

汉桃叶中苷类成分研究

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摘 要: 目的 研究鹅掌属植物汉桃叶(广西鹅掌柴 *Schefflera kwangsiensis*) 茎枝的苷类成分。方法 采用硅胶柱色谱、凝胶柱色谱等方法进行分离纯化, 通过光谱分析和理化性质鉴定化合物的结构。结果 从汉桃叶中分离得到 10 个化合物, 分别鉴定为野木瓜苷 C (1)、3-*O*-β-*D*-吡喃葡萄糖基常春藤苷元-28-*O*-α-*L*-吡喃鼠李糖基-(1→4)-β-*D*-吡喃葡萄糖基-(1→6)-β-*D*-吡喃葡萄糖苷 (2)、3-*O*-β-*D*-吡喃木糖基常春藤苷元-28-*O*-α-*L*-吡喃鼠李糖基-(1→4)-*O*-β-*D*-吡喃葡萄糖基-(1→6)-*O*-β-*D*-吡喃葡萄糖苷 (3)、刺楸皂苷 B (4)、3-*O*-β-*D*-吡喃木糖基-(1→3)-*O*-α-*L*-吡喃鼠李糖基-(1→2)-*O*-α-*L*-吡喃阿拉伯糖-常春藤苷元-28-*O*-α-*L*-吡喃鼠李糖基-(1→4)-β-*D*-吡喃葡萄糖基-(1→6)-*O*-β-*D*-吡喃葡萄糖酯苷 (5)、3-*O*-[*O*-吡喃阿拉伯糖基-(1→4)-*O*-吡喃阿拉伯糖基-(1→3)-*O*-吡喃鼠李糖基-(1→2)-吡喃阿拉伯糖基]-齐墩果酸-*O*-吡喃鼠李糖基-(1→4)-*O*-β-*D*-吡喃葡萄糖基-(1→6)-β-*D*-吡喃葡萄糖酯苷(6)、刺楸皂苷 G(7)、3-*O*-[*O*-吡喃阿拉伯糖基-(1→4)-*O*-吡喃阿拉伯糖基-(1→3)-*O*-吡喃鼠李糖基-(1→2)-吡喃阿拉伯糖基]常春藤苷(8)、3-*O*-β-*D*-吡喃葡萄糖基-(1→4)-*O*-β-*D*-吡喃木糖基 1-(1→3)-*O*-α-*L*-吡喃鼠李糖基-(1→2)-*O*-α-*L*-吡喃阿拉伯糖-齐墩果酸-28-*O*-α-*L*-吡喃鼠李糖基-(1→4)-β-*D*-吡喃葡萄糖基-(1→6)-*O*-β-*D*-吡喃葡萄糖酯苷 (9)、3-*O*-β-*D*-吡喃葡萄糖基-(1→4)-*O*-β-*D*-吡喃木糖基 1-(1→3)-*O*-α-*L*-吡喃鼠李糖基-(1→2)-*O*-α-*L*-吡喃阿拉伯糖-齐墩果酸-28-*O*-α-*L*-吡喃鼠李糖基-(1→4)-β-*D*-吡喃葡萄糖基-(1→6)-*O*-6-*O*-乙酰基-β-*D*-吡喃葡萄糖酯苷 (10)。结论 化合物 1、4、5、7、9、10 为首次从该植物中分离得到。

关键词: 汉桃叶; 鹅掌属; 野木瓜苷 C; 刺楸皂苷 B; 刺楸皂苷 G

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Study on glycosides from stems of *Schefflera kwangsiensis*

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Key words: stems of *Schefflera kwangsiensis* Merr. ex Li; *Schefflera* J. R. & G. Forst; staunoside C; kalopanaxsaponin B; kalopanaxsaponin G

汉桃叶为五加科鹅掌属植物广西鹅掌柴 *Schefflera kwangsiensis* Merr. ex Li 的茎枝, 又名鹅掌藤、七叶莲。主产于广西、福建, 其味微苦、温。有祛风止痛、舒筋活络功能。用于三叉神经痛、神经性头痛、坐骨神经痛、风湿关节痛及胃、肠、胆道疼痛等症^[1]。汉桃叶是中药痛安注射液中的主要药味, 其化学成分研究报道较少^[2-3], 为进一步研究汉桃叶药效物质基础, 本实验对其水溶性成分进行研究, 共分离得到 10 个苷类化合物, 分别鉴定为野木瓜苷 C (staunoside C, 1)、3-*O*-β-*D*-吡喃葡萄糖基常春藤苷元-28-*O*-α-*L*-吡喃鼠李糖基-(1→4)-β-*D*-

