兴安升麻根茎的化学成分研究

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摘 要：目的 研究兴安升麻 *Cimicifuga dahurica* 根茎的化学成分。**方法** 通过硅胶柱色谱、开放 ODS 柱色谱、Sephadex LH-20 以及半制备液相色谱等方法，对兴安升麻根茎的醋酸乙酯萃取部位及水层部位进行了分离，并通过理化性质及核磁共振波谱数据鉴定化合物结构。**结果** 从兴安升麻醋酸乙酯萃取部位及水层部位中分离并鉴定了 15 个化合物，分别为 20(*R*),23(*R*),24(*R*),25(*S*),26(*S*)-16β:23;23:26;24:25-三环氧-12β-乙酰基-3β,26-二羟基-9,19-环阿屯-7-烯-3-*O*-β-*D*-木糖苷（**1**）、小升麻苷 B（**2**）、23-*O*-乙酰升麻烷-3-*O*-β-*D*-木糖苷（**3**）、7,8-二去氢-24-*O*-乙酰氢化升麻醇-3-*O*-β-*D*-木糖苷（**4**）、24-表-升麻醇-3-*O*-β-*D*-木糖苷（**5**）、24-*O*-乙酰兴安升麻醇-3-*O*-β-*D*-木糖苷（**6**）、24-表-24-*O*-乙酰氢化升麻醇-3-*O*-β-*D*-木糖苷（**7**）、12β-*O*-乙酰升麻醇-3-*O*-β-*D*-木糖苷（**8**）、23-*O*-乙酰基-7,8-二去氢升麻烷-3-*O*-β-*D*-木糖苷（**9**）、7,8-二去氢-25-脱氢升麻醇-3-*O*-β-*D*-木糖苷（**10**）、25-*O*-乙基升麻醇-3-*O*-β-*D*-木糖苷（**11**）、3,4-二羟基苯甲酸（**12**）、24-*O*-异兴安升麻醇-3-*O*-α-*L*-阿拉伯糖苷（**13**）、番石榴酸-1-乙酯（**14**）和番石榴酸-4-乙酯（**15**）。**结论** 化合物 **6**、**11**、**12**、**14**、**15** 为首次从升麻属植物中分离得到，化合物 **1**、**4**、**5**、**8**～**10**、**13** 为首次从兴安升麻中分离得到。

关键词：兴安升麻；番石榴酸-1-乙酯；番石榴酸-4-乙酯；25-*O*-乙基升麻醇-3-*O*-β-*D*-木糖苷；3,4-二羟基苯甲酸

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Chemical constituents from rhizomes of *Cimicifuga dahurica*

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Abstract: Objective To study the chemical constituents from the rhizomes of *Cimicifuga dahurica*. **Methods** The chemical constituents from the rhizomes of *C. dahurica* in ethyl acetate extraction phase and H_2O fraction were isolated and purified by chromatographic methods, such as silica gel, opening ODS column, Sephadex LH-20, ODS and semi-preparative HPLC. Which stucture were identified by NMR and physicochemical analysis. **Results** Fifteen compounds were isolated and identified as 20(*R*),23(*R*),24(*R*),25(*S*),26(*S*)-16β:23; 23:26; 24:25-triepoxy-12β-acetoxy-3β,26-dihydroxy-9,19-cyclolanost-7-ene-3-*O*-β- *D*-xylopyranoside (**1**), cimiaceroside B (**2**), 23-*O*-acetylshengmanol-3-*O*-β-*D*-xylopyranoside (**3**), 7,8-didehydro-24-*O*-acetylhydroshengmanol-3-*O*-β-*D*-xylopyranoside (**4**), 24-*epi*-cimigenol-3-*O*-β-*D*-xylopyranoside (**5**), 24-*O*-acetyldahurinol-3-*O*-β-*D*-xylopyranoside (**6**), 24-*epi*-24-*O*-acetylhydroshengmanol-3-*O*-β-*D*-xylopyranoside (**7**), 12β-*O*-acetylcimigenol-3-*O*-β-*D*-xylopyranoside (**8**), 23-*O*-acetyl-7,8-didehydroshengmanol-3-*O*-β-*D*-xylopyranoside (**9**), 7,8-didehydro-25-dehydrocimigenol-3-*O*-β-*D*-xylopyranoside (**10**), 25-*O*-ethylcimigenol-3-*O*-β-*D*-xylopyranoside (**11**), 3,4-dihydroxybenzoic acid (**12**), 24-*O*-acetylisodahurinol-3-*O*-α-*L*-arabinopyranoside (**13**), 2,3-dihydroxy-2-[(4-hydroxyphenyl) methyl]-1-ethyl ester (**14**), and 2,3-dihydroxy-2-[(4-hudroxyphenyl) methyl]-4-ethyl ester (**15**). **Conclusion** Compounds **6**, **11**—**12**, and **14**—**15** are isolated from *Cimicifuga* genus for the first time. Compounds **1**, **4**—**5**, **8**—**10**, and **13** are isolated from *C. dahurica* for the first time.

