·化学成分·

兴安升麻根茎的化学成分研究

卢 青[1]，李海波[2]，姚新生[1]，于 洋[1*]

1. 暨南大学中药及天然药物研究所，广东 广州 510632
2. 江苏康缘药业股份有限公司 中药制药过程新技术国家重点实验室，江苏 连云港 222001

摘 要：目的 研究兴安升麻 *Cimicifuga dahurica* 根茎的化学成分。**方法** 运用 HP-20 大孔吸附树脂、硅胶、ODS 和 Sephadex LH-20 等柱色谱以及反相半制备型 HPLC 等各种现代色谱分离技术进行系统的分离纯化，根据化合物的光谱数据和理化性质进行结构鉴定。**结果** 从兴安升麻根茎大孔吸附树脂 30%乙醇水洗脱部位中共分离得到了 20 个化合物，分别鉴定为 cimicifugaside F（**1**）、(+)-(2*S*,3*R*)-2-(4-羟基-3-甲氧基苯基)-3-[(β-*D*-吡喃葡萄糖氧基) 甲基]-7-甲氧基苯并呋喃-5-丙烯酸（**2**）、5-羟基-2-甲氧基苯甲酸（**3**）、苯甲酸-4-*O*-β-*D*-葡萄糖苷（**4**）、异阿魏酸（**5**）、阿魏酸（**6**）、阿魏酸-4-*O*-β-*D*-阿洛糖苷（**7**）、阿魏酸-4-*O*-β-*D*-葡萄糖苷（**8**）、芥子酸-4-*O*-β-*D*-葡萄糖苷（**9**）、6,6′-二-*O*-芥子酰基蔗糖（**10**）、番石榴酸（**11**）、蜂斗菜酸（**12**）、*N*-反式对羟基苯乙基阿魏酰胺-4-*O*-β-*D*-阿洛糖苷（**13**）、*N*-反式-3′-甲氧基-4′-羟基苯乙基阿魏酰胺-4-*O*-β-*D*-阿洛糖苷（**14**）、*N*-反式-3′-甲氧基-4′-羟基苯乙基阿魏酰胺-4-*O*-β-*D*-葡萄糖苷（**15**）、grevilloside G（**16**）、丁香脂素（**17**）、丁香脂素-4,4′-*O*-β-*D*-双阿洛糖苷（**18**）、(+)-异落叶松树脂素-3a-*O*-β-*D*-葡萄糖苷（**19**）、(−)-5′-甲氧基异落叶松树脂素-3a-*O*-β-*D*-葡萄糖苷（**20**）。**结论** 化合物 **1** 为 1 个新的木脂素苷类化合物，化合物 **2**～**4**、**8**～**10**、**15**～**17**、**20** 为首次从升麻属植物中分离得到。

关键词：兴安升麻；5-羟基-2-甲氧基苯甲酸；苯甲酸-4-*O*-β-*D*-葡萄糖苷；阿魏酸-4-*O*-β-*D*-葡萄糖苷；芥子酸-4-*O*-β-*D*-葡萄糖苷；丁香脂素

中图分类号：R284.1 **文献标志码：**A **文章编号：**0253 - 2670(2019)14 - 3261 - 08

DOI: 10.7501/j.issn.0253-2670.2019.14.001

Chemical constituents from rhizomes of *Cimicifuga dahurica*

LU Qing[1], LI Hai-bo[2], YAO Xin-sheng[1], YU Yang[1]

1. Institute of Traditional Chinese Medicine and Natural Products, Jinan University, Guangzhou 510632, China
2. State Key Laboratory of New-tech for Chinese Medicine Pharmaceutical Process, Kanion Pharmaceutical Co., Ltd., Lianyungang 222001, China

Abstract: Objective To isolate and identify the chemical constituents from the rhizome of *Cimicifuga dahurica*. **Methods** The isolation and purification of 60% EtOH extract of the rhizomes of *C. dahurica* were carried out through various modern chromatographic separation techniques: HP-20, silica gel, ODS, Sephadex LH-20 column and semi-preparative HPLC. And the structures of the compounds were identified based on spectroscopic data and physicochemical properties. **Results** Twenty compounds were isolated and identified as cimicifugaside F (**1**), (+) (2*S*,3*R*)-2-(4-hydroxy-3-methoxyphenyl)-3-[(β-*D*-glucopyranosyloxy) methyl]-7-methoxybenzofuran-5-propenoic acid (**2**), 5-hydroxy-2-methoxybenzoic acid (**3**), benzoic acid 4-*O*-β-*D*-glucoside (**4**), isoferulic acid (**5**), ferulic acid (**6**), *trans*-ferulic acid 4-*O*-β-*D*-allopyranoside (**7**), *trans*-ferulic acid 4-*O*-β-*D*-glucoside (**8**), (*E*)-sinapic acid 4-*O*-β-*D*-glucoside (**9**), 6,6′-di-*O*-sinapoylsurcose (**10**), piscidic acid (**11**), fukinolic acid (**12**), *N*-*trans*-feruloyltyramine 4-*O*-β-*D*-allopyranoside (**13**), *N*-*trans*-3′-methoxy-4′-feruloyltyramine-4-*O*-β-*D*-allopyranoside (**14**), *N*-*trans*-3′-methoxy-4′-feruloyltyramine-4-*O*-β-*D*-glucoside (**15**), grevilloside G (**16**), (−)-syringaresinol (**17**), (−)-syringaresinol 4,4′-di-*O*-β-*D*-allopyranoside (**18**), (+)-isolarisiresinol 3a-*O*-β-*D*–glucoside (**19**), (−)-5′-methoxyisolariciresinol 3a-*O*-β-*D*-glucoside (**20**). **Conclusion** Compound **1** was identified as a new lignan, and compounds **2**—**4**, **8**—**10**, **15**—**17** and **20** were isolated from

收稿日期：2019-04-05

基金项目：国家自然科学基金重点项目（81602984）；国家自然科学基金重点项目（81630097）

作者简介：卢 青（1994—），女，湖北天门人，硕士研究生，研究方向为中药及天然药物的活性成分研究。E-mail: 17817311993@163.com

*通信作者 于 洋，副研究员，硕士生导师，研究方向为中药及天然药物活性成分研究。Tel: (020)5225849 E-mail: 1018yuyang@163.com

Cimicifuga genus for the first time.

Key words: *Cimicifuga dahurica* (Turcz.) Maxim.; 5-hydroxy-2-methoxybenzoic acid; benzoic acid 4-*O*-β-*D*-glucoside; *trans*-ferulic acid 4-*O*-β-*D*-glucoside; (*E*)-sinapic acid 4-*O*-β-*D*-glucoside; (−)-syringaresinol