吡喃葡萄糖基-(1→6)-β-*D*-吡喃葡萄糖苷 (tauroside St-H₁, 2)、3-*O*-β-*D*-吡喃木糖基常春藤苷元-28-*O*-α-*L*-吡喃鼠李糖基-(1→4)-*O*-β-*D*-吡喃葡萄糖基-(1→6)-*O*-β-*D*-吡喃葡萄糖苷 (saponins HCS-B, 3)、刺楸皂苷 B (kalopanaxsaponin B, 4)、3-*O*-β-*D*-吡喃木糖基-(1→3)-*O*-α-*L*-吡喃鼠李糖基-(1→2)-*O*-α-*L*-吡喃阿拉伯糖-常春藤苷元-28-*O*-α-*L*-吡喃鼠李糖基-(1→4)-β-*D*-吡喃葡萄糖基-(1→6)-*O*-β-*D*-吡喃葡萄糖酯苷 [hederagenin 3-*O*-β-*D*-xylopyranosyl-(1→3)-*O*-α-*L*-rhamnopyranosyl-(1→2)-*O*-α-*L*-arabinopyranoside-28-*O*-α-*L*-rhamnopyranosyl-(1→4)-β-*D*-glucopyra-

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nosyl-(1→6)-*O*-β-*D*-glucopyranosyl ester, **5**], 3-*O*-[*O*-吡喃阿拉伯糖基-(1→4)-*O*-吡喃阿拉伯糖基-(1→3)-*O*-吡喃鼠李糖基-(1→2)-吡喃阿拉伯糖基]-齐墩果酸-*O*-吡喃鼠李糖基-(1→4)-*O*-β-吡喃葡萄糖基-(1→6)-β-吡喃葡萄糖基酯 (scheffarboside **D**, **6**)、刺楸皂苷 **G** (kalopanaxsaponin **G**, **7**)、3-*O*-[*O*-吡喃阿拉伯糖基-(1→4)-*O*-吡喃阿拉伯糖基-(1→3)-*O*-吡喃鼠李糖基-(1→2)-吡喃阿拉伯糖基]常春藤苷 (scheffarboside **C**, **8**)、3-*O*-β-*D*-吡喃葡萄糖基-(1→4)-*O*-β-*D*-吡喃木糖基 1-(1→3)-*O*-α-*L*-吡喃鼠李糖基-(1→2)-*O*-α-*L*-吡喃阿拉伯糖-齐墩果酸-28-*O*-α-*L*-吡喃鼠李糖基-(1→4)-β-*D*-吡喃葡萄糖基-(1→6)-*O*-β-*D*-吡喃葡萄糖酯苷 [oleanolic acid 3-*O*-β-*D*-glucopyranosyl-(1→4)-*O*-β-*D*-xylopyranosyl-(1→3)-*O*-α-*L*-rhamnopyranosyl-(1→2)-*O*-α-*L*-arabinopyranoside-28-*O*-α-*L*-rhamnopyranosyl-(1→4)-*O*-β-*D*-glucopyranosyl-(1→6)-*O*-β-*D*-glucopyranosyl ester, **9**]、3-*O*-β-*D*-吡喃葡萄糖基-(1→4)-*O*-β-*D*-吡喃木糖基 1-(1→3)-*O*-α-*L*-吡喃鼠李糖基-(1→2)-*O*-α-*L*-吡喃阿拉伯糖-齐墩果酸-28-*O*-α-*L*-吡喃鼠李糖基-(1→4)-β-*D*-吡喃葡萄糖基-(1→6)-*O*-6-*O*-乙酰基-β-*D*-吡喃葡萄糖酯苷 [oleanolic acid-3-*O*-β-*D*-glucopyranosyl-(1→4)-*O*-β-*D*-xylopyranosyl-(1→3)-*O*-α-*L*-rhamnopyranosyl-(1→2)-*O*-α-*L*-arabinopyranoside-28-*O*-α-*L*-rhamnopyranosyl-(1→4)-*O*-6-*O*-acetyl-β-*D*-glucopyranosyl-(1→6)-*O*-β-*D*-glucopyranosyl ester, **10**]。其中化合物 **1**、**4**、**5**、**7**、**9**、**10** 为首次从该植物中分得。

1 仪器与材料

Finnigan LC—10Advp 高效液相色谱仪, 电喷雾离子化接口, 三重四极杆质谱仪 (Finnigan TSQ Quantum Discovery MAX); Bruker AV—300 型核磁共振仪 (Bruker 公司); Agilent 1100 型制备 HPLC, Zorbax SB C₁₈ (250 mm×9.4 mm, 5 μm) 柱。凝胶 Sephadex LH-20 (Pharmacia 公司生产); D-101 型大孔吸附树脂 (天津农药总厂); R30030B 反相 C₁₈ 填料 (40~63 μm, 上海安普科学仪器有限公司); 柱色谱用硅胶 (200~300 目) 和硅胶 GF254 均为青岛海洋化工厂生产。所用试剂均为分析纯或色谱纯。

