

贵州苗药吉祥草中皂苷类化学成分研究

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摘要: 目的 研究贵州苗药吉祥草 *Reineckia carnea* 中的皂苷类成分。方法 用95%乙醇提取, 萃取后利用常规硅胶柱、大孔树脂、ODS C₁₈、Sephadex LH-20及Pre-HPLC等进行分离纯化, 通过理化性质、HR-ESI-MS和核磁共振谱进行结构鉴定。结果 从吉祥草的正丁醇部位分离得到10个皂苷类化合物, 分别鉴定为(1 β ,3 β ,16 β ,22 S)-cholest-5-ene-1,3,16,22-tetrol-1,16-di-(β -D-glucopyranoside)(**1**)、(1 β ,3 β ,16 β ,22 S)-cholest-5-ene-1,3,16,22-tetrol-1-[O- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- β -D-glucopyranoside]-16-(β -D-glucopyranoside)(**2**)、(20 S ,22 R)-spirost-25(27)-en-1 β ,3 β ,4 β ,5 β -tetraol-5-O- β -D-glucopyranoside(**3**)、kitigenin 5-O- β -D-glucopyranoside(**4**)、蜘蛛抱蛋苷A(**5**)、(17,20- S -trans)-5 β -pregn-16-en-1 β ,3 β -diol-20-one-1-O- β -D-xylopyranosyl-(1 $\rightarrow$ 2)-[α -L-rhamnopyranosyl]-3-O- α -L-rhamnopyranoside(**6**)、薯蓣皂苷元-3-O- β -D-吡喃葡萄糖苷(**7**)、麦冬皂苷T(**8**)、prosaikogenin D(**9**)、柴胡皂苷b₂(**10**)。结论 化合物**3**、**5**、**8**~**10**均为首次从吉祥草中分离得到, 为进一步阐明和开发吉祥草中皂苷类成分提供了一定的参考。

关键词: 吉祥草; 皂苷; 蜘蛛抱蛋苷A; 麦冬皂苷T; 柴胡次皂苷D; 柴胡皂苷b₂

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Study on saponins from *Reineckia carnea* belongs to Guizhou Miao medicineXU Xu¹, WU Bei², LI Yan¹, ZHAN Yan-zhi¹, WEN Quan¹, TAN Ting¹, FENG Yu-lin¹, ZHONG Guo-yue¹, YANG Shi-lin³

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Abstract: Objective To study the saponins from *Reineckia carnea* of Guizhou Miao medicine. **Methods** The chemical constituents from 95% EtOH extract were isolated and purified by repeated silica gel column chromatography, macroporous resin, ODS C₁₈, Sephadex LH-20 gel column chromatography, and Pre-HPLC, and their structures were identified on the basis of physical and chemical properties, HR-ESI-MS and NMR spectral analysis. **Results** Ten compounds were isolated and identified as (1 β ,3 β ,16 β ,22 S)-cholest-5-ene-1,3,16,22-tetrol-1,16-di-(β -D-glucopyranoside)(**1**), (1 β ,3 β ,16 β ,22 S)-cholest-5-ene-1,3,16,22-tetrol-1-[O- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- β -D-glucopyranoside]-16-(β -D-glucopyranoside)(**2**), (20 S ,22 R)-spirost-25(27)-en-1 β ,3 β ,4 β ,5 β -tetraol-5-O- β -D-glucopyranoside(**3**), kitigenin 5-O- β -D-glucopyranoside(**4**), aspidistrin A(**5**), (17,20- S -trans)-5 β -pregn-16-en-1 β ,3 β -diol-20-one-1-O- β -D-xylopyranosyl-(1 $\rightarrow$ 2)-[α -L-rhamnopyranosyl]-3-O- α -L-rhamnopyranoside(**6**), diosgenin-3-O- β -D-glucopyranoside(**7**), ophiopogonin T(**8**), prosaikogenin D(**9**), and saikosaponin b₂(**10**). **Conclusion** Compounds **3**, **5**, **8**, **9**, and **10** are isolated from this plant for the first time, which provided some reference for further elucidation and development of saponins from *R. carnea*.

