

绿玉树化学成分研究

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摘要: 采用正相硅胶、Sephadex LH-20 和 HPLC 等色谱手段对绿玉树 *Euphorbia tirucalli* 化学成分进行分离纯化, 从绿玉树地上部分 70% 丙酮提取物中分离得到 12 个化合物。利用 MS、¹H NMR 和 ¹³C NMR 等现代波谱技术确定化合物结构为 4 α -去氧-巴豆醇-13-乙酸酯(1)、对映-3 β , 13S-二羟基-16-烯-14-阿替森酮(2)、羊毛甾醇(3)、3-表-粘霉烯醇(4)、齐墩果烷-9(11)、12-二烯-3-酮(5)、 β -香树烯酮(6)、齐墩果烷-18-烯-3-酮(7)、无羁萜(8)、4-豆甾烯-3-酮(9)、 β -谷甾醇(10)、山奈酚-3-O- α -L-鼠李糖苷(11)和东莨菪内酯(12)。其中, 化合物 1、2、5~7、9 和 12 为首次从该植物中分离得到。

关键词: 绿玉树; 二萜; 三萜

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Chemical Constituents from *Euphorbia tirucalli*

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Abstract: Twelve compounds including a tiglane diterpene ester, 4 α -deoxy-phorbol-13-acetate(1), a atisane diterpene, ent-(3 β , 13S)-dihydroxyatis-16-en-14-one(2), together with six triterpenoids, lanosterol(3), 3-*epi*-glutinol(4), olean-9(11), 12-dien-3-one(5), β -amyrenone(6), olean-18-en-3-one(7), friedelin(8), and four other compounds, stigmast-4-en-3-one(9), β -sitosterol(10), kaempferol 3-O- α -L-rhamnoside(11) and scopoletin(12), were isolated from the 70% acetone extract of *Euphorbia tirucalli*. Their structures were elucidated by spectroscopic analysis, including 1D NMR, 2D NMR and ESI-MS. Among them, compounds 1, 2, 5, 7, 9 and 12 were isolated from *E. tirucalli* for the first time.

Key words: *Euphorbia tirucalli*; diterpenoids; triterpenoids

绿玉树 *Euphorbia tirucalli* 为大戟科 Euphorbiaceae 大戟属 *Euphorbia* 植物, 原产非洲东部(安哥拉), 广泛栽培于热带和亚热带, 我国南北方均有栽培^[1]。许多国家用作传统药物, 在非洲和亚洲用作催泻和治疗神经痛、风湿病、牙痛等^[2]。研究表明, 绿玉树的乳汁有毒, 且对皮肤和粘膜有很强的刺激性, 高度不饱和的大戟二萜醇酯为其毒性的主要成分^[3-7]。为了弄清云南产绿玉树的化学成分, 发现更多活性好的化合物, 作者对采自云南西双版纳的绿玉树地上部分进行了化学成分的研究。从其 70% 丙酮提取物中分离得到 12 个化合物, 其中, 化合物 1、2、5~7、9 和 12 为首次从该植物中分离得到。

1 仪器与材料

Bruker DRX-500 型超导核磁共振仪; VG Auto spec-3000 质谱仪; 色谱正相硅胶(200~300目, 青岛海洋化工厂); 高效薄层板 TLC GF₂₅₄(青岛海洋化工厂); Sephadex LH-20(瑞典 Pharmacia 公司)。

植物样品于 2009 年 8 月采自云南西双版纳, 由云南中医学院杨耀文教授鉴定为绿玉树 *Euphorbia tirucalli*。植物标本(标本号: YTCM 20090803)存放于云南中医学院标本室。

2 提取与分离

干燥的绿玉树地上部分 4.8 kg, 粉碎后用 70% 丙酮室温浸提 3 次, 每次 24 h, 回收丙酮, 依次用石油醚、乙酸乙酯、正丁醇萃取, 回收溶剂后分别得石油醚浸膏(120 g)、乙酸乙酯浸膏(70 g)。

