类叶牡丹化学成分的研究

李国玉[1,2]，徐 娜[1]，刘晓燕[2]，武 震[3]，吕邵娃[1]，匡海学[1*]

1. 黑龙江中医药大学 教育部重点实验室，黑龙江 哈尔滨 150040
2. 哈尔滨医科大学药学院，黑龙江 哈尔滨 150081
3. 黑龙江省中医药管理局，黑龙江 哈尔滨 150030

摘 要：目的 对类叶牡丹 *Caulophyllum robustum* 根中化学成分进行研究。**方法** 利用反复硅胶柱色谱、中压柱色谱及半制备液相色谱等方法分离纯化，通过核磁共振谱、质谱等光谱数据鉴定化合物结构。**结果** 从类叶牡丹根中分离得到 10 个化合物，分别鉴定为刺囊酸-3-*O*-β-*D*-葡萄吡喃糖-(1→2)-α-*L*-吡喃阿拉伯糖苷（**1**）、3-*O*-α-*L*-吡喃阿拉伯糖-常春藤皂苷元-28-*O*-β-*D*-葡萄吡喃糖-(1→6)-β-*D*-吡喃葡萄糖苷（**2**）、HN-saponin H（**3**）、ciwujianosides A_1（**4**）、glycoside L-K_1（**5**）、3-*O*-β-*D*-吡喃葡萄糖-(1→3)-α-*L*-吡喃阿拉伯糖-常春藤皂苷元-28-*O*-α-*L*-吡喃鼠李糖-(1→4)-β-*D*-吡喃葡萄糖-(1→6)-β-*D*-吡喃葡萄糖苷（**6**）、leonticin F（**7**）、3-*O*-β-*D*-吡喃葡萄糖-(1→3) [β-*D*-吡喃葡萄糖-(1→2)]-α-*L*-吡喃阿拉伯糖-刺囊酸-28-*O*-α-*L*-吡喃鼠李糖-(1→4)-β-*D*-吡喃葡萄糖-(1→6)-β-*D*-吡喃葡萄糖苷（**8**）、leonticin A（**9**）、莫诺苷（**10**）。**结论** 化合物 **10** 是环烯醚萜类，其余化合物为皂苷类；化合物 **1**、**10** 首次从红毛七属植物中分离得到，化合物 **2**～**9** 首次从该植物中分离得到。

关键词：类叶牡丹；刺囊酸-3-*O*-β-*D*-葡萄吡喃糖-(1→2)-α-*L*-吡喃阿拉伯糖苷；3-*O*-α-*L*-吡喃阿拉伯糖-常春藤皂苷元-28-*O*-β-*D*-葡萄吡喃糖-(1→6)-β-*D*-吡喃葡萄糖苷；HN-saponin H；莫诺苷

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Saponin constituents from roots and rhizomes of *Caulophyllum robustum*

LI Guo-yu[1,2], XU Na[1], LIU Xiao-yan[2], WU Zhen[3], LV Shao-wa[1], KUANG Hai-xue[1]

1. Key Laboratory of Chinese Medicines, Ministry of Education, Heilongjiang University of Chinese Medicines, Harbin 150040, China
2. Pharmaceutical College, Harbin Medical University, Harbin 150081, China
3. Administration of Traditional Chinese Medicine of Heilongjiang, Harbin 150030, China

Abstract: Objective To separate the saponins from the roots and rhizomes of *Caulophyllum robustum* and determine their chemical structures. **Methods** The chemical constituents were isolated by repeated silica gel chromatography, medium pressure column chromatography, and semi-preparative liquid chromatography. Their structures were elucidated by the data of NMR and MS. **Results** Ten compounds were isolated from the roots and rhizomes of *C. robustum* and the structures of compounds **1**—**10** were identified as echinocystic acid-3-*O*-β-*D*-glucopyranosyl-(1→2)-α-*L*-arabinopyranoside (**1**), 3-*O*-α-*L*-arabinopyranosylhederagenin-28-*O*-β-*D*-glucopyranosyl-(1→6)-β-*D*-glucopyranoside (**2**), HN-saponin H (**3**), ciwujianosides A_1 (**4**), glycoside L-K_1 (**5**), 3-*O*-β-*D*-glucopyranosyl-(1→3)-α-*L*-arabinopyranosyl-hederagenin-28-*O*-α-*L*-rhamnopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→6)-β-*D*-glucopyranoside (**6**), leonticin F (**7**), 3-*O*-β-*D*-glucopyranosyl-(1→3) [β-*D*-glucopyranosyl-(1→2)] α-*L*-arabinopyranosyl-echinocystic acid-28-*O*-α-*L*-rhamnopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→6)-β-*D*-glucopyranoside (**8**), leonticin A (**9**), and morroniside (**10**). **Conclusion** Compound **10** is a iridoid. Compounds **1** and **10** are firstly isolated from the plants of *Caulophyllum* Maxim., compouds **2**—**9** are isolated from this plant for the first time.

