千里香化学成分研究

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摘　要:研究千里香的化学成分。采用硅胶、ODS、Sephadex LH-20、制备液相等多种色谱分离技术进行分离纯化,通过波谱数据分析进行结构鉴定。从千里香 70% 乙醇提取物中分离得到 26 个化合物,分别鉴定为千里香脂素(**1**)、8-去甲基川陈皮素(**2**)、ficusal(**3**)、lariciresinol-4′-monomethy ether(**4**)、(±)-5′-methoxy-4′-*O*-methyllariciresinol(**5**)、diospyrosin(**6**)、(-)-9′-*O*-*E*-feruloyl-lyoniresinol(**7**)、7-*O*-methylphellodenol-B(**8**)、欧芹烯酮酚甲醚(**9**)、3,4′-二羟基-3′,5′-二甲氧基苯丙酮(**10**)、4′-羟基-5,7-二甲氧基二氢黄酮(**11**)、5-羟基-6,7,3′,4′-四甲氧基二氢黄酮(**12**)、4′-羟基-5,7,3′-三甲氧基二氢黄酮(**13**)、5,7,3′,4′,5′-五甲氧基二氢黄酮(**14**)、2′,4-二羟基-3′,4′,6′-三甲氧基查尔酮(**15**)、2′,3-二羟基-4,4′,6′-三甲氧基查尔酮(**16**)、楝叶吴萸素 B(**17**)、2′-羟基-3,4,5,4′,6′-五甲氧基查尔酮(**18**)、2′-羟基-3,4,4′,6′-四甲氧基查尔酮(**19**)、5,8-二羟基-6,7,3′,4′-四甲氧基黄酮(**20**)、3′-羟基-5,6,7,8,4′,5′-六甲氧基黄酮(**21**)、5,3′,5′-三羟基-7,4′-二甲氧基黄酮(**22**)、5,7,3′-三羟基-8,4′-二甲氧基黄酮(**23**)、3′-羟基-5,6,7,4′-四甲氧基黄酮(**24**)、5,7,3′,4′,5′-五甲氧基黄酮(**25**)、5-羟基-6,7,8,3′,4′-五甲氧基黄酮(**26**),其中化合物 **1**、**2** 为新化合物,化合物 **3**~**8**、**10**~**13**、**15**、**16**、**20**~**24** 为首次从九里香属植物中分离得到,化合物 **17** 为首次从千里香中分离得到。

关键词:千里香;化学成分;木脂素;黄酮;香豆素

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Chemical constituents of *Murraya paniculata* (L.) Jack.

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Abstract: To study the chemical constituents of *Murraya paniculata* (L.) Jack, two new compounds, named as murrayanin (**1**) and 8-demethylnobiletin (**2**), along with twenty-four known compounds (**3-26**) were isolated from the 70% EtOH extract of *M. paniculata* by various chromatographic techniques such as silica gel, ODS, Sephadex-LH 20, Pre-HPLC, their structures was elucidated by spectral data analysis. The known compounds were identified as ficusal (**3**), lariciresinol-4′-monomethy ether (**4**), (±)-5′-methoxy-4′-*O*-methyllariciresinol (**5**), diospyrosin (**6**), (-)-9′-*O*-*E*-feruloyl-lyoniresinol (**7**), 7-*O*-methylphellodenol-B (**8**), osthenon (**9**), 3,4′-dihydroxy-3′,5′-dimethoxyphenylacetone (**10**), 4′-hydroxy-5,7-dimethoxyflavanone (**11**), cystosiphonin (**12**), 4′-hydroxy-5,7,3′-trimethoxyflavanone (**13**), 5,7,3′,4′,5′-pentamethoxyflavanone (**14**), 2′,4-dihydroxy-3′,4′,6′-trimethoxychalcone (**15**), 2′,3-dihydroxy-4,4′,6′-trimethoxychalcone (**16**), evofolin B (**17**), 2′-hydroxy-3,4,5,4′,6′-pentamoxychalcone (**18**), 2′-hydroxy-3,4,4′,6′-tetramethoxychalone (**19**), 5,8-dihydroxy-6,7,3′,4′-tetramethoxyflavone (**20**), 3′-hydroxy-5,6,7,8,4′,5′-hexamethoxyflavone (**21**), 5,3′,5′-trihydroxy-7,4′-dimethoxyflavone (**22**), 5,7,3′-trihydroxy-8,4′-dimethoxyflavone (**23**), 8-hydroxy-5,6,7,3′,4′-pentamoxyflavone (**23**), 3′-hydroxy-5,6,7,4′-tetramethoxyflavone (**24**), 5,7,3′,4′,5′-pentamethoxyflavone (**25**) and 5-hydroxy-6,7,8,3′,4′-pentamethoxyflavone (**26**), respectively. Compounds **3-8**, **10-13**, **15**, **16**, **20-24** were obtained from the genus *Murraya* for the first time, and compound **17** were isolated from *M. paniculata* for the first time.

Key words: *Murraya paniculata* (L.) Jack.; chemical constituent; lignan; flavone; coumarin

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千里香 *Murraya paniculata*(L.)Jack. 又名九树香、七里香、万里香、过山香,是芸香科九里香属植物。千里香为中药九里香基原植物之一,其入药部位为干燥叶和带叶嫩枝,具有行气止痛,活血散瘀之功效[1]。千里香主要分布于中国云南、广东、广西、福建、台湾等地[2]。常用于治疗多种疾病,特别是炎症性病变、风湿性关节痛以及胃痛。现代药理学研究发现其具抗炎镇痛、抗生育、降血糖,麻醉及抗肿瘤[3-6]等作用。目前报道的千里香的化学成分主要为黄酮类、香豆素类、生物碱类及挥发油类[7-10],黄酮类与香豆素类是其主要成分,主要存在于枝和叶中,多甲氧基黄酮是其特征之一,生物碱类主要存在于根和皮中,多为吲哚类[10]。目前现行的中国药典中仅有性状、理化鉴别及水分检查项,无定性定量鉴别,目前药材市场中,九里香商品药材的主流品种为千里香,为了后续开展其质量标准及药效物质基础研究,提高其资源综合利用效率,对千里香进行系统性化学研究。本研究从千里香中分离鉴定的化合物,以多甲氧基黄酮类化合物为主,前人报道该类成分有较好的生物活性[6],本研究不仅丰富了千里香中化学成分的信息,也为其活性筛选提供了物质基础,同时可为其质量标准研究提供指标性成分。

