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粘叶莸的化学成分研究

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摘　要:综合利用多种色谱方法从粘叶莸(*Caryopteris glutinosa*)的乙醇提取物中分离得到 13 个化合物,并通过多种波谱学手段鉴定它们的结构分别为:caryopterpene J(**1**)、5-羟基-7,3′,4′-三甲氧基黄酮(**2**)、5-羟基-7,8,4′-三甲氧基黄酮(**3**)、5-羟基-7,4′-二甲氧基黄酮(**4**)、8-甲氧基芹菜素(**5**)、5,4′-二羟基-7,8,3′-三甲氧基黄酮(**6**)、5,4′-二羟基-7,8-二甲氧基黄酮(**7**)、5-羟基-7,8,3′,4′-四甲氧基黄酮(**8**)、acteoside(**9**)、N-*trans*-feruloyl 3-*O*-methyldopamine(**10**)、secoisolariciresinol(**11**)、isolariciresinol(**12**)和 dehydroconiferyl alcohol(**13**)。其中,化合物 **1** 为新化合物,其它化合物除 **9** 以外均为首次从莸属植物中分离得到。

关键词:粘叶莸;环烯醚萜;木脂素;化学成分;马鞭草科

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Chemical Components from *Caryoptesis glutinosa*

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Abstract:Thirteen compounds were obtained from the ethanol extract of *Caryopteris glutinosa* by applying various chromatographic methods. Their structures were elucidated and identified as caryopterpene J (**1**),5-hydroxy-7,3′,4′-trimethoxyflavone (**2**),5-hydroxy-7,8,4′-trimethoxyflavone (**3**),5-hydroxy-7,4′-dimethoxyflavone (**4**),8-methoxyapigenin (**5**),5,4′-dihydroxy-7,8,3′-trimethoxyflavone (**6**),5,4′-dihydroxy-7,8-dimethoxyflavone (**7**),5-hydroxy-7,8,3′,4′-tetramethoxyflavone (**8**),acteoside (**9**),N-*trans*-feruloyl-3-*O*-methyldopamine (**10**),secoisolariciresinol (**11**),isolariciresinol (**12**) and dehydroconiferyl alcohol (**13**),respectively,based on the spectral data. Among them,compound **1** was a new compound. The rest compounds excluding **9** were obtained from *Caryopteris* genus for the first time.

Key words:*Caryopteris glutinosa*;iridoids;lignans;chemical composition;Verbenaceae

粘叶莸(*Caryopteris glutinosa*)为马鞭草科(*Verbenaceae*)莸属(*Caryopteris*)落叶灌木,目前仅发现在四川省有分布,且大多生于海拔 1800 m 左右的山谷[1]。作为羌族民族药,粘叶莸主要用于治疗崩漏、白带、月经不调等妇科疾病;用于消化不良、腹胀、风湿关节炎、酒疮、湿疹等疾病的治疗[2,3]。迄今为止,对莸属的其它植物进行了化学成分研究,并从中发现了一些具有抗肿瘤、抗菌和昆虫拒食活性的天然小分子化合物[4-7]。然而,对粘叶莸的化学成分研究报道甚少,仅对其挥发油的烃类成分进行了分析[8],对其中的环烯醚萜和二萜成分进行了分离和鉴定[9,10]。为进一步明确粘叶莸中的化学成分,遂对其 95% 乙醇提取物展开了系统地研究,从中共分离鉴定化合物 13 个,其中新化合物 1 个,首次从莸属植物中分离的化合物 11 个。

1　仪器与材料

核磁共振谱图由 Bruker Ascend 400 核磁共振仪在室温下测定,以 TMS 为内标;低分辨质谱采用 Waters Xevo TQ 质谱仪测定;高分辨质谱采用 Bruker Bio TOF IIIQ 质谱仪测定;柱层析硅胶(160 ~ 200,200 ~ 300 目)和薄层层析硅胶 GF_{254} 均购于青岛海洋化工厂;C_{18} 反相硅胶购于 YMC 公司;Sephadex LH-20 购于 GE Healthcare Bio-Sciences AB 公司;制备型 HPLC 为北京创新通恒科技有限公司的 LC3000 液相色谱仪,配备有 UV/VIS 检测器和 YMC 公司的 C_{18} 高效液相色谱柱(20 × 250 mm,10 μm);半制备型 HPLC 为 Perkin-Elmer 200 液相色谱仪,配备有 UV/VIS 检测器和 Welch 公司的 C_{18} 高效