Key words: *Reineckia carnea* (Andr.) Kunth; saponins; aspidistrin A; ophiopogonin T; prosaikogenin D; saikosaponin b₂

吉祥草为百合科植物吉祥草 *Reineckia carnea* (Andr.) Kunth 的全草, 为贵州省道地药材, 是我国西南苗族地区常用的传统草药之一, 属于苗药中比较重要的品种, 在贵州地区别名为观音草、小叶万

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年青等^[1-2]。在地方收录为全草入药,能润肺止咳、平喘、祛风解毒。可用于治疗肺结核咳嗽,临床上可用于慢性支气管炎、哮喘、风湿性关节炎以及咯血等。国内外研究表明吉祥草主要含有甾体类成分、萜类及木脂素类成分^[3-9],但主要药效物质以皂苷类成分为主^[10-11]。为进一步阐明吉祥草中皂苷类的类型,本研究从吉祥草的正丁醇部位分离得到8个甾体皂苷和2个三萜皂苷,分别鉴定为(1 β ,3 β ,16 β ,22 S)-cholest-5-ene-1,3,16,22-tetrol-1,16-di-(β -*D*-glucopyranoside) (**1**)、(1 β ,3 β ,16 β ,22 S)-cholest-5-ene-1,3,16,22-tetrol-1-[*O*- α -*L*-rhamnopyranosyl-(1 $\rightarrow$ 2)- β -*D*-glucopyranoside]-16-(β -*D*-glucopyranoside) (**2**)、(20 S ,22 R)-spirost-25(27)-en-1 β ,3 β ,4 β ,5 β -tetraol-5-*O*- β -*D*-glucopyranoside (**3**)、kitigenin 5-*O*- β -*D*-glucopyranoside (**4**)、蜘蛛抱蛋苷 A (aspidistrin A, **5**)、(17,20-*S-trans*)-5 β -pregn-16-en-1 β ,3 β -diol-20-one-1-*O*- β -*D*-xylopyranosyl-(1 $\rightarrow$ 2)-[α -*L*-rhamnopyranosyl]-3-*O*- α -*L*-rhamnopyranoside (**6**)、薯蓣皂苷元-3-*O*- β -*D*-吡喃葡萄糖苷 (diosgenin-3-*O*- β -*D*-glucopyranoside, **7**)、麦冬皂苷 T (ophiopogonin T, **8**)、prosaikogenin D (**9**)、柴胡皂苷 b₂ (saikosaponin b₂, **10**), 其中化合物 **3**、**5**、**8**~**10** 为首次从吉祥草中分离得到。

1 仪器与材料

Triple-TOF 5600⁺ 高分辨质谱仪 (美国 AB SCIEX 公司); Bruker avance 600 型核磁共振仪 (德国布鲁克公司); 旋转蒸发仪 (日本 EYALA 公司); DHG-9036A 型电热恒温鼓风干燥箱 (上海精宏实验设备有限公司); EL204 电子天平 [梅特勒-托利多仪器 (上海) 有限公司]; Waters 2487 半制备液相色谱仪、Waters 2487 制备液相色谱 (美国 Waters 公司); SHI-D III 循环水式真空泵 (巩义市英裕予华仪器厂); 大孔吸附树脂 HP20 (日本三菱公司); Sephadex LH-20 凝胶 (美国 GE 公司); 柱色谱硅胶、薄层色谱硅胶板 (青岛海洋化工厂分厂); 用于半制备液相和制备液相的试剂为色谱纯, 其他均为分析纯。

吉祥草药材于2014年3月采自贵州省安顺市紫云县, 由南昌市食品药品检验所吴蓓副主任药师鉴定为百合科吉祥草属植物吉祥草 *Reineckia carnea* (Andr.) Kunth 的全草, 标本 (Z-10310-01) 保存在江西中医药大学民族药资源中心。

