

# 美洲凌霄花的三萜类成分研究

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**摘要:** 利用硅胶、ODS、Sephadex LH-20、Amberchrom CG<sup>161M</sup>等柱色谱对美洲凌霄花 70% 乙醇提取物进行了系统的化学成分研究。从美洲凌霄花中分离得到了 14 个化合物, 通过波谱手段, 分别鉴定为熊果醇(1)、3  $\beta$ -hydroxy-18, 19  $\alpha$ -urs-20-en-28-oic acid (2)、熊果酸(3)、齐墩果酸(4)、19  $\alpha$ -羟基熊果酸(5)、常春藤皂苷元(6)、山楂酸(7)、科罗索酸(8)、委陵菜酸(9)、蔷薇酸(10)、铁冬青酸(11)、阿江榄仁树葡萄糖苷 II (12)、rengyolone (13)、(3 $\alpha$ R)-hexahydro-3 $\alpha$ -hydroxybenzo-furan-6 (2H)-one (14)。化合物 1, 2, 5, 10 ~ 12, 14 为首次从美洲凌霄花中分离得到, 化合物 1, 2, 5, 10 ~ 12, 14 为本属植物中首次分离得到。

**关键词:** 美洲凌霄花; 三萜类成分; 结构鉴定

中图分类号: R284. 2

文献标识码: A

DOI: 10. 16333/j. 1001-6880. 2017. S. 007

## Triperpenoids of *Campsis radicans*

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**Abstract:** The components of *Campsis radicans* (L.) Seem. were separated by means of repeated chromatography on silica gel, ODS, Amberchrom CG<sup>161M</sup> and Sephadex LH-20. Their structures were identified on the basis of spectroscopic analysis and chemical evidence. Fourteen compounds were isolated and identified as ursol (1), 3  $\beta$ -hydroxy-18, 19  $\alpha$ -urs-20-en-28-oic acid (2), ursolic acid (3), oleanolic acid (4), 19  $\alpha$ -hydroxy-ursolic acid (5), hederagenin (6), maslinic acid (7), corosolic acid (8), tormentic acid (9), euscaphic acid (10), rotundic acid (11), arjunglucoside II (12), rengyolone (13), (3 $\alpha$ R)-hexahydro-3 $\alpha$ -hydroxybenzo-furan-6 (2H)-one (14). Compounds 1, 2 and 5 ~ 14 were isolated from this plant for the first time. Compounds 1, 2, 5, 10 ~ 12 and 14 were isolated from the *Campsis* for the first time.

**Key words:** *Campsis radicans* (L.) Seem.; triperpenoids; structural identification

美洲凌霄花为紫葳科凌霄属植物美洲凌霄 *Campsis radicans* (L.) Seem. 的干燥花, 江苏、上海、湖南等地有栽培; 性味甘、酸、寒, 归肝、心包经, 有凉血、化淤、祛风之功效, 主治血滞经闭、痛经、崩中漏下、血热风痒等<sup>[1]</sup>。凌霄属是紫葳科植物, 中国有该属两种植物, 分别为凌霄 [*Campsis grandiflora* (Thunb.) K. Schum.] 和美洲凌霄 [*Campsis radicans* (L.) Seem.]<sup>[1]</sup>。2015 版药典收录的中药凌霄花即为紫葳科植物凌霄或美洲凌霄的干燥花<sup>[2]</sup>。对凌霄花的化学成分及其药理活性研究较多<sup>[3]</sup>, 但对于美洲凌霄花的化学成分研究较少。本课题组曾对美洲凌霄花进行了化学研究, 分离得到鼠李柠檬素等

黄酮<sup>[4]</sup>, 在此基础上, 本课题组对其进一步化学成分研究, 从中分离得到 14 个化合物, 主要为三萜类成分, 分别鉴定为熊果醇(1)、3  $\beta$ -hydroxy-18, 19  $\alpha$ -urs-20-en-28-oic acid (2)、熊果酸(3)、齐墩果酸(4)、19  $\alpha$ -羟基熊果酸(5)、常春藤皂苷元(6)、山楂酸(7)、科罗索酸(8)、委陵菜酸(9)、蔷薇酸(10)、铁冬青酸(11)、阿江榄仁树葡萄糖苷 II (12)、rengyolone (13)、(3 $\alpha$ R)-hexahydro-3  $\alpha$ -hydroxybenzo-furan-6 (2H)-one (14); 其中, 化合物 1, 2, 5 ~ 14 为首次从美洲凌霄花中分离得到, 化合物 1, 2, 5, 10 ~ 12, 14 为本属植物中首次分离得到。

