTS-135红外光谱仪, SEPA-300旋光仪, Bruker Am-400型超导核磁共振仪; Fonnegan-4510质谱仪。柱色谱材料为青岛海洋化工厂生产的 200～300目硅胶; Kieselgel 60 HF254(德国 Merk公司);薄层色谱材料为青岛海洋化工厂生产的 GF254硅胶板, Sephadex LH-20(瑞典 Pharmacia公司)。

滇丁香 *L. pinceana*于 2001年 7月采自云南省大理地区,经中国科学院昆明植物所彭华研究员鉴定为茜草科滇丁香属植物,标本存于中国科学院昆明植物所标本馆(KUN No 0358685)。

2 提取和分离

滇丁香干燥枝干 20 kg,粉碎后,用 95%的工业乙醇冷浸 3次,过滤,回收乙醇,将浓缩的提取物分散于水,依次用醋酸乙酯、正丁醇各萃取 3次,得醋酸乙酯提取物(300 g),正丁醇提取物(450 g),取正丁醇部位进行反复硅胶常压柱色谱,中压柱色谱, Kieselgel 60 HF_{254}常压柱色谱, Sephadex LH-20凝胶色谱及 RP-18反相柱色谱,分离得到化合物 **1** (31 mg), **2** (16 mg), **3** (34 mg), **4** (25 mg), **5** (62 mg), **6** (13 mg), **7** (43 mg)。

3 结构与鉴定

化合物 1 白色针状晶(甲醇), mp 113～116 ℃。Negative FAB-MS *m/z*(%) 387[M-H]$^+$ (46), 325(16), 225(23), 155(100), 111(10), 80(7)。^{1}H-NMR(400 MHz, C_5D_5N) δ: 5.45(2H m, H-1, H-8), 7.51(1H, d, *J* = 2.0 Hz, H-3), 3.08(1H, m, H-5), 2.67(1H, ddd, *J* = 13.4, 4.2, 2.4 Hz, H-6eq), 1.30(1H, ddd, *J* = 13.8, 13.8, 9.6 Hz, H-6ax), 5.31(1H, dd, *J* = 9.6, 2.4 Hz, H-7), 5.33(2H, m, H-10), 4.51(1H, d, *J* = 7.7 Hz, H-1′), 3.48(3H, s, 7-OCH_3), 2.95-3.75(6H, m, H-5, H-2′, H-3′, H-4′, H-5′, H-6′)。^{13}C-NMR(100 MHz, C_5D_5N) δ: 95.6(C-1), 151.6(C-3), 103.8(C-4), 23.6(C-5), 29.8(C-6), 98.1(C-7), 132.0(C-8), 41.3(C-9), 120.4(C-10), 163.9(C-11), 55.9(OMe), 61.0(C-6′), 102.9(C-1′), 73.0(C-2′), 76.3(C-3′), 70.0(C-4′), 77.2(C-5′)。以上数据与文献[8]报道数据一致,确定化合物为 vogeloside。

化合物 2 白色针状晶(甲醇), mp 108～110 ℃。Negative FAB-MS *m/z*(%) 387[M-H]$^+$ (67), 283(5), 255(26), 155(100), 111(20), 69(20)。^{1}H-NMR(400 MHz, C_5D_5N) δ: 5.48(2H m, H-1, H-8), 7.52(1H, d, *J* = 2.5 Hz, H-3), 1.84(1H, ddd, *J* = 13.8, 5.0, 2.0 Hz, H-6eq), 1.58(1H, ddd, *J* = 13.8, 13.8, 2.9 Hz, H-6ax), 5.31(1H, dd, *J* = 2.9, 2.0 Hz, H-7), 2.62(1H, ddd, *J* = 7.0, 5.4, 1.6 Hz, H-9), 5.26(2H, m, H-10), 4.54(1H, d, *J* = 7.7 Hz, H-1′), 3.44(3H, s, 7-OCH_3), 2.90～3.80(6H, m, H-5, H-2′, H-3′, H-4′, H-5′, H-6′)。^{13}C-NMR(100 MHz, C_5D_5N) δ: 96.2(C-1), 151.9(C-3), 103.7(C-4), 21.2(C-5), 28.3(C-6), 98.7(C-7), 132.2(C-8), 41.1(C-9), 120.2(C-10), 163.3(C-11), 55.9(OMe), 100.9(C-1′), 72.9(C-2′), 76.7(C-3′), 69.9(C-4′), 77.2(C-5′), 60.9(C-6′)。以上数据与文献[8]报道数据一致,确定化合物为 epi-vogeloside。