石油醚萃取物用硅胶(200~300目)柱层析分离, 以石油醚/乙酸乙酯(1:0~0:1, V/V) 进行梯度

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洗脱, TLC 对照合并相似流分得组分 A ~ E。B 组分 (13.5 g) 用硅胶 (200 ~ 300 目) 上柱, 以石油醚/乙酸乙酯 (99:1 ~ 10:1) 梯度洗脱, 经 TLC 检测后合并相似流分后得 4 个组分 B1 ~ B4, 组分 B1 有晶体析出, 经重结晶后得到化合物 **3** (182 mg)。组分 B3 经石油醚/乙酸乙酯 (40:1) 洗脱, 得到化合物 **4** (200 mg)。C 组分 (8.3 g) 用硅胶 (200 ~ 300 目) 柱层析, 以石油醚/乙酸乙酯 (50:1) 梯度洗脱, 经 TLC 检测后合并相似流分得组分 C1 ~ C3, C1 再经石油醚/乙酸乙酯 (50:1) 洗脱, 得到化合物 **5** (25 mg)。C2 经 Sephadex LH-20 (甲醇/氯仿 1:1) 分离后, 再经硅胶 (200 ~ 300 目) 柱层析以石油醚/乙酸乙酯 (30:1) 洗脱, 得到化合物 **7** (40 mg)。组分 C3 经 Sephadex LH-20 (甲醇/氯仿 1:1) 分离后, 再经 PTLC (石油醚/乙酸乙酯 10:1) 纯化得到化合物 **6** (15 mg) 和化合物 **8** (10 mg)。D 组分 (4.1 g) 上硅胶 (200 ~ 300 目) 柱, 石油醚/乙酸乙酯 (20:1) 梯度洗脱部分经 Sephadex LH-20 (甲醇/氯仿 1:1) 分离后, 再经 PTLC (石油醚/丙酮 3:1) 得到化合物 **9** (15 mg) 和化合物 **10** (10 mg)。

乙酸乙酯萃取物 (70 g) 利用硅胶 (200 (300 目) 柱层析, 以氯仿/丙酮 (1:0 ~ 0:1) 梯度洗脱, TLC 检测合并相似流分, 得到 6 个组分 F ~ K。G 组分 (3.6 g) 经硅胶 (200 ~ 300 目) 柱层析, 以石油醚/丙酮梯度 (1:0 ~ 0:1) 洗脱, 石油醚/丙酮 (10:1) 洗脱部分, 再经 Sephadex LH-20 (氯仿/甲醇 1:1) 分离, 再经硅胶 (300 ~ 400 目) 柱层析, 以石油醚/丙酮 (5:1) 洗脱, 最后再经 PTLC (石油醚/丙酮 2:1) 得到化合物 **2** (3 mg)。I 组分经硅胶 (200 ~ 300 目) 柱层析, 以石油醚/乙酸乙酯梯度洗脱, 石油醚/乙酸乙酯 (2:1) 洗脱部分合并, 再经硅胶 (200 ~ 300 目) 柱层析, 以氯仿/丙酮 (3:1) 洗脱, 得到化合物 **12** (15 mg) 和 **1** (11 mg)。

3 结构鉴定

化合物 **1** 无色针晶 (CH₃OH); ¹H NMR (CD₃OD, 500 MHz) δ: 7.34 (1H, s, H-1), 5.14 (1H, br s, H-7), 3.97 (1H, d, *J* = 10.0 Hz, H-12), 3.87 (2H, m, H-20), 3.51 (1H, m, H-10), 3.30 (1H, m, H-5β), 2.74 (1H, m, H-4), 2.27 (1H, dd, *J* = 15.2, 4.6 Hz, H-5α), 2.10 (3H, s, 13-OAc), 1.95 (1H, m, H-8), 1.75 (3H, s, Me-19), 1.68 (1H, m, H-11), 1.25 (3H, d, *J* = 5.2 Hz, Me-18), 1.24 (3H, s, Me-16),