## 1 材料、试剂与仪器

Bruker DRX-300、DRX-400、DRX-500 型核磁共振仪(内标为 TMS); 柱层析硅胶(300 ~ 400 目)和硅胶 GF<sub>254</sub> 薄层预制板(青岛海洋化工厂); Sephadex

LH-20 ( GE Healthcare ); ODS 反相柱层析材料 (  $C_{18}$ , 50 ~ 70  $\mu\text{m}$ , Daisogel ); Amberchrom CG<sup>161M</sup> ( Rohmhaas ); 所用试剂均为分析纯; 药材购自江苏省连云港, 经苏州大学药学院陆叶老师鉴定为美洲凌霄 *Campsis radicans* ( L. ) Seem. 的干燥花。

## 2 提取分离

美洲凌霄花 20 kg, 用 70% 的乙醇回流提取两次, 合并提取液并浓缩, 浓缩液依次用氯仿、正丁醇萃取, 得氯仿部位 (170 g)、正丁醇部位 (250 g)。氯仿部位 (170 g), 经硅胶柱层析, 以石油醚-乙酸乙酯系统 (100:1 ~ 1:1) 梯度洗脱分为五个部分 (Fr. 1-Fr. 5)。Fr. 2 经硅胶柱层析, 以石油醚-乙酸乙酯梯度 (30:1 ~ 5:1) 洗脱, 得到三个部分  $A_1$ - $A_3$ 。其中  $A_3$  经硅胶柱层析, 以石油醚-乙酸乙酯 (10:1) 洗脱后, 再经 ODS 柱层析, 以甲醇-水 (80:20) 洗脱, 经反复重结晶得到化合物 **1** (100 mg)、**2** (7 mg)。Fr. 3 经硅胶柱层析, 以石油醚-乙酸乙酯 (8:1) 洗脱, 得到 4 个部分  $A_4$ - $A_7$ ,  $A_4$  部分经硅胶柱层析, 以石油醚-乙酸乙酯 (5:1) 洗脱, 合并流份经 ODS 柱层析, 以甲醇-水 (75:25) 洗脱, 得到化合物 **3** (800 mg)、**4** (180 mg);  $A_5$  部分先经 Amberchrom CG<sup>161M</sup>, 甲醇-水 (75:25) 洗脱, 再经硅胶柱层析, 石油醚-乙酸乙酯 (3:1) 洗脱, 经重结晶得到化合物 **5** (57 mg)、**6** (170 mg);  $A_6$  部分先经 Amberchrom CG<sup>161M</sup>, 甲醇-水 (75:25) 洗脱, 再经 ODS 柱层析, 甲醇-水 (80:20) 洗脱, 得到化合物 **7** (13 mg)、**8** (10 mg)。Fr. 5 先经 ODS 柱层析甲醇-水 (50:50 ~ 70:30) 梯度洗脱, 再经硅胶柱层析, 氯仿-甲醇 (20:1) 洗脱, 得到油状物, 将其通过凝胶 Sephadex LH-20, 甲醇洗脱, 得到无色油状物, 为化合物 **13**, **14**, 共重 (1.8 g)。正丁醇部分 (250 g) 经硅胶减压柱层析, 氯仿-甲醇-水 (50:1:0 ~ 0:80:20) 梯度洗脱分为 7 个部分 (Fr. 6-Fr. 12), Fr. 7 先经硅胶柱层析, 氯仿-甲醇 (30:1 ~ 10:1) 梯度洗脱, 得到  $E_1$ - $E_3$  部分,  $E_2$ 、 $E_3$  再分别经 ODS 柱层析, 甲醇-水 (70:30) 洗脱, 从  $E_2$  中分离得到化合物 **9** (22 mg)、**11** (19 mg),  $E_3$  中分离得到化合物 **10** (13 mg)。Fr. 9 先通过 Amberchrom CG<sup>161M</sup>, 甲醇-水 (50:50) 洗脱, 再经 ODS 柱层析, 甲醇-水 (40:60 ~ 70:30) 梯度洗脱, 得到一化合物及黄色粉末状固体, 将此化合物反复重结晶得到化合物 **12** (17 mg)。