汉桃叶药材由南京中医药大学吴启南教授鉴定为广西鹅掌柴 *Schefflera kwangsiensis* Merr. ex Li 的茎枝。

2 提取与分离

汉桃叶茎枝 8 kg, 水煎煮提取 2 次, 每次 2 h, 提取液减压浓缩的浸膏经乙醇处理 2 次, 第 1 次为

65%乙醇, 第 2 次为 80%乙醇。醇沉浓缩液调节 pH 值至中性, 加乙醇使含醇量达 85%, 滤过, 滤液减压浓缩, 真空干燥, 得提取物 208 g。

取汉桃叶提取物 200 g 加 800 mL 水溶解, 醋酸乙酯提取 (800 mL×3), 合并提取液, 减压浓缩得浸膏 16 g; 醋酸乙酯提取母液用水饱和正丁醇提取 (800 mL×3), 合并提取液, 减压浓缩得浸膏 43 g。水饱和正丁醇提取后母液备用。

正丁醇提取物经硅胶柱色谱分离, 氯仿-甲醇 (100:0→10:90) 梯度洗脱, 得 5 个组分 (Fr. 1~5)。Fr. 5 经硅胶柱色谱, 氯仿-甲醇-水 (4:1:0.1) 洗脱得到化合物 **1** (49 mg); Fr. 3 经硅胶柱色谱, 氯仿-甲醇-水 (5:1:0.1→2:1:0.1) 洗脱, 再经反相 C₁₈ 柱 (30%~100%甲醇)、凝胶 Sephadex LH-20 纯化得化合物 **2** (61 mg)、**3** (53 mg)、**4** (48 mg)、**5** (30 mg); Fr. 4 经硅胶柱色谱, 氯仿-甲醇-水 (5:1:0.1→2:1:0.1) 梯度洗脱, 再经反相 C₁₈ 柱 (30%~100%甲醇)、凝胶 Sephadex LH-20 纯化得化合物 **6** (40 mg)、**7** (57 mg)、**8** (68 mg)。

水饱和正丁醇提取后母液通过 D-101 大孔树脂, 分别用水、30%、80%乙醇洗脱, 收集 80%乙醇洗脱部分浓缩除醇, 水溶解, 经 C₁₈ 柱, 水-甲醇梯度洗脱, 收集甲醇洗脱部分; 经凝胶 Sephadex LH-20 纯化, 收集 1~4 流分; 再经硅胶柱色谱, 氯仿-甲醇-水 (65:35:10) 洗脱, 100 mL 为 1 流分, 合并 19~35 流分, 浓缩, 水溶解, 经高效液相色谱制备, 得化合物 **9** (152 mg)、**10** (75 mg)。

3 结构鉴定

化合物 **1**: 白色粉末。ESI-MS m/z : 1 215 [2M+Na]⁺, 619 [M+Na]⁺。¹H-NMR (300 MHz, pyridine-*d*₅) δ: 7.26 (2H, s, H-2', 6'), 7.23 (2H, s, H-2'', 6''), 5.43 (1H, d, $J = 7.8$ Hz, Glc-H-1), 3.85 (6H, s, 3', 5'-OCH₃), 3.76 (6H, s, 3'', 5''-OCH₃); ¹³C-NMR (75 MHz, pyridine-*d*₅) δ: 98.6 (C-1), 88.1 (C-2), 70.9 (C-4), 60.4 (C-5), 87.7 (C-6), 74.7 (C-8), 127.2 (C-1'), 131.4 (C-1''), 107.7 (C-2'), 104.8 (C-2''), 148.0 (C-3'), 148.5 (C-3''), 137.3 (C-4'), 137.3 (C-4''), 148.0 (C-5'), 148.8 (C-5''), 107.7 (C-6'), 104.9 (C-6''), 56.3 (3', 5'-OCH₃), 56.3 (3'', 5''-OCH₃), 100.4 (Glc-C-1), 74.9 (Glc-C-2), 79.0 (Glc-C-3), 71.5 (Glc-C-4), 78.8 (Glc-C-5), 62.7 (Glc-C-6)。以上数据与文献报道一致^[4], 故鉴定化合物 **1** 为野木瓜苷 C。