Key words: *Cimicifuga dahurica* (Turcz.) Maxim.; 2,3-dihydroxy-2-[(4-hydroxyphenyl) methyl]-1-ethyl ester; 2,3-dihydroxy-2-[(4-hudroxyphenyl) methyl]-4-ethyl ester; 25-*O*-ethylcimigenol-3-*O*-β-*D*-xylopyranoside; 3,4-dihydroxybenzoic acid

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兴安升麻 *Cimicifuga dahurica* (Turcz.) Maxim. 为毛茛科（Ranunculaceae）升麻属 *Cimicifuga* L. 植物，幼苗可食，根茎入药，俗称窟窿牙、地龙牙，为《中国药典》2015 年版收载的中药升麻 3 种基原植物之一[1]。其广泛分布于河北、内蒙古、辽宁、吉林、黑龙江等地，味辛、微甘，性微寒，具有清热解毒、发表透疹、升举阳气等功效，用于治疗风热头疼、齿痛、口疮、咽喉肿痛、胃痛等疾病[2]。研究表明，兴安升麻主要含有三萜皂苷类、苯丙素类、色原酮类、生物碱类等化学成分[3-4]。现代药理活性研究表明兴安升麻中的三萜类成分具有解毒、抑制核苷转运、抗病毒、抗骨质疏松等活性，而苯丙素类及其衍生物具有显著的抗炎、抗氧化等生理活性[5-6]。为了进一步研究兴安升麻的药效物质基础，明确兴安升麻的活性成分，本课题组对兴安升麻根茎 70%乙醇提取物的醋酸乙酯及水层萃取物进行研究，分离得到了 15 个化合物，分别鉴定为 20(*R*),23(*R*),24(*R*),25(*S*),26(*S*)-16β:23;23:26;24:25- 三环氧-12β-乙酰基-3β,26-二羟基-9,19-环阿屯-7-烯-3-*O*-β-*D*- 木糖苷 [20(*R*),23(*R*),24(*R*),25(*S*),26(*S*)-16β:23;23:26;24:25-triepoxy-12β-acetoxy-3β,26-dihydroxy-9,19-cyclolanost-7-ene-3-*O*-β-*D*-xylopyranoside，**1**]、小升麻苷 B（cimiaceroside B，**2**）、23-*O*-乙酰升麻烷-3-*O*-β-*D*-木糖苷（23-*O*-acetylshengmanol-3-*O*-β-*D*-xylopyranoside，**3**）、7,8-二去氢-24-*O*-乙酰氢化升麻醇-3-*O*-β-*D*-木糖苷（7,8-didehydro-24-*O*-acetylhydro-shengmanol-3-*O*-β-*D*-xylopyranoside，**4**）、24-表-升麻醇-3-*O*-β-*D*-木糖苷（24-*epi*-cimigenol-3-*O*-β-*D*-xylopyranoside，**5**）、24-*O*-乙酰兴安升麻醇-3-*O*-β-*D*-木糖苷（24-*O*-acetyldahurinol-3-*O*-β-*D*-xylopyranoside，**6**）、24-表-24-*O*-乙酰氢化升麻醇-3-*O*-β-*D*-木糖苷（24-*epi*-24-*O*-acetylhydroshengmanol-3-*O*-β-*D*-xylopyranoside，**7**）、12β-*O*-乙酰升麻醇-3-*O*-β-*D*-木糖苷（12β-*O*-acetylcimigenol-3-*O*-β-*D*-xylopyranoside，**8**）、23-*O*-乙酰基-7,8-二去氢升麻烷-3-*O*-β-*D*-木糖苷（23-*O*-acetyl-7,8-didehydro-shengmanol-3-*O*-β-*D*-xylopyranoside，**9**）、7,8-二去氢-25-脱氢升麻醇-3-*O*-β-*D*-木糖苷（7,8-didehydro-25-dehydrocimigenol-3-*O*-β-*D*-xylopyranoside，**10**）、25-*O*-乙基升麻醇-3-*O*-β-*D*-木糖苷（25-*O*-ethylcimigenol-3-*O*-β-*D*-xylopyranoside，**11**）、3,4-二羟基苯甲酸（3,4-dihydroxybenzoic acid，**12**）、24-*O*-异兴安升麻醇-3-*O*-α-*L*-阿拉伯糖苷（24-*O*-acetylisodahurinol-3-*O*-α-*L*-arabinopyranoside，**13**）、番石榴酸-1-乙酯（2,3-dihydroxy-2-[(4-hydroxyphenyl)methyl]-1-ethyl ester，**14**）和番石榴酸-4-乙酯（2,3-dihydroxy-2-[(4-hudroxyphenyl)methyl]-4-ethyl ester，**15**）。其中，化合物 **6**、**11**、**12**、**14**、**15** 为首次从升麻属植物中分离得到，化合物 **1**、**4**、**5**、**8**～**10**、**13** 为首次从该植物中分离得到。

