

连翘的化学成分研究

聂承冬^{1,2}, 沙冬梅^{1,3,4}, 何晓勇^{1,3,4}, 何斌^{1,3,4}, 田玉寒^{1,3,4}, 刘圆^{1,3,4}, 李莹^{3,4}, 张绍山^{1,3,4}, 冯景秋^{1,3,4}, 李娟^{1,3,4}, 阎新佳^{1,3,4*}, 温静^{2,5}

1. 西南民族大学 青藏高原研究院, 四川 成都 610041
2. 哈尔滨商业大学药学院, 黑龙江 哈尔滨 150076
3. 四川省羌彝药用资源保护与利用技术工程实验室, 四川 成都 610225
4. 青藏高原民族药用资源保护与利用国家民委重点实验室, 四川 成都 610225
5. 四川中医药高等专科学校, 四川 绵阳 621000

摘要: 目的 研究连翘 *Forsythia suspensa* 的化学成分及其体外抗肿瘤活性。方法 采用多种色谱技术进行分离纯化, 通过理化性质和波谱学手段 (NMR 和 MS) 鉴定化合物结构, 测试各化合物对 HepG-2 和 MCF-7 细胞的细胞毒性。结果 从连翘 75%乙醇提取物中共分离鉴定出 26 个化合物, 分别为 2-(4-羟基苯基)乙基-6-O-[4-(4-羟基苯基)乙酰基]-β-D-吡喃葡萄糖苷 (**1**)、木通苯乙醇苷 **2**、2-(4-羟基苯基)乙基-6-O-(E)-咖啡酰-β-D-吡喃葡萄糖苷 (**3**)、6'-O-香豆酰-1'-O-[2-(3,4-二羟基苯基)乙基]-β-D-吡喃葡萄糖苷 (**4**)、(+)-松脂素 (**5**)、8-羟基松脂素 (**6**)、松脂素-4-O-β-D-吡喃葡萄糖苷 (**7**)、(+)-表松脂素 (**8**)、(+)-1-羟基-2-表松脂素 (**9**)、连翘脂素 (**10**)、(+)-表松脂素-4'-O-β-D-吡喃葡萄糖苷 (**11**)、(+)-落叶松脂素 (**12**)、(-)-落叶松脂素 (**13**)、rel-(7R,8'R,8S)-forsythialan C (**14**)、rel-(7R,8'R,8R)-forsythialan C (**15**)、(7'S,8R,8'R)-异落叶松脂素 (**16**)、罗汉松脂素 (**17**)、罗汉松脂素-4'-O-β-D-吡喃葡萄糖苷 (**18**)、(-)-甘密树皮素 B-β-D-吡喃葡萄糖苷 (**19**)、(7R,7'R,8S,8'R)-4,4'-二羟基-3,3'-二甲氧基-7,7'-环氧木脂素-4-O-β-D-吡喃葡萄糖苷 (**20**)、(7R,7'R,8S,8'R)-4,4'-二羟基-3,3'-二甲氧基-7,7'-环氧木脂素-4'-O-β-D-吡喃葡萄糖苷 (**21**)、10-O-β-D-桃金娘烯醇苷 (**22**)、neryl-β-D-glucopyranoside (**23**)、α-松油醇-8-O-β-D-吡喃葡萄糖苷 (**24**)、连翘环己醇酮 (**25**) 和阿魏酸甲酯 (**26**)。结论 化合物 **1**、**3**、**4** 和 **19~24**、**26** 为首次从连翘属植物中分离得到。在 40 μmol/L 浓度下化合物 **5~18** 对 HepG-2 和 MCF-7 细胞系具有一定的细胞毒性活性。

关键词: 连翘; 苯乙醇苷; 单萜苷; 木脂素; 抗肿瘤活性; 2-(4-羟基苯基)乙基-6-O-(E)-咖啡酰-β-D-吡喃葡萄糖苷; (+)-松脂素; 罗汉松脂素-4'-O-β-D-吡喃葡萄糖苷; α-松油醇-8-O-β-D-吡喃葡萄糖苷

中图分类号: R284.1 **文献标志码:** A **文章编号:** 0253-2670(2023)17-5487-11

DOI: 10.7501/j.issn.0253-2670.2023.17.003

Study on chemical constituents from *Forsythia suspensa*

NIE Cheng-dong^{1,2}, SHA Dong-mei^{1,3,4}, HE Xiao-yong^{1,3,4}, HE Bin^{1,3,4}, TIAN Yu-han^{1,3,4}, LIU Yuan^{1,3,4}, LI Ying^{3,4}, ZHANG Shao-shan^{1,3,4}, FENG Jing-qiu^{1,3,4}, LI Juan^{1,3,4}, YAN Xin-jia^{1,3,4}, WEN Jing^{2,5}

1. Institute of Qinghai-Tibetan Plateau, Southwest Minzu University, Chengdu 610041, China
2. College of Pharmacy, Harbin University of Commerce, Harbin 150076, China
3. Sichuan Provincial Qiang-Yi Medicinal Resources Protection and Utilization Technology Engineering Laboratory, Chengdu 610225, China
4. Key Laboratory of Protection and Utilization of Ethnic Medicinal Resources in Qinghai-Tibet Plateau, State Ethnic Affairs Commission, Chengdu 610225, China
5. School of Pharmacy, Sichuan College of Traditional Chinese Medicine, Mianyang 621000, China

Abstract: Objective To study the chemical constituents from Lianqiao [*Forsythia suspensa* (Thunb.) Vahl]. **Methods** The

收稿日期: 2023-01-19

基金项目: 国家自然科学基金青年基金项目 (81803696); 西南民族大学中央高校基本科研业务费专项资金项目资助 (ZYN2023068)

作者简介: 聂承冬, 男, 硕士研究生, 研究方向为中药药效物质基础研究。Tel: (028)89165778 E-mail: 13591776911@163.com

*通信作者: 阎新佳, 男, 博士, 教授, 研究方向为中药药效物质基础研究。Tel: (028)89165778 E-mail: yanxinjia@yeah.net

温静, 女, 博士, 工程师, 研究方向为中药药效物质基础研究。Tel: (028)89165778 E-mail: dachitu@yeah.net

compounds were separated and purified by various chromatographic techniques, and their structures were identified by physical and chemical properties and spectroscopic methods (NMR and MS). The cytotoxicity of each compound on HepG-2 and MCF-7 cells was tested. **Results** A total of 26 compounds were isolated and identified as 2-(4-hydroxyphenyl)ethyl-6-O-[(4-hydroxyphenyl)acetyl]- β -D-glucopyranoside (**1**), calceolarioside B (**2**), 2-(4-hydroxyphenyl)ethyl-6-O-(E)-caffeyl- β -D-glucopyranoside (**3**), 6'-O-coumaroyl-1'-O-[2-(3,4-dihydroxyphenyl)ethyl]- β -D-glucopyranoside (**4**), (+)-pinoresinol (**5**), 8-hydroxypinoresinol (**6**), pinoresinol-4-O- β -D-glucopyranoside (**7**), (+)-epipinoresinol (**8**), (+)-1-hydroxy-2-epipinoresinol (**9**), phillygenin (**10**), (+)-epipinoresinol-4'-O- β -D-glucopyranoside (**11**), (+)-lariciresinol (**12**), (-)-lariciresinol (**13**), rel-(7R,8'R,8S)-forsythian C (**14**), rel-(7R,8'R,8R)-forsythian C (**15**), (7'S,8R,8'R)-isolariciresinol (**16**), matairesinol (**17**), martairesinol-4'-O- β -D-glucopyranoside (**18**), (-)-nectandrin B- β -D-glucopyranoside (**19**), (7R,7'R,8S,8'R)-4,4'-dihydroxy-3,3'-dimethoxy-7,7'-epoxylignan-4-O- β -D-glucopyranoside (**20**), (7R,7'R,8S,8'R)-4,4'-dihydroxy-3,3'-dimethoxy-7,7'-epoxylignan-4'-O- β -D-glucopyranoside (**21**), myrtenyl-O- β -D-glucopyranoside (**22**), neryl- β -D-glucopyranoside (**23**), α -terpineol-8-O- β -D-glucopyranoside (**24**), rengyolone (**25**) and methyl ferulate (**26**). **Conclusion** Compounds **1**, **3**, **4**, **19**—**24** and **26** are separated from the genus of *Forsythia* for the first time. All compounds are evaluated for cytotoxic activities against MCF-7 and HepG-2 cell lines by MTT assay, and the results showed that compounds **5**–**18** have potential inhibitory activity on MCF-7 and HepG-2 cell lines at 40 μ mol/L.

Key words: *Forsythia suspensa* (Thunb.) Vahl.; phenylethanol glycoside; monoterpane glycoside; lignan; antitumor activity; 2-(4-hydroxyphenyl)ethyl-6-O-(E)-caffeyl- β -D-glucopyranoside; (+)-pinoresinol; martairesinol-4'-O- β -D-glucopyranoside; α -terpineol-8-O- β -D-glucopyranoside

连翘 *Forsythia suspensa* (Thunb.) Vahl. 为木犀科 (Oleaceae) 连翘属 *Forsythia* Vahl. 植物，气微香，味苦，微寒。归小肠、心、肺经。古人称其为“疮家圣药”，主要用于清热解毒，消肿散结，主治痈疽瘰疬，乳痈丹毒等症^[1-2]。目前国内学者从连翘中发现多种化学成分（苯乙醇苷类、木脂素类、萜类黄酮类成分和其他类成分等）和多种药理活性（抗肿瘤、抗炎、抗病毒和抗氧化等）^[3]。研究表明，连翘属植物具有较好的抗肿瘤活性，但研究对象主要局限于其提取物^[4-8]，无法全面反映连翘属植物中各类化学成分的活性特点，导致活性成分不够明确，药效物质难以阐明。为进一步阐明中药连翘抗肿瘤的药效物质，深入挖掘连翘中抗肿瘤活性成分，本实验对连翘进行了系统的化学成分研究，利用液液萃取方法和多种色谱手段（硅胶柱色谱、开放 ODS 柱色谱和高效液相色谱等）对连翘 75% 乙醇提取物进行分离，基于理化性质和波谱学手段进行化学结构的鉴定。从连翘 75% 乙醇提取物中分离鉴定出 26 个化合物，分别为 2-(4-羟基苯基)乙基-6-O-[(4-羟基苯基)乙酰基]- β -D-吡喃葡萄糖苷 (2-(4-hydroxyphenyl)ethyl-6-O-[(4-hydroxyphenyl) acetyl]- β -D-glucopyranoside, **1**)、木通苯乙醇苷 B (calceolarioside B, **2**)、2-(4-羟基苯基)乙基-6-O-(E)-咖啡酰- β -D-吡喃葡萄糖苷 [2-(4-hydroxyphenyl)ethyl-6-O-(E)-caffeyl- β -D-glucopyranoside, **3**]、6'-O-香豆酰-1'-O-[2-(3,4-二羟基苯基)乙基]- β -D-吡喃葡

