三叶木通正丁醇部位化学成分分离鉴定

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［摘要］ **目的**：研究三叶木通藤茎正丁醇萃取物的化学成分。**方法**：取三叶木通的藤茎 100 kg，采用 75% 乙醇加热回流提取 3 次，减压回收溶剂成浸膏。浸膏加适量的水混匀后，依次用二氯甲烷、乙酸乙酯、正丁醇进行萃取。正丁醇层萃取物经大孔树脂柱色谱，硅胶柱色谱，LH-20 型羟丙基葡聚糖凝胶（Sephadex LH-20）柱色谱，ODS 柱色谱和半制备高效液相色谱法进行分离纯化，并通过理化性质、质谱、核磁共振技术（^{1}H 和 ^{13}C-NMR）和相关文献数据等对所得化合物进行结构鉴定。**结果**：从三叶木通正丁醇部位分离并鉴定出 14 个化合物，分别鉴定为木通皂苷 B（**1**），木通皂苷 C（**2**），皂苷 PH（**3**），卵叶银莲花苷 A（**4**），2α，3β，23-三羟基齐墩果烷-30-去甲基-12，19-双烯-28-*O*-β-*D*-吡喃木糖-（1→3）-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（**5**），akemisaponins D（**6**），akemisaponins E（**7**），积雪草苷（**8**），皂苷 PJ1（**9**），scheffoleoside A（**10**），symplocosneolignan A（**11**），刺楸皂苷 D（**12**），leonticin E（**13**），ciwujianoside A_1（**14**）。**结论**：化合物 **1**～**4**，**11**，**13**，**14** 均为首次从该植物中分离得到，以上化合物的发现进一步丰富了三叶木通的化学成分组成，为综合开发和利用三叶木通植物资源提供前期的实验基础。

［关键词］ 木通；三叶木通；木通属；正丁醇部位
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Chemical Constituents of *n*-Butanol Extract Part of *Akebia trifoliata* Caulis

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［**Abstract**］ **Objective**: To study the chemical constituents from *n*-butanol extract of *Akebia trifoliata* caulis. **Method**: The 100 kg caulis of *A. trifoliata* was extracted with 75% ethanol (EtOH) for three times by heating reflux. These 3 extracts were decompressed and concentrated, and then dissolved in water. The solvent was successively extracted with dichloromethane, ethyl acetate and *n*-butanol. The chemical constituents from the *n*-butanol fraction were isolated by macroporous, silica gel, sephadex LH-20 and ODS columns, and semi-preparative high performance liquid chromatography, and their chemical structures were determined through MS, NMR analysis (^{1}H and ^{13}C-NMR) and spectroscopic data from literatures. **Result**: Totally 14 compounds were isolated and identified as mutongsaponin B (**1**), mutongsaponin C (**2**), saponin PH (**3**), begoniifolide A

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(**4**), 2α, 3β, 23-trihydroxy-30-noroleana-12, 19-dien-28-oicacid-*O*-β-*D*-xylopyranosyl-(1 → 3)-α-*L*-rhamnopyranosyl-(1 → 4)-β-*D*-glucopyranosyl-(1 → 6)-β-*D*-glucopyranosyl ester (**5**), akemisaponins D (**6**), akemisaponins E (**7**), asiaticoside (**8**), saponin PJ1 (**9**), scheffoleoside A (**10**), symplocosneolignan A (**11**), kalopanax-saponins D (**12**), leonticin E (**13**), ciwujianoside A_1 (**14**). **Conclusion**: Compounds **1-4**, **11**, **13**, **14** were isolated from this plant for the first time. The discovery of these compounds further enriched the chemical constituents of *A. trifoliata*, and provided experimental and scientific basis for the comprehensive development and utilization of *A. trifoliata*.

[**Key words**] Akebiae Caulis; *Akebia trifoliata*; *Akebia*; *n*-butanol extract

三叶木通是木通科木通属藤本植物,原产于中国和日本,在中国主要分布于陕西与湖北西部、河南南部及甘肃、四川等地[1-2],为 2015 年版《中国药典》收录的 3 个木通属植物之一,具有利尿通淋、清火除烦、通经下乳的功效,用于治疗心烦尿赤、水肿、淋症、经闭乳少等症状[3-4]。三叶木通化学成分丰富复杂,包括三萜类、三萜皂苷类、木脂素类、苯丙素类和酚醇苷类等[5],三萜皂苷类为其主要化学成分,现研究表明三萜皂苷在利尿抗水肿、抗菌消炎、抑制肿瘤细胞生长等多方面均有潜在的开发应用价值[6-8],为更好地开发利用该植物药用资源,本课题组对三叶木通进行较为系统的化学成分研究。采用三叶木通 75% 乙醇提取物通过硅胶柱色谱、凝胶、高压制备技术分离鉴定了 14 个化合物。分别为木通皂苷 B(**1**),木通皂苷 C(**2**),皂苷 PH(**3**),卵叶银莲花苷 A(**4**),2α,3β,23-三羟基齐墩果烷-30-去甲基-12,19-双烯-28-*O*-β-*D*-吡喃木糖-(1→3)-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(**5**),akemisaponins D(**6**),akemisaponins E(**7**),积雪草苷(**8**),皂苷 PJ1(**9**),scheffoleoside A(**10**),symplocosneolignan A(**11**),刺楸皂苷 D(**12**),leonticin E(**13**),ciwujianoside A_1(**14**)。化合物 **1** ~ **4**,**11**,**13**,**14** 均为首次从该植物中分离得到。结构式见图 1。

