

东北铁线莲地上部位化学成分研究

王 威^{1*}, 刘小红¹, 高 华¹, 张英华², 李相成¹, 范美玲¹, 董方言²

1. 青岛大学药学院, 山东 青岛 266021

2. 吉林省中医药科学院植物化学研究所, 吉林 长春 130012

摘要:目的 研究东北铁线莲 *Clematis manshurica* 地上部位的化学成分。方法 采用硅胶柱色谱、ODS 柱色谱和制备 HPLC 等技术方法进行分离纯化, 运用理化性质和波谱数据鉴定化合物结构。结果 从东北铁线莲地上部位乙醇提取物中分离得到 17 个化合物, 分别鉴定为 (+)-表松脂醇 (1)、(+)-松脂醇 (2)、(-)-表丁香树脂醇 (3)、(+)-椴皮树脂醇 (4)、(+)-松脂醇-4-O-β-D-吡喃葡萄糖苷 (5)、(+)-丁香树脂醇-4-O-β-D-吡喃葡萄糖苷 (6)、(+)-表丁香树脂醇-4-O-β-D-吡喃葡萄糖苷 (7)、罗汉松脂素 (8)、(+)-珍珠花环木脂素 (9)、(+)-异落叶松脂素 (10)、(7R, 8R)-4, 7, 9, 9'-四羟基-3, 3'-二甲氧基-8-O-4'-新木脂素 (11)、(7R, 8S)-4, 7, 9, 9'-四羟基-3, 3'-二甲氧基-8-O-4'-新木脂素 (12)、(7S, 8R)-二氢脱氢双松柏醇 (13)、木犀草素 (14)、3''-O-(2'''-甲基丁酰基) 异当药苷 (15)、2''-O-(2'''-甲基丁酰基) 异当药苷 (16)、6''-O-(2'''-甲基丁酰基) 异当药苷 (17)。结论 所有化合物均为首次从该植物地上部位中分离得到, 其中化合物 1、3、4、7~9、11、12、15~17 为首次从该属植物中分离得到。**关键词:** 毛茛科; 东北铁线莲; 地上部位; (+)-表松脂醇; (-)-表丁香树脂醇; 2''-O-(2'''-甲基丁酰基) 异当药苷

中图分类号: R284.1

文献标志码: A

文章编号: 0253-2670(2014)17-2440-07

DOI: 10.7501/j.issn.0253-2670.2014.17.004

Chemical constituents from aerial parts of *Clematis manshurica*

WANG Wei¹, LIU Xiao-hong¹, GAO Hua¹, ZHANG Ying-hua², LI Xiang-cheng¹, FAN Mei-ling¹, DONG Fang-yan²

1. College of Pharmacy, Qingdao University, Qingdao 266021, China

2. Institute of Phytochemistry, Jilin Academy of Chinese Medicine Sciences, Changchun 130012, China

Abstract: Objective To investigate the chemical constituents from the ethanol extract of aerial parts of *Clematis manshurica*.

Methods The compounds were isolated and purified by chromatography on silica gel, ODS, and preparative HPLC. Their structures were elucidated on the basis of chemical and spectroscopic methods, including MS, 1D, and 2D NMR spectral techniques. **Results** Seventeen compounds were isolated from the ethanol extract of the aerial parts of *C. manshurica*, and were identified as (+)-epipinoresinol (1), (+)-pinoresinol (2), (-)-episyningaresinol (3), (+)-medioresinol (4), (+)-pinoresinol-4-O-β-D-glucopyranoside (5), (+)-syningaresinol-4-O-β-D-glucopyranoside (6), (+)-episyningaresinol-4-O-β-D-glucopyranoside (7), matairesinol (8), (+)-lyoniresinol (9), (+)-isolariciresinol (10), (7R, 8R)-4, 7, 9, 9'-tetrahydroxy-3, 3'-diethoxy-8-O-4'-neolignan (11), (7R, 8S)-4, 7, 9, 9'-tetrahydroxy-3, 3'-diethoxy-8-O-4'-neolignan (12), (7S, 8R)-dihydrodehydroconiferyl alcohol (13), luteolin (14), 3''-O-(2'''-methylbutyryl) isoswertisin (15), 2''-O-(2'''-methylbutyryl) isoswertisin (16), and 6''-O-(2'''-methylbutyryl) isoswertisin (17).

Conclusion All compounds are obtained from the aerial parts of this plant for the first time, and compounds 1, 3, 4, 7-9, 11, 12, and 15-17 are firstly isolated from the plants of *Clematis* L.

Key words: Ranunculaceae; *Clematis manshurica* Rupr.; aerial parts; (+)-epipinoresinol; (-)-episyningaresinol; 2''-O-(2'''-methylbutyryl) isoswertisin

毛茛科 (Ranunculaceae) 铁线莲属 *Clematis* L. 植物为多年生木质藤本, 少数为草本、灌木或亚灌木。在全世界约有 355 种, 主要分布在热带、亚热

带以及寒带地区。我国约有 150 种, 分布于全国各地^[1]。东北铁线莲 *Clematis manshurica* Rupr. 分布于我国山西、辽宁、吉林、黑龙江、内蒙古, 其干燥

收稿日期: 2014-06-12

基金项目: 国家“十一五”科技支撑计划资助项目 (2007BAI38B05)

