杜仲中的一个新环烯醚萜类化合物

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摘要: 利用硅胶、Sephadex LH-20 和 Toyopearl HW-40C 等柱色谱及半制备液相等分离纯化方法, 从杜仲中分离得到 11 个化合物。运用现代波谱学方法确定化合物的结构, 分别鉴定为 neoeucommiate A (**1**)、(7*S*,8*R*)-dihydrodehydrodiconiferyl alcohol (**2**)、urolignoside (**3**)、ficusal (**4**)、tiruneesiin (**5**)、glochidioboside (**6**)、forsythialansides B (**7**)、ecdysanol B (**8**)、(+)-syringaresinol-4-*O*-*β*-*D*-glucopyranoside (**9**)、(+)-pinoresinol-4-*O*-[6″-*O*-vanilloyl]-*β*-*D*-glucopyranoside (**10**) 和 samsesquinoside (**11**)。其中化合物 **1** 为新化合物, 化合物 **3**～**7**、**10**、**11** 为首次从杜仲中分离得到。

关键词: 杜仲; neoeucommiate A; 环烯醚萜; 木脂素; 化学成分

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A new iridoid from *Eucommia ulmoides*

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Abstract: Eleven compounds were isolated from *Eucommia ulmoides* by silica gel, Sephadex LH-20, HW-40C column chromatography and semi-preparative HPLC. Their structures were identified by modern spectroscopic methods as neoeucommiate A (**1**), (7*S*, 8*R*)-dihydrodehydrodiconiferyl alcohol (**2**), urolignoside (**3**), ficusal (**4**), tiruneesiin (**5**), glochidioboside (**6**), forsythialansides B (**7**), ecdysanol B (**8**), (+)-syringaresinol-4-*O*-*β*-*D*-glucopyranoside (**9**), (+)-pinoresinol 4-*O*-[6″-*O*-vanilloyl]-*β*-*D*-glucopyranoside (**10**), samsesquinoside (**11**). Compound **1** is a new compound, compounds **3**−**7**, **10** and **11** were isolated from *Eucommia ulmoides* for the first time.

Key words: *Eucommia*; neoeucommiate A; iridoids; lignans; chemical composition

杜仲 (*Eucommia ulmoides* Oliv.), 又名思仙、木棉、思仲等, 为单科单属种植物, 是我国特有的经济树种, 广泛分布于河南、四川、湖南、贵州、云南等省[1]。杜仲来源于杜仲的干燥树皮,《神农本草经》将其列为上品, 味甘, 性温。归肝、肾经, 具有补肝肾、强筋骨、安胎的功效, 常用于肝肾不足、腰膝酸痛、筋骨无力、头晕目眩、妊娠漏血、胎动不安等症[2]。杜仲的现代药理活性主要表现为抗骨质疏松、抗炎、神经保护、降血压、降血糖等[3]。现有研究表明, 杜仲的化学成分主要有木脂素类、环烯醚萜类、黄酮类、酚类、三萜类及甾体类

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等[4]。近年来, 杜仲作为一种药食同源资源, 其叶、籽、雄花等部分已开发成多种保健品及食品原料[5], 极大丰富了杜仲的应用价值, 其巨大的开发前景也引起了社会广泛关注。为了进一步了解杜仲的化学成分, 本实验以杜仲为研究对象, 对其进行系统的化学成分研究, 从中分离得到了1个环烯醚萜类化合物, 10个木脂素类化合物, 结构见图1。化合物**1**为新化合物, 化合物**3**～**7**、**10**、**11**为首次从杜仲中分离得到。

结果与讨论

1 结构鉴定

化合物**1**为淡黄色油状物, $[\alpha]_D^{20}$ +89.196 (*c* 0.084, CH_3OH); UV在202 nm处有最大吸收; IR光谱显示出酯羰基 (1 793 cm^{-1}) 吸收; HR-ESI-MS给出其准分子离子峰 *m*/*z* 283.117 6 $[M+H]^+$ (calcd for $C_{14}H_{19}O_6$, 283.117 6), 提示化合物**1**的分子式为$C_{14}H_{18}O_6$, 计算不饱和度为6。^{1}H NMR谱中 (500 MHz, DMSO-d_6) 谱中, 在 δ_H 5.71 (1H, s, H-7) 出现烯氢质子信号, δ_H 4.65 (1H, m, H-10a), 4.61 (1H, d, *J* = 13.5 Hz, H-10b), 4.40 (1H, dd, *J* = 12.5, 4.0 Hz, H-1a), 4.35 (1H, m, H-1b), 4.30 (1H, dd, *J* = 11.5, 6.0 Hz, H-11a), 4.03 (1H, dd, *J* = 11.5, 7.5 Hz, H-11b) 为3个连氧亚甲基的氢质子信号, δ_H 3.28 (1H, m, H-4), 3.18 (1H, m, H-9), 3.12 (1H, m, H-5) 为3个次甲基的氢质子信号, δ_H 2.03 (3H, s, H-15), 2.03 (3H, s, H-13) 为2个甲基的氢质子信号, δ_H 2.42 (1H, m, H-6a), 1.90 (1H, m, H-6b) 为1个亚甲基的氢质子信号。分析^{13}C NMR (125 MHz, DMSO-d_6) 谱并结合DEPT-135和HSQC谱可知, 化合物**1**中共有14个碳, 其中 δ_C 172.6 (C-3), 170.2 (C-12), 170.1 (C-14) 为3个羰基碳信号, δ_C 137.1 (C-8), 129.9 (C-7) 为一组双键的碳信号, δ_C 66.5 (C-1), 61.1 (C-11), 60.5 (C-10) 为3个连氧亚甲基的碳信号, δ_C 44.5 (C-9), 40.6 (C-4), 34.3 (C-6), 33.9 (C-5) 为1个亚甲基和3个次甲基的碳信号, δ_C 20.3 (C-13, 15) 为两个甲基的碳信号。^{1}H-^{1}H COSY谱中 (图2) 显示H-9 (δ_H 3.18) 与H-1 (δ_H 4.40, 4.35) 和H-5 (δ_H 3.12) 的相关信号, 说明该结构中含有一个-O-CH_2-CH-CH-的结构片段, H-6 (δ_H 2.42, 1.90) 与H-7 (δ_H 5.71) 和H-5 (δ_H 3.12) 具有相关、H-4 (δ_H 3.28) 与H-11 (δ_H 4.30, 4.03) 和H-5 (δ_H 3.12) 具有相关, 推测结构中含有一个-C=CH-CH_2-CH-CH-CH_2-O-的结构片段。

