

• 化学成分 •

五味子中 1 个新的联苯环辛烯类木脂素

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摘要: 目的 研究中药五味子 *Schisandra chinensis* 的木脂素类化学成分。方法 采用硅胶柱色谱、中压反相柱色谱、半制备和制备液相对五味子中富含木脂素类成分的石油醚萃取部位进行分离、纯化, 通过波谱数据鉴定化合物的结构。结果 从五味子中分离得到了 26 个化合物, 分别鉴定为绿叶五味子素 B (1)、sphaerandrin A (2)、sieverlignan E (3)、arisanschinin G (4)、widdaranal F (5)、戈米辛 A (6)、戈米辛 B (7)、戈米辛 D (8)、戈米辛 G (9)、(-)-戈米辛 K₁ (10)、(+)-戈米辛 K₂ (11)、(-)-戈米辛 L₁ (12)、(+)-戈米辛 M₁ (13)、戈米辛 N (14)、当归酰戈米辛 H (15)、当归酰戈米辛 O (16)、当归酰戈米辛 Q (17)、苯甲酰戈米辛 Q (18)、五味子醇甲 (19)、五味子甲素 (20)、五味子乙素 (21)、五味子丙素 (22)、五味子酯丙 (23)、neglschisandrin E (24)、7(18)-dehydroschisandro A (25)、安五脂素 (26), 其中 24 个为联苯环辛烯类木脂素 (1~4、6~25)。结论 化合物 1 为新化合物, 化合物 2~5 为首次从该植物中分离得到。

关键词: 五味子; 绿叶五味子素 B; 联苯环辛烯类木脂素; sphaerandrin A; sieverlignan E; arisanschinin G; widdaranal F; 五味子醇甲

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A new dibenzocyclooctadiene lignan from *Schisandra chinensis*DI Tong-lian¹, LIU Xiao-qing², WU Nan¹, CHEN Xiao-yuan¹, FAN Jun-ting³, TAN Ning-hua¹

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Abstract: Objective To study the lignans in *Schisandra chinensis*. **Methods** The petroleum ether extract mainly contained lignans of *S. chinensis* was isolated and purified by silica gel column chromatography, medium pressure reversed phase column chromatography, semi-prepared and prepared liquid chromatography. The structures of compounds were identified by spectral data. **Results** Twenty-six compounds were obtained, in which 24 were dibenzocyclooctadiene lignans. They were identified as schiviridin B (1), sphaerandrin A (2), sieverlignan E (3), arisanschinin G (4), widdaranal F (5), gomisin A (6), gomisin B (7), gomisin D (8), gomisin G (9), (-)-gomisin K₁ (10), (+)-gomisin K₂ (11), (-)-gomisin L₁ (12), (+)-gomisin M₁ (13), gomisin N (14), angeloylgomisin H (15), angeloylgomisin O (16), angeloylgomisin Q (17), benzoylgomisin Q (18), schisandrin (19), schisandrin A (20), γ -schisandrin (21), schisandrin C (22), schisantherin C (23), neglschisandrin E (24), 7(18)-dehydroschisandro A (25), and anwulignan (26). **Conclusion** Compound 1 is new and compounds 2—5 are isolated from this plant for the first time.

Key words: *Schisandra chinensis* (Turcz.) Baill.; schiviridin B; dibenzocyclooctadiene lignans; sphaerandrin A; sieverlignan E; arisanschinin G; widdaranal F; schisandrin

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五味子为木兰科植物五味子 *Schisandra chinensis* (Turcz.) Baill. 的干燥成熟果实, 始载于《神农本草经》, 列为上品, 习称“北五味子”, 道地产区为黑龙江、吉林、辽宁等地。五味子具有收敛固涩、益气生津、补肾宁心等功效, 可用于治疗久咳虚喘、久泻不止、津伤口渴等症^[1]。五味子中富含木脂素、萜类、挥发油、多糖、酚酸、黄酮、植物甾醇等多类成分, 其中木脂素类是其特征活性成分^[2]。五味子作为苏黄止咳胶囊复方中的臣药, 研究发现其木脂素类成分具有舒张气管平滑肌^[3]、抗炎^[4-6]、抗纤维化^[7-8]、镇咳平喘^[9-11]的功效, 可能是该中成药发挥药效的活性成分。前期课题组利用 LC-MS 技术对苏黄止咳胶囊的化学成分进行分析和药材溯源, 鉴定出 300 多个化合物^[12-13], 其中包含 29 个木脂素并主要来源于五味子, 且研究结果表明五味子醇甲是影响该药质量的主要成分^[14]。因此本研究苏黄止咳胶囊臣药五味子的化学成分, 有助于进一步阐明苏黄止咳胶囊的药效物质基础及其质量标准研究。

本实验采用硅胶柱色谱、中压反相柱色谱、半制备和制备液相对五味子水提物富含木脂素的石油醚萃取部位进行分离纯化, 共得到 25 个木脂素和 1 个倍半萜, 包括 24 个联苯环辛烯类木脂素 (1~4、6~25), 分别鉴定为绿叶五味子素 B (schiviridin B, 1)、sphaerandrin A (2)、sieverlignan E (3)、arisanschinin G (4)、widdaranal F (5)、戈米辛 A (gomisin A, 6)、戈米辛 B (gomisin B, 7)、戈米辛 D (gomisin D, 8)、戈米辛 G (gomisin G, 9)、(-)-戈米辛 K₁ [(-)-gomisin K₁, 10]、(+)-戈米辛 K₂ [(+)-gomisin K₂, 11]、(-)-戈米辛 L₁ [(-)-gomisin L₁, 12]、(+)-戈米辛 M₁ [(+)-gomisin M₁, 13]、戈米辛 N (gomisin N, 14)、当归酰戈米辛 H (angeloylgomisin H, 15)、当归酰戈米辛 O (angeloylgomisin O, 16)、当归酰戈米辛 Q (angeloylgomisin Q, 17)、苯甲酰戈米辛 Q (benzoylgomisin Q, 18)、五味子醇甲 (schisandrin, 19)、五味子甲素 (schisandrin A, 20)、五味子乙素 (γ -schisandrin, 21)、五味子丙素 (schisandrin C, 22)、五味子酯丙 (schisantherin C, 23)、neglschisandrin E (24)、7(18)-dehydroschisandro A (25)、安五脂素 (anwulignan, 26)。其中化合物 1 为新化合物, 化合物 2~5 为首次从该药材中分离得到。

1 药材、仪器与材料

五味子 (10 kg) 由扬子江药业集团北京海燕药

业有限公司提供, 样品 (ID-210831) 保存于中国药科大学中药学院谭宁华教授团队实验室, 经中国药科大学中药学院秦民坚教授鉴定为植物五味子 *S. chinensis* (Turcz.) Baill. 的干燥成熟果实。

Shimadzu UV-2600i 型紫外光谱仪 (日本 Shimadzu 有限公司); Bruker AV-400 型核磁共振仪 (德国 Bruker 公司); Rudolph Autopl IV 型旋光仪 (美国 Rudolph 有限公司); Bruker Tensor-27 型红外光谱仪 (德国 Bruker 公司); Japan Jasco J810 型圆二光谱仪 (日本分光 JASCO 公司); Angilent 1260-6230 TOF 液质联用仪 (美国 Angilent 公司); Waters Xevo TQD 质谱仪 (美国 Waters 公司); LC 3000 I 型制备型 HPLC (北京创新通恒科技有限公司)。半制备型液相色谱柱、制备型液相色谱柱以及分析型液相色谱柱分别为 YMC-Pack ODS-A C₁₈ 柱系列 (250 mm×10 mm, 5 μ m, 日本 YMC 公司)、YMC-Pack ODS-A C₁₈ 柱系列 (250 mm×20 mm, 5 μ m, 日本 YMC 公司)、Waters ACQUITY UPLC HSS T3 色谱柱 (100 mm×2.1 mm, 1.8 μ m, 美国 Waters 公司)。柱色谱硅胶 (100~200、200~300 目) 以及 GF254 薄层板 (青岛裕明源硅胶试剂厂); 反相材料 Lichroprep RP-18 (40~63 μ m, 美国 Merck 公司); 显色剂为 5% 硫酸乙醇溶液; 实验所用试剂均为分析纯 (无锡市亚盛集团化学试剂有限公司) 和色谱纯 (美国 TEDIA 公司和 Merck 公司); LC-MS 级甲酸 (德国 Sigma-Aldrich 公司)。

2 提取与分离

干燥的五味子 10 kg, 粉碎, 用 10 倍量的水煎煮 3 次, 每次 1 h, 水提液减压浓缩得浸膏。浸膏以水溶解, 用石油醚、醋酸乙酯、正丁醇依次萃取 3~4 次, 萃取液减压浓缩得各萃取部位浸膏。各萃取部位浸膏经 TLC、LC-MS 检测, 确定所需木脂素类成分主要集中在石油醚萃取部位。然后石油醚部位 (80.4 g) 首先通过硅胶柱色谱 (200~300 目硅胶), 以石油醚-醋酸乙酯 (10:0~0:10) 梯度洗脱, 减压浓缩, TLC、LC-MS 检测合并, 得到 6 个流分 (Fr. 1~6)。