Key words: roots and rhizomes of *Caulophyllum robustum*; echinocystic acid-3-*O*-β-*D*-glucopyranosyl-(1→2)-α-*L*-arabinopyranoside; 3-*O*-α-*L*-arabinopyranosy-hederagenin-28-*O*-β-*D*-glucopyranosyl-(1→6)-β-*D*-glucopyranosyl ester; HN-saponin H; morroniside

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作者简介：李国玉（1972—），男，博士，副教授，主要从事天然药物资源及药效物质基础研究。E-mail: leegy@163.com

***通讯作者** 匡海学，男，教授，主要从事中药基本理论及药效物质基础研究。E-mail: hxkuang@hotmail.com

类叶牡丹 *Caulophyllum robustum* Maxim. 是小檗科（Berberidaceae）红毛七属 *Caulophyllum* Maxim. 植物类叶牡丹的根及根茎，别名红毛七、葳严仙、红毛细辛等，可栽培。广泛分布于中国黑龙江、辽宁、吉林、山西、甘肃和四川等地，红毛七属现有 3 种植物，分别为主产于东北亚的类叶牡丹 *Caulophyllum robustum* Maxim.、主产东北美的兰籽类叶牡丹 *Caulophyllum thalictroi* Des (L.) Michx. (blue cohosh) 和大类叶牡丹 *Caulophyllum gianteum* Maxim.，前 2 种作为被民间广泛用于风湿性关节炎、胃腹疼痛、跌打损伤及妇科疾病等的治疗。在《全国中草药汇编》中记载该药具有理气止痛、祛风活血的功效。《中药大辞典》描述类叶牡丹性温，味辛、苦，具有理气止痛及祛风活血功效的。根据文献报道[1]，该植物主要含三萜皂苷和生物碱类成分。本实验对类叶牡丹根的化学成分进行研究，共分离得到 10 个化合物，分别鉴定为刺囊酸-3-*O*-β-*D*-葡萄吡喃糖-(1→2)-α-*L*-吡喃阿拉伯糖苷 [echinocystic acid-3-*O*-β-*D*-glucopyranosyl-(1 → 2)-α-*L*-arabinopyranoside，**1**）、3-*O*-α-*L*-吡喃阿拉伯糖-常春藤皂苷元-28-*O*-β-*D*-葡萄吡喃糖-(1→6)-β-*D*-吡喃葡萄糖苷 [3-*O*-α-*L*-arabinopyranosyl-hederagenin-28-*O*-β-*D*-glucopyranosyl-(1→6)-β-*D*-glucopyranoside，**2**]、HN-saponin H（**3**）、ciwujianosides A_1（**4**）、glycoside L-K_1（**5**）、3-*O*-β-*D*-吡喃葡萄糖-(1→3)-α-*L*-吡喃阿拉伯糖-常春藤皂苷元-28-*O*-α-*L*-吡喃鼠李糖-(1→4)-β-*D*-吡喃葡萄糖-(1→6)-β-*D*-吡喃葡萄糖苷 [3-*O*-β-*D*-glucopyranosyl-(1→3)-α-*L*-arabinopyranosyl-hederagenin-28-*O*-α-*L*-rhamnopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→6)-β-*D*-glucopyranoside，**6**]、leonticin F（**7**）、3-*O*-β-*D*-吡喃葡萄糖-(1→3) [β-*D*-吡喃葡萄糖-(1→2)]-α-*L*-吡喃阿拉伯糖-刺囊酸-28-*O*-α-*L*-吡喃鼠李糖-(1→4)-β-*D*-吡喃葡萄糖-(1→6)-β-*D*-吡喃葡萄糖苷（3-*O*-β-*D*-glucopyranosyl-(1→3) [β-*D*-glucopyranosyl-(1 → 2)] α-*L*-arabinopyranosyl-echinocystic acid-28-*O*-α-*L*-rhamnopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→6)-β-*D*-glucopyranosyl ester，**8**）、leonticin A（**9**）、莫诺苷（morroniside，**10**）。其中，化合物 **1**、**10** 为首次从红毛七属植物中分离得到，化合物 **2**～**9** 首次从该植物中分离得到。

1 仪器与材料

INOVA-400/Bruker-400 超导核磁共振光谱仪（德国布鲁克公司）；MAT LCQ 质谱仪（美国 Finnigan 公司）；Delta-600-2487 制备高效液相色谱仪（Waters 公司）；Senshu Pak 半制备型色谱柱（250 mm×10 mm，10 μm）；制备色谱柱（300 mm×20 mm，10 μm，大连依利特公司）；柱色谱硅胶（青岛海洋化工厂）；薄层色谱用硅胶板及 RP-18 反相板（德国 Merck）；柱色谱反相 ODS（YMC 公司）；AB-8 大孔吸附树脂（南开大学化工厂）；其余试剂为分析纯（天津试剂一厂）。

本实验所用类叶牡丹采自黑龙江省绥棱林业局，经黑龙江中医药大学王振月教授鉴定为类叶牡丹 *Caulophyllum robustum* Maxim. 的干燥根及根茎。样品标本（ZYYH-No. 20060809）保存于黑龙江中医药大学药学院。