萄糖苷 (6'-O-coumaroyl-1'-O-[2-(3,4-dihydroxyphenyl)ethyl]- β -D-glucopyranoside, **4**)、(+)-松脂素 [(+)-pinoresinol, **5**]、8-羟基松脂素 (8-hydroxypinoresinol, **6**)、松脂素-4-O- β -D-吡喃葡萄糖苷 (pinoresinol-4-O- β -D-glucopyranoside, **7**)、(+)-表松脂素 [(+)-epipinoresinol, **8**]、(+)-1-羟基-2-表松脂素 [(+)-1-hydroxy-2-epipinoresinol, **9**]、连翘脂素 (phillygenin, **10**)、(+)-表松脂素-4'-O- β -D-吡喃葡萄糖苷 [(+)-epipinoresinol-4'-O- β -D-glucopyranoside, **11**]、(+)-落叶松脂素 [(+)-lariciresinol, **12**]、(-)-落叶松脂素 [(-)-lariciresinol, **13**]、rel-(7R,8'R,8S)-forsythian C (**14**)、rel-(7R,8'R,8R)-forsythian C (**15**)、(7'S,8R,8'R)-异落叶松脂素 [(7'S,8R,8'R)-isolariciresinol, **16**]、罗汉松脂素 (matairesinol, **17**)、罗汉松脂素-4'-O- β -D-吡喃葡萄糖苷 (martairesinol-4'-O- β -D-glucopyranoside, **18**)、(-)-甘密树皮素 B- β -D-吡喃葡萄糖苷 [(-)-nectandrin B- β -D-glucopyranoside, **19**]、(7R,7'R,8S,8'R)-4,4'-二羟基-3,3'-二甲氧基-7,7'-环氧木脂素-4-O- β -D-吡喃葡萄糖苷 [(7R,7'R,8S,8'R)-4,4'-dihydroxy-3,3'-di-methoxy-7,7'-epoxylignan-4-O- β -D-glucopyranoside, **20**]、(7R,7'R,8S,8'R)-4,4'-二羟基-3,3'-二甲氧基-7,7'-环氧木脂素-4'-O- β -D-吡喃葡萄糖苷 [(7R,7'R,8S,8'R)-4,4'-dihydroxy-3,3'-dimethoxy-7,7'-epoxylignan-4'-O- β -D-glucopyranoside, **21**]、10-O- β -D-桃金娘烯醇苷 (myrtenyl-O- β -D-

glucopyranoside, **22**)、neryl- β -D-glucopyranoside (**23**)、 α -松油醇-8-O- β -D-吡喃葡萄糖苷(α -terpineol-8-O- β -D-glucopyranoside, **24**)、连翘环己醇酮(rengyolone, **25**)和阿魏酸甲酯(methyl ferulate, **26**)。其中化合物**1**、**3**、**4**和**19~24**、**26**为首次从连翘属植物中分离得到。对分离得到的化合物进行了体外抗肿瘤活性测试,结果显示在 40 $\mu\text{mol/L}$ 浓度下化合物**5~18**对 HepG-2 和 MCF-7 细胞系具有一定的细胞毒性活性。

1 仪器与材料

Waters 2487 紫外检测器和 Waters 515 高效液相色谱仪(美国 Waters 公司), UPLC-Waters SYNG2SIHD TOF 超高效液相-高分辨飞行时间质谱(美国 Waters 公司), Bruker avance III600 核磁共振波谱仪(德国 Bruker 公司)和 P850 型旋光仪(中国济南海能仪器股份有限公司)。

柱色谱硅胶(100~200、200~300 目)和薄层硅胶 GF₂₅₄(青岛海洋化工有限公司),聚酰胺(60~90 目, 江苏长丰化工有限公司),MCI GEL CHP20P 填料(日本三菱化学),开放柱 ODS 填料(日本三菱公司)和 YMC-Pack ODS-A 反相色谱柱(日本三菱公司)。

连翘药材采购于哈尔滨三棵树药材市场,经沈阳药科大学中药学院吕重宁副教授鉴定为木犀科连翘属植物连翘 *F. suspensa* (Thunb.) Vahl 的干燥果实。样品(FS-201909)保存于西南民族大学敬文园 B 栋 221 实验室。

2 提取与分离

75%乙醇水溶液超声提取连翘果实(11.8 kg),减压浓缩后,用水复溶,依次用氯仿、醋酸乙酯和正丁醇试剂按照 1:1 的比例进行萃取,得到氯仿层(650.9 g)、醋酸乙酯层(213.2 g)和正丁醇层(700.3 g)。对醋酸乙酯萃取层采用 HP20 色谱柱进行分离,流动相为体积分数 10%、30%、50%、70%、90% 甲醇水以及纯甲醇梯度洗脱,得到 7 个流分(E-1~E-7)。E-2 首先经硅胶柱色谱进行初步分离,二氯甲烷-甲醇(40:1、20:1、10:1、8:1、4:1、0:1)梯度洗脱,得到 7 个流分(E-2-1~E-2-7)。E-2-2 经凝胶柱色谱分离,纯甲醇等度洗脱,得到 8 个流分(E-2-2-1~E-2-2-8),对 E-2-2-7 采用 pHPLC 进行等度洗脱,流动相为 55% 甲醇水,得到化合物**22**(E-2-2-7-2-1, $t_{\text{R}}=60 \text{ min}$, 10.5 mg)、**23**($t_{\text{R}}=62 \text{ min}$, 7.2 mg) 和 **24**($t_{\text{R}}=62 \text{ min}$, 5.9 mg); E-2-3 经凝胶

柱色谱分离,流动相依次为纯甲醇,洗脱 7 个保留体积,合并浓缩后得到 5 个流分(E-2-3-1~E-2-3-5),对 E-2-3-4 采用 pHPLC 进行等度洗脱,流动相为 40% 甲醇水,得到化合物**1**($t_{\text{R}}=30 \text{ min}$, 15.8 mg)。E-2-4 经聚酰胺柱色谱分离,流动相二氯甲烷-甲醇(30:1、25:1、15:1、10:1、5:1、0:1)梯度洗脱,得到 10 个流分(E-2-4-1~E-2-4-10)。E-2-4-4 经硅胶柱色谱分离,二氯甲烷-甲醇-水(15:1:0.05、8:2:0.2、7:3:0.5)进行洗脱,得到 3 个流分(E-2-4-4-1~E-2-4-4-3)。对 E-2-4-4-2 采用 pHPLC 进行等度洗脱,流动相为 38% 甲醇水,得到化合物**7**($t_{\text{R}}=40 \text{ min}$, 12.5 mg)、**11**($t_{\text{R}}=45 \text{ min}$, 25.1 mg)、**18**($t_{\text{R}}=50 \text{ min}$, 6.1 mg)。E-2-4-9, 经硅胶柱色谱分离,流动相为二氯甲烷:甲醇:水=15:1:0.05、8:2:0.2 和 7:3:0.5 进行洗脱,得到 4 个流分(E-2-4-9-1~E-2-4-9-4),对 E-2-4-9-3 采用 pHPLC 进行等度洗脱,流动相为 36% 甲醇水,得到化合物**3**($t_{\text{R}}=51 \text{ min}$, 15.1 mg)、**4**($t_{\text{R}}=52 \text{ min}$, 10.2 mg); E-2-5 经聚酰胺柱色谱分离,流动相为二氯甲烷-甲醇(30:1、25:1、15:1、10:1、5:1、0:1)梯度洗脱,得到 4 个流分(E-2-5-1~E-2-5-4)。E-2-5-3 经硅胶柱色谱分离,流动相二氯甲烷-甲醇-水(15:1:0.05、8:2:0.2、7:3:0.5)洗脱,得到 6 个流分(E-2-5-3-1~E-2-5-3-6)。对 E-2-5-3-4 采用 pHPLC 进行等度洗脱,流动相为 29% 甲醇水,得到化合物**2**($t_{\text{R}}=37 \text{ min}$, 13.4 mg)。E-7 首先经硅胶柱色谱进行初步的分离,开放柱流动相依次为二氯甲烷-甲醇(40:1、20:1、10:1、8:1、4:1、0:1)梯度洗脱,得到 5 个流分(E-7-1~E-7-5)。E-7-4 经聚酰胺柱色谱分离,流动相二氯甲烷-甲醇(30:1、25:1、15:1、10:1、5:1、0:1)梯度洗脱,得到 6 个流分(E-7-4-1~E-7-4-6)。E-7-4-5-6 通过 ODS 开放柱色谱,以甲醇-水(40%~100%)为流动相梯度洗脱,得到 6 个流分(E-7-4-5-6-1~E-7-4-5-6-5)。E-7-4-5-6-4 在经 pHPLC 进行等度洗脱,流动相为 32% 甲醇水,得到化合物**19**($t_{\text{R}}=19 \text{ min}$, 7.2 mg)、**20**($t_{\text{R}}=23 \text{ min}$, 15 mg)、**21**($t_{\text{R}}=26 \text{ min}$, 20 mg)。

对氯仿萃取层采用 HP20 色谱柱进行分离,流动相依次为体积分数为 30%~90% 甲醇水以及纯甲醇,进行梯度洗脱,得到 7 个流分(D-1~D-7)。D-3 经硅胶柱色谱,流动相二氯甲烷-醋酸乙酯(40:1、30:1、20:1、15:1、10:1、2:1)梯