Fr. 2 (5.936 g) 经硅胶柱色谱, 以石油醚-醋酸乙酯 5 个梯度 (80:1、40:1、20:1、10:1、0:1) 进行洗脱, 利用 TLC 和 LC-MS 检测, 合并获得 7 个亚流分 (Fr. 2-1~2-7)。Fr. 2-3 (473 mg) 经反复硅胶柱色谱及制备型 HPLC (75% 乙腈) 纯化得到化合物 16 (34 mg, t_R =51.6 min)、22 (18 mg,

$t_R=38.8$ min)、**26** (33 mg, $t_R=23.1$ min)。Fr. 2-5 (3.7 g) 经反复硅胶柱色谱及制备型 HPLC (72%乙腈) 纯化得到化合物 **14** (958 mg, $t_R=33.0$ min)、**21** (304 mg, $t_R=35.3$ min)。Fr. 3 (22.555 g) 经硅胶柱色谱, 石油醚-醋酸乙酯 (50:1、40:1、20:1、10:1、5:1、3:1、0:1) 梯度洗脱, 得到 9 个亚流分 (Fr. 3-1~3-9)。Fr. 3-5 (5.385 g) 经反复硅胶柱色谱及制备型 HPLC (60%乙腈) 纯化得到化合物 **1** (8 mg, $t_R=33.6$ min)、**5** (56 mg, $t_R=41.6$ min)、**10** (16 mg, $t_R=27.6$ min)、**11** (10 mg, $t_R=24.9$ min)、**12** (19 mg, $t_R=54.0$ min)、**13** (35 mg, $t_R=55.8$ min)、**20** (206 mg, $t_R=29.6$ min)、**24** (22 mg, $t_R=21.0$ min)、**25** (16 mg, $t_R=22.5$ min)。Fr. 3-7 (8.056 g) 经反复硅胶柱色谱及制备型 HPLC (60%乙腈) 纯化得到化合物 **9** (24 mg, $t_R=36.6$ min)。Fr. 4 (22.91 g) 经硅胶柱色谱, 石油醚-醋酸乙酯 (20:1、10:1、5:1、3:1、0:1) 梯度洗脱, 得到 5 个亚流分 Fr. 4-1~4-5。Fr. 4-2 (2.474 g) 经制备型 HPLC (60%乙腈) 纯化得到化合物 **4** (6 mg, $t_R=38.2$ min)、**6** (252 mg, $t_R=19.1$ min)、**7** (51 mg, $t_R=34.5$ min)、**17** (217 mg, $t_R=26.5$ min)、**23** (21 mg, $t_R=31.4$ min)。Fr. 4-3 (15.896 g) 经 RP-18

中压反相柱色谱, 甲醇-水 (30%~100%) 梯度洗脱, 利用 TLC 和 LC-MS 检测合并, 得到 4 个亚流分 Fr. 4-3-1~4-3-4, 其中 Fr. 4-3-2 (10.202 g) 经检测为化合物 **19** (10.202 g)。Fr. 4-3-3 (1.802 g) 经制备型 HPLC (60%乙腈) 纯化得到化合物 **2** (15 mg, $t_R=19.7$ min)、**3** (21 mg, $t_R=23.8$ min)、**8** (71 mg, $t_R=15.8$ min)、**15** (608 mg, $t_R=25.6$ min)、**18** (57 mg, $t_R=27.1$ min)。

3 结构鉴定

化合物 **1**: 黄色固体 (甲醇), 易溶于三氯甲烷。 $[\alpha]_D^{20} +82.1^\circ$ (c 0.067, MeOH), HR-ESI-MS (m/z 519.197 31 $[M+Na]^+$; 计算值 519.198 94), 可确定化合物 **1** 分子式为 $C_{28}H_{32}O_8$, 不饱和度为 13。紫外光谱显示其在 225 nm 处有最大吸收, 表明化合物结构中存在较强的共轭系统。红外光谱在 3398、1641、1456、1396、1033 cm^{-1} 处有吸收, 提示分子中含有苯环、羰基、双键。化合物 **1** 的 1H -NMR 和 ^{13}C -NMR 谱 (表 1) 与 schiviridin A^[15] 较为相似, 提示其为联苯环辛烯类木脂素。

化合物 **1** 的 1H -NMR 谱 (表 1) 显示 2 个芳环质子信号 δ_H 6.73 (1H, s), 6.48 (1H, s); 1 个连酯基质子信号 δ_H 6.42 (1H, s); 1 个亚甲二氧基质子信号 δ_H

表 1 化合物 **1** 的 1H -NMR 和 ^{13}C -NMR 数据 (400/100 MHz, $CDCl_3$)

Table 1 1H -NMR and ^{13}C -NMR of compound **1** (400/100 MHz, $CDCl_3$)

碳位	δ_C	δ_H	碳位	δ_C	δ_H
1	141.4 (C)		15	122.0 (C)	
2	137.2 (C)		16	122.6 (C)	
3	148.7 (C)		17	20.3 (CH ₃)	1.21 (3H, d, $J=6.8$ Hz)
4	105.0 (CH)	6.73 (1H, s)	18	111.3 (CH ₂)	4.83 (1H, s, H-18a) 4.60 (1H, s, H-18b)
5	132.9 (C)		1'	166.3 (C)	
6	78.6 (CH)	6.42 (1H, s)	2'	127.5 (C)	
7	149.2 (C)		3'	139.6 (CH)	5.95 (1H, m)
8	39.9 (CH)	2.58 (1H, overlapped)	4'	15.8 (CH ₃)	1.87 (3H, dq, $J=7.2, 1.6$ Hz)
9	41.1 (CH ₂)	2.54 (1H, overlapped, H-9 α) 2.24 (1H, dd, $J=12.2, 9.6$ Hz, H-9 β)	5'	20.1 (CH ₃)	1.51 (3H, q, $J=1.6$ Hz)
10	136.4 (C)		1-OCH ₃	59.8 (CH ₃)	3.78 (3H, s)
11	107.0 (CH)	6.48 (1H, s)	2,3-OCH ₂ O	101.4 (CH ₂)	5.99 (1H, d, $J=1.4$ Hz) 5.97 (1H, d, $J=1.4$ Hz)
12	153.3 (C)	/	12-OCH ₃	56.1 (CH ₃)	3.88 (3H, s)
13	140.0 (C)	/	13-OCH ₃	60.9 (CH ₃)	3.84 (3H, s)
14	151.9 (C)	/	14-OCH ₃	60.6 (CH ₃)	3.61 (3H, s)

5.99 (1H, d, $J = 1.4$ Hz), 5.97 (1H, d, $J = 1.4$ Hz); 2 个末端烯氢质子信号 δ_{H} 4.83 (1H, s), 4.60 (1H, s); 4 个甲氧基质子信号 δ_{H} 3.88 (3H, s), 3.84 (3H, s), 3.78 (3H, s), 3.61 (3H, s); 1 个次甲基质子信号 δ_{H} 2.58 (1H, overlapped); 1 个亚甲基质子信号 δ_{H} 2.54 (1H, overlapped), 2.24 (1H, dd, $J = 12.2, 9.6$ Hz); 1 个甲基质子信号 δ_{H} 1.21 (3H, d, $J = 6.8$ Hz); 还具有偶合系统的质子信号 δ_{H} 5.95 (1H, m), 1.87 (3H, dq, $J = 7.2, 1.6$ Hz), 1.51 (3H, q, $J = 1.6$ Hz), 结合 ^{13}C -NMR 谱 (表 1) 的酯基碳 (δ_{C} 166.3) 和烯碳 (δ_{C} 139.6, 127.5), 以及 ^1H - ^1H COSY 谱中 H-3'/H-4' 相关信号, 可以推导为当归酰基信号。 ^{13}C -NMR 结合 HSQC 谱显示化合物 **1** 中有 28 个碳信号, 包括 4 个甲氧基、3 个甲基、1 个亚甲二氧基、2 个亚甲基、5 个次甲基、12 个季碳、1 个酯基。

^1H - ^1H COSY 谱中 (图 1), H-8 与 H-9、H-17

相关, 表明 C-8、C-9、C-17 相连。HMBC 谱中 (图 1) 显示, H-6 (δ_{H} 6.42) 与 C-4、C-5、C-7、C-8、C-16、C-18、C-1' 相关; H-9 (δ_{H} 2.24, 2.54) 与 C-11、C-8、C-10、C-15、C-7 存在相关信号; 芳环 H-4 (δ_{H} 6.73) 与 C-2、C-3、C-16 相关, 芳环氢 H-11 (δ_{H} 6.48) 与 C-12、C-13、C-15 相关; 这些相关信号提示含有联苯环辛烯类木脂素的基本骨架。其中, H-6 与 C-1' 存在相关信号, 表明 C-6 位是当归酰基取代; H-6 还与 C-18 相关, 显示末端烯键连接在 C-7 位; 亚甲二氧基 δ_{H} 5.99、5.97 分别与 C-2、C-3 相关, 表明亚甲二氧基与 C-2、C-3 连接; 4 个甲氧基 δ_{H} 3.61、3.78、3.84、3.88 分别与 C-14、C-1、C-13、C-12 相关, 确定了甲氧基的连接位置。综上所述, 化合物 **1** 的平面结构得以确定。