化合物 3 mp 168 ℃, $[\alpha]_D^{20}$ - 86.2(*c* 0.5,

H_2O)。Negative FAB-MS *m/z* (%) 375 [M-H]$^+$ (30), 339 (25), 286 (10), 255 (14), 225 (17), 201 (18), 115 (100), 73 (68)。^{1}H-NMR (400 MHz, CD_3OD) δ: 5.74 (1H, d, *J* = 4.5 Hz, H-1), 8.56 (1H, s, H-3), 3.50 (1H, d, *J* = 7.20 Hz, H-5), 2.63, 1.72 (2H, dd, *J* = 13.75, 7.80 Hz, H-6), 4.24 (1H, m, H-7), 2.45 (1H, ddd, *J* = 4.5, 6.0, 8.9 Hz, H-9), 1.18 (3H, d, *J* = 6.81 Hz, H-10), 5.39 (1H, d, *J* = 7.8 Hz, H-1′), 4.08 (1H, t, *J* = 8.0 Hz, H-2′), 4.28 (1H, t, *J* = 8.1 Hz, H-3′), 4.02 (2H, overlap, H-4′, H-5′), 4.39, 4.36 (2H, m, H-6′)。^{13}C-NMR (100 MHz, CD_3OD) δ: 97.5 (C-1), 150.8 (C-3), 114.4 (C-4), 32.2 (C-5), 43.2 (C-6), 74.9 (C-7), 41.8 (C-8), 46.1 (C-9), 13.8 (C-10), 169.9 (COOH), 100.9 (C-1′), 73.6 (C-2′), 78.6 (C-3′), 71.5 (C-4′), 79.0 (C-5′), 62.7 (C-6′)。以上数据与文献 [9] 报道数据一致,确定化合物为 loganoside。

化合物 4 白色片状晶体 (甲醇), mp 223 ℃, $[\alpha]_D^{20}$ - 83 (*c* 0.5, H_2O)。EHMS *m/z* (%) 228 (34), 210 (32), 197 (15), 179 (67), 163 (34), 139 (55), 127 (30), 71 (100)。^{1}H-NMR (400 MHz, CD_3OD) δ: 5.25 (1H, d, *J* = 4.8 Hz, H-1), 7.37 (1H, d, *J* = 1.6 Hz, H-3), 3.0 (1H, m, H-5), 1.61, 2.22 (2H, m, H-6), 3.87 (1H, m, H-7), 1.86 (1H, m, H-8), 2.01 (1H, ddd, *J* = 4.5, 6.0, 8.9 Hz, H-9), 1.08 (3H, d, *J* = 8.8 Hz, H-10), 3.60 (3H, s, $COOCH_3$)。^{13}C-NMR (100 MHz, CD_3OD) δ: 97.6 (C-1), 152.1 (C-3), 114.0 (C-4), 32.1 (C-5), 42.6 (C-6), 74.7 (C-7), 42.8 (C-8), 46.4 (C-9), 13.4 (C-10), 169.5 (COOH), 51.7 (OMe), 100.0 (C-1′), 75.0 (C-2′), 77.9 (C-3′), 71.5 (C-4′), 78.3 (C-5′), 62.7 (C-6′)。以上数据与文献 [9] 报道数据一致,确定化合物为 loganin。