2 提取与分离

取吉祥草全草药材 20 kg, 用 80% 乙醇加热回

流提取 3 次, 提取时间分别为 2、2、1 h, 将 3 次提取液合并, 滤过, 减压浓缩成浸膏。浸膏加适量的蒸馏水溶解后, 依次用石油醚、醋酸乙酯、水饱和的正丁醇多次萃取, 各部分萃取液经减压浓缩, 干燥, 得石油醚部位浸膏 28 g、醋酸乙酯部位浸膏 305 g、正丁醇部位浸膏 812 g。

取正丁醇部位浸膏加适量的蒸馏水溶解后经大孔吸附树脂 HP20 分离, 依次用 30%、60%、95% 乙醇洗脱, 浓缩, 干燥, 得 30% 乙醇洗脱部位 188 g、60% 乙醇洗脱部位 241 g、95% 乙醇洗脱部位 79 g。取 60% 乙醇洗脱部位浸膏 241 g 经硅胶柱色谱分离, 以二氯甲烷-甲醇 (20:1、10:1、5:1、2:1、1:1、0:1) 梯度洗脱, 得到 6 个流分 Fr. 1~6。Fr. 3 经中压 ODS 反相柱色谱, 甲醇-水 (10%、20%、30%、40%、50%、60%、70%、80%、90%、100%) 梯度洗脱, 再经制备型 HPLC (乙腈-0.1% 甲酸水 35:65) 制备, 得化合物 **3** (34.4 mg)、**6** (11.0 mg)、**7** (2.1 mg), 经制备型 HPLC (乙腈-0.1% 甲酸水 21:79) 制备, 得化合物 **4** (2.8 mg)、**5** (4.5 mg), 经制备型 HPLC (乙腈-0.1% 甲酸水 17:83) 制备, 得化合物 **9** (2.7 mg)、**10** (6.4 mg)。Fr. 4 经中压 ODS 反相柱色谱, 甲醇-水 (10%、20%、30%、40%、50%、60%、70%、80%、90%、100%) 梯度洗脱, 再经制备型 HPLC (乙腈-0.1% 甲酸水 21:79) 制备, 得化合物 **1** (230.2 mg)、**2** (28.0 mg)、**8** (10.2 mg)。

3 结构鉴定

化合物 **1**: 白色粉末, ESI-MS m/z : 757.4 [$M-H$]⁻, 分子式为 C₃₉H₆₆O₁₄。¹H-NMR (600 MHz, CD₃OD) δ : 3.80 (1H, m, H-1), 3.75 (1H, m, H-3), 5.47 (1H, d, J = 5.8 Hz, H-6), 4.10 (1H, m, H-16), 1.88 (1H, m, H-17), 0.84 (3H, s, 18-CH₃), 1.01 (3H, s, 19-CH₃), 2.34 (1H, m, H-20), 1.12 (3H, d, J = 6.2 Hz, 21-CH₃), 3.82 (1H, m, H-22), 0.82 (3H, d, J = 6.4 Hz, 26-CH₃), 0.82 (3H, d, J = 6.4 Hz, 27-CH₃), 4.10 (1H, d, J = 7.6 Hz, 1-*O*-Glc-H-1'), 4.25 (1H, d, J = 7.6 Hz, 16-*O*-Glc-H-1'); ¹³C-NMR (150 MHz, CD₃OD) δ : 83.7 (C-1), 38.1 (C-2), 69.4 (C-3), 43.6 (C-4), 139.9 (C-5), 126.5 (C-6), 32.8 (C-7), 34.4 (C-8), 51.5 (C-9), 43.6 (C-10), 25.0 (C-11), 41.8 (C-12), 43.2 (C-13), 56.6 (C-14), 37.4 (C-15), 83.4 (C-16), 59.2 (C-17), 14.1 (C-18), 15.1 (C-19), 36.6 (C-20), 12.4 (C-21), 74.6 (C-22), 34.5 (C-23), 37.3 (C-24), 30.1 (C-25), 23.4 (C-26), 23.5 (C-27), 101.3 (1-*O*-Glc-C-1'), 75.7