在HMBC谱 (图2) 中, H-11 (δ_H 4.30, 4.03) 与C-3 (δ_C 172.6)、C-12 (δ_C 170.2) 具有远程相关, H-13 (δ_H 2.03)与C-12 (δ_C 170.2) 有远程相关, H-1 (δ_H 4.40, 4.35) 与C-3 (δ_C 172.6)、C-5 (δ_C 33.9) 具有远程相关, 提示结

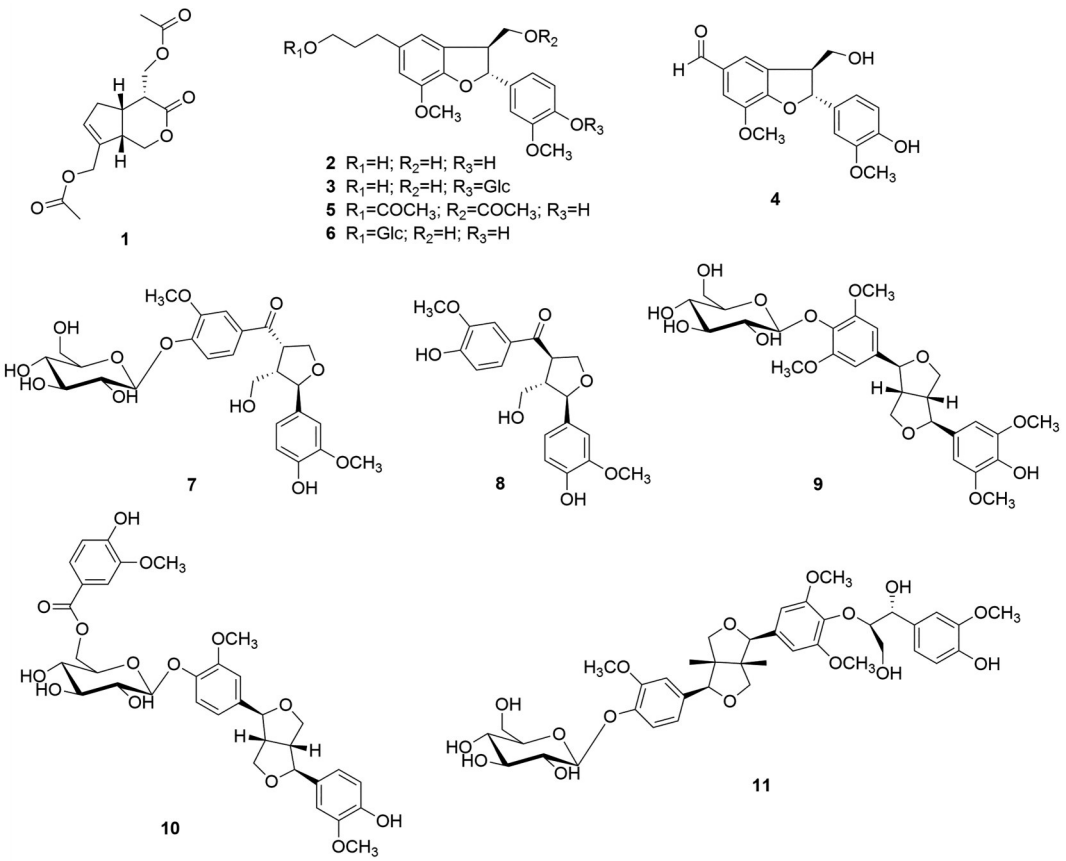

Figure 1 Structures of compound **1**–**11**

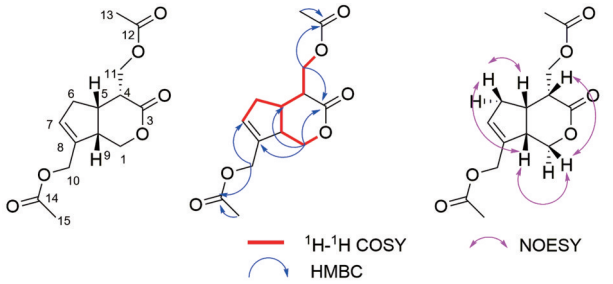

Figure 2 Structure of compound **1** and its key ^{1}H-^{1}H COSY, HMBC, and NOESY correlations