度洗脱, 得 9 个流分 (D-3-1~D-3-9)。D-3-3 通过 Sephadex LH-20 柱色谱分离, 流动相为纯甲醇, 得到 5 个流分 (D-3-3-1~D-3-3-5), D-3-3-3 通过 pHPLC 等度洗脱, 流动相为 45% 甲醇水, 得到化合物 **5** ($t_R=17$ min, 15.4 mg)、**17** ($t_R=19$ min, 10.2 mg)、**8** ($t_R=22$ min, 9.1 mg)、**12** ($t_R=24$ min, 4.4 mg) 和 **10** ($t_R=36$ min, 11.6 mg)。D-3-5 通过 pHPLC 等度洗脱, 流动相为 30% 甲醇水, 得到化合物 **9** ($t_R=19$ min, 9 mg)、**6** ($t_R=26$ min, 16.9 mg) 和 **13** ($t_R=31$ min, 10 mg)。D-3-7 通过 ODS 开放柱色谱, 以甲醇-水 (40%~100%) 为流动相梯度洗脱, 得到 6 个流分 (D-3-7-1~D-3-7-6), D-3-7-2 经 pHPLC 进行等度洗脱, 流动相为 35% 甲醇水, 得到化合物 **14** ($t_R=17$ min, 6.2 mg)、**15** ($t_R=32$ min, 22.5 mg) 和 **16** ($t_R=38$ min, 5.6 mg)。D-6 经硅胶柱色谱进行初步的分离, 流动相二氯甲烷-醋酸乙酯 (40:1、30:1、20:1、15:1、10:1、2:1) 梯度洗脱, 得到 7 个流分 (D-6-1~D-6-7)。D-6-2 通过 ODS 开放柱色谱, 以甲醇-水 (40%~100%) 为流动相梯度洗脱, 得到 5 个流分 (D-6-2-1~D-6-2-5), D-6-2-3 在经 pHPLC 进行等度洗脱, 流动相为 35% 甲醇水, 得到化合物 **26** ($t_R=38$ min, 5.9 mg)。D-6-4 经聚酰胺柱色谱分离, 流动相二氯甲烷-甲醇 (40:1、25:1、15:1、10:1、4:1) 梯度洗脱, 得到 6 个流分 (D-6-4-1~D-6-4-6), D-6-4-4 通过 ODS 开放柱色谱, 以甲醇-水 (40%~100%) 为流动相梯度洗脱, 得到 6 个流分 (D-6-4-4-1~D-6-4-4-6)。D-6-6 经聚酰胺柱色谱, 以二氯甲烷-甲醇 (40:1、30:1、20:1、15:1、10:1、4:1) 为流动相, 梯度洗脱得到 5 个流分 (D-6-6-1~D-6-6-5), D-6-6-2 通过 ODS 开放柱色谱以甲醇-水 (40%~100%) 为流动相梯度洗脱, 得到 6 个流分 (D-6-6-2-1~D-6-6-2-6), D-6-6-2-4 在经 pHPLC 进行等度洗脱, 流动相为 37% 甲醇水, 得到化合物 **25** ($t_R=35$ min, 4.1 mg)。

3 结构鉴定

化合物 1: 白色无定形粉末 (氯仿-甲醇)。ESI-MS m/z 457.146 8 [$M+Na$]⁺ (Calcd. 457.146 8, $C_{22}H_{26}O_9Na$), 分子式为 $C_{22}H_{26}O_9$ 。¹H-NMR (600 MHz, DMSO-*d*₆) δ : 9.31 (1H, s, OH), 9.18 (1H, s, OH), 7.02 (2H, dd, $J=9.0, 2.0$ Hz, H-2), 6.67 (2H, dd, $J=9.0, 2.0$ Hz, H-3), 2.73 (2H, t, $J=6.7$ Hz, H-7), 3.78 (1H, td, $J=9.8, 8.1, 6.7$ Hz, H-8a), 3.58~3.56

(1H, m, H-8b), 4.19 (1H, d, $J=7.8$ Hz, H-1'), 2.97 (1H, t, $J=7.8$ Hz, H-2'), 3.18~3.13 (1H, m, H-3'), 3.06 (1H, t, $J=9.4$ Hz, H-4'), 3.33 (1H, dd, $J=11.8, 6.9, 2.0$ Hz, H-6'a), 4.05 (1H, dd, $J=11.8, 6.9$ Hz, H-6'b), 7.04 (2H, dd, $J=9.0, 2.0$ Hz, H-2''), 6.65 (2H, dd, $J=9.0, 2.0$ Hz, H-3''), 3.52 (2H, d, $J=2.5$ Hz, H-7''); ¹³C-NMR (150 MHz, DMSO-*d*₆) δ : 129.1 (C-1), 130.2 (C-2), 115.6 (C-3), 156.1 (C-4), 115.6 (C-5), 130.2 (C-6), 35.3 (C-7), 70.5 (C-8), 103.3 (C-1'), 74.1 (C-2'), 76.9 (C-3'), 70.6 (C-4'), 73.8 (C-5'), 64.4 (C-6'), 124.8 (C-1''), 130.7 (C-2''), 115.5 (C-3''), 156.7 (C-4''), 115.5 (C-5''), 130.7 (C-6''), 40.0 (C-7''), 172.0 (C-8'')。

以上数据与文献对照^[9], 鉴定化合物 **1** 为 2-(4-hydroxyphenyl)ethyl-6-*O*-[(4-hydroxyphenyl)acetyl]- β -D-glucopyranoside。

化合物 2: 棕色无定形粉末 (氯仿-甲醇)。ESI-MS m/z 501.136 4 [$M+Na$]⁺ (Calcd. 501.137 3, $C_{22}H_{26}O_{11}Na$), 分子式为 $C_{22}H_{26}O_{11}$ 。¹H-NMR (600 MHz, CD₃OD) δ : 6.67 (1H, d, $J=2.0$ Hz, H-2), 6.63 (1H, d, $J=8.0$ Hz, H-5), 6.53 (1H, dd, $J=8.0, 2.0$ Hz, H-6), 2.79~2.77 (2H, m, H-7), 3.97~3.95 (1H, m, H-8a), 3.71~3.69 (1H, m, H-8b), 4.32 (1H, d, $J=7.8$, H-1'), 3.22 (1H, t, $J=7.8$ Hz, H-2'), 3.38~3.36 (1H, m, H-3'), 3.37~3.35 (1H, m, H-4'), 3.52~3.50 (1H, m, H-5'), 4.50 (1H, dd, $J=11.9, 2.2$ Hz, H-6'a), 4.32 (1H, dd, $J=11.9, 6.0$ Hz, H-6'b), 7.03 (1H, d, $J=2.1$ Hz, H-2''), 6.77 (1H, d, $J=8.2$ Hz, H-5''), 6.88 (1H, dd, $J=8.2, 2.1$ Hz, H-6''), 7.56 (1H, d, $J=15.9$ Hz, H-7''), 6.28 (1H, d, $J=15.9$ Hz, H-8''); ¹³C-NMR (150 MHz, CD₃OD) δ : 130.0 (C-1), 115.7 (C-2), 144.7 (C-3), 143.3 (C-4), 115.0 (C-5), 119.9 (C-6), 35.3 (C-7), 71.0 (C-8), 103.2 (C-1'), 73.7 (C-2'), 76.5 (C-3'), 70.3 (C-4'), 74.1 (C-5'), 63.2 (C-6'), 126.3 (C-1''), 113.6 (C-2''), 145.8 (C-3''), 148.3 (C-4''), 115.1 (C-5''), 121.8 (C-6''), 145.4 (C-7''), 113.4 (C-8''), 167.8 (C-9'')。

以上数据与文献对照^[10], 鉴定化合物 **2** 为 calceolarioside B。

化合物 3: 淡黄色粉状物 (氯仿-甲醇)。¹H-NMR (600 MHz, CD₃OD) δ : 4.33 (1H, d, $J=7.2$ Hz, H-1), 3.24 (1H, t, $J=8.2$ Hz, H-2), 3.39~3.38 (1H, m, H-3), 3.37~3.36 (1H, m, H-4), 3.54 (1H, ddd, $J=8.6, 6.1, 2.0$ Hz, H-5), 4.50 (1H, dd, $J=8.1, 2.0$ Hz, H-6a),

4.34~4.32 (1H, m, H-6b), 7.04 (1H, d, $J = 2.0$ Hz, H-2'), 6.78 (1H, d, $J = 8.4$ Hz, H-5'), 6.90 (1H, dd, $J = 8.4, 2.0$ Hz, H-6'), 7.57 (1H, d, $J = 15.9$ Hz, H-7'), 6.30 (1H, d, $J = 15.9$ Hz, H-8'), 7.03 (2H, d, $J = 8.0$ Hz, H-2'', 6''), 6.66 (2H, d, $J = 8.0$ Hz, H-3'', 5''), 2.84~2.82 (2H, m, H-7''), 3.95~3.94 (1H, m, H-8'a), 3.75~3.72 (1H, m, H-8'b); ^{13}C -NMR (150 MHz, CD₃OD) δ : 103.2 (C-1), 74.1 (C-2), 76.6 (C-3), 71.1 (C-4), 73.8 (C-5), 63.4 (C-6), 126.4 (C-1'), 115.2 (C-2'), 145.5 (C-3'), 148.4 (C-4'), 113.6 (C-5'), 121.9 (C-6'), 146.0 (C-7'), 113.8 (C-8'), 167.9 (C-9'), 129.3 (C-1''), 114.9 (C-2''), 129.5 (C-3''), 155.5 (C-4''), 129.6 (C-5''), 114.9 (C-6''), 35.2 (C-7''), 70.5 (C-8'')。

以上数据与文献对照^[11], 鉴定化合物 3 为 2-(4-hydroxyphenyl)ethyl-6-O-(E)-caffeooyl- β -D-glucopyranoside。

化合物 4: 淡黄色粉状(氯仿-甲醇)。 ^1H -NMR (600 MHz, CD₃OD) δ : 6.59 (1H, d, $J = 2.0$ Hz, H-2), 6.55 (1H, d, $J = 8.0$ Hz, H-5), 6.45 (1H, dd, $J = 8.0, 2.0$ Hz, H-6), 2.70 (2H, t, $J = 7.6$ Hz, H-7), 3.86 (1H, dt, $J = 9.9, 7.6$ Hz, H-8a), 3.63~3.62 (1H, m, H-8b), 4.25 (1H, d, $J = 7.7$ Hz, H-1'), 3.13 (1H, t, $J = 8.3$ Hz, H-2'), 3.32~3.31 (1H, m, H-3'), 3.27~3.26 (1H, m, H-4'), 3.43~3.42 (1H, m, H-5'), 4.42 (1H, dd, $J = 11.8, 2.2$ Hz, H-6'a), 4.23~4.22 (1H, m, H-6'b), 7.31 (2H, d, $J = 8.5$ Hz, H-2'', 6''), 6.71 (2H, d, $J = 8.5$ Hz, H-3'', 5''), 7.53 (1H, d, $J = 15.9$ Hz, H-7''), 6.25 (1H, d, $J = 15.9$ Hz, H-8''); ^{13}C -NMR (150 MHz, CD₃OD) δ : 130.1 (C-1), 115.8 (C-2), 143.4 (C-3), 145.6 (C-4), 113.6 (C-5), 119.9 (C-6), 35.4 (C-7), 71.2 (C-8), 103.3 (C-1'), 73.8 (C-2'), 76.6 (C-3'), 70.5 (C-4'), 74.1 (C-5'), 63.4 (C-6'), 125.8 (C-1''), 115.6 (C-2''), 129.9 (C-3''), 159.9 (C-4''), 129.9 (C-5''), 115.6 (C-6''), 144.8 (C-7''), 115.1 (C-8''), 167.9 (C-9'')。