(C-2'), 78.5 (C-3'), 72.7 (C-4'), 78.0 (C-5'), 63.9 (C-6'), 107.0 (16-*O*-Glc-C-1''), 75.8 (C-2''), 78.8 (C-3''), 71.9 (C-4''), 78.1 (C-5''), 63.1 (C-6'')。以上数据与文献报道基本一致^[12], 故鉴定化合物 **1** 为 (1 β ,3 β ,16 β ,22*S*)-cholest-5-ene-1,3,16,22-tetrol-1,16-di-(β -*D*-glucopyranoside)。

化合物 **2**: 白色粉末, ESI-MS m/z : 903.5 [$M-H$]⁻, 分子式为 C₄₅H₇₆O₁₈。¹H-NMR (600 MHz, CD₃OD) δ : 3.80 (1H, m, H-1), 3.76 (1H, m, H-3), 5.47 (1H, d, J = 5.8 Hz, H-6), 4.10 (1H, m, H-16), 1.89 (1H, m, H-17), 0.84 (3H, s, 18-CH₃), 1.01 (3H, s, 19-CH₃), 2.35 (1H, m, H-20), 1.17 (3H, d, J = 6.2 Hz, 21-CH₃), 3.82 (1H, m, H-22), 0.82 (3H, d, J = 6.6 Hz, 26-CH₃), 0.82 (3H, d, J = 6.6 Hz, 27-CH₃), 4.30 (1H, d, J = 7.6 Hz, 1-*O*-Glc-H-1'), 4.12 (1H, d, J = 7.6 Hz, 16-*O*-Glc-H-1''), 5.89 (1H, m, 2'-*O*-Rha-H-1'''); ¹³C-NMR (150 MHz, CD₃OD) δ : 84.6 (C-1), 38.1 (C-2), 69.4 (C-3), 43.7 (C-4), 139.8 (C-5), 126.6 (C-6), 32.7 (C-7), 34.5 (C-8), 51.5 (C-9), 43.5 (C-10), 25.1 (C-11), 41.8 (C-12), 43.2 (C-13), 56.6 (C-14), 37.6 (C-15), 83.5 (C-16), 59.2 (C-17), 14.1 (C-18), 15.5 (C-19), 36.6 (C-20), 12.4 (C-21), 74.4 (C-22), 34.5 (C-23), 37.4 (C-24), 30.0 (C-25), 23.5 (C-26), 23.5 (C-27), 100.3 (1-*O*-Glc-C-1'), 80.2 (C-2'), 77.8 (C-3'), 72.4 (C-4'), 78.0 (C-5'), 64.1 (C-6'), 107.0 (16-*O*-Glc-C-1''), 75.8 (C-2''), 78.8 (C-3''), 71.9 (C-4''), 78.0 (C-5''), 63.1 (C-6''), 101.7 (2'-*O*-Rha-C-1'''), 72.6 (C-2'''), 72.9 (C-3'''), 74.6 (C-4'''), 70.0 (C-5'''), 18.7 (C-6''')。以上数据与文献报道基本一致^[12], 故鉴定化合物 **2** 为 (1 β ,3 β ,16 β ,22*S*)-cholest-5-ene-1,3,16,22-tetrol-1-[*O*- α -*L*-rhamnopyranosyl-(1 $\rightarrow$ 2)- β -*D*-glucopyranoside]-16-(β -*D*-glucopyranoside)。