*通信作者 王 威 (1972—), 男, 教授, 博士研究生导师, 研究方向为天然产物活性成分与创新药物研究。

Tel: (0532)82991172 E-mail: w.w.wangwei@263.net

根和根茎入药,性温,味辛、咸,具有祛风除湿、通络止痛的功效,用于风湿痹痛、肢体麻木、筋脉拘挛、屈伸不利、骨哽咽喉等症^[2]。已从其根和根茎中分离得到三萜皂苷、酚苷和大环苷类化合物,但目前未见其地上部位化学成分和药理作用的研究报道^[3]。本课题组前期研究结果表明东北铁线莲地上部位乙醇提取物对弗氏完全佐剂关节炎模型大鼠继发性炎症和角又菜胶性足肿胀模型大鼠急性炎症有明显抑制作用,明显降低血清中肿瘤坏死因子- α (TNF- α)、白细胞介素(IL)-1 β 和IL-6的量。为开发利用东北铁线莲地上部位植物资源,本实验对长白山产东北铁线莲地上部位的化学成分进行了研究,从乙醇提取物中分离鉴定了17个化合物,其中包括木脂烷类化合物8个:(+)-表松脂醇 [(+)-epipinoresinol, **1**]、(+)-松脂醇 [(+)-pinoresinol, **2**]、(-)-表丁香树脂醇 [(-)-episyringaresinol, **3**]、(+)-椴皮树脂醇 [(+)-medioresinol, **4**]、(+)-松脂醇-4-*O*- β -D-吡喃葡萄糖苷 [(+)-pinoresinol-4-*O*- β -D-glucopyranoside, **5**]、(+)-丁香树脂醇-4-*O*- β -D-吡喃葡萄糖苷 [(+)-syringaresinol-4-*O*- β -D-glucopyranoside, **6**]、(+)-表丁香树脂醇-4-*O*- β -D-吡喃葡萄糖苷 [(+)-episyringaresinol-4-*O*- β -D-glucopyranoside, **7**]、罗汉松脂素 (matairesinol, **8**); 环木脂烷类化合物2个:(+)-珍珠花环木脂素 [(+)-lyoniresinol, **9**]、(+)-异落叶松脂素 [(+)-isolariciresinol, **10**]; 新木脂烷类化合物3个:(7*R*, 8*R*)-4, 7, 9, 9'-四羟基-3, 3'-二甲氧基-8-*O*-4'-新木脂素 [(7*R*, 8*R*)-4, 7, 9, 9'-tetrahydroxy-3, 3'-diethoxy-8-*O*-4'-neolignan, **11**]、(7*R*, 8*S*)-4, 7, 9, 9'-四羟基-3, 3'-二甲氧基-8-*O*-4'-新木脂素 [(7*R*, 8*S*)-4, 7, 9, 9'-tetrahydroxy-3, 3'-diethoxy-8-*O*-4'-neolignan, **12**]、(7*S*, 8*R*)-二氢脱氢双松柏醇 [(7*S*, 8*R*)-dihydrodehydroconiferyl alcohol, **13**]; 黄酮苷元类化合物1个:木犀草素 (luteolin, **14**); 黄酮碳苷类化合物3个:3''-*O*-(2'''-甲基丁酰基)异当药苷 [3''-*O*-(2'''-methylbutyryl) isoswertisin, **15**]、2''-*O*-(2'''-甲基丁酰基)异当药苷 [2''-*O*-(2'''-methylbutyryl) isoswertisin, **16**]、6''-*O*-(2'''-甲基丁酰基)异当药苷 [6''-*O*-(2'''-methylbutyryl) isoswertisin, **17**]。所有化合物均为首次从该植物地上部位分离得到,其中化合物**1**、**3**、**4**、**7**~**9**、**11**、**12**、**15**~**17**为首次从该属植物中分离得到。

1 仪器与材料

Bruker AV—500型核磁共振波谱仪(德国

Bruker公司); Bruker micro TOFQ飞行时间质谱仪(德国Bruker公司); HORIBA SEPA—300型旋光仪(日本堀场制作所); Jasco J—500型圆二色谱仪(日本分光公司); Shimadzu LC—6AD制备液相色谱仪(日本岛津制作所); Shim-Pack ODS色谱柱(250 mm×21.2 mm, 10 μ m, No. 2025B09, 日本岛津制作所); Kromasil 100-10-C₁₈色谱柱(250 mm×10 mm, 5 μ m, No. 81474, 瑞典阿克苏诺贝尔公司); 柱色谱硅胶(200~300目, 青岛海洋化工厂); 柱色谱用ODS(PEGASIL Prep ODS-5015-12A, 日本Senshu科学株式会社); 柱色谱用Sephadex LH-20(美国Pharmacia公司); 薄层色谱用ODS板(RP₁₈F₂₅₄, 德国默克公司); 色谱纯甲醇和乙腈(美国Fisher公司); 水为重蒸馏水; 其他试剂均为分析纯。

东北铁线莲地上部位药材于2008年8月采集于吉林省磐石市烟筒山,经吉林省中医药科学院严仲恺研究员鉴定为毛茛科铁线莲属植物东北铁线莲 *Clematis manshurica* Rupr. 的干燥地上部位,标本(2008TXL01)存放于青岛大学药学院。

2 提取与分离

东北铁线莲地上部位45 kg,加12倍量60%乙醇回流提取2次,每次2 h,分次滤过,合并滤液,减压回收乙醇得乙醇提取物10.3 kg。取乙醇提取物6.9 kg,加水16 L使溶解,依次用石油醚、氯仿、醋酸乙酯、正丁醇振荡提取4次,每次12 L,提取液减压回收,得石油醚分离部位273.5 g、氯仿分离部位153.1 g、醋酸乙酯分离部位144.1 g、正丁醇分离部位910.4 g。

取氯仿分离部位50 g,经硅胶柱色谱,以石油醚-氯仿(1:1),氯仿-甲醇(100:0、99:1、49:1、19:1、9:1、0:100)梯度洗脱得10个分离组分Fr. C-1~C-10。Fr. C-4经ODS柱色谱,以甲醇-水(4:6、10:0)洗脱,结合制备HPLC得化合物**1**(2.82 mg)、**2**(1.34 mg)、**3**(6.78 mg)、**4**(2.74 mg)、**8**(7.2 mg); Fr. C-5经ODS柱色谱,以甲醇-水(4:6、6:4、10:0)洗脱,结合制备液相色谱得化合物**9**(7.71 mg)、**10**(11.94 mg)、**11**(7.71 mg)、**12**(7.99 mg)、**13**(19.26 mg); Fr. C-7经ODS柱色谱,以甲醇-水(5:5、7:3、10:0)洗脱,结合制备液相色谱得化合物**6**(18.52 mg)、**7**(2.63 mg)。

取醋酸乙酯分离部位50 g,经硅胶柱色谱,以氯仿-甲醇(99:1、98:2、19:1、9:1、0:100)梯度洗脱得13个组分Fr. E-1~E-13。Fr. E-7~E-11

经 ODS 柱色谱, 以甲醇-水 (3 : 7、5 : 5、7 : 3、10 : 0) 洗脱, 结合制备 HPLC 得化合物 **5** (5.30 mg)、**14** (13.26 mg)、**15** (3.73 mg)、**16** (10.45 mg)、**17** (14.12 mg)。