1.24 (3H, s, Me-17), 0.83 (1H, d, *J* = 5.3 Hz, H-14); ¹³C NMR (CD₃OD, 125 MHz) δ: 214.5 (s, C-3), 175.5 (s, 13-OAc), 159.4 (d, C-1), 143.9 (s, C-2), 137.3 (s, C-6), 125.4 (d, C-7), 79.4 (s, C-9), 75.6 (d, C-12), 69.2 (t, C-20), 68.9 (s, C-13), 50.3 (d, C-4), 48.6 (d, C-10), 46.2 (d, C-11), 42.4 (d, C-8), 37.3 (d, C-14), 27.2 (t, C-5), 26.3 (s, C-15), 24.5 (q, C-16), 21.1 (q, 13-OAc), 16.7 (q, C-17), 12.6 (q, C-18), 10.2 (q, C-19); ESI-MS: *m/z* 413 [M + Na]⁺, *m/z* 803 [2M + Na]⁺。以上数据与文献^[8]报道一致, 故鉴定为 4α-去氧-巴豆醇-13-乙酰胺。

化合物 **2** 白色粉末 (CH₃OH); ¹H NMR (CD₃OD, 600 MHz) δ: 4.96 (1H, d, *J* = 1.6 Hz, H-17b), 4.81 (1H, d, *J* = 1.6 Hz, H-17a), 3.83 (1H, d, *J* = 3.0 Hz, H-13), 3.18 (1H, m, H-3), 2.69 (1H, dd, *J* = 6.3, 2.9 Hz, H-12), 2.31 (1H, overlapped, H-7a), 2.29 (2H, m, H-15), 1.91 (1H, ddd, *J* = 14.3, 11.5, 3.9 Hz, H-11a), 1.78 (1H, ddd, *J* = 14.3, 6.5, 2.4 Hz, H-11b), 1.65 (1H, m, H-1a), 1.62 (1H, d, *J* = 6.6 Hz, H-9), 1.59 (2H, overlapped, H-2), 1.56 (1H, overlapped, H-6a), 1.42 (1H, m, H-6b), 1.06 (1H, m, H-1b), 1.00 (3H, s, Me-18), 0.94 (1H, td, *J* = 13.3, 4.9 Hz, H-7b), 0.89 (1H, dd, *J* = 12.3, 2.2 Hz, H-5), 0.77 (3H, s, Me-19), 0.71 (3H, s, Me-20); ¹³C NMR (CD₃OD, 150 MHz) δ: 219.3 (s, C-14), 145.1 (s, C-16), 110.8 (t, C-17), 79.7 (d, C-3), 76.2 (d, C-13), 55.9 (d, C-5), 53.4 (d, C-9), 48.7 (s, C-8), 47.4 (d, C-12), 44.5 (t, C-15), 39.9 (s, C-4), 39.1 (s, C-10), 37.8 (t, C-1), 32.3 (t, C-7), 29.1 (q, C-18), 27.7 (t, C-2), 26.8 (t, C-11), 20.1 (t, C-6), 16.5 (q, C-19), 14.4 (q, C-20); ESI-MS: *m/z* 341 [M + Na]⁺。以上数据与文献^[9,10]报道一致, 故鉴定为对映-3β, 13S-二羟基-16-烯-14-阿替森酮。

化合物 **3** 白色针晶 (CHCl₃); ¹H NMR (CDCl₃, 500 MHz) δ: 5.09 (1H, m, H-24), 3.24 (1H, dd, *J* = 11.7, 4.5 Hz, H-3), 1.68 (3H, br s, H-27), 1.60 (3H, br s, H-26), 1.00 (3H, s, H-29), 0.95 (3H, s, H-19), 0.87 (3H, s, H-28), 0.85 (3H, d, *J* = 6.3 Hz, H-21), 0.80 (3H, s, H-18), 0.75 (3H, s, H-30); ¹³C NMR (CDCl₃, 125 MHz) δ: 134.1 (s, C-8), 133.5 (s, C-9), 130.9 (s, C-25), 125.2 (d, C-24), 79.0 (d, C-3), 51.0 (d, C-5), 50.0 (s, C-14), 49.6 (d, C-17), 44.1 (s, C-13), 38.9 (s, C-4), 37.3 (s, C-