化合物 **3**: 白色粉末, ESI-MS m/z : 623.3 [$M-H$]⁻, 分子式为 C₃₃H₅₂O₁₁。¹H-NMR (600 MHz, DMSO-*d*₆) δ : 4.16 (1H, m, H-1), 4.03 (1H, m, H-3), 4.32 (1H, d, J = 3.8 Hz, H-4), 1.00 (3H, s, 18-CH₃), 1.46 (3H, s, 19-CH₃), 1.16 (3H, d, J = 6.9 Hz, 21-CH₃), 5.02 (1H, s, H-27a), 5.05 (1H, s, H-27b), 4.79 (1H, d, J = 7.6 Hz, 5-*O*-Glc-H-1'); ¹³C-NMR (150 MHz, DMSO-*d*₆) δ : 72.2 (C-1), 33.1 (C-2), 70.5 (C-3), 66.7 (C-4), 86.5 (C-5), 24.0 (C-6), 27.8 (C-7), 34.3 (C-8), 45.4 (C-9), 46.3 (C-10), 21.0 (C-11), 39.3 (C-12), 40.2 (C-13), 55.2 (C-14), 32.4 (C-15), 80.7

(C-16), 62.1 (C-17), 16.3 (C-18), 13.2 (C-19), 41.2 (C-20), 14.8 (C-21), 109.1 (C-22), 31.6 (C-23), 28.3 (C-24), 143.5 (C-25), 64.2 (C-26), 108.8 (C-27), 96.0 (5-*O*-Glc-C-1'), 74.6 (C-2'), 76.9 (C-3'), 70.2 (C-4'), 77.0 (C-5'), 61.1 (C-6')。以上数据与文献报道基本一致^[13], 故鉴定化合物 **3** 为 (20*S*,22*R*)-spirost-25(27)-en-1 β ,3 β ,4 β ,5 β -tetraol-5-*O*- β -*D*-glucopyranoside。

化合物 **4**: 白色粉末, ESI-MS m/z : 625.4 [$M-H$]⁻, 分子式为 C₃₃H₅₄O₁₁。¹H-NMR (600 MHz, C₅D₅N) δ : 4.15 (1H, m, H-1), 4.08 (1H, m, H-3), 4.30 (1H, d, J = 3.8 Hz, H-4), 1.02 (3H, s, 18-CH₃), 1.46 (3H, s, 19-CH₃), 1.15 (3H, d, J = 6.9 Hz, 21-CH₃), 0.82 (3H, d, J = 6.8 Hz, 27-CH₃), 4.78 (1H, d, J = 7.6 Hz, 5-*O*-Glc-H-1'); ¹³C-NMR (150 MHz, C₅D₅N) δ : 72.3 (C-1), 31.2 (C-2), 70.6 (C-3), 66.7 (C-4), 86.5 (C-5), 24.2 (C-6), 27.8 (C-7), 34.3 (C-8), 45.4 (C-9), 46.3 (C-10), 21.0 (C-11), 39.3 (C-12), 40.2 (C-13), 55.2 (C-14), 32.4 (C-15), 80.7 (C-16), 62.1 (C-17), 16.3 (C-18), 13.2 (C-19), 41.2 (C-20), 14.8 (C-21), 109.1 (C-22), 31.6 (C-23), 28.3 (C-24), 29.2 (C-25), 64.2 (C-26), 16.8 (C-27), 96.0 (5-*O*-Glc-C-1'), 74.6 (C-2'), 76.9 (C-3'), 70.2 (C-4'), 77.0 (C-5'), 61.1 (C-6')。以上数据与文献报道基本一致^[3], 故鉴定化合物 **4** 为 kitigenin 5-*O*- β -*D*-glucopyranoside。