1 材料与方法

1.1 仪器与试剂

Bruker AVANCE-III(400 MHz)型核磁共振波谱仪;Waters UPLC Premior Q-TOF 质谱仪;Agilent 1260 制备型高效液相色谱仪(Pre-HPLC,安捷伦,美国,体积流量 10 mL/min);中压液相色谱仪(MPLC,Grace,美国,体积流量 6 mL/min);制备色谱柱(Shiseido Capcellpak C_{18},250 mm × 20 mm,5 μm,资生堂,日本);MCI gel CHP20P(75 ~ 150 μm,三菱化学有限公司,日本);凝胶 Sephadex LH-20(25 ~ 100 μm,通用电器医疗集团,美国);YMC gel ODS-AQ(50 μm,YMC 有限公司,日本);柱色谱硅胶(100 ~ 200、200 ~ 300、300 ~ 400 目,青岛海洋化工厂),薄层色谱及制备型薄层色谱 $HSGF_{254}$ 硅胶板(烟台江友硅胶开发有限公司,中国);CD_3OD、$CDCl_3$(Cambridge Isotope Laborato-ries,美国);乙腈、甲醇(Dikma 公司,色谱级,美国);薄层色谱用分析纯有机试剂为国药集团上海化学试剂公司生产;柱色谱用石油醚、乙酸乙酯、二氯甲烷、甲醇为上海润捷化学试剂有限公司生产的工业用有机试剂。

1.2 材料

实验用千里香的干燥枝叶采自广西,并由上海中医药大学吴立宏研究员鉴定为千里香 *Murraya paniculata*(L.)Jack. 的枝叶,标本保存于上海中医药大学中药研究所。

1.3 提取与分离

干燥的千里香枝叶粉碎成粗粉(23 kg),用 70% 乙醇加热回流提取 3 次,减压浓缩得总浸膏约 3.03 kg。将千里香总浸膏混悬于温水中,依次用石油醚、二氯甲烷、乙酸乙酯、正丁醇萃取,减压回收溶剂后得到不同极性的萃取部位。

二氯甲烷部位(798.5 g)与等量硅胶(100 ~ 200 目)拌样后经 10 倍量硅胶(200 ~ 300 目)装填的硅胶柱色谱,石油醚-乙酸乙酯系统(100∶1→0∶1)和乙酸乙酯-甲醇系统(10∶1→0∶1)不同比例梯度洗脱得到 B-1 ~ B-18。B-15(187 g)经硅胶色谱柱以二氯甲烷-甲醇(100∶1→0∶1)不同比例梯度洗脱得到 B-15-1 ~ B-15-18。B-15-8(16 g)经中压色谱柱,水-甲醇(3∶1→0∶1)梯度洗脱得 B-15-8-1 ~ B-15-8-13。B-15-8-3 经 Sephadex LH-20 凝胶柱色谱,石油醚-二氯甲烷-甲醇(5∶5∶1)洗脱、经制备液相(乙腈-水 45∶55)洗脱,得到化合物 **1**(2 mg)。B-15-8-5 ~ B-15-8-13 分别经 Sephadex LH-20 凝胶柱色谱,石油醚-二氯甲烷-甲醇(5∶5∶1)洗脱、经制备薄层板、制备液相分离得到化合物 **4**(5 mg)、**5**(3 mg)、**6**(3 mg)、**7**(9 mg)、**20**(13 mg)、**21**(8 mg)、**22**(25 mg)、**23**(7 mg)、**2**(6 mg)、**24**(150 mg)。B-15-7(22 g)经中压色谱柱,水-甲醇(3∶1→0∶1)梯度洗脱得 B15-7-1 ~ B-15-7-16。B-15-7-3 ~ B-15-7-12 分别经 Sephadex LH-20 凝胶柱色谱,石油醚-二氯甲烷-甲醇(5∶5∶1)洗脱、经制备薄层板、制备液相分离得到化合物 **3**(8 mg)、**8**(5 mg)、**9**(3 mg)、**10**(3 mg)、**11**(5 mg)、**12**(7 mg)。B-15-4(7.6 g)经 MCI 色谱柱[水-甲醇(3∶1→0∶1)]、Sephadex LH-20 凝胶柱色谱以及制备液相分离得 **13**(90 mg)、**14**(126 mg)、**15**(5 mg)、**16**(23 mg)、**17**(15 mg)、**18**(20 mg)、**19**(50 mg)。B-16(5.5 g)经硅胶柱色谱,石油醚-乙酸乙酯系统(10∶1→0∶1)不同比例梯度洗脱得到 B-16-1 ~ B-16-8。B-16-1,B-16-7 分别经制备薄层板、制备液相分离得到化合物 **25**(30 mg)、**26**(13 mg)。

2 结构鉴定

化合物 1 无色油状,易溶于甲醇;$[\alpha]_D^{20}$ +6.0(*c* 0.1,MeOH);HR-ESI-MS:*m/z* 471.199 1 [M +

Na]$^+$(calcd for $C_{24}H_{32}O_8Na$,471.198 9),确定其分子式为 $C_{24}H_{32}O_8$。红外光谱可见羟基吸收带(3 374 cm^{-1})。化合物 **1** 的^{1}H NMR(CD_3OD,400 MHz)谱中,可见苯环上对称的芳香质子信号 δ_H 6.65(2H,s,H-2′,H-6′),6.54(2H,s,H-2,H-6),结合^{13}C NMR(CD_3OD,100 MHz)谱数据 δ_C138.3(C-1),106.9(C-2,C-6),154.5(C-3,C-5),137.3(C-4),140.7(C-1′),103.9(C-2′,C-6′),154.5(C-3′,C-5′),138.1(C-4′),表明 1 具有两个 1,3,4,5-四取代的苯环。此外,还可见 6 个甲氧基信号 δ_H 3.83(6H,s,3′-OCH_3,5′-OCH_3),3.82(6H,s,3-OCH_3,5-OCH_3),3.75(3H,s,4′-OCH_3),3.74(3H,s,4-OCH_3)(见表 1)。在 HMBC 中,甲氧基 δ_H 3.83(3′-OCH_3,5′-OCH_3),3.82(3-OCH_3,5-OCH_3),3.75(4′-OCH_3),3.74(4-OCH_3)分别于 δ_C154.5(C-3,C-5),154.5(C-3′,C-5′),138.1(C-4′),137.3(C-4)有相关,提示化合物 **1** 存在两个具 3,4,5-三甲氧基的四取代苯环。此外,**1** 的^{1}H 和^{13}C NMR 谱结合 HMQC 谱,尚可观察到 1 个亚甲基信号 δ_H2.96(1H,dd,J = 13.3,4.8 Hz,H-7a),2.55(1H,dd,J = 13.3,11.2 Hz,H-7b),δ_C34.4(C-7);2 个连氧亚甲基信号 δ_H4.03(1H,dd,J = 8.3,6.5,H-9a),3.77(1H,dd,J = 8.3,6.5 Hz,H-9b),δ_C 73.6(C-9)和 δ_H3.86(1H,dd,J = 11.0,7.5 Hz,H-9′a),3.69(1H,dd,J = 11.0,6.9 Hz,H-9′b),δ_C60.5(C-6);1 个连氧次甲基信号 δ_H 4.83(1H,d,J = 6.5 Hz,H-7′),δ_C84.0(C-7′);以及 2 个次甲基信号 δ_H 2.75(1H,m,H-8),δ_C43.6(C-8)和 δ_H 2.38(1H,m,H-8′),δ_C54.2(C-8′)。上述信息表明化合物 **1** 是单环氧木脂素类化合物。化合物 **1** 的^{1}H-^{1}H COSY 谱显示 H_2-7/H-8/H_2-9,H-7′/H-8′/H_2-9′以及 H-8/H-8′有相关,进一步表明 **1** 为 7′-*O*-9 型单环氧木脂素类化合物。在 HMBC 中,可见 H_2-7 与 C-1、C-2 和 C-6 相关,H-7′与 C-1′、C-2′和 C-6′相关。综合上述信息,推导出 **1** 的平面结构如图 1 所示,与已知化合物(-)-seselinone[11] 的结构十分相似,唯一不同之处在于(-)-seselinone 的 7 位为羰基而化合物 **1** 的 7 位为亚甲基。在 1 的 NOESY 谱中,可见 H-7′与 H-7b 和 H_2-9′相关信号,H-8 和 H-8′在相对的一侧,为 α 取向。化合物 **1** 的绝对构型通过比较 TDDFT ECD 实验和计算 ECD 确定的,在化合物 **1** 的实验 ECD 谱中,可见在 200 ~ 230 nm 之间出现正 Cotton 效应,在 230 ~ 260 nm 之间出现负 Cotton 效应,与 7′*S*、8*R*、8′*R* 构型计算的 ECD 曲线基本吻合(见图 2),故确定其构型为 7′*S*、8*R*、8′*R*。因此化合物 **1** 被鉴定为(7′*S*,8*R*,8′*R*)-7′α-(3,4,5-三甲氧基苯基)-8′β-羟甲基-8β-(3,4,5-三甲氧基苄基)-四氢呋喃。经 SciFinder^n 检索确定 **1** 为新化合物,命名为千里香脂素(murrayanin)。化合物 **1** 和 **2** 的详细结构鉴定数据原始图谱可从本刊官网免费下载(www.trcw.ac.cn)。