1 仪器与材料

Bruker ARX 300、Bruker AV 600 型核磁共振波谱仪（瑞士 Bruker 公司）；Agilent1260 高效液相色谱仪（美国 Agilent 公司）；制备高效液相色谱：SPD-20A 紫外检测器和 LC-6AD 泵（日本岛津公司）。

YMC-Pack ODS-A 制备型色谱柱（200 mm×100 mm，15 μm，日本 YMC 公司）；薄层色谱硅胶和柱色谱硅胶（青岛海洋化工厂）；ODS C_{18} 柱色谱填料（日本 YMC 公司）；色谱甲醇（天津康科德有限公司），分析纯试剂（山东禹王试剂有限公司）。

兴安升麻药材于 2013 年 9 月采于辽宁凤城，经沈阳药科大学路金才教授鉴定为升麻属兴安升麻 *Cimicifuga dahurica* (Turcz.) Maxim. 的干燥根茎。凭证标本（20130926001）保存于沈阳药科大学生药学实验室。

2 提取与分离

兴安升麻药材 16.0 kg，粉碎后用 70%的乙醇回流提取 3 次，合并提取液，减压回收溶剂得总浸膏。将总浸膏分散于水中，依次用石油醚、醋酸乙酯、正丁醇萃取，水层萃取物经 HPD-400 大孔树脂分离，以水-乙醇（100∶0→10∶90）梯度洗脱得到 4 个组分 Fr. A～D。Fr. A 经 ODS 柱色谱，甲醇-水（10∶90→90∶10）梯度洗脱后得到 3 个组分 Fr. A_1～A_3。Fr. A_2 经制备液相纯化，甲醇-水（25∶75）洗脱得到化合物 **14**（13.6 mg）、**15**（7.5 mg）。醋酸乙酯萃取物经硅胶柱色谱分离，以二氯甲烷-甲醇（100∶1→100∶100）梯度洗脱，得 6 个流分 Fr. E_1～E_6。Fr. E_3（二氯甲烷-甲醇 100∶3→100∶10）经硅胶柱色谱分离后，经甲醇反复重结晶得化合物 **3**（12.4 mg）、**4**（7.8 mg）；再经 Sephadex LH-20 凝胶柱色谱及制备液相纯化（甲醇-水 85∶15）得化合物 **1**（9.4 mg），**2**（7.9 mg）和 **5**（8.2 mg）。Fr. E_4（二氯甲烷-甲醇 100∶4→100∶10）经硅胶柱色谱分离后，得到 5 个组分 Fr. $E_{4.1}$～$E_{4.5}$。Fr. $E_{4.3}$ 经制备液相纯化（甲醇-水 85∶15）得化合物 **6**（28.6 mg）、**7**（9.2 mg）和 **8**（7.6 mg）。Fr. E_5 经反复硅胶柱色谱

分离后，甲醇重结晶及制备液相纯化（甲醇-水 75∶25）得化合物 **9**（9.6 mg）、**10**（7.2 mg）、**11**（9.6 mg）和 **13**（10.2 mg）。Fr. E_6 经 ODS 柱色谱分离后制备液相纯化（甲醇-水 65∶35）得化合物 **12**（21.5 mg）。

