

续断的化学成分研究

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摘要: **目的** 研究续断的化学成分。**方法** 运用大孔树脂、反相硅胶及制备高效液相等色谱技术进行分离纯化, 并根据理化性质和波谱数据鉴定化合物的结构。**结果** 分离得到 13 个化合物, 其中 7 个环烯醚萜苷和 6 个木脂素类化合物, 分别鉴定为马钱苷(1)、獐牙菜苷(2)、6'-*O*- β -D-apiofuranosyl-sweroside(3)、续断苷 H(4)、续断苷 F(5)、续断苷 E(6)、triplostoside A(7)、(7*R*, 8*S*, 7'*R*, 8'*S*)-5-methoxyprinsepiol-4-*O*- β -D-glucopyranoside(8)、(7*R*, 8*S*, 7'*R*, 8'*S*)-prinsepiol-4-*O*- β -D-glucopyranoside(9)、acanthoside D(10)、(7*R*, 8*S*, 7'*R*, 8'*S*)-fraxiresinol-4'-*O*- β -D-glucopyranoside(11)、(7*R*, 8*S*, 7'*R*, 8'*S*)-8-hydroxypinoresinol-4'-*O*- β -D-glucopyranoside(12)、(7*R*, 8*S*, 7'*R*, 8'*S*)-8-hydroxypinoresinol-4-*O*- β -D-glucopyranoside(13)。**结论** 其中化合物 8、9、11、12、13 为首次从川续断属植物中分离得到。

关键词: 续断; 环烯醚萜苷; 木脂素; (7*R*, 8*S*, 7'*R*, 8'*S*)-5-methoxyprinsepiol-4-*O*- β -D-glucopyranoside; (7*R*, 8*S*, 7'*R*, 8'*S*)-prinsepiol-4-*O*- β -D-glucopyranoside

中图分类号: R284.1 文献标志码: A 文章编号: 1674-5515(2014)05-0459-06

DOI: 10.7501/j.issn.1674-5515.2014.05.003

Chemical constituents of *Dipsaci Radix*

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Abstract: Objective To study the chemical constituents of *Dipsaci Radix*. **Methods** The compounds were isolated by macroporous resin, reverse phase C₁₈ silica gel, and semi-preparative HPLC. Their structures were identified on the basis of physicochemical properties and spectroscopic data. **Results** Thirteen compounds were separated, seven of which were iridoid glycosides, and six of which were lignans, identified as loganin (1), sweroside (2), 6'-*O*- β -D-apiofuranosyl-sweroside (3), dipsanoside H (4), dipsanoside F (5), dipsanoside E (6), triplostoside A (7), (7*R*, 8*S*, 7'*R*, 8'*S*)-5-methoxyprinsepiol-4-*O*- β -D-glucopyranoside (8), (7*R*, 8*S*, 7'*R*, 8'*S*)-prinsepiol-4-*O*- β -D-glucopyranoside (9), acanthoside D (10), (7*R*, 8*S*, 7'*R*, 8'*S*)-fraxiresinol-4'-*O*- β -D-glucopyranoside (11), (7*R*, 8*S*, 7'*R*, 8'*S*)-8-hydroxypinoresinol-4'-*O*- β -D-glucopyranoside (12), and (7*R*, 8*S*, 7'*R*, 8'*S*)-8-hydroxypinoresinol-4-*O*- β -D-glucopyranoside (13), respectively. **Conclusion** Compounds 8, 9, and 11—13 are isolated from this genus for the first time.

Key words: *Dipsaci Radix*; iridoid glycosides; lignans; (7*R*, 8*S*, 7'*R*, 8'*S*)-5-methoxyprinsepiol-4-*O*- β -D-glucopyranoside; (7*R*, 8*S*, 7'*R*, 8'*S*)-prinsepiol-4-*O*- β -D-glucopyranoside

续断为川续断科植物川续断 *Dipsacus asper* Wall. ex Henry 的干燥根, 作为传统中药, 具有补肝肾、强筋骨、续折伤等功效, 临床上常用于治疗骨质疏松、腰腿酸软、骨折、流产等疾病^[1]。研究表明, 续断中化学成分主要为三萜皂苷类、环烯醚萜苷类、黄酮类、挥发油类等^[2]。本实验对续断中化

学成分进行研究, 运用大孔树脂、反相硅胶及制备高效液相等色谱技术进行分离纯化, 并根据理化性质和波谱数据鉴定化合物的结构。分离得到 13 个化合物, 其中 7 个环烯醚萜苷和 6 个木脂素类化合物, 分别鉴定为马钱苷(1)、獐牙菜苷(2)、6'-*O*- β -D-apiofuranosyl-sweroside(3)、续断苷 H(4)、续断