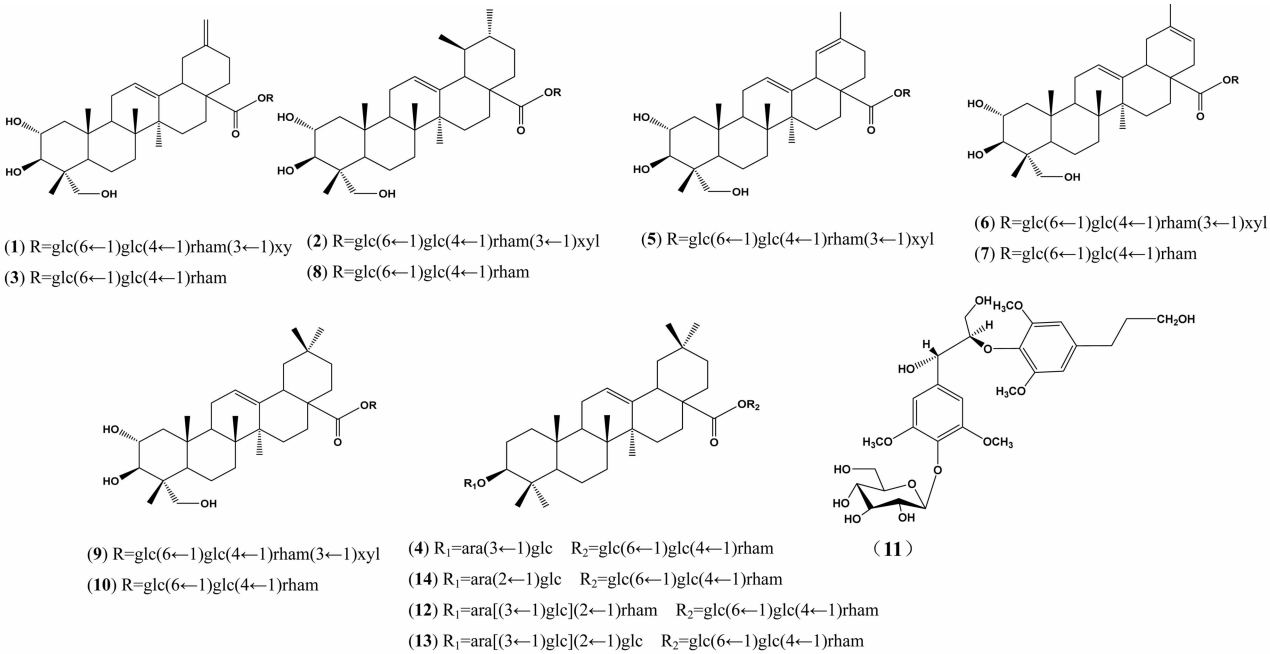

图 1 化合物 1 ~ 14 结构式

Fig. 1 Compound 1-14 structural formula

1 材料

1260 型高效液相色谱仪,1200 型制备高效液相色谱仪(美国安捷伦公司);中压液相制备色谱仪(瑞士步琪公司);BP211D 型电子天平(德国赛托利斯集团);SB-1000 型旋转蒸发仪(日本 EYELA 公司);电热恒温水浴锅(上海跃进医疗器械厂);UNITY INOVA 600 型超导核磁共振仪(美国 Varian 公司),ZabSpec 型质谱仪(美国 Micromass 公司);

C_{18}反相填料(日本 YMC 公司),柱色谱硅胶、薄层色谱硅胶(青岛海洋化工厂),其他所用试剂均为分析纯或色谱纯。

三叶木通药材由江西南昌济生制药厂提供,经江西省药品检验检测研究院周国平主任中药师鉴定为木通科木通属植物三叶木通 *Akebia trifoliata* 的干燥藤茎。标本保存在江西省药品检验检测研究院中药室标本馆。

2 提取与分离

三叶木通药材(100 kg),粉碎后用 75% 乙醇回流提取 3 次,每次 2 h,提取液合并减压浓缩至无醇味,得干浸膏 20 kg。然后加适量水使成混悬液,依次用等体积的二氯甲烷、乙酸乙酯、正丁醇分别萃取 2 次,减压浓缩至干,得正丁醇部分 3 kg。

取正丁醇部分 2 kg 上 D_{101} 大孔树脂,分别用 10%,30%,50%,70%,95% 乙醇梯度洗脱。收集 30% 乙醇洗脱液,减压浓缩至干,称质量 555 g,该馏分样品经硅胶柱色谱(100 ~ 200 目),以三氯甲烷-甲醇(2∶1)洗脱,经薄层色谱检视,合并相近的组分,得馏分 F_1 ~ F_{16}。馏分 F_{12}(95 g)经硅胶柱色谱,以三氯甲烷-甲醇(5∶1 ~ 1∶1)梯度洗脱,得到馏分 $F_{12\text{-}1}$ ~ $F_{12\text{-}8}$,$F_{12\text{-}1}$(700 mg)经 LH-20 型羟丙基葡聚糖凝胶柱(Sephadex LH-20)得馏分($F_{12\text{-}1\text{-}1}$ ~ $F_{12\text{-}1\text{-}4}$),$F_{12\text{-}1\text{-}2}$(42 mg)经反相高效制备液相色谱,乙腈-水(14∶86)为流动相,得化合物 **4**(5 mg),**10**(7 mg),$F_{12\text{-}4}$(10 g)过 C_{18} 中压柱,以乙腈-水(25∶75 ~ 29∶71)梯度洗脱,经高效液相色谱检测后,合并为 4 个部分($F_{12\text{-}4\text{-}1}$ ~ $F_{12\text{-}4\text{-}4}$)。$F_{12\text{-}4\text{-}2}$(200 mg)经反相高效制备液相色谱,以乙腈-水(21∶79)为流动相,得化合物 **3**(60 mg),$F_{12\text{-}5}$过 C_{18}中压柱,乙腈-水(21∶79 ~ 23∶77)梯度洗脱,经高效液相色谱检测后,合并为 7 个部分($F_{12\text{-}5\text{-}1}$ ~ $F_{12\text{-}5\text{-}7}$)。$F_{12\text{-}5\text{-}2}$(127 mg)经反相高效制备液相色谱,以乙腈-水(18∶82)为流动相,得化合物 **12**(18 mg),**13**(13 mg)。$F_{12\text{-}5\text{-}3}$(2.81 g)经反相高效制备液相色谱,以乙腈-水(21∶79)为流动相,得化合物 **1**(26 mg),**5**(13 mg),**6**(37 mg),**7**(9 mg),**9**(24 mg)。$F_{16\text{-}5\text{-}5}$(639 mg)经反相高效制备液相色谱,以乙腈-水(22∶78)为流动相,得化合物 **2**(86 mg),**8**(34 mg)。$F_{12\text{-}5\text{-}6}$(160 mg)经反相高效制备液相色谱,以乙腈-水(29∶71)为流动相,得化合物 **11**(24 mg)。$F_{12\text{-}4}$(10 g)过 C_{18} 中压柱,以乙腈-水(25∶75 ~ 29∶71)梯度洗脱,经高效液相色谱检测后,合并为 2 个部分($F_{12\text{-}4\text{-}1}$ ~ $F_{12\text{-}4\text{-}2}$)。$F_{12\text{-}4\text{-}2}$(56 mg)经反相高效制备液相色谱,以乙腈-水(22∶78)为流动相,得化合物 **14**(18 mg)。