化合物 **1** 的立体结构利用 CD 光谱和 ROESY 谱来确定。文献报道 *S* 型联苯环辛烯类木脂素的 CD

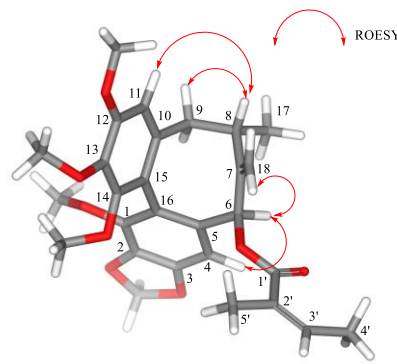
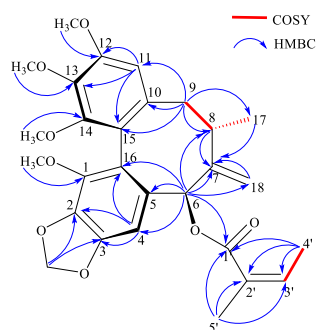


图 1 化合物 **1** 的结构及其主要 ^1H - ^1H COSY、HMBC 和 ROESY 相关信号

Fig. 1 Structure of compound **1** and its key ^1H - ^1H COSY, HMBC, ROESY correlations

光谱在 215~225 nm 为正 Cotton 效应, 在 235~255 nm 为负 Cotton 效应, 而 *R* 型的 CD 光谱则相反^[15]。化合物 **1** 的实验 ECD 光谱显示在 222 nm 有正 Cotton 效应, 在 243 nm 有负 Cotton 效应, 表明 **1** 是 *S* 型联苯环辛烯类木脂素。同时, ROESY 谱中 (图 1) H-4/H-6、H-6/H-18 相关, 显示 H-4、H-6 和 H-18 处于同侧; H-11/H-8、H-8/H-9 β 相关, 也显示 H-8、H-9 β 和 H-11 处于同侧。最后, 通过计算 ECD 和实验 ECD 比较 (图 2), 确定其绝对构型为 6*R*、8*S*。与已知化合物 schiviridin A^[15] 的结构进行比对, 二者苯环上的 4 个甲氧基和亚甲二氧基取代位置存在差异, 且 schiviridin A 的绝对构型是 6*R*、8*R*。因此, 化合物 **1** 的结构鉴定为 (a*S*)-(5*R*,7*S*)-5,6,7,8-四氢-1,11,12,13-四甲氧基-7-甲基-6-亚甲苯并[3',4']环辛基[1',2':4,5]苯并[1,2-*f*][1,3]二氧-5-基(2*Z*)-2-甲基-丁烯酸酯。经 SciFinder 检索为未见文

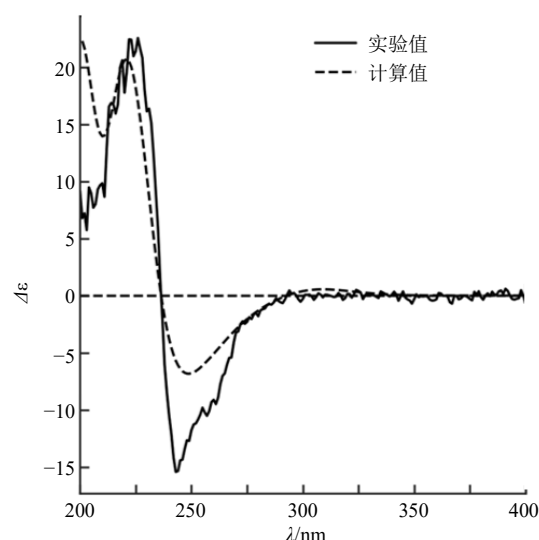


图 2 化合物 **1** 的计算 ECD 和实验 ECD 图谱

Fig. 2 Calculated and experimental ECD spectra of **1**

献报道的新化合物, 命名为绿叶五味子素 B (schiviridin B)。

化合物 2: 白色晶体(甲醇); $[\alpha]_D^{20} -42.3^\circ$ (c 0.052, MeOH); $C_{27}H_{32}O_9$; ESI-MS m/z : 523.25 $[M+Na]^+$ 。 1H -NMR (400 MHz, $CDCl_3$) δ : 6.86 (1H, s, H-4), 5.51 (1H, s, H-6), 2.00 (1H, m, H-8), 2.26 (1H, dd, $J = 14.1, 9.6$ Hz, H-9 β), 2.18 (1H, dd, $J = 14.1, 1.3$ Hz, H-9 α), 6.48 (1H, s, H-11), 1.14 (3H, d, $J = 7.1$ Hz, H-17), 1.36 (3H, s, H-18), 5.95 (1H, m, H-3'), 1.84 (3H, dq, $J = 7.3, 1.5$ Hz, H-4'), 1.42 (3H, d, $J = 1.5$ Hz, H-5'), 3.55 (3H, s, 1-OCH₃), 3.93 (3H, s, 2-OCH₃), 3.93 (3H, s, 3-OCH₃), 5.97 (1H, d, $J = 1.4$ Hz, 12, 13-OCH₂O), 5.89 (1H, d, $J = 1.4$ Hz, 12, 13-OCH₂O), 5.15 (1H, s, 14-OH); ^{13}C -NMR (100 MHz, $CDCl_3$) δ : 150.9 (C-1), 142.0 (C-2), 152.6 (C-3), 111.5 (C-4), 132.5 (C-5), 84.8 (C-6), 72.3 (C-7), 42.6 (C-8), 36.6 (C-9), 135.7 (C-10), 102.2 (C-11), 148.6 (C-12), 133.6 (C-13), 136.7 (C-14), 118.5 (C-15), 120.0 (C-16), 20.0 (C-17), 28.4 (C-18), 166.2 (C-1'), 126.9 (C-2'), 140.1 (C-3'), 15.9 (C-4'), 18.8 (C-5'), 61.5 (1-OCH₃), 61.3 (2-OCH₃), 56.1 (3-OCH₃), 101.4 (12, 13-OCH₂O)。以上数据与文献报道对比基本一致^[16], 鉴定化合物 2 为 sphaerandrin A。

化合物 3: 白色晶体 (甲醇); $[\alpha]_D^{20} +126.6^\circ$ (c 0.064, MeOH); $C_{28}H_{36}O_8$; ESI-MS m/z : 501.25 $[M+H]^+$ 。 1H -NMR (400 MHz, $CDCl_3$) δ : 6.55 (1H, s, H-4), 2.71 (1H, d, $J = 13.7$ Hz, H-6 α), 2.33 (1H, d, $J = 13.7$ Hz, H-6 β), 1.89 (1H, m, H-8), 2.69 (1H, dd, $J = 14.2, 1.8$ Hz, H-9 α), 2.41 (1H, dd, $J = 14.2, 7.6$ Hz, H-9 β), 6.68 (1H, s, H-11), 0.85 (3H, d, $J = 7.3$ Hz, H-17), 1.24 (3H, s, H-18), 6.82 (1H, m, H-3'), 1.71 (3H, overlapped, H-4'), 1.69 (3H, overlapped, H-5'), 3.50 (3H, s, 1-OCH₃), 3.83 (3H, s, 2-OCH₃), 3.87 (3H, s, 3-OCH₃), 3.82 (3H, s, 13-OCH₃), 3.90 (3H, s, 14-OCH₃); ^{13}C -NMR (100 MHz, $CDCl_3$) δ : 152.0 (C-1), 140.5 (C-2), 152.6 (C-3), 110.3 (C-4), 133.2 (C-5), 40.8 (C-6), 72.1 (C-7), 42.1 (C-8), 34.4 (C-9), 133.9 (C-10), 112.9 (C-11), 142.8 (C-12), 140.0 (C-13), 151.8 (C-14), 123.3 (C-15), 123.1 (C-16), 16.0 (C-17), 30.0 (C-18), 165.9 (C-1'), 128.1 (C-2'), 138.3 (C-3'), 12.2 (C-4'), 14.5 (C-5'), 61.0 (1-OCH₃), 61.1 (2-OCH₃), 56.2 (3-OCH₃), 60.8 (13-OCH₃), 56.2 (14-OCH₃)。以上数据与文献报道对比基本一致^[17],