收稿日期: 2014-03-11

基金项目: 国家科技重大专项资助项目(2011ZX09201-201-05); 中国医学科学院药用植物研究所创新团队发展计划资助项目

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昔 F (5)、续断昔 E (6)、triplostoside A (7)、(7*R*, 8*S*, 7'*R*, 8'*S*)-5-methoxyprinsepiol-4-*O*-β-*D*-glucopyranoside (8)、(7*R*, 8*S*, 7'*R*, 8'*S*)-prinsepiol-4-*O*-β-*D*-glucopyranoside (9)、acanthoside D (10)、(7*R*, 8*S*, 7'*R*, 8'*S*)-fraxiresinol-4'-*O*-β-*D*-glucopyranoside (11)、(7*R*, 8*S*, 7'*R*, 8'*S*)-8-hydroxypinoresinol-4'-*O*-β-*D*-glucopyranoside (12)、(7*R*, 8*S*, 7'*R*, 8'*S*)-8-hydroxypinoresinol-4-*O*-β-*D*-glucopyranoside (13)。其中化合物 8、9、11、12、13 均为首次从该属植物中分离得到。

1 仪器与材料

Bruker Av-600MHz 超导核磁共振仪 (瑞士 Bruker 公司); Thermo Fisher LTQ-Orbitrap XL 型质谱仪 (美国 Thermo Finnigan 公司); Waters 高效液相色谱仪, 包括 Waters 2535 型泵, Waters 2998 检测器, Empower III 色谱工作站 (美国 Waters 公司); Agela Cheetah™ 中压制备液相色谱仪 (天津博纳艾杰尔科技有限公司); 三菱 MCI GEL CHP20P 树脂 (北京绿百草科技有限公司); YMC Pack ODS 中压色谱柱、YMC Pack ODS-A 半制备色谱柱 (日本 YMC 公司)。

实验材料采自贵州, 由中国医学科学院药用植物研究所郭宝林教授鉴定为川续断 *Dipsacus asper* Wall. ex Henry 的干燥根。

2 提取与分离

续断干燥根 20 kg, 砍成小段, 用 70%乙醇回流提取 3 次, 每次 2 h, 浓缩得棕褐色浸膏 2 620 g。取浸膏 1 320 g 经大孔树脂色谱分离, 以乙醇-水 (0:30:70、50:50、100) 系统梯度洗脱。30%乙醇洗脱部分经 MCI 树脂色谱柱分离, 甲醇-水 (10:90~90:10) 洗脱得组分 Fr. A~E。Fr. A 经 ODS 中压色谱柱分离, 甲醇-水 (15:85~30:70) 洗脱得组分 Fr. A1~3。Fr. A2 经 HPLC 制备色谱分离, 甲醇-水 (25:75) 洗脱得到化合物 1 (35 mg)、2 (42 mg); Fr. A2 经 HPLC 制备色谱分离, 乙腈-水 (17:83) 洗脱得到化合物 3 (11 mg)、4 (10 mg)。Fr. B 经 ODS 中压色谱柱分离, 甲醇-水 (20:80~80:20) 洗脱得组分 Fr. B1~5。Fr. B1 经 HPLC 制备色谱分离, 乙腈-水 (16:84) 洗脱得到化合物 8 (12 mg)、9 (20 mg)、13 (16 mg)。Fr. B2 经 HPLC 制备色谱分离, 乙腈-水 (18:82) 洗脱, 得化合物 10 (22 mg)、11 (15 mg)、12 (12 mg)。Fr. B4 经 HPLC 制备色谱分离, 乙腈-水 (23:77) 洗脱得到化合物 5 (10