化合物 **5**: 白色粉末, ESI-MS m/z : 639.3 [$M-H$]⁻。¹H-NMR (600 MHz, CD₃OD) δ : 4.01 (1H, d, J = 3.8 Hz, H-1), 4.36 (1H, m, H-2), 3.75 (1H, m, H-3), 4.03 (1H, d, J = 3.8 Hz, H-4), 0.75 (3H, s, 18-CH₃), 1.29 (3H, s, 19-CH₃), 0.87 (3H, d, J = 7.4 Hz, 21-CH₃), 4.66 (1H, s, H-27a), 4.69 (1H, s, H-27b), 4.60 (1H, d, J = 7.8 Hz, 5-*O*-Glc-H-1'); ¹³C-NMR (150 MHz, CD₃OD) δ : 78.2 (C-1), 68.8 (C-2), 76.9 (C-3), 68.0 (C-4), 88.7 (C-5), 25.7 (C-6), 29.4 (C-7), 36.0 (C-8), 47.4 (C-9), 47.6 (C-10), 22.8 (C-11), 41.0 (C-12), 41.8 (C-13), 57.1 (C-14), 34.3 (C-15), 82.7 (C-16), 64.1 (C-17), 17.1 (C-18), 13.8 (C-19), 43.2 (C-20), 15.1 (C-21), 110.9 (C-22), 33.0 (C-23), 29.8 (C-24), 145.5 (C-25), 66.1 (C-26), 109.3 (C-27), 97.5 (5-*O*-Glc-C-1'), 76.1 (C-2'), 78.9 (C-3'), 71.4 (C-4'), 78.5 (C-5'), 62.4 (C-6')。以上数据与文献报道基本一致^[14], 故鉴定化合物 **5** 为蜘蛛抱蛋苷 A。

化合物 **6**: 白色粉末, ESI-MS m/z : 755.4 [$M-H$]⁻。¹H-NMR (600 MHz, DMSO-*d*₆) δ : 3.69 (1H, m,

H-1), 3.86 (1H, m, H-3), 6.86 (1H, dd, $J = 1.6, 2.8$ Hz, H-16), 0.80 (3H, s, 18-CH₃), 0.96 (3H, s, 19-CH₃), 2.20 (3H, s, 21-CH₃), 4.20 (1H, d, $J = 7.2$ Hz, 1-*O*-Xyl-H-1'), 5.21 (1H, brs, 3-*O*-Rha-H-1''), 4.61 (1H, brs, 2'-*O*-Rha-H-1'''); ¹³C-NMR (150 MHz, DMSO-*d*₆) δ : 77.5 (C-1), 29.1 (C-2), 68.9 (C-3), 30.4 (C-4), 34.4 (C-5), 25.7 (C-6), 26.4 (C-7), 32.4 (C-8), 45.8 (C-9), 38.8 (C-10), 21.8 (C-11), 35.0 (C-12), 45.6 (C-13), 56.5 (C-14), 32.0 (C-15), 145.3 (C-16), 154.7 (C-17), 16.0 (C-18), 16.3 (C-19), 196.4 (C-20), 27.2 (C-21), 98.2 (1-*O*-Xyl-C-1'), 78.2 (C-2'), 75.5 (C-3'), 70.2 (C-4'), 66.0 (C-5'), 99.8 (3-*O*-Rha-C-1''), 70.5 (C-2''), 70.9 (C-3''), 72.4 (C-4''), 68.8 (C-5''), 18.4 (C-6''), 97.8 (2'-*O*-Rha-C-1'''), 70.5 (C-2'''), 70.8 (C-3'''), 72.3 (C-4'''), 68.0 (C-5'''), 18.1 (C-6'''). 以上数据与文献报道基本一致^[15], 故鉴定化合物 **6** 为 (17,20-*S-trans*)-5 β -pregn-16-en-1 β ,3 β -diol-20-one-1-*O*- β -*D*-xylopyranosyl-(1 $\rightarrow$ 2)-[α -*L*-rhamnopyranosyl]-3-*O*- α -*L*-rhamnopyranoside。