构中含有一个六元氧杂环和一个CH_3-CO-O-CH_2-的结构片段。H-1 (δ_H 4.40, 4.35) 与 C-8 (δ_C 137.1)、C-5 (δ_C 33.9) 具有远程相关, 提示结构中含有一个不饱和五元环并与六元氧杂环相连。H-10 (δ_H 4.65, 4.61) 与 C-14 (δ_C 170.1)、C-7 (δ_C 129.9) 具有远程相关, H-15 (δ_H 2.03) 与 C-14 (δ_C 170.1) 有远程相关, 提示结构中含有另一个CH_3-CO-O-CH_2-的结构片段与C-8 (δ_C 137.1) 相连。

化合物**1**的相对构型通过NOESY谱确定, 在NOESY谱中 (图2), H-4和H-9与H-1a相关, H-5和H-9与H-6a相关, 确定H-4、H-5和H-9在同侧。化合物**1**的绝对构型通过电子圆二色性计算与实验ECD对比来确定, 在TDDFT/B3LYP/6-31G(d,p)水平下使用SMD模式并添加色散校正计算。结果显示实验ECD曲线与构型为(4*R*,5*S*,9*S*)的曲线吻合较好 (图3)。最终确定化合物**1**的结构得到确定, 命名为neoeucommiate A。

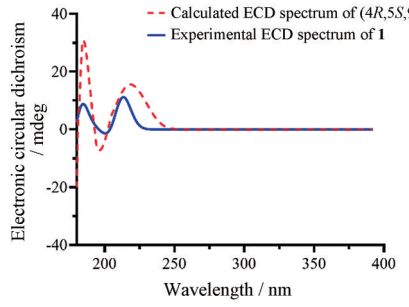

Figure 3 Calculated and experimental ECD spectra of compound **1**

2 讨论

本研究从杜仲中分离得到1个环烯醚萜类化合物, 10个木脂素类化合物, 其中木脂素类化合物结构涉及苯骈呋喃型木脂素、单环氧木脂素和双环氧木脂素, 1个环烯醚萜类化合物为新化合物, 7个木脂素类化合物为首次从杜仲中分离得到, 进一步丰富了杜仲的化学成分。前期研究报道杜仲在抗炎、抗肿瘤及抗氧化方面具有一定的药理活性, 化合物**2**、**9**～**11**具有较显著的抗氧化活性[6]; 化合物**3**、**8**具有较显著的抗炎活性[7], 化合物6能诱导真菌细胞凋亡[8]; 化合物**10**对PANC-1人胰腺癌细胞系具有细胞毒性[9]。

综上所述, 本研究丰富了杜仲的化学成分, 为探究杜仲的药效物质基础提供科学依据。

实验部分

Bruker AVANCE III 500型核磁共振仪 (TMS内标) 和Bruker maxis HD型飞行时间质谱 (德国布鲁克公司); Thermo EVO300型紫外分光光度计和Thermo Nicolet IS 10傅里叶变换红外光谱仪 (美国Thermo Scientific公司); Chirascan qCD圆二色光谱仪 (英国Applied Photophysics公司); Autopol IV全自动旋光仪 (美国鲁道夫公司); 赛谱锐思LC-52型高压制备液相色谱仪 (赛谱锐思北京科技有限公司); N-1111型冷冻水循环装置和N-1001型旋转蒸发仪 (上海埃朗仪器有限公司); 柱色谱填料Sephadex LH-20 (GE Healthcare公司); COSMOSIL 5C18-MS-Ⅱ色谱柱 (250 mm × 10 mm, 5 μm; 日本Nacalai Tesque公司); MCI gel CHP-20、Diaion HP-20大孔吸附树脂 (日本三菱化学公司); Toyopearl HW-40C (日本TOSOH公司); 柱色谱硅胶 (100～200和200～300目, 青岛海洋化工厂); 甲醇、乙腈 (色谱纯, 天津市富宇精细化工有限公司)。

杜仲药材购自安徽亳州药材市场, 经河南中医药大学董诚明教授鉴定为杜仲科杜仲属植物杜仲 (*Eucommia ulmoides* Oliv.) 的干燥树皮, 药材标本 (NO.20210603) 保存于河南省中药开发工程技术研究中心。

1 提取分离

杜仲的干燥树皮 (50 kg) 粉碎成粗颗粒, 用95%乙醇回流提取3次,减压浓缩得到浸膏。浸膏加适量水分散, 依次用石油醚、乙酸乙酯、正丁醇萃取, 得到石油醚部位 (600.5 g)、乙酸乙酯部位 (2.0 kg)、正丁醇部位 (260.4 g)。

乙酸乙酯部位 (2.0 kg) 用硅胶柱色谱分离, 并用石油醚−丙酮 (50∶1→1∶1) 进行梯度洗脱, 得到A～H共8个组分。对组分E (467.0 g) 进行硅胶柱色谱分离, 先以石油醚−丙酮 (200∶1→20∶1) 进行梯度洗脱, 再用二氯甲烷−甲醇 (200∶1→1∶1) 进行梯度洗脱, 通过TLC检识合并相同流分得到5个组分, 即Fr.1～Fr.5。对Fr.1 (60.3 g) 用硅胶柱色谱分离, 用石油醚−乙酸乙酯 (40∶1→1∶1) 进行梯度洗脱, 通过TLC检识合并相同流分得到9个组分, 即Fr.1-1～Fr.1-9。Fr.1-9 (6.5 g) 经MCI柱色谱分离, 用甲醇−水 (30∶70→100∶0) 进行梯度洗脱, 通过TLC检识合并相同流分得到11个组分, 即Fr.1-9-1～Fr.1-9-11。Fr.1-9-7 (1.1 g) 经半制备