化合物 **2**: 白色粉末。ESI-MS m/z : 1 127 [M+

$\text{Na}]^+$, 1 103 $[\text{M}-\text{H}]^-$ 。 $^1\text{H-NMR}$ (300 MHz, pyridine- d_5) δ : 6.21 (1H, d, $J = 9.0$ Hz, 28-*O*-Glc-H-1), 5.11 (1H, d, $J = 9.0$ Hz, 3-*O*-Glc-H-1), 0.84~1.16 (18H, s, $6\times\text{-CH}_3$); $^{13}\text{C-NMR}$ (75 MHz, pyridine- d_5) δ : 38.6 (C-1), 26.0 (C-2), 82.2 (C-3), 43.4 (C-4), 47.6 (C-5), 18.2 (C-6), 32.4 (C-7), 39.9 (C-8), 48.1 (C-9), 36.9 (C-10), 23.3 (C-11), 122.8 (C-12), 144.1 (C-13), 42.1 (C-14), 28.2 (C-15), 23.8 (C-16), 46.1 (C-17), 41.6 (C-18), 46.9 (C-19), 30.7 (C-20), 33.9 (C-21), 32.7 (C-22), 64.7 (C-23), 13.6 (C-24), 16.2 (C-25), 17.5 (C-26), 25.8 (C-27), 176.5 (C-28), 33.0 (C-29), 23.6 (C-30), 105.8 (3-*O*-Glc-C-1), 75.8 (3-*O*-Glc-C-2), 78.6 (3-*O*-Glc-C-3), 71.5 (3-*O*-Glc-C-4), 78.1 (3-*O*-Glc-C-5), 62.7 (3-*O*-Glc-C-6), 95.6 (28-*O*-Glc-C-1), 73.9 (28-*O*-Glc-C-2), 78.3 (28-*O*-Glc-C-3), 70.7 (28-*O*-Glc-C-4), 78.0 (28-*O*-Glc-C-5), 69.1 (28-*O*-Glc-C-6), 104.8 (Glc'-C-1), 75.3 (Glc'-C-2), 76.4 (Glc'-C-3), 78.3 (Glc'-C-4), 77.1 (Glc'-C-5), 61.2 (Glc'-C-6), 102.7 (Rha-C-1), 72.5 (Rha-C-2), 72.7 (Rha-C-3), 73.8 (Rha-C-4), 70.3 (Rha-C-5), 18.5 (Rha-C-6)。以上数据与文献报道一致^[5], 故鉴定化合物 **2** 为 3-*O*- β -*D*-吡喃葡萄糖基常春藤苷元-28-*O*- α -*L*-吡喃鼠李糖基-(1 $\rightarrow$ 4)- β -*D*-吡喃葡萄糖基-(1 $\rightarrow$ 6)- β -*D*-吡喃葡萄糖苷。

化合物 **3**: 白色粉末。ESI-MS m/z : 1 097 $[\text{M}+\text{Na}]^+$, 1 073 $[\text{M}-\text{H}]^-$ 。 $^1\text{H-NMR}$ (300 MHz, pyridine- d_5) δ : 6.23 (1H, d, $J = 9.0$ Hz, 28-*O*-Glc-H-1), 4.97 (1H, d, $J = 9.0$ Hz, Glc'-H-1), 0.86~1.15 (18H, s, $6\times\text{-CH}_3$); $^{13}\text{C-NMR}$ (75 MHz, pyridine- d_5) δ : 38.7 (C-1), 26.0 (C-2), 81.8 (C-3), 43.4 (C-4), 47.5 (C-5), 18.1 (C-6), 32.7 (C-7), 39.8 (C-8), 48.1 (C-9), 36.9 (C-10), 23.8 (C-11), 122.8 (C-12), 144.0 (C-13), 42.0 (C-14), 28.2 (C-15), 23.3 (C-16), 47.5 (C-17), 41.6 (C-18), 46.1 (C-19), 30.7 (C-20), 33.9 (C-21), 32.4 (C-22), 64.3 (C-23), 13.6 (C-24), 16.2 (C-25), 17.5 (C-26), 26.0 (C-27), 176.5 (C-28), 33.0 (C-29), 23.6 (C-30), 106.7 (3-*O*-Xyl-C-1), 75.3 (3-*O*-Xyl-C-2), 78.0 (3-*O*-Xyl-C-3), 70.2 (3-*O*-Xyl-C-4), 67.0 (3-*O*-Xyl-C-5), 95.6 (28-*O*-Glc-C-1), 74.0 (28-*O*-Glc-C-2), 78.7 (28-*O*-Glc-C-3), 70.7 (28-*O*-Glc-C-4), 78.1 (28-*O*-Glc-C-5), 69.1 (28-*O*-Glc-C-6), 104.8 (Glc'-C-1), 75.3 (Glc'-C-2), 76.4 (Glc'-C-3), 78.7 (Glc'-C-4), 77.1 (Glc'-C-5), 61.2 (Glc'-C-6), 102.7 (Rha-C-1), 72.5 (Rha-C-2), 72.7 (Rha-C-3), 73.8 (Rha-C-4), 70.7 (Rha-C-5), 18.5

(Rha-C-6)。以上数据与文献报道一致^[6], 故鉴定化合物 **3** 为 3-*O*- β -*D*-吡喃木糖基常春藤苷元-28-*O*- α -*L*-吡喃鼠李糖基-(1 $\rightarrow$ 4)-*O*- β -*D*-吡喃葡萄糖基-(1 $\rightarrow$ 6)-*O*- β -*D*-吡喃葡萄糖苷。