## 3 结构鉴定

化合物 **1** 白色针晶 (氯仿); mp. 229.5 ~ 231.8  $^{\circ}\text{C}$ 。<sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.10 (3H, s,  $\text{CH}_3$ ), 0.99 (3H, d,  $J = 5.1$  Hz,  $\text{CH}_3$ ), 0.98 (3H, d,  $J = 5.1$  Hz,  $\text{CH}_3$ ), 0.93 (3H, s,  $\text{CH}_3$ ), 0.81 (3H, s,  $\text{CH}_3$ ), 0.79 (3H, s,  $\text{CH}_3$ ), 0.77 (3H, s,  $\text{CH}_3$ ), 3.53 (1H, d,  $J = 11.0$  Hz, H-28), 3.19 (1H, d,  $J = 11.0$  Hz, H-28), 3.22 (1H, m, H-3), 5.13 (1H, t,  $J = 3.6$  Hz, H-12); <sup>13</sup>C NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 38.8 (C-1), 27.2 (C-2), 79.0 (C-3), 38.0 (C-4), 55.1 (C-5), 18.3 (C-6), 32.8 (C-7), 39.3 (C-8), 47.6 (C-9), 46.5 (C-10), 23.3 (C-11), 125.0 (C-12), 138.7 (C-13), 42.0 (C-14), 26.0 (C-15), 29.7 (C-16), 36.9 (C-17), 54.0 (C-18), 39.4 (C-19), 40.0 (C-20), 35.2 (C-21), 30.6 (C-22), 28.1 (C-23), 15.6 (C-24), 15.7 (C-25), 16.8 (C-26), 23.4 (C-27), 69.6 (C-28), 17.3 (C-29), 21.3 (C-30)。经与文献<sup>[5]</sup>核对, 确定为熊果醇 (uvqol)。

化合物 **2** 白色针晶 (氯仿); mp. 250.3 ~ 252.1  $^{\circ}\text{C}$ 。<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.62 (3H, s,  $\text{CH}_3$ ), 1.01 (3H, d,  $J = 6.5$  Hz,  $\text{CH}_3$ ), 0.97 (6H, s,  $2 \times \text{CH}_3$ ), 0.94 (3H, s,  $\text{CH}_3$ ), 0.84 (3H, s,  $\text{CH}_3$ ), 0.76 (3H, s,  $\text{CH}_3$ ), 3.21 (1H, dd,  $J = 5.0, 11.5$  Hz, H-3), 2.33 (1H, m, H-13), 2.50 (1H, dd,  $J = 7.0, 15.5$  Hz,  $\text{H}_\beta$ -22), 2.09 (1H, t,  $J = 6.5$  Hz, H-19), 5.26 (1H, d,  $J = 7.0$  Hz, H-21); <sup>13</sup>C NMR (125 MHz, pyridine- $d_5$ )  $\delta$ : 39.9 (C-1), 28.4 (C-2), 78.6 (C-3), 39.8 (C-4), 56.4 (C-5), 19.3 (C-6), 35.2 (C-7), 41.8 (C-8), 51.6 (C-9), 38.0 (C-10), 22.5 (C-11), 34.1 (C-12), 40.0 (C-13), 42.8 (C-14), 28.8 (C-15), 30.1 (C-16), 16.9 (C-17), 49.9 (C-18), 38.4 (C-19), 143.6 (C-20), 118.4 (C-21), 38.9 (C-22), 28.1 (C-23), 29.1 (C-24), 17.1 (C-25), 16.8 (C-26), 15.5 (C-27), 178.6 (C-28), 24.2 (C-29), 22.7 (C-30)。经与文献<sup>[6]</sup>核对, 确定为 3 $\beta$ -hydroxy-18,19 $\alpha$ -urs-20-en-28-oic acid。

化合物 **3** 白色粉末; <sup>1</sup>H NMR (300 MHz,  $\text{DM-SO}-d_6$ )  $\delta$ : 1.04 (3H, s,  $\text{CH}_3$ ), 0.90 (3H, d,  $J = 6.0$  Hz,  $\text{CH}_3$ ), 0.89 (3H, s,  $\text{CH}_3$ ), 0.86 (3H, s,  $\text{CH}_3$ ), 0.81 (3H, d,  $J = 6.3$  Hz,  $\text{CH}_3$ ), 0.74 (3H, s,  $\text{CH}_3$ ), 0.67 (3H, s,  $\text{CH}_3$ ), 2.99 (1H, m, H-3), 5.12