3 结构鉴定

化合物 **1** 白色无定形粉末(甲醇)。ESI-MS *m/z* 1 097 $[M + Na]^+$。^{1}H-NMR(600 MHz, C_5D_5N) δ:6.22(1H, d, J = 7.8 Hz, glc-H-1),5.91(1H, br s, rham-H-1),5.44(1H, br s, H-12),5.27(1H, d, J = 7.8, 1.8 Hz, xyl-H-1),4.95(1H, d, J = 7.8 Hz, glc′-H-1),4.71(1H, s, H-29a),4.66(1H, s, H-29b),4.22(1H, d, J = 10.8 Hz, H-23a),3.72(1H, d, J = 10.8 Hz, H-23b),1.68(3H, d, J = 6.0 Hz, rham-H-6),1.14(3H, s, H-26),1.13(3H, s, H-27),1.12(3H, s, H-25),1.09(3H, s, H-24);^{13}C-NMR(150 MHz, C_5D_5N) δ:48.0(C-1),69.3(C-2),78.4(C-3),44.1(C-4),48.3(C-5),19.0(C-6),32.3(C-7),40.5(C-8),48.6(C-9),38.9(C-10),24.4(C-11),123.0(C-12),144.0(C-13),42.6(C-14),28.7(C-15),24.0(C-16),48.3(C-17),47.8(C-18),42.1(C-19),148.8(C-20),30.5(C-21),38.1(C-22),66.8(C-23),14.9(C-24),18.0(C-25),18.1(C-26),26.5(C-27),176.3(C-28),107.8(C-29),96.2(glc-C-1),74.3(glc-C-2),78.9(glc-C-3),71.5(glc-C-4),78.4(glc-C-5),69.8(glc-C-6),105.4(glc′-C-1),75.9(glc′-C-2),76.8(glc′-C-3),77.7(glc′-C-4),77.7(glc′-C-5),61.7(glc′-C-6),102.8(rham-C-1),72.6(rham-C-2),83.8(rham-C-3),73.4(rham-C-4),70.3(rham-C-5),18.9(rham-C-6),107.9(xyl-C-1),76.1(xyl-C-2),79.1(xyl-C-3),71.3(xyl-C-4),67.8(xyl-C-5)。以上数据与文献[9]报道的数据一致,因此鉴定化合物 **1** 为木通皂苷 B。

化合物 **2** 白色无定形粉末(甲醇)。ESI-MS *m/z* 1 113 $[M + Na]^+$。^{1}H-NMR(600 MHz, C_5D_5N) δ:6.22(1H, d, J = 7.8 Hz, glc-H-1),5.91(1H, br s, rham-H-1),5.44(1H, br s, H-12),5.27(1H, d, J = 7.8, 1.8 Hz, xyl-H-1),4.95(1H, d, J = 7.8 Hz, glc′-H-1),4.22(1H, d, J = 10.8 Hz, H-23a),3.72(1H, d, J = 10.8 Hz, H-23b),1.68(3H, d, J = 6.0 Hz, rham-H-6),1.20(3H, s, H-26),1.14(3H, s, H-25),1.09(3H, s, H-27),1.08(3H, s, H-24),0.92(3H, d, J = 6.0 Hz, H-29),0.88(3H, d, J = 6.0 Hz, H-30);^{13}C-NMR(150 MHz, C_5D_5N) δ:48.1(C-1),69.0(C-2),78.2(C-3),43.6(C-4),47.9(C-5),18.5(C-6),33.2(C-7),40.2(C-8),48.2(C-9),38.3(C-10),23.8(C-11),126.0(C-12),138.6(C-13),42.5(C-

14), 28.6 (C-15), 24.5 (C-16), 48.3 (C-17), 53.2 (C-18), 39.3 (C-19), 39.1 (C-20), 36.7 (C-21), 30.8 (C-22), 66.5 (C-23), 14.4 (C-24), 17.7 (C-25), 17.8 (C-26), 23.7 (C-27), 176.3 (C-28), 17.4 (C-29), 21.2 (C-30), 95.6 (glc-C-1), 73.8 (glc-C-2), 78.9 (glc-C-3), 71.1 (glc-C-4), 77.8 (glc-C-5), 69.6 (glc-C-6), 105.2 (glc′-C-1), 75.5 (glc′-C-2), 76.4 (glc′-C-3), 77.2 (glc′-C-4), 77.2 (glc′-C-5), 61.3 (glc′-C-6), 102.1 (rham-C-1), 72.2 (rham-C-2), 83.5 (rham-C-3), 73.0 (rham-C-4), 70.0 (rham-C-5), 18.4 (rham-C-6), 107.5 (xyl-C-1), 75.7 (xyl-C-2), 78.4 (xyl-C-3), 71.1 (xyl-C-4), 67.3 (xyl-C-5)。以上数据与文献[9]报道的数据一致,因此鉴定化合物 **2** 为木通皂苷 C。