3 结构鉴定

化合物 **1**：白色粉末，^{1}H-NMR (600 MHz, C_5D_5N) δ: 0.56 (1H, d, J = 4.0 Hz, H-19), 1.08 (1H, d, J = 4.0 Hz, H-19), 0.97 (3H, d, J = 6.0 Hz, H-21), 1.32 (3H, s, H-18), 1.79 (3H, s, H-27), 1.04 (3H, s, H-28), 1.43 (3H, s, H-29), 1.02 (3H, s, H-30), 5.06 (1H, d, J = 7.9 Hz, H-7), 2.18 (3H, s, H-12)；^{13}C-NMR (150 MHz, C_5D_5N) δ: 30.6 (C-1), 29.8 (C-2), 88.2 (C-3), 40.7 (C-4), 42.8 (C-5), 22.0 (C-6), 114.3 (C-7), 148.1 (C-8), 21.6 (C-9), 28.6 (C-10), 37.0 (C-11), 77.1 (C-12), 48.4 (C-13), 50.9 (C-14), 42.7 (C-15), 73.5 (C-16), 57.2 (C-17), 15.2 (C-18), 29.1 (C-19), 26.2 (C-20), 21.3 (C-21), 37.7 (C-22), 106.2 (C-23), 63.7 (C-24), 66.0 (C-25), 98.8 (C-26), 13.5 (C-27), 27.1 (C-28), 26.1 (C-29), 14.6 (C-30), 107.8 (C-1′), 75.9 (C-2′), 78.9 (C-3′), 71.6 (C-4′), 67.4 (C-5′)。以上波谱数据与文献报道基本一致[7]，故化合物 **1** 鉴定为 20(*R*), 23(*R*), 24(*R*), 25(*S*), 26(*S*)-16β: 23;23:26;24:25-三环氧-12β-乙酰基-3β,26-二羟基-9,19-环阿屯-7-烯-3-*O*-β-*D*-木糖苷。

化合物 **2**：白色粉末，^{1}H-NMR (600 MHz, C_5D_5N) δ: 0.23 (1H, d, J = 4.1 Hz, H-19), 0.51 (1H, d, J = 3.8 Hz, H-19), 1.25 (3H, d, J = 6.6 Hz, H-21), 1.27 (3H, s, H-18), 1.80 (3H, s, H-26), 1.72 (3H, s, H-27), 0.89 (3H, s, H-28), 1.36 (3H, s, H-29), 1.08 (3H, s, H-30)；^{13}C-NMR (150 MHz, C_5D_5N) δ: 31.9 (C-1), 29.9 (C-2), 88.2 (C-3), 41.1 (C-4), 47.3 (C-5), 20.7 (C-6), 26.0 (C-7), 47.3 (C-8), 19.5 (C-9), 26.4 (C-10), 26.2 (C-11), 33.2 (C-12), 46.6 (C-13), 45.0 (C-14), 43.1 (C-15), 72.2 (C-16), 52.1 (C-17), 20.4 (C-18), 30.0 (C-19), 34.5 (C-20), 17.3 (C-21), 86.7 (C-22), 105.8 (C-23), 83.1 (C-24), 83.4 (C-25), 27.5 (C-26), 24.6 (C-27), 19.5 (C-28), 25.5 (C-29), 15.2 (C-30), 107.4 (C-1′), 75.4 (C-2′), 78.4 (C-3′), 71.1 (C-4′), 66.9 (C-5′)。以上波谱数据与文献报道基本一致[8]，故化合物 **2** 鉴定为小升麻苷 B。

化合物 **3**：白色粉末，^{1}H-NMR (600 MHz, C_5D_5N) δ: 0.31 (1H, d, J = 3.5 Hz, H-19), 0.56 (1H, d, J = 3.9 Hz, H-19), 1.24 (3H, d, J = 6.3 Hz, H-21), 1.23 (3H, s, H-18), 1.14 (3H, s, H-26), 1.38 (3H, s, H-27), 1.36 (3H, s, H-28), 1.29 (3H, s, H-29), 1.06 (3H, s, H-30)；^{13}C-NMR (150 MHz, C_5D_5N) δ: 32.7 (C-1), 30.9 (C-2), 88.8 (C-3), 41.7 (C-4), 47.9 (C-5), 21.4 (C-6), 26.1 (C-7), 48.7 (C-8), 20.5 (C-9), 27.2 (C-10), 27.1 (C-11), 33.5 (C-12), 42.0 (C-13), 46.5 (C-14), 83.3 (C-15), 220.3 (C-16), 60.4 (C-17), 20.2 (C-18), 30.5 (C-19), 28.4 (C-20), 20.7 (C-21), 37.4 (C-22), 72.5 (C-23), 65.6 (C-24), 58.9 (C-25), 25.1 (C-26), 19.8 (C-27), 12.4 (C-28), 26.1 (C-29), 15.9 (C-30), 108.0 (C-1′), 76.0 (C-2′), 79.0 (C-3′), 71.7 (C-4′), 67.2 (C-5′), 171.0 (C = O), 21.4 ($COCH_3$)。以上波谱数据与文献报道基本一致[9]，故化合物 **3** 鉴定为 23-*O*-乙酰升麻烷-3-*O*-β-*D*-木糖苷。