mg)、6 (8 mg)。Fr. C 经 ODS 中压制备色谱及 HPLC 制备色谱分离, 乙腈-水 (25:75) 洗脱得到化合物 7 (20 mg)。

3 结构鉴定

化合物 1: 白色无定型粉末, ESI-MS m/z : 413 $[M+Na]^+$, 分子式为 $C_{17}H_{26}O_{10}$ 。 1H -NMR (600 MHz, CD_3OD) δ : 5.27 (1H, d, $J=4.5$ Hz, H-1), 7.39 (1H, s, H-3), 3.11 (1H, d, $J=8.5$ Hz, H-5), 1.62 (1H, m, H-6), 1.84~1.91 (1H, m, H-6), 2.01~2.05 (1H, m, H-8), 2.25 (1H, m, H-9), 1.10 (3H, d, $J=6.5$ Hz, H-10), 4.65 (1H, d, $J=5.0$ Hz, Glu-H-1)。 ^{13}C -NMR (150 MHz, CD_3OD) δ : 97.8 (C-1), 152.3 (C-3), 114.3 (C-4), 32.4 (C-5), 42.9 (C-6), 42.4 (C-8), 46.7 (C-9), 13.6 (C-10), 169.4 (C-11), 51.8 (OCH₃), 100.3 (Glu-C-1), 74.9 (Glu-C-2), 75.2 (Glu-C-3), 74.9 (Glu-C-4), 77.8 (Glu-C-5), 63.0 (Glu-C-6)。与文献报道^[3]数据基本一致, 确定化合物 1 为马钱昔。

化合物 2: 白色无定型粉末, ESI-MS m/z : 381 $[M+Na]^+$, 分子式为 $C_{16}H_{22}O_9$ 。 1H -NMR (600 MHz, CD_3OD) δ : 5.55 (1H, d, $J=4.5$ Hz, H-1), 7.59 (1H, s, H-3), 3.14~3.21 (1H, m, H-5), 1.67~1.80 (2H, m, H-6), 5.52~5.59 (1H, m, H-8), 2.70 (1H, dd, $J=5.5$ 、8.5 Hz, H-9), 5.31 (1H, d, $J=20.5$ Hz, H-10), 5.27 (1H, d, $J=10.5$ Hz, H-10), 4.68 (1H, d, $J=8.0$ Hz, Glu-H-1)。 ^{13}C -NMR (150 MHz, CD_3OD) δ : 98.2 (C-1), 154.1 (C-3), 106.2 (C-4), 28.6 (C-5), 26.1 (C-6), 69.9 (C-7), 133.5 (C-8), 44.0 (C-9), 121.0 (C-10), 168.7 (C-11), 99.9 (Glu-C-1), 74.9 (Glu-C-2), 77.6 (Glu-C-3), 71.7 (Glu-C-4), 78.1 (Glu-C-5), 62.9 (Glu-C-6)。与文献报道^[4]数据基本一致, 确定化合物 2 为獐牙菜昔。

化合物 3: 白色无定型粉末, ESI-MS m/z : 513 $[M+Na]^+$, 分子式为 $C_{21}H_{30}O_{13}$ 。 1H -NMR (600 MHz, CD_3OD) δ : 5.55 (1H, d, $J=3.0$ Hz, H-1), 7.60 (1H, s, H-3), 3.13~3.21 (1H, m, H-5), 1.67~1.80 (2H, m, H-6), 5.51~5.57 (1H, m, H-8), 2.70~2.74 (1H, m, H-9), 5.34 (1H, d, $J=17.5$ Hz, H-10), 5.28 (1H, d, $J=10.5$ Hz, H-10), 4.67 (1H, d, $J=8.0$ Hz, Glu-H-1), 4.99 (1H, d, $J=3.0$ Hz, Api-H-1)。 ^{13}C -NMR (150 MHz, CD_3OD) δ : 98.4 (C-1), 154.1 (C-3), 106.2 (C-4), 28.6

(C-5), 26.1 (C-6), 69.9 (C-7), 133.4 (C-8), 44.1 (C-9), 121.2 (C-10), 168.7 (C-11), 100.1 (Glu-H-1), 78.0 (Glu-H-2), 80.7 (Glu-H-3), 71.7 (Glu-H-4), 78.1 (Glu-H-5), 68.8 (Glu-H-6), 111.2 (Api-H-1), 78.0 (Api-H-2), 80.7 (Api-H-3), 75.2 (Api-H-4), 65.7 (Api-H-5)。与文献报道^[5]数据基本一致, 确定化合物 **3** 为 6'-O-β-D-apiofuranosyl-sweroside。