化合物 5 白色粉末, $[\alpha]_D^{15.9}$ +65.7 (*c* 0.035, MeOH); Negative FAB-MS *m/z* 647 [M - H]$^-$, 485 [M - H - 162]$^-$, 441 [M - H - 162 - 44]$^-$。^{1}H-NMR (400 MHz, C_5D_5N) δ: 3.55 (1H, dd, *J* = 5.4, 11.3 Hz, H-3), 5.80 (1H, br s, H-12), 6.37 (1H, d, *J* = 8.1 Hz, H-1′), 4.41 (1H, t, *J* = 8.0 Hz, H-4′), 4.26 (1H, t, *J* = 8.0 Hz, H-3′), 4.18 (1H, t, *J* = 8.0 Hz, H-2′), 4.09 (1H, m, H-5′), 4.46, 4.43 (2H, dd, dd, *J* = 12.1, 2.0 Hz, H-6′), 1.20 (3H, s, H-26), 1.13 (3H, s, H-23), 0.93 (3H, s, H-24), 0.88 (3H, s, H-25), 0.84 (3H, s, H-30), 0.70 (3H, s, H-29)。^{13}C-NMR (100 MHz, C_5D_5N) δ: 39.3 (C-1), 28.2 (C-2), 79.3 (C-3), 40.2 (C-4), 55.8 (C-5), 18.9 (C-6), 37.6 (C-7), 40.8 (C-8), 47.4 (C-9), 37.4 (C-10), 23.5 (C-11), 126.6 (C-12), 137.4 (C-13), 56.0 (C-14), 26.2 (C-15), 25.2 (C-16), 49.0 (C-17), 54.7 (C-18), 39.1 (C-19), 30.5 (C-20), 30.3 (C-21), 36.5 (C-22), 28.6 (C-23), 17.1 (C-24), 16.6 (C-25), 19.1 (C-26), 178.8 (C-27), 176.8 (C-28), 32.2 (C-29), 23.6 (C-30), 95.7 (C-1′), 74.2 (C-2′), 78.0 (C-3′), 71.2 (C-4′), 78.9 (C-5′), 62.5 (C-6′)。以上数据与文献 [10] 报道数据一致,确定化合物为 cincholic acid 28-*O*-β-*D*-glucopyranosyl ester。

化合物 6 白色粉末。Negative FAB-MS *m/z* (%) 810 [M]$^+$ (13), 647 (34), 603 (17), 574 (35), 425 (37), 381 (18), 189 (19)。^{1}H-NMR (400 MHz, C_5D_5N) δ: 6.36 (1H, d, *J* = 8.2 Hz, H-1″), 5.98 (1H, brs, H-12), 4.67 (1H, d, *J* = 7.8 Hz, H-1′), 4.58 (1H, d, *J* = 11.6, H-6″), 4.45 (1H, dd, *J* = 11.6, 5.3 Hz, H-6″), 4.38 (1H, t, *J* = 8.3 Hz, H-4″), 4.31 (1H, t, *J* = 7.8, H-2″), 4.23 (1H, t, *J* = 7.8 Hz, H-3″), 4.10 (1H, t, *J* = 7.8 Hz, H-3′), 4.04 (1H, m, H-5″), 3.79 (1H, m, H-5″), 3.70 (1H, t, *J* = 7.8 Hz, H-4′), 3.16 (1H, dd, *J* = 11.3, 4.6 Hz, H-3), 2.68 (1H, d, *J* = 11.8 Hz), 1.66 (3H, d, *J* = 6.0 Hz, H-6′), 1.16, 1.20, 1.11, 0.92, 0.88, 0.73 (s, CH_3 ×6)。^{13}C-NMR (100 MHz, C_5D_5N) δ: 38.6 (C-1), 28.8 (C-2), 88.3 (C-3), 39.2 (C-4), 55.9 (C-5), 18.6 (C-6), 32.9 (C-7), 39.5 (C-8), 47.5 (C-9), 37.1 (C-10), 23.3 (C-11), 125.9 (C-12), 138.4 (C-13), 56.6 (C-14), 27.2 (C-15), 25.0 (C-16), 48.5 (C-17), 52.7 (C-18), 39.5 (C-19), 31.4 (C-20), 31.6 (C-21), 36.8 (C-22), 28.0 (C-23), 17.4 (C-24), 16.6 (C-25), 23.9 (C-26), 178.6 (C-27), 176.6 (C-28), 32.2 (C-29), 23.4 (C-30), 105.7 (C-1′), 75.1 (C-2′), 78.4 (C-3′), 71.5 (C-4′), 78.6 (C-5′), 62.2 (C-6′), 95.7 (C-1″), 74.2 (C-2″), 78.0 (C-3″), 71.2 (C-4″), 78.9 (C-5″), 62.5 (C-6″)。以上数据与文献 [10] 报道数据一致,确定化合物为 cincholic acid-3-*O*-β-*D*-glucopyranoside, 28-*O*-β-*D*-glucopyranosyl ester。