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液相色谱柱(10 × 250 mm,5 μm);HPLC 的检测波长均采用 208 nm;所有溶剂在使用前均经过蒸馏处理。

粘叶莸于 2012 年 7 月在四川省汶川县整株采集,由中国科学院成都生物研究所傅发鼎研究员鉴定。样本标本(2012-07)存于中国科学院成都生物研究所。样品在室温下风干后粉碎,室温保存备用。

2 提取与分离

取干燥并粉碎过的粘叶莸 25 kg,以 95% 乙醇在室温下冷浸提取 3 次,每次 7 d。完毕,回收提取溶剂得总浸膏 3.3 kg。取总浸膏 1.5 kg,分散于 1.7 L 热水中,并依次以乙酸乙酯(1.5 L×3 次)和正丁醇(1.5 L×3 次)萃取,分别回收溶剂得乙酸乙酯萃取物 780 g。乙酸乙酯萃取物经硅胶柱层析,以石油醚/丙酮(1∶0 ~0∶1)梯度洗脱得组分 E1-E17。组分 E4(16 g)经硅胶柱层析,以石油醚/丙酮(10∶1)等度洗脱得化合物 **4**(13 mg)。组分 E7(19 g)经凝胶 Sephadex LH-20 柱层析,以氯仿/甲醇(1∶1)洗脱得组分 E7A-E7E。组分 E7D 经半制备型 HPLC,以甲醇/水(70∶30;流速 3 mL/min)洗脱得化合物 **2**(7 mg)和组分 E7D5 和 E7D9。组分 E7D5 经半制备型 HPLC,以乙腈/水(65∶35;流速 4 mL/min)洗脱得化合物 **3**(10 mg)。组分 E7D9 经硅胶柱层析,以石油醚/丙酮(5∶1)洗脱得化合物 **1**(5 mg)。组分 E11(25 g)经凝胶 Sephadex LH-20 柱层析,以氯仿/甲醇(1∶1)洗脱得组分 E11E。组分 E11E 进一步经硅胶柱层析,以氯仿/甲醇(30∶1)洗脱得化合物 **5**(13 mg)。组分 E13(30 g)先后经凝胶 Sephadex LH-20 柱层析(氯仿/甲醇 1∶1)、C_{18}反相柱层析(甲醇/水 65∶35)和硅胶柱层析得组分 E13A1-E13A3。组分 E13A1 经半制备型 HPLC,以乙腈/水(71∶29;流速 3 mL/min)洗脱得化合物 **6**(5 mg;t_R = 9 min)和 **8**(3 mg;t_R = 14 min)。组分 E13A3 经半制备型 HPLC,以乙腈/水(63∶37;流速 3 mL/min)洗脱得化合物 **7**(6 mg;t_R = 11 min)。组分 E14(24 g)先后经凝胶 Sephadex LH-20 柱层析(氯仿/甲醇,1∶1)和制备型 HPLC(乙腈/水,35∶65;流速 15 mL/min)分离得化合物 **10**(5 mg;t_R = 19 min)。组分 E17(80 g)先后经凝胶 Sephadex LH-20 柱层析(氯仿/甲醇,1∶1)和硅胶柱层析(氯仿/甲醇,4∶1)分离得到组分 E17F 和 E17I。组分 E17F 经制备型 HPLC,以乙腈/水(18∶82;流速 15 mL/min)洗脱得化合物 **13**(7 mg;t_R = 33 min)和 **11**(9 mg;t_R = 36 min)。组分 E17I 的甲醇溶解部分先后经制备型 HPLC(甲醇/水 39∶61;流速 15 mL/min)和半制备型 HPLC(乙腈/水 15∶85;流速 4 mL/min)分离得到化合物 **12**(7 mg;t_R = 17 min)和 **9**(50 mg;t_R = 38 min)。