化合物 **4**: 白色无定型粉末, ESI-MS m/z : 543 $[M+Na]^+$, 分子式为 $C_{22}H_{32}O_{14}$ 。 1H -NMR (600 MHz, CD_3OD) δ : 5.55 (1H, d, $J=4.0$ Hz, H-1), 7.60 (1H, s, H-3), 3.13~3.21 (1H, m, H-5), 1.67~1.80 (2H, m, H-6), 3.87~3.91 (1H, m, H-7), 4.35~4.39 (1H, m, H-7), 5.52~5.57 (1H, m, H-8), 2.70~2.74 (1H, m, H-9), 5.32 (1H, d, $J=20.5$ Hz, H-10), 5.28 (1H, d, $J=10.5$ Hz, H-10), 4.73 (1H, d, $J=8.0$ Hz, Glu-H-1'), 4.67 (1H, d, $J=3.0$ Hz, Glu-H-1'')。 ^{13}C -NMR (150 MHz, CD_3OD) δ : 98.3 (C-1), 154.1 (C-3), 105.4 (C-4), 28.7 (C-5), 26.1 (C-6), 69.9 (C-7), 133.5 (C-8), 44.0 (C-9), 121.0 (C-10), 168.7 (C-11), 99.7 (Glu-C-1'), 74.3 (Glu-C-2'), 87.6 (Glu-C-3'), 70.2 (Glu-C-4'), 78.0 (Glu-C-5'), 62.8 (Glu-C-6'), 106.2 (Glu-C-1''), 75.7 (Glu-C-2''), 78.3 (Glu-C-3''), 71.8 (Glu-C-4''), 78.4 (Glu-C-5''), 62.8 (Glu-C-6'')。与文献报道^[6]数据基本一致, 确定化合物 **4** 为续断苷 H。

化合物 **5**: 白色无定型粉末, ESI-MS m/z : 843 $[M+Na]^+$, 分子式为 $C_{22}H_{32}O_{14}$ 。 1H -NMR (600 MHz, CD_3OD) δ : unit A: 5.54 (1H, d, $J=6.0$ Hz, H-1), 7.44 (1H, s, H-3), 3.13 (1H, m, H-5), 1.72~1.80 (1H, m, H-6), 1.83~1.99 (1H, m, H-6), 4.66 (1H, q, $J=6.0$ Hz, H-7), 5.74~5.82 (1H, m, H-8), 2.66 (1H, dd, $J=6.0$ 、9.0 Hz, H-9), 5.57 (1H, d, $J=18.0$ Hz, H-10), 5.24 (1H, d, $J=10.0$ Hz, H-10), 3.86 (1H, m, H-12), 3.26~3.40 (1H, m, H-12), 3.58 (1H, m, H-13), 3.91 (1H, m, H-14), 3.26~3.40 (1H, m, H-14), 4.71 (1H, d, $J=8.0$ Hz, Glu-H-1'); unit B: 5.29 (1H, d, $J=4.5$ Hz, H-1), 7.42 (1H, s, H-3), 3.20 (1H, br d, $J=8.0$ Hz, H-5), 1.72~1.80 (1H, m, H-6), 2.31 (1H, dd, $J=8.0$ 、14.0 Hz, H-6), 5.20 (1H, dd, $J=4.5$ 、5.0 Hz, H-7), 2.06~2.17 (1H, m, H-8), 2.06~2.17 (1H, m, H-9), 1.08 (3H, d, $J=6.5$ Hz, H-10), 3.70 (3H, s, OCH_3), 4.66 (1H,

d, $J=8.0$ Hz, Glu-H-1)。 ^{13}C -NMR (150 MHz, CD_3OD) δ : unit A: 97.9 (C-1), 153.5 (C-3), 113.6 (C-4), 31.3 (C-5), 36.2 (C-6), 102.5 (C-7), 136.1 (C-8), 45.6 (C-9), 119.8 (C-10), 168.6 (C-11), 72.6 (C-12), 65.2 (C-13), 72.5 (C-14), 100.4 (Glu-C-1), 74.9 (Glu-C-2), 78.2 (Glu-C-3), 71.7 (Glu-C-4), 78.5 (Glu-C-5), 63.0 (Glu-C-6); unit B: 97.6 (C-1), 152.6 (C-3), 112.4 (C-4), 32.6 (C-5), 40.6 (C-6), 78.6 (C-7), 41.2 (C-8), 47.3 (C-9), 13.9 (C-10), 169.6 (OCH_3), 100.4 (Glu-C-1), 74.9 (Glu-C-2), 78.2 (Glu-C-3), 71.7 (Glu-C-4), 78.5 (Glu-C-5), 63.0 (Glu-C-6)。与文献报道^[6]数据基本一致, 确定化合物 **5** 为续断苷 F。

