

## 巴西人参化学成分的研究

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**摘要:** 目的 研究引种的巴西人参 *Pfaffia paniculata* 根中的化学成分。方法 采用色谱分离技术进行分离和纯化, 并根据谱学数据鉴定化合物的结构。结果 从引种的巴西人参根部的甲醇提取物中分离得到 14 个化合物, 包括 11 个 30-降齐墩果烷型三萜和 3 个蜕皮激素类物质, 分别鉴定为 pfaffianol A (1)、3-oxo-akebanoic acid (2)、16 $\beta$ -hydroxyl-3-oxo-akebanoic acid (3)、pfaffiaglycoside A (4)、pfameric acid (5)、2 $\alpha$ ,3 $\beta$ ,20 $\alpha$ -trihydroxy-30-norolean-12-en-28-oic acid (6)、2 $\alpha$ ,3 $\beta$ -dihydroxy-23-oxo-30-norolean-12,20(29)-dien-28-oic acid (7)、2 $\alpha$ ,3 $\beta$ -dihydroxy-30-norolean-12,20(29)-dien-28-oic acid (8)、2 $\alpha$ ,3 $\alpha$ -dihydroxy-30-norolean-12,20(29)-dien-28-oic acid (9)、木通种酸 (10)、3 $\beta$ -hydroxy-30-norhederagenin (11)、diaulusterol B (12)、20,22-didehydrotaxisterone (13) 和蜕皮甾酮 (14)。结论 化合物 10~12 为首次从巴西人参中分离得到, 化合物 6~9 和 13 为首次从法菲亚属植物中分离得到。

**关键词:** 巴西人参; 30-降齐墩果烷型三萜; 蜕皮激素; 木通种酸; 蜕皮甾酮

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## Chemical constituents from *Pfaffia paniculata*

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**Abstract: Objective** To study the chemical constituents from the roots of *Pfaffia paniculata*. **Methods** The compounds were isolated and purified by means of chromatographic separation techniques and their structures were identified based on spectral features. **Results** Fourteen known compounds, including 11 30-noroleanane triterpenoids and three ecdysterones, named pfaffianol A (1), 3-oxo-akebanoic acid (2), 16 $\beta$ -hydroxyl-3-oxo-akebanoic acid (3), pfaffiaglycoside A (4), pfameric acid (5), 2 $\alpha$ ,3 $\beta$ ,20 $\alpha$ -trihydroxy-30-norolean-12-en-28-oic acid (6), 2 $\alpha$ ,3 $\beta$ -dihydroxy-23-oxo-30-norolean-12,20(29)-dien-28-oic acid (7), 2 $\alpha$ ,3 $\beta$ -dihydroxy-30-norolean-12,20(29)-dien-28-oic acid (8), 2 $\alpha$ ,3 $\alpha$ -dihydroxy-30-norolean-12,20(29)-dien-28-oic acid (9), quinatic acid (10), 3 $\beta$ -hydroxy-30-norhederagenin (11), diaulusterol B (12), 20,22-didehydrotaxisterone (13), and ecdysterone (14) were isolated from the roots of *P. paniculata*. **Conclusion** Compounds 10—12 are obtained from *P. paniculata* for the first time. Compounds 6—9, and 13 are isolated from the genus of *Pfaffia* for the first time.

**Key words:** *Pfaffia paniculata* (Mart) Kuntze; 30-noroleanane triterpenoids; ecdysterones; quinatic acid; ecdysterone