液相色谱 (乙腈−水, 21∶79) 等度洗脱, 得到化合物 **1** (t_R = 53.0 min, 3.2 mg)。Fr.1-9-10 (837.6 mg) 经半制备液相色谱 (甲醇−水, 58∶42) 等度洗脱, 得到化合物 **5** (t_R = 43.3 min, 2.0 mg)。

正丁醇部位 (260.4 g) 上大孔吸附树脂柱 Diaion HP-20, 依次用水、20% 乙醇、40% 乙醇、60% 乙醇、80% 乙醇、95% 乙醇进行梯度洗脱, 对 40% 乙醇部位 (85.0 g) 上硅胶柱色谱分离, 用二氯甲烷−甲醇 (50∶1→1∶1) 进行梯度洗脱, 通过 TLC 检识合并相同流分得到 13 个组分, 即 D4-1～D4-13。D4-2 (2.8 g) 经 Sephadex LH-20 凝胶柱色谱分离, 用甲醇进行等度洗脱, 经 TLC 检识合并相同流分得到 4 个组分, 即 D4-2-1～D4-2-4。D4-2-3 (750.3 mg) 经半制备液相色谱 (甲醇−水, 34∶66) 等度洗脱, 得到化合物 **4** (t_R = 44.6 min, 3.2 mg)。D4-3 (1.6 g) 经 Toyopearl HW-40C 凝胶柱色谱分离, 用甲醇进行等度洗脱, 经 TLC 检识合并相同流分得到 5 个组分, 即 D4-3-1～D4-3-5。D4-3-3 (432.3 mg) 经半制备液相色谱 (甲醇−水, 36∶64) 等度洗脱, 得到化合物 **2** (t_R = 40.6 min, 8.0 mg)。D4-3-5 (131.1 mg) 经半制备液相色谱 (甲醇−水, 35∶65) 等度洗脱, 得到化合物 **8** (t_R = 37.6 min, 4.1 mg)。D4-4 (3.5 g) 经 Toyopearl HW-40C 凝胶柱色谱分离, 用甲醇进行等度洗脱, 经 TLC 检识合并相同流分得到 4 个组分, 即 D4-4-1～D4-4-4。D4-4-4 (1.9 g) 经硅胶柱色谱分离, 用二氯甲烷−甲醇 (30∶1→1∶1) 进行梯度洗脱, 通过 TLC 检识合并相同流分得到 5 个组分, 即 D4-4-4-1～D4-4-4-5。D4-4-4-2 (310.3 mg) 经半制备液相色谱 (甲醇−水, 46∶54) 等度洗脱, 得到化合物 **10** (t_R = 30.4 min, 4.2 mg)。D4-4-4-3 (523.6 mg) 经半制备液相色谱 (乙腈−水, 17∶83) 等度洗脱, 得到化合物 **9** (t_R = 37.0 min, 50.6 mg)。D4-6 (5.2 g) 经 Toyopearl HW-40C 凝胶柱色谱分离, 用甲醇−水 (60∶40) 进行等度洗脱, 经 TLC 检识合并相同流分得到 4 个组分, 即 D4-6-1～D4-6-4。D4-6-4 (835.7 mg) 经半制备液相色谱 (乙腈-水, 17∶83) 等度洗脱, 得到 5 个组分, 即 D4-6-4-1～D4-6-4-5, D4-6-4-3 即为化合物 **6** (t_R = 30.4 min, 6.0 mg)。D4-6-4-4 (71.3 mg) 经半制备液相色谱 (乙腈−水, 20∶80) 等度洗脱, 得到化合物 **11** (t_R = 46.0 min, 3.2 mg)。D4-7 (4.3 mg) 经 Sephadex LH-20 凝胶柱色谱分离, 用甲醇−水 (60∶40) 进行等度洗脱, 经 TLC 检识合并相同流分得到 4 个组分, 即 D4-7-1～D4-7-4。D4-7-1 (620.3 mg) 经半制备液相色谱 (乙腈−水, 17.∶83) 等度洗脱, 得到化合物 **3** (t_R = 21.0 min, 3.1 mg)。D4-7-2 (806.3 mg) 经半制备液相色谱 (乙腈−水, 13∶87) 等度洗脱, 得到化合物 **7** (t_R = 39.0 min, 5.6 mg)。

2 结构鉴定

化合物 **1** 黄色油状物, 易溶于甲醇, $[\alpha]_D^{20}$ +89.196 (*c* 0.084, CH_3OH); UV (CH_3OH) λ_{max} (log ε): 202 (3.65); IR ν_{max}: 1 793, 1 246, 1 158, 1 030 cm^{-1}, HR-ESI-MS *m*/*z*: 283.117 6 $[M+H]^+$ (计算值为 283.117 6.); ^1H NMR (500 MHz, DMSO-d_6) 和 ^{13}C NMR (125 MHz, DMSO-d_6) 数据见表 1。

Table 1 ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) data of compound **1** in DMSO-d_6