化合物 **4**：白色粉末，^{1}H-NMR (600 MHz, C_5D_5N) δ: 0.51 (1H, d, J = 3.9 Hz, H-19), 1.05 (1H, d, J = 4.0 Hz, H-19), 0.98 (3H, d, J = 6.6 Hz, H-21), 0.93 (3H, s, H-18), 1.33 (3H, s, H-26), 1.22 (3H, s, H-27), 1.03 (3H, s, H-28), 0.96 (3H, s, H-29), 0.86 (3H, s, H-30), 6.06 (1H, d, J = 7.5 Hz, H-7), 2.02 (3H, s, H-24)；^{13}C-NMR (150 MHz, C_5D_5N) δ: 30.5 (C-1), 29.9 (C-2), 88.5 (C-3), 40.8 (C-4), 42.8 (C-5), 21.7 (C-6), 114.3 (C-7), 147.1 (C-8), 21.4 (C-9), 28.3 (C-10), 25.1 (C-11), 33.6 (C-12), 40.3 (C-13), 49.1 (C-14), 80.2 (C-15), 106.2 (C-16), 61.0 (C-17), 22.0 (C-18), 28.7 (C-19), 26.1 (C-20), 20.5 (C-21), 33.2 (C-22), 72.4 (C-23), 79.4 (C-24), 76.0 (C-25), 32.3 (C-26), 27.1 (C-27), 18.4 (C-28), 26.2 (C-29), 14.1 (C-30), 107.9 (C-1′), 76.0 (C-2′), 79.0 (C-3′), 71.6 (C-4′), 67.5 (C-5′), 170.9 (C = O), 21.7 ($COCH_3$)。以上波谱数据与文献报道基本一致[10]，故化合物 **4** 鉴定为 7,8-二去氢-24-*O*-乙酰氢化升麻醇-3-*O*-β-*D*-木糖苷。

化合物 **5**：白色粉末，^{1}H-NMR (600 MHz, C_5D_5N) δ: 0.30 (1H, d, J = 4.0 Hz, H-19), 0.55 (1H, d, J = 4.2 Hz, H-19), 0.96 (3H, d, J = 6.2 Hz, H-21), 1.20 (3H, s, H-18), 1.44 (3H, s, H-26), 1.28 (3H, s, H-27), 1.06 (3H, s, H-28), 1.35 (3H, s, H-29), 1.06 (3H, s, H-30)；^{13}C-NMR (150 MHz, C_5D_5N) δ: 32.8 (C-1), 30.0 (C-2), 88.7 (C-3), 41.5 (C-4), 48.1 (C-5), 21.5 (C-6), 26.4 (C-7), 49.1 (C-8), 20.1 (C-9), 26.9 (C-10), 26.7 (C-11), 34.3 (C-12), 41.8 (C-13), 47.8 (C-14), 81.2 (C-15), 112.6 (C-16), 61.0 (C-17), 20.0 (C-18),

30.6 (C-19), 23.8 (C-20), 20.0 (C-21), 30.0 (C-22), 74.1 (C-23), 84.4 (C-24), 69.0 (C-25), 31.8 (C-26), 26.1 (C-27), 12.1 (C-28), 26.0 (C-29), 15.9 (C-30), 107.9 (C-1′), 75.9 (C-2′), 79.1 (C-3′), 71.5 (C-4′), 67.6 (C-5′)。以上波谱数据与文献报道基本一致[11]，故化合物 **5** 鉴定为 24-表-升麻醇-3-*O*-β-*D*-木糖苷。

化合物 **6**：白色粉末，^{1}H-NMR (600 MHz, C_5D_5N) δ: 0.28 (1H, d, J = 4.1 Hz, H-19), 0.51 (1H, d, J = 3.7 Hz, H-19), 0.95 (3H, d, J = 6.4 Hz, H-21), 1.20 (3H, s, H-18), 1.52 (3H, s, H-26), 1.52 (3H, s, H-27), 1.09 (3H, s, H-28), 1.34 (3H, s, H-29), 1.05 (3H, s, H-30), 2.12 (3H, s, H-24)；^{13}C-NMR (150 MHz, C_5D_5N) δ: 32.9 (C-1), 30.5 (C-2), 88.8 (C-3), 41.7 (C-4), 47.8 (C-5), 21.2 (C-6), 26.3 (C-7), 44.0 (C-8), 20.4 (C-9), 27.4 (C-10), 26.4 (C-11), 31.5 (C-12), 40.4 (C-13), 55.5 (C-14), 214.2 (C-15), 84.5 (C-16), 52.8 (C-17), 20.7 (C-18), 31.7 (C-19), 33.4 (C-20), 20.4 (C-21), 38.2 (C-22), 80.0 (C-23), 80.6 (C-24), 72.0 (C-25), 27.4 (C-26), 27.5 (C-27), 17.9 (C-28), 26.1 (C-29), 15.8 (C-30), 108.0 (C-1′), 76.0 (C-2′), 79.0 (C-3′), 71.6 (C-4′), 67.5 (C-5′), 170.7 (C = O), 21.3 ($COCH_3$)。以上波谱数据与文献报道基本一致[12]，故化合物 **6** 鉴定为 24-*O*-乙酰兴安升麻醇-3-*O*-β-*D*-木糖苷。