化合物 **4**: 白色粉末。ESI-MS m/z : 1 244 $[\text{M}+\text{Na}]^+$, 1 220 $[\text{M}-\text{H}]^-$ 。 $^1\text{H-NMR}$ (300 MHz, pyridine- d_5) δ : 6.23 (1H, d, $J = 9.0$ Hz, 28-*O*-Glc-H-1), 0.84~1.14 (18H, s, $6\times\text{-CH}_3$); $^{13}\text{C-NMR}$ (75 MHz, pyridine- d_5) δ : 39.0 (C-1), 26.1 (C-2), 80.9 (C-3), 43.4 (C-4), 47.6 (C-5), 18.1 (C-6), 32.4 (C-7), 39.8 (C-8), 48.1 (C-9), 36.8 (C-10), 23.7 (C-11), 123.0 (C-12), 144.0 (C-13), 42.0 (C-14), 28.2 (C-15), 23.3 (C-16), 46.9 (C-17), 41.6 (C-18), 46.1 (C-19), 30.7 (C-20), 34.0 (C-21), 32.7 (C-22), 63.8 (C-23), 13.9 (C-24), 16.1 (C-25), 17.5 (C-26), 26.1 (C-27), 176.5 (C-28), 33.0 (C-29), 23.7 (C-30), 104.3 (3-*O*-Ara-C-1), 75.7 (3-*O*-Ara-C-2), 74.6 (3-*O*-Ara-C-3), 69.5 (3-*O*-Ara-C-4), 65.9 (3-*O*-Ara-C-5), 101.5 (Rha-C-1), 72.3 (Rha-C-2), 72.5 (Rha-C-3), 74.1 (Rha-C-4), 69.6 (Rha-C-5), 18.5 (Rha-C-6), 95.6 (28-*O*-Glc-C-1), 75.3 (28-*O*-Glc-C-2), 78.4 (28-*O*-Glc-C-3), 70.2 (28-*O*-Glc-C-4), 76.4 (28-*O*-Glc-C-5), 70.9 (28-*O*-Glc-C-6), 104.8 (Glc'-C-1), 73.9 (Glc'-C-2), 78.1 (Glc'-C-3), 78.6 (Glc'-C-4), 77.1 (Glc'-C-5), 61.2 (Glc'-C-6), 102.6 (Rha-C-1), 72.5 (Rha-C-2), 72.5 (Rha-C-3), 74.0 (Rha-C-4), 69.1 (Rha-C-5), 18.4 (Rha-C-6)。以上数据与文献报道一致^[7], 故鉴定化合物 **4** 为刺楸皂苷 B。

化合物 **5**: 白色粉末。ESI-MS m/z : 1 375 $[\text{M}+\text{Na}]^+$, 1 351 $[\text{M}-\text{H}]^-$ 。 $^1\text{H-NMR}$ (300 MHz, pyridine- d_5) δ : 6.21 (1H, d, $J = 9.0$ Hz, 28-*O*-Glc-H-1), 0.84~1.16 (18H, s, $6\times\text{-CH}_3$); $^{13}\text{C-NMR}$ (75 MHz, pyridine- d_5) δ : 39.0 (C-1), 26.3 (C-2), 81.0 (C-3), 43.5 (C-4), 47.5 (C-5), 18.0 (C-6), 32.7 (C-7), 39.8 (C-8), 48.1 (C-9), 36.8 (C-10), 23.8 (C-11), 122.8 (C-12), 144.0 (C-13), 42.0 (C-14), 28.2 (C-15), 23.3 (C-16), 46.9 (C-17), 41.6 (C-18), 46.1 (C-19), 30.7 (C-20), 33.9 (C-21), 32.4 (C-22), 63.9 (C-23), 14.2 (C-24), 16.1 (C-25), 17.4 (C-26), 26.0 (C-27), 176.5 (C-28), 33.0 (C-29), 23.6 (C-30), 104.8 (3-*O*-Ara-C-1), 75.3 (3-*O*-Ara-C-2), 75.3 (3-*O*-Ara-C-3), 69.5 (3-*O*-Ara-C-4), 66.3 (3-*O*-Ara-C-5), 101.2 (Rha-C-1), 71.9 (Rha-C-2), 82.8 (Rha-C-3), 72.9 (Rha-C-4), 69.8 (Rha-C-5), 18.5 (Rha-C-6), 107.5 (Xyl-C-1), 75.6

(Xyl-C-2), 78.1 (Xyl-C-3), 71.0 (Xyl-C-4), 67.3 (Xyl-C-5), 95.6 (28-O-Glc-C-1), 73.8 (28-O-Glc-C-2), 78.6 (28-O-Glc-C-3), 70.7 (28-O-Glc-C-4), 77.9 (28-O-Glc-C-5), 69.1 (28-O-Glc-C-6), 104.8 (Glc'-C-1), 75.3 (Glc'-C-2), 76.4 (Glc'-C-3), 78.4 (Glc'-C-4), 77.1 (Glc'-C-5), 61.2 (Glc'-C-6), 102.6 (Rha-C-1), 72.5 (Rha-C-2), 72.7 (Rha-C-3), 73.9 (Rha-C-4), 70.2 (Rha-C-5), 18.4 (Rha-C-6)。以上数据与文献报道一致^[8], 故鉴定化合物 **5** 为 3-O-β-D-吡喃木糖基-(1→3)-O-α-L-吡喃鼠李糖基-(1→2)-O-α-L-吡喃阿拉伯糖-常春藤苷元-28-O-α-L-吡喃鼠李糖基-(1→4)-β-D-吡喃葡萄糖基-(1→6)-O-β-D-吡喃葡萄糖酯苷。