以上数据与文献对照^[12], 鉴定化合物 4 为 6'-O-coumaroyl-1'-O-[2-(3,4-dihydroxyphenyl)ethyl]- β -D-glucopyranoside。

化合物 5: 白色粉末(氯仿-甲醇), $[\alpha]_D^{20} + 164.3$ ($c 0.05$, MeOH), ESI-MS m/z 357.134 6 [$\text{M}-\text{H}]^-$ (Calcd. 357.133 8, C₂₀H₂₁O₆), 分子式为 C₂₀H₂₂O₆。 ^1H -NMR (600 MHz, DMSO-*d*₆) δ : 6.90 (2H, d, $J = 8.4$ Hz, H-2, 2'), 6.74 (2H, d, $J = 1.8$ Hz, H-5, 5'), 6.76 (2H, dd, $J = 8.4, 1.8$ Hz, H-6, 6'), 4.62 (2H, d, $J = 4.3$ Hz, H-7, 7'), 3.06~3.01 (2H, m, H-8, 8'), 3.73 (2H,

dd, $J = 3.7, 3.2$ Hz, H-9, 9'), 3.77 (12H, s, 4×OCH₃); ^{13}C -NMR (150 MHz, DMSO-*d*₆) δ : 132.8 (C-1, 2'), 111.0 (C-2, 2'), 148.1 (C-3, 3'), 146.5 (C-4, 4'), 115.7 (C-5, 5'), 119.2 (C-6, 6'), 85.7 (C-7, 7'), 56.2 (C-8, 8'), 71.5 (C-9, 9'), 54.2 (2×OCH₃)。以上数据与文献对照^[13], 鉴定化合物 5 为 (+)-pinoresinol。

化合物 6: 黄色油状物(氯仿-甲醇), ESI-MS m/z 373.129 6 [$\text{M}-\text{H}]^-$ (Calcd. 373.128 7, C₂₀H₂₁O₇), 分子式为 C₂₀H₂₂O₇。 ^1H -NMR (600 MHz, CD₃OD) δ : 7.05 (1H, d, $J = 8.0$ Hz, H-2), 6.85 (1H, d, $J = 1.9$ Hz, H-5), 6.86 (1H, dd, $J = 8.0, 1.9$ Hz, H-6), 4.68 (1H, brs, H-7), 3.87 (1H, m, H-9a), 3.76 (2H, dd, $J = 9.1, 6.2$ Hz, H-9b), 6.88 (1H, d, $J = 2.0$ Hz, H-2'), 6.73 (1H, d, $J = 8.1$ Hz, H-5'), 6.79 (1H, dd, $J = 8.1, 2.0$ Hz, H-6'), 4.87 (1H, d, $J = 5.2$ Hz, H-7'), 4.04 (1H, d, $J = 9.3$ Hz, H-9'a), 4.46 (1H, dd, $J = 9.3, 8.2$ Hz, H-9'b), 3.02~3.05 (1H, m, H-8'), 3.87 (3H, s, -OCH₃), 3.86 (3H, s, -OCH₃); ^{13}C -NMR (150 MHz, DMSO-*d*₆) δ : 132.3 (C-1), 111.4 (C-2), 147.5 (C-3), 146.2 (C-4), 115.0 (C-5), 120.3 (C-6), 88.0 (C-7), 91.5 (C-8), 74.8 (C-9), 127.9 (C-1'), 110.0 (C-2'), 147.4 (C-3'), 146.1 (C-4'), 114.7 (C-5'), 119.2 (C-6'), 86.5 (C-7'), 61.1 (C-8'), 70.7 (C-9'), 55.1 (-OCH₃), 55.0 (-OCH₃)。以上数据与文献对照^[14], 鉴定化合物 6 为 8-hydroxypinoresinol。

化合物 7: 黄色胶体(氯仿-甲醇), ESI-MS m/z 543.183 4 [$\text{M}+\text{Na}]^+$ (Calcd. 543.184 2, C₂₆H₃₂O₁₁Na), 分子式为 C₂₆H₃₂O₁₁。 ^1H -NMR (600 MHz, CD₃OD) δ : 6.94 (1H, d, $J = 1.9$ Hz, H-2), 6.76 (1H, d, $J = 8.1$ Hz, H-5), 6.80 (1H, dd, $J = 8.1, 1.9$ Hz, H-6), 4.70 (1H, d, $J = 4.2$ Hz, H-7), 3.14~3.12 (1H, m, H-8), 4.24~4.22 (1H, m, H-9a), 3.86~3.85 (1H, m, H-9b), 7.02 (1H, d, $J = 2.1$ Hz, H-2'), 7.14 (1H, d, $J = 8.3$ Hz, H-5'), 6.91 (1H, dd, $J = 8.3, 2.1$ Hz, H-6'), 4.75 (1H, d, $J = 4.0$ Hz, H-7), 3.15~3.13 (1H, m, H-8'), 4.23~4.21 (1H, m, H-9'a), 3.85~3.84 (1H, m, H-9'b), 4.88 (1H, d, $J = 8.0$ Hz, H-1''), 3.40~3.38 (1H, m, H-2''), 3.47~4.45 (1H, m, H-3''), 3.39~3.37 (1H, m, H-4''), 3.52~3.47 (1H, m, H-5''), 3.34 (1H, m, H-6'b), 3.68 (1H, dd, $J = 11.9, 3.6$ Hz, H-6'a), 3.86 (3H, s, -OCH₃), 3.85 (3H, s, -OCH₃); ^{13}C -NMR (150 MHz, CD₃OD) δ : 136.1 (C-1), 110.2 (C-2), 149.6 (C-3), 146.1 (C-4), 116.6 (C-5), 118.4 (C-6), 85.7 (C-7), 54.1

(C-8), 71.3 (C-9), 132.4 (C-1'), 109.6 (C-2'), 147.7 (C-3'), 145.9 (C-4'), 114.7 (C-5'), 118.7 (C-6'), 86.1 (C-7'), 54.0 (C-8'), 71.3 (C-9'), 101.4 (C-1''), 73.5 (C-2''), 76.4 (C-3''), 69.9 (C-4''), 76.8 (C-5''), 61.1 (C-6''), 55.3 (-OCH₃), 55.0 (-OCH₃)。以上数据与文献对照^[15], 鉴定化合物 7 为 pinoresinol-4-O-β-D-glucopyranoside。

化合物 8: 白色粉末(氯仿-甲醇)。 $[\alpha]_D^{20} + 32 (c\ 0.05, \text{MeOH})$; ¹H-NMR (600 MHz, CD₃OD) δ: 6.83 (1H, d, *J* = 1.7 Hz, H-2), 6.81 (1H, d, *J* = 7.2 Hz, H-5), 6.96 (1H, dd, *J* = 7.2, 1.7 Hz, H-6), 4.42 (1H, d, *J* = 6.9 Hz, 1H, H-7), 4.10 (1H, dd, *J* = 8.4, 1.3 Hz, H-9), 6.77 (1H, d, *J* = 1.8 Hz, H-2'), 6.79 (1H, d, *J* = 7.2 Hz, H-5'), 6.80 (1H, dd, *J* = 7.2, 1.8 Hz, H-6'), 4.86 (1H, d, *J* = 6.1 Hz, H-7'), 2.93~2.92 (1H, m, H-8'), 3.78~3.76 (1H, m, H-9a'), 3.36~3.34 (1H, m, H-9b'); 3.86 (3H, s, -OCH₃), 3.86 (3H, s, -OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ: 132.5 (C-1), 109.6 (C-2), 147.9 (C-3), 145.4 (C-4), 114.8 (C-5), 118.9 (C-6), 88.2 (C-7), 54.3 (C-8), 70.7 (C-9), 130.0 (C-1'), 109.2 (C-2'), 147.6 (C-3'), 146.3 (C-4'), 114.8 (C-5'), 118.1 (C-6'), 82.2 (C-7'), 50.0 (C-8'), 70.7 (C-9'), 55.1 (-OCH₃), 55.0 (-OCH₃)。以上数据与文献对照^[16], 鉴定化合物 8 为 (+)-epipinoresinol。

化合物 9: 黄色油状物(氯仿-甲醇), $[\alpha]_D^{20} + 68.7 (c\ 0.05, \text{CD}_3\text{OD})$, ESI-MS *m/z* 373.129 8 [M-H]⁻ (Calcd. 373.128 7, C₂₀H₂₂O₇), 分子式为 C₂₀H₂₂O₇。¹H-NMR (600 MHz, CD₃OD) δ: 4.39 (1H, brs, H-2), 5.17 (1H, d, *J* = 5.2 Hz, H-3), 3.06~3.10 (1H, m, H-4), 3.89 (1H, t, *J* = 9.1 Hz, H-5a), 3.61 (1H, d, *J* = 9.2 Hz, H-5b), 4.13 (1H, d, *J* = 9.1 Hz, H-6a), 3.22 (1H, t, *J* = 9.2 Hz, H-6b), 7.04 (1H, d, *J* = 2.0 Hz, H-2'), 6.76~6.79 (3H, m, H-5', 6', 6''), 6.95 (1H, d, *J* = 2.0 Hz, H-2''), 6.85 (1H, dd, *J* = 8.1, 2.0 Hz, H-5''), 3.86 (3H, s, -OCH₃), 3.86 (3H, s, -OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ: 90.3 (C-1), 89.5 (C-2), 81.5 (C-3), 57.4 (C-4), 67.8 (C-5), 75.5 (C-6), 127.7 (C-1'), 109.1 (C-2'), 147.4 (C-3'), 145.4 (C-4'), 114.3 (C-5'), 117.7 (C-6'), 129.8 (C-1''), 111.5 (C-2''), 147.6 (C-3''), 146.2 (C-4''), 114.8 (C-5''), 120.3 (C-6''), 55.1 (-OCH₃), 55.0 (-OCH₃)。以上数据与文献对照^[14], 鉴定化合物 9 为 (+)-1-hydroxy-2-epipinoresinol。