3 结构鉴定

化合物 **1**: 无色固体 (甲醇), $[\alpha]_{\text{D}}^{25} +108.6^{\circ}$ (c 0.21, CH₃OH), ESI-MS m/z : 381 [M+Na]⁺, 结合 ¹³C-NMR 谱数据推测分子式为 C₂₀H₂₂O₆。¹H-NMR (500 MHz, CD₃OD) δ : 6.97 (1H, d, $J = 1.8$ Hz, H-2'), 6.95 (1H, d, $J = 1.8$ Hz, H-2), 6.82 (1H, dd, $J = 8.0, 1.8$ Hz, H-6), 6.80 (1H, dd, $J = 8.0, 1.8$ Hz, H-6'), 6.78 (1H, d, $J = 8.0$ Hz, H-5'), 6.77 (1H, d, $J = 8.0$ Hz, H-5), 4.86 (1H, d, $J = 6.0$ Hz, H-7'), 4.43 (1H, d, $J = 7.0$ Hz, H-7), 4.10 (1H, d, $J = 9.4$ Hz, H-9a), 3.86 (3H, s, 3-OCH₃), 3.86 (3H, s, 3'-OCH₃), 3.85 (1H, m, H-9b), 3.79 (1H, m, H-9'a), 3.38 (1H, m, H-8'), 3.29 (1H, m, H-9'b), 2.94 (1H, m, H-8); ¹³C-NMR (125 MHz, CD₃OD) δ : 149.2 (C-3), 148.9 (C-3'), 147.4 (C-4), 146.7 (C-4'), 133.9 (C-1), 131.4 (C-1'), 120.2 (C-6), 119.4 (C-6'), 116.1 (C-5), 116.0 (C-5'), 111.0 (C-2), 110.6 (C-2'), 89.4 (C-7), 83.6 (C-7'), 72.0 (C-9), 70.6 (C-9'), 56.4 (3, 3'-OCH₃), 55.6 (C-8), 51.3 (C-8')。以上数据与文献报道基本一致^[4], 故鉴定化合物 **1** 为 (+)-表松脂醇。

化合物 **2**: 无色固体 (甲醇), $[\alpha]_{\text{D}}^{25} +80.6^{\circ}$ (c 0.32, CH₃OH), ESI-MS m/z : 381 [M+Na]⁺, 结合 ¹³C-NMR 谱数据推测分子式为 C₂₀H₂₂O₆。¹H-NMR (500 MHz, CD₃OD) δ : 6.95 (2H, d, $J = 1.8$ Hz, H-2, 2'), 6.81 (2H, dd, $J = 8.0, 1.8$ Hz, H-6, 6'), 6.77 (2H, d, $J = 8.0$ Hz, H-5, 5'), 4.71 (2H, d, $J = 4.4$ Hz, H-7, 7'), 4.23 (2H, m, H-9a, 9'a), 3.86 (6H, s, 3, 3'-OCH₃), 3.85 (2H, m, H-9b, 9'b), 3.14 (2H, m, H-8, 8'); ¹³C-NMR (125 MHz, CD₃OD) δ : 149.2 (C-3, 3'), 147.4 (C-4, 4'), 133.8 (C-1, 1'), 120.1 (C-6, 6'), 116.1 (C-5, 5'), 111.0 (C-2, 2'), 87.5 (C-7, 7'), 72.6 (C-9, 9'), 56.4 (3, 3'-OCH₃), 55.4 (C-8, 8')。以上数据与文献报道基本一致^[5], 故鉴定化合物 **2** 为 (+)-松脂醇。

化合物 **3**: 无色固体 (甲醇), $[\alpha]_{\text{D}}^{25} -94.5^{\circ}$ (c 0.26, CH₃OH), ESI-MS m/z : 441 [M+Na]⁺, 结合 ¹³C-NMR 谱数据推测分子式为 C₂₂H₂₆O₈。¹H-NMR (500 MHz, CD₃OD) δ : 6.67 (2H, s, H-2, 6), 6.66 (2H, s, H-2', 6'), 4.86 (1H, d, $J = 6.0$ Hz, H-7), 4.44 (1H, d, $J = 6.8$ Hz, H-7'), 4.14 (1H, d, $J = 9.4$ Hz, H-9'a), 3.88 (1H, m,

H-9'b), 3.85 (12H, s, 3, 3', 5, 5'-OMe), 3.81 (1H, m, H-9a), 3.41 (1H, m, H-8), 3.31 (1H, m, H-9b), 2.95 (1H, m, H-8'); ¹³C-NMR (125 MHz, CD₃OD) δ : 149.4 (C-3', 5'), 149.2 (C-3, 5), 136.4 (C-4'), 135.6 (C-4), 133.2 (C-1'), 130.6 (C-1), 104.6 (C-2', 6'), 104.2 (C-2, 6), 89.6 (C-7'), 83.6 (C-7), 72.1 (C-9'), 70.7 (C-9), 56.8 (3, 5, 3', 5'-OMe), 55.7 (C-8'), 51.2 (C-8)。以上数据与文献报道基本一致^[6], 故鉴定化合物 **3** 为 (-)-表丁香树脂醇。

化合物 **4**: 无色固体 (甲醇), $[\alpha]_{\text{D}}^{25} +20.6^{\circ}$ (c 0.25, CH₃OH), ESI-MS m/z : 411 [M+Na]⁺, 结合 ¹³C-NMR 谱数据推测分子式为 C₂₁H₂₄O₇。¹H-NMR (500 MHz, CD₃OD) δ : 6.95 (1H, d, $J = 1.8$ Hz, H-2), 6.82 (1H, dd, $J = 8.0, 1.8$ Hz, H-6), 6.77 (1H, d, $J = 8.2$ Hz, H-5), 6.66 (2H, s, H-2', 6'), 4.72 (2H, d, $J = 4.3$ Hz, H-7, 7'), 4.25 (2H, m, H-9a, 9'a), 3.88 (2H, m, H-9b, 9'b), 3.86 (3H, s, 3-OCH₃), 3.85 (6H, s, 3', 5'-OCH₃), 3.14 (2H, m, H-8, 8'); ¹³C-NMR (125 MHz, CD₃OD) δ : 149.4 (C-3', 5'), 149.2 (C-3), 147.4 (C-4, 4'), 136.3 (C-4'), 133.8 (C-1), 133.2 (C-1'), 120.1 (C-6), 116.1 (C-5), 111.0 (C-2), 104.6 (C-2', 6'), 87.7 (C-7), 87.5 (C-7'), 72.8 (C-9), 72.6 (C-9'), 56.8 (3', 5'-OCH₃), 56.5 (3-OCH₃), 55.6 (C-8'), 55.3 (C-8)。以上数据与文献报道基本一致^[7], 故鉴定化合物 **4** 为 (+)-椴皮树脂醇。

