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银叶巴豆的化学成分研究*

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摘要：对产自云南思茅银叶巴豆（*Croton cascarilloides*）的化学成分进行了研究.利用反复硅胶柱层析、重结晶等分离手段从中分离纯化得到8个化合物，通过现代波谱技术和理化常数测定鉴定了结构，它们是3个二萜，2个芳香类化合物，1个黄酮苷和β-谷甾醇及β-胡萝卜苷.

关键词：巴豆属；银叶巴豆；化学成分
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银叶巴豆（*Croton cascarilloides*）系大戟科（Euphorbiaceae）巴豆属（*Croton*）植物，该属植物全球约800多种，广泛分布于热带、亚热带地区，我国有21种，主要分布于南部各省区[1]. 在民间，巴豆属植物的枝叶、皮、根均可入药，可以用于治疗痛经，便秘（巴豆种），消化不良（巴豆树皮），疟疾，跌打损伤，蛇伤（巴豆叶）[2]. 前人主要报道了从巴豆属的其它植物中分离到了二萜类化合物[3~5]. 银叶巴豆的化学成分研究未见报道.

作为对滇产药用植物研究的一部分，我们对采自云南思茅的银叶巴豆的化学成分进行了深入的研究，从中分离到了8个化合物，并用波谱学方法确定了他们的结构，分别是：*ent*-8，9-7α-hydroxy-11β-acetoxykaura-8(14)，16-dien-9，15-dione(1)；*ent*-8，9-*seco*-7α-hydroxykaura-8(14)，16-dien-9，15-dione(2)；*ent*-8，9-*seco*-8，14-epoxy-7α-hydroxy-11β-acetoxy-16-kauren-9，15-dione(3)；luteolin-7-O-α-L-rhamnoside(4)；vanillin(5)；anisicacid(6)；β-sitosterol(7)；β-daucosterol(8). 以上化合物均为首次从该植物中分离得到.

1　实验部分

1.1　仪器和材料　熔点用XT-4双目显微熔点测定仪测定（温度计未校正）；MS用VG Autospec-3000质谱仪测定；NMR实验用Bruker AV-300型超导核磁共振仪测定（TMS内标）；柱层析用青岛海洋化工厂生产的0.15~0.075 mm和0.075~0.038 mm硅胶，薄层层析（TLC）采用该厂生产的GF_{254}高效硅胶层析板；显色剂用5%硫酸-乙醇溶液. 所用试剂均为化学纯或分析纯. 样品于2003年4月采自云南思茅，经中国科学院昆明植物研究所植物标本馆陈渝研究员鉴定为银叶巴豆.

1.2　提取分离　样品粗粉8 kg用90%的工业乙醇冷浸提取5次（每次4 d），合并提取液，减压蒸馏得粗提物. 将其悬浮于水中，分别用石油醚、乙酸乙酯、正丁醇萃取，得石油醚部分21 g，乙酸乙酯部分96 g，正丁醇部分78 g. 乙酸乙酯部分经反复硅胶柱层析分离和纯化得到8个化合物.

2　结构鉴定

2.1　化合物（**1**）　无色针状晶体（氯仿），m.p.156~158 ℃；分子式为$C_{22}H_{30}O_5$；EI-MS *m/z*：374[M]$^+$；^{1}HNMR（300 MHz，$CDCl_3$）δ：4.68（1H，dd，*J*=11.6，4.7 Hz，H-7），4.75（1H，d，*J*=4.1 Hz，H-11），3.6（1H，d，*J*=2.4 Hz，H-13），7.25