化合物 **6**: 白色粉末。ESI-MS m/z : $[M+H]^+$ 1 491。¹H-NMR (300 MHz, pyridine- d_5) δ : 6.1 (1H, brs, Rha-H-1), 0.76~1.16 (18H, s, 6×-CH₃); ¹³C-NMR (75 MHz, pyridine- d_5) δ : 38.5 (C-1), 26.1 (C-2), 88.4 (C-3), 39.4 (C-4), 55.5 (C-5), 17.9 (C-6), 31.9 (C-7), 39.1 (C-8), 47.6 (C-9), 36.5 (C-10), 23.2 (C-11), 122.4 (C-12), 143.8 (C-13), 41.7 (C-14), 27.7 (C-15), 22.8 (C-16), 45.8 (C-17), 41.2 (C-18), 45.8 (C-19), 30.3 (C-20), 33.5 (C-21), 32.7 (C-22), 27.7 (C-23), 16.7 (C-24), 15.2 (C-25), 17.0 (C-26), 25.6 (C-27), 176.5 (C-28), 32.7 (C-29), 23.2 (C-30), 104.6 (3-O-Ara-C-1), 75.0 (3-O-Ara-C-2), 73.5 (3-O-Ara-C-3), 68.6 (3-O-Ara-C-4), 64.7 (3-O-Ara-C-5), 100.8 (Rha-C-1), 71.1 (Rha-C-2), 81.6 (Rha-C-3), 72.0 (Rha-C-4), 69.2 (Rha-C-5), 17.9 (Rha-C-6), 106.0 (Ara'-C-1), 74.5 (Ara'-C-2), 75.8 (Ara'-C-3), 76.0 (Ara'-C-4), 64.0 (Ara'-C-5), 102.6 (Ara''-C-1), 70.9 (Ara''-C-2), 73.5 (Ara''-C-3), 68.6 (Ara''-C-4), 66.6 (Ara''-C-5), 95.1 (28-O-Glc-C-1), 73.1 (28-O-Glc-C-2), 77.9 (28-O-Glc-C-3), 69.9 (28-O-Glc-C-4), 77.5 (28-O-Glc-C-5), 68.6 (28-O-Glc-C-6), 104.6 (Glc'-C-1), 74.5 (Glc'-C-2), 76.0 (Glc'-C-3), 77.9 (Glc'-C-4), 76.3 (Glc'-C-5), 60.6 (Glc'-C-6), 102.1 (Rha-C-1), 71.7 (Rha-C-2), 72.0 (Rha-C-3), 73.5 (Rha-C-4), 69.9 (Rha-C-5), 17.9 (Rha-C-6)。以上数据与文献报道一致^[9], 故鉴定化合物 **6** 为 3-O-[O-吡喃阿拉伯糖基-(1→4)-O-吡喃阿拉伯糖基-(1→3)-O-吡喃鼠李糖基-(1→2)-吡喃阿拉伯糖基]-齐墩果酸-O-吡喃鼠李糖基-(1→4)-O-β-吡喃葡萄糖基-(1→6)-β-吡喃葡萄糖酯苷。

化合物 **7**: 白色粉末。ESI-MS m/z : 965 $[M+Na]^+$, 941 $[M-H]^-$ 。提示相对分子质量为 942。

¹H-NMR (300 MHz, pyridine- d_5) δ : 6.25 (1H, d, J = 7.8 Hz, 28-O-Glc-H-1), 6.0 (1H, s, Rha-H-1), 5.41 (1H, s, H-12), 4.98 (1H, d, J = 9.0 Hz, Glc-H-1), 1.68 (3H, d, J = 5.4 Hz, Rha-H-6), 0.99~1.33 (18H, s, 6×-CH₃); ¹³C-NMR (75 MHz, pyridine- d_5) δ : 38.8 (C-1), 27.6 (C-2), 73.8 (C-3), 42.9 (C-4), 48.4 (C-5), 18.5 (C-6), 32.4 (C-7), 39.8 (C-8), 48.1 (C-9), 37.2 (C-10), 23.3 (C-11), 122.9 (C-12), 144.1 (C-13), 42.1 (C-14), 28.2 (C-15), 23.8 (C-16), 47.0 (C-17), 41.6 (C-18), 46.1 (C-19), 30.7 (C-20), 33.9 (C-21), 33.0 (C-22), 67.6 (C-23), 13.1 (C-24), 16.0 (C-25), 17.5 (C-26), 26.0 (C-27), 176.5 (C-28), 33.0 (C-29), 23.8 (C-30), 95.6 (28-O-Glc-C-1), 73.8 (28-O-Glc-C-2), 78.1 (28-O-Glc-C-3), 70.7 (28-O-Glc-C-4), 78.1 (28-O-Glc-C-5), 69.1 (28-O-Glc-C-6), 104.8 (Glc'-C-1), 75.3 (Glc'-C-2), 76.4 (Glc'-C-3), 78.7 (Glc'-C-4), 77.1 (Glc'-C-5), 61.2 (Glc'-C-6), 102.7 (Ara-C-1), 72.5 (Ara-C-2), 72.7 (Ara-C-3), 74.0 (Ara-C-4), 70.3 (Ara-C-5), 18.5 (Ara-C-6)。以上数据与文献报道一致^[10], 故鉴定化合物 **7** 为刺楸皂苷 G。