2 提取与分离

类叶牡丹干燥粉末 10 kg，用 70%乙醇回流提取后，得到乙醇提取物，将此提取物经大孔吸附树脂柱色谱，依次用水及 70%、95%乙醇洗脱，分别得到各自洗脱物。将 70%乙醇洗脱部分取出 150 g 溶于水，分别用醋酸乙酯和水饱和正丁醇萃取，取正丁醇提取物 118 g，将正丁醇提取物（50 g）以硅胶柱色谱进行分离，二氯甲烷-甲醇-水梯度洗脱得 5 个部分 Fr. 1～5，其中 Fr. 1（二氯甲烷-甲醇 10∶1 洗脱部分）得到化合物 **1**（20.3 mg）、**10**（7.2 mg）。Fr. 2（二氯甲烷-甲醇-水 4∶1∶0.1 洗脱部分）经反相开放 ODS 柱分离和 HPLC 制备得到化合物 **2**（5.6 mg）、**3**（6.2 mg）。Fr. 4（二氯甲烷-甲醇-水 65∶35∶10 洗脱部分）经反相开放 ODS 和 HPLC 制备得到化合物 **4**（7.7 mg）、**5**（5.8 mg）、**6**（5.5 mg）。Fr.5（二氯甲烷-甲醇-水 1∶1∶0.3 洗脱部分）经 ODS 和 HPLC 制备得到化合物 **7**（6.3 mg）、**8**（5.3 mg）、**9**（4.7 mg）。

3 结构鉴定

化合物 **1**：白色粉末（甲醇），分子式为 $C_{11}H_{66}O_{15}$，Liebermann-Burchard 和 Molish 反应呈阳性。ESI-MS *m*/*z*: 789.6 $[M+Na]^+$, 1 555.4 $[2M+Na]^+$。^{1}H-NMR (400 MHz, C_5D_5N) *δ*: 3.21 (1H, dd, *J* = 11.6, 4.4 Hz, H-3), 0.73 (1H, brd, *J* = 11.6 Hz, H-5), 5.63 (1H, brs, H-12), 5.23 (1H, brs, H-16), 3.61 (1H, dd, *J* = 13.7, 4.4 Hz, H-18), 1.19 (3H, s, H-23), 1.02 (3H, s, H-24), 0.86 (3H, s, H-25), 1.00 (3H, s, H-26), 1.82 (3H, s, H-27), 1.05 (3H, s, H-29), 1.17 (3H, s, H-30), 4.94 (1H, d, *J* = 5.6 Hz, Ara H-1), 5.16 (1H, d, *J* = 7.6 Hz, Glc H-1)；^{13}C-NMR (100 MHz, C_5D_5N) *δ*: 38.8 (C-1), 26.5 (C-2), 88.9 (C-3), 39.5

(C-4), 55.9 (C-5), 18.5 (C-6), 33.5 (C-7), 39.9 (C-8), 47.2 (C-9), 37.0 (C-10), 23.8 (C-11), 122.3 (C-12), 145.2 (C-13), 42.1 (C-14), 36.2 (C-15), 74.8 (C-16), 48.9 (C-17), 41.5 (C-18), 47.3 (C-19), 31.1 (C-20), 36.1 (C-21), 32.8 (C-22), 28.2 (C-23), 16.8 (C-24), 15.6 (C-25), 17.5 (C-26), 27.2 (C-27), 180.3 (C-28), 33.4 (C-29), 24.8 (C-30); Ara: 104.8 (C-1), 80.9 (C-2), 73.4 (C-3), 68.3 (C-4), 64.9 (C-5); Glc: 105.9 (C-1), 76.4 (C-2), 78.2 (C-3), 71.5 (C-4), 78.2 (C-5), 62.5 (C-6)。经与文献数据比较[2]，鉴定化合物 **1** 为刺囊酸-3-*O*-β-*D*-葡萄吡喃糖-(1→2)-α-*L*-阿拉伯吡喃糖苷。