化合物 10: 无色针状结晶(氯仿-甲醇)。

¹H-NMR (600 MHz, DMSO-d₆) δ: 3.77, 3.76, 3.75 (9H, s, 3, 3', 4'-OCH₃), 6.72~6.93 (6H, m, H-2, 2', 5, 5', 6, 6'), 4.32 (1H, d, *J* = 7.0 Hz, H-7), 2.81~2.85 (m, 1H, H-8), 4.07 (1H, d, *J* = 9.3 Hz, H-9a), 3.73 (1H, m, 1H, H-9b), 4.80 (1H, d, *J* = 5.9 Hz, 1H, H-7'), 3.36~3.41 (1H, m, H-8', 9a'), 3.73 (1H, m, H-9b'); ¹³C-NMR (150 MHz, DMSO-d₆) δ: 132.9 (C-1), 110.8 (C-2), 148.1 (C-3), 148.1 (C-4), 115.7 (C-5), 119.2 (C-6), 87.6 (C-7), 54.5 (C-8), 69.4 (C-9), 131.8 (C-1'), 110.0 (C-2'), 149.0 (C-3'), 146.5 (C-4'), 112.1 (C-5'), 118.1 (C-6'), 81.8 (C-7'), 49.9 (C-8'), 70.9 (C-9'), 56.1 (-OCH₃), 56.0 (-OCH₃), 54.5 (-OCH₃)。以上数据与文献对照^[17], 鉴定化合物 10 为 phillygenin。

化合物 11: 黄色胶体(氯仿-甲醇), $[\alpha]_D^{20} + 20.8 (c\ 0.4, \text{MeOH})$, ESI-MS *m/z* 543.184 3 [M+Na]⁺ (Calcd. 543.184 2, C₂₆H₃₂O₁₁Na), 分子式为 C₂₆H₃₂O₁₁。¹H-NMR (600 MHz, DMSO-d₆) δ: 6.96 (1H, brs, H-2), 7.05 (1H, d, *J* = 9.0 Hz, H-5), 6.71 (1H, dd, *J* = 9.0, 1.1 Hz, H-6), 4.31 (1H, t, *J* = 5.7 Hz, H-7), 2.85~2.83 (1H, m, H-8), 4.01 (1H, d, *J* = 9.9 Hz, H-9a), 3.68~3.66 (1H, m, H-9b), 6.84 (1H, brs, H-2'), 6.66 (1H, d, *J* = 7.7 Hz, H-5'), 6.81 (1H, dd, *J* = 7.7, 2.7 Hz, H-6'), 4.79 (1H, d, *J* = 5.3 Hz, H-7'), 3.29~3.27 (1H, m, H-8'), 3.60~3.58 (1H, m, H-9'a), 3.15~3.11 (1H, m, H-9'b), 4.75 (1H, d, *J* = 7.0 Hz, H-1''), 3.21~3.19 (1H, m, H-2''), 3.22~3.20 (1H, m, H-3''), 3.21~3.19 (1H, m, H-4''), 3.22~3.20 (1H, m, H-5''), 3.40~3.37 (1H, m, H-6''a), 3.39~3.36 (1H, m, H-6''b), 3.77 (3H, s, OCH₃), 3.75 (3H, s, OCH₃); ¹³C-NMR (150 MHz, DMSO-d₆) δ: 132.7 (C-1), 109.1 (C-2), 147.0 (C-3), 145.3 (C-4), 113.9 (C-5), 118.0 (C-6), 87.3 (C-7), 53.5 (C-8), 69.9 (C-9), 131.6 (C-1'), 108.7 (C-2'), 148.5 (C-3'), 144.8 (C-4'), 115.6 (C-5'), 117.2 (C-6'), 81.0 (C-7'), 49.0 (C-8'), 68.4 (C-9'), 100.6 (C-1''), 72.7 (C-2''), 75.6 (C-3''), 69.1 (C-4''), 76.0 (C-5''), 60.3 (C-6''), 54.5 (-OCH₃), 54.2 (-OCH₃)。以上数据与文献对照^[18], 鉴定化合物 11 为 (+)-epipinoresinol-4'-O-β-D-glucopyranoside。

化合物 12: 白色粉末(氯仿-甲醇)。 $[\alpha]_D^{20} + 48.7 (c\ 0.05, \text{MeOH})$ 。¹H-NMR (600 MHz, CD₃OD) δ: 6.91 (1H, d, *J* = 1.9 Hz, H-2), 6.72 (1H, d, *J* = 8.0 Hz, H-5), 6.78 (1H, dd, *J* = 8.0, 1.9 Hz, H-6), 4.75 (1H, d, *J* =

6.9 Hz, H-7), 2.73~2.72 (1H, m, H-8), 3.84 (1H, m, H-9a), 3.64 (1H, dd, $J = 11.0, 6.5$ Hz, H-9b), 6.77 (1H, d, $J = 1.9$ Hz, H-2'), 6.71 (1H, d, $J = 8.1$ Hz, H-5'), 6.65 (1H, dd, $J = 8.1, 1.9$ Hz, H-6'), 2.94 (1H, dd, $J = 13.5, 4.9$ Hz, H-7b'), 2.50 (1H, dd, $J = 13.5, 11.2$ Hz, H-7a'), 2.75~2.72 (1H, m, H-8'), 3.98 (1H, dd, $J = 8.4, 6.4$ Hz, H-9'a), 3.72 (1H, dd, $J = 8.4, 5.9$ Hz, H-9'b), 3.85 (3H, s, -OCH₃), 3.83 (3H, s, -OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 134.5 (C-1), 109.4 (C-2), 147.7 (C-3), 145.8 (C-4), 114.9 (C-5), 118.5 (C-6), 82.8 (C-7), 52.8 (C-8), 59.2 (C-9), 132.2 (C-1'), 112.1 (C-2'), 147.7 (C-3'), 144.5 (C-4'), 114.7 (C-5'), 120.9 (C-6'), 32.4 (C-7'), 42.6 (C-8'), 72.2 (C-9'), 55.1 (-OCH₃), 55.0 (-OCH₃)。以上数据与文献对照^[19], 鉴定化合物 **14** 为 *rel*-(7*R*,8'*R*,8*S*)-forsythian C。

化合物 13: 白色粉末(氯仿-甲醇), $[\alpha]_D^{20} -48.1$ (*c* 0.05, MeOH)。¹H-NMR (600 MHz, DMSO-*d*₆) δ : 8.83 (1H, s, -OH), 8.70 (1H, s, -OH), 6.83 (1H, d, $J = 1.9$ Hz, H-2), 6.72 (1H, d, $J = 8.1$ Hz, H-5), 6.71 (1H, dd, $J = 8.1, 1.9$ Hz, H-6), 4.67 (1H, d, $J = 6.2$ Hz, H-7), 2.60~2.56 (1H, m, H-8), 3.89 (1H, dd, $J = 6.6, 6.5$ Hz, H-9a), 3.56 (1H, dd, $J = 6.6, 6.5$ Hz, H-9b), 6.75 (1H, d, $J = 8.1$ Hz, H-2'), 6.70 (1H, d, $J = 1.9$ Hz, H-5'), 6.59 (1H, dd, $J = 8.1, 1.9$ Hz, H-6'), 2.43 (1H, dd, $J = 10.9, 4.9$ Hz, H-7a'), 2.83 (1H, dd, $J = 13.2, 4.9$ Hz, H-7b'), 3.76 (6H, s, 2×OCH₃); ¹³C-NMR (150 MHz, DMSO-*d*₆) δ : 135.3 (C-1), 110.5 (C-2), 147.9 (C-3), 145.1 (C-4), 115.6 (C-5), 118.8 (C-6), 82.3 (C-7), 53.0 (C-8), 59.2 (C-9), 132.3 (C-1'), 113.3 (C-2'), 148.0 (C-3'), 146.1 (C-4'), 115.9 (C-5'), 121.2 (C-6'), 32.7 (C-7'), 42.6 (C-8'), 72.4 (C-9'), 56.1 (-OCH₃), 56.0 (-OCH₃)。以上数据与文献对照^[20], 鉴定化合物 **13** 为 (-)-lariciresinol。

化合物 14: 白色粉末(氯仿-甲醇), ESI-MS *m/z* 357.134 7 [M-H]⁻ (Calcd. 357.133 8, C₂₀H₂₁O₆) 分子式为 C₂₀H₂₂O₆。¹H-NMR (600 MHz, CD₃OD) δ : 7.52 (1H, d, $J = 2.1$ Hz, H-2), 6.96 (1H, d, $J = 8.1$ Hz, H-5), 7.57 (1H, dd, $J = 8.1, 2.1$ Hz, H-6), 4.46 (1H, d, $J = 8.4$ Hz, H-8), 4.42 (1H, dd, $J = 9.0, 6.5$ Hz, H-9a), 4.28 (1H, dd, $J = 6.5, 4.1$ Hz, H-9b), 6.81 (1H, d, $J = 1.8$ Hz, H-2'), 6.80 (1H, d, $J = 8.5$ Hz, H-5'), 6.77 (1H, dd, $J = 8.5, 1.8$ Hz, H-6'), 2.55~2.48 (1H, m, H-8'), 0.79 (3H, d, $J = 7.1$ Hz, 9'-CH₃), 3.88 (3H, s, -OCH₃),

3.87 (3H, s, -OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 132.1 (C-1), 110.1 (C-2), 147.8 (C-3), 149.2 (C-4), 115.5 (C-5), 124.7 (C-6), 199.4 (C-7), 46.0 (C-8), 69.6 (C-9), 127.4 (C-1'), 109.7 (C-2'), 146.2 (C-3'), 145.1 (C-4'), 114.7 (C-5'), 119.2 (C-6'), 87.7 (C-7), 48.6 (C-8'), 11.7 (C-9'), 55.1 (-OCH₃), 54.9 (-OCH₃)。以上数据与文献对照^[21], 鉴定化合物 **14** 为 *rel*-(7*R*,8'*R*,8*S*)-forsythian C。