化合物 **7**：白色粉末，^{1}H-NMR (600 MHz, C_5D_5N) δ: 0.31 (1H, d, J = 4.1 Hz, H-19), 0.59 (1H, d, J = 3.9 Hz, H-19), 0.98 (3H, d, J = 5.9 Hz, H-21), 1.24 (3H, s, H-18), 1.52 (3H, s, H-26), 1.49 (3H, s, H-27), 1.25 (3H, s, H-28), 1.34 (3H, s, H-29), 1.06 (3H, s, H-30), 2.13 (3H, s, H-24)；^{13}C-NMR (150 MHz, C_5D_5N) δ: 31.1 (C-1), 31.1 (C-2), 88.8 (C-3), 41.7 (C-4), 47.1 (C-5), 34.4 (C-6), 26.1 (C-7), 49.4 (C-8), 20.4 (C-9), 27.8 (C-10), 26.9 (C-11), 32.7 (C-12), 42.6 (C-13), 47.9 (C-14), 82.7 (C-15), 103.4 (C-16), 61.3 (C-17), 21.5 (C-18), 30.5 (C-19), 27.1 (C-20), 21.9 (C-21), 33.3 (C-22), 74.5 (C-23), 81.6 (C-24), 72.6 (C-25), 27.5 (C-26), 27.5 (C-27), 12.2 (C-28), 27.0 (C-29), 15.8 (C-30), 108.0 (C-1′), 76.0 (C-2′), 79.0 (C-3′), 71.7 (C-4′), 67.5 (C-5′), 170.8 (C = O), 20.7 ($COCH_3$)。以上波谱数据与文献报道基本一致[13]，故化合物 **7** 鉴定为 24-表-24-*O*-乙酰氢化升麻醇-3-*O*-β-*D*-木糖苷。

化合物 **8**：白色粉末，^{1}H-NMR (600 MHz, C_5D_5N) δ: 0.30 (1H, d, J = 3.4 Hz, H-19), 0.62 (1H, d, J = 3.4 Hz, H-19), 0.91 (3H, d, J = 5.8 Hz, H-21), 1.30 (3H, s, H-18), 1.48 (3H, s, H-26), 1.50 (3H, s, H-27), 1.33 (3H, s, H-28), 1.24 (3H, s, H-29), 1.04 (3H, s, H-30), 2.14 (3H, s, H-12)；^{13}C-NMR (150 MHz, C_5D_5N) δ: 32.5 (C-1), 30.3 (C-2), 88.7 (C-3), 41.6 (C-4), 47.1 (C-5), 20.7 (C-6), 25.9 (C-7), 47.5 (C-8), 20.2 (C-9), 26.7 (C-10), 37.2 (C-11), 77.6 (C-12), 46.9 (C-13), 48.4 (C-14), 79.1 (C-15), 112.2 (C-16), 59.7 (C-17), 12.0 (C-18), 30.3 (C-19), 24.3 (C-20), 20.1 (C-21), 38.4 (C-22), 71.2 (C-23), 90.4 (C-24), 71.2 (C-25), 25.6 (C-26), 25.7 (C-27), 12.0 (C-28), 27.5 (C-29), 15.7 (C-30), 107.8 (C-1′), 75.8 (C-2′), 78.8 (C-3′), 71.5 (C-4′), 67.3 (C-5′), 170.7 (C = O), 21.6 ($COCH_3$)。以上波谱数据与文献报道基本一致[14]，故化合物 **8** 鉴定为 12β-*O*-乙酰升麻醇-3-*O*-β-*D*-木糖苷。

化合物 **9**：白色粉末，^{1}H-NMR (600 MHz, C_5D_5N) δ: 0.56 (1H, d, J = 3.9 Hz, H-19), 1.22 (1H, d, J = 4.0 Hz, H-19), 1.24 (3H, d, J = 6.6 Hz, H-21), 1.28 (3H, s, H-18), 1.32 (3H, s, H-26), 1.43 (3H, s, H-27), 1.45 (3H, s, H-28), 1.38 (3H, s, H-29), 1.10 (3H, s, H-30), 6.13 (1H, d, J = 6.4 Hz, H-7), 2.04 (3H, s, H-23)；^{13}C-NMR (150 MHz, C_5D_5N) δ: 30.7 (C-1), 29.9 (C-2), 88.5 (C-3), 40.8 (C-4), 43.0 (C-5), 21.8 (C-6), 115.5 (C-7), 147.6 (C-8), 21.4 (C-9), 28.9 (C-10), 25.6 (C-11), 33.9 (C-12), 41.2 (C-13), 49.9 (C-14), 81.3 (C-15), 220.8 (C-16), 60.5 (C-17), 22.2 (C-18), 28.3 (C-19), 28.9 (C-20), 19.8 (C-21), 37.7 (C-22), 72.4 (C-23), 65.6 (C-24), 68.9 (C-25), 25.1 (C-26), 19.2 (C-27), 19.2 (C-28), 26.2 (C-29), 14.7 (C-30), 107.9 (C-1′), 76.0 (C-2′), 79.1 (C-3′), 71.7 (C-4′), 67.6 (C-5′), 170.8 (C = O), 21.6 ($COCH_3$)。以上波谱数据与文献报道基本一致[15]，故化合物 **9** 鉴定为 23-*O*-乙酰基-7,8-二去氢升麻烷-3-*O*-β-*D*-木糖苷。