化合物 **2**：白色粉末（甲醇），分子式为 $C_{47}H_{76}O_{18}$，Liebermann-Burchard 和 Molish 反应呈阳性。ESI-MS *m*/*z*: 951.3 $[M+Na]^+$。^{1}H-NMR (400 MHz, C_5D_5N) δ: 5.46 (1H, brs, H-12), 3.22 (1H, brd, J = 13.2 Hz, H-18), 1.02 (3H, s, H-24), 0.98 (3H, s, H-25), 1.17 (3H, s, H-26), 1.21 (3H, s, H-27), 0.90 (3H, s, H-29), 0.90 (3H, s, H-30), 5.03 (1H, d, J = 6.4 Hz, Ara H-1), 6.32 (1H, d, J = 8.0 Hz, Glc H-1′), 5.09 (1H, d, J = 7.2 Hz, Glc H-1″)；^{13}C-NMR (100 MHz, C_5D_5N) δ: 37.4 (C-1), 24.7 (C-2), 80.5 (C-3), 42.1 (C-4), 46.4 (C-5), 16.8 (C-6), 31.4 (C-7), 38.5 (C-8), 46.8 (C-9), 35.5 (C-10), 22.5 (C-11), 121.5 (C-12), 142.7 (C-13), 40.7 (C-14), 26.9 (C-15), 21.9 (C-16), 45.6 (C-17), 40.2 (C-18), 44.8 (C-19), 29.3 (C-20), 32.5 (C-21), 31.1 (C-22), 63.0 (C-23), 12.2 (C-24), 14.8 (C-25), 16.2 (C-26), 24.6 (C-27), 175.1 (C-28), 31.7 (C-29), 22.3 (C-30); Ara: 105.3 (C-1), 71.7 (C-2), 73.3 (C-3), 68.3 (C-4), 65.6 (C-5); 28-*O*-inner Glc: 94.3 (C-1′), 72.5 (C-2′), 76.9 (C-3′), 69.5 (C-4′), 76.6 (C-5′), 67.9 (C-6′); terminal Glc: 103.9 (C-1″), 73.8 (C-2″), 77.1 (C-3″), 70.1 (C-4″), 77.3 (C-5″), 61.2 (C-6″)。经与文献数据比较[3]，鉴定化合物 **2** 为 3-*O*-α-*L*-阿拉伯吡喃糖-常春藤皂苷元-28-*O*-β-*D*-葡萄吡喃糖-(1→6)-β-*D*-葡萄吡喃糖苷。

化合物 **3**：白色粉末（甲醇），分子式为 $C_{48}H_{78}O_{18}$，Liebermann-Burchard 和 Molish 反应呈阳性。ESI-MS *m*/*z*: 941.3 $[M-H]^-$。^{1}H-NMR (400 MHz, C_5D_5N) δ: 5.43 (1H, brs, H-12), 1.08 (3H, s, H-24), 1.02 (3H, s, H-25), 1.16 (3H, s, H-26), 1.19 (3H, s, H-27), 0.87 (3H, s, H-29), 0.89 (3H, s, H-30), 1.72 (3H, d, J = 6.2 Hz, Rha-6-CH_3)；^{13}C-NMR (100 MHz, C_5D_5N) δ: 38.8 (C-1), 27.7 (C-2), 73.3 (C-3), 42.9 (C-4), 48.2 (C-5), 18.6 (C-6), 32.9 (C-7), 39.9 (C-8), 48.5 (C-9), 37.2 (C-10), 23.9 (C-11), 122.8 (C-12), 144.2 (C-13), 42.2 (C-14), 28.3 (C-15), 23.4 (C-16), 47.0 (C-17), 41.7 (C-18), 46.2 (C-19), 30.8 (C-20), 34.0 (C-21), 32.5 (C-22), 67.8 (C-23), 13.2 (C-24), 16.1 (C-25), 17.6 (C-26), 26.1 (C-27), 176.6 (C-28), 33.1 (C-29), 23.7 (C-30); 28-*O*-inner Glc: 95.7 (C-1′), 74.0 (C-2′), 78.8 (C-3′), 70.9 (C-4′), 78.1 (C-5′), 69.2 (C-6′); 6′-Glc: 104.9 (C-1″), 75.4 (C-2″), 76.5 (C-3″), 78.2 (C-4″), 77.2 (C-5″), 61.3 (C-6″); Rha: 102.8 (C-1), 72.6 (C-2), 72.8 (C-3), 73.9 (C-4), 70.3 (C-5), 18.6 (C-6)。经与文献数据比较[4]，鉴定化合物 **3** 为 HN-saponin H。

化合物 **4**：白色粉末（甲醇），分子式为 $C_{59}H_{96}O_{25}$，Liebermann-Burchard 和 Molish 反应呈阳性。ESI-MS *m*/*z*: 1 243.3 $[M+Na]^+$。^{1}H-NMR (400 MHz, CD_3OD) δ: 3.17 (1H, overlap, H-3), 0.69 (1H, brd, J = 11.2 Hz, H-5), 1.58 (1H, t, J = 8.6 Hz, H-9), 5.40 (1H, brs, H-12), 3.17 (1H, o, H-18), 1.20 (3H, s, H-23), 1.03 (3H, s, H-24), 0.86 (3H, s, H-25), 1.08 (3H, s, H-26), 1.21 (3H, s, H-27), 0.88 (3H, s, H-29), 0.87 (3H, s, H-30), 4.94 (1H, d, J = 5.6 Hz, Ara H-1), 5.17 (1H, d, J = 7.6 Hz, Glc H-1), 6.23 (1H, d, J = 8.0 Hz, Glc H-1′), 4.98 (1H, d, J = 7.6 Hz, Glc H-1″), 5.84 (1H, s, Rha H-1), 1.69 (3H, d, J = 6.0 Hz, Rha 6-CH_3), ^{13}C-NMR (100 MHz, C_5D_5N) δ: 39.9 (C-1), 27.6 (C-2), 90.0 (C-3), 40.6 (C-4), 56.9 (C-5), 19.7 (C-6), 34.3 (C-7), 41.0 (C-8), 49.2 (C-9), 38.1 (C-10), 24.9 (C-11), 124.0 (C-12), 145.3 (C-13), 43.2 (C-14), 29.3 (C-15), 24.5 (C-16), 48.2 (C-17), 42.8 (C-18), 47.4 (C-19), 31.9 (C-20), 35.1 (C-21), 33.6 (C-22), 29.3 (C-23), 17.9 (C-24), 16.7 (C-25), 18.6 (C-26), 27.2 (C-27), 177.7 (C-28), 34.3 (C-29), 24.8 (C-30); Ara: 105.9 (C-1), 82.0 (C-2), 74.6 (C-3), 69.4 (C-4), 66.1 (C-5); Glc:107.1 (C-1), 77.5 (C-2), 79.3 (C-3), 72.7 (C-4), 79.3 (C-5), 63.7 (C-6); 28-*O*-inner Glc: 96.8 (C-1′), 75.1 (C-2′), 79.8 (C-3′), 71.9 (C-4′), 79.1 (C-5′), 70.3 (C-6′); 6′-Glc: 105.9 (C-1″), 76.4 (C-2″), 77.6 (C-3″), 79.3 (C-4″), 78.3 (C-5″), 62.4 (C-6″); Rha: 103.8 (C-1), 73.7 (C-2), 73.9 (C-3), 75.0 (C-4), 71.4 (C-5), 19.7 (C-6)。经与文献数据比较[5]，鉴定化合物 **4** 为 ciwujianosides A_1。