No.	δ_H (*J* in Hz)	δ_C	No.	δ_H (*J* in Hz)	δ_C
1a	4.40, dd (12.5, 4.0)	66.5	9	3.18, m	44.5
1b	4.35, m		10a	4.65, m	60.5
3	−	172.6	10b	4.61, d (13.5)	
4	3.28, m	40.6	11a	4.30, dd (11.5, 6.0)	61.1
5	3.12, m	33.9	11b	4.03, dd (11.5, 7.5)	
6a	2.42, m	34.3	12	−	170.2
6b	1.90, m		13	2.03, s	20.3
7	5.71, s	129.9	14	−	170.1
8	−	137.1	15	2.03, s	20.3

化合物 **2** 白色无定形粉末, 易溶于甲醇, ESI-MS *m*/*z* 383 $[M+Na]^+$, 分子式为 $C_{20}H_{24}O_6$。^1H NMR (500 MHz, CD_3OD) δ_H: 6.95 (1H, d, *J* = 2.0 Hz, H-2), 6.83 (1H, dd, *J* = 8.0, 2.0 Hz, H-6), 6.76 (1H, d, *J* = 8.0 Hz, H-5), 6.73 (2H, s, H-2′, 6′), 5.49 (1H, d, *J* = 6.5 Hz, H-7), 3. 85 (3H, s, 3′-OMe), 3.84 (1H, m, H-9a), 3.81 (3H, s, 3-OMe), 3.75 (1H, m, H-9b), 3.57 (2H, t, *J* = 6.5 Hz, H-9′), 3.47 (1H, t, *J* = 6.0 Hz, H-8), 2.62 (2H, m, H-7′), 1.81 (2H, m, H-8′); ^{13}C NMR (125 MHz, CD_3OD) δ_C: 134.8 (C-1), 110.5 (C-2), 149.1 (C-3), 147.5 (C-4), 116.1 (C-5), 119.7 (C-6), 88.9 (C-7), 55.4 (C-8), 65.0 (C-9), 136.33 (C-1′), 114.1 (C-2′), 145.2 (C-3′), 147.5 (C-4′), 129.9 (C-5′), 117.9 (C-6′), 32.9 (C-7′), 35.8 (C-8′), 62.2 (C-9′), 56.7 (3-OMe), 56.4 (3′-OMe)。以上数据与文献[10]对比, 确定化合物 **2** 为 (7*S*, 8*R*)-dihydrodehydrodiconiferyl alcohol。

化合物 **3** 白色无定形粉末, 易溶于甲醇, ESI-MS *m*/*z* 545 $[M+Na]^+$, 分子式为 $C_{26}H_{34}O_{11}$。^1H NMR (500 MHz, CD_3OD) δ_H: 7.14 (1H, d, *J* = 8.0 Hz, H-5), 7.03 (1H, d, *J* = 2.0 Hz, H-2), 6.93 (1H, dd, *J* = 8.0, 2.0 Hz, H-6), 6.74 (1H, s, H-6′), 6.72 (1H, s, H-2′), 5.56 (1H, d, *J* = 5.8 Hz, H-7), 4.89 (1H, d, *J* = 7.0 Hz, H-1″), 3.86 (3H, s, 3-OMe), 3.83 (3H, s, 3′-OMe), 3.75 (1H, dd, *J* = 11.0, 7.5 Hz, H-9a), 3.68 (1H, dd, *J* = 11.0, 4.0 Hz, H-6″a), 3.57 (2H, t, *J* = 6.5 Hz, H-9′), 3.50 (1H, m, H-9b), 3.45 (1H, m, H-8), 3.40 (1H, m, H-6″b), 3.33 (1H, m, H-5″), 3.28 (1H, m, H-4″), 3.25 (1H, m, H-3″),

3.16 (1H, m, H-2″), 2.62 (2H, t, *J* = 8.0 Hz, H-7′), 1.81 (2H, m, H-8′); ^{13}C NMR (125 MHz, CD_3OD) δ_C: 129.6 (C-1), 114.2 (C-2), 145.2 (C-3), 147.6 (C-4), 137.1 (C-5), 117.9 (C-6), 32.9 (C-7), 35.8 (C-8), 62.2 (C-9), 138.3 (C-1′), 111.1 (C-2′), 147.5 (C-3′), 150.9 (C-4′), 118.0 (C-5′), 119.4 (C-6′), 88.4 (C-7′), 55.7 (C-8′), 65.0 (C-9′), 102.7 (C-1″), 74.9 (C-2″), 78.2 (C-3″), 71.3 (C-4″), 77.8 (C-5″), 62.5 (C-6″), 56.7 (3-OMe), 56.7 (3′-OMe)。以上数据与文献[11]对比, 确定化合物**3**为urolignoside。

化合物**4** 黄色油状物, 易溶于甲醇, ESI-MS *m*/*z* 331 $[M+H]^+$, 分子式为$C_{18}H_{18}O_6$。^{1}H NMR (500 MHz, CD_3OD) δ_H: 9.76 (1H, s, H-7′), 7.52 (1H, s, H-2′), 7.46 (1H, s, H-6′), 6.95 (1H, d, *J* = 2.0 Hz, H-2), 6.84 (1H, dd, *J* = 8.0, 2.0 Hz, H-6), 6.79 (1H, d, *J* = 8.0 Hz, H-5), 5.66 (1H, d, *J* = 6.5 Hz, H-7), 3.93 (3H, s, 5′-OMe), 3.87 (2H, m, H-9), 3.82 (3H, s, 3-OMe), 3.61 (1H, m, H-8); ^{13}C NMR (125 MHz, CD_3OD) δ_C: 133.6 (C-1), 110.6 (C-2), 149.2 (C-3), 147.9 (C-4), 116.3 (C-5), 119.8 (C-6), 90.6 (C-7), 54.3 (C-8) 64.4 (C-9), 132.7 (C-1′), 122.3 (C-2′), 131.2 (C-3′), 155.6 (C-4′), 146.3 (C-5′), 113.8 (C-6′), 192.7 (C-7′) , 56.4 (3-OMe), 56.7 (5′-OMe)。以上数据与文献[12]对比, 确定化合物**4**为ficusal。