化合物 **8**: 白色粉末。ESI-MS m/z : 1 037 $[M+Na]^+$, 1 013 $[M-H]^-$ 。提示相对分子质量为 1 014。¹H-NMR (300 MHz, pyridine- d_5) δ : 6.28 (1H, brs, H-1'), 5.44 (1H, brs, H-12), 1.24~1.31 (9H, s, 3×-CH₃), 1.1 (3H, s), 0.98 (3H, s), 0.90 (3H, s); ¹³C-NMR (75 MHz, pyridine- d_5) δ : 38.9 (C-1), 26.3 (C-2), 81.0 (C-3), 43.5 (C-4), 47.5 (C-5), 18.0 (C-6), 32.7 (C-7), 39.6 (C-8), 48.1 (C-9), 36.8 (C-10), 23.5 (C-11), 122.5 (C-12), 144.7 (C-13), 42.0 (C-14), 28.2 (C-15), 23.7 (C-16), 46.5 (C-17), 41.8 (C-18), 46.3 (C-19), 30.8 (C-20), 34.1 (C-21), 33.2 (C-22), 63.8 (C-23), 14.0 (C-24), 16.0 (C-25), 17.3 (C-26), 26.1 (C-27), 180.2 (C-28), 33.2 (C-29), 23.7 (C-30), 104.6 (3-O-Ara-C-1), 75.1 (3-O-Ara-C-2), 75.1 (3-O-Ara-C-3), 69.3 (3-O-Ara-C-4), 66.3 (3-O-Ara-C-5), 101.3 (Rha-C-1), 71.8 (Rha-C-2), 82.8 (Rha-C-3), 72.8 (Rha-C-4), 69.4 (Rha-C-5), 18.3 (Rha-C-6), 107.0 (Ara'-C-1), 75.4 (Ara'-C-2), 75.8 (Ara'-C-3), 76.0 (Ara'-C-4), 64.7 (Ara'-C-5), 103.5 (Ara''-C-1), 71.2 (Ara''-C-2), 74.2 (Ara''-C-3), 69.7 (Ara''-C-4), 67.2 (Ara''-C-5)。以上数据与文献报道一致^[9], 故鉴定化合物 **8** 为 3-O-[O-吡喃阿拉伯糖基-(1→4)-O-吡喃阿拉伯糖基-(1→3)-O-吡喃鼠李糖基-(1→2)-吡喃阿拉伯糖基] 常春藤苷。

化合物 **9**: 白色粉末。ESI-MS m/z : 1 499 $[M+H]^+$ 。 1H -NMR (300 MHz, pyridine- d_5) δ : 6.21 (1H, d, $J = 7.8$ Hz, 28-*O*-Glc-H-1), 0.83~1.15 (18H, s, $6\times-CH_3$); ^{13}C -NMR (75 MHz, pyridine- d_5) δ : 39.0 (C-1), 26.3 (C-2), 81.0 (C-3), 43.5 (C-4), 47.6 (C-5), 18.1 (C-6), 32.7 (C-7), 39.8 (C-8), 48.1 (C-9), 36.8 (C-10), 23.8 (C-11), 122.8 (C-12), 144.0 (C-13), 42.0 (C-14), 28.2 (C-15), 23.3 (C-16), 46.9 (C-17), 41.6 (C-18), 46.1 (C-19), 30.6 (C-20), 33.9 (C-21), 32.4 (C-22), 63.9 (C-23), 14.0 (C-24), 16.1 (C-25), 17.5 (C-26), 26.3 (C-27), 176.5 (C-28), 33.0 (C-29), 23.8 (C-30), 104.5 (3-*O*-Ara-C-1), 75.4 (3-*O*-Ara-C-2), 74.9 (3-*O*-Ara-C-3), 69.5 (3-*O*-Ara-C-4), 66.0 (3-*O*-Ara-C-5), 101.2 (Rha-C-1), 71.8 (Rha-C-2), 82.8 (Rha-C-3), 72.8 (Rha-C-4), 69.5 (Rha-C-5), 18.4 (Rha-C-6), 107.0 (Xyl-C-1), 75.4 (Xyl-C-2), 76.0 (Xyl-C-3), 77.9 (Xyl-C-4), 64.7 (Xyl-C-5), 103.5 (Glc-C-1), 74.2 (Glc-C-2), 78.2 (Glc-C-3), 71.8 (Glc-C-4), 78.6 (Glc-C-5), 61.2 (Glc-C-6), 95.5 (28-*O*-Glc-C-1), 73.8 (28-*O*-Glc-C-2), 78.6 (28-*O*-Glc-C-3), 70.7 (28-*O*-Glc-C-4), 77.9 (28-*O*-Glc-C-5), 69.1 (28-*O*-Glc-C-6), 104.7 (Glc'-C-1), 75.2 (Glc'-C-2), 76.4 (Glc'-C-3), 78.6 (Glc'-C-4), 77.0 (Glc'-C-5), 61.2 (Glc'-C-6), 102.6 (Rha-C-1), 72.4 (Rha-C-2), 72.6 (Rha-C-3), 73.8 (Rha-C-4), 70.2 (Rha-C-5), 18.4 (Rha-C-6)。以上数据与文献报道一致^[8], 故鉴定化合物 **9** 为 3-*O*- β -D-吡喃葡萄糖基-(1 $\rightarrow$ 4)-*O*- β -D-吡喃木糖基 1-(1 $\rightarrow$ 3)-*O*- α -L-吡喃鼠李糖基-(1 $\rightarrow$ 2)-*O*- α -L-吡喃阿拉伯糖-齐墩果酸-28-*O*- α -L-吡喃鼠李糖基-(1 $\rightarrow$ 4)- β -D-吡喃葡萄糖基-(1 $\rightarrow$ 6)-*O*- β -D-吡喃葡萄糖酯苷。