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(1H, d, J = 2.6 Hz, H-14), 6.1(1H, s, H-17), 5.4(1H, s, H-17), 1.01(3H, s, CH_3(18)), 0.99(3H, s, CH_3(19)), 1.08(3H, s, CH_3(20)), 1.98(3H, s, CH_3(2′)); ^{13}CNMR(75 MHz, $CDCl_3$) δ: 26.0(t, C-1), 24.0(t, C-2), 34.5(t, C-3), 34.6(s, C-4), 39.4(d, C-5), 34.6(t, C-6), 64.1(d, C-7), 148.7(s, C-8), 211.9(s, C-9), 56.4(s, C-10), 73.5(d, C-11), 36.4(t, C-12), 39.4(d, C-13), 160.1(d, C-14), 195.6(s, C-15), 146.5(s, C-16), 116.4(t, C-17), 33.7(q, C-18), 23.7(q, C-19), 17.7(q, C-20), 169.8(s, C-1′), 21.8(q, C-2′). 以上波谱数据与 *ent*-8,9-7α-hydroxy-11β-acetoxykaura-8(14),16-dien-9,15-dione[5] 一致, 故鉴定该化合物为 *ent*-8,9-7α-hydroxy-11β-acetoxykaura-8(14),16-dien-9,15-dione.

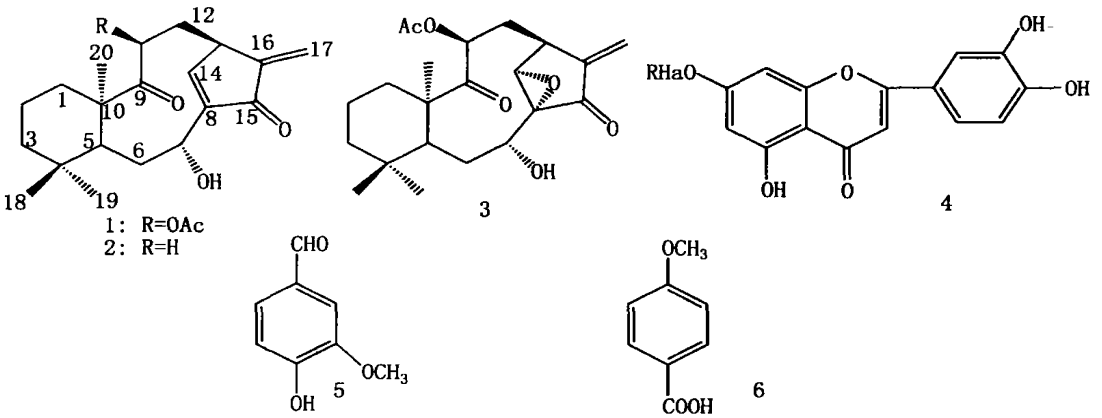

图 1 化合物 1~6 结构

Fig. 1 The structure of compounds 1—6

2.2 化合物(**2**) 无色油状液体, 分子式 $C_{20}H_{28}$ $C_{20}H_{28}O_3$; EI-MS m/z: 316[M]$^+$; ^{1}HNMR(300 MHz, $CDCl_3$) δ: 4.62(1H, dd, J = 12.1, 4.6 Hz, H-7), 3.5(1H, brs, H-13), 7.21(1H, d, J = 2.46 Hz, H-14), 6.06(1H, s, H-17), 5.39(1H, s, H-17), 0.95(3H, s, CH_3(18)), 0.87(3H, s, CH_3(19)), 0.89(3H, s, CH_3(20)); ^{13}CNMR(75 MHz, $CDCl_3$) δ: 36.6(t, C-1), 17.0(t, C-2), 40.3(t, C-3), 33.6(s, C-4), 42.4(d, C-5), 33.0(t, C-6), 63.2(d, C-7), 147.5(s, C-8), 214.4(s, C-9), 52.8(s, C-10), 29.7(d, C-11), 24.7(t, C-12), 41.3(d, C-13), 158.8(d, C-14), 194.3(s, C-15), 144.9(s, C-16), 115.9(t, C-17), 32.6(q, C-18), 21.3(q, C-19), 15.5(q, C-20). 以上波谱数据与 *ent*-8,9-*seco*-7α-hydroxykaura-8(14),16-dien-9,15-dione[6] 一致, 故鉴定该化合物为 *ent*-8,9-*seco*-7α-hydroxykaura-8(14),16-dien-9,15-dione.