化合物 **5**: 无色固体 (甲醇), $[\alpha]_{\text{D}}^{25} +14.2^{\circ}$ (c 0.18, CH₃OH), ESI-MS m/z : 543 [M+Na]⁺, 结合 ¹³C-NMR 谱数据推测分子式为 C₂₆H₃₂O₁₁。¹H-NMR (500 MHz, CD₃OD) δ : 7.15 (1H, d, $J = 8.4$ Hz, H-5), 7.03 (1H, d, $J = 1.8$ Hz, H-2), 6.95 (1H, d, $J = 1.8$ Hz, H-2'), 6.92 (1H, dd, $J = 8.4, 1.8$ Hz, H-6), 6.81 (1H, dd, $J = 8.2, 1.8$ Hz, H-6'), 6.77 (1H, d, $J = 8.2$ Hz, H-5'), 4.88 (1H, d, $J = 7.4$ Hz, H-1''), 4.76 (1H, d, $J = 4.1$ Hz, H-7), 4.71 (1H, d, $J = 4.4$ Hz, H-7'), 4.25 (2H, m, H-9a, 9'a), 3.87 (3H, s, 3-OCH₃), 3.86 (2H, m, H-9b, 9'b), 3.86 (3H, s, 3'-OCH₃), 3.86 (1H, m, H-6''a), 3.69 (1H, m, H-6''b), 3.49 (1H, m, H-2''), 3.45 (1H, m, H-3''), 3.39 (2H, m, H-4'', 5''), 3.13 (2H, m, H-8, 8'); ¹³C-NMR (125 MHz, CD₃OD) δ : 151.0 (C-4), 149.2 (C-4'), 147.5 (C-3'), 147.4 (C-3), 137.5 (C-1), 133.8 (C-1'), 120.1 (C-6'), 119.8 (C-6), 118.2 (C-5), 116.1 (C-5'), 111.7 (C-2), 111.0 (C-2'), 102.9 (C-1''), 87.5 (C-7'), 87.1 (C-7), 78.2 (C-5''), 77.9

(C-3''), 74.9 (C-2''), 72.7 (C-9), 72.7 (C-9'), 71.4 (C-4''), 62.5 (C-6''), 56.8 (3-OCH₃), 56.4 (3'-OCH₃), 55.6 (C-8'), 55.4 (C-8)。以上数据与文献报道基本一致^[8], 故鉴定化合物 **5** 为 (+)-松脂醇-4-*O*-β-*D*-吡喃葡萄糖苷。

化合物 **6**: 无色固体(甲醇), $[\alpha]_{\text{D}}^{25} +21.2^{\circ}$ (*c* 0.20, CH₃OH), ESI-MS *m/z*: 603 [M+Na]⁺, 结合 ¹³C-NMR 谱数据推测分子式为 C₂₈H₃₆O₁₃。¹H-NMR (500 MHz, CD₃OD) δ : 6.72 (2H, s, H-2, 6), 6.66 (2H, s, H-2', 6'), 4.87 (1H, d, *J* = 7.8 Hz, H-1''), 4.77 (1H, d, *J* = 4.1 Hz, H-7), 4.72 (1H, d, *J* = 4.4 Hz, H-7'), 4.28 (2H, m, H-9a, 9'a), 3.91 (2H, m, H-9b, 9'b), 3.86 (6H, s, 3, 5-OCH₃), 3.84 (6H, s, 3', 5'-OCH₃), 3.77 (1H, dd, *J* = 12.0, 2.4 Hz, H-6''a), 3.67 (1H, dd, *J* = 12.0, 5.2 Hz, H-6''b), 3.48 (1H, m, H-2''), 3.41 (2H, m, H-3'', 4''), 3.20 (1H, m, H-5''), 3.13 (2H, m, H-8, 8'); ¹³C-NMR (125 MHz, CD₃OD) δ : 154.4 (C-3, 5), 149.4 (C-3', 5'), 139.6 (C-1), 136.3 (C-4'), 135.7 (C-4), 133.1 (C-1'), 105.4 (C-1''), 104.9 (C-2, 6), 104.6 (C-2', 6'), 87.6 (C-7'), 87.2 (C-7), 78.3 (C-5''), 77.8 (C-3''), 75.7 (C-2''), 72.9 (C-9), 72.9 (C-9'), 71.4 (C-4''), 62.6 (C-6''), 57.1 (3, 5-OCH₃), 56.9 (3', 5'-OCH₃), 55.7 (C-8'), 55.5 (C-8)。以上数据与文献报道基本一致^[9], 故鉴定化合物 **6** 为 (+)-丁香树脂醇-4-*O*-β-*D*-吡喃葡萄糖苷。