鉴定化合物 3 为 sieverlignan E。

化合物 4: 白色晶体(甲醇); $[\alpha]_D^{20} -24.1^\circ$ (c 0.058, MeOH); $C_{22}H_{28}O_6$; ESI-MS m/z : 411.36 $[M+Na]^+$ 。 1H -NMR (400 MHz, $CDCl_3$) δ : 6.37 (1H, s, H-4), 2.24 (1H, dd, $J = 13.3, 9.4$ Hz, H-6 β), 2.04 (1H, d, $J = 13.3$ Hz, H-6 α), 1.81 (1H, m, H-7), 1.89 (1H, m, H-8), 2.56 (1H, dd, $J = 13.5, 7.4$ Hz, H-9 β), 2.44 (1H, d, $J = 13.5, 1.9$ Hz, H-9 α), 6.66 (1H, s, H-11), 0.73 (3H, d, $J = 7.1$ Hz, H-17), 1.00 (3H, d, $J = 7.1$ Hz, H-18), 5.74 (1H, s, 1-OH), 3.87 (3H, s, 2-OCH₃), 3.90 (3H, s, 3-OCH₃), 5.68 (1H, s, 12-OH), 3.93 (3H, s, 13-OCH₃), 3.60 (3H, s, 14-OCH₃); ^{13}C -NMR (100 MHz, $CDCl_3$) δ : 146.7 (C-1), 133.5 (C-2), 151.9 (C-3), 104.0 (C-4), 140.0 (C-5), 35.6 (C-6), 41.0 (C-7), 33.9 (C-8), 38.9 (C-9), 135.5 (C-10), 113.8 (C-11), 147.9 (C-12), 137.7 (C-13), 150.3 (C-14), 121.6 (C-15), 115.9 (C-16), 12.6 (C-17), 22.0 (C-18), 61.2 (2-OCH₃), 55.9 (3-OCH₃), 61.2 (13-OCH₃), 60.6 (14-OCH₃)。以上数据与文献报道对比基本一致^[18], 鉴定化合物 4 为 arisanschinin G。

化合物 5: 白色针晶(甲醇); $[\alpha]_D^{20} -82.6^\circ$ (c 0.086, MeOH); $C_{15}H_{22}O_2$; ESI-MS m/z : 235.25 $[M+H]^+$ 。 1H -NMR (400 MHz, $CDCl_3$) δ : 2.24 (2H, m, H-1), 7.10 (1H, m, H-2), 2.34 (1H, m, H-4a), 1.84 (1H, m, H-4b), 1.54 (2H, m, H-5), 1.78 (1H, m, H-8a), 1.19 (1H, m, H-8b), 2.08 (1H, m, H-9a), 1.41 (1H, m, H-9b), 2.16 (2H, m, H-10), 4.86 (1H, s, H-12a), 4.36 (1H, s, H-12b), 0.88 (3H, s, H-13), 0.85 (3H, s, H-14); ^{13}C -NMR (100 MHz, $CDCl_3$) δ : 30.1 (C-1), 142.2 (C-2), 128.9 (C-3), 21.8 (C-4), 23.7 (C-5), 45.0 (C-6), 37.3 (C-7), 37.0 (C-8), 25.6 (C-9), 32.1 (C-10), 148.5 (C-11), 110.9 (C-12), 23.2 (C-13), 25.0 (C-14), 173.0 (C-15)。以上数据与文献报道对比基本一致^[19], 鉴定化合物 5 为 widdaranal F。

化合物 6: 白色晶体 (甲醇); $[\alpha]_D^{20} +59.5^\circ$ (c 0.074, MeOH); $C_{23}H_{28}O_7$; ESI-MS m/z : 439.26 $[M+Na]^+$ 。 1H -NMR (400 MHz, $CDCl_3$) δ : 6.61 (1H, s, H-4), 2.67 (1H, d, $J = 13.5$ Hz, H-6 α), 2.35 (1H, d, $J = 13.5$ Hz, H-6 β), 2.00 (1H, s, 7-OH), 1.85 (1H, m, H-8), 2.57 (1H, dd, $J = 14.1, 1.6$ Hz, H-9 α), 2.32 (1H, dd, $J = 14.1, 7.4$ Hz, H-9 β), 6.47 (1H, s, H-11), 0.81 (3H, d, $J = 7.3$ Hz, H-17), 1.25 (3H, s, H-18), 3.51 (3H, s, 1-OCH₃), 3.90 (3H, s, 2-OCH₃), 3.91 (3H, s, 3-OCH₃), 5.96 (2H, s, 12, 13-OCH₂O), 3.83 (3H, s,

14-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ: 152.2 (C-1), 140.8 (C-2), 152.4 (C-3), 110.4 (C-4), 132.1 (C-5), 40.6 (C-6), 71.7 (C-7), 42.1 (C-8), 33.8 (C-9), 132.6 (C-10), 106.1 (C-11), 148.0 (C-12), 135.0 (C-13), 141.3 (C-14), 121.9 (C-15), 124.2 (C-16), 15.9 (C-17), 30.2 (C-18), 60.7 (1-OCH₃), 61.1 (2-OCH₃), 56.1 (3-OCH₃), 101.0 (12, 13-OCH₂O), 59.8 (14-OCH₃)。以上数据与文献报道对比基本一致^[20], 鉴定化合物 **6** 为 gomisin A。

化合物 **7**: 白色晶体(甲醇); $[\alpha]_D^{20}$ -20.9° (c 0.067, MeOH); C₂₈H₃₄O₉; ESI-MS m/z : 537.35 [M+Na]⁺。 ¹H-NMR (400 MHz, CDCl₃) δ: 6.76 (1H, s, H-4), 5.61 (1H, s, H-6), 1.93 (1H, m, H-8), 2.29 (1H, dd, J = 14.0, 9.7 Hz, H-9β), 2.13 (1H, d, J = 14.0 Hz, H-9α), 6.45 (1H, s, H-11), 1.12 (3H, d, J = 7.1 Hz, H-17), 1.32 (3H, s, H-18), 5.99 (1H, m, H-3'), 1.84 (3H, dq, J = 7.3, 1.6 Hz, H-4'), 1.38 (3H, q, J = 1.6 Hz, H-5'), 3.72 (3H, s, 1-OCH₃), 3.88 (3H, s, 2-OCH₃), 3.89 (3H, s, 3-OCH₃), 5.89 (1H, d, J = 1.4 Hz, 12, 13-OCH₂O), 5.86 (1H, d, J = 1.4 Hz, 12, 13-OCH₂O), 3.55 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ: 152.2 (C-1), 141.8 (C-2), 152.0 (C-3), 109.9 (C-4), 130.7 (C-5), 84.5 (C-6), 72.3 (C-7), 42.5 (C-8), 36.5 (C-9), 135.3 (C-10), 102.8 (C-11), 148.8 (C-12), 134.3 (C-13), 140.6 (C-14), 121.3 (C-15), 122.3 (C-16), 19.1 (C-17), 28.2 (C-18), 166.0 (C-1'), 127.2 (C-2'), 140.1 (C-3'), 15.8 (C-4'), 19.9 (C-5'), 60.8 (1-OCH₃), 61.0 (2-OCH₃), 55.9 (3-OCH₃), 100.7 (12, 13-OCH₂O), 59.2 (14-OCH₃)。以上数据与文献报道对比基本一致^[21], 鉴定化合物 **7** 为 gomisin B。

化合物 **8**: 白色晶体(甲醇); $[\alpha]_D^{20}$ -47.4° (c 0.076, MeOH); C₂₈H₃₄O₁₀; ESI-MS m/z : 553.36 [M+Na]⁺。 ¹H-NMR (400 MHz, CDCl₃) δ: 6.79 (1H, s, H-4), 5.72 (1H, s, H-6), 1.76 (1H, m, H-8), 2.37 (1H, dd, J = 14.1, 8.3 Hz, H-9β), 2.00 (1H, d, J = 14.1 Hz, H-9α), 6.47 (1H, s, H-11), 1.05 (3H, d, J = 7.0 Hz, H-17), 1.22 (3H, s, H-18), 1.65 (1H, m, H-21), 3.71 (2H, m, H-22), 1.28 (3H, s, H-23), 1.14 (3H, d, J = 7.2 Hz, H-24), 3.56 (3H, s, 1-OCH₃), 3.84 (3H, s, 2-OCH₃), 3.91 (3H, s, 3-OCH₃), 6.00 (1H, d, J = 1.4 Hz, 12, 13-OCH₂O), 5.91 (1H, d, J = 1.4 Hz, 12, 13-OCH₂O); ¹³C-NMR (100 MHz, CDCl₃) δ: 152.0 (C-1), 142.5 (C-2), 152.2 (C-3), 110.9 (C-4), 130.3 (C-5), 87.6

(C-6), 72.2 (C-7), 44.0 (C-8), 36.1 (C-9), 136.5 (C-10), 102.7 (C-11), 148.6 (C-12), 137.3 (C-13), 138.4 (C-14), 121.4 (C-15), 122.6 (C-16), 19.0 (C-17), 27.6 (C-18), 177.7 (C-19), 75.0 (C-20), 37.9 (C-21), 73.0 (C-22), 24.8 (C-23), 11.4 (C-24), 60.8 (1-OCH₃), 60.9 (2-OCH₃), 56.1 (3-OCH₃), 101.2 (12, 13-OCH₂O)。以上数据与文献报道对比基本一致^[22], 鉴定化合物 **8** 为 gomisin D。