2.3 化合物(**3**) 无色针状晶体(氯仿), m.p. 218 ~ 220 ℃; 分子式为 $C_{22}H_{30}O_6$; EI-MS m/z: 390 [M]$^+$; ^{1}HNMR(300 MHz, $CDCl_3$) δ: 4.64(1H, dd, J = 11.5, 4.26 Hz, H-7), 4.84(1H, t, J = 4.5 Hz, H-11), 3.24(1H, s, H-13), 3.68(1H, s, H-14), 6.31(1H, s, H-17), 5.52(1H, d, J = 1.2, H-17), 1.15(3H, s, CH_3(18)), 1.02(3H, s, CH_3(19)), 1.07(3H, s, CH_3(20)), 2.01(3H, s, CH_3(2′)); ^{13}CNMR(75 MHz, $CDCl_3$) δ: 32.8(t, C-1), 24.1(t, C-2), 35.1(t, C-3), 34.9(s, C-4), 39.9(d, C-5), 34.7(t, C-6), 61.9(d, C-7), 64.7(s, C-8), 211.2(s, C-9), 56.2(s, C-10), 73.3(d, C-11), 25.4(t, C-12), 38.0(d, C-13), 60.6(d, C-14), 197.0(s, C-15), 145.7(s, C-16), 122.3(t, C-17), 33.6(q, C-18), 23.3(q, C-19), 17.5(q, C-20), 169.6(s, C-1′), 21.8(q, C-2′) 以上波谱数据与 *ent*-8,9-*seco*-8,14-*epoxy*-7α-hydroxy-11β-acetoxy-16-kauren-9,15-dione[5] 一致, 故鉴定该化合物为 *ent*-8,9-*seco*-8,14-epoxy-7α-hydroxy-11β-ace-

toxy- 16- kauren- 9, 15- dione.

2.4 化合物(**4**)　黄色油状液体, 分子式 $C_{21}H_{20}O_{10}$; FAB- MS *m/z*: 431[M- 1]$^-$; ^{1}HNMR(300 M Hz, CD_3OD) δ: 7.44(1H, d, *J*= 1.9 Hz, H- 2′), 7.31(1H, dd, *J*= 8.3, 2.0 Hz, H- 6′), 6.91(1H, d, *J*= 8.2, H- 5′), 6.47(1H, d, *J*= 2.0 Hz, H- 8), 6.55(1H, s, H- 3), 6.21(1H, d, *J*= 2.0 Hz, H- 6), 5.35(1H, brs, H- 1″), 0.94(3H, d, *J*= 5.9 Hz, CH_3); ^{13}CNMR(75 M Hz, CD_3CD) δ: 163.2(s, C- 2), 103.6(d, C- 3), 179.7(s, C- 4), 159.3(s, C- 5), 94.6(d, C- 6), 165.9(s, C- 7), 94.7(d, C- 8), 158.5(s, C- 9), 104.4(s, C- 10), 136.2(s, C- 1′), 116.4(d, C- 2′), 149.8(s, C- 3′), 146.4(s, C- 4′), 117.0(d, C- 5′), 122.9(d, C- 6′), 99.8(d, C- 1″), 72.0(d, C- 2″), 72.1(d, C- 3″), 73.3(d, C- 4″), 71.9(d, C- 5″), 17.6(q, C- 6″). 以上波谱数据与 luteolin- 7- O- α- L- rhamnoside[7] 一致, 故鉴定该化合物为 luteolin- 7- O- α- L- rhamnoside.

