·化学与分析·

太白楤木的化学成分分离鉴定

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[摘要] **目的**：对太白楤木 *Aralia taibaiensis* 根皮 70% 乙醇部位进行系统的化学成分研究，从物质基础的角度探寻其作为药用资源的可能性。**方法**：取太白楤木药材 3 kg，70% 乙醇浸泡提取，经减压浓缩后得到太白楤木浸膏，将浸膏加适量水分散，得到太白楤木上样液，将上样液经 101 大孔树脂柱色谱吸附，依次用水和 70% 乙醇洗脱，得到 2 个部位。对其 70% 乙醇部分通过硅胶柱色谱，Sephadex LH-20 凝胶柱色谱，半制备 HPLC 及重结晶等方法进行分离纯化，并且利用 NMR，MS 等现代波谱技术以及化合物的理化性质并结合参考文献确定化合物的结构。**结果**：从太白楤木 70% 乙醇部位中分离得到 12 个三萜皂苷类化合物，分别鉴定为 araliasaponin Ⅻ(**1**)，竹节参皂苷 1(**2**)，竹节参皂苷Ⅳa(**3**)，tarasaponin Ⅴ(**4**)，蕷知子皂苷Ⅳ(**5**)，elatoside F(**6**)，araliasaponin Ⅱ(**7**)，araliasaponin Ⅵ(**8**)，araliasaponin Ⅲ(**9**)，楤木皂苷 A(**10**)，银莲花苷(**11**)，3-*O*-[*β*-*D*-rhamnopyranosy(1→2)-*α*-*L*-arabinopyranosy]-28-*O*-[*β*-*D*-glucopyrannoside(1→6)-*β*-*D*-glucopyrannoside]oleanlic acid(**12**)。**结论**：化合物 **6**～**9**，**12** 为首次从该植物中分离得到，化合物 **5** 为首次从楤木属植物中分离得到。

[关键词] 太白楤木；三萜皂苷；结构鉴定；蕷知子皂苷Ⅳ
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Isolation and Identification of Chemical Constituents from *Aralia taibaiensis* Cortex

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[**Abstract**] **Objective**: To study the chemical constituents from 70% ethanol fraction of *Aralia taibaiensis* cortex and evaluate its potential in sustainable utilization as medicinal resources from pharmacodynamics. **Method**: The 3 kg *A. taibaiensis* cortex medicinal materials were crushed into coarse powder, extracted by 70% ethanol, and concentrated under reduced pressure to obtain extract. The extract was added with appropriate amount of water to get the sample solution which was then adsorbed by 101 macroporous resin column chromatography. Water and 70% ethanol were used for elution and two corresponding fractions were obtained. The 70% ethanol fraction was separated and purified by silica gel column chromatography, Sephadex LH-20 gel column chromatography, semi-preparative HPLC and recrystallization, and their structures were identified by NMR and MS, physicochemical properties and reference literature. **Result**: Twelve triterpenoid saponin compounds were obtained and elucidated

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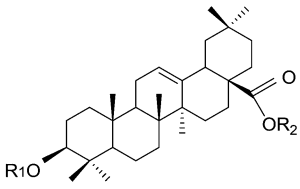
as araliasaponin Ⅻ (**1**), chikusetsusaponin 1 (**2**), chikusetsusaponin Ⅳa (**3**), tarasaponin Ⅴ (**4**), yuzhizioside Ⅳ (**5**), elatoside F (**6**), araliasaponin Ⅱ (**7**), araliasaponin Ⅵ (**8**), araliasaponin Ⅲ (**9**), araloside A (**10**), narcissiflorine (**11**), and 3-*O*-[*β*-*D*-rhamnose (1→2) -*α*-*L*-arabinose] -28-*O*-[*β*-*D*-glucose (1→6) -*β*-*D*-glucose] oleanlic acid (**12**). **Conclusion**: Compounds **6-9** and **12** were isolated from *Aralia taibaiensis* for the first time. Compound **5** was isolated from *A. chinensis* cortex for the first time.

[**Key words**] *Aralia taibaiensis* cortex; triterpenoid saponin; structural identification; yuzhizioside Ⅳ