(1H, s, H-12), 11.95 (1H, s, -COOH); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ: 38.45 (C-1), 27.0 (C-2), 76.8 (C-3), 38.40 (C-4), 54.8 (C-5), 18.0 (C-6), 32.7 (C-7), 41.3 (C-8), 46.8 (C-9), 36.3 (C-10), 22.8 (C-11), 124.5 (C-12), 138.2 (C-13), 41.6 (C-14), 28.2 (C-15), 23.8 (C-16), 47.0 (C-17), 52.3 (C-18), 38.5 (C-19), 38.2 (C-20), 30.2 (C-21), 36.5 (C-22), 27.5 (C-23), 15.2 (C-24), 16.1 (C-25), 16.9 (C-26), 23.3 (C-27), 178.3 (C-28), 17.0 (C-29), 21.1 (C-30)。经与文献<sup>[7]</sup>核对,确定为熊果酸(ursolic acid)。

**化合物 4** 白色粉末; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 1.09 (3H, s, CH<sub>3</sub>), 0.89 (3H, s, CH<sub>3</sub>), 0.87 (6H, s, 2 × CH<sub>3</sub>), 0.85 (3H, s, CH<sub>3</sub>), 0.71 (3H, s, CH<sub>3</sub>), 0.67 (3H, s, CH<sub>3</sub>), 2.99 (1H, m, H-3), 5.15 (1H, brs, H-12), 12.03 (1H, s, -COOH); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ: 38.90 (C-1), 27.2 (C-2), 76.8 (C-3), 38.1 (C-4), 54.8 (C-5), 18.0 (C-6), 32.1 (C-7), 38.4 (C-8), 47.1 (C-9), 36.6 (C-10), 22.6 (C-11), 121.5 (C-12), 143.8 (C-13), 41.3 (C-14), 27.0 (C-15), 22.9 (C-16), 45.7 (C-17), 40.8 (C-18), 45.5 (C-19), 30.4 (C-20), 33.3 (C-21), 32.4 (C-22), 28.2 (C-23), 16.1 (C-24), 15.1 (C-25), 16.9 (C-26), 25.6 (C-27), 178.6 (C-28), 32.8 (C-29), 23.4 (C-30)。经与文献<sup>[7]</sup>核对,确定为齐墩果酸(oleanolic acid)。

**化合物 5** 白色粉末; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 1.28 (3H, s, CH<sub>3</sub>), 1.07 (3H, s, CH<sub>3</sub>), 0.89 (3H, s, CH<sub>3</sub>), 0.68 (3H, s, CH<sub>3</sub>), 0.85 (3H, s, CH<sub>3</sub>), 0.84 (3H, d, *J* = 6.9 Hz, CH<sub>3</sub>), 0.70 (3H, s, CH<sub>3</sub>), 2.36 (1H, s, H-18), 3.00 (1H, m, H-3), 5.16 (1H, s, H-16), 11.86 (1H, s, -COOH); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ: 38.1 (C-1), 27.1 (C-2), 76.9 (C-3), 38.4 (C-5), 54.9 (C-5), 18.1 (C-6), 32.7 (C-7), 40.4 (C-8), 46.7 (C-9), 37.3 (C-10), 23.1 (C-11), 126.8 (C-12), 138.6 (C-13), 41.4 (C-14), 28.3 (C-15), 25.2 (C-16), 46.9 (C-17), 53.2 (C-18), 71.6 (C-19), 41.1 (C-20), 25.9 (C-21), 36.6 (C-22), 28.1 (C-23), 15.1 (C-24), 16.0 (C-25), 16.6 (C-26), 23.9 (C-27), 179.0 (C-28), 26.4 (C-29), 16.3 (C-30)。经与文献<sup>[8]</sup>核对,确定为 19 α-羟基熊果酸(19α-hydroxy-ursolic acid)。