化合物 **5**：白色粉末（甲醇），分子式为

$C_{59}H_{96}O_{25}$，Liebermann-Burchard 和 Molish 反应均呈阳性。ESI-MS *m/z*: 1 243.3 $[M+Na]^+$。^{1}H-NMR (400 MHz, CD_3OD) δ: 3.33 (1H, dd, *J* = 11.6, 4.0 Hz, H-3), 0.79 (1H, brd, *J* = 11.6 Hz, H-5), 1.62 (1H, t, *J* = 8.8 Hz, H-9), 5.40 (1H, brs, H-12), 3.17 (1H, dd, *J* = 13.4, 3.4 Hz, H-18), 1.29 (3H, s, H-23), 0.97 (3H, s, H-24), 0.86 (3H, s, H-25), 1.08 (3H, s, H-26), 1.24 (3H, s, H-27), 0.88 (3H, s, H-29), 0.88 (3H, s, H-30), 4.74 (1H, d, *J* = 7.2 Hz, Ara H-1), 5.39 (1H, d, *J* = 7.9 Hz, Glc H-1), 6.24 (1H, d, *J* = 8.1 Hz, Glc H-1′), 4.98 (1H, d, *J* = 8.0 Hz, Glc H-1″), 5.85 (1H, s, Rha H-1), 1.69 (3H, d, *J* = 6.0 Hz, Rha 6-CH_3)；^{13}C-NMR (100 MHz, C_5D_5N) δ: 38.8 (C-1), 26.7 (C-2), 88.7 (C-3), 39.6 (C-4), 55.9 (C-5), 18.5 (C-6), 33.1 (C-7), 39.9 (C-8), 48.1 (C-9), 37.0 (C-10), 23.8 (C-11), 122.9 (C-12), 144.1 (C-13), 42.1 (C-14), 28.3 (C-15), 23.4 (C-16), 47.1 (C-17), 41.7 (C-18), 46.2 (C-19), 30.8 (C-20), 34.0 (C-21), 32.5 (C-22), 28.1 (C-23), 16.9 (C-24), 15.6 (C-25), 17.5 (C-26), 26.1 (C-27), 176.5 (C-28), 33.1 (C-29), 23.7 (C-30); Ara: 107.4 (C-1), 71.6 (C-2), 84.1 (C-3), 69.3 (C-4), 66.9 (C-5); Glc: 106.3 (C-1), 75.7 (C-2), 78.3 (C-3), 71.9 (C-4), 78.4 (C-5), 62.7 (C-6); 28-*O*-inner Glc: 95.7 (C-1′), 73.9 (C-2′), 78.7 (C-3′), 70.8 (C-4′), 78.0 (C-5′), 69.2 (C-6′); 6′-Glc: 104.8 (C-1″), 75.3 (C-2″), 76.5 (C-3″), 78.7 (C-4″), 77.2 (C-5″), 61.3 (C-6″); Rha: 102.8 (C-1), 72.6 (C-2), 72.8 (C-3), 74.0 (C-4), 70.3 (C-5), 18.5 (C-6)。经与文献数据比较[6]，鉴定化合物 **5** 为 glycoside L-K_1。