太白楤木又名飞天蜈蚣七,系五加科楤木属植物太白楤木的干燥根皮。生于海拔 400 ~ 2 700 m 的山坡灌木丛、沟旁或林间,有着丰富的野生资源。根皮是太白楤木主要药用部位,又称楤木白皮,药用历史悠久,其性平味辛,入肺、肾经,具有祛风湿、利小便、散瘀血、消肿痛之功效。主要用于治疗风湿性关节炎、肾炎水肿、肝炎等,民间还用于小儿豆疹、干咳等[1-2]。太白楤木中含有皂苷、多糖、挥发油和微量元素等。其中皂苷类是太白楤木的主要化学成分,具有保肝,体外抗 HBV,降血糖,降血脂及抗氧化作用等多方面的药理活性[3]。太白楤木还具有脑、心脏、肝脏保护和抗菌抗病毒作用[4]。太白楤木总皂苷对体外人白血病 K562 细胞有抑制增殖的作用,从而表现出抗肿瘤活性[5]。楤木属植物太白楤木中研究最多的为三萜皂苷类成分,大多数皂苷元为五环三萜类,包括齐墩果酸型等,洪良健[6]从太白楤木中分离皂苷类化合物 14 种,本实验在此基础上做进一步分离。为开发利用该植物资源,探索新的化合物结构及其活性成分,明确其药效物质基础,本实验对太白楤木中的化学成分进行了研究,从中共分离得到 12 个三萜皂苷类化合物,根据理化性质和波谱数据分别鉴定为 araliasaponin Ⅻ(**1**),竹节参皂苷 1(**2**),竹节参皂苷Ⅳa (**3**), tarasaponin Ⅴ (**4**), 蒴知子皂苷Ⅳ (yuzhizioside Ⅳ,**5**), elatoside F(**6**), araliasaponin Ⅱ (**7**), araliasaponin Ⅵ(**8**), araliasaponin Ⅲ(**9**), 楤木皂苷 (araloside A, **10**), 银莲花苷 (narcissiflorine, **11**), 3-*O*-[*β*-*D*-rhamnose (1→2)-*α*-*L*-arabinose]-28-*O*-[*β*-*D*-glucos (1→6)-*β*-*D*-glucose] oleanlic acid (**12**),其中化合物**6** ~ **9**,**12** 为首次从该植物中分离得到,化合物 **5** 为首次从楤木属植物中分离得到,所有化合物的结构见图 1。



	R1	R2
1.	- ara (2→) glc, (3→) glc	- glc
2.	- H	- glc
3.	- glcA	- glc
4.	- glcA (2→) xyl, (3→) glc	- glc
5.	- ara (2→) xyl	- glc (6→) glc
6.	- ara (2→) xyl, (3→) glc	- glc
7.	- ara (3→) glc	- glc (6→) glc
8.	- gal (2→) xyl, (3→) glc	- glc
9.	- ara (2→) xyl, (3→) glc	- glc (6→) glc
10.	- glcA (4→) ara(f)	- glc
11.	- glcA (4→) ara(f)	- H
12.	- ara (2→) rha	- glc (6→) glc

Glc. *β*-*D*-glucopyranosyl; Rha. *α*-*L*-rhamnopyranosyl; Gal. *β*-*D*-galactopyranosyl; Xyl. *β*-*D*-xylopyranosyl; Ara (f). *α*-*L*-arabinofuranosyl; Glu A. *β*-*D*-glucuronic acid

图 1 化合物 1 ~ 12 的结构

Fig. 1 Structures of compounds 1-12

1 材料

Bruker-AVANCE 400 型核磁共振仪[四甲基硅烷(TMS)为内标,德国 Bruker 公司];LC-3000 型高效半制备液相色谱仪(Alltima C_{18} 10 μm, Allsphere ODS 10 mm × 250 mm, 5 μm);HB10 digital 型旋转蒸发仪(德国 IKA 公司);WFH-203 型三用紫外分析仪(上海精科实业有限公司); Agilent Technologies 6550 型 Q-TOF(美国安捷伦公司); LH-20 羟丙基葡聚糖凝胶(Sephadex LH-20,瑞典 GE Healthcare Bio-Sciences AB 公司);柱色谱硅胶(100 ~ 200,200 ~ 300 目)均为青岛海洋化工厂产品;薄层硅胶板(烟台江友硅胶发展有限公司);所用试剂分析纯均为天津天力试剂公司产品,色谱纯均为天津科密欧试剂公司产品,液相用水为娃哈哈纯净水。

太白楤木药材于 2014 年 1 月采自陕西秦岭太白山等地,经陕西中医药大学王继涛高级实验师鉴定为五加科楤木属植物太白楤木 *Aralia taibaiensis* 的干燥根皮。