化合物 **9**: 白色晶体(甲醇); $[\alpha]_D^{20}$ -126.5° (c 0.068, MeOH); C₃₀H₃₂O₉; ESI-MS m/z : 559.25 [M+Na]⁺。 ¹H-NMR (400 MHz, CDCl₃) δ: 6.77 (1H, s, H-4), 5.88 (1H, s, H-6), 2.13 (1H, m, H-8), 2.48 (1H, dd, J = 14.0, 10.1 Hz, H-9β), 2.28 (1H, d, J = 14.0 Hz, H-9α), 6.69 (1H, s, H-11), 1.20 (3H, d, J = 7.0 Hz, H-17), 1.33 (3H, s, H-18), 7.36 (5H, overlapped, H-2'~6'), 3.39 (3H, s, 1-OCH₃), 6.00 (2H, d, J = 1.6 Hz, 2, 3-OCH₂O), 3.98 (3H, s, 12-OCH₃), 3.81 (3H, s, 13-OCH₃), 3.14 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ: 141.8 (C-1), 137.2 (C-2), 148.2 (C-3), 107.4 (C-4), 128.9 (C-5), 84.5 (C-6), 72.6 (C-7), 42.3 (C-8), 36.9 (C-9), 136.6 (C-10), 106.3 (C-11), 153.4 (C-12), 140.0 (C-13), 150.8 (C-14), 122.4 (C-15), 121.9 (C-16), 19.1 (C-17), 28.4 (C-18), 164.9 (-CO), 129.6 (C-1'), 129.3 (C-2', 6'), 128.2 (C-3', 5'), 133.3 (C-4'), 60.0 (1-OCH₃), 101.5 (2, 3-OCH₂O), 56.2 (12-OCH₃), 60.2 (13-OCH₃), 59.8 (14-OCH₃)。以上数据与文献报道对比基本一致^[21], 鉴定化合物 **9** 为 gomisin G。

化合物 **10**: 白色晶体(甲醇); $[\alpha]_D^{20}$ -112.5° (c 0.056, MeOH); C₂₃H₃₀O₆; ESI-MS m/z : 403.30 [M+H]⁺。 ¹H-NMR (400 MHz, CDCl₃) δ: 6.54 (1H, s, H-4), 2.54 (2H, m, H-6), 1.84 (1H, overlapped, H-7), 1.84 (1H, overlapped, H-8), 2.22 (1H, dd, J = 13.1, 9.4 Hz, H-9β), 2.01 (1H, dd, J = 13.1, 1.3 Hz, H-9α), 6.62 (1H, s, H-11), 0.96 (3H, d, J = 7.1 Hz, H-17), 0.72 (3H, d, J = 7.1 Hz, H-18), 3.54 (3H, s, 1-OCH₃), 3.88 (3H, s, 2-OCH₃), 3.88 (3H, s, 3-OCH₃), 5.86 (1H, s, 12-OH), 3.90 (3H, s, 13-OCH₃), 3.55 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ: 151.6 (C-1), 140.1 (C-2), 151.6 (C-3), 110.6 (C-4), 134.2 (C-5), 39.3 (C-6), 33.8 (C-7), 40.9 (C-8), 35.3 (C-9), 140.1 (C-10), 110.1 (C-11), 148.8 (C-12), 137.4 (C-13), 150.3 (C-14), 121.5 (C-15), 123.3 (C-16), 21.8

(C-17), 12.7 (C-18), 60.6 (1-OCH₃), 61.1 (2-OCH₃), 56.0 (3-OCH₃), 61.0 (13-OCH₃), 60.2 (14-OCH₃)。以上数据与文献报道对比基本一致^[20], 鉴定化合物 **10** 为 (-)-gomisin K₁。

化合物 **11**: 白色晶体 (甲醇); $[\alpha]_D^{20} + 3.8^\circ$ (*c* 0.053, MeOH); C₂₃H₃₀O₆; ESI-MS *m/z*: 403.31 [M+H]⁺。¹H-NMR (400 MHz, CDCl₃) δ : 6.54 (1H, s, H-4), 2.16 (2H, m, H-6), 1.84 (1H, overlapped, H-7), 1.84 (1H, overlapped, H-8), 2.51 (2H, m, H-9), 6.62 (1H, s, H-11), 0.73 (3H, d, *J* = 7.1 Hz, H-17), 0.99 (3H, d, *J* = 7.1 Hz, H-18), 3.55 (3H, s, 1-OCH₃), 3.89 (3H, s, 2-OCH₃), 3.92 (3H, s, 3-OCH₃), 5.70 (1H, s, 12-OH), 3.88 (3H, s, 13-OCH₃), 3.55 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ : 151.5 (C-1), 139.9 (C-2), 153.0 (C-3), 107.4 (C-4), 139.5 (C-5), 35.7 (C-6), 41.0 (C-7), 33.9 (C-8), 38.9 (C-9), 134.8 (C-10), 113.1 (C-11), 147.6 (C-12), 137.7 (C-13), 150.4 (C-14), 122.7 (C-15), 122.3 (C-16), 12.6 (C-17), 22.0 (C-18), 60.7 (1-OCH₃), 61.1 (2-OCH₃), 56.0 (3-OCH₃), 61.1 (13-OCH₃), 60.2 (14-OCH₃)。以上数据与文献报道对比基本一致^[23], 鉴定化合物 **11** 为 (+)-gomisin K₂。

化合物 **12**: 白色晶体 (甲醇); $[\alpha]_D^{20} - 5.9^\circ$ (*c* 0.051, MeOH); C₂₂H₂₆O₆; ESI-MS *m/z*: 387.26 [M+H]⁺。¹H-NMR (400 MHz, CDCl₃) δ : 6.51 (1H, s, H-4), 2.51 (2H, m, H-6), 1.84 (1H, overlapped, H-7), 1.84 (1H, overlapped, H-8), 2.16 (2H, m, H-9), 6.37 (1H, s, H-11), 1.00 (3H, d, *J* = 7.2 Hz, H-17), 0.73 (3H, d, *J* = 7.2 Hz, H-18), 3.87 (3H, s, 1-OCH₃), 5.95 (2H, d, *J* = 1.6 Hz, 2, 3-OCH₂O), 3.90 (3H, s, 12-OCH₃), 3.90 (3H, s, 13-OCH₃), 5.72 (1H, s, 14-OH); ¹³C-NMR (100 MHz, CDCl₃) δ : 141.3 (C-1), 135.1 (C-2), 148.0 (C-3), 106.6 (C-4), 133.2 (C-5), 39.1 (C-6), 34.0 (C-7), 40.9 (C-8), 35.5 (C-9), 140.1 (C-10), 104.0 (C-11), 151.8 (C-12), 133.2 (C-13), 146.8 (C-14), 115.8 (C-15), 121.4 (C-16), 22.1 (C-17), 12.4 (C-18), 59.9 (1-OCH₃), 101.0 (2, 3-OCH₂O), 55.8 (12-OCH₃), 61.2 (13-OCH₃)。以上数据与文献报道对比基本一致^[24], 鉴定化合物 **12** 为 (-)-gomisin L₁。

化合物 **13**: 白色晶体 (甲醇); $[\alpha]_D^{20} + 3.2^\circ$ (*c* 0.062, MeOH); C₂₂H₂₆O₆; ESI-MS *m/z*: 387.26 [M+H]⁺。¹H-NMR (400 MHz, CDCl₃) δ : 6.51 (1H, s, H-4), 2.14 (2H, m, H-6), 1.84 (1H, overlapped, H-7), 1.84

(1H, overlapped, H-8), 2.55 (2H, m, H-9), 6.38 (1H, s, H-11), 0.75 (3H, d, *J* = 7.2 Hz, H-17), 0.97 (3H, d, *J* = 7.2 Hz, H-18), 3.87 (3H, s, 1-OCH₃), 5.95 (1H, d, *J* = 1.5 Hz, 2, 3-OCH₂O), 5.93 (1H, d, *J* = 1.5 Hz, 2, 3-OCH₂O), 3.91 (3H, s, 12-OCH₃), 3.89 (3H, s, 13-OCH₃), 5.72 (1H, s, 14-OH); ¹³C-NMR (100 MHz, CDCl₃) δ : 141.1 (C-1), 134.6 (C-2), 149.0 (C-3), 103.6 (C-4), 138.5 (C-5), 35.8 (C-6), 40.9 (C-7), 33.6 (C-8), 39.3 (C-9), 134.8 (C-10), 107.3 (C-11), 150.5 (C-12), 133.6 (C-13), 147.0 (C-14), 116.7 (C-15), 120.3 (C-16), 13.0 (C-17), 21.6 (C-18), 59.9 (1-OCH₃), 100.9 (2, 3-OCH₂O), 55.8 (12-OCH₃), 61.1 (13-OCH₃)。以上数据与文献报道对比基本一致^[25], 鉴定化合物 **13** 为 (+)-gomisin M₁。