10), 35.9 (d, C-20), 35.4 (t, C-1), 35.3 (t, C-22), 30.9 (t, C-15), 29.8 (t, C-16), 28.2 (t, C-2), 28.1 (q, C-29), 27.9 (t, C-7), 27.7 (t, C-12), 25.7 (q, C-26), 24.8 (t, C-23), 24.5 (q, C-28), 21.5 (t, C-6), 20.1 (q, C-21), 19.0 (t, C-11), 18.9 (q, C-19), 17.7 (q, C-27), 15.6 (q, C-18), 15.5 (q, C-30)。以上数据与文献^[11]报道一致,故鉴定为羊毛甾醇。

化合物 4 无色针晶 (CHCl₃) ;¹H NMR (CDCl₃, 500 MHz) δ : 5.63 (1H, d, $J = 6.0$ Hz, H-6), 3.47 (1H, br s, H-3), 1.16, 1.14, 1.09, 1.04, 1.00, 0.99, 0.95, 0.85 (each 3H, s, 8 \times CH₃) ;¹³C NMR (CDCl₃, 125 MHz) δ : 141.6 (s, C-5), 122.1 (d, C-6), 76.3 (d, C-3), 49.7 (d, C-10), 47.4 (d, C-8), 43.1 (d, C-18), 40.8 (s, C-4), 39.3 (s, C-14), 39.0 (t, C-22), 37.8 (s, C-13), 36.0 (t, C-19), 34.9 (s, C-9), 35.1 (t, C-16), 34.6 (t, C-15), 34.5 (q, C-30), 33.1 (t, C-11), 32.4 (q, C-28), 32.0 (q, C-29), 32.1 (t, C-21), 30.4 (t, C-12), 30.1 (s, C-17), 29.0 (q, C-23), 28.3 (s, C-20), 27.8 (t, C-2), 25.6 (q, C-24), 23.7 (t, C-7), 19.6 (q, C-27), 18.4 (q, C-26), 18.2 (t, C-1), 16.2 (q, C-25) ;ESI-MS m/z : 449 [M + Na]⁺。以上数据与文献^[12]报道一致,故鉴定为 3-表-粘霉烯醇。

化合物 5 白色针晶 (CHCl₃) ;¹H NMR (CDCl₃, 500 MHz) δ : 5.63 (1H, d, $J = 5.8$ Hz, H-11), 5.53 (1H, d, $J = 5.8$ Hz, H-12), 1.26, 1.17, 1.12, 1.07, 1.00, 0.90, 0.89, 0.88 (each 3H, s, 8 \times CH₃) ;¹³C NMR (CDCl₃, 125 MHz) δ : 217.7 (s, C-3), 152.3 (s, C-9), 147.7 (s, C-13), 120.6 (d, C-12), 117.5 (d, C-11), 51.8 (d, C-5), 47.3 (s, C-4), 46.9 (t, C-19), 45.6 (d, C-18), 43.0 (s, C-14), 40.7 (s, C-8), 38.2 (s, C-10), 37.8 (t, C-22), 37.0 (t, C-1), 34.6 (t, C-21), 34.6 (t, C-2), 33.2 (q, C-29), 32.2 (s, C-17), 32.1 (s, C-20), 31.3 (t, C-7), 28.7 (q, C-28), 27.2 (t, C-15), 26.9 (q, C-23), 25.7 (t, C-16), 25.3 (q, C-27), 23.7 (q, C-30), 21.3 (q, C-24), 20.6 (q, C-25), 19.7 (q, C-26), 19.6 (t, C-6)。以上数据与文献^[13]报道一致,故鉴定为齐墩果烷-9(11),12-二烯-3-酮。

化合物 6 白色粉末 (CHCl₃) ;¹H NMR (CDCl₃, 500 MHz) δ : 5.20 (1H, t, $J = 3.5$ Hz, H-12), 1.14 (3H, s, Me-27), 1.09 (3H, s, Me-23), 1.07 (3H, s, Me-26), 1.05 (3H, s, Me-25), 1.02 (3H, s,