化合物 **3**　白色无定形粉末(甲醇)。ESI-MS *m/z* 947 [M + Na]$^+$。^{1}H-NMR (600 MHz, C_5D_5N) δ: 6.21 (1H, d, *J* = 7.8 Hz, glc-H-1), 5.90 (1H, br s, rham-H-1), 5.44 (1H, br s, H-12), 4.94 (1H, d, *J* = 7.8 Hz, glc′-H-1), 4.70 (1H, s, H-29a), 4.66 (1H, s, H-29b), 4.22 (1H, d, *J* = 10.8 Hz, H-23a), 3.72 (1H, d, *J* = 10.8 Hz, H-23b), 1.68 (3H, d, *J* = 6.0 Hz, rham-H-6), 1.15 (3H, s, H-26), 1.13 (3H, s, H-27), 1.11 (3H, s, H-25), 1.10 (3H, s, H-24); ^{13}C-NMR (150 MHz, C_5D_5N) δ: 48.0 (C-1), 69.4 (C-2), 78.6 (C-3), 44.1 (C-4), 48.3 (C-5), 19.0 (C-6), 32.3 (C-7), 40.5 (C-8), 48.6 (C-9), 38.9 (C-10), 24.4 (C-11), 123.0 (C-12), 144.0 (C-13), 42.6 (C-14), 28.7 (C-15), 24.0 (C-16), 48.3 (C-17), 47.8 (C-18), 42.1 (C-19), 148.8 (C-20), 30.5 (C-21), 38.1 (C-22), 66.8 (C-23), 14.9 (C-24), 18.0 (C-25), 18.1 (C-26), 26.5 (C-27), 176.3 (C-28), 107.9 (C-29), 96.2 (glc-C-1), 74.3 (glc-C-2), 79.1 (glc-C-3), 71.5 (glc-C-4), 78.6 (glc-C-5), 69.8 (glc-C-6), 105.4 (glc′-C-1), 75.9 (glc′-C-2), 77.0 (glc′-C-3), 78.4 (glc′-C-4), 77.6 (glc′-C-5), 61.7 (glc′-C-6), 102.8 (rham-C-1), 73.1 (rham-C-2), 73.2 (rham-C-3), 74.4 (rham-C-4), 70.3 (rham-C-5), 18.8 (rham-C-6)。以上数据与文献[9]报道的数据一致,因此鉴定化合物 **3** 为皂苷 PH。

化合物 **4**　白色无定形粉末(甲醇)。ESI-MS *m/z* 1 097 [M + Na]$^+$。^{1}H-NMR (600 MHz, C_5D_5N) δ: 6.26 (1H, d, *J* = 7.8 Hz, glc-H-1), 5.88 (1H, br s, rham-H-1), 5.42 (1H, br s, H-12), 5.40 (1H, d, *J* = 7.8 Hz, glc″-H-1), 5.21 (1H, br s, H-21), 5.00 (1H, d, *J* = 7.8 Hz, glc′-H-1), 4.73 (1H, d, *J* = 7.2 Hz, ara-H-1), 3.36 (1H, dd, *J* = 4.8, 12.0 Hz, H-3), 1.71 (3H, d, *J* = 6.0 Hz, rham-H-6), 1.31 (3H, s, H-30), 1.26 (3H, s, H-29), 1.11 (3H, s, H-27), 1.00 (3H, s, H-26), 0.91 (3H, s, H-25), 0.90 (3H, s, H-24), 0.89 (3H, s, H-23); ^{13}C-NMR (150 MHz, C_5D_5N) δ: 39.1 (C-1), 27.0 (C-2), 89.0 (C-3), 40.0 (C-4), 56.2 (C-5), 18.8 (C-6), 33.5 (C-7), 40.2 (C-8), 48.4 (C-9), 37.4 (C-10), 24 (C-11), 123.2 (C-12), 144.4 (C-13), 42.4 (C-14), 28.6 (C-15), 23.7 (C-16), 47.4 (C-17), 42.0 (C-18), 46.5 (C-19), 31.1 (C-20), 34.3 (C-21), 32.9 (C-22), 28.4 (C-23), 17.3 (C-24), 15.9 (C-25), 17.8 (C-26), 26.4 (C-27), 176.8 (C-28), 33.5 (C-29), 24.1 (C-30), 107.7 (ara-C-1), 71.9 (ara-C-2), 84.4 (ara-C-3), 69.5 (ara-C-4), 67.3 (ara-C-5), 106.7 (glc-C-1), 76.1 (glc-C-2), 78.5 (glc-C-3), 72.2 (glc-C-4), 78.7 (glc-C-5), 62.9 (glc-C-6), 96.0 (glc′-C-1), 74.2 (glc′-C-2), 79.0 (glc′-C-3), 71.2 (glc′-C-4), 78.4 (glc′-C-5), 69.6 (glc′-C-6), 105.2 (glc″-C-1), 75.7 (glc″-C-2), 76.8 (glc″-C-3), 79.1 (glc″-C-4), 77.5 (glc″-C-5), 61.6 (glc″-C-6), 103.0 (rham-C-1), 72.9 (rham-C-2), 72.8 (rham-C-3), 74.3 (rham-C-4), 70.6 (rham-C-5), 18.8 (rham-C-6)。以上数据与文献[10]报道的数据一致,因此鉴定化合物 **4** 为卵叶银莲花苷 A。