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巴西人参 *Pfaffia paniculata* (Mart) Kuntze 为苋科(Amaranthaceae)法菲亚属 *Pfaffia* Pedersen 植物, 原产于南美洲亚马逊河流域如巴西、厄瓜多尔、巴拿马、巴拉圭、秘鲁和委内瑞拉等热带雨林地区。2001 年以来, 我国在浙江、广西、四川等地先后引种成功巴西人参<sup>[1]</sup>。巴西人参在民间作为一种重要的植物药已有 300 多年的应用历史, 现代研究表明, 巴西人参的根有多种药理作用如壮阳、镇静、抗肿瘤, 治疗溃疡、风湿性关节炎和降血糖等<sup>[2]</sup>。近年来国内外学者对巴西人参化学成分的研究表明, 巴西人参中的主要化学成分有三萜类、降三萜类和甾体类等<sup>[3]</sup>。为进一步探索巴西人参根部的化学成分, 以及充分利用该植物资源提供物质基础指导, 本实验对引种的巴西人参根部的化学成分进行了研究, 从其甲醇提取物中分离得到 14 个化合物, 包括 11 个 30-降齐墩果烷型三萜和 3 个蜕皮激素类物质, 其结构分别鉴定为 pfaffianol A(1)、3-oxo-akebonoic acid (2)、16 $\beta$ -hydroxyl-3-oxo-akebonoic acid (3)、pfaffiaglycoside A (4)、pfameric acid (5)、2 $\alpha$ ,3 $\beta$ ,20 $\alpha$ -trihydroxy-30-norolean-12-en-28-oic acid (6)、2 $\alpha$ ,3 $\beta$ -dihydroxy-23-oxo-30-norolean-12,20(29)-dien-28-oic acid (7)、2 $\alpha$ ,3 $\beta$ -dihydroxy-30-norolean-12,20(29)-dien-28-oic acid (8)、2 $\alpha$ ,3 $\alpha$ -dihydroxy-30-norolean-12,20(29)-dien-28-oic acid (9)、木通种酸 (quinatic acid, 10)、3 $\beta$ -hydroxy-30-norhederagenin (11)、diaulusterol B (12)、20,22-didehydrotaxisterone (13) 和蜕皮甾酮 (ecdysterone, 14)。其中, 化合物 10~12 为首次从巴西人参中分离得到, 化合物 6~9 和 13 为首次从法菲亚属植物中分离得到。

## 1 仪器与材料

XRC-1 型显微熔点仪 (四川大学科仪厂); Bruker DRX-500 型核磁共振仪 (Bruker 公司); 柱色谱用硅胶 (100~200、200~300 目) 和薄层色谱用硅胶 GF<sub>254</sub> 均由青岛海洋化工厂生产; 反相色谱用材料 RP<sub>18</sub> 为 Merck 公司产品; Sephadex LH-20 由 Fluka 公司生产; 其余试剂均为分析纯。

本实验所用引种的巴西人参采自浙江省宁波市象山县, 由中国中医科学院中药研究所杨建博士鉴定为苋科法菲亚属植物巴西人参 *Pfaffia paniculata* (Mart) Kuntze, 植物标本 (ZA20180203) 保存于浙江农林大学天然产物研究室。

## 2 提取与分离

干燥的巴西人参块根 (5 kg), 粉碎, 用甲醇室

温浸提, 合并提取液, 减压浓缩得到甲醇总浸膏。将甲醇提取物分散在蒸馏水中悬浮, 分别用石油醚、醋酸乙酯和正丁醇等不同极性的溶剂进行萃取, 浓缩后分别得到石油醚浸膏 (64 g), 醋酸乙酯浸膏 (65 g) 和正丁醇浸膏 (78 g)。醋酸乙酯提取物用粗硅胶 (100~200 目) 拌样后, 经过硅胶 (200~300 目) 柱色谱, 氯仿-甲醇梯度洗脱 (100:0→0:100), 薄层色谱 (TLC) 检测合并为 7 个组分 (Fr. 1~Fr. 7)。Fr. 3 进行硅胶柱色谱分离, 用氯仿-甲醇 (19:1→8:2) 梯度洗脱, 再用制备 TLC (展开剂为氯仿-甲醇 9:1) 分离得到化合物 1 (9.0 mg)、2 (7.2 mg) 和 3 (8.6 mg)。Fr. 4 反复进行硅胶柱色谱分离, 用氯仿-甲醇 (9:1→1:1) 梯度洗脱, 再用 Sephadex LH-20 (甲醇) 分离得到化合物 8 (7.8 mg)、9 (9.0 mg)、10 (6.5 mg) 和 4 (12.9 mg)。Fr. 5 进行 RP<sub>18</sub> 分离, 用甲醇-水 (30:70→90:10) 梯度洗脱, 再用 Sephadex LH-20 (甲醇) 分离得到化合物 5 (8.6 mg)、6 (9.5 mg)、7 (11.7 mg) 和 12 (13.1 mg)。Fr. 6 进行 RP<sub>18</sub> 分离, 用甲醇-水 (20:80→90:10) 梯度洗脱, 再用 Sephadex LH-20 (甲醇) 和 MCI 柱色谱分离得到化合物 11 (8.9 mg)、13 (10.7 mg) 和 14 (11.1 mg)。