2.5 化合物(**5**)　白色针状晶体(氯仿), m.p. 78 ~ 80 ℃; 分子式为 $C_8H_8O_3$; EI- MS *m/z*: 152[M]$^+$; ^{1}HNMR(300 M Hz, $CDCl_3$) δ: 9.81(1H, s, CHO), 7.41(2H, m, H- 2, H- 6), 7.03(1H, d, *J*= 8.8 Hz, H- 5), 6.47(1H, brs, OH), 3.95(3H, s, OCH_3); ^{13}CNMR(75 M Hz, $CDCl_3$) δ: 129.9(s, C- 1), 108.9(d, C- 2), 147.3(s, C- 3), 151.9(s, C- 4), 114.5(d, C- 5), 127.7(d, C- 6), 191.2(s, CHO), 56.2(q, OCH_3). 以上波谱数据与 vanillin[8] 一致, 故鉴定该化合物为 vanillin.

2.6 化合物(**6**)　无色针状晶体(仿), m.p. 182~184 ℃; 分子式为 $C_8H_8O_3$; EI- MS *m/z*: 152[M]$^+$; ^{1}HNMR(300 Hz, $CDCl_3$) δ: 3.88(3H, s, OCH_3), 8.08(2H, d, *J*= 8.9 Hz, H- 2, H- 6), 6.96(2H, d, *J*= 7.0 Hz, H- 3, H- 5); ^{13}CNMR(75 M Hz, $CDCl_3$) δ: 171.9(s, C═O), 164.3(s, C- 4), 132.5(d, C- 2, C- 6), 121.9(s, C- 1), 113.9(d, C- 3, C- 5), 55.6(q, OCH_3). 以上波谱数据与 anisic acid[9] 一致, 故鉴定该化合物为 anisic acid.

2.7 化合物(**7**)　无色针状晶体(氯仿), m.p. 136 ~ 137 ℃, 与 β- 谷甾醇标准品进行对照, 混合熔点不下降; 在多种体系中进行薄层层析(TLC)检测, R_f 值一致, 且显色相同, 故确定为 β- 谷甾醇(β- sitosterol).

2.8 化合物(**8**)　白色粉末, 与 β- 胡萝卜苷准品进行对照, 混合熔点不下降; 在多种体系中进行薄层层析(TLC)检测, R_f 值一致, 且显色相同, 故确定为 β- 胡萝卜苷(β- daucosterol).

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Studies on chemical constituents of *Croton cascarilloides*

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Abstract: The chemical constituents of *Croton cascarilloides* were studied and eight compounds were isolated. The structure of these compounds were elucidated as *ent*-8,9-7α-hydroxy-11β-acetoxykaura-8(14),16-dien-9,15-dione(1); *ent*-8,9-*seco*-7α-hydroxykaura-8(14),16-dien-9,15-dione(2); *ent*-8,9-*seco*-8,14-epoxy-7α-hydroxy-11β-acetoxy-16-kauren-9,15-dione(3); luteolin-7-O-α-L-rhamnoside(4); vanillin(5); anisic acid(6); β-sitosterol(7) and β-daucosterol(8) by spectral analysis.

Key words: croton; *Croton Cascarilloids*; chemical constituents

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Analysis of chemical constituents of the volatile oils from *Stenoloma chusanum* (L.) Chingand their antibacterial activity

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Abstract: The chemical constituents of volatile oils from the *Stenoloma chusanum* (L.) Ching were analyzed and test was for their antibacterial activity. The volatile oils were obtained by steam distillation, its chemical components were determined by GC/MS analysis, and its antibacterial activity was carried out with paper scrip method. 36 components were checked out and 24 compounds were identified, in which the main ingredients were L-linalool (24.76%), α-terpineol (7.24%) and geraniol (6.06%). The test for the antibacterial activity showed that volatile oils had obvious inhibition to *Bacillus subtilis* and *Salmonella typhi*, and had little inhibitory while almost no inhibition activity to *Psedomonas aeruginose*, *Escherichia cdi*, *Staphylococcus aureus* and *Sarcina lutea*. The main constituents in the volatile oils of *Stenoloma chusanum* (L.) Ching were monoterpene and 72.0 percent of them was identified. It was presumed that volatile oils from this plant contain some antibacterial constituents.

Key words: *Stenoloma chusanum* (L.) Ching; volatile oils; chemical constituents; antibacterial activity