化合物 **6**: 白色无定型粉末, ESI-MS m/z : 843 $[M+Na]^+$, 分子式为 $C_{22}H_{32}O_{14}$ 。 1H -NMR (600 MHz, CD_3OD) δ : unit A: 5.52 (1H, d, $J=6.0$ Hz, H-1), 7.44 (1H, s, H-3), 2.99 (1H, ddd, $J=4.5$ 、5.0、10.0 Hz, H-5), 1.72~1.78 (1H, m, H-6), 1.94 (1H, ddd, $J=6.0$ 、8.0、14.0 Hz, H-6), 4.56 (1H, dd, $J=4.4$ 、5.0 Hz, H-7), 5.73~5.78 (1H, m, H-8), 2.67 (1H, $J=5.5$ 、6.0、9.0 Hz, ddd, H-9), 5.30 (1H, d, $J=18.0$ Hz, H-10), 5.25 (1H, d, $J=10.0$ Hz, H-10), 4.03 (1H, ddd, $J=1.5$ 、5.0、10.5 Hz, H-12), 3.19~3.32 (1H, m, H-12), 3.72 (1H, dd, $J=5.0$ 、10.0 Hz, H-13), 4.07 (1H, ddd, $J=1.5$ 、5.0、10.5 Hz, H-14), 3.19~3.32 (1H, m, H-14), 4.69 (1H, d, $J=8.0$ Hz, Glu-H-1); unit B: 5.34 (1H, d, $J=4.5$ Hz, H-1), 7.41 (1H, s, H-3), 3.13 (1H, br d, $J=8.0$ Hz, H-5), 1.72~1.78 (1H, m, H-6), 2.23 (1H, dd, $J=8.0$ 、14.0 Hz, H-6b), 5.17 (1H, dd, $J=4.5$ 、5.0 Hz, H-7), 2.08~2.14 (1H, m, H-8), 2.23 (1H, ddd, $J=4.0$ 、9.0、9.0 Hz, H-9), 1.08 (3H, d, $J=6.5$ Hz, H-10), 3.70 (3H, s, OCH_3), 4.66 (1H, d, $J=8.0$ Hz, Glu-H-1)。 ^{13}C -NMR (150 MHz, CD_3OD) δ : unit A: 97.9 (C-1), 153.5 (C-3), 113.8 (C-4), 30.1 (C-5), 35.9 (C-6), 101.9 (C-7), 136.2 (C-8), 45.7 (C-9), 119.8 (C-10), 168.6 (C-11a), 72.8 (C-12a), 62.1 (C-13a), 72.7 (C-14), 100.4 (Glu-C-1), 74.9 (Glu-C-2), 78.2 (Glu-C-3), 72.7 (Glu-C-4), 78.6 (Glu-C-5), 63.0 (Glu-C-6); unit B: 97.4 (C-1), 152.4 (C-3), 112.3 (C-4), 32.3 (C-5), 40.7 (C-6), 78.8 (C-7), 41.1 (C-8), 47.1 (C-9), 13.4 (C-10), 169.6 (OCH_3),

100.3 (Glu-C-1), 74.8 (Glu-C-2), 78.2 (Glu-C-3), 71.6 (Glu-C-4), 78.5 (Glu-C-5), 62.8 (Glu-C-6)。与文献报道^[6]数据基本一致, 确定化合物 **6** 为续断苷 E。

化合物 **7**: 白色无定型粉末, ESI-MS m/z : 815 $[M+Na]^+$, 分子式为 $C_{22}H_{32}O_{14}$ 。 1H -NMR (600 MHz, CD_3OD) δ : unit A: 5.54 (1H, d, $J=6.6$ Hz, H-1), 7.47 (1H, s, H-3), 2.94 (1H, q, $J=7.2$ Hz, H-5), 1.74~1.80 (1H, m, H-6), 2.07~2.18 (1H, m, H-6), 4.54 (1H, dd, $J=4.0$ 、7.0 Hz, H-7), 5.73~5.81 (1H, m, H-8), 2.69~2.73 (1H, m, H-9), 5.34 (1H, d, $J=18.0$ Hz, H-10), 5.29 (1H, d, $J=10.0$ Hz, H-10), 3.31 (6H, s, $2\times OCH_3$), 4.54 (1H, d, $J=7.2$ Hz, Glu-H-1); unit B: 5.32 (1H, d, $J=4.4$ Hz, H-1), 7.45 (1H, s, H-3), 3.24 (1H, dd, $J=4.0$ 、8.0 Hz, H-5), 1.64~1.70 (1H, m, H-6), 2.13~2.18 (1H, m, H-6), 5.20 (1H, t, $J=7.6$ Hz, H-7), 2.13~2.18 (1H, m, H-8), 2.32 (3H, d, $J=8.0$ 、8.5 Hz, H-9), 1.09 (3H, d, $J=6.5$ Hz, H-10), 3.71 (3H, s, OCH_3 -11), 4.46 (1H, d, $J=6.8$ Hz, Glu-H-1)。 ^{13}C -NMR (150 MHz, CD_3OD) δ : unit A: 97.7 (C-1), 153.4 (C-3), 112.2 (C-4), 32.7 (C-5), 33.5 (C-6), 104.5 (C-7), 136.0 (C-8), 45.6 (C-9), 120.0 (C-10), 168.5 (C-11), 53.0 (C-12), 53.8 (C-13), 100.3 (Glu-C-1), 74.8 (Glu-C-2), 78.2 (Glu-C-3), 71.8 (Glu-C-4), 78.5 (Glu-C-5), 63.0 (Glu-C-6), unit B: 98.1 (C-1), 152.7 (C-3), 113.5 (C-4), 29.7 (C-5), 40.5 (C-6), 78.6 (C-7), 41.2 (C-8), 47.3 (C-9), 14.0 (C-10), 169.5 (OCH_3 -11), 51.9 (C-12b), 100.4 (Glu-C-1), 74.9 (Glu-C-2), 78.2 (Glu-C-3), 71.7 (Glu-C-4), 78.6 (Glu-C-5), 63.0 (Glu-C-6)。与文献报道^[3]数据基本一致, 确定化合物 **7** 为 triplostoside A。