化合物 15: 白色粉末(氯仿-甲醇), ESI-MS *m/z* 357.134 9 [M-H]⁻ (Calcd. 357.133 8, C₂₀H₂₁O₆) 分子式为 C₂₀H₂₂O₆。¹H-NMR (600 MHz, CD₃OD) δ : 7.58 (1H, d, $J = 2.0$ Hz, H-2), 6.96 (1H, d, $J = 8.3$ Hz, H-5), 7.61 (1H, dd, $J = 8.3, 2.0$ Hz, H-6), 3.84 (1H, dt, $J = 10.3, 9.0$ Hz, H-8), 4.09 (1H, dd, $J = 8.4, 6.9$ Hz, H-9a), 4.01 (1H, dd, $J = 9.0, 6.9$ Hz, H-9b), 6.93 (1H, d, $J = 1.8$ Hz, H-2'), 6.89 (1H, d, $J = 8.4$ Hz, H-5'), 6.81 (1H, dd, $J = 8.4, 1.8$ Hz, H-6'), 4.38 (1H, d, $J = 9.6$ Hz, H-7'), 2.44~2.43 (1H, m, H-8'), 1.02 (3H, d, $J = 6.6$ Hz, H-9'), 3.93 (3H, s, -OCH₃), 3.88 (3H, s, -OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 131.5 (C-1), 110.8 (C-2), 146.4 (C-3), 149.3 (C-4), 114.8 (C-5), 124.0 (C-6), 198.8 (C-7), 53.6 (C-8), 70.2 (C-9), 132.5 (C-1'), 109.7 (C-2'), 147.9 (C-3'), 146.8 (C-4'), 114.6 (C-5'), 119.8 (C-6'), 89.1 (C-7'), 46.4 (C-8'), 13.8 (C-9'), 55.2 (-OCH₃), 54.1 (-OCH₃)。以上数据与文献对照^[21], 鉴定化合物 **15** 为 *rel*-(7*R*,8'*R*,8*R*)-forsythian C。

化合物 16: 黄色无定形粉末(氯仿-甲醇), ESI-MS *m/z* 359.150 5 [M-H]⁻ (Calcd. 359.149 5, C₂₀H₂₃O₆) 分子式为 C₂₀H₂₄O₆。¹H-NMR (600 MHz, CD₃OD) δ : 6.66 (1H, s, H-2), 6.19 (1H, s, H-5), 2.78 (2H, d, $J = 7.8$ Hz, H-7), 2.02~1.98 (m, 1H, H-8), 3.68~3.66 (1H, m, H-9a), 3.66~3.64 (1H, m, H-9b), 6.68 (1H, d, $J = 2.0$ Hz, H-2'), 6.75 (1H, d, $J = 8.0$ Hz, H-5'), 6.62 (1H, dd, $J = 8.0, 2.0$ Hz, H-6'), 3.81~3.79 (1H, m, H-7'), 1.77~1.75 (1H, m, H-8'), 3.71 (1H, dd, $J = 11.3, 4.9$ Hz, H-9'a), 3.40 (1H, dd, $J = 11.3, 4.1$ Hz, H-9'b), 3.81 (3H, s, -OCH₃), 3.78 (3H, s, -OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 138.8 (C-1'), 113.9 (C-2'), 149.2 (C-3'), 146.1 (C-4'), 115.9 (C-5'), 123.3 (C-6'), 48.2 (C-7'), 48.1 (C-8'), 62.3 (C-9'), 129.1 (C-1), 112.5 (C-2), 147.3 (C-3), 145.4 (C-4), 117.5 (C-5), 134.3 (C-6), 33.7 (C-7), 40.1 (C-8),

66.1 (C-9), 56.5 (-OCH₃), 56.5 (-OCH₃)。以上数据与文献对照^[22], 鉴定化合物 **16** 为 (7'S,8R,8'R)-isolariciresinol。

化合物 17: 淡黄色油状物(氯仿-甲醇), ESI-MS *m/z* 357.135 1 [M-H]⁻ (Calcd. 357.133 8, C₂₀H₂₁O₆), 分子式 C₂₀H₂₂O₆。¹H-NMR (600 MHz, CD₃OD) δ: 6.57 (1H, d, *J* = 2.0 Hz, H-2), 6.53 (1H, d, *J* = 7.6 Hz, H-5), 6.69 (1H, dd, *J* = 7.6, 2.0 Hz, H-6), 2.82 (2H, d, *J* = 7.0 Hz, H-7), 2.54~2.52 (1H, m, H-8), 4.18 (1H, d, *J* = 7.4 Hz, H-9a), 4.16 (1H, d, *J* = 7.4 Hz, H-9b), 6.70 (1H, d, *J* = 2.0 Hz, H-2'), 6.51 (1H, d, *J* = 7.0 Hz, 1H, H-5'), 6.59 (1H, dd, *J* = 7.0, 2.0 Hz, H-6'), 2.90 (2H, dd, *J* = 5.4, 2.0 Hz, H-7'), 2.68~2.66 (1H, m, H-8'), 3.80 (3H, s, -OCH₃), 3.79 (3H, s, -OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ: 129.5 (C-1), 112.6 (C-2), 147.8 (C-3), 145.1 (C-4), 114.9 (C-5), 121.8 (C-6), 37.6 (C-7), 46.5 (C-8), 71.6 (C-9), 130.2 (C-1'), 112.0 (C-2'), 147.7 (C-3'), 144.9 (C-4'), 114.8 (C-5'), 120.9 (C-6'), 34.1 (C-7'), 41.2 (C-8'), 180.4 (C-9'), 55.0 (-OCH₃), 55.0 (-OCH₃)。以上数据与文献对照^[23], 鉴定化合物 **17** 为 matairesinol。

化合物 18: 黄色无定型粉末(氯仿-甲醇), ESI-MS *m/z* 543.184 1 [M+Na]⁺ (Calcd. 543.184 2, C₂₆H₃₂O₁₁Na), 分子式 C₂₆H₃₂O₁₁。¹H-NMR (600 MHz, DMSO-*d*₆) δ: 6.62 (1H, d, *J* = 2.0 Hz, H-2), 6.99 (1H, d, *J* = 8.0 Hz, H-5), 6.49 (1H, dd, *J* = 8.0, 2.0 Hz, H-6), 2.42 (1H, d, *J* = 5.4 Hz, H-8), 4.09 (1H, m, H-9a), 3.86 (1H, t, *J* = 8.5 Hz, H-9b), 6.68 (1H, d, *J* = 2.0 Hz, H-2'), 6.65 (1H, d, *J* = 8.0 Hz, H-5'), 6.78 (1H, dd, *J* = 8.0, 2.0 Hz, H-6'), 2.43 (1H, d, *J* = 9.0 Hz, H-7'a), 2.81~2.80 (1H, m, H-7'b), 2.73 (1H, dt, *J* = 8.9, 6.0 Hz, H-8'), 4.84 (1H, d, *J* = 7.2 Hz, H-1'), 3.26~3.25 (1H, m, H-2'), 3.27~3.26 (1H, m, H-3'), 3.15~3.14 (1H, m, H-4'), 3.23~3.22 (1H, m, H-5'), 3.65 (1H, dd, *J* = 11.7, 2.1 Hz, H-6'a), 3.44 (1H, dd, *J* = 11.7, 5.6 Hz, H-6'b), 3.72 (3H, s, -OCH₃), 3.71 (3H, s, -OCH₃); ¹³C-NMR (150 MHz, DMSO-*d*₆) δ: 132.2 (C-1), 113.1 (C-2), 149.1 (C-3), 145.4 (C-4), 115.5 (C-5), 121.2 (C-6), 37.3 (C-7), 41.3 (C-8), 71.2 (C-9), 130.0 (C-1'), 114.3 (C-2'), 148.0 (C-3'), 145.7 (C-4'), 115.8 (C-5'), 121.8 (C-6'), 33.9 (C-7'), 46.0 (C-8'), 178.9 (C-9'), 100.6 (C-1'), 73.7 (C-2'), 77.4 (C-3'), 70.1 (C-4'), 77.3 (C-5'), 61.1 (C-6'), 56.1 (-OCH₃), 56.0

(-OCH₃)。以上数据与文献对照^[24], 鉴定化合物 **18** 为 matairesinol-4'-*O*-β-*D*-glucopyranoside。

化合物 19: 淡黄色油状(氯仿-甲醇), [α]_D²⁰-98.4 (*c* 0.05, MeOH)。¹H-NMR (600 MHz, CD₃OD) δ: 7.07 (1H, d, *J* = 2.0 Hz, H-2), 6.96 (1H, dd, *J* = 8.4, 2.0 Hz, H-5), 7.17 (1H, d, *J* = 8.4 Hz, H-6), 4.67 (2H, dd, *J* = 12.0, 2.0 Hz, H-7), 1.82~1.81 (1H, m, H-8, 8'), 1.03 (6H, dd, *J* = 11.6, 6.0 Hz, H-9, 9'), 6.99 (1H, d, *J* = 1.9 Hz, H-2'), 6.79 (1H, d, *J* = 8.4 Hz, H-5'), 6.85 (1H, dd, *J* = 8.4, 1.9 Hz, H-6'), 4.66 (2H, dd, *J* = 16.0, 2.0 Hz, H-7'), 4.90 (1H, d, *J* = 7.4 Hz, H-1'), 3.51 (2H, dd, *J* = 9.1, 7.4 Hz, H-2'), 3.48~3.47 (1H, m, H-3'), 3.41~3.40 (1H, m, H-4'), 3.40~3.39 (1H, m, H-5'), 3.86~3.84 (1H, m, H-6'a), 3.70~3.69 (1H, m, H-6'b), 3.90 (3H, s, -OCH₃), 3.88 (3H, s, -OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ: 136.9 (C-1), 110.5 (C-2), 149.6 (C-3), 146.1 (C-4), 114.7 (C-5), 119.1 (C-6), 88.9 (C-7), 50.7 (C-8), 12.5 (C-9), 133.3 (C-1'), 109.8 (C-2'), 147.8 (C-3'), 146.3 (C-4'), 116.6 (C-5'), 119.3 (C-6'), 88.4 (C-7'), 50.9 (C-8'), 12.6 (C-9'), 101.6 (C-1'), 73.6 (C-2'), 76.6 (C-3'), 70.0 (C-4'), 76.9 (C-5'), 61.2 (C-6'), 55.1 (-OCH₃), 55.5 (-OCH₃)。以上数据与文献对照^[25], 鉴定化合物 **19** 为 (-)-nectandrin B-β-*D*-glucopyranoside。