2 提取分离

取太白楤木药材 3 kg,用 70% 的乙醇提取 3 次,每次 60 min,合并提取液,减压回收乙醇至无醇味,以蒸馏水分散至 20 L,得到太白楤木上样液。将太白楤木上样液经 D101 大孔吸附树脂柱色谱吸附,依次用水和 70% 乙醇洗脱,得到两个部位。70% 乙醇部位经硅胶柱色谱,以二氯甲烷-甲醇(1∶0~0∶1)梯度洗脱共得到 8 个部分(Fr. 1 ~ Fr. 8)。Fr. 2 经反复硅胶柱色谱及 Sephadex LH-20 柱色谱得到化合物 **2** 和 **3**。Fr. 4 经硅胶柱色谱,以三氯甲烷-甲醇梯度洗脱,得到 5 个部分(Fr. 4-1 ~ Fr. 4-5),Fr. 4-3 经 HPLC 半制备柱制备(紫外检测波长 203 nm,流动相 75% 甲醇,流速 1 mL·min^{-1})得到化合物 **10** 和 **11**。Fr. 4-5 经 HPLC 半制备柱制备(紫外检测波长 203 nm,流动相 72% 甲醇,流速 1 mL·min^{-1})得到化合物 **5**,**7** 和 **12**。Fr. 7 经硅胶柱色谱,以三氯甲烷-甲醇(1∶0~0∶1)梯度洗脱,得到 4 个部分(Fr. 7-1 ~ Fr. 7-4),Fr. 7-3 经 HPLC 半制备柱制备(紫外检测波长 203 nm,流动相 68% 甲醇,流速 1 mL·min^{-1})得到化合物 **1** 和 **4**。Fr. 7-4 经 HPLC 半制备柱制备(紫外检测波长 203 nm,流动相 65% 甲醇,流速 1 mL·min^{-1})得到化合物 **6**,**8** 和 **9**。

3 结构鉴定

化合物 **1** 白色无定形粉末,HR-ESI-MS *m/z* 1 074.561 1 [M]$^+$,分子式为 $C_{53}H_{86}O_{22}$。^{1}H-NMR (400 MHz, Pyr-d_5) δ: 6.35 (1H, d, *J* = 8.0 Hz, 28-Glc-H-1), 5.53 (1H, d, *J* = 7.8 Hz, glc-H-1′), 5.53 (1H, d, *J* = 7.7 Hz, Glc-H-1), 4.80 (1H, d, *J* = 6.7 Hz, Ara-H-1), 5.44 (1H, s, H-12), 3.23 (1H, m, H-3), 1.27, 1.26 (各 3H, s, CH_3 ×2), 1.10 (6H, s), 0.93, 0.9, 0.84 (各 3H, s, CH_3 ×3)。^{13}C-NMR (100 MHz, Pyr-d_5) δ: 38.6 (C-1), 26.2 (C-2), 89.1 (C-3), 39.8 (C-4), 56.0 (C-5), 18.6 (C-6), 33.3 (C-7), 40.0 (C-8), 48.2 (C-9), 37.1 (C-10), 23.8 (C-11), 123.1 (C-12), 144.2 (C-13), 42.3 (C-14), 28.4 (C-15), 23.8 (C-16), 47.1 (C-17), 41.9 (C-18), 46.3 (C-19), 31.0 (C-20), 33.3 (C-21), 32.7 (C-22), 28.2 (C-23), 16.9 (C-24), 15.7 (C-25), 17.6 (C-26), 26.2 (C-27), 176.6 (C-28), 33.3 (C-29), 23.8 (C-30); 3-*O*-*α*-*L*-Ara: 105.6 (C-1), 77.6 (C-2), 83.1 (C-3), 69.0 (C-4), 63.1 (C-5); Glc (1→2): 104.5 (C-1′), 76.3 (C-2′), 78.7 (C-3′), 72.5 (C-4′), 78.5 (C-5′), 62.7 (C-6′); Glc (1→3): 105.1 (C-1″), 75.4 (C-2″), 79.0 (C-3″), 71.7 (C-4″), 79.5 (C-5″), 62.3 (C-6″); 28-*β*-*D*-Glc: 96.0 (C-1), 74.3 (C-2), 78.7 (C-3), 71.3 (C-4), 79.5 (C-5), 62.3 (C-6)。与文献 [7] 对比确定该化合物为 araliasaponin Ⅻ。

化合物 **2** 白色粉末,HR-ESI-MS *m/z* 618.413 2 [M]$^+$,分子式为 $C_{36}H_{58}O_8$。^{1}H-NMR (400 MHz, Pyr-d_5) δ: 6.34 (1H, d, *J* = 7.9 Hz, 28-Glc-H-1), 5.34 (1H, s, H-12), 1.34, 1.31, 1.27, 1.10, 0.97, 0.93, 0.90 (各 3H, s, CH_3 ×7)。^{13}C-NMR (100 MHz, Pyr-d_5) δ: 37.1 (C-1), 28.2 (C-2), 79.0 (C-3), 39.7 (C-4), 55.8 (C-5), 18.6 (C-6), 33.3 (C-7), 40.0 (C-8), 46.6 (C-9), 37.1 (C-10), 23.8 (C-11), 122.9 (C-12), 144.3 (C-13), 41.9 (C-14), 30.1 (C-15), 23.5 (C-16), 47.1 (C-17), 42.3 (C-18), 46.3 (C-19), 30.9 (C-20), 33.3 (C-21), 32.7 (C-22), 28.4 (C-23), 17.1 (C-24), 15.7 (C-25), 17.6 (C-26), 26.3 (C-27), 176.6 (C-28), 34.1 (C-29), 20.3 (C-30); 28-*β*-*D*-Glc: 95.9 (C-1), 74.3 (C-2), 79.1 (C-3), 71.3 (C-4), 78.6 (C-5), 62.3 (C-6)。以上数据与文献[8]对比确定该化合物为竹节参皂苷 1,即齐墩果酸-28-*β*-*D*-吡喃葡萄糖苷。