化合物 **5**　白色无定形粉末(甲醇)。ESI-MS *m/z* 1 097 [M + Na]$^+$。^{1}H-NMR (600 MHz, C_5D_5N) δ: 6.30 (1H, d, *J* = 7.8 Hz, glc-H-1), 5.91 (1H, br s, rham-H-1), 5.55 (1H, br s, H-12), 5.26 (1H, d, *J* = 7.8 Hz, xyl-H-1), 5.19 (1H, br s, H-19), 4.93 (1H, d, *J* = 7.8 Hz, glc′-H-1), 4.23 (1H, d, *J* = 10.2 Hz, H-23a), 3.71 (1H, d, *J* = 10.2 Hz, H-23b), 1.69 (3H, d, *J* = 6.0 Hz, rham-H-6), 1.57 (3H, s, H-29), 1.16 (3H, s, H-26), 1.13 (3H, s, H-25), 1.09 (3H, s, H-27), 1.07 (3H, s, H-24); ^{13}C-NMR (150 MHz, C_5D_5N) δ: 48.0 (C-1), 69.0 (C-2), 78.3 (C-3), 44.0 (C-4), 48.0 (C-5), 18.4 (C-6), 33.4 (C-7), 39.7 (C-8), 48.1 (C-9), 38.5 (C-10), 23.8 (C-11), 123.5 (C-12), 142.7 (C-13), 43.2 (C-14), 28 (C-15), 22.9 (C-16), 45.9 (C-17), 46.0 (C-18), 129.5 (C-19), 129.7 (C-20), 26.2 (C-21), 32.6 (C-22), 66.4 (C-23), 14.6 (C-24), 17.8 (C-25), 17.9 (C-26), 23.6 (C-27), 176.3 (C-28), 23.2 (C-29), 95.8 (glc-C-1), 73.3 (glc-C-2), 78.7 (glc-C-3), 70.7 (glc-C-4), 77.9

(glc-C-5), 69.4 (glc-C-6), 105.2 (glc′-C-1), 75.5 (glc′-C-2), 76.4 (glc′-C-3), 78.5 (glc′-C-4), 77.2 (glc′-C-5), 61.2 (glc′-C-6), 102.4 (rham-C-1), 72.2 (rham-C-2), 83.2 (rham-C-3), 73 (rham-C-4), 70.1 (rham-C-5), 18.5 (rham-C-6), 107.4 (xyl-C-1), 75.4 (xyl-C-2), 77.2 (xyl-C-3), 71.1 (xyl-C-4), 67.3 (xyl-C-5)。以上数据与文献[11]报道的数据一致,因此鉴定化合物 **5** 为 2α,3β,23-三羟基齐墩果烷-30-去甲基-12,19-双烯-28-*O*-β-*D*-吡喃木糖-(1→3)-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。

化合物 **6**　白色无定形粉末(甲醇)。ESI-MS *m/z* 1 097 $[M+Na]^+$。^{1}H-NMR (600 MHz, C_5D_5N) δ: 6.23 (1H, d, *J* = 7.8 Hz, glc-H-1), 5.90 (1H, br s, rham-H-1), 5.44 (1H, br s, H-12), 5.26 (1H, d, *J* = 7.8 Hz, xyl-H-1), 5.21 (1H, br s, H-21), 4.94 (1H, d, *J* = 7.8 Hz, glc′-H-1), 4.17 (1H, m, H-23a), 3.71 (1H, d, *J* = 10.2 Hz, H-23b), 1.68 (3H, d, *J* = 6.0 Hz, rham-H-6), 1.60 (3H, s, H-29), 1.20 (3H, s, H-27), 1.16 (3H, s, H-26), 1.13 (3H, s, H-25), 1.09 (3H, s, H-24); ^{13}C-NMR (150 MHz, C_5D_5N) δ: 47.8 (C-1), 69.0 (C-2), 78.4 (C-3), 43.8 (C-4), 48.1 (C-5), 18.8 (C-6), 32.9 (C-7), 40.1 (C-8), 48.3 (C-9), 38.5 (C-10), 24.1 (C-11), 123.1 (C-12), 143.8 (C-13), 42.2 (C-14), 28.7 (C-15), 26 (C-16), 45.3 (C-17), 42.2 (C-18), 36.9 (C-19), 132.7 (C-20), 117.5 (C-21), 36.8 (C-22), 66.7 (C-23), 14.3 (C-24), 17.6 (C-25), 17.8 (C-26), 27.0 (C-27), 176.2 (C-28), 23.3 (C-29), 95.8 (glc-C-1), 73.9 (glc-C-2), 78.9 (glc-C-3), 71.1 (glc-C-4), 77.9 (glc-C-5), 69.6 (glc-C-6), 105.2 (glc′-C-1), 75.5 (glc′-C-2), 76.5 (glc′-C-3), 77.6 (glc′-C-4), 77.2 (gl′-C-5), 61.5 (glc′-C-6), 102.5 (rham-C-1), 72.2 (rham-C-2), 83.5 (rham-C-3), 73.0 (rham-C-4), 70.1 (rham-C-5), 18.5 (rham-C-6), 107.3 (xyl-C-1), 75.7 (xyl-C-2), 78.4 (xyl-C-3), 71.1 (xyl-C-4), 67.3 (xyl-C-5)。以上数据与文献[12]报道的数据一致,因此鉴定化合物 **6** 为 akemisaponins D。

化合物 **7**　白色无定形粉末(甲醇)。ESI-MS *m/z* 965 $[M+Na]^+$。^{1}H-NMR (600 MHz, C_5D_5N) δ: 6.23 (1H, d, *J* = 7.8 Hz, glc-H-1), 5.89 (1H, br s, rham-H-1), 5.45 (1H, br s, H-12), 5.21 (1H, br s, H-21), 4.99 (1H, d, *J* = 7.8 Hz, glc′-H-1), 4.17 (1H, m, H-23a), 3.71 (1H, d, *J* = 10.2 Hz, H-23b), 1.72 (3H, d, *J* = 6.0 Hz, rham-H-6), 1.60 (3H, s, H-29), 1.19 (3H, s, H-27), 1.16 (3H, s, H-26), 1.14 (3H, s, H-25), 1.10 (3H, s, H-24); ^{13}C-NMR (150 MHz, C_5D_5N) δ: 47.8 (C-1), 69.0 (C-2), 78.3 (C-3), 43.8 (C-4), 48.1 (C-5), 18.7 (C-6), 32.6 (C-7), 40.2 (C-8), 48.3 (C-9), 38.5 (C-10), 24.1 (C-11), 123.2 (C-12), 143.7 (C-13), 42.2 (C-14), 28.7 (C-15), 26.0 (C-16), 45.2 (C-17), 42.2 (C-18), 36.9 (C-19), 132.8 (C-20), 117.5 (C-21), 36.8 (C-22), 66.8 (C-23), 14.4 (C-24), 17.6 (C-25), 17.7 (C-26), 27.1 (C-27), 176.3 (C-28), 23.3 (C-29), 95.8 (glc-C-1), 73.9 (glc-C-2), 78.4 (glc-C-3), 71.1 (glc-C-4), 78.7 (glc-C-5), 69.6 (glc-C-6), 105.2 (glc′-C-1), 75.4 (glc′-C-2), 76.6 (glc′-C-3), 78.6 (glc′-C-4), 77.2 (glc′-C-5), 61.5 (glc′-C-6), 102.8 (rham-C-1), 72.6 (rham-C-2), 72.8 (rham-C-3), 74.1 (rham-C-4), 70.4 (rham-C-5), 18.5 (rham-C-6)。以上数据与文献[12]报道的数据一致,因此鉴定化合物 **7** 为 akemisaponins E。