化合物 **10**：白色粉末，^{1}H-NMR (600 MHz, C_5D_5N) δ: 0.59 (1H, d, J = 3.9 Hz, H-19), 1.20 (1H, d, J = 4.0 Hz, H-19), 0.90 (3H, d, J = 6.5 Hz, H-21), 1.17 (3H, s, H-18), 4.89, 5.36 (1H, brs, H-26), 1.87 (3H, s, H-27), 1.34 (3H, s, H-28), 1.49 (3H, s, H-29), 1.08 (3H, s, H-30), 6.16 (1H, d, J = 6.2 Hz, H-7)；^{13}C-NMR (150 MHz, C_5D_5N) δ: 32.1 (C-1), 30.7 (C-2), 88.7 (C-3), 41.5 (C-4), 43.1 (C-5), 21.7 (C-6), 114.7 (C-7), 148.4 (C-8), 20.0 (C-9), 26.2 (C-10), 26.2 (C-11), 34.4

(C-12), 41.5 (C-13), 50.8 (C-14), 79.1 (C-15), 113.0 (C-16), 60.1 (C-17), 18.8 (C-18), 30.7 (C-19), 24.2 (C-20), 20.0 (C-21), 28.8 (C-22), 76.0 (C-23), 87.0 (C-24), 146.2 (C-25), 113.5 (C-26), 18.6 (C-27), 12.9 (C-28), 25.6 (C-29), 14.7 (C-30), 107.9 (C-1′), 75.6 (C-2′), 78.7 (C-3′), 71.6 (C-4′), 67.5 (C-5′)。以上波谱数据与文献报道基本一致[16]，故化合物 **10** 鉴定为7,8-二去氢-25-脱氢升麻醇-3-*O*-β-*D*-木糖苷。

化合物 **11**：白色粉末，^{1}H-NMR (600 MHz, C_5D_5N) δ: 0.31 (1H, d, J = 4.0 Hz, H-19), 0.56 (1H, d, J = 3.7 Hz, H-19), 0.86 (3H, d, J = 6.5 Hz, H-21), 1.16 (3H, s, H-18), 1.31 (3H, s, H-26), 1.31 (3H, s, H-27), 1.20 (3H, s, H-28), 1.34 (3H, s, H-29), 1.08 (3H, s, H-30), 3.45 (2H, dd, J = 6.9, 5.5 Hz, -OCH_2), 1.14 (3H, t, J = 6.8 Hz, -CH_3)；^{13}C-NMR (150 MHz, C_5D_5N) δ: 33.0 (C-1), 30.7 (C-2), 89.1 (C-3), 41.9 (C-4), 47.8 (C-5), 21.6 (C-6), 26.9 (C-7), 49.2 (C-8), 20.6 (C-9), 27.2 (C-10), 27.0 (C-11), 34.6 (C-12), 42.4 (C-13), 48.2 (C-14), 80.7 (C-15), 112.5 (C-16), 60.0 (C-17), 20.1 (C-18), 31.5 (C-19), 24.6 (C-20), 20.2 (C-21), 38.7 (C-22), 72.1 (C-23), 88.6 (C-24), 76.6 (C-25), 20.8 (C-26), 23.5 (C-27), 12.3 (C-28), 26.3 (C-29), 16.0 (C-30), 108.2 (C-1′), 76.1 (C-2′), 79.2 (C-3′), 71.8 (C-4′), 67.7 (C-5′), 57.5 (-OCH_2), 17.0 (-CH_3)。以上波谱数据与文献报道基本一致[17]，故化合物 **11** 鉴定为25-*O*-乙基升麻醇-3-*O*-β-*D*-木糖苷。