兴安升麻，别名北升麻，是毛茛科（Ranunculaceae）升麻属 *Cimicifuga* L. 植物兴安升麻 *Cimicifuga dahurica* (Turcz.) Maxim. 的根茎。兴安升麻在我国其主要分布于山西、河北、内蒙古、辽宁、吉林、黑龙江等地，具有发表透疹、清热解毒和升举阳气的作用，常用于治疗风热头痛、齿痛、口疮、麻疹不透和子宫脱垂等[1]。国内外研究表明兴安升麻中的化学成分主要包括环阿尔廷型三萜[2]、酚酸及其苷[3]、木脂素[4]，以及生物碱[5]等，具有抗肿瘤[6]、抗炎[7]、抗氧化[8]以及神经保护[9]等方面的药理活性。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的 60%乙醇水提取物经大孔吸附树脂柱色谱，30%乙醇水洗脱部位进行系统的化学成分研究，从中分离得到 20 个化合物，分别鉴定为 cimicifugaside F（**1**）、(+)-(2*S*,3*R*)-2-(4-羟基-3-甲氧基苯基)-3-[(β-*D*-吡喃葡萄糖氧基) 甲基]-7-甲氧基苯并呋喃-5-丙烯酸（(+) (2*S*,3*R*)-2-(4-hydroxy-3-methoxyphenyl)-3-[(β-*D*-glucopyranosyloxy) methyl]-7-methoxybenzofuran-5-propenoic acid，**2**）、5-羟基-2-甲氧基苯甲酸（5-hydroxy-2-methoxybenzoic acid，**3**）、苯甲酸-4-*O*-β-*D*-葡萄糖苷（benzoic acid 4-*O*-β-*D*-glucoside，**4**）、异阿魏酸（isoferulic acid，**5**）、阿魏酸（ferulic acid，**6**）、阿魏酸-4-*O*-β-*D*-阿洛糖苷（*trans*-ferulic acid 4-*O*-β-*D*-allopyranoside，**7**）、阿魏酸-4-*O*-β-*D*-葡萄糖苷（*trans*-ferulic acid 4-*O*-β-*D*-glucoside，**8**）、芥子酸-4-*O*-β-*D*-葡萄糖苷 [(*E*)-sinapic acid 4-*O*-β-*D*-glucoside，**9**]、6,6′-二-*O*-芥子酰基蔗糖苷（6,6′-di-*O*-sinapoylsurcose，**10**）、番石榴酸（piscidic acid，**11**）、蜂斗酸（fukinolic acid，**12**）、*N*-反式对羟基苯乙基阿魏酰胺-4-*O*-β-*D*-阿洛糖苷（*N*-*trans*-feruloyltyramine 4-*O*-β-*D*-allopyranoside，**13**）、*N*-反式-3′-甲氧基-4′-羟基苯乙基阿魏酰胺-4-*O*-β-*D*-阿洛糖苷（*N*-*trans*-3′-methoxy-4′-feruloyl-tyramine-4-*O*-β-*D*-allopyranoside，**14**）、*N*-反式-3′-甲氧基-4′-羟基苯乙基阿魏酰胺-4-*O*-β-*D*-葡萄糖苷（*N*-*trans*-3′-methoxy-4′-feruloyltyramine-4-*O*-β-*D*-glucoside，**15**）、3,5-二羟基苯乙醇-3-*O*-β-*D*-葡萄糖苷（grevilloside G，**16**）、丁香脂素 [(−)-syringaresinol，**17**]、丁香脂素-4,4′-*O*-β-*D*-双阿洛糖苷 [(−)-syringaresinol 4,4′-di-*O*-β-*D*-allopyranoside，**18**]、(+)-异落叶松树脂素-3a-*O*-β-*D*-葡萄糖苷 [(+)-isolarisiresinol 3a-*O*-β-*D*-glucoside，**19**]、(−)-5′-甲氧基异落叶松树脂素-3a-*O*-β-*D*-葡萄糖苷 [(−)-5′-methoxyisolariciresinol 3a-*O*-β-*D*-glucoside，**20**]。其中化合物 **1** 为新化合物，化合物 **2**～**4**、**8**～**10**、**15**～**17**、**20** 为首次从升麻属植物中分离得到。

1 仪器与材料

瑞士 BrukerAvance 81 600 全数字化超导核磁共振仪；分析型高效液相色谱仪（日本岛津）：LC20AB prominence LIQUID CHROMATOGRAPH 泵和 SPD-M20A prominence DIODE ARRAY AETECTOR 检测器；制备型高效液相色谱仪（日本岛津）：LC-6AD（SHIMADZU 公司，LIQUID CHROMATOGRAPH）泵和 SPD-20A（prominence UV/VIS DETECTOR）检测器。

分析型色谱柱 Phenomenex Gemini（C_{18}，250 mm×4.6 mm，5 μm）；半制备型色谱柱 Phenomenex Gemini（C_{18}，250 mm×10 mm，5 μm）；Diaion HP-20（Mitsubishi Chemical Co.，日本）；柱色谱硅胶（100～200、200～300 目），青岛海洋化工公司；RP-C_{18} 柱色谱填料（12 nm，S-50 μm），YMC；甲醇（色谱级）、乙腈（色谱级）、甲酸（分析纯），Oceanpack Alexative Chemicals 有限公司；氘代试剂，Cambridge Isotope Laboratories，Inc.（Saint Louis，美国）。

从黑龙江大兴安岭采集兴安升麻根茎样品 19.5 kg，由黑龙江中医药大学匡海学教授鉴定为兴安升麻 *Cimicifuga dahurica* (Turcz.) Maxim. 的干燥根茎。

2 提取与分离

兴安升麻干燥根茎 19.5 kg，经 120 L 60%乙醇水回流提取 2 次，每次 2 h，合并提取液，减压浓缩干燥得兴安升麻提取物 2.8 kg，经 HP-20 大孔吸附树脂柱色谱进行粗分离，乙醇-水（0∶100、70∶30、95∶5）梯度洗脱（每个梯度 25 L 流动相）得到 3 个洗脱部位 Fr. CD-1～CD-3。Fr. CD-2 经硅胶柱色谱，甲醇-二氯甲烷-水（100∶0∶0、97∶3∶0、95∶5∶0、90∶10∶1、85∶15∶1.5、70∶30∶5、60∶

40∶8、50∶50∶10、0∶100∶0）梯度洗脱，得到 13 个馏份（2A～2M）。再经过硅胶柱色谱、ODS 柱色谱、半制备 HPLC 以及重结晶等方法分离纯化。从 Fr. 2B 得到化合物 **3**（6.3 mg）、**5**（3.3 g）、**6**（323 mg），从 Fr. 2H 得到化合物 **7**（753.2 mg）、**9**（91.0 mg）、**13**（75.4 mg）、**14**（270.5 mg），从 Fr. 2I 得到化合物 **1**（44.9 mg）、**2**（39.2 mg）、**8**（36.4 mg）、**15**（30.7 mg），从 Fr. 2J 得到化合物 **4**（3.2 mg）、**10**（7.8 mg）、**16**（70.2 mg）、**17**（2.7 mg）、**18**（10.4 mg）、**19**（10.0 mg）、**20**（3.3 mg），从 Fr. 2L 得到化合物 **11**（13.7 mg）、**12**（15.5 mg）。

3 结构鉴定

化合物 **1**：黄色膏状体，HR-ESI-MS 给出 *m*/*z* 557.163 8 $[M+Na]^+$（计算值 557.163 5），确定分子式为 $C_{26}H_{30}O_{12}$，不饱和度为 12。