表 1 化合物 1 的^{1}H NMR 和^{13}C NMR 数据(CD_3OD,400 和 100 MHz)

Table 1 ^{1}H NMR and ^{13}C NMR data of compound **1** (CD_3OD,400 and 100 MHz)

位置 Position	δ_H(J in Hz)	δ_C	位置 Position	δ_H(J in Hz)	δ_C
1		138.3	1′		140.7
2	6.54,s	106.9	2′	6.65,s	103.9
3		154.5	3′		154.5
4		137.3	4′		138.1
5		154.5	5′		154.5
6	6.54,s	106.9	6′	6.65,s	103.9
7a	2.96,dd(13.3,4.8)	34.4	3-OCH_3	3.82,s	56.5
7b	2.55,dd(13.3,11.2)				
8	2.75,m	43.6	4-OCH_3	3.74,s	61.0
9a	4.03,dd(8.3,6.5)	73.6	5-OCH_3	3.82,s	56.5
9b	3.77,dd(8.3,6.5)				
7′	4.83,d(6.5)	84.0	3′-OCH_3	3.83,s	56.5
8′	2.38,m	54.2	4′-OCH_3	3.75,s	61.0
9′a	3.86,dd(11.0,7.5)	60.5	5′-OCH_3	3.83,s	56.5
9′b	3.69,dd(11.0,6.9)				

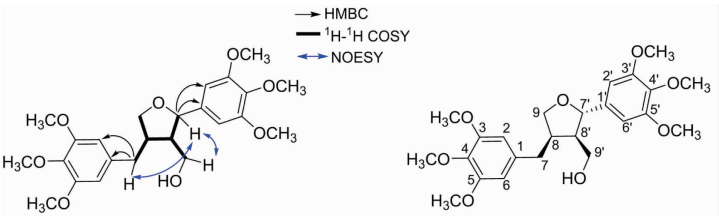

图 1　化合物 1 的结构及关键相关信号

Fig. 1　Chemical structure and key correlations of compound **1**

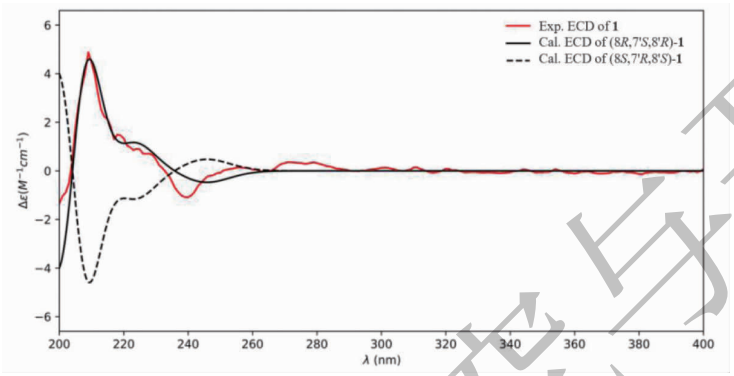

图 2　化合物 1 的 ECD 谱

Fig. 2　ECD spectra of compound **1**

化合物 2　淡黄色粉末，易溶于甲醇，通过高分辨质谱 HR-ESI-MS *m/z* 389.123 4 [M + H]$^+$ (calcd for $C_{20}H_{21}O_8$, 389.123 1)，确定其分子式为 $C_{20}H_{20}O_8$。化合物 **2** 的^{1}H NMR 谱示有一个单峰氢信号 δ_H 6.64(1H, s, H-3)，一组 ABX 偶合系统芳香质子信号 δ_H 7.67 (1H, dd, J = 8.5, 2.2 Hz, H-6′)，7.57 (1H, d, J = 2.2 Hz, H-2′)，7.08 (1H, d, J = 8.5 Hz, H-5′)以及 5 个甲氧基信号(见表 2)。^{13}C NMR 谱中共有 20 个碳信号(见表 2)，其中羰基信号 δ_C 180.1 (C-4) 以及两个烯碳信号 δ_C 163.9 (C-2)，106.6 (C-3)为黄酮的特征信号峰，提示 **2** 具有黄酮骨架。**2** 与已知化合物 8-羟基-3,5,6,7,3′,4′-六甲氧基黄酮[12]极为相似，唯一不同之处在于已知化合物的氢谱信号无单峰氢信号，表明已知化合物的 C-3 位有甲氧基取代，而 **2** 的 C-3 位氢未被取代。进一步由 HMBC 相关信号证实，**2** 的五个甲氧基 δ_H 4.02、3.94、3.93、3.90、3.85 分别位于 C-5、C-7、C-3′、C-4′、C-6 位上(见图 3)。综上所述，鉴定 **2** 为 8-羟基-5,6,7,3′,4′-五甲氧基黄酮，并命名为 8-去甲基川陈皮素，经 SciFinder^n 检索确定化合物 **2** 为新化合物。

表 2　化合物 2 的^{1}H NMR 和^{13}C NMR 数据(CD_3OD, 400 和 100 MHz)

Table 2　^{1}H NMR and ^{13}C NMR data of compound **2** (CD_3OD, 400 and 100 MHz)