化合物 **6**：白色粉末（甲醇-醋酸乙酯），分子式为 $C_{59}H_{96}O_{27}$，Liebermann-Burchard 和 Molish 反应呈阳性。ESI-MS *m/z*: 1 259.2 $[M+Na]^+$, 1 235.0 $[M-H]^-$。^{1}H-NMR (400 MHz, C_5D_5N) δ: 5.39 (1H, brs, H-12), 3.14 (1H, dd, *J* = 13.2, 3.8 Hz, H-18), 0.92 (3H, s, H-24), 0.95 (3H, s, H-25), 1.09 (3H, s, H-26), 1.17 (3H, s, H-27), 0.85 (3H, s, H-29), 0.86 (3H, s, H-30), 4.96 (1H, d, *J* = 6.5 Hz, Ara H-1), 5.30 (1H, d, *J* = 7.9 Hz, Glc H-1), 6.22 (1H, d, *J* = 8.1 Hz, Glc H-1′), 4.98 (1H, d, *J* = 7.6 Hz, Glc H-1″), 5.84 (1H, s, Rha H-1), 1.68 (3H, d, *J* = 6.0 Hz, Rha 6-CH_3)；^{13}C-NMR (100 Hz, C_5D_5N) δ: 40.3 (C-1), 22.7 (C-2), 83.3 (C-3), 45.0 (C-4), 49.0 (C-5), 19.6 (C-6), 34.0 (C-7), 41.4 (C-8), 49.7 (C-9), 38.4 (C-10), 25.4 (C-11), 124.4 (C-12), 145.6 (C-13), 43.6 (C-14), 29.8 (C-15), 24.8 (C-16), 48.5 (C-17), 43.1 (C-18), 47.7 (C-19), 32.2 (C-20), 35.4 (C-21), 34.3 (C-22), 65.7 (C-23), 15.2 (C-24), 17.7 (C-25), 19.1 (C-26), 27.6 (C-27), 178.1 (C-28), 34.6 (C-29), 25.2 (C-30); Ara: 108.0 (C-1), 73.0 (C-2), 85.7 (C-3), 70.8 (C-4), 68.5 (C-5); Glc: 107.7 (C-1), 77.2 (C-2), 79.7 (C-3), 73.5 (C-4), 80.2 (C-5), 64.2 (C-6); 28-*O*-inner Glc: 97.1 (C-1′), 75.3 (C-2′), 80.2 (C-3′), 72.3 (C-4′), 79.5 (C-5′), 70.6 (C-6′); 6′-Glc: 106.3 (C-1″), 76.8 (C-2″), 78.0 (C-3″), 79.8 (C-4″), 78.6 (C-5″), 62.7 (C-6″); Rha: 104.2 (C-1), 74.1 (C-2), 74.2 (C-3), 75.5 (C-4), 71.8 (C-5), 20.0 (C-6)。经与文献数据比较[7]，鉴定化合物 **6** 为 3-*O*-β-*D*-葡萄吡喃糖-(1→3)-α-*L*-阿拉伯吡喃糖-常春藤皂苷元-28-*O*-α-*L*-鼠李吡喃糖-(1→4)-β-*D*-葡萄吡喃糖-(1→6)-β-*D*-葡萄吡喃糖苷。

化合物 **7**：白色粉末（甲醇），分子式为 $C_{65}H_{106}O_{32}$，Liebermann-Burchard 和 Molish 反应呈阳性。ESI-MS *m/z*: 1 421.2 $[M+Na]^+$, 1 397.0 $[M-H]^-$。^{1}H-NMR (400 MHz, C_5D_5N) δ: 5.38 (1H, brs, H-12), 3.14 (1H, dd, *J* = 13.2, 4.0 Hz, H-18), 1.06 (3H, s, H-24), 0.92 (3H, s, H-25), 1.08 (3H, s, H-26), 1.14 (3H, s, H-27), 0.85 (3H, s, H-29), 0.86 (3H, s, H-30), 5.00 (1H, d, *J* = 5.6 Hz, Ara H-1), 5.52 (1H, d, *J* = 7.7 Hz, Glc H-1), 5.25 (1H, d, *J* = 7.7 Hz, Glc H-1‴), 6.23 (1H, d, *J* = 7.9 Hz, Glc H-1′), 4.98 (1H, d, *J* = 8.4 Hz, Glc H-1″), 5.85 (1H, s, Rha H-1), 1.69 (3H, d, *J* = 6.0 Hz, Rha 6-CH_3)；^{13}C-NMR (100 Hz, C_5D_5N) δ: 38.8 (C-1), 26.0 (C-2), 82.4 (C-3), 43.6 (C-4), 47.9 (C-5), 18.2 (C-6), 32.8 (C-7), 39.9 (C-8), 48.2 (C-9), 36.9 (C-10), 23.8 (C-11), 123.0 (C-12), 144.1 (C-13), 42.1 (C-14), 28.3 (C-15), 23.4 (C-16), 47.0 (C-17), 41.7 (C-18), 46.2 (C-19), 30.7 (C-20), 33.9 (C-21), 32.5 (C-22), 64.7 (C-23), 13.4 (C-24), 16.2 (C-25), 17.5 (C-26), 26.0 (C-27), 176.5 (C-28), 33.1 (C-29), 23.7 (C-30); Ara: 104.3 (C-1), 77.6 (C-2), 83.5 (C-3), 68.6 (C-4), 65.8 (C-5); Glc (2-position of Ara): 104.3 (C-1), 76.1 (C-2), 78.5 (C-3), 72.0 (C-4), 77.4 (C-5), 62.9 (C-6); Glc (3-position of Ara): 104.8 (C-1′), 75.2 (C-2′), 78.7 (C-3′), 71.5 (C-4′), 78.3 (C-5′), 62.5 (C-6′); 28-*O*-inner Glc: 95.6 (C-1″), 74.0 (C-2″), 78.7 (C-3″), 70.9 (C-4″), 78.0 (C-5″), 69.2 (C-6″); 6″-Glc: 104.9 (C-1‴), 75.3 (C-2‴), 76.5 (C-3‴), 78.3 (C-4‴), 77.2