化合物 **8**: 白色无定型粉末, HR-ESI-MS m/z : 605 $[M+Na]^+$, 分子式为 $C_{27}H_{34}O_{14}$ 。 1H -NMR (600 MHz, CD_3OD) δ : 6.72 (1H, s, H-2), 6.72 (1H, s, H-6), 5.01 (1H, s, H-7), 4.01 (1H, d, $J=9.5$ Hz, H-9), 4.13 (1H, t, $J=9.5$ Hz, H-9), 3.85 (3H, s, OCH_3 -3), 3.85 (3H, s, OCH_3 -5), 7.11 (1H, d, $J=1.5$ Hz, H-2'), 7.15 (1H, d, $J=8.0$ Hz, H-5'), 6.95 (1H, dd, $J=1.5$ 、8.0 Hz, H-6'), 4.97 (1H, s, H-7'), 4.01 (1H, d, $J=9.5$ Hz, H-9'), 4.13 (1H, t, $J=9.5$ Hz, H-9'), 3.87 (3H, s, OCH_3 -3'),

4.87 (1H, d, $J=7.5$ Hz, Glu-H-1)。 ^{13}C -NMR (150 MHz, CD_3OD) δ : 128.9 (C-1), 106.5 (C-2), 149.1 (C-3), 136.6 (C-4), 149.1 (C-5), 106.5 (C-6), 89.3 (C-7), 89.4 (C-8), 77.0 (C-9), 56.0 (OCH_3 -3), 128.9 (C-1'), 113.8 (C-2'), 150.6 (C-3'), 147.9 (C-4'), 117.7 (C-5'), 121.6 (C-6'), 88.9 (C-7'), 89.4 (C-8'), 77.0 (C-9'), 55.7 (OCH_3 -3'), 103.1 (Glu-C-1), 75.1 (Glu-C-2), 78.0 (Glu-C-3), 71.6 (Glu-C-4), 78.4 (Glu-C-5), 62.7 (Glu-C-6)。与文献报道^[7]数据基本一致, 确定化合物 **8** 为 (7*R*, 8*S*, 7'*R*, 8'*S*)-5-methoxyprinsepiol-4-*O*- β -*D*-glucopyranoside, 首次从川续断属植物中分离得到。

化合物 **9**: 白色无定型粉末, HR-ESI-MS m/z : 575 $[M+Na]^+$, 分子式为 $C_{26}H_{32}O_{13}$ 。 1H -NMR (600 MHz, CD_3OD) δ : 7.11 (1H, d, $J=1.5$ Hz, H-2), 7.15 (1H, d, $J=8.0$ Hz, H-5), 6.95 (1H, dd, $J=1.5$ 、8.0 Hz, H-6), 5.01 (1H, s, H-7), 4.12 (1H, d, $J=9.5$ Hz, H-9), 3.99 (1H, d, $J=9.5$ Hz, H-9), 3.87 (3H, s, $3-OCH_3$), 7.04 (1H, d, $J=1.5$ Hz, H-2'), 6.78 (1H, d, $J=8.0$ Hz, H-5'), 6.95 (1H, dd, $J=1.5$ 、8.0 Hz, H-6'), 4.89 (1H, s, H-7'), 4.12 (1H, d, $J=9.5$ Hz, H-9'), 3.99 (1H, d, $J=9.5$ Hz, H-9'), 3.86 (3H, s, OCH_3 -3'), 4.89 (1H, d, $J=7.5$ Hz, Glu-H-1)。 ^{13}C -NMR (150 MHz, CD_3OD) δ : 133.4 (C-1), 113.8 (C-2), 150.6 (C-3), 147.9 (C-4), 117.7 (C-5), 121.6 (C-6), 88.9 (C-7), 89.5 (C-8), 77.0 (C-9), 57.0 (OCH_3 -3), 129.7 (C-1'), 113.0 (C-2'), 148.9 (C-3'), 147.7 (C-4'), 115.9 (C-5'), 121.8 (C-6'), 89.2 (C-7'), 89.3 (C-8'), 77.0 (C-9'), 56.6 (OCH_3 -3'), 103.1 (Glu-C-1), 75.1 (Glu-C-2), 78.0 (Glu-C-3), 71.6 (Glu-C-4), 78.4 (Glu-C-5), 62.7 (Glu-C-6)。与文献报道^[8]数据基本一致, 确定化合物 **9** 为 (7*R*, 8*S*, 7'*R*, 8'*S*)-prinsepiol-4-*O*- β -*D*-glucopyranoside, 首次从川续断属植物中分离得到。