化合物 **8**　白色无定形粉末(甲醇)。ESI-MS *m/z* 957 $[M-H]^-$。^{1}H-NMR (600 MHz, C_5D_5N) δ: 6.20 (1H, d, *J* = 7.8 Hz, glc-H-1), 5.89 (1H, br s, rham-H-1), 5.42 (1H, br s, H-12), 4.99 (1H, d, *J* = 7.8 Hz, glc′-H-1), 4.18 (1H, m, H-23a), 3.72 (1H, d, *J* = 10.8 Hz, H-23b), 1.71 (3H, d, *J* = 6.0 Hz, rham-H-6), 1.19 (3H, s, H-26), 1.13 (3H, s, H-25), 1.08 (3H, s, H-27), 1.08 (3H, s, H-24), 0.91 (3H, d, *J* = 6.0 Hz, H-29), 0.87 (3H, d, *J* = 6.0 Hz, H-30); ^{13}C-NMR (150 MHz, C_5D_5N) δ: 48.0 (C-1), 69.0 (C-2), 78.2 (C-3), 43.6 (C-4), 48 (C-5), 18.5 (C-6), 33.2 (C-7), 40.2 (C-8), 48.1 (C-9), 38.4 (C-10), 23.9 (C-11), 126.0 (C-12), 138.6 (C-13), 42.5 (C-14), 28.7 (C-15), 24.6 (C-16), 48.4 (C-17), 53.2 (C-18), 39.3 (C-19), 39.1 (C-20), 36.8 (C-21), 30.9 (C-22), 66.6 (C-23), 14.4 (C-24), 17.7 (C-25), 17.8 (C-26), 23.8 (C-27), 176.3 (C-28), 23.8 (C-29), 21.2 (C-30), 95.6 (glc-C-1), 73.8 (glc-C-2), 78.9 (glc-C-3), 71.1 (glc-C-4), 77.9 (glc-C-5), 69.5 (glc-C-6), 105.1 (glc′-C-1), 75.4 (glc′-C-2), 78.4 (glc′-C-3), 77.2 (glc′-C-4), 77.2 (glc′-C-5), 61.3 (glc′-C-6), 102.7 (rham-C-1), 72.6 (rham-C-2), 72.8 (rham-C-3), 74.0 (rham-C-4), 70.3 (rham-C-5), 18.4 (rham-C-6)。以上数据与文献[13]报道的数据一致,因此鉴定化合物 **8** 为积雪草苷。

化合物 **9**　白色无定形粉末(甲醇)。ESI-MS *m/z* 1 113 [M + Na]$^+$。^{1}H-NMR(600 MHz, C_5D_5N) δ:6.26(1H, d, *J* = 7.8 Hz, glc-H-1), 5.91(1H, br s, rham-H-1), 5.42(1H, br s, H-12), 5.27(1H, d, *J* = 7.8, 1.8 Hz, xyl-H-1), 4.97(1H, d, *J* = 7.8 Hz, glc′-H-1), 4.22(1H, d, *J* = 10.8 Hz, H-23a), 3.72(1H, d, *J* = 10.8 Hz, H-23b), 1.69(3H, d, *J* = 6.0 Hz, rham-H-6), 1.16(3H, s, H-27), 1.16(3H, s, H-26), 1.13(3H, s, H-25), 1.09(3H, s, H-24), 0.88(3H, s, H-29), 0.88(3H, s, H-30); ^{13}C-NMR(150 MHz, C_5D_5N) δ:47.7(C-1), 68.8(C-2), 78.2(C-3), 43.6(C-4), 47.8(C-5), 18.6(C-6), 34.0(C-7), 39.9(C-8), 48.1(C-9), 38.3(C-10), 23.9(C-11), 122.7(C-12), 144.0(C-13), 42.1(C-14), 28.2(C-15), 23.3(C-16), 46.8(C-17), 41.5(C-18), 46.1(C-19), 30.7(C-20), 32.7(C-21), 32.4(C-22), 66.3(C-23), 14.3(C-24), 17.4(C-25), 17.5(C-26), 25.9(C-27), 176.4(C-28), 32.9(C-29), 23.6(C-30), 95.6(glc-C-1), 73.8(glc-C-2), 78.7(glc-C-3), 71(glc-C-4), 77.9(glc-C-5), 69.2(glc-C-6), 105(glc′-C-1), 75.3(glc′-C-2), 76.3(glc′-C-3), 77.1(glc′-C-4), 77.1(glc′-C-5), 61.2(glc′-C-6), 102.4(rham-C-1), 72.1(rham-C-2), 83.3(rham-C-3), 73.0(rham-C-4), 70.0(rham-C-5), 18.5(rham-C-6), 107.4(xyl-C-1), 75.7(xyl-C-2), 78.3(xyl-C-3), 71.1(xyl-C-4), 67.3(xyl-C-5)。以上数据与文献[14]报道的数据一致,因此鉴定化合物 **9** 为皂苷 PJ1。