## 3 结构鉴定

化合物 1: 白色粉末。<sup>1</sup>H-NMR (500 MHz, pyridine-*d*<sub>5</sub>)  $\delta$ : 5.53 (1H, m, H-12), 4.82 (1H, s, H-29), 4.78 (1H, s, H-29), 4.66 (1H, dd, *J* = 11.5, 4.5 Hz, H-16), 3.45 (1H, dd, *J* = 11.5, 4.0 Hz, H-3), 1.37 (3H, s, H-27), 1.24 (3H, s, H-23), 1.02 (3H, s, H-26), 1.00 (3H, s, H-24), 0.88 (3H, s, H-25); <sup>13</sup>C-NMR (125 MHz, pyridine-*d*<sub>5</sub>)  $\delta$ : 180.1 (C-28), 148.4 (C-20), 144.7 (C-13), 123.6 (C-12), 107.6 (C-29), 78.1 (C-3), 65.0 (C-16), 55.8 (C-5), 50.6 (C-17), 49.7 (C-18), 47.2 (C-9), 44.4 (C-14), 41.6 (C-19), 39.9 (C-8), 39.2 (C-4), 38.8 (C-15), 38.2 (C-1), 37.1 (C-10), 33.2 (C-7), 32.8 (C-22), 29.9 (C-21), 28.7 (C-23), 28.0 (C-2), 26.8 (C-27), 23.8 (C-11), 18.7 (C-6), 17.3 (C-26), 16.6 (C-24), 15.5 (C-25)。以上数据与文献报道一致<sup>[4]</sup>, 故鉴定化合物 1 为 pfaffianol A。

化合物 2: 白色粉末。<sup>1</sup>H-NMR (500 MHz, pyridine-*d*<sub>5</sub>)  $\delta$ : 5.43 (1H, brs, H-12), 4.76 (1H, s, H-29), 4.70 (1H, s, H-29), 1.28 (3H, s, H-23), 1.24 (3H, s, H-27), 1.04 (3H, s, H-26), 0.96 (3H, s, H-24), 0.84 (3H, s, H-25); <sup>13</sup>C-NMR (125 MHz, pyridine-*d*<sub>5</sub>)

$\delta$ : 215.8 (C-3), 180.1 (C-28), 148.5 (C-20), 144.2 (C-13), 123.1 (C-12), 107.2 (C-29), 55.2 (C-5), 47.8 (C-17), 47.5 (C-18), 47.3 (C-9), 47.1 (C-4), 42.2 (C-14), 42.0 (C-19), 39.6 (C-8), 39.1 (C-1), 38.3 (C-22), 36.9 (C-10), 34.2 (C-2), 32.3 (C-7), 30.2 (C-21), 28.3 (C-15), 28.2 (C-23), 26.2 (C-27), 23.7 (C-16), 23.6 (C-11), 19.8 (C-6), 17.4 (C-26), 16.5 (C-24), 15.5 (C-25)。以上数据和文献报道一致<sup>[5]</sup>, 故鉴定化合物 2 为 3-oxo-akebonoic acid。