化合物 **10**: 白色无定型粉末, HR-ESI-MS m/z : 765 $[M+Na]^+$, 分子式为 $C_{34}H_{46}O_{18}$ 。由于该化合物结构的对称性, 核磁信号只显示一半信号。 1H -NMR (600 MHz, $DMSO-d_6$) δ : 6.66 (2H, s, H-2、2'), 6.66 (2H, s, H-6、6'), 4.67 (2H, d, H-7、7'), 3.09 (2H, m, H-8、8'), 4.20 (2H, m, H-9、9'), 3.83 (2H, d, $J=9.0$ Hz, H-9、9'), 3.76 (12H, s, OCH_3 -3、3'、5、5')。 ^{13}C -NMR (150 MHz, $DMSO-d_6$)

δ : 133.7 (C-1, 1'), 104.2 (C-2, 2'), 152.6 (C-3, 3'), 137.1 (C-4, 4'), 152.6 (C-5, 5'), 104.2 (C-6, 6'), 85.0 (C-7, 7'), 53.6 (C-8, 8'), 71.3 (C-9, 9'), 55.6 (OCH₃-3, 3', 5, 5'), 102.6 (Glu-C-1, Glu-C-1')。与文献报道^[9]数据基本一致, 确定化合物 **10** 为 acanthoside D。

化合物 **11**: 白色无定型粉末, HR-ESI-MS m/z : 589 [M+Na]⁺, 分子式为 C₂₇H₃₅O₁₃。¹H-NMR (600 MHz, CD₃OD) δ : 6.72 (1H, s, H-2), 6.72 (1H, s, H-6), 4.69 (1H, s, H-7), 4.09 (1H, d, J =9.0 Hz, H-9), 3.83 (1H, d, J =9.0 Hz, H-9), 3.86 (6H, s, OCH₃-3, 5), 7.12 (1H, d, J =1.5 Hz, H-2'), 7.16 (1H, d, J =8.0 Hz, H-5'), 6.97 (1H, dd, J =1.5、8.0 Hz, H-6'), 4.89 (1H, d, J =6.0 Hz, H-7'), 3.03 (1H, m, H-8'), 4.48 (1H, t, J =9.0 Hz, H-9'), 3.69 (1H, d, J =9.0 Hz, H-9'), 3.88 (3H, s, OCH₃-3'), 4.89 (1H, d, J =7.5 Hz, Glu-H-1)。¹³C-NMR (150 MHz, CD₃OD) δ : 128.4 (C-1), 106.5 (C-2), 149.2 (C-3), 136.7 (C-4), 149.2 (C-5), 106.5 (C-6), 89.6 (C-7), 93.1 (C-8), 76.4 (C-9), 57.0 (OCH₃-3, 5), 137.5 (C-1'), 112.2 (C-2'), 151.2 (C-3'), 147.8 (C-4'), 118.2 (C-5'), 120.4 (C-6'), 87.5 (C-7'), 62.7 (C-8'), 72.3 (C-9'), 57.0 (OCH₃-3'), 103.1 (Glu-C-1), 75.1 (Glu-C-2), 78.1 (Glu-C-3), 71.6 (Glu-C-4), 78.4 (Glu-C-5), 62.7 (Glu-C-6)。与文献报道^[8]数据基本一致, 确定化合物 **11** 为 (7*R*, 8*S*, 7'*R*, 8'*S*)-fraxiresinol-4'-*O*- β -D-glucopyranoside, 首次从川续断属植物中分离得到。