^{1}H-NMR (600 MHz, CD_3OD) 图谱中（表 1），低场区显示 1 组 1,2,4-三取代芳香质子信号 [δ_H 7.01 (1H, d, J = 2.0 Hz, H-2), 6.88 (1H, dd, J = 8.1, 2.0 Hz, H-6), 6.79 (1H, d, J = 8.1 Hz, H-5)]；1 组 1,2,3,5-四取代芳香质子信号 [δ_H 7.13 (1H, m, H-2′), 7.26 (1H, s, H-6′)]，1 组反式烯质子 [δ_H 7.64 (1H, d, J = 15.8 Hz, H-7′), 6.36 (1H, d, J = 15.8 Hz, H-8′)]，1 个糖端基质子信号 [δ_H 4.37 (1H, d, J = 7.8 Hz)]，以及 2 个甲氧基质子信号 [δ_H 3.91 (3H, s), 3.85 (3H, s)]。^{13}C-NMR (150 MHz, CD_3OD) 图谱中，共显示 26 个碳信号，除去 6 个糖基碳信号和 2 个甲氧基碳信号，还有 18 个碳信号，推测化合物 **1** 可能为木脂素类化合物。在 HMBC 谱中（图 1），H-7′/C-1′, 2′, 6′, 8′, 9′和 H-8′/C-1′, 7′, 9′ 两组相关信号，提示反式双键与四取代苯环和羰基相连，推出 1 个 C_6-C_3 单元。在 ^{1}H-^{1}H COSY 谱中，显示 1 组偶合信号 H-7 (δ_H 5.67) /H-8 (δ_H 3.72) /H-9 (δ_H 4.22)，结合 HMBC 图谱，H-7/C-1, 2, 6、H-8/C-1，连接出另一个 C_6-C_3 单元。此外，H-6′/C-8、H-7/C-4′, 5′、H-8/C-5′, 6′、H-9/C-5′有 HMBC 远程相关，表明化合物为苯骈呋喃型木脂素。在 HMBC 图谱中，CH_3O-(δ_H 3.82) 与 C-3 (δ_C 149.0) 相关，CH_3O-(δ_H 3.89) 与 C-3′ (δ_C 145.8) 相关，提示 2 个甲氧基分别与 2 个苯环的 3 和 3′位相连；糖端基质子 H-1″ (δ_H 4.37) 与 C-9 (δ_C 72.0) 相关，H-9 (δ_H 4.22, 3.83) 与糖基的 C-1 (δ_C 134.0) 相关，表明葡萄糖基与 C-9 位相连，因此确定了化合物 **1** 的平面结构。H-7 与 H-8 偶合常数 (J = 6.5Hz)，提示呋喃环 7,8 位的相对构型为反式[10]，CD 图谱（图 2）在 256 nm (−1.85) 和 351 nm (−1.62) 处显示负的 Cotton 效应，表明 7,8 位的绝对构型为 7*R*,8*S*[11]。综上所述，化合物 **1** 鉴定为如图 3 所示的结构，命名为兴安升麻苷 F（cimicifugaside F），为 1 个新的苯骈呋喃型木脂素苷。

表 1 化合物 1 的 ^{1}H-NMR 和 ^{13}C-NMR 数据 (^{1}H: 600 MHz; ^{13}C: 150 MHz, CD_3OD)

Table 1 ^{1}H-NMR and ^{13}C-NMR spectral data of compound 1 (^{1}H: 600 MHz; ^{13}C: 150 MHz, in CD_3OD)

碳位	1		碳位	1	
	δ_H	δ_C		δ_H	δ_C
1	—	134.0	5′	—	130.7
2	6.99 (d, J = 2.0 Hz)	110.7	6′	7.24 (s)	119.4
3	—	149.0	7′	7.62 (d, J = 15.8 Hz)	146.7
4	—	147.6	8′	6.34 (d, J = 15.8 Hz)	116.5
5	6.77 (d, J = 8.1 Hz)	116.1	9′	—	171.0
6	6.86 (dd, J = 8.1, 2.0 Hz)	119.8	1″	4.37 (d, J = 7.8 Hz)	104.4
7	5.66 (d, J = 6.5 Hz)	89.8	2″	3.25 (dd, J = 9.1, 7.8 Hz)	75.1
8	3.71 (q, J = 6.5 Hz)	52.5	3″	3.37 (t, J = 8.5 Hz)	78.2
9	3.83 (dd, J = 9.8, 5.8 Hz)	72.0	4″	3.32 (overlapped)	71.6
	4.22 (dd, J = 9.8, 5.8 Hz)		5″	3.31 (overlapped)	78.0
1′	—	129.8			
			6″	3.68 (dd, J = 12.0, 5.4 Hz)	62.8
2′	7.13 (s)	113.7		3.89 (dd, J = 9.8, 5.8 Hz)	
3′	—	145.8	3-OCH_3	3.82 (s)	56.4
4′	—	151.7	3′-OCH_3	3.89 (s)	56.8

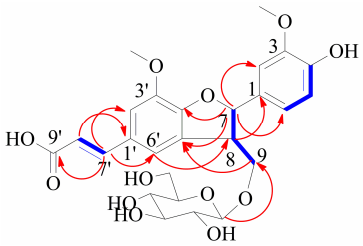

图 1 化合物 1 的关键 ^{1}H-^{1}H COSY 和 HMBC 相关

Fig. 1 Key ^{1}H-^{1}H COSY and HMBC correlations of compound 1

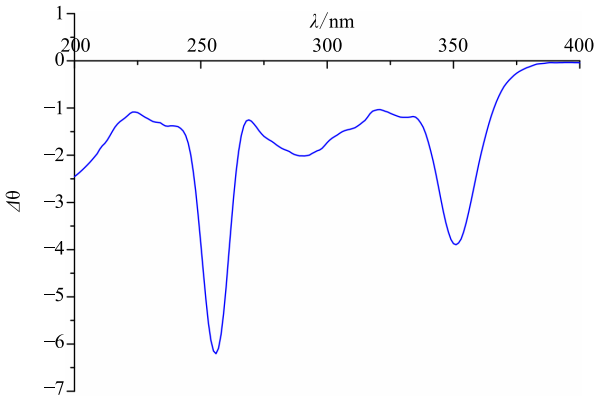

图 2 化合物 1 的 CD 图谱

Fig. 2 CD spectrum of compound 1

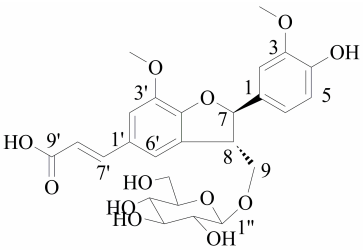

图 3 化合物 1 的结构

Fig. 3 Structure of compound 1

化合物 **2**：白色粉末，HR-ESI-MS *m*/*z* 557.161 8 [M＋Na]$^+$。^{1}H-NMR (600 MHz, CD_3OD) *δ*: 7.00 (1H, d, *J* = 2.0 Hz, H-2), 6.78 (1H, d, *J* = 8.1 Hz, H-5), 6.86 (1H, dd, *J* = 8.1, 2.0 Hz, H-6), 5.65 (1H, d, *J* = 6.8 Hz, H-7), 3.72 (1H, q, *J* = 6.6 Hz, H-8), 3.86 (1H, overlapped, H-9a), 4.18 (1H, dd, *J* = 9.7, 7.2 Hz, H-9b), 3.84 (3H, s, 3-OCH_3), 3.90 (3H, s, 3′-OCH_3), 7.13 (1H, d, *J* = 1.2 Hz, H-2′), 7.31 (1H, d, *J* = 1.2 Hz, H-6′), 7.63 (1H, d, *J* = 15.8 Hz, H-7′), 6.37 (1H, d, *J* = 15.8 Hz, H-8′), 4.37 (1H, d, *J* = 7.8 Hz, H-1″), 3.24 (1H, dd, *J* = 9.2, 7.8 Hz, H-2″), 3.37 (1H, t, *J* = 8.7 Hz, H-3″), 3.30 (1H, overlapped, H-4″), 3.28 (1H, overlapped, H-5″), 3.87 (1H, overlapped, H-6″a), 3.68 (1H, dd, *J* = 11.8, 5.3 Hz, H-6″b)；^{13}C-NMR (150 MHz, CD_3OD) *δ*: 133.9 (C-1), 110.8 (C-2), 149.1 (C-3), 147.7 (C-4), 116.1 (C-5), 119.9 (C-6), 90.0 (C-7), 52.4 (C-8), 72.1 (C-9), 56.5 (3-OCH_3), 56.8 (3′-OCH_3), 129.9 (C-1′), 113.8 (C-2′), 145.8 (C-3′), 151.7 (C-4′), 131.0 (C-5′), 119.3 (C-6′), 146.8 (C-7′), 116.6 (C-8′), 171.1 (C-9′), 104.3 (C-1″), 75.2 (C-2″), 78.2 (C-3″), 71.6 (C-4″), 78.1 (C-5″), 62.7 (C-6″)。CD 图谱在 256 nm（+1.97）和 351 nm（+1.75）处显示正的 cotton 效应，提示化合物 **2** 的 7,8 位的绝对构型为 7*S*,8*R*[11]。以上波谱数据与文献报道基本一致[12]，故鉴定化合物 **2** 为 (+)-(2*S*,3*R*)-2-(4-羟基-3-甲氧基苯基)-3-[(β-*D*-吡喃葡萄糖氧基) 甲基]-7-甲氧基苯并呋喃-5-丙烯酸。