化合物 20: 淡黄色油状物(氯仿-甲醇)。¹H-NMR (600 MHz, CD₃OD) δ: 7.17 (1H, d, *J* = 2.0 Hz, H-2), 6.96 (1H, dd, *J* = 8.1, 2.0 Hz, H-5), 7.22 (1H, d, *J* = 8.1 Hz, H-6), 5.14 (2H, dd, *J* = 12.1, 8.9 Hz, H-7), 1.83~1.81 (1H, m, H-8, 8'), 1.04 (6H, dd, *J* = 8.3, 6.5 Hz, H-9, 9'), 7.07 (1H, d, *J* = 2.0 Hz, H-2'), 6.83 (1H, d, *J* = 8.0 Hz, H-5'), 6.92 (1H, dd, *J* = 8.0, 2.0 Hz, H-6'), 4.40 (2H, dd, *J* = 12.4, 9.5 Hz, H-7'), 4.93 (1H, d, *J* = 7.4 Hz, H-1'), 3.71 (1H, dd, *J* = 5.2, 2.2 Hz, H-2'), 3.48~3.47 (1H, m, H-3'), 3.43~3.42 (1H, m, H-4'), 3.41~3.40 (1H, m, H-5'), 3.72~3.70 (1H, m, H-6'a), 3.70~3.69 (1H, m, H-6'b), 3.90 (3H, s, -OCH₃), 3.89 (3H, s, OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ: 132.5 (C-1), 112.4 (C-2), 149.6 (C-3), 146.0 (C-4), 116.7 (C-5), 119.4 (C-6), 87.8 (C-7), 45.3 (C-8), 14.0 (C-9), 136.0 (C-1'), 110.7 (C-2'), 147.8 (C-3'), 146.4 (C-4'), 114.9 (C-5'), 119.7 (C-6'), 87.3 (C-7'), 48.3 (C-8'), 13.9 (C-9'), 55.5 (OCH₃), 55.4 (-OCH₃), 101.5 (C-1'), 73.6 (C-2'),

76.6 (C-3''), 70.1 (C-4''), 76.9 (C-5''), 61.2 (C-6'')^o。以上数据与文献对照^[25]，鉴定化合物 **20** 为 (7*R*,7'*R*,8*S*,8'*R*)-4,4'-dihydroxy-3,3'-dimethoxy-7,7'-epoxylignan-4-*O*- β -D-glucopyranoside。

化合物 21：淡黄色油状物（氯仿-甲醇）。¹H-NMR (600 MHz, CD₃OD) δ : 6.81 (1H, d, J = 1.8 Hz, H-2), 6.94 (1H, dd, J = 8.1, 1.8 Hz, H-5), 6.80 (1H, d, J = 8.1 Hz, H-6), 5.14 (2H, dd, J = 12.1, 8.9 Hz, H-7), 1.77~1.75 (1H, m, H-8, 8'), 1.04 (6H, dd, J = 8.3, 6.5 Hz, H-9, 9'), 7.02 (1H, d, J = 2.0 Hz, H-2'), 7.18 (1H, d, J = 8.0 Hz, H-5'), 7.09 (1H, dd, J = 8.0, 2.0 Hz, H-6'), 4.91 (2H, d, J = 7.5 Hz, H-7'), 4.91 (1H, d, J = 7.5 Hz, H-1''), 3.41~3.40 (1H, m, H-2''), 3.49~3.48 (1H, m, H-3''), 3.43~3.42 (1H, m, H-4''), 3.71 (1H, dd, J = 5.2, 2.2 Hz, H-5''), 3.72~3.71 (1H, m, H-6'a), 3.48~3.47 (1H, m, H-6'b), 3.86 (3H, s, -OCH₃), 3.85 (3H, s, -OCH₃)；¹³C-NMR (150 MHz, CD₃OD) δ : 131.6 (C-1), 110.4 (C-2), 147.4 (C-3), 145.6 (C-4), 114.5 (C-5), 119.1 (C-6), 83.0 (C-7), 45.7 (C-8), 13.6 (C-9), 135.4 (C-1''), 111.0 (C-2''), 149.1 (C-3''), 146.3 (C-4''), 116.1 (C-5''), 119.6 (C-6''), 83.5 (C-7''), 48.1 (C-8''), 13.6 (C-9''), 55.2 (-OCH₃), 55.1 (-OCH₃), 101.5 (C-1''), 73.6 (C-2''), 76.6 (C-3''), 70.1 (C-4''), 76.6 (C-5''), 61.2 (C-6'')^o。以上数据与文献对照^[25]，鉴定化合物 **21** 为 (7*R*,7'*R*,8*S*,8'*R*)-4,4'-dihydroxy-3,3'-dimethoxy-7,7'-epoxylignan-4-*O*- β -D-glucopyranoside。

化合物 22：白色针状结晶（氯仿-甲醇），ESI-MS *m/z* 337.161 [M + Na]⁺ (Calcd. 337.162 7, C₁₆H₂₆O₆Na)，分子式 C₁₆H₂₆O₆。¹H-NMR (600 MHz, CD₃OD) δ : 2.23 (1H, td, J = 5.6, 1.4 Hz, H-1), 5.58~5.54 (1H, m, H-3), 2.29 (2H, dt, J = 11.7, 2.5 Hz, H-4), 2.11~2.06 (1H, m, H-5), 2.42 (1H, m, H-6a), 1.19 (1H, d, J = 8.6 Hz, H-6b), 1.30 (3H, s, H-8), 0.87 (3H, s, H-9), 4.23~4.21 (1H, m, H-10a), 4.02~4.00 (1H, m, H-10b), 4.27 (1H, d, J = 7.8 Hz, H-1''), 3.33 (1H, d, J = 8.9 Hz, H-2''), 3.28 (1H, dd, J = 9.1, 8.9 Hz, H-3''), 3.22~3.20 (1H, m, H-4''), 3.19~3.17 (1H, m, H-5''), 3.85 (1H, dd, J = 11.9, 2.3 Hz, H-6'a), 3.66 (1H, dd, J = 11.9, 5.7 Hz, H-6'b)；¹³C-NMR (150 MHz, CD₃OD) δ : 102.0 (C-1''), 73.7 (C-2''), 76.6 (C-3''), 71.2 (C-4''), 76.8 (C-5''), 61.4 (C-6''), 43.1 (C-1), 144.9 (C-2), 119.4 (C-3), 31.1 (C-4), 40.8 (C-5), 30.9

(C-6), 37.5 (C-7), 25.2 (C-8), 20.2 (C-9), 70.3 (C-10)^o。以上数据与文献对照^[26~28]，鉴定化合物 **22** 为 myrtenyl-*O*- β -D- glucopyranoside。

化合物 23：白色粉状物（氯仿-甲醇），¹H-NMR (600 MHz, CD₃OD) δ : 4.31~4.30 (1H, m, H-1), 5.40 (1H, m, H-2), 1.77~1.75 (3H, m, H-4), 2.15~2.12 (1H, m, H-5), 2.10 (1H, m, H-6), 5.12 (1H, m, H-7), 1.68 (3H, s, H-9), 1.62 (3H, s, H-10), 4.28 (1H, d, J = 7.8 Hz, H-1''), 3.86 (1H, dd, J = 8.1, 2.3 Hz, H-2''), 3.29 (1H, d, J = 8.1 Hz, H-3''), 3.68 (1H, dd, J = 11.9, 5.6 Hz, H-6'a), 3.34 (1H, m, H-6'b)；¹³C-NMR (150 MHz, CD₃OD) δ : 64.9 (C-1), 121.3 (C-2), 140.5 (C-3), 16.5 (C-4), 31.8 (C-5), 26.4 (C-6), 123.7 (C-7), 131.5 (C-8), 22.4 (C-9), 24.6 (C-10), 101.6 (C-1''), 73.8 (C-2''), 76.6 (C-3''), 70.3 (C-4''), 76.8 (C-5''), 61.4 (C-6')^o。以上数据与文献对照^[29]，鉴定化合物 **23** 为 neryl- β -D- glucopyranoside。

化合物 24：淡黄色无定形粉末（氯仿-甲醇）。¹H-NMR (600 MHz, CD₃OD) δ : 1.70~1.69 (1H, m, H-1), 1.30 (1H, ddd, J = 12.0, 9.5, 4.4 Hz, H-2), 2.01~1.99 (1H, m, H-3), 5.37 (1H, d, J = 2.3 Hz, H-5), 2.17~2.16 (1H, m, H-6), 1.21~1.20 (3H, m, H-7), 0.90 (3H, s, H-9), 0.88 (3H, d, J = 1.7 Hz, H-10), 4.25 (1H, d, J = 7.8 Hz, H-1''), 3.35~3.34 (1H, m, H-2''), 3.28 (1H, t, J = 9.1 Hz, H-3''), 3.22 (1H, m, H-4''), 3.16 (1H, dd, J = 9.1, 7.7 Hz, H-5''), 3.84 (1H, dd, J = 11.8, 2.4 Hz, H-6'a), 3.67 (1H, td, J = 11.8, 5.5 Hz, H-6'b)；¹³C-NMR (150 MHz, CD₃OD) δ : 43.9 (C-1), 22.3 (C-2), 30.8 (C-3), 133.5 (C-4), 120.6 (C-5), 26.4 (C-6), 21.7 (C-7), 83.1 (C-8), 23.8 (C-9), 23.8 (C-10), 101.8 (C-1''), 74.0 (C-2''), 76.2 (C-3''), 70.4 (C-4''), 77.1 (C-5''), 61.6 (C-6')^o。以上数据与文献对照^[30]，鉴定化合物 **24** 为 α -terpineol-8-*O*- β -D- glucopyranoside。

化合物 25：淡黄色无定形粉末（氯仿-甲醇）。¹H-NMR (600 MHz, DMSO-d₆) δ : 4.46 (1H, dd, J = 16.2, 8.4 Hz, H-2), 2.78 (1H, dd, J = 16.2, 4.2 Hz, H-3a), 2.60 (1H, ddd, J = 12.7, 3.0, 1.8 Hz, H-3b), 5.89 (1H, d, J = 10.1 Hz, H-5), 6.77 (1H, dd, J = 10.1, 1.7 Hz, H-6), 2.44 (1H, ddd, J = 10.5, 4.7, 4.6 Hz, H-7a), 2.15 (1H, ddd, J = 10.5, 2.2, 1.7 Hz, H-7b), 4.03 (1H, td, J = 4.7, 1.7 Hz, H-8a), 3.86 (1H, ddd, J = 4.7, 2.6, 1.7 Hz, H-8b)；¹³C-NMR (150 MHz,

DMSO-*d*₆) δ : 74.5 (C-1), 81.1 (C-2), 42.5 (C-3), 197.4 (C-4), 127.5 (C-5), 150.6 (C-6), 38.2 (C-7), 66.0 (C-8)。以上数据与文献对照^[31], 鉴定化合物 25 为 rengyolone。