位置 Position	δ_H (J in Hz)	δ_C	位置 Position	δ_H (J in Hz)	δ_C
1			2′	7.57, d(2.2)	110.5
2		163.9	3′		150.7
3	6.64, s	106.6	4′		153.8
4		180.1	5′	7.08, d(8.5)	112.6
5		147.5	6′	7.67, dd(8.5, 2.2)	121.4
6		144.6	5-OCH_3	4.02, s	61.8
7		145.7	6-OCH_3	3.85, s	62.6

续表 2(Continued Tab. 2)

位置 Position	δ_H (J in Hz)	δ_C	位置 Position	δ_H (J in Hz)	δ_C
8		138.5	7-OCH_3	3.94,s	62.0
9		145.0	3′-OCH_3	3.93,s	56.6
10		115.4	4′-OCH_3	3.90,s	56.4
1′		124.9			

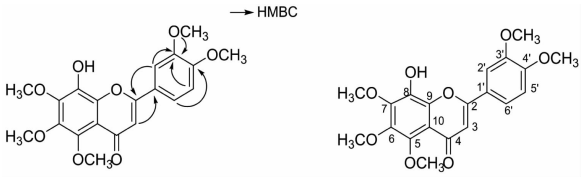

图 3　化合物 2 的结构及 HMBC 关键相关信号

Fig. 3　Chemical structure and key correlations of compound **2**

化合物 3　棕黄色粉末;^{1}H NMR(400 MHz, CD_3OD)δ:9.76(1H,s,H-7′),7.48(1H,d,J = 1.4 Hz,H-6′),7.41(1H,d,J = 1.4 Hz,H-2′),6.91(1H,d,J = 1.8 Hz,H-2),6.83(1H,dd,J = 8.2,1.8 Hz,H-6),6.79(1H,d,J = 8.2 Hz,H-5),5.66(1H,d,J = 6.6 Hz,H-7),3.92(3H,s,5′-OCH_3),3.86(2H,m,H-9),3.82(3H,s,3-OCH_3),3.64(1H,m,H-8);^{13}C NMR(100 MHz,CD_3OD)δ:132.8(C-1),110.1(C-2),147.2(C-3),148.5(C-4),115.8(C-5),119.6(C-6),90.3(C-7),53.6(C-8),64.0(C-9),131.9(C-1′),122.2(C-2′),130.4(C-3′),155.0(C-4′),145.7(C-5′),112.9(C-6′),192.3(C-7′),56.2(3-OCH_3),56.4(5′-OCH_3)。以上数据与文献[13]报道一致,故鉴定化合物 **3** 为 ficusal。

化合物 4　淡黄色油状液体;^{1}H NMR(400 MHz,CD_3OD)δ:6.94(1H,d,J = 1.3 Hz,H-2),6.92(1H,d,J = 8.2 Hz,H-5),6.88(1H,dd,J = 8.2,1.3 Hz,H-6),6.80(1H,d,J = 1.4 Hz,H-2′),6.72(1H,d,J = 8.0 Hz,H-5′),6.64(1H,dd,J = 8.0,1.4 Hz,H-6′),4.80(1H,d,J = 6.6 Hz,H-7),4.00(1H,dd,J = 8.2,6.6 Hz,H-9′a),3.85(1H,dd,J = 10.9,6.7 Hz,H-9a),3.83(6H,s,3-OCH_3,3′-OCH_3),3.82(3H,s,4-OCH_3),3.74(1H,dd,J = 8.2,6.6 Hz,H-9′b),3.65(1H,dd,J = 10.9,6.7 Hz,H-9b),2.92(1H,dd,J = 13.4,4.8 Hz,H-7′a),2.73(1H,m,H-8′),2.50(1H,dd,J = 13.4,11.3 Hz,H-7′b),2.37(1H,m,H-8);^{13}C NMR(100 MHz,CD_3OD)δ:137.3(C-1),110.8(C-2),150.5(C-3),149.0(C-4),113.3(C-5),119.5(C-6),83.9(C-7),54.0(C-8),60.4(C-9),133.5(C-1′),112.8(C-2′),149.9(C-3′),145.8(C-4′),116.2(C-5′),122.1(C-6′),33.6(C-7′),43.8(C-8′),73.6(C-9′),56.5(3-OCH_3),56.4(4-OCH_3),56.3(3′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **4** 为 lariciresinol-4′-monomethy ether[14]。

化合物 5　黄色油状液体;^{1}H NMR(400 MHz,$CDCl_3$)δ:6.79(1H,d,J = 1.4 Hz,H-2′),6.71(1H,d,J = 8.0 Hz,H-5′),6.63(1H,dd,J = 8.0,1.4 Hz,H-6′),6.64(2H,s,H-2,H-6),4.84(1H,d,J = 6.2 Hz,H-7),4.01(1H,dd,J = 8.2,6.7 Hz,H-9′a),3.88(1H,dd,J = 10.9,7.3 Hz,H-9a),3.83(9H,s,3-OCH_3,5-OCH_3,3′-OCH_3),3.75(3H,s,4-OCH_3),3.75(1H,dd,J = 8.2,6.7 Hz,H-9′b),3.68(1H,dd,J = 10.9,7.3 Hz,H-9b),2.90(1H,dd,J = 13.4,5.0 Hz,H-7′a),2.71(1H,m,H-8′),2.51(1H,dd,J = 13.4,11.1 Hz,H-7′b),2.35(1H,m,H-8);^{13}C NMR(100 MHz,$CDCl_3$)δ:133.4(C-1),103.9(C-2),154.5(C-3),140.8(C-4),154.5(C-5),103.9(C-6),84.1(C-7),54.1(C-8),60.5(C-9),138.1(C-1′),113.3(C-2′),149.0(C-3′),145.8(C-4′),116.2(C-5′),122.1(C-6′),33.6(C-7′),43.7(C-8′),73.7(C-9′),56.5(3-OCH_3,5-OCH_3),61.0(4-OCH_3),56.3(3′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **5** 为(±)-5′-methoxy-4′-*O*-methyllariciresinol[15]。

化合物 6　淡黄色油状液体;^{1}H NMR(400 MHz,CD_3OD)δ:9.58(1H,d,J = 7.8 Hz,H-9),7.62(1H,d,J = 15.7 Hz,H-7),7.29(1H,brs,H-6),7.23(1H,brs,H-2),6.95(1H,d,J = 1.8 Hz,H-6′),6.83(1H,dd,J = 8.1,1.8 Hz,H-4′),6.78(1H,d,J = 8.1 Hz,H-3′),6.69(1H,dd,J = 15.7,7.8 Hz,H-8),5.60(1H,d,J = 6.2 Hz,H-7′),3.91(3H,s,-OCH_3),3.84(2H,m,H-9′),3.82(3H,s,-OCH_3),3.56(1H,m,H-8′);^{13}C NMR(100 MHz,CD_3OD)δ:129.6(C-1),114.3(C-2),146.0(C-3),