化合物 **7**: 无色固体(甲醇), $[\alpha]_{\text{D}}^{25} +18.5^{\circ}$ (*c* 0.28, CH₃OH), ESI-MS *m/z*: 603 [M+Na]⁺, 结合 ¹³C-NMR 谱数据推测分子式为 C₂₈H₃₆O₁₃。¹H-NMR (500 MHz, CD₃OD) δ : 6.72 (2H, s, H-2, 6), 6.67 (2H, s, H-2', 6'), 4.85 (1H, d, *J* = 7.5 Hz, H-1''), 4.74 (1H, d, *J* = 5.8 Hz, H-7'), 4.50 (1H, d, *J* = 6.6 Hz, H-7), 4.18 (1H, d, *J* = 9.4 Hz, H-9a), 3.88 (2H, m, H-9'a, 9b), 3.86 (6H, s, 3, 5-OCH₃), 3.85 (6H, s, 3', 5'-OCH₃), 3.78 (1H, dd, *J* = 12.0, 2.4 Hz, H-6''a), 3.67 (1H, dd, *J* = 12.0, 5.2 Hz, H-6''b), 3.47 (1H, m, H-2''), 3.41 (2H, m, H-3'', 4''), 3.35 (1H, m, H-8'), 3.20 (1H, m, H-5''), 3.17 (1H, m, H-9'b), 2.94 (1H, m, H-8); ¹³C-NMR (125 MHz, CD₃OD) δ : 154.4 (C-3, 5), 149.2 (C-3', 5'), 139.7 (C-1), 135.7 (C-4'), 134.8 (C-4), 132.2 (C-1'), 105.4 (C-1''), 105.0 (C-2, 6), 104.2 (C-2', 6'), 89.1 (C-7), 83.6 (C-7'), 78.4 (C-5''), 77.8 (C-3''), 75.7 (C-2''), 72.1 (C-9), 71.4 (C-4''), 70.8 (C-9'), 62.6 (C-6''), 57.1 (3, 5-OCH₃), 56.8 (3', 5'-OCH₃), 55.9 (C-8),

51.3 (C-8')。以上数据与文献报道基本一致^[10], 故鉴定化合物 **7** 为 (+)-表丁香树脂醇-4-*O*-β-*D*-吡喃葡萄糖苷。

化合物 **8**: 无色固体(甲醇), ESI-MS *m/z*: 381 [M+Na]⁺, 结合 ¹³C-NMR 谱推测分子式为 C₂₀H₂₂O₆。¹H-NMR (500 MHz, CD₃OD) δ : 6.71 (1H, d, *J* = 8.0 Hz, H-5'), 6.69 (1H, d, *J* = 8.0 Hz, H-5), 6.68 (1H, d, *J* = 2.0 Hz, H-2'), 6.58 (1H, dd, *J* = 8.0, 2.0 Hz, H-6'), 6.56 (1H, d, *J* = 1.9 Hz, H-2), 6.51 (1H, dd, *J* = 8.0, 1.9 Hz, H-6), 4.16 (H, dd, *J* = 9.0, 7.4 Hz, H-9a), 3.92 (H, dd, *J* = 9.0, 7.7 Hz, H-9b), 3.79 (3H, brs, 3-OCH₃), 3.78 (3H, brs, 3'-OCH₃), 2.89 (1H, dd, *J* = 14.0, 5.4 Hz, H-7'a), 2.82 (1H, dd, *J* = 14.0, 7.0 Hz, H-7'b), 2.66 (1H, m, H-8'), 2.53 (2H, m, H-7), 2.50 (1H, m, H-8); ¹³C-NMR (125 MHz, CD₃OD) δ : 181.6 (C-9'), 149.1 (C-3'), 149.0 (C-3), 146.4 (C-4'), 146.2 (C-4), 131.5 (C-1), 130.8 (C-1'), 123.1 (C-6'), 122.3 (C-6), 116.2 (C-5), 116.1 (C-5'), 114.0 (C-2'), 113.4 (C-2), 72.9 (C-9), 56.4 (3-OCH₃), 56.3 (3'-OCH₃), 47.8 (C-8'), 42.6 (C-8), 38.9 (C-7), 35.4 (C-7')。以上数据与文献报道基本一致^[11], 故鉴定化合物 **8** 为罗汉松脂素。

化合物 **9**: 白色粉末(甲醇), ESI-MS *m/z*: 443 [M+Na]⁺, 结合 ¹³C-NMR 谱数据推测分子式为 C₂₂H₂₈O₈。¹H-NMR (500 MHz, CD₃OD) δ : 6.58 (1H, s, H-2'), 6.38 (2H, s, H-2, 6), 4.31 (1H, d, *J* = 5.6 Hz, H-7), 3.86 (3H, s, 3'-OCH₃), 3.74 (6H, brs, 3, 5-OCH₃), 3.59 (1H, dd, *J* = 10.8, 5.1 Hz, H-9'a), 3.49 (3H, m, H-9, H-9'b), 3.38 (3H, s, 5'-OCH₃), 2.70 (1H, dd, *J* = 15.0, 4.8 Hz, H-7'a), 2.57 (1H, dd, *J* = 14.9, 11.4 Hz, H-7'b), 1.97 (1H, m, H-8), 1.63 (1H, m, H-8'); ¹³C-NMR (125 MHz, CD₃OD) δ : 149.0 (C-3, 5), 148.7 (C-3'), 147.7 (C-5'), 139.3 (C-4'), 138.9 (C-1), 134.6 (C-4), 130.2 (C-1'), 126.3 (C-6'), 107.8 (C-2'), 107.0 (C-2, 6), 66.8 (C-9'), 64.3 (C-9), 60.2 (5'-OCH₃), 56.8 (3, 5-OCH₃), 56.6 (3'-OCH₃), 49.0 (C-8), 42.3 (C-7), 41.0 (C-8'), 33.6 (C-7')。以上数据与文献报道基本一致^[12], 故鉴定化合物 **9** 为 (+)-珍珠花环木脂素。

化合物 **10**: 白色粉末(甲醇), ESI-MS *m/z*: 383 [M+Na]⁺, 结合 ¹³C-NMR 谱数据推测分子式为 C₂₀H₂₄O₆。¹H-NMR (500 MHz, CD₃OD) δ : 6.74 (1H, d, *J* = 8.0 Hz, H-5), 6.68 (1H, d, *J* = 1.8 Hz, H-2), 6.66

(1H, s, H-2'), 6.61 (1H, dd, $J = 8.0, 1.8$ Hz, H-6), 6.19 (1H, s, H-5'), 3.81 (3H, s, 3-OCH₃), 3.80 (1H, d, $J = 10.2$ Hz, H-7), 3.77 (3H, s, 3'-OCH₃), 3.70 (1H, dd, $J = 11.0, 5.0$ Hz, H-9'a), 3.66 (2H, m, H-9a, 9'b), 3.40 (1H, dd, $J = 11.2, 4.1$ Hz, H-9b), 2.77 (2H, d, $J = 7.6$ Hz, H-7'), 2.00 (1H, m, H-8'), 1.77 (1H, m, H-8); ¹³C-NMR (125 MHz, CD₃OD) δ : 149.1 (C-3), 147.2 (C-3'), 146.0 (C-4), 145.3 (C-4'), 138.6 (C-1), 134.2 (C-6'), 129.0 (C-1'), 123.2 (C-6), 117.4 (C-5'), 116.0 (C-5), 113.9 (C-2), 112.4 (C-2'), 66.0 (C-9'), 62.3 (C-9), 56.4 (3'-OCH₃), 56.4 (3-OCH₃), 48.5 (C-7), 48.1 (C-8), 40.1 (C-8'), 33.6 (C-7')。以上数据与文献报道基本一致^[13], 故鉴定化合物 **10** 为 (+)-异落叶松脂素。