化合物**5** 黄色油状物, 易溶于甲醇, ESI-MS *m*/*z* 445 $[M+H]^+$, 分子式为$C_{24}H_{28}O_8$。^{1}H NMR (500 MHz, CD_3OD) δ_H: 6.95 (1H, d, *J* = 2.0 Hz, H-2), 6.83 (1H, dd, *J* = 8.1, 2.0 Hz, H-6), 6.78 (1H, d, *J* = 8.1 Hz, H-5), 6.75 (1H, s, H-2′), 6.71 (1H, s, H-6′), 5.44 (1H, d, *J* = 7.0 Hz, H-7), 4.41 (1H, dd, *J* = 11.0, 5.5 Hz, H-9a), 4.32 (1H, dd, *J* = 11.0, 7.5 Hz, H-9b), 4.06 (2H, t, *J* = 6.5 Hz, H-9′), 3.86 (3H, s, 3′-OMe), 3.82 (3H, s, 3-OMe), 3.71 (1H, m, H-8), 2.65 (2H, t, *J* = 7.5 Hz, H-7′), 2.03 (3H, s, 10′-OMe), 1.99 (3H, s, 10′-OMe), 1.94 (2H, m, H-8′); ^{13}C NMR (125 MHz, CD_3OD) δ_C: 133.9 (C-1), 110.6 (C-2), 149.2 (C-3), 147.7 (C-4), 116.2 (C-5), 120.1 (C-6), 89.6 (C-7), 51.9 (C-8), 66.7 (C-9), 172.6 (C-10), 20.7 (C-11), 136.4 (C-1′), 114.4 (C-2′), 145.4 (C-3′), 147.8 (C-4′), 128.9 (C-5′), 117.7 (C-6′), 32.9 (C-7′), 31.7 (C-8′), 64.9 (C-9′), 173.0 (C-10′), 20.8 (C-11′), 56.4 (3-OMe), 56.7 (3′-OMe)。以上数据与文献[13]对比, 确定化合物**5**为tiruneesiin。

化合物**6** 无色无定形粉末, 易溶于甲醇, ESI-MS *m*/*z* 521 $[M-H]^-$, 分子式为$C_{26}H_{34}O_{11}$。^{1}H NMR (500 MHz, CD_3OD) δ_H: 6.95 (1H, d, *J* = 2.0 Hz, H-2), 6.83 (1H, dd, *J* = 8.0, 2.0 Hz, H-6), 6.77 (1H, d, *J* = 8.0 Hz, H-5), 6.75 (2H, s, H-2′, H-6′), 5.49 (1H, d, *J* = 6.5 Hz, H-7), 4.26 (1H, m, H-1″), 3.90 (1H, m, H-9′a) 3.87 (1H, m, H-6″a), 3.85 (3H, s, 3′-OMe), 3.83 (1H, m, H-9a), 3.81 (3H, s, 3-OMe), 3.76 (1H, m, H-9b), 3.66 (1H, m, H-6″b), 3.54 (1H, m, H-9′b), 3.47 (1H, m, H-8), 3.36 (1H, m, H-3″), 3.29 (1H, m, H-4″), 3.26 (1H, m, H-5″), 3.20 (1H, m, H-2″), 2.68 (2H, t, *J* = 7.5 Hz, H-7′), 1.90 (2H, m, H-8′); ^{13}C NMR (125 MHz, CD_3OD) δ_C: 134.8 (C-1), 110.5 (C-2), 149.1 (C-3), 147.5 (C-4), 116.1 (C-5), 119.7 (C-6), 89.0 (C-7), 55.5 (C-8), 65.0 (C-9), 136.8 (C-1′), 114.2 (C-2′), 145.2 (C-3′), 147.5 (C-4′), 129.8 (C-5′), 118.1 (C-6′), 32.9 (C-7′), 32.9 (C-8′), 70.0 (C-9′), 104.5 (C-1″), 75.2 (C-2″), 78.1 (C-3″), 71.7 (C-4″), 77.9 (C-5″), 62.8 (C-6″) , 56.4 (3-OMe), 56.8 (3′-OMe)。以上数据与文献[14]对比, 确定化合物**6**为glochidioboside。