化合物 3: 白色粉末。<sup>1</sup>H-NMR (500 MHz, pyridine-*d*<sub>5</sub>)  $\delta$ : 5.53 (1H, brs, H-12), 4.82 (1H, s, H-29), 4.78 (1H, s, H-29), 4.65 (1H, dd, *J* = 11.5, 4.5 Hz, H-16), 1.36 (3H, s, H-27), 1.24 (3H, s, H-23), 1.02 (3H, s, H-26), 1.01 (3H, s, H-24), 0.86 (3H, s, H-25); <sup>13</sup>C-NMR (125 MHz, pyridine-*d*<sub>5</sub>)  $\delta$ : 215.8 (C-3), 180.0 (C-28), 148.4 (C-20), 144.5 (C-13), 123.4 (C-12), 107.5 (C-29), 65.0 (C-16), 55.2 (C-5), 50.8 (C-17), 49.7 (C-18), 47.3 (C-9), 47.1 (C-4), 44.4 (C-14), 41.6 (C-19), 39.6 (C-8), 39.0 (C-1), 38.9 (C-15), 36.9 (C-10), 34.3 (C-2), 32.9 (C-22), 32.3 (C-7), 30.0 (C-21), 28.6 (C-23), 26.8 (C-27), 23.8 (C-11), 19.8 (C-6), 17.3 (C-26), 16.5 (C-24), 15.6 (C-25)。以上数据与文献报道一致<sup>[5]</sup>, 故鉴定化合物 3 为 16 $\beta$ -hydroxyl-3-oxo-akebonoic acid。

化合物 4: 淡黄色粉末。<sup>1</sup>H-NMR (500 MHz, pyridine-*d*<sub>5</sub>)  $\delta$ : 6.10 (1H, *J* = 8.0 Hz, H-1'), 5.43 (1H, brs, H-12), 4.76 (1H, s, H-29), 4.71 (1H, s, H-29), 4.60 (1H, dd, *J* = 11.5, 4.5 Hz, H-16), 3.40 (1H, dd, *J* = 11.5, 4.0 Hz, H-3), 1.28 (3H, s, H-27), 1.19 (3H, s, H-23), 1.00 (3H, s, H-26), 0.98 (3H, s, H-24), 0.91 (3H, s, H-25); <sup>13</sup>C-NMR (125 MHz, pyridine-*d*<sub>5</sub>)  $\delta$ : 174.8 (C-28), 148.3 (C-20), 142.3 (C-13), 123.0 (C-12), 107.5 (C-29), 96.1 (C-1'), 79.2 (C-5'), 78.4 (C-3'), 78.0 (C-3), 73.9 (C-2'), 71.4 (C-4'), 65.1 (C-16), 62.4 (C-6'), 55.8 (C-5), 51.6 (C-17), 49.7 (C-18), 47.1 (C-9), 44.5 (C-14), 41.7 (C-19), 39.8 (C-8), 39.4 (C-15), 39.1 (C-4), 38.2 (C-1), 37.2 (C-10), 33.1 (C-7), 31.9 (C-22), 29.9 (C-21), 28.7 (C-23), 28.0 (C-2), 26.9 (C-27), 23.8 (C-11), 18.7 (C-6), 17.4 (C-26), 16.5 (C-24), 15.6 (C-25)。以上数据和文献报道一致<sup>[4]</sup>, 故鉴定化合物 4 为 pfaffiaglycoside A。