化合物 **3** 白色无定型粉末,HR-ESI-MS *m/z* 794.445 8 [M]$^+$,分子式为 $C_{42}H_{66}O_{14}$。^{1}H-NMR (400 MHz, Pyr-d_5) δ: 6.31 (1H, d, *J* = 8.0 Hz, 28-Glc-H-1), 5.03 (1H, d, *J* = 7.7 Hz, GlcA-H-1), 1.31, 1.28, 1.09, 0.99, 0.92, 0.89, 0.83 (各 3H, s, CH_3 ×7)。^{13}C-NMR (100 MHz, Pyr-d_5) δ: 38.7 (C-1), 26.1 (C-2), 89.1 (C-3), 41.7 (C-4), 55.8 (C-5), 17.5 (C-6), 32.5 (C-7), 39.5 (C-8), 47.0 (C-9), 36.9 (C-10), 23.7 (C-11), 122.9 (C-12), 144.1 (C-13), 42.1 (C-14), 28.2 (C-15), 23.4 (C-16), 46.2 (C-17), 39.9 (C-18), 48.0 (C-19), 30.8 (C-20), 34.0 (C-21), 33.1 (C-22), 26.6 (C-23), 15.5 (C-24), 17.0 (C-25), 18.5 (C-26), 23.8 (C-27), 176.5 (C-28), 33.1 (C-29), 23.7 (C-30); 3-*O*-*β*-*D*-GlcA: 107.2 (C-1), 73.4 (C-2), 76.0 (C-3), 71.1 (C-4), 79.3 (C-5), 172.9 (C-6); 28-*β*-*D*-Glc: 95.7 (C-1), 74.1 (C-2), 78.1 (C-3), 70.1 (C-4), 78.9 (C-5), 62.2 (C-6); 以上数据与文献[9]对照基本一致,故确定该化合物为竹节参Ⅳa。

化合物 **4** 白色结晶性粉末,HR-ESI-MS *m/z* 1 088.540 9 [M]$^+$,分子式为 $C_{53}H_{84}O_{23}$。^{1}H-NMR (400 MHz, Pyr-d_5) δ: 6.34 (1H, d, *J* = 8.0 Hz, 28-Glc-H-1), 4.91 (1H, d, *J* = 7.5 Hz, GlcA-H-1), 5.68

(1H, d, J = 7.8 Hz, Xyl-H-1), 5.42 (2H, m, Glc-H-1, H-12), 3.62 (1H, s, H-3), 1.26, 1.25, 1.11, 1.09, 1.03, 0.93, 0.89 (各 3H, s, CH_3 × 7)。^{13}C-NMR (100 MHz, Pyr-d_5) δ: 37.6 (C-1), 26.6 (C-2), 89.7 (C-3), 40.4 (C-4), 56.6 (C-5), 17.3 (C-6), 31.3 (C-7), 40.1 (C-8), 47.5 (C-9), 37.4 (C-10), 21.7 (C-11), 123.4 (C-12), 138.5 (C-13), 42.6 (C-14), 29.7 (C-15), 24.1 (C-16), 46.6 (C-17), 41.5 (C-18), 43.5 (C-19), 31.2 (C-20), 33.6 (C-21), 33.0 (C-22), 28.1 (C-23), 16.7 (C-24), 15.8 (C-25), 16.8 (C-26), 26.6 (C-27), 176.9 (C-28), 32.8 (C-29), 21.7 (C-30); 3-*O*-β-*D*-GlcA: 105.6 (C-1), 79.0 (C-2), 84.2 (C-3), 71.6 (C-4), 77.9 (C-5), 176.0 (C-6); Xyl(1→2): 105.7 (C-1′), 74.8 (C-2′), 76.8 (C-3′), 72.0 (C-4′), 67.6 (C-5′); Glc(1→3): 106.2 (C-1″), 74.7 (C-2″), 75.8 (C-3″), 69.5 (C-4″), 78.9 (C-5″), 62.8 (C-6″); 28-β-*D*-Glc: 96.3 (C-1), 75.7 (C-2), 79.5 (C-3), 69.5 (C-4), 79.8 (C-5), 62.8 (C-6)。以上数据与文献[10]对照基本一致,故确定该化合物为 tarasaponin Ⅴ。