化合物 **7**: 白色粉末, ESI-MS m/z : 575.3 [M-H]⁻。 ¹H-NMR (600 MHz, C₅D₅N) δ : 0.78 (3H, s, 18-CH₃), 0.89 (3H, s, 19-CH₃), 1.10 (3H, d, $J = 7.2$ Hz, 21-CH₃), 0.68 (3H, d, $J = 6.0$ Hz, 27-CH₃), 5.42 (1H, d, $J = 5.2$ Hz, H-6), 5.08 (1H, d, $J = 8.0$ Hz, 3-*O*-H-1'); ¹³C-NMR (150 MHz, C₅D₅N) δ : 38.2 (C-1), 30.5 (C-2), 79.1 (C-3), 40.0 (C-4), 141.5 (C-5), 121.7 (C-6), 33.0 (C-7), 32.6 (C-8), 51.0 (C-9), 37.8 (C-10), 21.8 (C-11), 40.6 (C-12), 41.3 (C-13), 57.3 (C-14), 33.1 (C-15), 81.7 (C-16), 63.7 (C-17), 17.1 (C-18), 20.0 (C-19), 42.9 (C-20), 15.8 (C-21), 110.0 (C-22), 33.0 (C-23), 29.9 (C-24), 31.2 (C-25), 68.1 (C-26), 18.2 (C-27), 103.1 (3-*O*-C-1'), 75.8 (C-2'), 79.2 (C-3'), 72.1 (C-4'), 78.9 (C-5'), 63.5 (C-6')。以上数据与文献报道基本一致^[16], 故鉴定化合物 **7** 为薯蓣皂苷元-3-*O*- β -*D*-吡喃葡萄糖苷。

化合物 **8**: 白色粉末, ESI-MS m/z : 1 033.5 [M-H]⁻。 ¹H-NMR (600 MHz, C₅D₅N) δ : 3.78 (1H, m, H-1), 3.75 (1H, m, H-3), 5.47 (1H, d, $J = 4.3$ Hz, H-6), 0.84 (3H, s, 18-CH₃), 1.01 (3H, s, 19-CH₃), 1.09 (3H, d, $J = 6.8$ Hz, 21-CH₃), 0.98 (3H, d, $J = 6.8$ Hz, H-27), 4.10 (1H, d, $J = 7.6$ Hz, 1-*O*-Fuc-H-1'), 5.32 (1H, brs, 2'-*O*-Rha-H-1''), 4.40 (1H, d, $J = 6.8$ Hz, 3'-*O*-Xyl-H-1'''), 4.24 (1H, d, $J = 7.6$ Hz, 26-*O*-Glc-H-1'''); ¹³C-NMR (150 MHz, C₅D₅N) δ : 84.3 (C-1), 37.8 (C-2), 69.3 (C-3), 43.2 (C-4), 139.8 (C-5), 126.2 (C-6), 32.6 (C-7), 34.2 (C-8), 51.5 (C-9), 43.3 (C-10), 24.8 (C-11), 41.3 (C-12), 41.7 (C-13), 58.1 (C-14), 33.0 (C-15), 82.3 (C-16), 65.7 (C-17), 17.7 (C-18), 14.3 (C-19), 41.5 (C-20), 14.9 (C-21), 114.0 (C-22), 37.8 (C-23), 29.1 (C-24), 35.4 (C-25), 75.9 (C-26), 17.5 (C-27), 99.4 (1-*O*-Fuc-C-1'), 74.0 (C-2'), 86.4 (C-3'), 72.2 (C-4'), 71.5 (C-5'), 17.2 (C-6'), 99.6 (2'-*O*-Rha-C-1''), 72.4 (C-2''), 73.2 (C-3''), 74.4 (C-4''), 69.8 (C-5''), 18.8 (C-6''), 105.5 (3'-*O*-Xyl-C-1'''), 78.0 (C-2'''), 75.0 (C-3'''), 71.2 (C-4'''), 67.3 (C-5'''), 105.0 (26-*O*-Glc-C-1'''), 75.4 (C-2'''), 78.2 (C-3'''), 71.4 (C-4'''), 78.5 (C-5'''), 63.2 (C-6''')。以上数据与文献报道基本一致^[17], 故鉴定化合物 **8** 为麦冬皂苷 T。