**化合物 6** 白色针晶(氯仿-甲醇); mp. 332.4

~ 333.6 °C。 <sup>1</sup>H NMR (400 MHz, pyridine-*d*<sub>5</sub>) δ: 1.23 (3H, s, CH<sub>3</sub>), 1.05 (3H, s, CH<sub>3</sub>), 1.05 (3H, s, CH<sub>3</sub>), 1.00 (3H, s, CH<sub>3</sub>), 0.97 (3H, s, CH<sub>3</sub>), 0.92 (3H, s, CH<sub>3</sub>), 4.19 (1H, m, H-3α), 4.18 (1H, d, *J* = 10.5 Hz, H-23), 3.72 (1H, d, *J* = 10.5 Hz, H-23), 3.30 (1H, dd, *J* = 3.6, 13.5 Hz, H-18), 5.49 (1H, s, H-12); <sup>13</sup>C NMR (100 MHz, pyridine-*d*<sub>5</sub>) δ: 38.3 (C-1), 27.1 (C-2), 72.9 (C-3), 42.4 (C-4), 48.1 (C-5), 18.1 (C-6), 32.5 (C-7), 39.2 (C-8), 47.7 (C-9), 36.7 (C-10), 23.3 (C-11), 122.1 (C-12), 144.3 (C-13), 41.7 (C-14), 27.2 (C-15), 23.1 (C-16), 46.1 (C-17), 42.4 (C-18), 45.9 (C-19), 30.4 (C-20), 33.7 (C-21), 32.7 (C-22), 67.3 (C-23), 12.6 (C-24), 15.4 (C-25), 17.0 (C-26), 25.7 (C-27), 179.7 (C-28), 32.7 (C-29), 23.2 (C-30)。经与文献<sup>[9]</sup>核对,确定为常春藤皂苷元(hederagenin)。

**化合物 7** 白色粉末; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 1.08 (3H, s, CH<sub>3</sub>), 0.92 (3H, s, CH<sub>3</sub>), 0.92 (3H, s, CH<sub>3</sub>), 0.92 (3H, s, CH<sub>3</sub>), 0.82 (3H, s, CH<sub>3</sub>), 0.75 (3H, s, CH<sub>3</sub>), 0.71 (3H, s, CH<sub>3</sub>), 4.30 (1H, s, H-2), 4.38 (1H, s, H-3), 5.17 (1H, brs, H-12); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 45.7 (C-1), 67.1 (C-2), 82.2 (C-3), 38.9 (C-4), 54.8 (C-5), 18.1 (C-6), 32.9 (C-7), 46.8 (C-8), 47.1 (C-9), 37.7 (C-10), 23.4 (C-11), 121.4 (C-12), 143.9 (C-13), 41.3 (C-14), 27.2 (C-15), 22.6 (C-16), 45.4 (C-17), 23.0 (C-18), 40.8 (C-19), 30.4 (C-20), 33.3 (C-21), 32.3 (C-22), 28.8 (C-23), 16.3 (C-24), 16.9 (C-25), 17.1 (C-26), 25.7 (C-27), 178.6 (C-28), 32.8 (C-29), 22.9 (C-30)。经与文献<sup>[10]</sup>核对,确定为山楂酸(maslinic acid)。

**化合物 8** 白色粉末; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 1.04 (3H, s, CH<sub>3</sub>), 0.91 (9H, brs, 3 × CH<sub>3</sub>), 0.81 (3H, d, *J* = 5.0 Hz, CH<sub>3</sub>), 0.74 (3H, s, CH<sub>3</sub>), 0.70 (3H, s, CH<sub>3</sub>), 2.74 (1H, d, *J* = 9.2 Hz, H-3), 3.42 (1H, s, H-2), 2.10 (1H, d, *J* = 10.5 Hz, H-18), 5.13 (1H, s, H-12); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ: 47.3 (C-1), 67.6 (C-2), 82.7 (C-3), 38.9 (C-4), 55.2 (C-5), 18.5 (C-6), 30.6 (C-7), 38.9 (C-8), 47.4 (C-9), 38.0 (C-10), 23.7 (C-11), 124.9 (C-12), 138.7 (C-13), 42.1 (C-14), 27.9 (C-15), 24.2 (C-16), 47.5 (C-17), 52.8 (C-

18), 39.5 (C-19), 39.3 (C-20), 33.1 (C-21), 36.8 (C-22), 29.3 (C-23), 17.4 (C-24), 17.4 (C-25), 16.9 (C-26), 23.4 (C-27), 178.8 (C-28), 17.6 (C-29), 21.5 (C-30)。经与文献<sup>[11]</sup>核对, 确定为科罗索酸 (corosolic acid)。