Me-24), 0.87 (6H, s, Me-29, 30), 0.84 (3H, s, Me-28) ;¹³C NMR (CDCl₃, 125 MHz) δ : 217.6 (s, C-3), 145.2 (s, C-13), 121.5 (d, C-12), 55.3 (d, C-5), 47.4 (d, C-9), 47.3 (d, C-18), 46.9 (s, C-4), 46.8 (t, C-19), 41.8 (s, C-14), 39.8 (s, C-8), 39.3 (t, C-1), 36.9 (t, C-22), 36.6 (s, C-10), 34.7 (t, C-21), 34.2 (t, C-2), 33.4 (q, C-29), 32.5 (s, C-17), 32.2 (t, C-7), 31.1 (s, C-20), 28.4 (t, C-15), 26.9 (q, C-28), 26.5 (t, C-16), 26.1 (q, C-23), 25.9 (q, C-27), 23.7 (q, C-30), 23.6 (t, C-11), 21.5 (q, C-24), 19.7 (t, C-6), 16.7 (q, C-26), 15.2 (q, C-25) ;ESI-MS m/z : 447 [M + Na]⁺。以上数据与文献^[14]报道一致,故鉴定为 β -香树烯酮。

化合物 7 白色粉末 (CHCl₃) ;¹H NMR (CDCl₃, 500 MHz) δ : 4.86 (1H, s, H-19), 1.10 (3H, s, Me-26), 1.07 (3H, s, Me-23), 1.03 (3H, s, Me-24), 1.02 (3H, s, Me-28), 0.96 (3H, s, Me-25), 0.94 (6H, s, Me-29, 30), 0.74 (3H, s, Me-27) ;¹³C NMR (CDCl₃, 125 MHz) δ : 218.1 (s, C-3), 142.5 (s, C-18), 129.9 (d, C-19), 54.8 (d, C-5), 50.5 (d, C-9), 47.2 (s, C-4), 43.3 (s, C-14), 40.6 (s, C-8), 39.8 (t, C-1), 38.5 (d, C-13), 37.6 (t, C-22), 37.4 (t, C-16), 36.9 (s, C-10), 34.3 (s, C-17), 34.0 (t, C-2), 33.8 (t, C-7), 33.3 (t, C-21), 32.4 (s, C-20), 31.4 (q, C-29), 29.2 (q, C-30), 27.5 (t, C-15), 26.9 (q, C-23), 26.2 (t, C-12), 25.3 (q, C-28), 21.7 (t, C-11), 20.9 (q, C-24), 19.7 (t, C-6), 16.6 (q, C-25), 15.9 (q, C-26), 14.5 (q, C-27) ;ESI-MS m/z : 447 [M + Na]⁺。以上数据与文献^[15]报道一致,故鉴定为齐墩果烷-18-烯-3-酮。

化合物 8 无色针晶 (CHCl₃) ;¹H NMR (CDCl₃, 500 MHz) δ : 1.18 (3H, s, Me-28), 1.05 (3H, s, Me-27), 1.01 (3H, s, Me-26), 1.00 (3H, s, Me-30), 0.95 (3H, s, Me-29), 0.88 (3H, d, $J = 7.0$ Hz, Me-23), 0.87 (3H, s, Me-25), 0.73 (3H, s, Me-24) ;¹³C NMR (CDCl₃, 125 MHz) δ : 213.4 (s, C-3), 59.5 (d, C-10), 58.2 (d, C-4), 53.1 (d, C-8), 42.8 (d, C-18), 42.2 (s, C-5), 41.5 (t, C-2), 41.3 (t, C-6), 39.7 (s, C-13), 39.3 (t, C-22), 38.3 (s, C-14), 37.5 (s, C-9), 36.0 (t, C-16), 35.6 (t, C-11), 35.4 (t, C-19), 35.0 (q, C-29), 32.8 (t, C-21), 32.4 (t, C-15), 32.1 (q, C-28), 31.8 (q, C-30), 30.5 (t, C-12), 30.0 (s, C-17), 28.2 (s, C-20), 22.3 (t, C-1), 20.3 (q, C-

26), 18.7 (q, C-27), 18.2 (t, C-7), 18.0 (q, C-25), 14.7 (q, C-24), 6.8 (q, C-23); ESI-MS m/z : 449 [M + Na]⁺。以上数据与文献^[16]报道一致,故鉴定为无羧萜。