3 结构鉴定

化合物 1 白色粉末。由其高分辨质谱(HR-ESI-MS)给出的准分子离子峰 *m/z* 267.1207 [M + Na]$^+$(cacld for $C_{12}H_{20}NaO_5$,267.1203)可推断其分子式为 $C_{12}H_{20}O_5$,不饱和度为 3。同时,还给出了 1 个碎片峰 *m/z* 207.0992 [M-$C_2H_4O_2$ + Na]$^+$(cacld for $C_{12}H_{20}NaO_5$,207.0992)。结合其核磁共振氢谱(表 1)和 HSQC 谱可知化合物 1 含有 1 个次甲基、3 个甲氧基、2 个-CH_2CH-的结构片段和 1 个甲基。核磁共振碳谱(表 1)中除了给出上述结构单元相对应的碳信号外,还存在 1 个四取代双键和 1 个季碳的碳信号。由以下关键 HMBC 谱(图 1)相关峰:H-1/C-3、C-5; H-4/C-3、C-5、C-6、C-9;H-7/C-5、C-6、C-9;H-10/C-7、C-9;1-OCH_3/C-1;3-OCH_3/C-3;8-OCH_3/C-8,可构建其 C-9 环烯醚萜的基本骨架,并确定化合物的平面结构,见图 1。这同时也解释了高分辨质谱中的碎片峰,为化合物 **1** 的 RDA 裂解产物。根据 NOESY 谱(图 1)中 H-10 与 H-1 和 H-7α 之间的相关峰可确定 H-1 和 8-CH_3 的 α 取向。此外,8-OCH_3 与 H-6 和 H-7β 之间的相关峰,表明 6-OH 为 α 取向,这与由偶合常数 $J_{H-6,H-7}$确定的 6-OH 的构型是相符的[11]。根据偶合常数 $J_{H-3,H-4}$的大小可推定 H-3 处于竖直键上,结合构象分析,可确定 3-OCH_3 为 β 取向。化合物 **1** 的结构如图 1 所示,命名为 caryopterpene J。将化合物 **1** 置于冰箱 4 ℃保存一段时间后,我们发现样品 **1** 不稳定:TLC 分析发发现有比 **1** 极性大的产物,我们曾尝试分离,但因样品量太少二无法获得纯品,故未能获得化合物 **1** 的紫外光谱、红外光谱和旋光等数据。

化合物 2 黄色固体;^{1}H NMR ($CDCl_3$,400 MHz) δ:12.78 (5-OH),7.51 (1H,br d,*J* = 8.2 Hz,H-6′),7.33 (1H,br s,H-2′),6.97 (1H,d,*J* = 8.5 Hz,H-5′),6.58 (1H,s,H-3),6.48 (1H,br s,H-8),6.36 (1H,br s,H-6),3.98 (3H,s,7-OCH_3),3.96 (3H,s,4′-OCH_3),3.88 (3H,s,3′-OCH_3);^{13}C NMR ($CDCl_3$,100 MHz) δ:182.5 (s,C-4),165.6

表 1 化合物 1 的核磁共振氢谱和碳谱数据[a]

Table 1 ^{1}H and ^{13}C NMR spectroscopic data of compound 1[a]

No.	δ_H (mult, J in Hz)	δ_C	No.	δ_H (mult, J in Hz)	δ_C
1	5.03 (s)	95.85	8		85.82
3	4.95 (dd, 8.8, 3.4)	96.12	9		137.61
4	2.51 (dd, 17.4, 3.4) 2.17 (dd, 17.4, 8.8)	29.33	10	1.43 (s)	27.04
5		143.63	1-OMe	3.53 (s)	55.69
6	4.71 (dd, 7.4, 4.5)	75.32	3-OMe	3.56 (s)	56.83
7	2.58 (dd, 14.9, 7.4) 1.67 (dd, 14.9, 4.5)	45.77	8-OMe	3.01 (s)	50.56

a) 分别在 400 MHz 和 100 MHz 条件下采集。

a) Recorded at 400 MHz and 100 MHz, respectively.