化合物 **9**: 白色粉末, ESI-MS m/z : 617.4 [M-H]⁻。 ¹H-NMR (600 MHz, CD₃OD) δ : 6.38 (1H, dd, $J = 10.6, 2.8$ Hz, H-11), 5.52 (1H, d, $J = 10.6$ Hz, H-12), 4.26 (1H, d, $J = 7.2$ Hz, 3-*O*-Fuc-H-1'), 1.17 (3H, s, H-27), 0.90 (3H, s, H-26), 0.88 (3H, s, H-25), 0.78 (3H, s, H-29), 0.66 (3H, s, H-30), 0.63 (3H, s, H-24), 1.20 (3H, d, $J = 6.4$ Hz, 6'-CH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 39.4 (C-1), 26.6 (C-2), 83.4 (C-3), 44.4 (C-4), 48.4 (C-5), 19.2 (C-6), 33.2 (C-7), 42.2 (C-8), 55.1 (C-9), 37.6 (C-10), 126.9 (C-11), 127.4 (C-12), 137.6 (C-13), 42.7 (C-14), 32.3 (C-15), 69.4 (C-16), 45.7 (C-17), 132.9 (C-18), 39.7 (C-19), 33.5 (C-20), 36.1 (C-21), 24.8 (C-22), 65.0 (C-23), 13.2 (C-24), 19.3 (C-25), 17.9 (C-26), 22.4 (C-27), 65.3 (C-28), 25.6 (C-29), 33.2 (C-30), 106.5 (3-*O*-Fuc-C-1'), 73.5 (C-2'), 75.7 (C-3'), 73.2 (C-4'), 72.1 (C-5'), 17.2 (C-6')。以上数据与文献报道基本一致^[18], 故鉴定化合物 **9** 为 prosaikogenin D。

化合物 **10**: 白色粉末, ESI-MS m/z : 779.5 [M-H]⁻。 ¹H-NMR (600 MHz, CD₃OD) δ : 6.38 (1H, dd, $J = 10.6, 2.8$ Hz, H-11), 5.52 (1H, d, $J = 10.6$ Hz, H-12), 4.33 (1H, d, $J = 7.6$ Hz, 3-*O*-Fuc-H-1'), 4.47 (1H, d, $J = 7.6$ Hz, 3'-*O*-Glc-H-1''), 1.17 (3H, s, H-27), 0.89 (3H, s, H-26), 0.87 (3H, s, H-25), 0.78 (3H, s, H-29), 0.66 (3H, s, H-30), 0.64 (3H, s, H-24), 1.20 (3H, d, $J = 6.4$ Hz, 6'-CH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 39.4 (C-1), 26.5 (C-2), 83.6 (C-3), 44.3 (C-4), 48.6 (C-5), 19.2 (C-6), 33.2 (C-7), 42.2 (C-8),

55.2 (C-9), 37.6 (C-10), 127.0 (C-11), 127.4 (C-12), 137.6 (C-13), 42.7 (C-14), 32.3 (C-15), 69.3 (C-16), 45.7 (C-17), 133.0 (C-18), 39.7 (C-19), 33.5 (C-20), 36.1 (C-21), 24.8 (C-22), 65.3 (C-23), 13.1 (C-24), 19.4 (C-25), 17.9 (C-26), 22.4 (C-27), 65.3 (C-28), 25.6 (C-29), 33.2 (C-30), 105.9 (3-O-Fuc-C-1'), 71.7 (C-2'), 85.5 (C-3'), 72.2 (C-4'), 71.5 (C-5'), 17.2 (C-6'), 106 (3'-O-Glc-C-1''), 75.7 (C-2''), 78.2 (C-3''), 72.7 (C-4''), 78.0 (C-5''), 62.7 (C-6'')。以上数据与文献报道基本一致^[19], 故鉴定化合物 **10** 为柴胡皂苷 b_2 。

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