化合物 **10**: 白色粉末。ESI-MS m/z : 1 541 $[M+H]^+$ 。 1H -NMR (300 MHz, pyridine- d_5) δ : 6.20 (1H, d, $J = 7.8$ Hz, 28-*O*-Glc-H-1), 0.86~1.28 (21H, s, $7\times-CH_3$); ^{13}C -NMR (75 MHz, pyridine- d_5) δ : 38.9 (C-1), 26.6 (C-2), 88.7 (C-3), 39.5 (C-4), 56.0 (C-5), 18.5 (C-6), 33.3 (C-7), 39.9 (C-8), 48.1 (C-9), 37.0 (C-10), 23.7 (C-11), 122.9 (C-12), 144.1 (C-13), 42.1 (C-14), 28.3 (C-15), 23.3 (C-16), 47.0 (C-17), 41.6 (C-18), 46.2 (C-19), 30.7 (C-20), 34.0 (C-21), 32.5 (C-22), 28.3 (C-23), 17.2 (C-24), 15.6 (C-25), 17.5 (C-26), 26.2 (C-27), 176.5 (C-28), 33.1 (C-29), 23.7 (C-30), 105.1 (3-*O*-Ara-C-1), 75.5 (3-*O*-Ara-C-2), 74.4 (3-*O*-Ara-C-3), 69.2 (3-*O*-Ara-C-4), 65.4 (3-*O*-

Ara-C-5), 101.4 (Rha-C-1), 71.9 (Rha-C-2), 83.0 (Rha-C-3), 72.9 (Rha-C-4), 69.6 (Rha-C-5), 18.5 (Rha-C-6), 107.1 (Xyl-C-1), 75.3 (Xyl-C-2), 76.2 (Xyl-C-3), 78.0 (Xyl-C-4), 64.9 (Xyl-C-5), 103.7 (Glc-C-1), 74.4 (Glc-C-2), 78.3 (Glc-C-3), 71.9 (Glc-C-4), 78.7 (Glc-C-5), 61.3 (Glc-C-6), 95.6 (28-*O*-Glc-C-1), 73.9 (28-*O*-Glc-C-2), 78.7 (28-*O*-Glc-C-3), 70.8 (28-*O*-Glc-C-4), 78.0 (28-*O*-Glc-C-5), 69.3 (28-*O*-Glc-C-6), 104.8 (Glc'-C-1), 75.1 (Glc'-C-2), 76.5 (Glc'-C-3), 78.7 (Glc'-C-4), 73.9 (Glc'-C-5), 61.3 (Glc'-C-6), 20.7 (-OAc), 170.8 (-C=O), 102.7 (Rha-C-1), 72.6 (Rha-C-2), 72.8 (Rha-C-3), 74.0 (Rha-C-4), 70.8 (Rha-C-5), 18.5 (Rha-C-6)。以上数据与文献报道一致^[8], 故鉴定化合物 **10** 为 3-*O*- β -D-吡喃葡萄糖基-(1 $\rightarrow$ 4)-*O*- β -D-吡喃木糖基 1-(1 $\rightarrow$ 3)-*O*- α -L-吡喃鼠李糖基-(1 $\rightarrow$ 2)-*O*- α -L-吡喃阿拉伯糖-齐墩果酸-28-*O*- α -L-吡喃鼠李糖基-(1 $\rightarrow$ 4)- β -D-吡喃葡萄糖基-(1 $\rightarrow$ 6)-*O*-6-*O*-乙酰基- β -D-吡喃葡萄糖酯苷。

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