化合物 **5** 白色针状结晶, HR-ESI-MS m/z 1 044.551 1 [M]$^+$, 分子式为 $C_{52}H_{84}O_{21}$。^{1}H-NMR (400 MHz, Pyr-d_5) δ: 6.27 (1H, d, J = 8.1 Hz, 28-Glc-H-1), 5.04 (1H, d, J = 7.8 Hz, 28-Glc-H-1′), 4.88 (1H, d, J = 6.1 Hz, Ara-H-1), 4.73 (1H, d, J = 10.6 Hz, Xyl-H-1), 5.43 (1H, s, H-12), 3.62 (1H, s, H-3), 1.26, 1.12, 1.09, 0.91, 0.9, 0.89, 0.88 (各 3H, s, CH_3 ×7)。^{13}C-NMR (100 MHz, Pyr-d_5) δ: 39.0 (C-1), 26.8 (C-2), 89.1 (C-3), 39.8 (C-4), 56.1 (C-5), 18.8 (C-6), 33.3 (C-7), 40.1 (C-8), 48.3 (C-9), 49.9 (C-10), 23.9 (C-11), 123.1 (C-12), 144.4 (C-13), 42.4 (C-14), 28.2 (C-15), 23.6 (C-16), 47.3 (C-17), 41.9 (C-18), 46.5 (C-19), 41.9 (C-20), 34.2 (C-21), 32.8 (C-22), 28.5 (C-23), 16.6 (C-24), 15.9 (C-25), 17.7 (C-26), 26.3 (C-27), 176.8 (C-28), 33.3 (C-29), 24.0 (C-30); 3-*O*-α-*L*-Ara: 107.0 (C-1), 81.8 (C-2), 74.0 (C-3), 68.8 (C-4), 65.9 (C-5); Xyl(1→2): 105.5 (C-1′), 76.4 (C-2′), 78.6 (C-3′), 71.1 (C-4′), 67.6 (C-5′); 28-β-*D*-Glc: 95.9 (C-1), 74.1 (C-2), 78.6 (C-3), 71.3 (C-4), 78.2 (C-5), 69.6 (C-6); Glc(1→6): 105.3 (C-1′), 75.4 (C-2′), 78.7 (C-3′), 71.7 (C-4′), 79.0 (C-5′), 62.8 (C-6′)。以上数据与文献[11]对照基本一致,故确定该化合物为蒺藜皂苷Ⅳ,即 yuzhizioside Ⅳ。

化合物 **6** 白色无定形粉末, HR-ESI-MS m/z 1 044.551 1 [M]$^+$, 分子式为 $C_{52}H_{84}O_{21}$。^{1}H-NMR (400 MHz, Pyr-d_5) δ: 6.34 (1H, d, J = 8.0 Hz, 28-Glc-H-1), 5.32 (1H, d, J = 7.7 Hz, Glc-H-1), 5.41 (1H, d, J = 7.7 Hz, Xyl-H-1), 4.76 (1H, d, J = 7.1 Hz, Ara-H-1), 5.43 (1H, s, H-12), 3.62 (1H, s, H-3), 1.29, 1.27 (各 3H, s, CH_3 × 2), 1.11 (6H, s), 0.93, 0.9, 0.87 (各 3H, s, CH_3 × 3)。^{13}C-NMR (100 MHz, Pyr-d_5) δ: 39.0 (C-1), 28.0 (C-2), 89.3 (C-3), 39.9 (C-4), 56.1 (C-5), 18.7 (C-6), 33.3 (C-7), 40.1 (C-8), 48.2 (C-9), 37.2 (C-10), 23.8 (C-11), 123.0 (C-12), 144.2 (C-13), 42.3 (C-14), 28.4 (C-15), 24.0 (C-16), 47.2 (C-17), 41.9 (C-18), 46.3 (C-19), 30.9 (C-20), 34.1 (C-21), 32.7 (C-22), 26.2 (C-23), 16.6 (C-24), 15.7 (C-25), 17.6 (C-26), 26.8 (C-27), 176.6 (C-28), 33.3 (C-29), 23.6 (C-30); 3-*O*-α-*L*-Ara: 105.3 (C-1), 79.5 (C-2), 83.8 (C-3), 69.1 (C-4), 66.3 (C-5); Xyl(1→2): 105.2 (C-1′), 76.1 (C-2′), 77.5 (C-3′), 71.7 (C-4′), 67.2 (C-5′); Glc(1→3): 105.8 (C-1″), 75.4 (C-2″), 78.6 (C-3″), 71.5 (C-4″), 78.5 (C-5″), 62.7 (C-6″); 28-β-*D*-Glc: 95.9 (C-1), 74.3 (C-2), 79.2 (C-3), 71.2 (C-4), 79.0 (C-5), 62.3 (C-6)。以上数据与文献[12]对照基本一致,故确定该化合物为 elatoside F。