**化合物 9** 白色针晶 (氯仿-甲醇); mp. 266.5 ~ 268.0 °C。<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 1.28 (3H, s, CH<sub>3</sub>), 1.07 (3H, s, CH<sub>3</sub>), 0.91 (3H, s, CH<sub>3</sub>), 0.90 (3H, s, CH<sub>3</sub>), 0.84 (3H, d, *J* = 5.7 Hz, CH<sub>3</sub>), 0.70 (3H, s, CH<sub>3</sub>), 0.69 (3H, s, CH<sub>3</sub>), 3.42 (1H, brs, *J* = 3.6, 9.3 Hz, H-2), 2.72 (1H, d, *J* = 9.3 Hz, H-3), 2.36 (1H, s, H-18), 5.16 (1H, s, H-12); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ: 46.9 (C-1), 67.1 (C-2), 82.3 (C-3), 37.3 (C-4), 54.8 (C-5), 18.2 (C-6), 32.6 (C-7), 37.6 (C-8), 46.7 (C-9), 37.1 (C-10), 23.2 (C-11), 126.7 (C-12), 138.6 (C-13), 41.2 (C-14), 28.1 (C-15), 25.2 (C-16), 47.0 (C-17), 53.2 (C-18), 71.6 (C-19), 41.4 (C-20), 26.4 (C-21), 36.9 (C-22), 28.8 (C-23), 16.4 (C-24), 16.8 (C-25), 17.2 (C-26), 24.0 (C-27), 178.9 (C-28), 25.9 (C-29), 16.6 (C-30)。经与文献<sup>[12]</sup>核对, 确定为委陵菜酸 (tormentic acid)。

**化合物 10** 白色粉末; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ: 1.29 (3H, s, CH<sub>3</sub>), 1.08 (3H, s, CH<sub>3</sub>), 0.89 (3H, s, CH<sub>3</sub>), 0.89 (3H, s, CH<sub>3</sub>), 0.84 (3H, d, *J* = 6.5 Hz, CH<sub>3</sub>), 0.78 (3H, s, CH<sub>3</sub>), 0.69 (3H, s, CH<sub>3</sub>), 3.16 (1H, s, H-18), 3.98 (1H, d, *J* = 2.0 Hz, H-3), 4.10 (1H, m, H-2), 5.57 (1H, m, H-12); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ: 44.0 (C-1), 64.6 (C-2), 77.9 (C-3), 37.8 (C-4), 48.5 (C-5), 17.7 (C-6), 32.6 (C-7), 41.3 (C-8), 46.8 (C-9), 41.3 (C-10), 23.1 (C-11), 126.8 (C-12), 138.6 (C-13), 46.5 (C-14), 27.9 (C-15), 25.9 (C-16), 47.6 (C-17), 53.1 (C-18), 71.6 (C-19), 41.5 (C-20), 26.4 (C-21), 37.9 (C-22), 28.8 (C-23), 21.9 (C-24), 16.2 (C-25), 16.6 (C-26), 24.0 (C-27), 178.8 (C-28), 25.1 (C-29), 16.0 (C-30)。经与文献<sup>[13]</sup>核对, 确定为蔷薇酸 (euscapic acid)。

**化合物 11** 白色粉末; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 1.29 (3H, s, CH<sub>3</sub>), 1.08 (3H, s, CH<sub>3</sub>), 0.87 (3H, s, CH<sub>3</sub>), 0.84 (3H, d, *J* = 6.6 Hz, CH<sub>3</sub>), 0.70 (3H, s, CH<sub>3</sub>), 0.54 (3H, s, CH<sub>3</sub>), 3.44 (1H, m, H-23), 4.16 (1H, d, *J* = 4.8 Hz, H-3),