化合物 5: 白色粉末。<sup>1</sup>H-NMR (500 MHz,

pyridine-*d*<sub>5</sub>)  $\delta$ : 5.54 (1H, m, H-12), 4.61 (1H, dd, *J* = 11.5, 4.5 Hz, H-16), 3.42 (1H, dd, *J* = 11.5, 4.5 Hz, H-3), 1.44 (3H, s, H-29), 1.36 (3H, s, H-27), 1.23 (3H, s, H-23), 1.04 (3H, s, H-26), 1.00 (3H, s, H-24), 0.87 (3H, s, H-25); <sup>13</sup>C-NMR (125 MHz, pyridine-*d*<sub>5</sub>)  $\delta$ : 181.2 (C-28), 143.9 (C-13), 122.8 (C-12), 78.2 (C-3), 68.3 (C-20), 64.9 (C-16), 55.8 (C-5), 50.5 (C-17), 47.6 (C-9), 46.3 (C-19), 44.6 (C-14), 43.5 (C-18), 39.9 (C-8), 39.5 (C-4), 39.1 (C-1), 38.7 (C-15), 37.3 (C-10), 34.2 (C-21), 33.5 (C-7), 32.4 (C-29), 28.8 (C-23), 28.2 (C-2), 27.3 (C-22), 27.2 (C-27), 24.0 (C-11), 18.8 (C-6), 17.7 (C-26), 16.8 (C-24), 15.6 (C-25)。以上数据和文献报道一致<sup>[6]</sup>, 故鉴定化合物 5 为 pfameric acid。

化合物 6: 白色粉末。<sup>1</sup>H-NMR (500 MHz, pyridine-*d*<sub>5</sub>)  $\delta$ : 5.28 (1H, t, *J* = 3.0 Hz, H-12), 3.76 (1H, td, *J* = 12.0, 9.5, 4.0 Hz, H-2), 3.08 (1H, d, *J* = 9.5 Hz, H-3), 1.33 (3H, s, H-29), 1.06 (3H, s, H-27), 1.03 (3H, s, H-23), 0.82 (3H, s, H-26), 0.80 (3H, s, H-24), 0.76 (3H, s, H-25); <sup>13</sup>C-NMR (125 MHz, pyridine-*d*<sub>5</sub>)  $\delta$ : 179.9 (C-28), 144.2 (C-13), 122.6 (C-12), 83.6 (C-3), 69.9 (C-20), 68.5 (C-2), 55.8 (C-5), 47.9 (C-9), 47.7 (C-1), 47.6 (C-19), 46.7 (C-17), 44.2 (C-18), 42.2 (C-14), 39.8 (C-4, 8), 38.4 (C-10), 36.2 (C-21), 35.0 (C-22), 33.2 (C-7), 29.2 (C-23), 28.3 (C-15), 25.8 (C-27), 25.5 (C-29), 23.9 (C-11), 23.7 (C-16), 18.7 (C-6), 17.6 (C-24), 17.4 (C-26), 16.6 (C-25)。以上数据和文献报道一致<sup>[7]</sup>, 故鉴定化合物 6 为 2 $\alpha$ ,3 $\beta$ ,20 $\alpha$ -trihydroxy-30-norolean-12-en-28-oic acid。

化合物 7: 白色粉末。<sup>1</sup>H-NMR (500 MHz, pyridine-*d*<sub>5</sub>)  $\delta$ : 9.66 (1H, s, 23-CHO), 5.46 (1H, t, *J* = 3.0 Hz, H-12), 4.80 (1H, s, H-29), 4.76 (1H, s, H-29), 4.23 (1H, td, *J* = 12.0, 9.5, 4.0 Hz, H-2), 4.06 (1H, d, *J* = 9.5 Hz, H-3), 1.43 (3H, s, H-24), 1.22 (3H, s, H-27), 1.00 (3H, s, H-25), 0.96 (3H, s, H-26); <sup>13</sup>C-NMR (125 MHz, pyridine-*d*<sub>5</sub>)  $\delta$ : 206.2 (C-23), 179.5 (C-28), 148.8 (C-20), 144.1 (C-13), 122.5 (C-12), 107.1 (C-29), 77.3 (C-3), 67.9 (C-2), 56.4 (C-4), 57.9 (C-5), 47.8 (C-1, 9), 47.3 (C-18), 46.8 (C-17), 42.0 (C-14), 41.9 (C-19), 39.8 (C-8), 38.3 (C-22), 38.2 (C-10), 32.4 (C-7), 30.3 (C-21), 28.2 (C-15), 26.0 (C-27), 23.8 (C-16), 23.7 (C-11), 20.4