化合物 **11**: 无色透明固体 (甲醇), ESI-MS m/z : 401 [M+Na]⁺, 结合 ¹³C-NMR 谱数据推测分子式为 C₂₀H₂₆O₇。 ¹H-NMR (500 MHz, CD₃OD) δ : 6.99 (1H, d, $J = 1.8$ Hz, H-2), 6.98 (1H, d, $J = 8.4$ Hz, H-5'), 6.85 (1H, m, H-6), 6.83 (1H, m, H-2'), 6.74 (1H, d, $J = 8.2$ Hz, H-5), 6.71 (1H, m, H-6'), 4.86 (1H, d, $J = 6.6$ Hz, H-7), 4.20 (1H, m, H-8), 3.86 (3H, s, 3'-OCH₃), 3.81 (3H, s, 3-OCH₃), 3.70 (1H, dd, $J = 11.8, 3.8$ Hz, H-9a), 3.56 (2H, t, $J = 6.5$ Hz, H-9'), 3.46 (1H, dd, $J = 11.9, 5.0$ Hz, H-9b), 2.62 (2H, t, $J = 7.2$ Hz, H-7'), 1.81 (2H, m, H-8'); ¹³C-NMR (125 MHz, CD₃OD) δ : 151.8 (C-3'), 149.3 (C-3), 148.6 (C-4'), 147.7 (C-4), 138.3 (C-1'), 133.0 (C-1), 122.1 (C-6'), 120.9 (C-6), 119.8 (C-5'), 116.3 (C-5), 114.1 (C-2'), 111.8 (C-2), 87.9 (C-8), 74.4 (C-7), 62.3 (C-9'), 62.0 (C-9), 56.6 (3'-OCH₃), 56.4 (3-OCH₃), 35.6 (C-8'), 32.8 (C-7')。以上数据与文献报道基本一致^[14], 故鉴定化合物 **11** 为 (7R, 8R)-4, 7, 9, 9'-四羟基-3, 3'-二甲氧基-8-O-4'-新木脂素。

化合物 **12**: 无色透明固体 (甲醇), ESI-MS m/z : 401 [M+Na]⁺, 结合 ¹³C-NMR 谱数据推测分子式为 C₂₀H₂₆O₇。 ¹H-NMR (500 MHz, CD₃OD) δ : 7.00 (1H, d, $J = 1.8$ Hz, H-2), 6.82 (1H, dd, $J = 8.0, 1.8$ Hz, H-6), 6.81 (1H, d, $J = 8.1$ Hz, H-5'), 6.79 (1H, d, $J = 1.8$ Hz, H-2'), 6.73 (1H, d, $J = 8.0$ Hz, H-5), 6.66 (1H, dd, $J = 8.2, 1.9$ Hz, H-6'), 4.83 (1H, overlapped, H-7), 4.28 (1H, m, H-8), 3.84 (1H, dd, $J = 11.9, 5.7$ Hz, H-9b), 3.80 (3H, s, 3-OCH₃), 3.78 (3H, s, 3'-OCH₃), 3.75 (1H, dd, $J = 11.9, 3.7$ Hz, H-9a), 3.55 (2H, t, $J =$

6.5 Hz, H-9'), 2.60 (2H, t, $J = 7.5$ Hz, H-7'), 1.79 (2H, m, H-8'); ¹³C-NMR (125 MHz, CD₃OD) δ : 151.9 (C-3'), 148.8 (C-3), 147.2 (C-4), 147.1 (C-4'), 138.1 (C-1'), 134.1 (C-1), 121.9 (C-6'), 121.0 (C-6), 119.6 (C-5'), 115.7 (C-5), 114.1 (C-2'), 111.8 (C-2), 86.6 (C-8), 74.2 (C-7), 62.2 (C-9, 9'), 56.5 (3-OCH₃), 56.4 (3'-OCH₃), 35.5 (C-8'), 32.7 (C-7')。以上数据与文献报道基本一致^[15], 故鉴定化合物 **12** 为 (7R, 8S)-4, 7, 9, 9'-四羟基-3, 3'-二甲氧基-8-O-4'-新木脂素。

化合物 **13**: 黄色油状物 (甲醇), ESI-MS m/z : 383 [M+Na]⁺, 结合 ¹³C-NMR 谱数据推测分子式为 C₂₀H₂₄O₆。 ¹H-NMR (500 MHz, CD₃OD) δ : 6.95 (1H, d, $J = 1.6$ Hz, H-2), 6.82 (1H, dd, $J = 8.0, 1.6$ Hz, H-6), 6.76 (1H, d, $J = 8.1$ Hz, H-5), 6.72 (1H, brs, H-6'), 6.68 (1H, brs, H-2'), 5.49 (1H, d, $J = 6.3$ Hz, H-7), 3.84 (3H, s, 3'-OCH₃), 3.84 (1H, dd, $J = 8.4, 3.0$ Hz, H-9a), 3.80 (3H, s, 3-OCH₃), 3.75 (1H, dd, $J = 11.0, 7.1$ Hz, H-9b), 3.57 (2H, t, $J = 6.5$ Hz, H-9'), 3.47 (1H, dt, $J = 12.4, 6.2$ Hz, H-8), 2.62 (2H, t, $J = 7.5$ Hz, H-7'), 1.82 (2H, m, H-8'); ¹³C-NMR (125 MHz, CD₃OD) δ : 149.1 (C-3), 147.5 (C-4'), 147.5 (C-4), 145.2 (C-3'), 136.9 (C-1'), 134.8 (C-1), 129.9 (C-5'), 119.7 (C-6), 117.9 (C-5), 116.2 (C-6'), 114.2 (C-2'), 110.6 (C-2), 89.0 (C-7), 65.0 (C-9), 62.2 (C-9'), 56.8 (3'-OCH₃), 56.4 (3-OCH₃), 55.4 (C-8), 35.8 (C-8'), 32.9 (C-7')。以上数据与文献报道基本一致^[16], 故鉴定化合物 **13** 为 (7S, 8R)-二氢脱氢双松柏醇。