化合物 **12**: 白色无定型粉末, HR-ESI-MS m/z : 559 [M+Na]⁺, 分子式为 C₂₆H₃₂O₁₂。¹H-NMR (600 MHz, CD₃OD) δ : 7.05 (1H, d, J =1.5 Hz, H-2), 7.15 (1H, d, J =8.0 Hz, H-5), 6.95 (1H, dd, J =1.5、8.0 Hz, H-6), 4.72 (1H, s, H-7), 4.06 (1H, d, J =9.0 Hz, H-9), 3.77 (1H, d, J =9.0 Hz, H-9), 3.88 (3H, s, OCH₃-3), 7.11 (1H, d, J =1.5 Hz, H-2'), 6.78 (1H, d, J =8.0 Hz, H-5'), 6.87 (1H, dd, J =1.5、8.0 Hz, H-6'), 4.84 (1H, d, J =6.0 Hz, H-7'), 3.04 (1H, m, H-8'), 4.47 (1H, t, J =9.0 Hz, H-9'), 3.68 (1H, d, J =9.0 Hz, H-9'), 3.86 (3H, s, OCH₃-3'), 4.88 (1H, d, J =7.5 Hz, Glu-H-1)。¹³C-NMR (150 MHz, CD₃OD) δ : 133.0 (C-1), 113.7 (C-2), 150.7 (C-3), 149.3 (C-4), 117.8 (C-5), 121.5 (C-6), 89.1 (C-7), 93.1 (C-8), 76.3 (C-9),

133.8 (C-1'), 111.5 (C-2'), 147.9 (C-3'), 147.6 (C-4'), 116.3 (C-5'), 120.7 (C-6'), 88.0 (C-7'), 62.7 (C-8'), 72.3 (C-9'), 103.1 (Glu-C-1), 75.1 (Glu-C-2), 78.0 (Glu-C-3), 71.5 (Glu-C-4), 78.4 (Glu-C-5), 62.6 (Glu-C-6)。与文献报道^[10]数据基本一致, 确定化合物 **12** 为 (7*R*, 8*S*, 7'*R*, 8'*S*)-8-hydroxypinoresinol-4'-*O*- β -D-glucopyranoside, 首次从川续断属植物中分离得到。

化合物 **13**: 无色不定型粉末, HR-ESI-MS m/z : 559 [M+Na]⁺, 分子式为 C₂₆H₃₂O₁₂。¹H-NMR (600 MHz, DMSO-*d*₆) δ : 7.02 (1H, d, J =1.5 Hz, H-2), 7.06 (1H, d, J =8.0 Hz, H-5), 6.90 (1H, dd, J =1.5、8.0 Hz, H-6), 4.52 (1H, s, H-7), 4.94 (1H, d, J =9.0 Hz, H-9), 3.73 (1H, d, J =9.0 Hz, H-9), 3.77 (3H, s, OCH₃-3), 6.95 (1H, d, J =1.5 Hz, H-2'), 6.70 (1H, d, J =8.0 Hz, H-5'), 6.76 (1H, dd, J =1.5、8.0 Hz, H-6'), 4.80 (1H, d, J =6.0 Hz, H-7'), 2.89 (1H, m, H-8'), 4.36 (1H, t, J =9.0 Hz, H-9'), 3.66 (1H, d, J =9.0 Hz, H-9'), 3.75 (3H, s, OCH₃-3'), 4.88 (1H, d, J =7.5 Hz, Glu-H-1)。¹³C-NMR (150 MHz, DMSO-*d*₆) δ : 128.0 (C-1), 110.9 (C-2), 146.9 (C-3), 145.9 (C-4), 114.5 (C-5), 118.3 (C-6), 87.1 (C-7), 91.0 (C-8), 74.7 (C-9), 55.7 (OCH₃-3), 135.3 (C-1'), 112.3 (C-2'), 148.9 (C-3'), 145.9 (C-4'), 115.2 (C-5'), 120.2 (C-6'), 85.1 (C-7'), 60.9 (C-8'), 70.3 (C-9'), 55.6 (OCH₃-3'), 100.1 (Glu-C-1), 73.2 (Glu-C-2), 76.8 (Glu-C-3), 69.7 (Glu-C-4), 77.0 (Glu-C-5), 60.7 (Glu-C-6)。与文献报道^[10]数据基本一致, 确定化合物 **13** 为 (7*R*, 8*S*, 7'*R*, 8'*S*)-8-hydroxypinoresinol-4'-*O*- β -D-glucopyranoside, 首次从川续断属植物中分离得到。

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