化合物 **14**: 白色晶体 (甲醇); $[\alpha]_D^{20} - 10.3^\circ$ (*c* 0.078, MeOH); C₂₃H₂₈O₆; ESI-MS *m/z*: 401.25 [M+H]⁺。¹H-NMR (400 MHz, CDCl₃) δ : 6.55 (1H, s, H-4), 2.58 (1H, dd, *J* = 13.6, 7.2 Hz, H-6 β), 2.51 (1H, dd, *J* = 13.6, 2.4 Hz, H-6 α), 1.84 (1H, overlapped, H-7), 1.84 (1H, overlapped, H-8), 2.23 (1H, dd, *J* = 13.3, 9.4 Hz, H-9 β), 2.02 (1H, dd, *J* = 13.3, 1.5 Hz, H-9 α), 6.48 (1H, s, H-11), 0.99 (3H, d, *J* = 7.2 Hz, H-17), 0.73 (3H, d, *J* = 7.2 Hz, H-18), 3.54 (3H, s, 1-OCH₃), 3.88 (3H, s, 2-OCH₃), 3.89 (3H, s, 3-OCH₃), 5.94 (2H, s, 12, 13-OCH₂O), 3.82 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ : 151.7 (C-1), 140.1 (C-2), 151.7 (C-3), 110.7 (C-4), 134.2 (C-5), 39.2 (C-6), 33.9 (C-7), 40.8 (C-8), 35.6 (C-9), 137.9 (C-10), 103.0 (C-11), 148.8 (C-12), 134.6 (C-13), 141.2 (C-14), 121.4 (C-15), 123.4 (C-16), 21.7 (C-17), 12.9 (C-18), 60.6 (1-OCH₃), 61.1 (2-OCH₃), 56.0 (3-OCH₃), 100.8 (12, 13-OCH₂O), 59.7 (14-OCH₃)。以上数据与文献报道对比基本一致^[26], 鉴定化合物 **14** 为 gomisin N。

化合物 **15**: 白色晶体 (甲醇); $[\alpha]_D^{20} + 2.2^\circ$ (*c* 0.091, MeOH); C₂₈H₃₆O₈; ESI-MS *m/z*: 523.20 [M+Na]⁺。¹H-NMR (400 MHz, CDCl₃) δ : 6.53 (1H, s, H-4), 2.71 (1H, d, *J* = 13.7 Hz, H-6 α), 2.30 (1H, d, *J* = 13.7 Hz, H-6 β), 1.84 (1H, m, H-8), 2.67 (1H, dd, *J* = 14.6, 1.8 Hz, H-9 α), 2.38 (1H, dd, *J* = 14.6, 7.6 Hz, H-9 β), 6.66 (1H, s, H-11), 0.81 (3H, d, *J* = 7.3 Hz, H-17), 1.21 (3H, s, H-18), 5.85 (1H, m, H-3'), 1.73 (3H, overlapped, H-4'), 1.72 (3H, overlapped, H-5'), 3.50 (3H, s, 1-OCH₃), 3.80 (3H, s, 2-OCH₃), 3.83 (3H,

s, 3-OCH₃), 3.87 (3H, s, 12-OCH₃), 3.80 (3H, s, 13-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ: 151.7 (C-1), 140.3 (C-2), 152.6 (C-3), 110.1 (C-4), 133.1 (C-5), 40.7 (C-6), 72.0 (C-7), 41.9 (C-8), 34.3 (C-9), 133.9 (C-10), 112.8 (C-11), 151.8 (C-12), 139.7 (C-13), 142.3 (C-14), 123.2 (C-15), 122.9 (C-16), 15.9 (C-17), 29.9 (C-18), 165.6 (C-1'), 127.6 (C-2'), 137.3 (C-3'), 15.3 (C-4'), 20.3 (C-5'), 60.6 (1-OCH₃), 60.9 (2-OCH₃), 56.0 (3-OCH₃), 56.0 (12-OCH₃), 60.8 (13-OCH₃)。以上数据与文献报道对比基本一致^[20], 鉴定化合物 **15** 为 angeloylgomisin H。

化合物 **16**: 白色晶体 (甲醇); $[\alpha]_D^{20} + 20.8^\circ$ (*c* 0.051, MeOH); C₂₈H₃₄O₈; ESI-MS *m/z*: 521.26 [M+Na]⁺。¹H-NMR (400 MHz, CDCl₃) δ: 6.75 (1H, s, H-4), 5.75 (1H, d, *J* = 8.5 Hz, H-6), 1.89 (1H, m, H-7), 1.89 (1H, m, H-8), 2.18 (2H, m, H-9), 6.40 (1H, s, H-11), 0.94 (3H, d, *J* = 6.9 Hz, H-17), 0.83 (3H, d, *J* = 6.9 Hz, H-18), 5.92 (1H, overlapped, H-3'), 1.84 (3H, d, *J* = 7.2 Hz, H-4'), 1.57 (3H, s, H-5'), 3.51 (3H, s, 1-OCH₃), 3.88 (3H, s, 2-OCH₃), 3.89 (3H, s, 3-OCH₃), 5.92 (2H, m, 12, 13-OCH₂O), 3.80 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ: 151.9 (C-1), 141.7 (C-2), 151.9 (C-3), 111.2 (C-4), 132.9 (C-5), 80.9 (C-6), 37.1 (C-7), 37.3 (C-8), 37.9 (C-9), 135.2 (C-10), 102.4 (C-11), 148.8 (C-12), 134.6 (C-13), 142.0 (C-14), 121.7 (C-15), 123.7 (C-16), 18.0 (C-17), 15.7 (C-18), 167.1 (C-1'), 128.1 (C-2'), 138.2 (C-3'), 15.7 (C-4'), 20.2 (C-5'), 60.5 (1-OCH₃), 61.0 (2-OCH₃), 56.1 (3-OCH₃), 100.1 (12, 13-OCH₂O), 59.4 (14-OCH₃)。以上数据与文献报道对比基本一致^[27], 鉴定化合物 **16** 为 angeloylgomisin O。

化合物 **17**: 白色晶体 (甲醇); $[\alpha]_D^{20} - 8.8^\circ$ (*c* 0.068, MeOH); C₂₉H₃₈O₉; ESI-MS *m/z*: 553.34 [M+Na]⁺。¹H-NMR (400 MHz, CDCl₃) δ: 6.78 (1H, s, H-4), 5.73 (1H, s, H-6), 1.90 (1H, m, H-8), 2.33 (1H, dd, *J* = 14.0, 9.8 Hz, H-9β), 2.18 (1H, d, *J* = 14.0 Hz, H-9α), 6.53 (1H, s, H-11), 1.15 (3H, d, *J* = 7.1 Hz, H-17), 1.31 (3H, s, H-18), 5.94 (1H, m, H-3'), 1.80 (3H, dq, *J* = 7.4, 1.7 Hz, H-4'), 1.29 (3H, q, *J* = 1.7 Hz, H-5'), 3.50 (3H, s, 1-OCH₃), 3.80 (3H, s, 2-OCH₃), 3.88 (3H, s, 3-OCH₃), 3.87 (3H, s, 12-OCH₃), 3.86 (3H, s, 13-OCH₃), 3.55 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ: 152.2 (C-1), 141.0 (C-2), 152.0

(C-3), 110.1 (C-4), 130.4 (C-5), 84.3 (C-6), 72.4 (C-7), 42.2 (C-8), 36.8 (C-9), 136.6 (C-10), 107.3 (C-11), 153.2 (C-12), 140.0 (C-13), 150.9 (C-14), 122.3 (C-15), 122.5 (C-16), 19.2 (C-17), 28.2 (C-18), 166.0 (C-1'), 127.0 (C-2'), 142.0 (C-3'), 15.7 (C-4'), 19.9 (C-5'), 60.6 (1-OCH₃), 60.9 (2-OCH₃), 55.9 (3-OCH₃), 56.2 (12-OCH₃), 60.8 (13-OCH₃), 60.3 (14-OCH₃)。以上数据与文献报道对比基本一致^[28-29], 鉴定化合物 **17** 为 angeloylgomisin Q。