152.9(C-4),131.3(C-5),119.9(C-6),156.0(C-7),127.1(C-8),196.1(C-9),133.9(C-1′),147.8(C-2′),116.2(C-3′),119.8(C-4′),149.1(C-5′),110.6(C-6′),90.1(C-7′),54.6(C-8′),64.5(C-9′),56.8(-OCH_3),56.4(-OCH_3)。以上数据与文献报道一致,故鉴定化合物**6**为diospyrosin[16]。

化合物7 淡黄色油状液体;^{1}H NMR(400 MHz,CD_3OD)δ:7.58(1H,d,J = 15.9 Hz,H-7″),7.19(1H,d,J = 2.2 Hz,H-2″),7.06(1H,dd,J = 8.2,2.2 Hz,H-6″),6.81(1H,d,J = 8.2 Hz,H-5″),6.60(1H,s,H-6),6.40(1H,d,J = 15.9 Hz,H-8″),6.36(2H,s,H-2′,H-6′),4.30(1H,J = 6.3 Hz,H-7′),4.30(1H,dd,J = 11.2,6.3 Hz,H-9′),4.11(1H,dd,J = 11.2,5.2 Hz,H-9′),3.88(3H,s,3″-OCH_3),3.87(3H,s,5-OCH_3),3.70(6H,s,3′-OCH_3,5′-OCH_3),3.62(1H,dd,J = 11.0,6.6 Hz,H-9),3.54(1H,dd,J = 11.0,6.6 Hz,H-9),3.35(3H,s,3-OCH_3),2.77(1H,dd,J = 15.1,4.7 Hz,H-7),2.65(1H,dd,J = 15.1,11.6 Hz,H-7),2.25(1H,m,H-8′),1.76(1H,m,H-8);^{13}C NMR(100 MHz,CD_3OD)δ:130.0(C-1),125.9(C-2),147.4(C-3),138.9(C-4),148.8(C-5),107.7(C-6),33.6(C-7),40.7(C-8),66.0(C-9),138.8(C-1′),106.5(C-2′),149.0(C-3′),134.6(C-4′),149.0(C-5′),106.5(C-6′),43.2(C-7′),45.8(C-8′),66.3(C-9′),127.6(C-1″),111.6(C-2″),149.4(C-3″),150.7(C-4″),116.4(C-5″),124.2(C-6″),147.0(C-7″),115.4(C-8″),169.3(C-9″),60.0(3-OCH_3),56.5(5-OCH_3),56.7(3′-OCH_3,5′-OCH_3),56.4(3″-OCH_3)。以上数据与文献报道一致,故鉴定化合物**7**为(-)-9′-*O*-*E*-feruloyl-lyoniresinol[17]。

化合物8 白色针状晶体(甲醇∶氯仿=1∶1);^{1}H NMR(400 MHz,$CDCl_3$)δ:7.76(1H,d,J = 9.4 Hz,H-4),7.41(1H,d,J = 8.6 Hz,H-5),6.92(1H,d,J = 8.6 Hz,H-6),6.23(1H,d,J = 9.4 Hz,H-3),3.91(3H,s,7-OCH_3),3.71(2H,t,J = 7.3 Hz,H-2′),3.09(2H,t,J = 7.3 Hz,H-1′);^{13}C NMR(100 MHz,$CDCl_3$)δ:163.2(C-2),113.4(C-3),145.5(C-4),127.8(C-5),108.3(C-6),161.5(C-7),114.9(C-8),153.7(C-9),112.6(C-10),26.6(C-1′),61.2(C-2′),56.4(7-OCH_3)。以上数据与文献报道一致,故鉴定化合物**8**为7-*O*-methylphellodenol-B[18]。

化合物9 淡黄色粉末;^{1}H NMR(400 MHz,$CDCl_3$)δ:7.98(1H,d,J = 16.7 Hz,H-1′),7.65(1H,d,J = 9.5 Hz,H-4),7.46(1H,d,J = 8.7 Hz,H-5),7.34(1H,d,J = 16.7 Hz,H-2′),6.91(1H,d,J = 8.7 Hz,H-6),6.31(1H,d,J = 9.5 Hz,H-3),4.00(3H,s,7-OCH_3),2.43(1H,s,H-4′);^{13}C NMR(100 MHz,$CDCl_3$)δ:160.2(C-2),111.7(C-3),143.7(C-4),130.2(C-5),107.8(C-6),161.8(C-7),113.6(C-8),113.0(C-9),153.9(C-10),132.6(C-1′),131.5(C-2′),199.9(C-3′),27.8(C-4′),56.4(7-OCH_3)。以上数据与文献报道一致,故鉴定化合物**9**为欧芹烯酮酚甲醚[19]。

化合物10 无色油状液体;^{1}H NMR(400 MHz,CD_3OD)δ:7.30(2H,s,H-3,H-5),3.94(2H,t,J = 6.2 Hz,H-9),3.90(6H,s,2-OCH_3,6-OCH_3),3.18(2H,t,J = 6.2 Hz,H-8);^{13}C NMR(100 MHz,CD_3OD)δ:129.2(C-1),148.9(C-2),107.1(C-3),142.4(C-4),107.1(C-5),148.9(C-6),199.6(C-7),41.6(C-8),58.9(C-9),56.8(2-OCH_3,6-OCH_3)。以上数据与文献报道一致,故鉴定化合物**10**为3,4′-二羟基-3′,5′-二甲氧基苯丙酮[20]。

化合物11 淡黄色粉末;^{1}H NMR(400 MHz,CD_3OD)δ:7.28(2H,s,H-2′,H-6′),6.82(2H,s,H-3′,H-5′),6.14(1H,d,J = 2.3 Hz,H-8),6.12(1H,d,J = 2.3 Hz,H-6),5.31(1H,dd,J = 13.1,2.9 Hz,H-2),3.84(3H,s,5-OCH_3),3.81(3H,s,7-OCH_3),3.01(1H,dd,J = 16.1,13.1 Hz,H-3),2.67(1H,dd,J = 16.1,2.9 Hz,H-3);^{13}C NMR(100 MHz,CD_3OD)δ:79.9(C-2),45.9(C-3),192.0(C-4),163.2(C-5),93.6(C-6),167.7(C-7),94.6(C-8),166.4(C-9),106.3(C-10),130.5(C-1′),128.6(C-2′),116.1(C-3′),158.4(C-4′),116.1(C-5′),128.6(C-6′),56.2(5-OCH_3),56.1(7-OCH_3)。以上数据与文献报道一致,故鉴定化合物**11**为4′-羟基-5,7-二甲氧基二氢黄酮[21]。

化合物12 淡黄色粉末;^{1}H NMR(400 MHz,CD_3OD)δ:7.15(1H,d,J = 1.9 Hz,H-2′),7.07(1H,dd,J = 8.3,1.9 Hz,H-6′),6.99(1H,d,J = 8.3 Hz,H-5′),6.16(1H,s,H-8),5.42(1H,dd,J = 12.6,3.1 Hz,H-2),3.86(6H,s,3-OCH_3),3.81(3H,s,3′-OCH_3),3.06(1H,dd,J = 16.7,12.6 Hz,H-3),2.74(1H,dd,J = 16.7,3.1 Hz,H-3),3.86