(C-5″), 61.3 (C-6″); Rha: 102.7 (C-1), 72.6 (C-2), 72.8 (C-3), 73.9 (C-4), 70.3 (C-5), 18.5 (C-6)。经与文献数据比较[8]，鉴定化合物 **7** 为 leonticin F。

化合物 **8**：白色粉末（甲醇-醋酸乙酯），分子式为 $C_{65}H_{106}O_{32}$，Liebermann-Burchard 和 Molish 反应呈阳性。ESI-MS *m/z*: 1 421.2 $[M+Na]^+$。^{1}H-NMR (400 MHz, C_5D_5N) *δ*: 3.26 (1H, dd, *J* = 11.2, 3.4 Hz, H-3), 0.78 (1H, brd, *J* = 11.6 Hz, H-5), 5.59 (brs, H-12), 5.30 (1H, brs, H-16), 3.50 (1H, dd, *J* = 14.0, 2.9 Hz, H-18), 1.24 (3H, s, H-23), 1.09 (3H, s, H-24), 0.89 (3H, s, H-25), 1.12 (3H, s, H-26), 1.82 (3H, s, H-27), 0.99 (3H, s, H-29), 1.05 (3H, s, H-30), 4.80 (1H, d, *J* = 6.7 Hz, Ara H-1), 5.52 (1H, d, *J* = 7.7 Hz, Glc H-1), 5.31 (1H, d, *J* = 7.6 Hz, Glc H-1‴), 6.25 (1H, d, *J* = 8.1 Hz, Glc H-1′), 4.98 (1H, d, *J* = 8.0 Hz, Glc H-1″), 5.86 (1H, s, Rha H-1), 1.71 (3H, d, *J* = 6.1 Hz, Rha 6-CH_3)；^{13}C-NMR (100 MHz, C_5D_5N) *δ*: 38.9 (C-1), 26.7 (C-2), 89.0 (C-3), 39.7 (C-4), 55.9 (C-5), 18.5 (C-6), 33.5 (C-7), 40.1 (C-8), 47.2 (C-9), 37.0 (C-10), 23.8 (C-11), 122.7 (C-12), 144.4 (C-13), 42.1 (C-14), 36.1 (C-15), 74.3 (C-16), 49.2 (C-17), 41.2 (C-18), 47.2 (C-19), 30.8 (C-20), 35.9 (C-21), 32.2 (C-22), 28.0 (C-23), 16.8 (C-24), 15.7 (C-25), 17.6 (C-26), 27.2 (C-27), 176.0 (C-28), 33.2 (C-29), 24.6 (H-30); Ara: 105.4 (C-1), 77.5 (C-2), 82.9 (C-3), 68.8 (C-4), 65.9 (C-5); Glc (2-position of Ara): 104.4 (C-1), 76.1 (C-2), 78.3 (C-3), 72.3 (C-4), 77.4 (C-5), 63.2 (C-6); Glc (3-position of Ara): 105.0 (C-1′), 75.3 (C-2′), 78.6 (C-3′), 71.5 (C-4′), 78.2 (C-5′), 62.5 (C-6′); 28-*O*-inner Glc: 95.8 (C-1″), 73.9 (C-2″), 78.7 (C-3″), 70.8 (C-4″), 78.0 (C-5″), 69.2 (C-6″); 6″-Glc: 105.0 (C-1‴), 75.3 (C-2‴), 76.5 (C-3‴), 78.5 (C-4‴), 77.1 (C-5‴), 61.4 (C-6‴); Rha: 102.7 (C-1), 72.6 (C-2), 72.7 (C-3), 73.9 (C-4), 70.3 (C-5), 18.5 (C-6)。经与文献数据比较[9]，鉴定化合物 **8** 为 3-*O*-β-*D*-葡萄吡喃糖-(1→3) [β-*D*-葡萄吡喃糖-(1→2)]-α-*L*-阿拉伯吡喃糖-刺囊酸-28-*O*-α-*L*-鼠李吡喃糖-(1→4)-β-*D*-葡萄吡喃糖-(1→6)-β-*D*-葡萄吡喃糖苷。