化合物 **18**: 白色晶体 (甲醇); $[\alpha]_D^{20} - 115.9^\circ$ (*c* 0.063, MeOH); C₃₁H₃₆O₉; ESI-MS *m/z*: 575.14 [M+Na]⁺。¹H-NMR (400 MHz, CDCl₃) δ: 6.83 (1H, s, H-4), 5.97 (1H, s, H-6), 2.14 (1H, m, H-8), 2.48 (1H, dd, *J* = 14.1, 10.0 Hz, H-9β), 2.28 (1H, d, *J* = 14.1 Hz, H-9α), 6.68 (1H, s, H-11), 1.20 (3H, d, *J* = 7.1 Hz, H-17), 1.34 (3H, s, H-18), 7.35 (5H, overlapped, H-2' ~ 6'), 3.16 (3H, s, 1-OCH₃), 3.57 (3H, s, 2-OCH₃), 3.97 (3H, s, 3-OCH₃), 3.89 (3H, s, 12-OCH₃), 3.88 (3H, s, 13-OCH₃), 3.38 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ: 152.3 (C-1), 142.1 (C-2), 152.0 (C-3), 110.3 (C-4), 130.1 (C-5), 84.5 (C-6), 72.6 (C-7), 42.4 (C-8), 36.9 (C-9), 136.5 (C-10), 107.2 (C-11), 153.2 (C-12), 140.1 (C-13), 150.7 (C-14), 122.5 (C-15), 122.6 (C-16), 19.1 (C-17), 28.2 (C-18), 165.0 (-CO), 129.3 (C-1'), 129.6 (C-2', 6'), 128.2 (C-3', 5'), 133.3 (C-4'), 60.2 (1-OCH₃), 60.9 (2-OCH₃), 56.0 (3-OCH₃), 56.2 (12-OCH₃), 60.8 (13-OCH₃), 59.9 (14-OCH₃)。以上数据与文献报道对比基本一致^[28], 鉴定化合物 **18** 为 benzoylgomisin Q。

化合物 **19**: 白色晶体 (甲醇); $[\alpha]_D^{20} + 87.1^\circ$ (*c* 0.124, MeOH); C₂₄H₃₂O₇; ESI-MS *m/z*: 455.36 [M+Na]⁺。¹H-NMR (400 MHz, CDCl₃) δ: 6.59 (1H, s, H-4), 2.63 (1H, d, *J* = 13.4 Hz, H-6β), 2.34 (1H, d, *J* = 13.4 Hz, H-6α), 1.97 (1H, s, 7-OH), 1.85 (1H, m, H-8), 2.57 (1H, dd, *J* = 14.2, 1.8 Hz, H-9α), 2.35 (1H, dd, *J* = 14.2, 7.7 Hz, H-9β), 6.51 (1H, s, H-11), 0.79 (3H, d, *J* = 7.3 Hz, H-17), 1.23 (3H, s, H-18), 3.51 (3H, s, 1-OCH₃), 3.85 (3H, s, 2-OCH₃), 3.88 (3H, s, 3-OCH₃), 3.86 (3H, s, 12-OCH₃), 3.86 (3H, s, 13-OCH₃), 3.56 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ: 151.8 (C-1), 140.7 (C-2), 152.4 (C-3), 110.4 (C-4), 131.9 (C-5), 40.8 (C-6), 71.8 (C-7), 41.8 (C-8), 34.2

(C-9), 133.9 (C-10), 110.0 (C-11), 152.0 (C-12), 140.1 (C-13), 151.6 (C-14), 124.2 (C-15), 122.7 (C-16), 15.9 (C-17), 29.9 (C-18), 60.7 (1-OCH₃), 61.0 (2-OCH₃), 56.0 (3-OCH₃), 55.9 (12-OCH₃), 61.0 (13-OCH₃), 60.6 (14-OCH₃)。以上数据与文献报道对比一致^[20], 鉴定化合物 **19** 为 schisandrin。

化合物 **20**: 白色针晶 (甲醇); $[\alpha]_D^{20} +9.3^\circ$ (*c* 0.086, MeOH); C₂₄H₃₂O₆; ESI-MS *m/z*: 417.36 [M+H]⁺。¹H-NMR (400 MHz, CDCl₃) δ : 6.55 (1H, s, H-4), 2.59 (1H, dd, *J* = 13.5, 7.3 Hz, H-6 β), 2.06 (1H, d, *J* = 13.5 Hz, H-6 α), 1.85 (1H, overlapped, H-7), 1.85 (1H, overlapped, H-8), 2.50 (1H, d, *J* = 13.2 Hz, H-9 α), 2.28 (1H, dd, *J* = 13.2, 9.5 Hz, H-9 β), 6.54 (1H, s, H-11), 0.74 (3H, d, *J* = 7.1 Hz, H-17), 1.00 (3H, d, *J* = 7.1 Hz, H-18), 3.59 (3H, s, 1-OCH₃), 3.87 (3H, s, 2-OCH₃), 3.89 (3H, s, 3-OCH₃), 3.88 (3H, s, 12-OCH₃), 3.88 (3H, s, 13-OCH₃), 3.59 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ : 151.4 (C-1), 139.9 (C-2), 152.7 (C-3), 107.0 (C-4), 139.0 (C-5), 35.4 (C-6), 40.6 (C-7), 33.6 (C-8), 39.0 (C-9), 133.8 (C-10), 110.3 (C-11), 151.5 (C-12), 139.6 (C-13), 151.3 (C-14), 123.2 (C-15), 122.2 (C-16), 12.5 (C-17), 21.7 (C-18), 60.4 (1-OCH₃), 60.8 (2-OCH₃), 55.7 (3-OCH₃), 55.7 (12-OCH₃), 60.8 (13-OCH₃), 60.4 (14-OCH₃)。以上数据与文献报道对比基本一致^[20], 鉴定化合物 **20** 为 schisandrin A。

化合物 **21**: 白色晶体 (甲醇); $[\alpha]_D^{20} 0^\circ$ (*c* 0.084, MeOH); C₂₃H₂₈O₆; ESI-MS *m/z*: 401.30 [M+H]⁺。¹H-NMR (400 MHz, CDCl₃) δ : 6.54 (1H, s, H-4), 2.31 (1H, dd, *J* = 13.2, 9.6 Hz, H-6 β), 2.04 (1H, dd, *J* = 13.2, 1.5 Hz, H-6 α), 1.83 (1H, overlapped, H-7), 1.83 (1H, overlapped, H-8), 2.55 (1H, dd, *J* = 13.5, 7.3 Hz, H-9 β), 2.43 (1H, dd, *J* = 13.5, 1.8 Hz, H-9 α), 6.48 (1H, s, H-11), 0.73 (3H, dd, *J* = 7.1 Hz, H-17), 0.99 (3H, d, *J* = 7.1 Hz, H-18), 3.54 (3H, s, 1-OCH₃), 3.88 (3H, s, 2-OCH₃), 3.89 (3H, s, 3-OCH₃), 5.95 (1H, d, *J* = 1.4 Hz, 12, 13-OCH₂O), 5.94 (1H, d, *J* = 1.4 Hz, 12, 13-OCH₂O), 3.83 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ : 151.5 (C-1), 139.8 (C-2), 152.9 (C-3), 107.5 (C-4), 139.5 (C-5), 35.5 (C-6), 40.8 (C-7), 33.9 (C-8), 38.9 (C-9), 132.6 (C-10), 106.0 (C-11), 147.7 (C-12), 134.9 (C-13), 141.3 (C-14), 122.3 (C-15), 122.5 (C-16), 12.5 (C-17), 22.1 (C-18),

60.7 (1-OCH₃), 61.1 (2-OCH₃), 55.9 (3-OCH₃), 100.8 (12, 13-OCH₂O), 59.7 (14-OCH₃)。以上数据与文献报道对比基本一致^[24], 鉴定化合物 **21** 为 γ -schisandrin。

化合物 **22**: 白色固体 (甲醇); $[\alpha]_D^{20} -8.7^\circ$ (*c* 0.072, MeOH); C₂₂H₂₄O₆; ESI-MS *m/z*: 385.32 [M+H]⁺。¹H-NMR (400 MHz, CDCl₃) δ : 6.48 (1H, s, H-4), 2.54 (1H, dd, *J* = 13.6, 7.2 Hz, H-6 β), 2.44 (1H, dd, *J* = 13.6, 1.9 Hz, H-6 α), 1.82 (1H, m, H-7), 1.82 (1H, m, H-8), 2.24 (1H, dd, *J* = 13.2, 9.5 Hz, H-9 β), 2.00 (1H, d, *J* = 13.2 Hz, H-9 α), 6.48 (1H, s, H-11), 0.96 (3H, d, *J* = 7.2 Hz, H-17), 0.73 (3H, d, *J* = 7.2 Hz, H-18), 3.82 (3H, s, 1-OCH₃), 5.94 (2H, overlapped, 2, 3-OCH₂O), 5.94 (2H, overlapped, 12, 13-OCH₂O), 3.83 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ : 141.4 (C-1), 134.8 (C-2), 147.7 (C-3), 106.2 (C-4), 132.9 (C-5), 38.9 (C-6), 33.7 (C-7), 40.8 (C-8), 35.4 (C-9), 138.3 (C-10), 103.3 (C-11), 148.8 (C-12), 134.5 (C-13), 141.1 (C-14), 121.1 (C-15), 122.3 (C-16), 21.9 (C-17), 12.7 (C-18), 59.8 (1-OCH₃), 100.8 (2, 3-OCH₂O), 100.8 (12, 13-OCH₂O), 59.8 (14-OCH₃)。以上数据与文献报道对比基本一致^[30], 故鉴定化合物 **22** 为 schisandrin C。