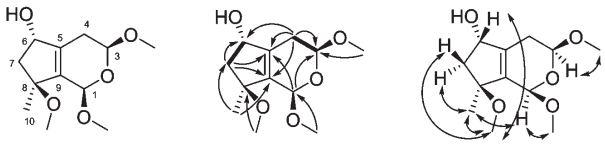

图 1 化合物 1 的结构及其 ^{1}H-^{1}H COSY(粗黑线)、HMBC(弧线箭头)和 NOESY(弧线双箭头)的关键相关信号

Fig. 1 Chemical structure, ^{1}H-^{1}H COSY (Bold Bonds), selected HMBC (Curved Arrows) and key NOESY (Curved Double Arrows) correlations of compound **1**

(s, C-2), 164.1 (s, C-7), 162.3 (s, C-9), 157.8 (s, C-5), 152.5 (s, C-3′), 149.5 (s, C-4′), 123.9 (s, C-1′), 120.3 (d, C-6′), 111.3 (d, C-5′), 109.0 (d, C-2′), 105.7 (s, C-10), 104.8 (d, C-3), 98.2 (d, C-6), 92.8 (d, C-8), 56.3 (q, 3′/4′-OCH_3), 56.0 (q, 7-OCH_3); ESI-MS *m/z* 327.09 [M-H]$^-$。将以上数据经与文献报道的数据进行比对后,该化合物被确定为 5-羟基-7,3′,4′-三甲氧基黄酮[12]。

化合物 3 黄色粉末;^{1}H NMR ($CDCl_3$, 400 MHz) δ: 12.66 (1H, s, 5-OH), 7.91 (2H, d, J = 7.7 Hz, H-2′/6′), 7.04 (2H, d, J = 7.9 Hz, H-3′/5′), 6.58 (1H, s, H-3), 6.42 (1H, s, H-6), 3.94 (6H, s, 7/4′-OCH_3), 3.90 (3H, s, 8-OCH_3); ESI-MS *m/z* 329.07 [M + H]$^+$, 351.07 [M + Na]$^+$。将以上数据与文献报道的数据进行比对后,该化合物被确定为 5-羟基-7,8,4′-三甲氧基黄酮[13]。

化合物 4 黄色粉末;^{1}H NMR ($CDCl_3$, 400 MHz) δ: 12.81 (1H, s, 5-OH), 7.85 (2H, d, J = 8.9 Hz, H-2′/6′), 7.04 (2H, d, J = 8.9 Hz, H-3′/5′), 6.58 (1H, s, H-3), 6.49 (1H, d, J = 2.1 Hz, H-8), 6.37 (1H, d, J = 2.1 Hz, H-6), 3.89 (3H, s, 4′-OCH_3), 3.88 (3H, s, 7-OCH_3); HR-ESI-MS *m/z* 299.0916 [M + H]$^+$ (cacld for $C_{17}H_{15}O_5$, 299.0914), 321.0738 [M + Na]$^+$ (cacld for $C_{17}H_{14}NaO_5$, 321.0733)。将以上数据经与文献报道的数据进行比对后,该化合物被确定为 5-羟基-7,4′-二甲氧基黄酮[14]。

化合物 5 黄色粉末;^{1}H NMR (DMSO-d_6, 400 MHz) δ: 12.63 (1H, s, 5-OH), 7.93 (2H, d, J = 8.8 Hz, H-2′/6′), 6.96 (2H, d, J = 8.8 Hz, H-3′/5′), 6.81 (1H, s, H-3), 6.28 (1H, s, H-6), 3.84 (3H, s, 8-OCH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 181.9 (s, C-4), 163.6 (s, C-2), 161.3 (s, C-4′), 157.1 (s, C-7), 156.2 (s, C-5), 149.5 (s, C-9), 128.5 (d, C-2′/6′), 127.7 (s, C-8), 121.3 (s, C-1′), 116.1 (d, C-3′/5′), 103.5 (s, C-10), 102.7 (d, C-3), 99.0 (d, C-6), 61.1 (q, 8-OCH_3); ESI-MS: *m/z* 301.14 [M + H]$^+$, 299.08 [M-H]$^-$;将以上数据与文献报道的数据进行比对后,该化合物被确定为 8-甲氧基芹菜素[15]。