化合物 **9**：白色粉末（甲醇-醋酸乙酯），分子式为 $C_{77}H_{126}O_{41}$，Liebermann-Burchard 和 Molish 反应呈阳性。ESI-MS *m/z*: 1 749.7 $[M+Na]^+$。^{1}H-NMR (400 MHz, C_5D_5N) *δ*: 5.41 (1H, brs, H-12), 3.17 (1H, brd, *J* = 12.3 Hz, H-18), 1.05 (3H, s, H-24), 0.97 (3H, s, H-25), 1.13 (3H, s, H-26), 1.16 (3H, s, H-27), 0.86 (3H, s, H-29), 0.87 (3H, s, H-30), 5.20 (1H, d, *J* = 5.7 Hz, Ara H-1), 5.22 (1H, d, *J* = 7.6 Hz, Glc H-1), 6.26 (1H, d, *J* = 8.0 Hz, Glc H-1′), 4.99 (1H, d, *J* = 7.5 Hz, Glc H-1″), 5.88 (1H, brs, Rha H-1), 1.85 (1H, d, *J* = 6.1 Hz, Rha H-6), 5.23 (1H, d, *J* = 7.5 Hz, Glc H-1‴), 5.01 (1H, d, *J* = 7.8 Hz, Glc H-1⁗), 5.88 (1H, brs, Rha H-1′), 1.73 (1H, d, *J* = 6.1 Hz, Rha H-6′)；^{13}C-NMR (100 MHz, C_5D_5N) *δ*: 38.8 (C-1), 26.0 (C-2), 82.1 (C-3), 43.5 (C-4), 47.8 (C-5), 18.2 (C-6), 32.7 (C-7), 39.9 (C-8), 48.1 (C-9), 36.9 (C-10), 23.8 (C-11), 122.9 (C-12), 144.1 (C-13), 42.1 (C-14), 28.3 (C-15), 23.3 (C-16), 46.9 (C-17), 41.6 (C-18), 46.2 (C-19), 30.7 (C-20), 33.9 (C-21), 32.5 (C-22), 64.8 (C-23), 13.4 (C-24), 16.2 (C-25), 17.5 (C-26), 26.0 (C-27), 176.5 (C-28), 33.1 (C-29), 23.7 (C-30); Ara: 103.9 (C-1), 81.3 (C-2), 74.0 (C-3), 68.4 (C-4), 65.1 (C-5); Glc: 105.9 (C-1), 76.3 (C-2), 78.0 (C-3), 71.4 (C-4), 78.2 (C-5), 62.5 (C-6); 28-*O*-inner Glc: 95.6 (C-1′), 73.9 (C-2′), 78.5 (C-3′), 70.7 (C-4′), 77.2 (GC-5′), 69.2 (C-6′); 6′-Glc: 104.9 (C-1″), 75.5 (C-2″), 76.5 (C-3″), 78.7 (C-4″), 77.2 (C-5″), 61.4 (C-6″); 4″-Rha: 102.0 (C-1), 72.1 (C-2), 72.6 (C-3), 84.7 (C-4), 68.4 (C-5), 18.6 (C-6); Glc (4-position of Ara): 106.2 (C-1‴), 76.2 (C-2‴), 78.3 (C-3‴), 71.2 (C-4‴), 77.2 (C-5‴), 69.9 (C-6‴); 6‴-Glc: 105.3 (C-1⁗), 75.4 (C-2⁗), 76.4 (C-3⁗), 78.0 (C-4⁗), 77.2 (C-5⁗), 61.2 (C-6⁗); 4⁗-Rha: 102.6 (C-1′), 72.7 (C-2′), 72.8 (C-3′), 73.7 (C-4′), 70.3 (C-5′), 18.5 (C-6′)。经与文献数据比较[10]，鉴定化合物 **9** 为 leonticin A。

化合物 **10**：白色粉末（甲醇），分子式为 $C_{17}H_{26}O_{11}$，Molish 反应呈阳性。ESI-MS *m/z*: 429.3 $[M+Na]^+$, 405.5 $[M-H]^-$。^{1}H-NMR (400 MHz CD_3OD) *δ*: 5.82 (1H, d, *J* = 9.2 Hz, H-1), 7.51 (1H, s, H-3), 2.82 (1H, dt, *J* = 13.0, 4.4 Hz, H-5), 2.02 (1H, ddd, *J* = 13.0, 4.4, 2.2 Hz, H-6), 1.17 (1H, ddd, *J* = 13.0, 9.6 Hz, H-6), 4.80 (1H, dd, *J* = 2.2, 9.6 Hz, H-7) 3.95 (1H, dq, *J* = 6.8, 2.0 Hz, H-8), 1.76 (1H, ddd, *J* = 9.2, 4.8, 2.0 Hz, H-9), 1.38 (3H, d, *J* = 6.8 Hz, H-10), 3.68 (3H, s, H-12), 4.77 (1H, d, *J* = 8.0 Hz, Glc H-1)；^{13}C-NMR (100 MHz, CD_3OD) *δ*: 95.9 (C-1), 154.5 (C-3), 110.9 (C-4), 32.0 (C-5), 37.3 (C-6), 97.1 (C-7), 74.2 (C-8), 39.9 (C-9), 19.9 (C-10), 168.7 (C-11), 51.8

(C-12)；Glc: 100.1 (C-1), 75.1 (C-2), 77.9 (C-3), 71.7 (C-4), 78.5 (C-5), 62.8 (C-6)。以上数据与文献报道一致[11]，故鉴定化合物 **10** 为莫诺苷。

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