化合物 **3**：棕黄色膏状体，HR-ESI-MS *m*/*z*: 191.033 4 [M＋Na]$^+$。^{1}H-NMR (600 MHz, DMSO-d_6) *δ*: 6.96 (1H, d, *J* = 8.3 Hz, H-3), 7.40 (1H, dd, *J* = 8.3, 2.0 Hz, H-4), 7.36 (1H, d, *J* = 2.0 Hz, H-6), 3.81 (3H, s, 2-OCH_3)；^{13}C-NMR (150 MHz, DMSO-d_6) *δ*: 124.2 (C-1), 151.2 (C-2), 111.2 (C-3), 121.4 (C-4), 146.0 (C-5), 116.1 (C-6), 167.7 (C = O), 55.6 (2-OCH_3)。以上波谱数据与文献报道基本一致[13]，故鉴定化合物 **3** 为 5-羟基-2-甲氧基苯甲酸。

化合物 **4**：浅黄色粉末，HR-ESI-MS *m*/*z*: 323.073 8 [M＋Na]$^+$。^{1}H-NMR (600 MHz, DMSO-d_6) *δ*: 7.87 (2H, d, *J* = 8.4 Hz, H-2, 6), 7.07 (2H, d, *J* = 8.4 Hz, H-3, 5), 4.97 (1H, d, *J* = 7.4 Hz, H-1′), 3.17～3.68 (5H, m, H-2′～6′)；^{13}C-NMR (150 MHz, DMSO-d_6) *δ*: 124.4 (C-1), 131.1 (C-2, 6), 115.7 (C-3, 5), 160.6 (C-4), 167.6 (C = O), 99.9 (C-1′), 73.2 (C-2′), 76.6 (C-3′), 69.6 (C-4′), 77.1 (C-5′), 60.6 (C-6′)。以上波谱数据与文献报道基本一致[14]，故鉴定化合物 **4** 为苯甲酸-4-*O*-β-*D*-葡萄糖苷。

化合物 **5**：白色针晶（甲醇）。HR-ESI-MS *m*/*z*: 195.065 8 [M＋H]$^+$。^{1}H-NMR (600 MHz, CD_3OD) *δ*: 7.07 (1H, d, *J* = 2.1 Hz, H-2), 6.94 (1H, d, *J* = 8.3 Hz, H-5), 7.04 (1H, dd, *J* = 8.3, 2.1 Hz, H-6), 7.55 (1H, d, *J* = 15.9 Hz, H-7), 6.27 (1H, d, *J* = 15.9 Hz, H-8), 3.88 (3H, s, 4-OCH_3)；^{13}C-NMR (150 MHz, CD_3OD) *δ*: 129.0 (C-1), 112.5 (C-2), 148.0 (C-3), 151.4 (C-4), 114.7 (C-5), 122.7 (C-6), 146.5 (C-7), 116.7 (C-8), 170.9 (C = O), 56.4 (4-OCH_3)。以上波谱数据与文献报道基本一致[15]，故鉴定化合物 **5** 为异阿魏酸。

化合物 **6**：白色针晶（甲醇）。HR-ESI-MS *m*/*z*: 195.065 8 $[M+H]^+$。^{1}H-NMR (600 MHz, CD_3OD) δ: 7.16 (1H, d, *J* = 2.0 Hz, H-2), 6.81 (1H, d, *J* = 8.2 Hz, H-5), 7.05 (1H, dd, *J* = 8.2, 2.0 Hz, H-6), 7.59 (1H, d, *J* = 15.9 Hz, H-7), 6.31 (1H, d, *J* = 15.9 Hz, H-8), 3.88 (3H, s, 3-OCH_3)；^{13}C-NMR (150 MHz, CD_3OD) δ: 127.8 (C-1), 111.6 (C-2), 149.3 (C-3), 150.4 (C-4), 116.0 (C-5), 123.9 (C-6), 146.8 (C-7), 116.4 (C-8), 171.2 (C = O), 56.4 (3-OCH_3)。以上波谱数据与文献报道基本一致[15]，故鉴定化合物 **6** 为阿魏酸。

化合物 **7**：白色粉末，HR-ESI-MS *m*/*z*: 379.100 1 $[M+Na]^+$。^{1}H-NMR (600 MHz, CD_3OD) δ: 7.24 (1H, d, *J* = 1.9 Hz, H-2), 7.18 (1H, d, *J* = 8.4 Hz, H-5), 7.16 (1H, d, *J* = 8.4, 1.9 Hz, H-6), 7.61 (1H, d, *J* = 16.0 Hz, H-7), 6.39 (1H, d, *J* = 16.0 Hz, H-8), 3.89 (3H, s, 3-OCH_3), 5.32 (1H, d, *J* = 7.9 Hz, H-1′), 3.66 (1H, dd, *J* = 7.9, 3.0 Hz, H-2′), 4.16 (1H, t, *J* = 3.0 Hz, H-3′), 3.61 (1H, dd, *J* = 9.7, 3.0 Hz, H-4′), 3.86 (1H, overlapped, H-5′), 3.86 (1H, overlapped, H-6′a), 3.69 (1H, dd, *J* = 12.6, 6.6 Hz, H-6′b)；^{13}C-NMR (150 MHz, CD_3OD) δ: 130.4 (C-1), 112.4 (C-2), 151.0 (C-3), 150.3 (C-4), 117.2 (C-5), 123.4 (C-6), 146.1 (C-7), 117.8 (C-8), 170.7 (C = O), 56.7 (3-OCH_3), 100.2 (C-1′), 72.0 (C-2′), 72.9 (C-3′), 68.6 (C-4′), 75.9 (C-5′), 62.8 (C-6′)。以上波谱数据与文献报道基本一致[16]，故鉴定化合物 **7** 为阿魏酸-4-*O*-β-*D*-阿洛糖苷。