化合物 **14**: 淡黄色粉末 (甲醇), 盐酸-镁粉反应呈阳性; ESI-MS m/z : 285 [M-H]⁻, 结合 ¹³C-NMR 谱数据推测分子式为 C₁₅H₁₀O₆。 ¹H-NMR (500 MHz, DMSO-*d*₆) δ : 12.95 (1H, s, 5-OH), 9.89 (1H, brs, 7-OH), 7.40 (1H, dd, $J = 8.1, 1.6$ Hz, H-6'), 7.39 (1H, d, $J = 1.6$ Hz, H-2'), 6.88 (1H, d, $J = 8.1$ Hz, H-5'), 6.64 (1H, s, H-3), 6.43 (1H, d, $J = 1.6$ Hz, H-6), 6.17 (1H, d, $J = 1.6$ Hz, H-6); ¹³C-NMR (125 MHz, DMSO-*d*₆) δ : 181.6 (C-4), 164.2 (C-7), 163.9 (C-2), 161.5 (C-9), 157.3 (C-5), 149.7 (C-4'), 145.8 (C-3'), 121.5 (C-1'), 119.0 (C-6'), 116.0 (C-5'), 113.4 (C-2'), 103.66 (C-10), 102.84 (C-3), 98.8 (C-6), 93.8 (C-8)。以上数据与文献报道基本一致^[17], 故鉴定化合物 **14** 为木犀草素。

化合物 **15**: 黄色粉末 (甲醇), 盐酸-镁粉反应呈阳性, Molish 反应呈阳性; ESI-MS m/z : 529 [M-

H]⁻, 结合¹³C-NMR 谱数据推测分子式为 C₂₇H₃₀O₁₁。 ¹H-NMR (500 MHz, DMSO-*d*₆) δ: 13.37 (1H, s, 5-OH), 10.74 (1H, brs, 7-OH), 8.06 (2H, d, *J* = 8.8 Hz, H-2', 6'), 6.91 (2H, d, *J* = 8.8 Hz, H-3', 5'), 6.83 (1H, s, H-3), 6.53 (1H, s, H-6), 4.89 (1H, t, *J* = 9.4 Hz, H-3''), 4.82 (1H, d, *J* = 9.8 Hz, H-1''), 4.00 (1H, t, *J* = 9.6 Hz, H-2''), 3.89 (3H, s, 7-OCH₃), 3.75 (1H, brd, *J* = 11.0 Hz, H-6''a), 3.60 (1H, dd, *J* = 11.0, 5.4 Hz, H-6''b), 3.60 (1H, t, *J* = 9.4 Hz, H-4''), 3.34 (1H, m, H-5''), 2.31 (1H, m, H-2'''), 1.54 (1H, m, H-3'''a), 1.35 (1H, m, H-3'''b), 1.05 (3H, d, *J* = 7.0 Hz, H-5'''), 0.80 (3H, t, *J* = 7.4 Hz, H-4'''); ¹³C-NMR (125 MHz, DMSO-*d*₆) δ: 182.2 (C-4), 175.2 (C-1'''), 164.4 (C-2), 163.3 (C-7), 161.7 (C-5), 161.5 (C-4'), 155.2 (C-9), 129.0 (C-2', 6'), 121.1 (C-1'), 115.9 (C-3', 5'), 104.8 (C-8), 104.4 (C-10), 102.4 (C-3), 94.9 (C-6), 81.8 (C-5''), 79.0 (C-3''), 73.4 (C-1''), 68.6 (C-2''), 68.2 (C-4''), 60.6 (C-6''), 56.5 (-OCH₃), 40.3 (C-2'''), 26.3 (C-3'''), 16.5 (C-5'''), 11.1 (C-4''')。以上数据与文献报道基本一致^[18], 故鉴定化合物 **15** 为 3''-O-(2'''-甲基丁酰基) 异当药苷。

化合物 **16**: 黄色粉末 (甲醇), 盐酸-镁粉反应呈阳性, Molish 反应呈阳性; ESI-MS *m/z*: 529 [M-H]⁻, 结合¹³C-NMR 谱数据推测分子式为 C₂₇H₃₀O₁₁。 ¹H-NMR (500 MHz, DMSO-*d*₆) δ: 13.34 (1H, s, 5-OH), 10.35 (1H, brs, 7-OH), 8.09 (2H, d, *J* = 8.8 Hz, H-2', 6'), 6.91 (2H, d, *J* = 8.8 Hz, H-3', 5'), 6.83 (1H, s, H-3), 6.48 (1H, s, H-6), 5.34 (1H, t, *J* = 10.1 Hz, H-2''), 4.88 (1H, d, *J* = 10.1 Hz, H-1''), 3.87 (3H, s, 7-OCH₃), 3.78 (1H, brd, *J* = 11.9 Hz, H-6''a), 3.58 (1H, dd, *J* = 11.9, 5.6 Hz, H-6''b), 3.49 (2H, m, H-3'', 4''), 3.32 (1H, m, H-5''), 2.03 (1H, m, H-2'''), 1.22 (1H, m, H-3'''a), 1.12 (1H, m, H-3'''b), 0.68 (3H, d, *J* = 7.0 Hz, H-5'''), 0.58 (3H, t, *J* = 7.4 Hz, H-4'''); ¹³C-NMR (125 MHz, DMSO-*d*₆) δ: 182.2 (C-4), 174.5 (C-1'''), 164.4 (C-2), 162.8 (C-7), 161.7 (C-5), 161.4 (C-4'), 155.6 (C-9), 129.1 (C-2', 6'), 121.4 (C-1'), 115.9 (C-3'', 5'), 104.2 (C-8), 103.3 (C-10), 102.4 (C-3), 94.6 (C-6), 82.0 (C-5''), 75.6 (C-3''), 71.6 (C-2''), 70.5 (C-1''), 70.5 (C-4''), 60.9 (C-6''), 56.5 (C-OCH₃), 40.0 (C-2'''), 25.7 (C-3'''), 16.4 (C-5'''), 11.1 (C-4''')。以上数据与文献报道基本一致^[18], 故鉴定化合物 **16** 为 2''-O-(2'''-甲基丁酰基) 异当药苷。