化合物**7** 黄色无定形粉末, 易溶于甲醇, ESI-MS *m*/*z* 559 $[M+Na]^+$, 分子式为$C_{26}H_{32}O_{12}$。^{1}H NMR (500 MHz, CD_3OD) δ_H: 7.69 (1H, d, *J* = 8.5, 2.0 Hz, H-6), 7.66 (1H, dd, *J* = 2.0 Hz, H-2), 7.26 (1H, d, *J* = 8.5 Hz, H-5), 7.05 (1H, d, *J* = 1.8 Hz, H-2′), 6.84 (1H, d, *J* = 8.0, 1.8 Hz, H-6′), 6.76 (1H, d, *J* = 8.0 Hz, H-5′), 5.06 (1H, d, *J* = 7.5 Hz, H-1″), 4.64 (1H, d, *J* = 8.5 Hz, H-7′), 4.27 (1H, m, H-8), 4.19 (1H, m, H-9a), 4.17 (1H, m, H-9b), 3.93 (3H, s, 3-OMe), 3.91 (1H, m, H-6″a), 3.88 (3H, s, 3′-OMe), 3.67 (1H, m, H-6″b), 3.64 (2H, m, H-9′a), 3.55 (1H, m, H-2″), 3.51 (1H, m, H-5″), 3.48 (1H, m, H-3″), 3.42 (1H, m, H-4″), 2.69 (1H, m, H-8′); ^{13}C NMR (125 MHz, CD_3OD) δ_C: 132.4 (C-1), 113.0 (C-2), 150.8 (C-3), 152.5 (C-4), 116.3 (C-5), 124.3 (C-6), 200.4 (C-7), 50.5 (C-8), 71.6 (C-9), 133.5 (C-1′), 111.4 (C-2′), 149.1 (C-3′), 147.5 (C-4′), 115.8 (C-5′), 121.0 (C-6′), 85.3 (C-7′), 54.6 (C-8′), 61.4 (C-9′), 101.8 (C-1″), 74.7 (C-2″), 78.4 (C-3″), 71.2 (C-4″), 77.8 (C-5″), 62.4 (C-6″), 56.7 (3-OMe), 56.4 (3′-OMe)。以上数据与文献[15]对比, 确定化合物**7**为forsythialansides B。

化合物**8** 黄色无定形粉末, 易溶于甲醇, ESI-MS *m*/*z* 373 $[M+Na]^+$, 分子式为$C_{20}H_{22}O_7$。^{1}H NMR (500 MHz, CD_3OD) δ_H: 7.62 (1H, overlapped, H-6), 7.61 (1H, overlapped, H-2), 7.06 (1H, d, *J* = 2.0 Hz, H-2′), 6.88 (1H, d, *J* = 8.5 Hz, H-5), 6.85 (1H, d, *J* = 8.0, 2.0 Hz, H-6′), 6.76 (1H, d, *J* = 8.0 Hz, H-5′), 4.64 (1H, d, *J* = 9.0 Hz, H-7′), 4.26 (1H, m, H-8), 4.19 (1H, t, *J* = 8.5 Hz, H-9a), 4.15 (1H, dd, *J* = 8.5, 5.5 Hz, H-9b), 3.92 (3H, s, 3-OMe), 3.88 (3H, s, 3′-OMe), 3.65 (1H, m, H-9′a), 3.60 (1H, m, H-9′b), 2.69 (1H, m, H-8′); ^{13}C NMR

(125 MHz, CD_3OD) δ_C: 129.8 (C-1), 112.4 (C-2), 154.1 (C-3), 149.3 (C-4), 116.0 (C-5), 125.1 (C-6), 200.3 (C-7), 50.2 (C-8), 61.2 (C-9), 133.5 (C-1′), 111.4 (C-2′), 149.1 (C-3′), 147.5 (C-4′), 115.8 (C-5′), 121.0 (C-6′), 85.3 (C-7′), 54.6 (C-8′) 71.8 (C-9′), 56.4 (3-OMe), 56.3 (3′-OMe)。以上数据与文献[16]对比, 确定化合物**8**为ecdysanol B。

化合物**9** 无色无定形粉末, 溶于甲醇, $[\alpha]_D^{20}$ +9.485 (*c* 0.2, CH_3OH); ESI-MS *m*/*z* 579 $[M-H]^-$, 分子式为 $C_{28}H_{36}O_{13}$。^{1}H NMR (500 MHz, DMSO-d_6) δ_H: 8.27 (1H, s, 4′-OH), 6.65 (2H, s, H-2, 6), 6.59 (2H, s, H-2′, 6′), 4.88 (1H, m, H-1″), 4.66 (1H, d, *J* = 4.5 Hz, H-7′), 4.93～4.15 (4H, m, 2″, 3″, 4″, 6″-OH), 4.61 (1H, dd, *J* = 4.5 Hz, H-7), 4.26 (1H, m, H-9a), 4.17 (1H, m, H-9b), 4.167 (1H, m, H-9′a), 3.81 (1H, m, H-9′b), 3.76 (6H, s, 3′, 5′-OMe), 3.75 (6H, s, 3, 5-OMe), 3.81-3.19 (6H, m, H-2″, 3″, 4″, 6″); ^{13}C NMR (125 MHz, DMSO-d_6) δ_C: 133.7 (C-1), 104.2 (C-2), 152.7 (C-3, 5), 134.9 (C-4), 104.2 (C-6), 85.2 (C-7), 53.8 (C-8), 71.2 (C-9), 131.4 (C-1′), 103.7 (C-2′, 6′), 147.9 (C-3′, 5′), 137.3 (C-4′), 85.4 (C-7′), 53.7 (C-8′), 71.3 (C-9′), 102.7 (C-1″), 74.2 (C-2″), 76.6 (C-3″), 70.0 (C-4″), 77.3 (C-5″), 60.9 (C-6″), 56.5 (3, 5-OMe), 56.1 (3′, 5′-OMe)。以上数据与文献[17]对比, 确定化合物**9**为 (+)-syringaresinol-4-*O*-*β*-*D*-glucopyranoside。