化合物 9 无色油状 (CHCl₃); ¹H NMR (CDCl₃, 500 MHz) δ : 5.72 (1H, s, H-4), 1.18 (3H, s, Me-19), 0.91 (3H, d, J = 6.1 Hz, Me-21), 0.83 (9H, overlapped, Me-29, 26, 27), 0.71 (3H, s, Me-18); ¹³C NMR (CDCl₃, 125 MHz) δ : 199.7 (s, C-3), 171.7 (s, C-5), 123.8 (d, C-4), 56.0 (d, C-14), 55.9 (d, C-17), 53.8 (d, C-9), 45.8 (d, C-24), 42.4 (s, C-13), 39.6 (t, C-12), 38.6 (s, C-10), 36.1 (d, C-20), 35.7 (t, C-1), 35.6 (d, C-8), 34.0 (t, C-2), 33.9 (t, C-22), 32.9 (t, C-6), 32.1 (t, C-7), 29.7 (t, C-16), 29.2 (d, C-25), 28.2 (t, C-23), 26.1 (t, C-15), 24.2 (t, C-28), 23.1 (t, C-11), 21.0 (q, C-26), 19.8 (q, C-27), 19.0 (q, C-19), 18.7 (q, C-21), 17.4 (q, C-18), 12.0 (q, C-29); ESI-MS m/z : 435 [M + Na]⁺。以上数据与文献^[17]报道一致,故鉴定为4-豆甾烯-3-酮。

化合物 10 白色针晶 (CHCl₃); 其 TLC 与标准品对照, 鉴定为 β -谷甾醇。

化合物 11 黄色粉末 (CH₃OH); ¹H NMR (CD₃OD, 500 MHz) δ : 7.70 (2H, d, J = 8.2 Hz, H-2', 6'), 6.90 (2H, d, J = 8.2 Hz, H-3', 5'), 6.28 (1H, br s, H-8), 6.13 (1H, br s, H-6), 5.36 (1H, d, J = 7.5 Hz, H-1"), 4.25 (1H, br s, H-2"), 3.75 (1H, m, H-3"), 3.34 (1H, m, H-4"), 3.30 (1H, m, H-5"), 0.93 (3H, d, J = 6.1 Hz, H-6"); ¹³C NMR (CD₃OD, 125 MHz) δ : 179.4 (s, C-4), 166.5 (s, C-7), 162.9 (s, C-5), 161.5 (s, C-4'), 159.1 (s, C-9), 158.4 (s, C-2), 136.1 (s, C-3), 131.9 (d, C-2', 6'), 122.6 (s, C-1'), 116.5 (d, C-3', 5'), 105.7 (s, C-10), 103.4 (d, C-1"), 100.2 (d, C-6), 95.1 (d, C-8), 73.3 (d, C-3"), 72.1 (d, C-5"), 72.0 (d, C-4"), 72.0 (d, C-2"), 17.7 (q, C-6"); ESI-MS m/z : 431 [M-H]⁻。以上数据与文献^[18]报道一致,故鉴定为山奈酚-3-O- α -L-鼠李糖苷。

化合物 12 无色针晶 (CH₃OH); ¹H NMR (CD₃OD, 500 MHz) δ : 7.87 (1H, d, J = 9.4 Hz, H-4), 7.12 (1H, s, H-5), 6.79 (1H, br s, H-8), 6.22 (1H, d, J = 9.4 Hz, H-3), 3.93 (3H, s, OCH₃); ¹³C NMR (CD₃OD, 125 MHz) δ : 162.6 (s, C-2), 151.5 (s, C-

9), 150.0 (s, C-7), 145.7 (s, C-6), 144.7 (d, C-4), 111.2 (d, C-3), 110.1 (s, C-10), 108.6 (d, C-5), 102.6 (d, C-8), 55.4 (q, OCH₃); ESI-MS m/z : 191 [M-H]⁻。以上数据与文献^[19]报道一致,故鉴定为东莨菪内酯。

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