(C-6), 17.3 (C-26), 16.9 (C-25), 10.7 (C-24)。以上数据和文献报道一致<sup>[7]</sup>, 故鉴定化合物 7 为 2 $\alpha$ ,3 $\beta$ -dihydroxy-23-oxo-30-norolean-12,20(29)-dien-28-oic acid。

化合物 8: 白色粉末。 $^1\text{H-NMR}$  (500 MHz, pyridine- $d_5$ )  $\delta$ : 5.48 (1H, t,  $J$  = 3.5 Hz, H-12), 4.81 (1H, s, H-29), 4.76 (1H, s, H-29), 4.11 (1H, td,  $J$  = 12.0, 9.5, 4.0 Hz, H-2), 3.42 (1H, d,  $J$  = 9.5 Hz, H-3), 1.29 (3H, s, H-23), 1.24 (3H, s, H-27), 1.09 (3H, s H-24), 1.00 (3H, s, H-26), 0.98 (3H, s, H-25);  $^{13}\text{C-NMR}$  (125 MHz, pyridine- $d_5$ )  $\delta$ : 179.5 (C-28), 149.0 (C-20), 144.3 (C-13), 122.9 (C-12), 107.1 (C-29), 83.8 (C-3), 68.5 (C-2), 55.9 (C-5), 48.2 (C-9), 47.9 (C-18), 47.8 (C-1), 47.0 (C-17), 42.2 (C-14), 41.9 (C-19), 39.8 (C-4, 8), 38.6 (C-10), 38.4 (C-22), 33.3 (C-7), 30.4 (C-21), 29.4 (C-23), 28.3 (C-15), 26.2 (C-27), 23.9 (C-11), 23.8 (C-16), 18.8 (C-6), 17.6 (C-24), 17.3 (C-26), 16.8 (C-25)。以上数据和文献报道一致<sup>[8]</sup>, 故鉴定化合物 8 为 2 $\alpha$ ,3 $\beta$ -dihydroxy-30-norolean-12,20(29)-dien-28-oic acid。

化合物 9: 白色粉末。 $^1\text{H-NMR}$  (500 MHz, pyridine- $d_5$ )  $\delta$ : 5.48 (1H, t,  $J$  = 3.5 Hz, H-12), 4.78 (1H, s, H-29), 4.74 (1H, s, H-29), 4.31 (1H, td,  $J$  = 12.0, 4.0, 3.0 Hz, H-2), 3.76 (1H, d,  $J$  = 3.0 Hz, H-3), 1.28 (3H, s, H-23), 1.15 (3H, s, H-27), 1.00 (3H, s H-26), 0.96 (3H, s, H-25), 0.91 (3H, s, H-24);  $^{13}\text{C-NMR}$  (125 MHz, pyridine- $d_5$ )  $\delta$ : 179.5 (C-28), 149.0 (C-20), 144.3 (C-13), 123.0 (C-12), 107.1 (C-29), 79.3 (C-3), 66.1 (C-2), 48.8 (C-5), 47.9 (C-9, 18), 47.0 (C-17), 42.9 (C-1), 42.1 (C-14), 41.9 (C-19), 40.0 (C-8), 38.9 (C-4), 38.8 (C-10), 38.4 (C-22), 33.3 (C-7), 30.4 (C-21), 29.5 (C-23), 28.2 (C-15), 26.2 (C-27), 23.8 (C-11, 16), 22.2 (C-24), 18.5 (C-6), 17.3 (C-26), 16.7 (C-25)。以上数据和文献报道一致<sup>[8]</sup>, 故鉴定化合物 9 为 2 $\alpha$ ,3 $\alpha$ -dihydroxy-30-norolean-12,20(29)-dien-28-oic acid。