化合物 **8**：棕黄色膏状体，HR-ESI-MS *m*/*z*: 379.101 3 $[M+Na]^+$。^{1}H-NMR (600 MHz, CD_3OD) δ: 7.23 (1H, d, *J* = 1.8 Hz, H-2), 7.17 (1H, d, *J* = 8.4 Hz, H-5), 7.15 (1H, d, *J* = 8.4, 1.8 Hz, H-6), 7.61 (1H, d, *J* = 15.9 Hz, H-7), 6.39 (1H, d, *J* = 15.9 Hz, H-8), 3.89 (3H, s, 3-OCH_3), 4.98 (1H, d, *J* = 7.5 Hz, H-1′), 3.53 (1H, dd, *J* = 9.2, 7.4 Hz, H-2′), 3.45 (1H, overlapped, H-3′), 3.61 (1H, overlapped, H-4′), 3.86 (1H, overlapped, H-5′), 3.88 (1H, overlapped, H-6′a), 3.71 (1H, dd, *J* = 12.0, 5.4 Hz, H-6′b)；^{13}C-NMR (150 MHz, CD_3OD) δ: 130.5 (C-1), 112.4 (C-2), 150.9 (C-3), 149.9 (C-4), 117.3 (C-5), 123.4 (C-6), 146.1 (C-7), 117.8 (C-8), 170.6 (C = O), 56.7 (3-OCH_3), 102.1 (C-1′), 74.8 (C-2′), 77.8 (C-3′), 71.2 (C-4′), 78.2 (C-5′), 62.4 (C-6′)。以上波谱数据与文献报道基本一致[17]，故鉴定化合物 **8** 为阿魏酸-4-*O*-β-*D*-葡萄糖苷。

化合物 **9**：白色粉末，HR-ESI-MS *m*/*z*: 409.110 9 $[M+Na]^+$。^{1}H-NMR (600 MHz, CD_3OD) δ: 6.94 (2H, s, H-2, 6), 7.58 (1H, d, *J* = 15.9 Hz, H-7), 6.45 (1H, d, *J* = 15.9 Hz, H-8), 3.89 (6H, s, 3, 5-OCH_3), 4.98 (1H, d, *J* = 7.6 Hz, H-1′), 3.49 (1H, m, H-2′), 3.42 (1H, overlapped, H-3′), 3.61 (1H, overlapped, H-4′), 3.22 (1H, ddd, *J* = 8.5, 5.4, 2.5 Hz, H-5′), 3.78 (1H, dd, *J* = 12.0, 2.4 Hz, H-6′a), 3.66 (1H, dd, *J* = 12.0, 5.2 Hz, H-6′b)；^{13}C-NMR (150 MHz, CD_3OD) δ: 132.5 (C-1), 107.1 (C-2, 6), 154.6 (C-3, 5), 137.9 (C-4), 145.5 (C-7), 120.0 (C-8), 171.1 (C = O), 57.1 (3, 5-OCH_3), 104.9 (C-1′), 75.7 (C-2′), 77.8 (C-3′), 71.3 (C-4′), 78.4 (C-5′), 62.5 (C-6′)。以上波谱数据与文献报道基本一致[18]，故鉴定化合物 **9** 为芥子酸-4-*O*-β-*D*-葡萄糖苷。

化合物 **10**：黄色粉末，HR-ESI-MS *m*/*z*: 777.217 2 $[M+Na]^+$。^{1}H-NMR (600 MHz, CD_3OD) δ: 6.90 (2H, s, H-2, 6), 7.60 (1H, d, *J* = 15.9 Hz, H-7), 6.47 (1H, d, *J* = 15.9 Hz, H-8), 6.77 (2H, s, H-2′, 6′), 7.50 (1H, d, *J* = 15.9 Hz, H-7′), 6.27 (1H, d, *J* = 15.9 Hz, H-8′), 3.83 (6H, s, 3, 5-OCH_3), 3.85 (6H, s, 3′, 5′-OCH_3), 5.42 (1H, d, *J* = 3.8 Hz, H-1″), 3.47 (1H, dd, *J* = 9.8, 3.8 Hz, H-2″), 3.75 (1H, m, H-3″), 3.26 (1H, m, H-4″), 4.19 (1H, overlapped, H-5″), 4.62 (1H, m, H-6″a), 4.20 (1H, overlapped, H-6″b), 3.64 (2H, d, *J* = 3.8 Hz, H-1‴), 4.13 (1H, d, *J* = 8.3 Hz, H-3‴), 4.20 (1H, overlapped, H-4‴), 4.02 (1H, td, *J* = 7.8, 3.8 Hz, H-5‴), 4.58 (1H, dd, *J* = 11.7, 3.8 Hz, H-6‴a), 4.47 (1H, *J* = 11.7, 7.8 Hz, H-6‴b)；^{13}C-NMR (150 MHz, CD_3OD) δ: 126.6 (C-1), 107.0 (C-2, 6), 149.3 (C-3, 5), 139.5 (C-4), 147.4 (C-7), 115.8 (C-8), 169.2 (9-C = O), 126.6 (C-1′), 106.8 (C-2′, 6′), 149.4 (C-3′, 5′), 139.5 (C-4′), 147.1 (C-7′), 115.6 (C-8′), 168.8 (9′-C = O), 56.8 (3, 5, 3′, 5′-OCH_3), 93.1 (C-1″), 73.3 (C-2″), 74.7 (C-3″), 72.3 (C-4″), 72.1 (C-5″), 65.7 (C-6″), 64.1 (C-1‴), 105.4 (C-2‴), 79.0 (C-3‴), 77.1 (C-4‴), 80.8 (C-5‴), 66.9 (C-6‴)。以上波谱数据与文献报道基本一致[19]，故鉴定化合物 **10** 为 6,6′-二-*O*-芥子酰基蔗糖。

化合物 **11**：棕黄色膏状体，HR-ESI-MS *m*/*z*: 279.048 2 $[M+Na]^+$。^{1}H-NMR (600 MHz, CD_3OD) δ: 4.52 (1H, s, H-2), 3.00 (1H, d, *J* = 13.8 Hz, H-4a), 3.14 (1H, d, *J* = 13.8 Hz, H-4b), 7.08 (2H, d, *J* = 8.0 Hz, H-2′, 6′), 6.66 (2H, d, *J* = 8.0 Hz, H-3′, 5′)；^{13}C-NMR (150 MHz, CD_3OD) δ: 174.7 (C-1), 76.4

(C-2), 81.4 (C-3), 41.9 (C-4), 175.9 (C-5), 128.0 (C-1′), 132.4 (C-2′, 6′), 115.7 (C-3′, 5′), 157.1 (C-4′)。以上波谱数据与文献报道基本一致[20]，故鉴定化合物 **11** 为番石榴酸。

化合物 **12**：棕黄色膏状体，HR-ESI-MS *m*/*z*: 295.042 4 $[M+Na]^+$。^{1}H-NMR (600 MHz, CD_3OD) δ: 4.48 (1H, s, H-2), 3.07 (1H, d, *J* = 13.8 Hz, H-4a), 2.94 (1H, d, *J* = 13.8 Hz, H-4b), 6.73 (1H, s, H-2′), 6.63 (1H, d, *J* = 8.0 Hz, H-5′), 6.58 (1H, d, *J* = 8.0 Hz, H-6′)；^{13}C-NMR (150 MHz, CD_3OD) δ: 174.9 (C-1), 76.6 (C-2), 81.4 (C-3), 42.1 (C-4), 176.2 (C-5), 128.7 (C-1′), 118.8 (C-2′), 145.6 (C-3′), 145.1 (C-4′), 115.9 (C-5′), 123.0 (C-6′)。以上波谱数据与文献报道基本一致[21]，故鉴定化合物 **12** 为蜂斗菜酸。