化合物 26: 黄色无定形粉末 (氯仿-甲醇), ESI-MS *m/z* 207.067 3 [M-H]⁻ (Calcd. 207.065 7, C₁₁H₁₁O₄), 分子式 C₁₁H₁₂O₄。¹H-NMR (600 MHz, CD₃OD) δ : 7.18 (1H, d, *J* = 2.0 Hz, H-2), 6.80 (1H, d, *J* = 8.2 Hz, H-3), 7.06 (1H, dd, *J* = 8.2, 2.0 Hz, H-6), 7.61 (1H, d, *J* = 15.9 Hz, H-7), 6.36 (1H, d, *J* = 15.9 Hz, H-8), 3.89 (3H, s, H-10), 3.76 (3H, s, H-11); ¹³C-NMR (150 MHz, CD₃OD) δ : 126.2 (C-1), 122.7 (C-2), 115.1 (C-3), 149.4 (C-4), 148.0 (C-5), 110.3 (C-6), 145.5 (C-7), 113.7 (C-8), 168.3 (C-9), 55.0 (C-10), 50.6 (C-11)。以上数据与文献对照^[32], 鉴定化合物 26 为 methyl ferulate。

4 体外抗肿瘤活性评价

取生长状态良好的细胞, 加胰酶细胞消化液使贴壁细胞消化脱落, 形成细胞混悬液, 对细胞进行计数, 并将细胞稀释到 1×10⁴ 个/mL。在 96 孔板上, 每孔接种 190 μL 细胞悬液, 置 37 °C、5% CO₂ 的恒温箱中培养, 培养 12 h 使细胞贴壁。倒掉培养液, 每孔加入 100 μL (含待测化合物浓度为 40 μmol/L) DMEM 高糖培养液, 在恒温箱中培养 48 h。吸去 100 μL 上清液, 加入 100 μL 新鲜 DMEM 高糖培养液, 再加入配制好的 10 μL MTT 溶液 (5 mg/mL、0.5% MTT), 继续在恒温箱中培养 4 h。吸去 100 μL 上清液, 每孔加入 100 μL 的甲酇溶解液, 置摇床上低速振荡 10 min, 在恒温箱中放置 4 h 左右。在酶联免疫检测仪 570 nm 处测量各个孔的吸光度 (A) 值, 按照公式计算抑制率。每组设定 4 个复孔, 同时设置空白组 (含有培养基和 MTT)、对照组 (含有细胞、培养液和 MTT) 和阳性对照组 (含有细胞、培养液、5-氟尿嘧啶和 MTT)。结果见表 1。

$$\text{抑制率} = [(A_{\text{对照}} - A_{\text{空白}}) - (A_{\text{给药}} - A_{\text{空白}})] / (A_{\text{对照}} - A_{\text{空白}})$$

5 讨论

本研究利用多种色谱分离手段对中药连翘进行了化学成分研究, 分离鉴定了共 26 个化合物, 其中 10 个属内首次分离的化合物, 化合物 1~4 为苯乙醇苷类, 5~21 为木脂素及其苷类, 22~24 为单萜苷类, 25 为环己酮类, 26 为简单苯丙素类化合物。活性测定结果表明, 在 40 μmol/L 下化合物 5~18 对 HepG-2 和 MCF-7 细胞具有一定的细胞毒活性。

表 1 化合物的抑制率

Table 1 Inhibition rate of compounds

化合物	抑制率/%	
	HepG-2	MCF-7
5	57.3±4.8	49.5±5.4
6	54.7±8.9	41.6±5.5
7	53.2±9.4	43.8±1.7
8	51.0±5.8	38.1±2.4
9	54.6±5.3	44.1±5.4
10	55.3±9.3	41.7±2.2
11	51.2±0.7	47.4±4.8
12	56.2±3.5	44.1±3.5
13	49.6±7.2	40.2±3.5
14	47.4±7.8	42.5±5.1
15	49.9±3.6	43.4±3.5
16	47.9±4.3	39.1±4.9
17	52.8±1.8	39.6±4.8
18	51.1±4.4	51.7±3.4
阳性对照	73.8±4.5	71.3±3.2

本研究丰富了连翘的化学成分, 为连翘抗肿瘤作用的活性成分发现提供科学依据。

利益冲突 所有作者均声明不存在利益冲突

参考文献

- 中国药典 [S]. 一部. 2020: 177-178.
- 中国科学院中国植物志编辑委员会. 中国植物志 (第八卷) [M]. 北京: 科学出版社, 1992: 42.
- Wang Z Y, Xia Q, Liu X, et al. Phytochemistry, pharmacology, quality control and future research of *Forsythia suspensa* (Thunb.) Vahl: A review [J]. *J Ethnopharmacol*, 2018, 210: 318-339.
- Zhao L M, Yan X, Shi J A, et al. Ethanol extract of *Forsythia suspensa* root induces apoptosis of esophageal carcinoma cells via the mitochondrial apoptotic pathway [J]. *Mol Med Rep*, 2015, 11(2): 871-880.
- Zhang W G, Liu Q, Lei C P. *Forsythia suspensa* extract has inhibitory effect on proliferation and apoptosis of A549 lung cancer cells [J]. *Trop J Pharm Res*, 2021, 18(9): 1949-1954.
- 李平, 张桂萍, 胡建燃. 连翘总黄酮对胃癌细胞 MGC80-3 增殖的影响 [J]. 生物技术通报, 2018, 34(6): 199-203.
- 阎新佳, 聂承冬, 江园园, 等. 连翘中 1 个新的苯乙醇苷 [J]. 中国中药杂志, 2022, 47(13): 3526-3529.
- 聂承冬, 阎新佳, 温静, 等. 基于分子对接和网络药理学方法筛选连翘抗肿瘤活性成分 [J]. 中草药, 2023, 54(17): 5496-5503.

- 学的连翘抗肿瘤的作用机制分析 [J]. 中国中药杂志, 2020, 45(18): 4455-4465.
- [9] Candido L P, Varela R M, Torres A, et al. Evaluation of the allelopathic potential of leaf, stem, and root extracts of *Ocotea pulchella* Nees et Mart [J]. *Chem Biodiversity*, 2016, 13(8): 1058-1067.
- [10] Damtoft S, Jensen S R. Three phenylethanoid glucosides of unusual structure from *Chirita sinensis* (Gesneriaceae) [J]. *Phytochemistry*, 1994, 37(2): 441-443.
- [11] Hanhineva K, Soininen P, Anttonen M J, et al. NMR and UPLC-qTOF-MS/MS characterisation of novel phenylethanol derivatives of phenylpropanoid glucosides from the leaves of strawberry (*Fragaria × ananassa* cv. Jonsook) [J]. *Phytochem Anal*, 2009, 20(5): 353-364.
- [12] 李骅轩. 厚皮香地上部分化学成分与镇痛活性研究 [D]. 大理: 大理大学, 2019.
- [13] 郭婷, 黄家宇, 董莉. 连翘的化学成分研究 [J]. 西北药学杂志, 2020, 35(5): 648-652.
- [14] Yeo H, Chin Y W, Park S Y, et al. Lignans of *Rosa multiflora* roots [J]. *Arch Pharm Res*, 2004, 27(3): 287-290.
- [15] 王福男. 中药连翘的化学成分研究 [D]. 北京: 中国协和医科大学, 2009.
- [16] Nishibe S, Tsukamoto H, Hisada S. Effects of *O*-methylation and *O*-glucosylation on carbon-13 nuclear magnetic resonance chemical shifts of matairesinol, (+)-pinoresinol and (+)-epipinoresinol [J]. *Chem Pharm Bull*, 1984, 32(11): 4653-4657.
- [17] Rahman M M A, Dewick P M, Jackson D E, et al. Lignans of *Forsythia intermedia* [J]. *Phytochemistry*, 1990, 29(6): 1971-1980.
- [18] 阎新佳, 江园园, 温静, 等. 连翘中双四氢呋喃木脂素类化学成分及其波谱特征 [J]. 天然产物研究与开发, 2020, 32(6): 995-999.
- [19] 赵明, 韩晶, 吕嵩岩, 等. 紫丁香树枝化学成分研究 [J]. 中草药, 2012, 43(2): 251-254.
- [20] Guo J R, Zhang J W, Shu P H, et al. Two new diterpenoids from the buds of *Wikstroemia chamaedaphne* [J]. *Molecules*, 2012, 17(6): 6424-6433.
- [21] Kuo P C, Wu T S. Chemical constituents and anti-inflammatory principles from the fruits of *Forsythia suspensa* [J]. *J Nat Prod*, 2017, 80(4): 1055-1064.
- [22] 包永睿, 阎新佳, 杨欣欣, 等. 白花败酱草的化学成分研究 [J]. 中药材, 2017, 40(2): 347-349.
- [23] 龙红萍, 谭桂山, 朱刚直, 等. 兖州卷柏苯丙素类和木脂素类化学成分研究 [J]. 中草药, 2016, 47(21): 3773-3778.
- [24] 张创峰, 沈硕, 宋联强, 等. 连花清瘟胶囊的化学成分研究 (II) [J]. 中草药, 2018, 49(14): 3222-3225.
- [25] Bu P B, Li Y R, Jiang M, et al. Glycosides from the bark of *Machilus robusta* [J]. *J Asian Nat Prod Res*, 2013, 15(5): 482-491.
- [26] 费永和. 菊花籽的化学成分研究 [D]. 苏州: 苏州大学, 2014.
- [27] Yin X M, Zhang J D, Wang S H. Chemical constituents of the stems of *Orostachys malacophyllus* [J]. *Chem Nat Compd*, 2020, 56(4): 740-742.
- [28] Kawahara E, Fujii M, Ida Y, et al. Chemoenzymatic synthesis of sacranosides A and B [J]. *Chem Pharm Bull*, 2006, 54(3): 387-390.
- [29] 杨勇勋, 张建平, 王群, 等. 贵州天名精的化学成分研究 [J]. 中草药, 2017, 48(15): 3037-3041.
- [30] Nham N X, Kim K C, Kim A D, et al. Phenylpropanoids from the leaves of *Acanthopanax koreanum* and their antioxidant activity [J]. *J Asian Nat Prod Res*, 2011, 13(1): 56-61.
- [31] Tuntiwachwuttikul P, Rayanil K, Taylor W C. Chemical constituents from the flowers of *Nyctanthes arbor-tristis* [J]. *Scienceasia*, 2003, 29: 21-30.
- [32] 刘晓艳, 徐嵬, 杨秀伟, 等. 鸡血藤非黄酮类化学成分的研究 [J]. 中国中药杂志, 2020, 45(5): 1120-1127.

[责任编辑 王文倩]