化合物 **7** 白色无定形粉末, HR-ESI-MS m/z 1 074.561 6 [M]$^+$, 分子式为 $C_{53}H_{86}O_{22}$。^{1}H-NMR (400 MHz, Pyr-d_5) δ: 6.28 (1H, d, J = 8.0 Hz, 28-Glc-H-1), 4.73 (1H, d, J = 10.2 Hz, 28-Glc-H-1′), 4.77 (1H, d, J = 7.3 Hz, Ara-H-1), 5.44 (1H, d, J = 9.4 Hz, Glc-H-1), 3.62 (1H, s, H-3), 1.34, 1.28, 1.27, 1.12, 1.00, 0.91, 0.90 (各 3H, s, CH_3 × 7)。^{13}C-NMR (100 MHz, Pyr-d_5) δ: 39.0 (C-1), 26.3 (C-2), 88.9 (C-3), 39.8 (C-4), 56.1 (C-5), 17.7 (C-6), 33.3 (C-7), 40.1 (C-8), 49.9 (C-9), 37.3 (C-10), 23.6 (C-11), 123.2 (C-12), 144.4 (C-13), 42.4 (C-14), 28.4 (C-15), 23.9 (C-16), 48.3 (C-17), 41.9 (C-18), 47.3 (C-19), 31.0 (C-20), 34.2 (C-21), 32.8 (C-22), 28.4 (C-23), 17.2 (C-24), 15.9 (C-25), 17.7 (C-26), 26.3 (C-27), 176.8 (C-28), 33.3 (C-29), 23.9 (C-30); 3-*O*-α-*L*-Ara: 107.6 (C-1), 71.8 (C-2), 84.3 (C-3), 69.5 (C-4), 67.2 (C-5); Glc(1→3): 106.6 (C-1′), 76.0

(C-2′), 78.6 (C-3′), 71.7 (C-4′), 78.7 (C-5′), 62.8 (C-6′); 28-*β*-*D*-Glc: 95.9 (C-1), 74.1 (C-2), 78.9 (C-3), 71.1 (C-4), 78.2 (C-5), 69.5 (C-6); Glc(1→6): 105.5 (C-1′), 75.4 (C-2′), 79.0 (C-3′), 72.1 (C-4′), 78.6 (C-5′), 62.9 (C-6′)。以上数据与文献[13]对照基本一致，故确定该化合物为 araliasaponin Ⅱ。

化合物 **8** 白色无定形粉末，HR-ESI-MS *m/z* 1 074.561 6 [M]$^+$，分子式为 $C_{53}H_{86}O_{22}$。^{1}H-NMR (400 MHz, Pyr-d_5) δ: 6.28 (1H, d, *J* = 8.0 Hz, 28-Glc-H-1), 5.31 (1H, d, *J* = 7.8 Hz, Glc-H-1), 5.44 (1H, d, *J* = 7.6 Hz, Xyl-H-1), 4.79 (1H, d, *J* = 7.6 Hz, Gal-H-1), 4.69 (1H, dd, *J* = 9.2, 8.0 Hz, Gal-H-2), 5.42 (t, H-12), 3.37 (1H, dd, *J* = 12.5, 12.3 Hz, H-3), 1.24, 1.23 (各 3H, s, CH_3 × 2), 1.05 (6H, s), 0.87, 0.84, 0.8 (各 3H, s, CH_3 × 3)。^{13}C-NMR (100 MHz, Pyr-d_5) δ: 38.8 (C-1), 26.1 (C-2), 89.4 (C-3), 39.7 (C-4), 55.9 (C-5), 18.6 (C-6), 33.2 (C-7), 39.9 (C-8), 48.1 (C-9), 37.0 (C-10), 23.7 (C-11), 122.9 (C-12), 144.2 (C-13), 42.2 (C-14), 28.3 (C-15), 23.8 (C-16), 47.0 (C-17), 41.8 (C-18), 46.3 (C-19), 30.8 (C-20), 34.0 (C-21), 32.6 (C-22), 27.9 (C-23), 16.5 (C-24), 15.6 (C-25), 17.5 (C-26), 26.7 (C-27), 176.5 (C-28), 33.2 (C-29), 23.4 (C-30); 3-*O*-*α*-*L*-Gal: 105.5 (C-1), 77.8 (C-2), 84.9 (C-3), 69.7 (C-4), 76.2 (C-5), 62.5 (C-6); Xyl(1→2): 105.2 (C-1′), 76.1 (C-2′), 79.1 (C-3′), 71.6 (C-4′), 67.1 (C-5′); Glc(1→3): 104.9 (C-1″), 75.4 (C-2″), 78.4 (C-3″), 71.1 (C-4″), 78.3 (C-5″), 62.4 (C-6″); 28-*β*-*D*-Glc: 95.8 (C-1), 74.2 (C-2), 78.9 (C-3), 71.4 (C-4), 79.3 (C-5), 62.2 (C-6)。以上数据与文献[13]对照基本一致，故确定该化合物为 araliasaponin Ⅵ。