化合物 **12**：白色粉末，^{1}H-NMR (600 MHz, DMSO-d_6) δ: 7.32 (1H, d, J = 1.8 Hz, H-2), 7.28 (1H, dd, J = 1.8, 8.2 Hz, H-6), 6.77 (1H, d, J = 8.2 Hz, H-5)；^{13}C-NMR (150 MHz, DMSO-d_6) δ: 121.7 (C-1), 116.6 (C-2), 144.9 (C-3), 150.0 (C-4), 115.1 (C-5), 121.8 (C-6), 167.3 (C-7)。以上波谱数据与文献报道基本一致[18]，故化合物 **12** 鉴定为3,4-二羟基苯甲酸。

化合物 **13**：白色粉末，^{1}H-NMR (600 MHz, C_5D_5N) δ: 0.23 (1H, d, J = 4.1 Hz, H-19), 0.51 (1H, d, J = 4.0 Hz, H-19), 0.90 (3H, d, J = 6.2 Hz, H-21), 1.15 (3H, s, H-18), 1.63 (3H, s, H-26), 1.68 (3H, s, H-27), 0.99 (3H, s, H-28), 1.30 (3H, s, H-29), 1.01 (3H, s, H-30), 2.16 (3H, s, H-24)；^{13}C-NMR (150 MHz, C_5D_5N) δ: 32.6 (C-1), 30.2 (C-2), 88.6 (C-3), 41.5 (C-4), 47.6 (C-5), 21.0 (C-6), 26.2 (C-7), 43.8 (C-8), 20.1 (C-9), 27.0 (C-10), 25.9 (C-11), 31.3 (C-12), 40.1 (C-13), 55.2 (C-14), 214.0 (C-15), 84.4 (C-16), 52.5 (C-17), 20.4 (C-18), 31.5 (C-19), 33.4 (C-20), 19.7 (C-21), 38.8 (C-22), 79.2 (C-23), 80.0 (C-24), 72.2 (C-25), 26.9 (C-26), 28.5 (C-27), 17.7 (C-28), 26.0 (C-29), 15.5 (C-30), 107.6 (C-1′), 73.1 (C-2′), 74.8 (C-3′), 69.7 (C-4′), 66.9 (C-5′), 170.6 (C = O), 21.1 ($COCH_3$)。以上波谱数据与文献报道基本一致[19]，故化合物 **13** 鉴定为24-*O*-异兴安升麻醇-3-*O*-α-*L*-阿拉伯糖苷。

化合物 **14**：淡黄色粉末，^{1}H-NMR (600 MHz, CD_3OD) δ: 2.97 (1H, d, J = 13.8 Hz, H-5), 3.14 (1H, d, J = 13.8 Hz, H-5), 6.65 (1H, d, J = 8.4 Hz, H-2′), 6.65 (1H, d, J = 8.4 Hz, H-6′), 7.07 (1H, d, J = 8.5 Hz, H-3′), 7.07 (1H, d, J = 8.5 Hz, H-5′), 4.94 (1H, brs, H-2), 1.23 (3H, t, J = 7.1 Hz, H-8′), 4.16 (2H, m, H-7′)；^{13}C-NMR (150 MHz, CD_3OD) δ: 175.8 (C-1), 76.4 (C-2), 81.6 (C-3), 172.9 (C-4), 41.9 (C-5), 127.9 (C-1′), 132.5 (C-2′), 115.7 (C-3′), 157.2 (C-4′), 115.7 (C-5′), 132.5 (C-6′), 62.4 (C-7′), 14.3 (C-8′)。以上波谱数据与文献报道基本一致[20]，故化合物 **14** 鉴定为番石榴酸-1-乙酯。

化合物 **15**：淡黄色粉末，^{1}H-NMR (600 MHz, DMSO-d_6) δ: 2.84 (1H, d, J = 13.8 Hz, H-5a), 2.92 (1H, d, J = 13.8 Hz, H-5b), 6.59 (1H, d, J = 8.4 Hz, H-2′), 6.59 (1H, d, J = 8.4 Hz, H-6′), 6.93 (1H, d, J = 8.5 Hz, H-3′), 6.93 (1H, d, J = 8.5 Hz, H-5′), 4.23 (1H, brs, H-2), 1.09 (3H, t, J = 7.1 Hz, H-8′), 3.94 (2H, m, H-7′)；^{13}C-NMR (150 MHz, DMSO-d_6) δ: 172.9 (C-1), 80.0 (C-2), 74.9 (C-3), 172.1 (C-4), 41.0 (C-5), 126.4 (C-1′), 131.1 (C-2′), 114.5 (C-3′), 155.8 (C-4′), 114.5 (C-5′), 131.1 (C-6′), 60.2 (C-7′), 13.9 (C-8′)。以上波谱数据与文献报道的基本一致[20]，故化合物 **15** 鉴定为番石榴酸-4-乙酯。

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