化合物 **13**：棕黄色膏状体，HR-ESI-MS *m*/*z*: 476.192 4 $[M+H]^+$。^{1}H-NMR (600 MHz, CD_3OD) δ: 7.18 (1H, d, *J* = 1.9 Hz, H-2), 7.17 (1H, d, *J* = 8.4 Hz, H-5), 7.12 (1H, d, *J* = 8.4, 1.9 Hz, H-6), 7.46 (1H, d, *J* = 15.7 Hz, H-7), 6.48 (1H, d, *J* = 15.7 Hz, H-8), 3.89 (3H, s, 3-OCH_3), 7.06 (2H, d, *J* = 8.4 Hz, H-2′, 6′), 6.72 (2H, d, *J* = 8.4 Hz, H-3′, 5′), 2.76 (2H, t, *J* = 7.4 Hz, H-7′), 3.47 (2H, t, *J* = 7.4 Hz, H-8′), 5.30 (1H, d, *J* = 7.9 Hz, H-1″), 3.65 (1H, dd, *J* = 7.9, 3.0 Hz, H-2″), 4.15 (1H, t, *J* = 3.0 Hz, H-3″), 3.61 (1H, dd, *J* = 9.9, 3.0 Hz, H-4″), 3.86 (1H, overlapped, H-5″), 3.86 (1H, overlapped, H-6″a), 3.68 (1H, dd, *J* = 12.2, 5.7 Hz, H-6″b)；^{13}C-NMR (150 MHz, CD_3OD) δ: 130.9 (C-1), 112.3 (C-2), 151.0 (C-3), 149.8 (C-4), 117.3 (C-5), 122.7 (C-6), 141.4 (C-7), 120.4 (C-8), 168.8 (C = O), 56.7 (3-OCH_3), 131.3 (C-1′), 130.7 (C-2′, 6′), 116.3 (C-3′, 5′), 156.9 (C-4′), 35.8 (C-7′), 42.6 (C-8′), 100.3 (C-1″), 72.0 (C-2″), 72.9 (C-3″), 68.6 (C-4″), 75.9 (C-5″), 62.8 (C-6″)。以上波谱数据与文献报道基本一致[16]，故鉴定化合物 **13** 为 *N*-反式对羟基苯乙基阿魏酰胺-4-*O*-β-*D*-阿洛糖苷。

化合物 **14**：棕黄色膏状体，HR-ESI-MS *m*/*z*: 506.203 3 $[M+H]^+$。^{1}H-NMR (600 MHz, CD_3OD) δ: 7.18 (1H, d, *J* = 1.9 Hz, H-2), 7.17 (1H, d, *J* = 8.5 Hz, H-5), 7.12 (1H, d, *J* = 8.5, 1.9 Hz, H-6), 7.46 (1H, d, *J* = 15.7 Hz, H-7), 6.48 (1H, d, *J* = 15.7 Hz, H-8), 3.89 (3H, s, 3-OCH_3), 3.83 (3H, s, 3′-OCH_3), 6.82 (1H, d, *J* = 1.9 Hz, H-2′), 6.72 (1H, d, *J* = 8.0 Hz, H-5′), 6.67 (1H, dd, *J* = 8.0, 1.9 Hz, H-6′), 2.77 (2H, t, *J* = 7.3 Hz, H-7′), 3.49 (2H, t, *J* = 7.3 Hz, H-8′), 5.30 (1H, d, *J* = 7.8 Hz, H-1″), 3.65 (1H, dd, *J* = 7.9, 3.0 Hz, H-2″), 4.15 (1H, t, *J* = 3.0 Hz, H-3″), 3.60 (1H, dd, *J* = 9.8, 3.0 Hz, H-4″), 3.86 (1H, overlapped, H-5″), 3.88 (1H, overlapped, H-6″a), 3.68 (1H, dd, *J* = 12.2, 5.7 Hz, H-6″b)；^{13}C-NMR (150 MHz, CD_3OD) δ: 130.9 (C-1), 112.3 (C-2), 151.0 (C-3), 149.8 (C-4), 117.4 (C-5), 122.3 (C-6), 141.4 (C-7), 120.4 (C-8), 168.8 (C = O), 56.7 (3-OCH_3), 56.3 (3′-OCH_3), 132.0 (C-1′), 113.4 (C-2′), 149.0 (C-3′), 146.1 (C-4′), 116.2 (5′), 122.3 (6′), 36.2 (C-7′), 42.5 (C-8′), 100.3 (C-1″), 72.0 (C-2″), 72.9 (C-3″), 68.6 (C-4″), 75.9 (C-5″), 62.8 (C-6″)。以上波谱数据与文献报道基本一致[4]，故鉴定化合物 **14** 为 *N*-反式-3′-甲氧基-4′-羟基苯乙基阿魏酰胺-4-*O*-β-*D*-阿洛糖苷。

化合物 **15**：棕黄色膏状体，HR-ESI-MS *m*/*z* 506.202 0 $[M+H]^+$。^{1}H-NMR (600 MHz, CD_3OD) δ: 7.18 (1H, d, *J* = 2.0 Hz, H-2), 7.17 (1H, d, *J* = 8.4 Hz, H-5), 7.12 (1H, d, *J* = 8.4, 2.0 Hz, H-6), 7.46 (1H, d, *J* = 15.7 Hz, H-7), 6.48 (1H, d, *J* = 15.7 Hz, H-8), 3.89 (3H, s, 3-OCH_3), 3.83 (3H, s, 3′-OCH_3), 6.82 (1H, d, *J* = 1.9 Hz, H-2′), 6.72 (1H, d, *J* = 8.0 Hz, H-5′), 6.67 (1H, dd, *J* = 8.0, 1.9 Hz, H-6′), 2.77 (2H, t, *J* = 7.4 Hz, H-7′), 3.49 (2H, t, *J* = 7.4 Hz, H-8′), 4.96 (1H, d, *J* = 7.5 Hz, H-1″), 3.51 (1H, dd, *J* = 9.6, 7.5 Hz, H-2″), 3.46 (1H, overlapped, H-3″), 3.41 (1H, m, H-4″), 3.46 (1H, overlapped, H-5″), 3.88 (1H, overlapped, H-6″a), 3.69 (1H, dd, *J* = 12.2, 5.4 Hz, H-6″b)；^{13}C-NMR (150 MHz, CD_3OD) δ: 131.1 (C-1), 112.3 (C-2), 151.0 (C-3), 149.5 (C-4), 117.6 (C-5), 122.7 (C-6), 141.4 (C-7), 120.5 (C-8), 168.8 (C = O), 56.7 (3-OCH_3), 56.3 (3′-OCH_3), 132.0 (C-1′), 113.4 (C-2′), 148.9 (C-3′), 146.1 (C-4′), 116.2 (5′), 122.3 (6′), 36.2 (C-7′), 42.5 (C-8′), 102.3 (C-1″), 74.8 (C-2″), 77.9 (C-3″), 71.3 (C-4″), 78.3 (C-5″), 62.5 (C-6″)。以上波谱数据与文献报道基本一致[22]，故鉴定化合物 **15** 为 *N*-反式-3′-甲氧基-4′-羟基苯乙基阿魏酰胺-4-*O*-β-*D*-葡萄糖苷。

化合物 **16**：棕黄色膏状体，HR-ESI-MS *m*/*z*: 339.105 8 $[M+Na]^+$。^{1}H-NMR (600 MHz, DMSO-d_6) δ: 6.95 (1H, s, H-2), 6.70 (2H, d, *J* = 1.0 Hz, H-4, 6), 2.59 (2H, t, *J* = 7.2 Hz, H-7), 3.53 (2H, t, *J* = 7.2 Hz, H-8), 4.64 (1H, d, *J* = 7.2 Hz, H-1′), 3.28 (1H, overlapped, H-2′), 3.28 (1H, overlapped, H-3′), 3.28