化合物 **9** 白色无定形粉末，HR-ESI-MS *m/z* 1 206.603 3 [M]$^+$，分子式为 $C_{58}H_{94}O_{26}$。^{1}H-NMR (400 MHz, Pyr-d_5) δ: 6.26 (1H, d, *J* = 8.1 Hz, 28-Glc-H-1), 5.32 (1H, d, *J* = 7.5 Hz, Glc-H-1), 5.41 (1H, d, *J* = 7.4 Hz, Xyl-H-1), 5.04 (1H, d, *J* = 7.6 Hz, 28-Glc-H-1′), 4.75 (1H, d, *J* = 7.1 Hz, Ara-H-1), 5.41 (t, H-12), 3.23 (1H, dd, *J* = 18.2, 16.8 Hz, H-3), 1.28, 1.25 (各 3H, s, CH_3 × 2), 1.1 (6H, s), 0.89 (9H, s)。^{13}C-NMR (100 MHz, Pyr-d_5) δ: 38.9 (C-1), 26.1 (C-2), 89.2 (C-3), 39.8 (C-4), 56.0 (C-5), 18.8 (C-6), 33.2 (C-7), 39.9 (C-8), 48.1 (C-9), 37.1 (C-10), 23.7 (C-11), 122.9 (C-12), 144.2 (C-13), 42.2 (C-14), 28.3 (C-15), 23.7 (C-16), 47.1 (C-17), 41.7 (C-18), 46.3 (C-19), 30.8 (C-20), 34.0 (C-21), 32.6 (C-22), 27.9 (C-23), 16.5 (C-24), 15.7 (C-25), 17.5 (C-26), 26.1 (C-27), 176.6 (C-28), 33.2 (C-29), 23.5 (C-30); 3-*O*-*α*-*L*-Ara: 105.7 (C-1), 77.4 (C-2), 83.7 (C-3), 69.0 (C-4), 66.2 (C-5); Xyl(1→2): 105.1 (C-1′), 76.1 (C-2′), 79.1 (C-3′), 71.6 (C-4′), 67.2 (C-5′); Glc(1→3): 105.2 (C-1″), 75.3 (C-2″), 78.4 (C-3″), 72.3 (C-4″), 78.5 (C-5″), 62.2 (C-6″); 28-*β*-*D*-Glc: 95.7 (C-1), 73.9 (C-2), 78.8 (C-3), 71.0 (C-4), 78.4 (C-5), 69.4 (C-6); Glc(1→6): 105.3 (C-1′), 75.2 (C-2′), 78.0 (C-3′), 70.1 (C-4′), 78.5 (C-5′), 62.7 (C-6′)。以上数据与文献[13]对照基本一致，故确定该化合物为 araliasaponin Ⅲ。

化合物 **10** 白色粉末，HR-ESI-MS *m/z* 926.487 5 [M]$^+$，分子式为 $C_{47}H_{74}O_{18}$。^{1}H-NMR (400 MHz, Pyr-d_5) δ: 6.34 (1H, d, *J* = 8.0 Hz, 28-Glc-H-1), 4.88 (1H, d, *J* = 9.3 Hz, GlcA-H-1), 6.28 (1H, s, Ara-H-1), 5.46 (1H, s, H-12), 3.23 (1H, s, H-3), 1.32, 1.25, 1.11, 0.97, 0.94, 0.92, 0.85 (各 3H, s, CH_3 × 7)。^{13}C-NMR (100 MHz, Pyr-d_5) δ: 37.2 (C-1), 26.4 (C-2), 89.4 (C-3), 39.7 (C-4), 55.9 (C-5), 17.7 (C-6), 34.3 (C-7), 40.1 (C-8), 48.2 (C-9), 37.2 (C-10), 23.9 (C-11), 123.2 (C-12), 144.4 (C-13), 42.4 (C-14), 28.4 (C-15), 23.9 (C-16), 47.2 (C-17), 42.0 (C-18), 47.2 (C-19), 31.0 (C-20), 33.4 (C-21), 32.8 (C-22), 28.5 (C-23), 17.2 (C-24), 15.8 (C-25), 17.2 (C-26), 26.4 (C-27), 176.7 (C-28), 33.4 (C-29), 23.9 (C-30); 3-*O*-*β*-*D*-GlcA: 107.1 (C-1), 74.3 (C-2), 75.7 (C-3), 78.7 (C-4), 75.7 (C-5), 176.7 (C-6); Ara(f)(1→4): 107.9 (C-1′), 82.5 (C-2′), 78.7 (C-3′), 89.4 (C-4′), 62.4 (C-5′); 28-*β*-*D*-Glc: 95.9 (C-1), 74.3 (C-2), 79.5 (C-3), 71.3 (C-4), 79.1 (C-5), 62.4 (C-6)。以上数据与文献[14]对照基本一致，故确定该化合物为楤木皂苷 A，即 araloside A。