(3H,s,4′-OCH_3),3.85(3H,s,3′-OCH_3),3.80(3H,s,7-OCH_3),3.76(3H,s,6-OCH_3);^{13}C NMR(100 MHz,CD_3OD)δ:80.4(C-2),46.1(C-3),192.1(C-4),159.5(C-5),130.7(C-6),159.5(C-7),94.1(C-8),158.2(C-9),106.0(C-10),133.1(C-1′),111.3(C-2′),150.7(C-3′),150.6(C-4′),112.8(C-5′),120.1(C-6′),61.4(6-OCH_3),56.1(7-OCH_3),56.5(3′-OCH_3,4′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **12** 为5-羟基-6,7,3′,4′-四甲氧基二氢黄酮[22]。

化合物 13 淡黄色油状液体;^{1}H NMR(400 MHz,$CDCl_3$)δ:6.95(1H,br s,H-2′),6.93(2H,m,H-5′,H-6′),6.13(1H,d,J = 2.3 Hz,H-8),6.08(1H,d,J = 2.3 Hz,H-6),5.31(1H,dd,J = 13.3,2.8 Hz,H-2),3.91(3H,s,3′-OCH_3),3.88(3H,s,5-OCH_3),3.80(3H,s,7-OCH_3),3.02(1H,dd,J = 16.5,13.3 Hz,H-3),2.75(1H,dd,J = 16.5,2.8 Hz,H-3);^{13}C NMR(100 MHz,$CDCl_3$)δ:79.4(C-2),45.6(C-3),189.6(C-4),162.5(C-5),93.2(C-6),166.0(C-7),93.6(C-8),165.1(C-9),106.0(C-10),130.6(C-1′),108.9(C-2′),146.8(C-3′),146.2(C-4′),114.6(C-5′),119.7(C-6′),56.2(5-OCH_3),55.7(7-OCH_3),56.1(3′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **13** 为4′-羟基-5,7,3′-三甲氧基二氢黄酮[23]。

化合物 14 白色粉末;^{1}H NMR(400 MHz,$CDCl_3$)δ:6.67(2H,s,H-2′,H-6′),6.17(1H,d,J = 2.3 Hz,H-6),6.10(1H,d,J = 2.3 Hz,H-8),5.33(1H,dd,J = 13.3,2.9 Hz,H-2),3.89(9H,s,5-OCH_3,3′-OCH_3,5′-OCH_3),3.85(3H,s,4′-OCH_3),3.82(3H,s,7-OCH_3),3.04(1H,dd,J = 16.5,13.3 Hz,H-3),2.77(1H,dd,J = 16.5,2.9 Hz,H-3);^{13}C NMR(100 MHz,$CDCl_3$)δ:79.5(C-2),45.8(C-3),189.2(C-4),162.4(C-5),93.7(C-6),166.1(C-7),93.3(C-8),164.9(C-9),106.0(C-10),134.4(C-1′),103.3(C-2′),153.6(C-3′),138.2(C-4′),153.6(C-5′),103.3(C-6′),56.3(5-OCH_3,3′-OCH_3,5′-OCH_3),55.7(7-OCH_3),60.9(4′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **14** 为5,7,3′,4′,5′-五甲氧基二氢黄酮[24]。

化合物 15 淡黄色粉末;^{1}H NMR(400 MHz,$CDCl_3$)δ:8.19(1H,d,J = 15.5 Hz,H-α),8.03(1H,d,J = 15.5 Hz,H-β),7.76(2H,d,J = 8.5 Hz,H-2,H-6),7.19(2H,d,J = 8.5 Hz,H-3,H-5),6.23(1H,s,H-5′),3.96(3H,s,3′-OCH_3),3.86(6H,s,4′-OCH_3,6′-OCH_3);^{13}C NMR(100 MHz,$CDCl_3$)δ:194.1(C = O),125.3(C-α),144.6(C-β),127.4(C-1),131.7(C-2),117.4(C-3),162.2(C-4),117.4(C-5),131.7(C-6),108.5(C-1′),159.3(C-2′),132.0(C-3′),158.9(C-4′),88.6(C-5′),159.0(C-6′),60.9(3′-OCH_3),56.4(4′-OCH_3),56.5(6′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **15** 为2′,4-二羟基-3′,4′,6′-三甲氧基查尔酮[25]。

化合物 16 橘黄色粉末;^{1}H NMR(400 MHz,$CDCl_3$)δ:14.41(1H,br s,-OH),7.77(1H,d,J = 15.5 Hz,H-α),7.76(1H,d,J = 15.5 Hz,H-β),7.21(1H,dd,J = 8.3,1.9 Hz,H-6),7.08(1H,d,J = 1.9 Hz,H-2),6.95(1H,d,J = 8.3 Hz,H-5),6.11(1H,d,J = 2.3 Hz,H-5′),5.96(1H,d,J = 2.3 Hz,H-3′),5.89(1H,brs,-OH),3.95(3H,s,4-OCH_3),3.91(3H,s,6′-OCH_3),3.84(3H,s,4′-OCH_3);^{13}C NMR(100 MHz,$CDCl_3$)δ:192.6(C = O),125.2(C-α),143.0(C-β),128.3(C-1),110.6(C-2),146.8(C-3),148.0(C-4),115.0(C-5),122.7(C-6),106.4(C-1′),162.5(C-2′),91.4(C-3′),166.1(C-4′),93.9(C-5′),168.5(C-6′),56.0(4-OCH_3),55.7(4′-OCH_3),55.9(6′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **16** 为2′,3-二羟基-4,4′,6′-三甲氧基查尔酮[26]。

化合物 17 棕黄色粉末;^{1}H NMR(400 MHz,CD_3OD)δ:7.61(1H,dd,J = 8.4,2.0 Hz,H-6),7.56(1H,d,J = 2.0 Hz,H-2),6.89(1H,d,J = 1.8 Hz,H-2′),6.80(1H,d,J = 8.4 Hz,H-5),6.76(1H,dd,J = 8.1,1.8 Hz,H-6′),6.72(1H,d,J = 8.1 Hz,H-5′),4.75(1H,dd,J = 8.7,5.2 Hz,H-7′),4.25(1H,dd,J = 10.7,5.2 Hz,H-8′),3.86(3H,s,3-OCH_3),3.81(3H,s,3′-OCH_3),3.71(1H,dd,J = 10.7,5.2 Hz,H-8′);^{13}C NMR(100 MHz,CD_3OD)δ:130.3(C-1),112.7(C-2),153.0(C-3),149.2(C-4),115.6(C-5),125.1(C-6),199.6(C-7),129.8(C-1′),112.5(C-2′),146.9(C-3′),148.9(C-4′),116.5(C-5′),122.1(C-6′),56.2(C-7′),65.4(C-8′),56.3(3-OCH_3),56.3(3′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **17** 为楝叶吴萸素 B[27]。