化合物 **23**: 白色晶体 (甲醇); $[\alpha]_D^{20} -150.0^\circ$ (*c* 0.056, MeOH); C₂₈H₃₄O₉; ESI-MS *m/z*: 537.28 [M+Na]⁺。¹H-NMR (400 MHz, CDCl₃) δ : 6.76 (1H, s, H-4), 5.67 (1H, s, H-6), 1.95 (1H, m, H-8), 2.30 (1H, dd, *J* = 14.0, 9.7 Hz, H-9 β), 2.15 (1H, d, *J* = 14.0 Hz, H-9 α), 6.50 (1H, s, H-11), 1.13 (3H, d, *J* = 7.0 Hz, H-17), 1.30 (3H, s, H-18), 6.01 (1H, m, H-3'), 1.67 (3H, d, *J* = 7.0 Hz, H-4'), 1.56 (3H, s, H-5'), 3.55 (3H, s, 1-OCH₃), 3.86 (3H, s, 2-OCH₃), 3.88 (3H, s, 3-OCH₃), 5.92 (1H, d, *J* = 1.4 Hz, 12, 13-OCH₂O), 5.86 (1H, d, *J* = 1.4 Hz, 12, 13-OCH₂O), 3.68 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ : 152.0 (C-1), 141.8 (C-2), 152.2 (C-3), 110.1 (C-4), 130.9 (C-5), 84.3 (C-6), 72.3 (C-7), 42.5 (C-8), 36.5 (C-9), 137.6 (C-10), 102.7 (C-11), 148.7 (C-12), 134.4 (C-13), 140.7 (C-14), 121.5 (C-15), 122.2 (C-16), 19.0 (C-17), 28.2 (C-18), 166.3 (C-1'), 127.7 (C-2'), 135.4 (C-3'), 14.4 (C-4'), 11.6 (C-5'), 60.8 (1-OCH₃), 61.0 (2-OCH₃), 56.0 (3-OCH₃), 100.6 (12, 13-OCH₂O), 59.1 (14-OCH₃)。以上数据与文献报道对比基本一

致^[31], 鉴定化合物 **23** 为 schisantherin C。

化合物 **24**: 白色晶体 (甲醇); $[\alpha]_D^{20} -13.5^\circ$ (c 0.052, MeOH); $C_{22}H_{26}O_6$; ESI-MS m/z : 387.26 $[M+H]^+$ 。¹H-NMR (400 MHz, $CDCl_3$) δ : 6.63 (1H, s, H-4), 2.25 (1H, dd, $J = 13.2, 9.4$ Hz, H-6 β), 2.00 (1H, d, $J = 13.2$ Hz, H-6 α), 1.83 (1H, overlapped, H-7), 1.83 (1H, overlapped, H-8), 2.55 (1H, dd, $J = 13.6, 7.3$ Hz, H-9 β), 2.44 (1H, dd, $J = 13.6, 1.8$ Hz, H-9 α), 6.49 (1H, s, H-11), 0.73 (3H, d, $J = 7.1$ Hz, H-17), 0.97 (3H, d, $J = 7.1$ Hz, H-18), 3.50 (3H, s, 1-OCH₃), 3.93 (3H, s, 2-OCH₃), 5.70 (1H, s, 3-OH), 5.96 (2H, d, $J = 1.4$ Hz, 12, 13-OCH₂O), 3.78 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, $CDCl_3$) δ : 150.4 (C-1), 137.5 (C-2), 148.8 (C-3), 110.3 (C-4), 140.4 (C-5), 35.2 (C-6), 41.0 (C-7), 33.9 (C-8), 39.1 (C-9), 132.8 (C-10), 106.3 (C-11), 147.8 (C-12), 135.2 (C-13), 141.4 (C-14), 121.6 (C-15), 122.6 (C-16), 12.5 (C-17), 22.0 (C-18), 60.3 (1-OCH₃), 61.2 (2-OCH₃), 100.9 (12, 13-OCH₂O), 59.8 (14-OCH₃)。以上数据与文献报道对比基本一致^[32], 鉴定化合物 **24** 为 neglschisandrin E。

化合物 **25**: 黄色粉末 (甲醇); $[\alpha]_D^{20} +117.9^\circ$ (c 0.056, MeOH); $C_{24}H_{30}O_6$; ESI-MS m/z : 415.30 $[M+H]^+$ 。¹H-NMR (400 MHz, $CDCl_3$) δ : 6.65 (1H, s, H-4), 3.00 (1H, d, $J = 12.3$ Hz, H-6 β), 2.93 (1H, d, $J = 12.3$ Hz, H-6 α), 2.70 (1H, m, H-8), 2.54 (2H, m, H-9), 6.55 (1H, s, H-11), 1.01 (3H, d, $J = 7.2$ Hz, H-17), 4.86 (1H, d, $J = 2.0$ Hz, H-18a), 4.72 (1H, d, $J = 2.0$ Hz, H-18b), 3.60 (3H, s, 1-OCH₃), 3.86 (3H, s, 2-OCH₃), 3.90 (3H, s, 3-OCH₃), 3.89 (3H, s, 12-OCH₃), 3.89 (3H, s, 13-OCH₃), 3.62 (3H, s, 14-OCH₃); ¹³C-NMR (100 MHz, $CDCl_3$) δ : 151.4 (C-1), 140.3 (C-2), 153.1 (C-3), 107.1 (C-4), 136.6 (C-5), 37.2 (C-6), 154.0 (C-7), 38.7 (C-8), 37.9 (C-9), 133.3 (C-10), 110.5 (C-11), 152.0 (C-12), 140.5 (C-13), 151.6 (C-14), 123.8 (C-15), 122.6 (C-16), 20.7 (C-17), 111.0 (C-18), 60.7 (1-OCH₃), 61.1 (2-OCH₃), 56.0 (3-OCH₃), 56.1 (12-OCH₃), 61.1 (13-OCH₃), 60.7 (14-OCH₃)。以上数据与文献报道对比基本一致^[33], 鉴定化合物 **25** 为 7(18)-dehydroschisandro A。

化合物 **26**: 棕色油状物 (甲醇); $[\alpha]_D^{20} +11.5^\circ$ (c 0.096, MeOH); $C_{20}H_{24}O_4$; ESI-MS m/z : 329.20 $[M+H]^+$ 。¹H-NMR (400 MHz, $CDCl_3$) δ : 6.62 (1H, d, $J =$

1.9 Hz, H-2), 6.83 (1H, d, $J = 7.9$ Hz, H-5), 6.63 (1H, dd, $J = 7.9, 1.9$ Hz, H-6), 2.74 (1H, dd, $J = 13.6, 6.0$ Hz, H-7a), 2.24 (1H, dd, $J = 13.6, 9.1$ Hz, H-7b), 1.73 (1H, overlapped, H-8), 0.84 (3H, d, $J = 6.8$ Hz, H-9), 3.87 (3H, s, 3-OCH₃), 5.45 (1H, s, 4-OH), 6.65 (1H, d, $J = 1.7$ Hz, H-2'), 6.73 (1H, d, $J = 7.9$ Hz, H-5'), 6.60 (1H, dd, $J = 7.9, 1.7$ Hz, H-6'), 2.70 (1H, dd, $J = 13.2, 6.4$ Hz, H-7'a), 2.29 (1H, dd, $J = 13.2, 9.1$ Hz, H-7'b), 1.73 (1H, overlapped, H-8'), 0.82 (3H, d, $J = 6.8$ Hz, H-9'), 5.92 (2H, s, 3', 4'-OCH₂O); ¹³C-NMR (100 MHz, $CDCl_3$) δ : 133.9 (C-1), 111.5 (C-2), 146.4 (C-3), 143.7 (C-4), 114.1 (C-5), 121.8 (C-6), 39.0 (C-7), 39.4 (C-8), 16.4 (C-9), 56.0 (3-OCH₃), 135.8 (C-1'), 109.5 (C-2'), 147.6 (C-3'), 145.6 (C-4'), 108.1 (C-5'), 121.8 (C-6'), 39.2 (C-7'), 39.5 (C-8'), 16.3 (C-9'), 100.9 (3', 4'-OCH₂O)。以上数据与文献报道对比基本一致^[34], 鉴定化合物 **26** 为 anwulignan。

4 讨论

近年来课题组对苏黄止咳胶囊改善气道重塑^[35]、痰阻塞^[36]、抑制炎症反应^[37]、以及治疗 CVA^[38-39]和 PIC^[40]等方面的药理机制进行了阐释, 其功效成分及机制正在研究中。本研究作为该项目的一部分, 进一步丰富了其臣药五味子化学成分多样性, 为后续开展苏黄止咳胶囊的药效物质基础研究及其质量控制奠定了基础。

利益冲突 所有作者均声明不存在利益冲突

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