化合物 **10**　白色无定形粉末(甲醇)。ESI-MS *m/z* 957[M + Na]$^+$。^{1}H-NMR(600 MHz, C_5D_5N) δ:6.23(1H, d, *J* = 7.8 Hz, glc-H-1), 5.85(1H, br s, rham-H-1), 5.38(1H, br s, H-12), 5.21(1H, br s, H-21), 4.98(1H, d, *J* = 7.8 Hz, glc′-H-1), 4.11(1H, m, H-23a), 3.65(1H, d, *J* = 10.2 Hz, H-23b), 1.69(3H, d, *J* = 6.0 Hz, rham-H-6), 1.12(3H, s, H-27), 1.12(3H, s, H-26), 1.10(3H, s, H-25), 1.06(3H, s, H-24), 0.85(3H, s, H-29), 0.83(3H, s, H-30); ^{13}C-NMR(150 MHz, C_5D_5N) δ:47.8(C-1), 69.0(C-2), 78.3(C-3), 43.8(C-4), 48.1(C-5), 18.7(C-6), 32.6(C-7), 40.2(C-8), 48.3(C-9), 38.5(C-10), 24.1(C-11), 123.2(C-12), 143.7(C-13), 42.2(C-14), 28.7(C-15), 26.0(C-16), 45.2(C-17), 42.2(C-18), 36.9(C-19), 132.8(C-20), 117.5(C-21), 36.8(C-22), 66.8(C-23), 14.4(C-24), 17.6(C-25), 17.7(C-26), 27.1(C-27), 176.3(C-28), 33.1(C-29), 23.7(C-30), 95.8(glc-C-1), 73.9(glc-C-2), 78.4(glc-C-3), 71.1(glc-C-4), 78.7(glc-C-5), 69.6(glc-C-6), 105.2(glc′-C-1), 75.4(glc′-C-2), 76.6(glc′-C-3), 78.6(glc′-C-4), 77.2(glc′-C-5), 61.5(glc′-C-6), 102.8(rham-C-1), 72.6(rham-C-2), 72.8(rham-C-3), 74.1(rham-C-4), 70.4(rham-C-5), 18.5(rham-C-6)。以上数据与文献[15]报道的数据一致,因此鉴定化合物 **10** 为 scheffoleoside A。

化合物 **11**　淡黄色粉末(甲醇)。ESI-MS *m/z* 623[M + Na]$^+$。^{1}H-NMR(600 MHz, CD_3OD) δ:6.61(2H, s, H-2′,6′), 6.53(2H, s, H-2,6), 4.30(1H, d, *J* = 7.8 Hz, glc-H-1), 3.84(6H, s, 3′,5′-OMe), 3.79(6H, s, 3,5-OMe)。^{13}C-NMR(150 MHz, CD_3OD) δ:139.5(C-1), 106.4(C-2), 153.9(C-3), 135.5(C-4), 153.9(C-5), 106.4(C-6), 73.9(C-7), 88.0(C-8), 61.8(C-9), 139.5(C-1′), 106.7(C-2′), 154.7(C-3′), 135.5(C-4′), 154.7(C-5′), 106.7(C-6′), 33.5(C-7′), 35.9(C-8′), 62.9(C-9′), 105.6(glc-C-1), 76.5(glc-C-2), 77.9(glc-C-3), 71.9(glc-C-4), 78.7(glc-C-5), 62.9(glc-C-6), 56.6(C-3,5-OMe), 56.9(C-3′,5′-OMe)。以上数据与文献[16]报道的数据一致,因此鉴定化合物 **11** 为 symplocosneolignan A。

化合物 **12**　白色无定形粉末(甲醇)。ESI-MS *m/z* 1 389[M + Na]$^+$。^{1}H-NMR(600 MHz, C_5D_5N) δ:6.26(1H, d, *J* = 7.8 Hz, glc-H-1), 5.87(1H, br s, rham-H-1), 5.62(1H, br s, rham′-H-1), 5.41(1H, br s, H-12), 5.40(1H, d, *J* = 7.8 Hz, glc″-H-1), 5.21(1H, br s, H-21), 5.01(1H, d, *J* = 7.8 Hz, glc′-H-1), 4.73(1H, d, *J* = 7.2 Hz, ara-H-1), 3.36(1H, dd, *J* = 4.8, 12.0 Hz, H-3), 1.71(3H, d, *J* = 6.0 Hz, rham-H-6), 1.62(3H, d, *J* = 6.0 Hz, rham′-H-6), 1.31(3H, s, H-30), 1.26(3H, s, H-29), 1.10(3H, s, H-27), 1.00(3H, s, H-26), 0.90(3H, s, H-25), 0.89(3H, s, H-24), 0.88(3H, s, H-23)。^{13}C-NMR(150 MHz, C_5D_5N) δ:39.1(C-1), 26.9(C-2), 89.2(C-3), 40.2(C-4), 56.4(C-5), 18.9(C-6), 32.8(C-7), 40.3(C-8), 48.3(C-9), 37.3(C-10), 24.1(C-11), 123.2(C-12), 144.4(C13), 42.4(C-14), 28.6(C-15), 23.7(C-16), 47.3(C-17), 42.0(C-18), 46.5(C-19), 31.1(C-20), 34.4(C-21), 33.2(C-22), 28.3(C-23), 17.5(C-24), 16.0(C-25), 17.9(C-26), 26.3(C-27), 176.8(C-28), 33.4(C-29),

24.0(C-30),96.3(glc-C-1),73.2(glc-C-2),79.2(glc-C-3),70.1(glc-C-4),77.7(glc-C-5),68.5(glc-C-6),105.7(glc′-C-1),74.4(glc′-C-2),75.8(glc′-C-3),78.3(glc′-C-4),77.0(glc′-C-5),61.8(glc′-C-6),103.2(rham-C-1),71.2(rham-C-2),73.1(rham-C-3),73.4(rham-C-4),69.9(rham-C-5),19.0(rham-C-6),105.1(ara-C-1),74.9(ara-C-2),83.1(ara-C-3),68.7(ara-C-4),65.5(ara-C-5),104.5(glc″-C-1),74.8(glc″-C-2),78.2(glc″-C-3),71.6(glc″-C-4),78.3(glc″-C-5),62.6(glc″-C-6),101.7(rham′-C-1),72.5(rham′-C-2),72.4(rham′-C-3),73.8(rham′-C-4),70.1(rham′-C-5),18.4(rham′-C-6)。以上数据与文献[17]报道的数据一致,因此鉴定化合物**12**为刺楸皂苷 D。