化合物 7 白色粉末, mp 278～280 ℃。$[\alpha]_D^{25}$

+ 36 (*c* 0.025, MeOH)。Negative FAB-MS *m/z* (%): 631 $[M - H]^+$ (7), 587 (100), 469 (8), 423 (5)。^{1}H-NMR (400 MHz, C_5D_5N) δ: 5.87 (1H, br s, H-12), 4.42 (1H, d, *J* = 7.8 Hz, H-1′), 3.43 (1H, t, *J* = 8.8 Hz, H-2′), 3.70 (1H, t, *J* = 8.8 Hz, H-3′), 3.84 (1H, t, *J* = 8.8 Hz, H-4′), 3.48 (2H, m, H-5′), 1.35 (3H, d, *J* = 6.04 Hz, H-6′), 3.33 (3H, dd, *J* = 11.08, 4.28 Hz, H-29), 0.94 (3H, s, H-25), 0.87 (3H, s, H-23), 0.76 (3H, s, H-29), 0.73 (3H, s, H-30), 0.67 (3H, s, H-24), 0.54 (3H, s, H-26)。^{13}C-NMR (100 MHz, C_5D_5N) δ: 39.3 (C-1), 28.2 (C-2), 88.6 (C-3), 40.1 (C-4), 55.9 (C-5), 18.7 (C-6), 37.6 (C-7), 39.8 (C-8), 47.3 (C-9), 37.1 (C-10), 23.5 (C-11), 126.1 (C-12), 137.0 (C-13), 56.0 (C-14), 26.2 (C-15), 25.2 (C-16), 49.0 (C-17), 54.7 (C-18), 39.1 (C-19), 30.5 (C-20), 30.3 (C-21), 36.5 (C-22), 28.6 (C-23), 17.1 (C-24), 16.6 (C-25), 19.2 (C-26), 178.6 (C-27), 180.2 (C-28), 32.2 (C-29), 23.6 (C-30), 106.6 (C-1′), 75.9 (C-2′), 78.4 (C-3′), 72.0 (C-4′), 78.4 (C-5′), 63.5 (C-6′)。以上数据与文献 [10] 报道数据一致,确定化合物为 cincholic acid-3-*O*-β-*D*-glucopyranoside。

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Terpenoid glycosides from stem of Luculia pinceana

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[Abstract] Objective: To study the chemical constituents from *n*-BuOH portion of ethanolic extract from the stem of *Luculia pinceana*. **Method:** The column chromatographic techniques were applied to isolate constituents. A combination of IR, FAB-MS, NMR and 2D NMR spectroscopy was used to identify structures. **Result:** Seven compounds were isolated from the *n*-BuOH fraction and their structures were elucidated as vogeloside (**1**), *epi*-vogeloside (**2**), loganoside (**3**), loganin (**4**), cincholic acid 28-*O*-β-*D*-glucopyranosyl ester (**5**), cincholic acid-3-*O*-β-*D*-glucopyranoside, 28-*O*-β-*D*-glucopyranosyl ester (**6**), cincholic acid-3-*O*-β-*D*-glucopyranoside (**7**). **Conclusion:** Compounds **1-7** were isolated from the genus for the first time.

[Key words] *Luculia pinceana*; triterpenoid glycosides; iridoid glycosides

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