(1H, overlapped, H-4′), 3.17 (1H, overlapped, H-5′), 3.71 (1H, dd, *J* = 12.0, 1.9 Hz, H-6′a), 3.47 (1H, dd, *J* = 12.0, 5.7 Hz, H-6′b)；^{13}C-NMR (150 MHz, DMSO-d_6) *δ*: 130.4 (C-1), 117.6 (C-2), 145.1 (C-3), 115.6 (C-4), 145.1 (C-5), 123.3 (C-6), 38.6 (C-7), 62.5 (C-8), 102.5 (C-1′), 73.5 (C-2′), 77.3 (C-3′), 69.9 (C-4′), 76.0 (C-5′), 60.9 (C-6′)。以上波谱数据与文献报道基本一致[23]，故鉴定化合物 **16** 为 3,5-二羟基苯乙醇-3-*O*-β-*D*-葡萄糖苷。

化合物 **17**：白色片晶（甲醇）。HR-ESI-MS *m*/*z*: 441.152 6 [M＋Na]$^+$。^{1}H-NMR (600 MHz, CD_3OD) *δ*: 6.66 (4H, s, H-2, 2′, 6, 6′), 4.72 (2H, d, *J* = 4.1 Hz, H-7, 7′), 3.15 (2H, m, H-8, 8′), 4.27 (1H, m, H-9a, 9′a), 3.89 (2H, dd, *J* = 9.1, 3.5 Hz, H-9b, 9′b), 3.85 (s, 12H, 3, 3′, 5, 5′-OCH_3)；^{13}C-NMR (150 MHz, CD_3OD) *δ*: 133.1 (C-1, 1′), 104.5 (C-2, 2′, 6, 6′), 149.3 (C-3, 3′, 5, 5′), 136.2 (C-4, 4′), 87.6 (C-7, 7′), 55.5 (C-8, 8′), 72.8 (C-9, 9′), 56.8 (3, 3′, 5, 5′-OCH_3)。以上波谱数据与文献报道基本一致[24]，故鉴定化合物 **17** 为丁香脂素。

化合物 **18**：白色粉末，HR-ESI-MS *m*/*z*: 765.259 0 [M＋Na]$^+$。^{1}H-NMR (600 MHz, CD_3OD) δ_H: 6.72 (4H, s, H-2, 2′, 6, 6′), 4.78 (2H, d, *J* = 3.9 Hz, H-7, 7′), 3.14 (2H, m, H-8, 8′), 4.31 (1H, m, H-9a, 9′a), 3.95 (2H, dd, *J* = 9.1, 3.3 Hz, H-9b, 9′b), 3.86 (s, 12H, 3, 3′, 5, 5′-OCH_3), 5.15 (2H, d, *J* = 7.7 Hz, H-1″, 1‴), 3.61 (2H, dd, *J* = 7.7, 2.9 Hz, H-2″, 2‴), 4.14 (2H, t, *J* = 2.9 Hz, H-3″, 3‴), 3.63 (2H, overlapped, H-4″, 4‴), 3.65 (2H, overlapped, H-5″, 5‴), 3.77 (2H, dd, *J* = 13.2, 3.0 Hz, H-6″a, 6‴a), 3.67 (2H, dd, *J* = 13.2, 4.8 Hz, H-6″b, 6‴b)；^{13}C-NMR (150 MHz, CD_3OD) *δ*: 139.4 (C-1, 1′), 104.7 (C-2, 2′, 6, 6′), 154.4 (C-3, 3′, 5, 5′), 135.9 (C-4, 4′), 87.2 (C-7, 7′), 55.7 (C-8, 8′), 73.0 (C-9, 9′), 57.1 (3, 3′, 5, 5′-OCH_3), 103.9 (C-1″, 1‴), 73.1 (C-2″, 2‴), 72.3 (C-3″, 3‴), 68.6 (C-4″, 4‴), 76.3 (C-5″, 5‴), 63.0 (C-6″, 6‴)。以上波谱数据与文献报道基本一致[4]，故鉴定化合物 **18** 为丁香脂素-4,4′-*O*-β-*D*-双阿洛糖苷。

化合物 **19**：白色片晶（甲醇），$[\alpha]_D^{25}$ +92.00°，HR-ESI-MS *m*/*z*: 545.198 0 [M＋Na]$^+$。^{1}H-NMR (600 MHz, CD_3OD) *δ*: 2.81 (2H, t, *J* = 7.9 Hz, H-1), 2.08 (1H, dq, *J* = 10.4, 5.2 Hz, H-2), 3.19 (2H, m, H-2a), 1.85 (1H, t, *J* = 10.4 Hz, H-3), 3.71 (1H, dd, *J* = 10.8, 6.0 Hz, H_a-3a), 3.64 (1H, dd, *J* = 12.0, 6.0 Hz, H_b-3a), 4.06 (1H, t, *J* = 11.6 Hz, H-4), 6.17 (1H, s, H-5), 6.63 (1H, overlapped, H-8), 3.79 (3H, s, 7-OCH_3), 3.79 (3H, s, 3′-OCH_3), 6.78 (1H, d, *J* = 1.9 Hz, H-2′), 6.73 (1H, d, *J* = 8.0 Hz, H-5′), 6.63 (1H, overlapped, H-6′), 4.11 (1H, d, *J* = 7.8 Hz, H-1″), 3.25～3.82 (5H, m, H-2′～6′)；^{13}C-NMR (150 MHz, CD_3OD) *δ*: 33.9 (C-1), 39.5 (C-2), 65.2 (C-2a), 45.9 (C-3), 69.5 (C-3a), 47.9 (C-4), 117.4 (C-5), 145.8 (C-6), 147.1 (C-7), 112.4 (C-8), 129.1 (C-9), 134.4 (C-10), 56.5 (7-OCH_3), 56.4 (3′-OCH_3), 138.7 (C-1′), 114.3 (C-2′), 148.9 (C-3′), 145.1 (C-4′), 116.1 (C-5′), 123.1 (C-6′), 105.2 (C-1″), 75.2 (C-2″), 78.1 (C-3″), 71.7 (C-4″), 77.9 (C-5″), 62.8 (C-6″)。以上波谱数据与文献报道基本一致[25]，故将该化合物鉴定为 (+)-异落叶松树脂素-3a-*O*-β-*D*-葡萄糖苷。