化合物 18 橘黄色粉末;^{1}H NMR(400 MHz, $CDCl_3$)δ:7.81(1H,d,J = 15.5 Hz,H-α),7.71(1H,d,J = 15.5 Hz,H-β),6.84(2H,s,H-2,H-6),6.12(1H,d,J = 2.4 Hz,H-3′),5.97(1H,d,J = 2.4 Hz,H-5′),3.92(6H,s,3-OCH_3,5-OCH_3),3.91(3H,s,6′-OCH_3),3.90(3H,s,4-OCH_3),3.84(3H,s,4′-OCH_3);^{13}C NMR(100 MHz,$CDCl_3$)δ:192.5(C=O),127.0(C-α),142.5(C-β),131.3(C-1),105.7(C-2),153.5(C-3),140.2(C-4),153.5(C-5),105.7(C-6),106.4(C-1′),168.5(C-2′),93.9(C-3′),166.3(C-4′),91.4(C-5′),162.5(C-6′),56.2(3-OCH_3,5-OCH_3),61.1(4-OCH_3),55.7(4′-OCH_3),55.9(6′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **18** 为 2′-羟基-3,4,5,4′,6′-五甲氧基查尔酮[28]。

化合物 19 橘黄色粉末;^{1}H NMR(400 MHz, $CDCl_3$)δ:7.78(1H,d,J = 15.5 Hz,H-α),7.75(1H,d,J = 15.5 Hz,H-β),7.21(1H,dd,J = 8.3,1.8 Hz,H-6),7.12(1H,d,J = 1.8 Hz,H-2),6.89(1H,d,J = 8.3 Hz,H-5),6.11(1H,d,J = 2.3 Hz,H-3′),5.96(1H,d,J = 2.3 Hz,H-5′),3.94(3H,s,4-OCH_3),3.93(3H,s,6′-OCH_3),3.91(3H,s,3-OCH_3),3.83(3H,s,4′-OCH_3);^{13}C NMR(100 MHz,$CDCl_3$)δ:192.5(C=O),125.5(C-α),142.7(C-β),128.7(C-1),110.5(C-2),149.2(C-3),151.2(C-4),111.2(C-5),122.7(C-6),106.4(C-1′),166.1(C-2′),91.4(C-3′),162.5(C-4′),93.9(C-5′),168.5(C-6′),55.9(3-OCH_3),55.9(4-OCH_3),56.1(4′-OCH_3),55.7(6′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **19** 为 2′-羟基-3,4,4′,6′-四甲氧基查尔酮[29]。

化合物 20 黄色粉末;^{1}H NMR(400 MHz, $CDCl_3$)δ:7.62(1H,dd,J = 8.6,2.1 Hz,H-6′),7.48(1H,d,J = 2.1 Hz,H-2′),6.98(1H,d,J = 8.6 Hz,H-5′),6.58(1H,s,H-3),4.03(3H,s,7-OCH_3),3.95(3H,s,4′-OCH_3),3.93(3H,s,3′-OCH_3),3.92(3H,s,6-OCH_3);^{13}C NMR(100 MHz,$CDCl_3$)δ:165.0(C-2),103.8(C-3),183.0(C-4),147.8(C-5),136.6(C-6),145.4(C-7),131.0(C-8),141.6(C-9),107.2(C-10),123.9(C-1′),109.5(C-2′),149.5(C-3′),152.7(C-4′),110.5(C-5′),120.9(C-6′),61.2(6-OCH_3),61.6(7-OCH_3),56.2(3′-OCH_3),56.2(4′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **20** 为 5,8-二羟基-6,7,3′,4′-四甲氧基黄酮[30]。

化合物 21 黄色粉末;^{1}H NMR(400 MHz, $CDCl_3$)δ:7.22(1H,d,J = 2.0 Hz,H-6′),7.03(1H,d,J = 2.0 Hz,H-2′),6.63(1H,s,H-3),4.10(3H,s,5′-OCH_3),4.02(3H,s,4′-OCH_3),3.99(3H,s,5-OCH_3),3.95(9H,s,6-OCH_3,7-OCH_3,8-OCH_3);^{13}C NMR(100 MHz,$CDCl_3$)δ:160.9(C-2),107.8(C-3),177.5(C-4),148.5(C-5),144.3(C-6),151.7(C-7),138.2(C-8),147.8(C-9),114.9(C-10),127.3(C-1′),102.2(C-2′),152.6(C-3′),138.4(C-4′),149.8(C-5′),106.5(C-6′),61.2(5-OCH_3),62.1(6-OCH_3),56.1(7-OCH_3),61.9(8-OCH_3),62.4(4′-OCH_3),61.8(5′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **21** 为 3′-羟基-5,6,7,8,4′,5′-六甲氧基黄酮[31]。

化合物 22 黄色粉末;^{1}H NMR(400 MHz, $CDCl_3$)δ:13.57(1H,s,5-OH),11.96(2H,s,3′-OH,5′-OH),7.54(2H,s,H-2′,H-6′),7.04(1H,s,H-3),6.62(1H,d,J = 2.3 Hz,H-6),6.53(1H,d,J = 2.3 Hz,H-8),4.04(3H,s,4′-OCH_3),3.77(3H,s,7-OCH_3);^{13}C NMR(100 MHz,$CDCl_3$)δ:165.2(C-2),106.0(C-3),183.3(C-4),158.5(C-5),93.2(C-6),166.3(C-7),99.0(C-8),163.1(C-9),106.4(C-10),127.8(C-1′),107.6(C-2′),153.4(C-3′),141.1(C-4′),153.4(C-5′),107.6(C-6′),56.3(7-OCH_3),60.7(4′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **22** 为 5,3′,5′-三羟基-7,4′-二甲氧基黄酮[32]。

化合物 23 黄色粉末;^{1}H NMR(400 MHz,DMSO-d_6)δ:12.63(1H,s,OH),10.77(1H,s,OH),9.59(1H,s,OH),7.56(1H,dd,J = 8.6,2.3 Hz,H-6′),7.48(1H,d,J = 2.3 Hz,H-2′),7.12(1H,d,J = 8.6 Hz,H-5′),6.79(1H,s,H-3),6.29(1H,s,H-6),3.87(3H,s,8-OCH_3),3.86(3H,s,4′-OCH_3);^{13}C NMR(100 MHz,DMSO-d_6)δ:163.3(C-2),103.3(C-3),181.9(C-4),156.2(C-5),99.0(C-6),157.1(C-7),127.7(C-8),149.5(C-9),103.5(C-10),123.1(C-1′),112.8(C-2′),146.8(C-3′),151.2(C-4′),112.2(C-5′),118.6(C-6′),55.7(8-OCH_3),61.1(4′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **23** 为 5,7,3′-三羟基-8,4′-二甲氧基黄酮[33]。