化合物 **11** 白色块晶，HR-ESI-MS *m/z* 764.434 7 [M]$^+$，分子式为 $C_{41}H_{64}O_{13}$。^{1}H-NMR (400 MHz, Pyr-d_5) δ: 6.18 (1H, s, Ara-H-1), 4.73 (1H, d, *J* = 9.7 Hz, GlcA-H-1), 5.47 (1H, s, H-12), 3.29 (1H, m, H-3), 1.33, 1.31, 1.02, 0.99, 0.98, 0.97, 0.8 (各 3H, s, CH_3 × 7)。^{13}C-NMR (100 MHz, Pyr-

d_5) δ: 40.0 (C-1), 27.1 (C-2), 89.6 (C-3), 40.2 (C-4), 56.2 (C-5), 18.9 (C-6), 33.7 (C-7), 39.1 (C-8), 48.5 (C-9), 37.4 (C-10) 24.2 (C-11), 123.0 (C-12), 145.3 (C-13), 42.6 (C-14), 28.8 (C-15), 24.2 (C-16), 46.9 (C-17), 42.5 (C-18), 47.2 (C-19), 31.5 (C-20), 34.7 (C-21), 33.8 (C-22), 28.7 (C-23), 17.4 (C-24), 15.9 (C-25), 17.7 (C-26), 26.7 (C-27), 173.2 (C-28), 33.7 (C-29), 24.2 (C-30); 3-*O*-β-*D*-GlcA: 107.6 (C-1), 75.8 (C-2), 76.6 (C-3), 77.1 (C-4), 76.7 (C-5), 180.7 (C-6); Ara (f) (1→4): 109.1 (C-1′), 83.0 (C-2′), 79.3 (C-3′), 88.3 (C-4′), 63.2 (C-5′)。以上数据与文献[15]对照基本一致,故确定该化合物为银莲花苷,即 narcissiflorine。

化合物 **12** 白色粉末, HR-ESI-MS *m/z* 1 088.540 9 [M]$^+$, 分子式为 $C_{53}H_{84}O_{23}$。^{1}H-NMR (400 MHz, Pyr-d_5) δ: 6.29 (1H, d, *J* = 8.0 Hz, 28-Glc-H-1), 5.05 (1H, d, *J* = 7.6 Hz, 28-Glc-H-1′), 4.92 (1H, d, *J* = 4.9 Hz, Ara-H-1), 6.15 (1H, s, Rha-H-1), 1.64 (1H, d, *J* = 5.93 Hz, Rha-H-CH_3), 5.43 (t, H-12), 3.62 (1H, s, H-3), 1.27, 1.18 (各 3H, s, CH_3 ×2), 1.12 (6H, s), 1.09 (9H, s)。^{13}C-NMR (100 MHz, Pyr-d_5) δ: 39.1 (C-1), 26.7 (C-2), 89.0 (C-3), 39.7 (C-4), 56.1 (C-5), 18.8 (C-6), 33.3 (C-7), 40.1 (C-8), 48.3 (C-9), 37.2 (C-10), 23.9 (C-11), 123.1 (C-12), 144.4 (C-13), 42.4 (C-14), 28.3 (C-15), 23.9 (C-16), 47.3 (C-17), 41.9 (C-18), 46.5 (C-19), 31.0 (C-20), 34.2 (C-21), 32.8 (C-22), 28.5 (C-23), 17.2 (C-24), 15.9 (C-25), 17.7 (C-26), 26.3 (C-27), 176.8 (C-28), 33.3 (C-29), 23.9 (C-30); 3-*O*-α-*L*-Ara: 105.0 (C-1), 76.2 (C-2), 73.9 (C-3), 69.6 (C-4), 64.8 (C-5); Rha (1→2): 102.0 (C-1′), 72.8 (C-2′), 72.6 (C-3′), 74.1 (C-4′), 68.8 (C-5′), 18.8 (C-6′); 28-β-*D*-Glc: 95.9 (C-1), 74.3 (C-2), 78.6 (C-3), 70.1 (C-4), 78.2 (C-5), 69.9 (C-6); Glc (1→6): 105.5 (C-1′), 75.4 (C-2′), 78.7 (C-3′), 71.7 (C-4′), 79.0 (C-5′), 62.8 (C-6′)。以上数据与文献[16]对照基本一致,故确定该化合物为 3-*O*-[β-*D*-rhamnopyranosy (1→2-α-*L*-arabinopyranosy]-28-*O*-[β-*D*-glucopyrannoside (1→6)-β-*D*-glucopyrannoside] oleanlic acid。

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