化合物 6 黄色粉末;^{1}H NMR (DMSO-d_6, 400 MHz) δ: 12.77 (1H, s, 5-OH), 7.93 (2H, d, J = 8.8 Hz, H-2′/6′), 6.96 (2H, d, J = 8.8 Hz, H-3′/5′), 6.83 (1H, s, H-3), 6.57 (1H, s, H-6), 3.91 (3H, s, 7-OCH_3), 3.83 (3H, s, 8-OCH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 182.1 (s, C-4), 164.0 (s, C-2), 161.4 (s, C-4′), 158.3 (s, C-7), 156.7 (s, C-5), 148.7 (s, C-9), 128.5 (s, C-8), 128.5 (d, C-2′/6′), 121.2 (s, C-1′), 116.1 (d, C-3′/5′), 103.9 (s, C-10), 102.7 (d, C-3), 96.0 (d, C-6), 61.1 (q, 8-OCH_3), 56.5 (q, 7-OCH_3); HR-ESI-MS *m/z* 313.0718 [M-H]$^-$ (cacld for $C_{17}H_{13}O_6$, 313.0718)。将以上数据经与文献报道的数据进行比对后,该化合物被确定为 5,4′-二羟基-7,8-二甲氧基黄

酮[15,16]。

化合物 7 黄色固体;^{1}H NMR (DMSO-d_6,400 MHz) δ:12.79 (1H,s,5-OH),7.57 (2H,m,H-2′/6′),6.95 (1H,d,J = 8.5 Hz,H-5′),6.93 (1H,s,H-3),6.55 (1H,s,H-6),3.90 (3H,s,7-OCH_3),3.88 (3H,s,3′-OCH_3),3.84 (3H,s,8-OCH_3);^{13}C NMR (DMSO-d_6,100 MHz) δ:182.2 (s,C-4),163.5 (s,C-2),158.3 (s,C-7),156.7 (s,C-5),151.5 (s,C-4′),148.8 (s,C-9),148.1 (s,C-3′),128.4 (s,C-8),121.1 (s,C-1′),120.4 (d,C-6′),116.0 (d,C-5′),110.0 (d,C-2′),103.9 (s,C-10),102.8 (d,C-3),95.9 (d,C-6),61.1 (q,8-OCH_3),56.5 (q,7-OCH_3),55.8 (q,3′-OCH_3);HMBC 谱关键相关峰:H-3/C-2、C-10、C-1′;H-6/C-5、C-7、C-8、C-10;H-2′/C-2、C-4′、C-6′;H-5′/C-1′、C-3′;H-6′/C-2、C-2′、C-4′;7-OCH_3/C-7;8-OCH_3/C-8;3′-OCH_3/C-3′;HR-ESI-MS m/z 343.0818 [M-H]$^-$(cacld for $C_{18}H_{15}O_7$,343.0823)。将以上数据与文献报道的数据进行比对后,该化合物被确定为 5,4′-二羟基-7,8,3′-三甲氧基黄酮[17]。

化合物 8 黄色粉末;^{1}H NMR ($CDCl_3$,400 MHz) δ:12.61 (1H,s,5-OH),7.60 (1H,dd,J = 8.5,2.2 Hz,H-6′),7.43 (1H,d,J = 2.1 Hz,H-2′),7.00 (1H,d,J = 8.5 Hz,H-5′),6.59 (1H,s,H-3),6.43 (1H,s,H-6),3.98 (3H,s,7-OCH_3),3.97 (3H,s,4′-OCH_3),3.95 (3H,s,3′-OCH_3),3.94 (3H,s,8-OCH_3);ESI-MS m/z 359.04 [M + H]$^+$,357.18 [M-H]$^-$。将以上数据与文献报道的数据进行比对后,该化合物被确定为 5-羟基-7,8,3′,4′-四甲氧基黄酮[13]。