化合物 **17**: 黄色粉末 (甲醇), 盐酸-镁粉反应呈阳性, Molish 反应呈阳性; ESI-MS *m/z*: 529 [M-H]⁻, 结合¹³C-NMR 谱数据推测分子式为 C₂₇H₃₀O₁₁。 ¹H-NMR (500 MHz, DMSO-*d*₆) δ: 7.97 (2H, d, *J* = 8.8 Hz, H-2', 6'), 6.92 (2H, d, *J* = 8.8 Hz, H-3', 5'), 6.82 (1H, s, H-3), 6.51 (1H, s, H-6), 4.74 (1H, d, *J* = 10.0 Hz, H-1''), 4.34 (1H, brd, *J* = 11.4 Hz, H-6''a), 4.09 (1H, dd, *J* = 11.4, 5.0 Hz, H-6''b), 3.87 (3H, s, 7-OCH₃), 2.16 (1H, m, H-2'''), 1.43 (1H, m, H-3'''a), 1.27 (1H, m, H-3'''b), 0.91 (3H, d, *J* = 7.0 Hz, H-5'''), 0.69 (3H, t, *J* = 7.4 Hz, H-4'''); ¹³C-NMR (125 MHz, DMSO-*d*₆) δ: 182.2 (C-4), 175.8 (C-1'''), 164.3 (C-2), 163.4 (C-7), 161.6 (C-5), 161.4 (C-4'), 155.2 (C-9), 128.7 (C-2', 6'), 121.2 (C-1'), 115.9 (C-3'', 5'), 105.3 (C-8), 104.4 (C-10), 102.4 (C-3), 95.0 (C-6), 78.4 (C-5''), 78.3 (C-3''), 73.3 (C-1''), 70.7 (C-2''), 70.5 (C-4''), 63.6 (C-6''), 56.6 (-OCH₃), 40.0 (C-2'''), 26.1 (C-3'''), 16.2 (C-5'''), 11.0 (C-4''')。以上数据与文献报道基本一致^[19], 故鉴定化合物 **17** 为 6''-O-(2'''-甲基丁酰基) 异当药苷。

参考文献

- [1] 中国科学院中国植物志编辑委员会. 中国植物志 (第28卷) [M]. 北京: 科学出版社, 1980.
- [2] 中国药典 [S]. 一部. 2010.
- [3] Chawla R, Kumar S, Sharma A. The genus *Clematis* (Ranunculaceae): Chemical and pharmacological perspectives [J]. *J Ethnopharmacol*, 2012, 143(1): 116-150.
- [4] 张凡, 赵明波, 李军, 等. 独蒜兰的化学成分研究 [J]. 中草药, 2013, 44(12): 1529-1523.
- [5] Xie L H, Akao T, Hamasaki K, et al. Biotransformation of pinoresinol diglucoside to mammalian lignans by human intestinal microflora, and isolation of *Enterococcus faecalis* strain PDG-1 responsible for the transformation of (+)-pinoresinol to (+)-pLariciresinol [J]. *Chem Pharm Bull*, 2003, 51(5): 508-515.
- [6] 丛悦, 王艳, 王天晓, 等. 功劳木的化学成分研究 [J]. 中成药, 2011, 33(6): 1008-1010.
- [7] 刘可鑫, 周翎, 刘攀峰, 等. 盐制对杜仲化学成分含量变化的影响 [J]. 中成药, 2011, 33(2): 280-284.
- [8] Kim D K, Lim J P, Kim J W, et al. Antitumor and antiinflammatory constituents from *Celtis sinensis* [J]. *Arch Pharm Res*, 2005, 28(1): 39-43.
- [9] Shahat A A, Abdel-Azim N S, Pieters L, et al. Isolation and NMR spectra of syringaresinol-β-D-glucoside from

- Cressa cretica* [J]. *Fitoterapia*, 2004, 75(7/8): 771-773.
- [10] Li X C, Barnes D L, Khan I A. A new lignan glycoside from *Eleutherococcus senticosus* [J]. *Planta Med*, 2001, 67(8): 776-778.
- [11] Rahman M M A, Dewick P M, Jackson D E, *et al.* Lignans of *Forsythia intermedia* [J]. *Phytochemistry*, 1990, 29: 1971-1980.
- [12] Ouyang M A, Wein Y S, Su R K, *et al.* Rhusemialins A—C, new cycloligan esters from the roots of *Rhus javanica* var. *roxburghiana* [J]. *Chem Pharm Bull*, 2007, 55(5): 804-807.
- [13] Erdemoglu N, Sener B, Ozcan Y, *et al.* Structural and spectroscopic characteristics of two new dibenzylbutane type lignans from *Taxus baccata* L. [J]. *J Mol Struct*, 2003, 655(3): 459-466.
- [14] Matsuda N, Kikuchi M. Studies on the constituents of *Lonicera* species. X. Neolignan glycosides from the leaves of *Lonicera gracilipes* var. *glandulosa* Maxim. [J]. *Chem Pharm Bull*, 1996, 44(9): 1676-1679.
- [15] Sinkkonen J, Karonen M, Liimatainen J, *et al.* Lignans from the bark extract of *Pinus sylvestris* L. [J]. *Mag Reson Chem*, 2006, 44(6): 633-636.
- [16] Lee D Y, Song M C, Yoo K H, *et al.* Lignans from the fruits of *Cornus kousa* Burg. and their cytotoxic effects on human cancer cell lines [J]. *Arch Pharm Res*, 2007, 30(4): 402-407.
- [17] 靳鑫, 时圣明, 张东方, 等. 穿心莲化学成分的研究 (II) [J]. *中草药*, 2014, 45(2): 164-169.
- [18] Zou J H, Yang J S, Zhou L. Acylated flavone C-glycosides from *Trollius ledebouri* [J]. *J Nat Prod*, 2004, 67(4): 664-667.
- [19] Dong F Y, Guan L N, Zhang Y H, *et al.* Acylated flavone C-glycosides from *Hemistepa lyrata* [J]. *J Asian Nat Prod Res*, 2010, 12(9): 776-780.