化合物**13** 白色无定形粉末(甲醇)。ESI-MS *m/z* 1 405[M + Na]$^+$。^{1}H-NMR(600 MHz,C_5D_5N)δ:6.24(1H,d,*J* = 7.8 Hz,glc-H-1),5.86(1H,br s,rham-H-1),5.50(1H,d,*J* = 7.8 Hz,glc‴-H-1),5.41(1H,br s,H-12),5.33(1H,d,*J* = 7.8 Hz,glc″-H-1),5.21(1H,br s,H-21),5.01(1H,d,*J* = 7.8 Hz,glc′-H-1),4.73(1H,d,*J* = 7.2 Hz,ara-H-1),3.36(1H,dd,*J* = 4.8,12.0 Hz,H-3),1.71(3H,d,*J* = 6.0 Hz,rham-H-6),1.30(3H,s,H-30),1.26(3H,s,H-29),1.10(3H,s,H-27),1.00(3H,s,H-26),0.91(3H,s,H-25),0.90(3H,s,H-24),0.89(3H,s,H-23)。^{13}C-NMR(150 MHz,C_5D_5N)δ:39.1(C-1),26.9(C-2),89.3(C-3),40.2(C-4),56.4(C-5),18.9(C-6),32.8(C-7),40.3(C-8),48.3(C-9),37.3(C-10),24.1(C-11),123.1(C-12),144.4(C-13),42.4(C-14),28.6(C-15),23.7(C-16),47.3(C-17),42.0(C-18),46.5(C-19),31.1(C-20),34.4(C-21),33.2(C-22),28.3(C-23),17.5(C-24),16.0(C-25),17.9(C-26),26.3(C-27),176.9(C-28),33.4(C-29),24.0(C-30),96.5(glc-C-1),73.5(glc-C-2),79.0(glc-C-3),70.0(glc-C-4),77.5(glc-C-5),68.6(glc-C-6),105.7(glc′-C-1),74.4(glc′-C-2),75.8(glc′-C-3),78.3(glc′-C-4),77.0(glc′-C-5),61.8(glc′-C-6),103.2(rham-C-1),71.2(rham-C-2),73.2(rham-C-3),73.4(rham-C-4),69.9(rham-C-5),18.9(rham-C-6),105.2(ara-C-1),77.4(ara-C-2),83.3(ara-C-3),68.8(ara-C-4),65.9(ara-C-5),105.3(glc″-C-1),75.7(glc″-C-2),78.6(glc″-C-3),72.1(glc″-C-4),77.5(glc″-C-5),63.1(glc″-C-6),104.4(glc‴-C-1),76.7(glc‴-C-2),78.3(glc‴-C-3),71.0(glc‴-C-4),78.6(glc‴-C-5),62.7(glc‴-C-6)。以上数据与文献[18]报道的数据一致,因此鉴定化合物**13**为 leonticin E。

化合物**14** 白色无定形粉末(甲醇)。ESI-MS *m/z* 1 097 [M + Na]$^+$。^{1}H-NMR(600 MHz,C_5D_5N)δ:6.26(1H,d,*J* = 7.8 Hz,glc-H-1),5.88(1H,br s,rham-H-1),5.40(1H,br s,H-12),4.96(1H,d,*J* = 7.8 Hz,glc‴-H-1),5.21(1H,br s,H-21),5.00(1H,d,*J* = 7.8 Hz,glc′-H-1),4.78(1H,d,*J* = 7.2 Hz,ara-H-1),3.36(1H,dd,*J* = 4.8,12.0 Hz,H-3),1.69(3H,d,*J* = 6.0 Hz,rham-H-6),1.31(3H,s,H-30),1.25(3H,s,H-29),1.11(3H,s,H-27),1.01(3H,s,H-26),0.91(3H,s,H-25),0.89(3H,s,H-24),0.88(3H,s,H-23)。^{13}C-NMR(150 MHz,C_5D_5N)δ:39.2(C-1),27.4(C-2),89.2(C-3),40.2(C-4),56.4(C-5),18.9(C-6),33.7(C-7),40.3(C-8),48.6(C-9),37.6(C-10),24.4(C-11),123.2(C-12),144.3(C-13),42.4(C-14),28.9(C-15),23.9(C-16),47.5(C-17),41.8(C-18),46.7(C-19),30.6(C-20),34.8(C-21),32.7(C-22),28.8(C-23),17.6(C-24),16.3(C-25),17.9(C-26),26.8(C-27),176.9(C-28),33.7(C-29),24.4(C-30),96.5(glc-C-1),73.5(glc-C-2),79.0(glc-C-3),70.0(glc-C-4),77.5(glc-C-5),68.6(glc-C-6),105.7(glc′-C-1),74.5(glc′-C-2),75.8(glc′-C-3),78.3(glc′-C-4),77.2(glc′-C-5),61.8(glc′-C-6),103.2(rham-C-1),71.2(rham-C-2),73.2(rham-C-3),73.4(rham-C-4),69.9(rham-C-5),18.9(rham-C-6),105.7(ara-C-1),81.1(ara-C-2),83.2(ara-C-3),69.2(ara-C-4),67.5(ara-C-5),105.3(glc″-C-1),75.7(glc″-C-2),76.8(glc″-C-3),79.7(glc″-C-4),77.7(glc″-C-5),61.6(glc″-C-6)。以上数据与文献[19]报道的数据一致,因此鉴定化合物**14**为 ciwujianoside A_1。

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