化合物 9 淡黄色粉末;^{1}H NMR (MeOH-d_4,400 MHz) δ:7.59 (1H,d,J = 15.8 Hz,H-7′),7.06 (1H,d,J = 2.1 Hz,H-2′),6.96 (1H,dd,J = 8.3,2.1 Hz,H-6′),6.78 (1H,d,J = 8.2 Hz,H-5′),6.70 (1H,d,J = 2.0 Hz,H-2),6.68 (1H,d,J = 8.0 Hz,H-5),6.57 (1H,dd,J = 8.1,2.1 Hz,H-6),6.28 (1H,d,J = 15.8 Hz,H-8′),5.19 (1H,d,J = 1.8 Hz,H-1′′′),4.92 (1H,m,H-4′′),4.38 (1H,d,J = 7.9 Hz,H-1′′),2.80 (1H,m,H-7),1.09 (3H,d,J = 6.2 Hz,H-6′′′);^{13}C NMR (MeOH-d_4,100 MHz) δ:168.3 (s,C-9′),149.8 (s,C-4′),148.0 (d,C-7′),146.8 (s,C-3′),146.1 (s,C-4),144.7 (s,C-3),131.5 (s,C-1),127.7 (s,C-1′),123.2 (d,C-6′),121.3 (d,C-6),117.1 (d,C-5),116.5 (d,C-2),116.3 (d,C-5′),115.2 (d,C-8′),114.7 (d,C-2′),104.2 (d,C-1′′),103.0 (d,C-1′′′),81.6 (d,C-3′′),76.2 (d,C-2′′),76.0 (d,C-5′′),73.8 (d,C-4′′′),72.3 (d,C-3′′′),72.3 (t,C-8),72.0 (d,C-2′′′),70.6 (d,C-4′′),70.4 (d,C-5′′′),62.4 (t,C-6′′),36.6 (t,C-7),18.5 (q,C-6′′′);ESI-MS m/z 646.88 [M + Na]$^+$,662.77 [M + K]$^+$,622.80 [M-H]$^-$。将以上数据与文献报道的数据进行比对后,该化合物被确定为 acteoside[18]。

化合物 10 淡黄色油状物;^{1}H NMR (MeOH-d_4,400 MHz) δ:7.44 (1H,d,J = 15.7 Hz,H-7′),7.11 (1H,d,J = 1.9 Hz,H-2′),7.02 (1H,dd,J = 8.2,2.0 Hz,H-6′),6.82 (1H,d,J = 1.9 Hz,H-2),6.79 (1H,d,J = 8.2 Hz,H-5′),6.72 (1H,d,J = 8.0 Hz,H-5),6.67 (1H,d,J = 8.0,1.9 Hz,H-6),6.41 (1H,d,J = 15.7 Hz,H-8′),3.48 (2H,m,H-8),2.77 (2H,t,J = 7.3 Hz,H-7);^{13}C NMR (MeOH-d_4,100 MHz) δ:169.2 (s,C-9′),150.0 (s,C-3′),149.3 (s,C-3),149.0 (s,C-4′),146.1 (s,C-4),142.1 (d,C-7′),132.0 (s,C-1),128.2 (s,C-1′),123.2 (s,C-6′),122.3 (s,C-6),118.7 (d,C-8),116.5 (d,C-5′),116.2 (d,C-5),113.4 (d,C-2),111.5 (d,C-2′),56.4 (q,3′-OCH_3),56.3 (q,3-OCH_3),42.5 (t,C-8),36.2 (t,C-7);ESI-MS m/z 382.00 [M + K]$^+$,342.00 [M-H]$^-$。将以上数据与文献报道的数据进行比对后,该化合物被确定为 N-*trans*-feruloyl 3-*O*-methyldopamine[19]。