化合物 10: 白色粉末。 $^1\text{H-NMR}$  (500 MHz, pyridine- $d_5$ )  $\delta$ : 5.52 (1H, t,  $J$  = 3.5 Hz, H-12), 4.79 (1H, s, H-29), 4.75 (1H, s, H-29), 4.09 (1H, d,  $J$  = 11.0 Hz, H-24), 3.85 (1H, d,  $J$  = 11.0 Hz, H-24), 3.24 (1H, dd,  $J$  = 13.5, 4.5 Hz, H-3), 1.64 (3H, s, H-27), 1.17 (3H, s, H-23), 1.03 (3H, s, H-26), 0.98 (3H, s, H-25);  $^{13}\text{C-NMR}$  (125 MHz, pyridine- $d_5$ )  $\delta$ : 179.5 (C-28),

149.1 (C-20), 144.2 (C-13), 123.0 (C-12), 107.0 (C-29), 70.1 (C-3), 66.0 (C-24), 50.3 (C-5), 48.2 (C-9), 48.1 (C-18), 47.2 (C-17), 44.0 (C-4), 42.3 (C-14), 42.1 (C-19), 40.2 (C-8), 38.4 (C-21), 37.5 (C-10), 34.1 (C-7), 33.9 (C-1), 30.5 (C-22), 28.4 (C-15), 26.6 (C-2), 26.2 (C-27), 24.1 (C-16), 23.9 (C-11), 23.4 (C-23), 19.3 (C-6), 17.4 (C-26), 16.0 (C-25)。以上数据和文献报道一致<sup>[9]</sup>, 故鉴定化合物 10 为木通种酸。

化合物 11: 白色粉末。 $^1\text{H-NMR}$  (500 MHz, pyridine- $d_5$ )  $\delta$ : 5.51 (1H, t,  $J$  = 3.5 Hz, H-12), 4.80 (1H, s, H-29), 4.75 (1H, s, H-29), 4.20 (1H, d,  $J$  = 11.0 Hz, H-23), 3.74 (1H, d,  $J$  = 11.0 Hz, H-23), 3.24 (1H, dd,  $J$  = 11.5, 4.0 Hz, H-3), 1.21 (3H, s, H-27), 1.06 (3H, s, H-24), 1.03 (3H, s, H-26), 0.97 (3H, s, H-25);  $^{13}\text{C-NMR}$  (125 MHz, pyridine- $d_5$ )  $\delta$ : 179.4 (C-28), 148.6 (C-20), 144.9 (C-13), 122.5 (C-12), 107.0 (C-29), 73.5 (C-3), 68.1 (C-23), 48.7 (C-5), 48.1 (C-9), 48.0 (C-18), 47.1 (C-17), 42.9 (C-4), 42.1 (C-14), 42.0 (C-19), 39.8 (C-8), 38.8 (C-1), 38.4 (C-21), 37.3 (C-10), 33.0 (C-7), 30.4 (C-22), 28.3 (C-15), 27.7 (C-2), 26.2 (C-27), 23.8 (C-16), 23.7 (C-11), 18.7 (C-6), 17.6 (C-26), 16.0 (C-25), 13.1 (C-24)。以上数据和文献报道一致<sup>[10]</sup>, 故鉴定化合物 11 为 3 $\beta$ -hydroxy-30-norhederagenin。