化合物**10** 无色无定形粉末, 易溶于甲醇, $[\alpha]_D^{20}$ +15.359 (*c* 0.4, CH_3OH); ESI-MS *m*/*z* 693 $[M+Na]^+$, 分子式为 $C_{34}H_{38}O_{14}$。^{1}H NMR (500 MHz, CD_3OD) δ_H: 7.82 (1H, dd, *J* = 8.0, 1.9 Hz, H-6′), 7.58 (1H, dd, *J* = 8.5, 1.9 Hz, H-6‴), 7.54 (1H, d, *J* = 1.9 Hz, H-2‴), 6.98 (1H, d, *J* = 1.9 Hz, H-2′), 6.97 (1H, overlapped, H-5), 6.95 (1H, overlapped, H-2), 6.87 (1H, d, *J* = 8.5 Hz, H-5‴), 6.78 (1H, d, *J* = 8.0 Hz, H-5′), 6.44 (1H, dd, *J* = 8.5, 2.0 Hz, H-6), 4.87 (1H, overlapped, H-1″), 4.67 (2H, m, H-7, 7′), 4.63 (1H, m, H-6″a), 4.46 (1H, m, H-6″b), 4.24 (2H, dd, *J* = 9.0, 7.2 Hz, H-9a, 9′a), 3.87 (3H, s, 3′-OMe), 3.83 (6H, s, 3′, 3‴-OMe), 3.82 (1H, m, H-9′b), 3.80 (1H, m, H-9b), 3.76 (1H, m, H-5″), 3.54 (1H, m, H-2″), 3.49 (1H, m, H-3″), 3.41 (1H, t, *J* = 9.5 Hz, H-4″), 3.08 (1H, m, H-8′), 2.98 (1H, m, H-8); ^{13}C NMR (125 MHz, CD_3OD) δ_C: 137.4 (C-1), 111.6 (C-2), 150.7 (C-3), 147.1 (C-4), 117.7 (C-5), 119.3 (C-6), 87.0 (C-7), 55.4 (C-8), 72.8 (C-9), 133.7 (C-1′), 111.0 (C-2′), 149.1 (C-3′), 147.3 (C-4′), 116.1 (C-5′), 120.2 (C-6′), 87.6 (C-7′), 55.3 (C-8′), 72.5 (C-9′), 102.4 (C-1″), 74.8 (C-2″), 77.8 (C-3″), 72.2 (C-4″), 75.6 (C-5″), 65.0 (C-6″), 122.5 (C-1‴), 113.9 (C-2‴), 148.8 (C-3‴), 153.0 (C-4‴), 116.0 (C-5‴), 125.3 (C-6‴), 167.7 (C-7‴), 56.7 (3-OMe), 56.4 (3′-OMe), 56.5 (3‴-OMe)。以上数据与文献[18]对比, 确定化合物**10**为 (+)-pinoresinol-4-*O*-[6″-*O*-vanilloyl]-*β*-*D*-glucopyranoside。

化合物**11** 黄色无定形粉末, 易溶于甲醇, ESI-MS *m*/*z* 769 $[M+Na]^+$, 分子式为 $C_{37}H_{46}O_{16}$。^{1}H NMR (500 MHz, CD_3OD) δ_H: 7.09 (1H, d, *J* = 8.5 Hz, H-5″), 7.04 (1H, d, *J* = 2.0 Hz, H-2″), 6.95 (1H, d, *J* = 2.0 Hz, H-2), 6.89 (1H, dd, *J* = 8.5, 2.0 Hz, H-6″), 6.81 (1H, dd, *J* = 8.0, 2.0 Hz, H-6), 6.78 (1H, d, *J* = 8.0 Hz, H-5), 6.66 (2H, s, H-2′, 6′), 4.91 (1H, d, *J* = 6.0 Hz, H-7″), 4.88 (1H, overlapped, H-1‴), 4.74 (1H, d, *J* = 4.0 Hz, H-7′), 4.71 (1H, m, H-7), 4.29 (1H, m, H-8″), 4.27 (2H, m, H-9), 3.89 (1H, m, H-9″a), 3.87 (2H, m, H-9′), 3.86 (3H, s, 3″-OMe), 3.83 (3H, s, 3-OMe), 3.81 (6H, s, 3′, 5′-OMe), 3.84 (1H, m, H-6‴a), 3.68 (1H, m, H-6‴b), 3.60 (1H, m, H-9″b), 3.47 (1H, m, H-2‴), 3.45 (1H, m, H-5‴), 3.41 (1H, m, H-4‴), 3.38 (1H, m, H-3‴), 3.14 (2H, m, H-8, H-8′); ^{13}C NMR (125 MHz, CD_3OD) δ_C: 133.7 (C-1), 110.1 (C-2), 149.1 (C-3), 147.3 (C-4), 116.1 (C-5), 120.0 (C-6), 87.4 (C-7), 55.3 (C-8), 72.9 (C-9), 138.9 (C-1′), 104.2 (C-2′, 6′), 154.4 (C-3′, 5′), 136.0 (C-4′), 87.3 (C-7′), 55.7 (C-8′), 72.7 (C-9′), 137.3 (C-1″), 112.3 (C-2″), 150.3 (C-3″), 147.2 (C-4″), 117.2 (C-5″), 120.9 (C-6″), 73.8 (C-7″), 86.9 (C-8″), 62.5 (C-9″), 102.7 (C-1‴), 74.9 (C-2‴), 78.2 (C-3‴), 71.4 (C-4‴), 77.8 (C-5‴), 61.7 (C-6‴), 56.7 (3, 3′-OMe), 56.6 (5″-OMe), 56.4 (3″-OMe)。以上数据与文献[19]对比, 确定化合物**11**为samsesquinoside。

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