4.41 (1H, dd, *J* = 10.2, 3.9 Hz, H-23), 5.16 (1H, s, H-12); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 38.0 (C-1), 26.4 (C-2), 70.4 (C-3), 41.8 (C-4), 46.7 (C-5), 17.6 (C-6), 32.3 (C-7), 39.2 (C-8), 46.4 (C-9), 36.3 (C-10), 23.2 (C-11), 126.7 (C-12), 138.6 (C-13), 41.1 (C-14), 28.1 (C-15), 25.2 (C-16), 46.9 (C-17), 53.2 (C-18), 71.6 (C-19), 41.4 (C-20), 25.9 (C-21), 37.3 (C-22), 64.5 (C-23), 12.6 (C-24), 16.6 (C-25), 16.3 (C-26), 24.0 (C-27), 178.9 (C-28), 26.6 (C-29), 15.5 (C-30)。经与文献<sup>[14]</sup>核对, 确定为铁冬青酸 (rotundic acid)。

**化合物 12** 白色针状结晶 (甲醇); mp. 252.0 ~ 252.8 °C。<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 1.08 (3H, s, CH<sub>3</sub>), 0.91 (3H, s, CH<sub>3</sub>), 0.88 (3H, s, CH<sub>3</sub>), 0.87 (3H, s, CH<sub>3</sub>), 0.68 (3H, s, CH<sub>3</sub>), 0.53 (3H, s, CH<sub>3</sub>), 3.62 (1H, dd, *J* = 11.0, 5.2 Hz, H-23), 4.14 (1H, d, *J* = 3.8 Hz, H-3), 4.22 (1H, d, *J* = 4.3 Hz, H-2), 4.40 (1H, dd, *J* = 12.0, 5.6 Hz, H-23), 5.18 (1H, s, H-12); 5.23 (1H, d, *J* = 8.0 Hz, glu H-1), 3.14 ~ 3.50 (6H, m); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ: 46.0 (C-1), 67.4 (C-2), 75.5 (C-3), 42.5 (C-4), 46.8 (C-5), 17.4 (C-6), 31.8 (C-7), 39.5 (C-8), 47.1 (C-9), 37.4 (C-10), 23.1 (C-11), 121.6 (C-12), 143.6 (C-13), 41.4 (C-14), 27.2 (C-15), 23.4 (C-16), 45.9 (C-17), 40.7 (C-18), 45.6 (C-19), 31.6 (C-20), 32.8 (C-21), 31.7 (C-22), 63.9 (C-23), 13.8 (C-24), 16.9 (C-25), 16.8 (C-26), 25.6 (C-27), 175.2 (C-28), 30.3 (C-29), 22.5 (C-30); 94.0 (glu C-1'), 72.4 (glu C-2'), 77.7 (glu C-3'), 69.6 (glu C-4'), 76.7 (glu C-5'), 60.7 (glu C-6')。经与文献<sup>[15]</sup>核对, 确定为阿江榄仁树葡萄糖苷 II (arjunglucoside II)。

**化合物 13** 无色油状物 (丙酮); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 6.78 (1H, dd, *J* = 10.2, 1.7 Hz, H-6), 5.88 (1H, d, *J* = 10.2 Hz, H-5), 4.13 (1H, td, *J* = 4.5, 1.6 Hz, H-2), 3.92 (1H, m, H-8a), 3.78 (1H, dd, *J* = 15.6, 8.0 Hz, H-8b), 2.72 (1H, dd, *J* = 4.2, 16.7 Hz, H-3b), 2.49 (1H, dd, *J* = 16.7, 4.7 Hz, H-3a), 2.26 (1H, m, H-7a), 2.18 (1H, m, H-7b); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 75.0 (C-1), 81.7 (C-2), 40.2 (C-3), 197.4 (C-4), 128.2 (C-5), 149.9 (C-6), 40.1 (C-7), 66.3 (C-8)。经与文献<sup>[16]</sup>核对, 确定为 renyolone。

**化合物 14** 无色油状物(丙酮)。<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 4.34 (1H, m, H-2), 3.85 (2H, m, H-8), 2.87 (1H, m, H-3a), 2.70 (1H, m, H-3b), 2.38 (1H, m, H'-5a), 2.27 (1H, m, H'-7a), 2.16 (2H, m, H-6), 2.05 (1H, m, H-7b), 1.56 (1H, m, H-5b); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 77.2 (C-1), 84.3 (C-2), 42.8 (C-3), 210.4 (C-4), 33.8 (C-5), 35.5 (C-6), 40.6 (C-7), 66.2 (C-8)。经与文献<sup>[16]</sup>核对,确定为(3 αR)-hexahydro-3 α-hydroxybenzo-furan-6 (2 H)-one。

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