化合物 11 淡黄色粉末;^{1}H NMR (MeOH-d_4,400 MHz) δ:6.68 (2H,d,J = 7.9 Hz,H-5/5′),6.60 (2H,d,J = 1.9 Hz,H-2/2′),6.56 (2H,dd,J = 7.9,1.8 Hz,H-6/6′),3.75 (6H,s,3/3′-OCH_3),3.60 (4H,m,H-9/9′),2.68 (2H,dd,J = 13.8,6.9 Hz,H-7a/7′a),2.57 (2H,dd,J = 13.6,7.8 Hz,H-7b/7′b),1.91 (2H,m,H-8/8′);^{13}C NMR (MeOH-d_4,100 MHz) δ:148.8 (s,C-3/3′),145.4 (s,C-4/4′),133.9 (s,C-1/1′),122.7 (d,C-6/6′),115.8 (d,C-5/5′),113.3 (d,C-2/2′),62.1 (t,C-9/9′),56.1 (q,3/3′-OCH_3),44.0 (d,C-8/8′),36.0 (t,C-7/7′);ESI-MS m/z 385.17 [M + Na]$^+$。将以上数据与文献报道的数据进行比对后,该化合物被确定为 secoisolariciresinol[20]。

化合物 12 淡黄色粉末;^{1}H NMR (MeOH-d_4,

400 MHz) δ:6.76 (1H,d,J = 8.0 Hz,H-5),6.69 (1H,d,J = 2.0 Hz,H-2),6.67 (1H,s,H-2′),6.63 (1H,dd,J = 8.1,2.0 Hz,H-6),6.20 (1H,s,H-5′),3.83 (3H,s,3′-OCH_3),3.83 (1H,d,J = 9.5 Hz,H-7),3.79 (3H,s,3-OCH_3),3.42 (1H,dd,J = 11.2,4.0 Hz,H-9a),2.80 (2H,d,J = 7.7 Hz,H-7′),2.02 (1H,ddt,J = 13.1,7.9,3.7 Hz,H-8′),1.78 (1H,tt, J = 10.1,3.6 Hz,H-8);^{13}C NMR (MeOH-d_4,100 MHz) δ:149.0 (s,C-3),147.2 (s,C-3′),145.9 (s,C-4),145.3 (s,C-4′),138.6 (s,C-1),134.1 (s,C-6′),129.0 (s,C-1′),123.2 (d,C-6),117.3 (d,C-5′),116.0 (d,C-5),113.7 (d,C-2),112.3 (d,C-2′),65.9 (t,C-9′),62.1 (t,C-9),56.3 (q,3′/3-OCH_3),48.0 (d,C-7),48.0 (d,C-8),39.9 (d,C-8′),33.6 (t,C-7′);ESI-MS m/z 361.23 [M + H]$^+$,383.15 [M + Na]$^+$。将以上数据与文献报道的数据进行比对后,该化合物被确定为 isolariciresinol[21]。

化合物 13 淡黄色粉末;^{1}H NMR (MeOH-d_4, 400 MHz) δ:6.97 (1H,d,J = 1.4 Hz,H-2),6.84 (1H,dd,J = 8.1,1.8 Hz,H-6),6.78 (1H,d,J = 8.1 Hz,H-5),6.75 (2H,s,H-4′/6′),5.51 (1H,d,J = 6.2 Hz,H-7),3.87 (3H,s,3′-OCH_3),3.83 (3H,s,3-OCH_3),3.77 (1H,dd,J = 11.0,7.1 Hz,H-9a),3.59 (2H,t,J = 6.5 Hz,H-9′),3.49 (1H,dd,J = 12.3,6.2 Hz,H-8),2.65 (2H,m,H-7′),1.84 (2H,m,H-8′);^{13}C NMR (MeOH-d_4,100 MHz) δ:149.1 (s,C-3),147.5 (s,C-4/2′),145.2 (s,C-3′),136.9 (s,C-5′),134.8 (s,C-1),129.9 (s,C-1′),119.7 (d,C-6),117.9 (d,C-6′),116.1 (d,C-5),114.0 (d,C-4′),110.5 (d,C-2),89.0 (d,C-7),65.0 (t,C-9),62.2 (t,C-9′),56.7 (q,3-OCH_3),56.3 (q,3′-OCH_3),55.5 (d,C-8),35.8 (t,C-8′),32.9 (t,C-7′);ESI-MS m/z 383.11 [M + Na]$^+$。将以上数据与文献报道的数据进行比对后,该化合物被确定为 dehydroconiferyl alcohol[20]。

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