化合物 12: 无色针状结晶(丙酮)。 $^1\text{H-NMR}$  (500 MHz, DMSO- $d_6$ )  $\delta$ : 6.25 (1H, d,  $J$  = 5.5 Hz, H-4), 5.66 (1H, d,  $J$  = 2.0 Hz, H-7), 3.98 (1H, m, H-3), 3.64 (1H, m, H-2), 1.05 (6H, s, H-26, 27), 1.02 (3H, s, H-19), 0.94 (3H, d,  $J$  = 6.5 Hz, H-21), 0.58 (3H, s, H-18);  $^{13}\text{C-NMR}$  (125 MHz, DMSO- $d_6$ )  $\delta$ : 187.9 (C-6), 166.8 (C-8), 143.8 (C-5), 130.3 (C-4), 122.6 (C-7), 68.9 (C-25), 65.9 (C-2), 64.5 (C-3), 55.4 (C-17), 55.0 (C-14), 46.8 (C-9), 44.1 (C-24), 43.8 (C-13), 39.8 (C-10), 38.1 (C-1), 37.9 (C-12), 36.0 (C-22), 35.5 (C-20), 29.4 (C-26, 27), 27.3 (C-16), 22.2 (C-15), 21.5 (C-11), 20.7 (C-19), 20.2 (C-23), 18.6 (C-21), 12.2 (C-18)。以上数据与文献报道基本一致<sup>[11]</sup>, 故鉴定化合物 12 为 diaulusterol B。

化合物 13: 无色针状结晶(甲醇)。 $^1\text{H-NMR}$  (500 MHz, CD<sub>3</sub>OD)  $\delta$ : 5.82 (1H, d,  $J$  = 2.0 Hz, H-7), 5.30 (1H, t,  $J$  = 7.0 Hz, H-22), 3.97 (1H, m, H-3), 3.85 (1H, m, H-2), 1.68 (3H, s, H-21), 1.21 (6H, s, H-26, 27),

0.96 (3H, s, H-19), 0.58 (3H, s, H-18);  $^{13}\text{C}$ -NMR (125 MHz, CD<sub>3</sub>OD)  $\delta$ : 206.8 (C-6), 167.9 (C-8), 134.8 (C-20), 127.6 (C-22), 121.9 (C-7), 85.0 (C-14), 71.6 (C-25), 68.9 (C-2), 68.7 (C-3), 54.3 (C-17), 52.0 (C-5), 48.8 (C-13), 45.0 (C-24), 39.5 (C-10), 37.6 (C-1), 35.5 (C-9), 33.0 (C-4), 32.2 (C-15), 31.1 (C-12), 29.3 (C-26, 27), 24.6 (C-19), 24.4 (C-23), 24.1 (C-16), 21.8 (C-11), 18.4 (C-21), 17.8 (C-18)。以上数据与文献报道基本一致<sup>[12]</sup>, 故鉴定化合物 **13** 为 20,22-didehydrotaxisterone。

化合物 **14**: 无色针状结晶(甲醇)。 $^1\text{H}$ -NMR (500 MHz, pyridine-*d*<sub>5</sub>)  $\delta$ : 6.22 (1H, d, *J* = 2.0 Hz, H-7), 4.18 (1H, m, H-3), 3.86 (1H, dd, *J* = 8.5, 1.5 Hz, H-22), 3.22 (1H, m, H-2), 1.58 (3H, s, H-21), 1.36 (6H, s, H-26, 27), 1.21 (3H, s, H-18), 1.06 (3H, s, H-18);  $^{13}\text{C}$ -NMR (125 MHz, pyridine-*d*<sub>5</sub>)  $\delta$ : 203.4 (C-6), 166.2 (C-8), 121.8 (C-7), 84.5 (C-14), 77.8 (C-22), 77.0 (C-20), 69.9 (C-25), 68.2 (C-3), 68.1 (C-2), 51.4 (C-5), 50.1 (C-17), 48.3 (C-13), 42.6 (C-24), 38.9 (C-10), 38.0 (C-1), 34.6 (C-9), 32.6 (C-4), 32.1 (C-12), 31.8 (C-15), 30.0 (C-26, 27), 27.6 (C-23), 24.5 (C-19), 21.8 (C-21), 21.6 (C-16), 21.2 (C-11), 17.9 (C-18)。以上数据与文献报道基本一致<sup>[13]</sup>, 故鉴定化合物 **14** 为 脱皮甾酮。

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