化合物 24　淡黄色粉末;^{1}H NMR(400 MHz, DMSO-d_6)δ:9.84(1H,s,OH),7.54(1H,dd,J = 8.9,2.6 Hz,H-6′),7.53(1H,d,J = 2.6 Hz,H-5′),7.21(1H,s,H-8),6.91(1H,d,J = 8.9 Hz,H-2′),6.74(1H,s,H-3),3.95(3H,s,3′-OCH_3),3.90(3H,s,7-OCH_3),3.80(3H,s,5-OCH_3),3.76(3H,s,6-OCH_3);^{13}C NMR(100 MHz,DMSO-d_6)δ:160.5(C-2),105.8(C-3),175.6(C-4),151.5(C-5),139.6(C-6),157.3(C-7),97.2(C-8),153.8(C-9),111.9(C-10),121.7(C-1′),109.8(C-2′),150.1(C-3′),147.9(C-4′),115.6(C-5′),119.7(C-6′),61.7(5-OCH_3),60.9(6-OCH_3),55.9(7-OCH_3),56.3(3′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **24** 为3′-羟基-5,6,7,4′-四甲氧基黄酮[34]。

化合物 25　白色粉末;^{1}H NMR(400 MHz,CD_3OD)δ:7.23(2H,s,H-2′,H-6′),6.83(1H,d,J = 2.3 Hz,H-8),6.68(1H,s,H-3),6.51(1H,d,J = 2.3 Hz,H-6),3.95(9H,s,3′-OCH_3,5′-OCH_3,7-OCH_3),3.91(3H,s,5-OCH_3),3.85(3H,s,4′-OCH_3);^{13}C NMR(100 MHz,CD_3OD)δ:162.0(C-2),108.6(C-3),179.9(C-4),163.0(C-5),97.4(C-6),166.5(C-7),94.3(C-8),161.3(C-9),109.3(C-10),127.8(C-1′),104.8(C-2′),155.0(C-3′),142.3(C-4′),155.0(C-5′),104.8(C-6′),56.6(5-OCH_3),56.5(7-OCH_3),56.9(3′-OCH_3),61.2(4′-OCH_3),56.9(5′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **25** 为5,7,3′,4′,5′-五甲氧基黄酮[35]。

化合物 26　淡黄色粉末;^{1}H NMR(400 MHz,$CDCl_3$)δ:7.59(1H,dd,J = 8.5,2.1 Hz,H-6′),7.42(1H,d,J = 2.1 Hz,H-2′),7.01(1H,d,J = 8.5 Hz,H-5′),6.62(1H,s,H-3),4.11(3H,s,7-OCH_3),3.98(9H,s,8-OCH_3,3′-OCH_3,4′-OCH_3),3.96(3H,s,6-OCH_3);^{13}C NMR(100 MHz,$CDCl_3$)δ:164.0(C-2),104.1(C-3),183.1(C-4),149.5(C-5),136.7(C-6),153.1(C-7),133.0(C-8),145.9(C-9),107.1(C-10),123.8(C-1′),108.8(C-2′),149.6(C-3′),152.5(C-4′),111.3(C-5′),120.2(C-6′),61.3(6-OCH_3),61.8(7-OCH_3),56.1(8-OCH_3),56.2(3′-OCH_3),62.2(4′-OCH_3)。以上数据与文献报道一致,故鉴定化合物 **26** 为5-羟基-6,7,8,3′,4′-五甲氧基黄酮[35]。

化合物 **1** ~ **26** 的化学结构见图4。

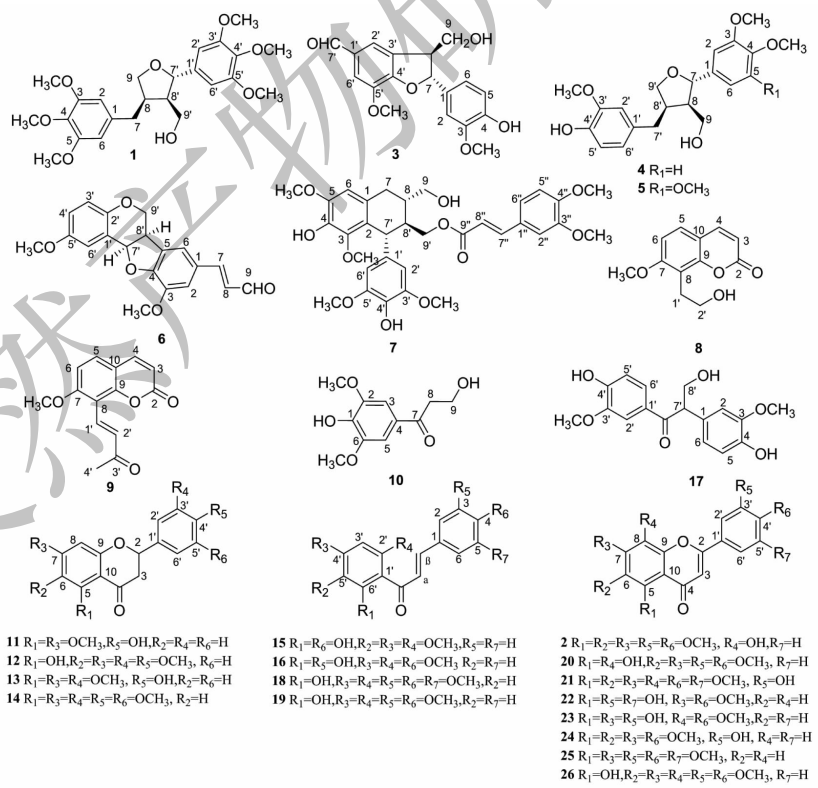

图4　化合物 1 ~ 26 的化学结构

Fig. 4　Chemical structures of compounds **1-26**

3 结论

研究表明,千里香中主要成分为香豆素类及黄酮类化合物。香豆素类成分具有良好的抗炎镇痛活性[36],是千里香抗炎镇痛作用的潜在有效成分,此外还具有抑菌,降血糖[37]的作用。多甲氧基黄酮是甲基化程度较高的黄酮类成分,是九里香属植物的特征性成分之一,其生物活性显著,对 MCF-7 人胸腺癌细胞、MDA-MB-468 人乳腺癌细胞和人胃癌 AGS 细胞等多种癌细胞具有较强的抗增殖活性,此外还具有抗炎、抑制血管生成[38]等活性。本文的研究结果也进一步表明千里香富含多甲氧基黄酮类成分,同时也是其主要的活性成分,如本文分离得到的 2 个多甲氧基黄酮 5,7,3′,4′,5′-五甲氧基黄酮(**25**)和去甲基川陈皮素(**26**)对乙醇诱导的胃上皮细胞(GES-1)损伤均具有显著的抗炎作用[39]。

本文共分离得到两个新化合物,并首次从九里香属发现 17 个化合物。该研究结果不仅丰富了千里香中化学成分的信息,也为其活性筛选提供了物质基础,同时可为其质量标准研究提供指标性成分。

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