化合物 **20**：棕黄色膏状体，$[\alpha]_D^{25}$ −50.30°，HR-ESI-MS *m*/*z*: 575.213 0 [M＋Na]$^+$。^{1}H-NMR (600 MHz, DMSO-d_6) *δ*: 2.74 (1H, d, *J* = 9.0 Hz, H-1a), 2.65 (1H, dd, *J* = 16.0, 3.6 Hz, H-1b), 1.84 (1H, qt, *J* = 8.7, 6.1, 4.7 Hz, H-2), 3.55 (2H, t, *J* = 4.6 Hz, H-2a), 1.85 (1H, qt, *J* = 8.7, 6.1, 4.7 Hz, H-3), 3.59 (1H, dd, *J* = 7.8, 3.0 Hz, H_a-3a), 3.47 (1H, dd, *J* = 10.2, 1.8 Hz, H_b-3a), 3.75 (1H, d, *J* = 6.4 Hz, H-4), 6.13 (1H, s, H-5), 6.61 (1H, s, H-8), 3.71 (3H, s, 7-OCH_3), 3.69 (6H, s, 3′, 5′-OCH_3), 6.34 (2H, s, H-2′, 6′), 3.96 (1H, d, *J* = 7.8 Hz, H-1″), 2.94 (1H, overlapped, H-2″), 3.09 (1H, overlapped, H-3″), 3.08 (1H, overlapped, H-4″), 2.93 (1H, overlapped, H-5″), 3.57 (1H, overlapped, H-6″a), 3.44 (1H, dd, *J* = 11.4, 5.6 Hz, H-6″b)；^{13}C-NMR (150 MHz, DMSO-d_6) *δ*: 32.2 (C-1), 38.9 (C-2), 63.3 (C-2a), 43.3 (C-3), 68.7 (C-3a), 46.8 (C-4), 116.2 (C-5), 144.1 (C-6), 145.6 (C-7), 111.7 (C-8), 127.2 (C-9), 132.0 (C-10), 55.5 (7-OCH_3), 56.1 (3′, 5′-OCH_3), 136.0 (C-1′), 106.7 (C-2′, 6′), 147.8 (C-3′, 5′), 133.8 (C-4′), 102.8 (C-1″), 73.5 (C-2″), 76.8 (C-3″), 69.8 (C-4″), 76.9 (C-5″), 60.8 (C-6″)。以上波谱数据与文献报道基本一致[26]，故鉴定化合物 **20** 为 (−)-5′-甲氧基异落叶松树脂素-3a-*O*-β-*D*-葡萄糖苷。

参考文献

[1] 中国药典 [S]. 一部. 2015.

[2] Thao N P, Kim J H, Luyen B T T, *et al*. In silico

investigation of cycloartane triterpene derivatives from *Cimicifuga dahurica* (Turcz.) Maxim. roots for the development of potent soluble epoxide hydrolase inhibitors [J]. *Int J Biol Macromol*, 2017, 98: 526-534.

[3] Iwanaga A, Kusano G, Warashina T, *et al*. Hyaluronidase inhibitors from "*Cimicifugae Rhizoma*" (a mixture of the rhizomes of *Cimicifuga dahurica* and *C. heracleifolia*) [J]. *J Nat Prod*, 2010, 73(4): 573-578.

[4] Huyen C, Luyen B, Khan G, *et al*. Chemical constituents from *Cimicifuga dahurica* and their anti-proliferative effects on MCF-7 breast cancer cells [J]. *Molecules*, 2018, 23(5): 1083-1098.

[5] Thao N P, Luyen B T T, Lee J S, *et al*. Soluble epoxide hydrolase inhibitors of indolinone alkaloids and phenolic derivatives from *Cimicifuga dahurica* (Turcz.) Maxim [J]. *Bioorg Med Chem Lett*, 2017, 27(8): 1874-1879.

[6] Nian Y, Wang H Y, Zhou L, *et al*. Cytotoxic cycloartane triterpenes of the traditional Chinese medicine "shengma" (*Cimicifuga dahurica*) [J]. *Planta Med*, 2013, 79(1): 60-69.

[7] Thao N P, Luyen B T T, Lee J S, *et al*. Inhibition potential of cycloartane-type glycosides from the roots of *Cimicifuga dahurica* against soluble epoxide hydrolase [J]. *J Nat Prod*, 2017, 80(6): 1867-1875.

[8] Qin R, Zhao Y, Zhao Y, *et al*. Polyphenolic compounds with antioxidant potential and neuro-protective effect from *Cimicifuga dahurica* (Turcz.) Maxim [J]. *Fitoterapia*, 2016, 115: 52-56.

[9] Lv C, Yang F, Qin R, *et al*. Bioactivity-guided isolation of chemical constituents against H_2O_2-induced neurotoxicity on PC12 from *Cimicifuga dahurica* (Turcz.) Maxim [J]. *Bioorg Med Chem Lett*, 2017, 27(15): 3305-3309.

[10] Kim K H, Moon E, Sun Y K. Lignans from the tuber-barks of *Colocasia antiquorum var. esculenta* and their antimelanogenic activity [J]. *J Agric Food Chem*, 2010, 58(8): 4779-4785.

[11] Xiong L, Zhu C, Li Y, *et al*. Lignans and neolignans from *Sinocalamus affinis* and their absolute configurations [J]. *Jf Nat Prod*, 2011, 74(5): 1188-1200.

[12] 李金晟, 王光寅, 郭夫江, 等. 水茄果实中的一个新木脂素苷 [J]. 中国中药杂志, 2014, 39(14): 2670-2673.

[13] M Iqbal C, Saima J, Sarfraz Ahmad N, *et al*. Antiinflammatory and lipoxygenase inhibitory compounds from *Vitex agnus-castus* [J]. *Phytother Res*, 2010, 24(1): 1336-1339.

[14] Leong G, Uzio R, Derbesy M. Synthesis, identification and determination of glucosides present in green vanilla beans (*Vanilla fragrans Andrews*) [J]. *Flav Fragr J*, 2010, 4(4): 163-167.

[15] Da M J, Hyun A J, Hye S K, *et al*. Peroxynitrite scavengers from *Phellinus linteus* [J]. *Nat Prod Sci*, 2008, 14(1): 1-11.

[16] Yim S H, Kim H J, Jeong N R, *et al*. Structure-guided identification of novel phenolic and phenolic amide allosides from the rhizomes of *Cimicifuga heracleifolia* [J]. *Bull Korean Chem Soc*, 2012, 33(4): 1253-1258.

[17] Struijs K, Vincken J P, Verhoef R, *et al*. The flavonoid herbacetin diglucoside as a constituent of the lignan macromolecule from *flaxseed hulls* [J]. *Phytochemistry*, 2007, 68(8): 1227-1235.

[18] Karina W, Jürgen S, Victor W, *et al*. Profiling of phenylpropanoids in transgenic low-sinapine oilseed rape (*Brassica napus*) [J]. *Phytochemistry*, 2010, 71(10): 1076-1084.

[19] Chen H, Zhou Y Z, Qiao L, *et al*. Two new compounds from *Cynanchum amplexicaule* [J]. *J Asian Nat Prod Res*, 2008, 10(3): 248-251.

[20] Takahira M, Kusano A, Shibano M, *et al*. Piscidic acid and fukiic acid esters from *Cimicifuga simplex* [J]. *Phytochemistry*, 1998, 49(7): 2115-2119.

[21] Takahira M, Kusano A, Shibano M, *et al*. Three new fukiic acid esters, cimicifugic acids A, B and C, from *Cimicifuga Simplex* WORMSK [J]. *Chem Pharm Bull*, 1998, 46(2): 362-365.

[22] Yang L, Jiang H, Wang Q H, *et al*. A new feruloyl tyramine glycoside from the roots of *Achyranthes bidentata* [J]. *Chin J Nat Med*, 2012, 10(1): 16-19.

[23] 晏 晨, 汪 冶, 郝小江. 秃叶黄皮树果实中的水溶性化学成分研究 [J]. 中国中药杂志, 2009, 34(22): 2895-2897.

[24] Park H B, Lee K H, Kim K H, *et al*. Lignans from the Roots of *Berberis amurensis* [J]. *Nat Prod Sci*, 2009, 15(1): 17-21.

[25] Chu H B, Zeng G Z, Zhu M J, *et al*. Chemical constituents of *Pedicularis densispica* Franch [J]. *Zeitschrift Naturforschung B*, 2011, 66(6): 641-646.

[26] Wen Q, Lin X, Liu Y, *et al*. Phenolic and lignan glycosides from the butanol extract of *Averrhoa carambola* L. root [J]. *Molecules*, 2012, 17(10): 12330-12340.