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长叶马兜铃的化学成分研究

王 欣,史国茹,刘彦飞,陈若芸,于德泉*

中国医学科学院、北京协和医学院药物研究所,天然药物活性物质与功能国家重点实验室,北京 100050

摘 要:采用硅胶、Sephadex LH-20、RP-C_{18}柱色谱等方法从长叶马兜铃块根的95%乙醇提取物中分离得到16个化合物,根据化合物的波谱数据分别鉴定为 debilon (**1**)、1α-羟基-9-马兜铃稀-8-酮(**2**)、(4*S*)-4-hydroxyl-1,10-seco-muurol-5-ene-1,10-dione (**3**)、千年健醇 A (**4**)、环-(*L*-亮氨酸-*L*-脯氨酸) (**5**)、lasiodiplodin (**6**)、oxyphyllenodiol A (**7**)、(7*R*,9*R*,10*R*)-3,9-di-hydroxycalameneno (**8**)、1β,11-2 羟基-5-桉叶稀 (**9**)、吐叶醇 (**10**)、苏式-2,3-双-(4-羟基-3-甲氧基苯基)-3-乙氧基丙烷-1-醇 (**11**)、pollenfuran A (**12**)、N-芥子酰基酪胺 (**13**)、N-阿魏酰基酪胺 (**14**)、1,2-二氢-6,8-二甲氧基-7-羟基-1-(3,5 - 二甲氧基-4-羟苯基)-N^1,N^2-双-[2-(4-羟苯基]-2,3-萘酰胺 (**15**)、克罗酰胺 (**16**)。其中化合物 **1** ~ **16** 均为首次从该植物中分离得到,化合物 **3** ~ **9**、**11**、**12**、**15**、**16** 为首次从该属植物中分离得到。

关键词:马兜铃属;长叶马兜铃;化学成分

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Chemical Constituents from Roots of *Aristolochia championii*

WANG Xin, SHI Guo-ru, LIU Yan-fei, CHEN Ruo-yun, YU De-quan*

State Key Laboratory of Bioactive Substance and Function of Natural Medicines, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100050, China

Abstract: Chemical investigation of roots of *Aristolochia championii* lead to the isolation of sixteen compounds by various chromatographies such as silica gel, Sephadex LH-20, and RP-C_{18} column chromatography. Their structures were determined to be: debilon (**1**), 1α-hydroxy-9-aristolen-8-one (**2**), (4*S*)-4-hydroxyl-1, 10-seco-muurol-5-ene-1, 10-dione (**3**), homalomenol (**4**), cyclo-(*L*-Leu-*L*-Pro) (**5**), lasiodiplodin (**6**), oxyphyllenodiol A (**7**), (7*R*,9*R*,10*R*)-3,9-di-hydroxycalameneno (**8**), 1β,11-dihydroxy-5-eudesmene (**9**), vomifoliol (**10**), *threo*-2,3-bis(4-hydroxy-3-methoxyphenyl)-3-ethoxypropan-1-ol (**11**), pollenfuran A (**12**), N-*trans*-sinapoyltyramine (**13**), N-*trans*-feruloyltyramine (**14**), 1,2-dihydro-6,8-dimethoxy-7-hydroxy-1-(3,5-dimethoxy-4-hydroxyphenyl)-N^1,N^2-bis-[2-(4-hydroxyphenyl) ethyl]-2,3-naphthalene dicarboxamide (**15**), grossamide (**16**), respectively, based on the spectral analysis such as NMR, MS, *etc*. Compounds **1-16** were isolated from this plant for the first time. Compounds **3-9**, **11**, **12**, **15** and **16** were obtained from this genus for the first time.

Key words: *Aristolochia*; *Aristolochia championii*; chemical constituents

长叶马兜铃 *Aristolochia championii* 是马兜铃科(Aristolochiaceae)马兜铃属(*Aristolochia*)植物,别名“三筒管”、“绊藤香”,主要分布于我国广西、云南、四川等地区,块根入药,有清热解毒之功效,用于治疗喉痛、痢疾、胃肠炎等[1]。长期以来,对马兜铃属植物的化学成分研究较多,从马兜铃属中分离到多种化合物,主要有马兜铃酸、萜类、黄酮类等化合物[2-5],但对长叶马兜铃的报道较少。本实验对长叶马兜铃块根的95%乙醇提取部位进行了系统化学成分研究,采用硅胶、凝胶 LH-20 层析和高效液相等色谱方法,共分离得到16个化合物,采用波谱手段分别鉴定为 debilon (**1**)、1α-羟基-9-马兜铃稀-8-酮(**2**)、(4*S*)-4-hydroxyl-1, 10-seco-muurol-5-ene-1, 10-dione (**3**)、千年健醇 A (**4**)、环-(*L*-亮氨酸-*L*-脯氨酸) (**5**)、lasiodiplodin (**6**)、oxyphyllenodiol A (**7**)、(7*R*,9*R*,10*R*)-3,9-di-hydroxycalameneno (**8**)、1β,11-2 羟基-5-桉叶稀 (**9**)、吐叶醇 (**10**)、苏式-2,3-双-(4-羟基-3-甲氧基苯基)-3-乙氧基丙烷-1-醇 (**11**)、pollenfuran A (**12**)、N-芥子酰基酪胺 (**13**)、N-

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* 通信作者 Tel:86-10-63030807;E-mail:dqyu@imm.ac.cn

阿魏酰基酪胺（**14**）、1,2-二氢-6,8-二甲氧基-7-羟基-1-(3,5 -二甲氧基-4-羟苯基)-N^1,N^2-双-[2-(4-羟苯基]-2,3-萘酰胺（**15**）、克罗酰胺（**16**）。其中化合物 **1** ~ **16** 均为首次从该植物中分离得到,化合物 **3** ~ **9**、**11**、**12**、**15**、**16** 为首次从该属植物中分离得到。

1　仪器与材料

BRUKER AV-500 核磁共振仪(瑞士布鲁克拜厄斯宾有限公司);HP1100 系列 LC/MSD Trap-SL 型质谱仪(安捷伦公司);Gilson 302 型中压色谱仪(吉尔森公司);岛津 LC-6AD 制备液相色谱仪(岛津公司);反相柱色谱硅胶 RP-C_{18}(40 ~ 60 μm)为 Merk 公司生产;薄层色谱硅胶 GF_{254}及柱色谱硅胶为青岛海洋化工厂产品;葡聚糖凝胶 Sephadex LH-20 为 Pharmacia 公司产品。制备液相用试剂为色谱纯,其余试剂为分析纯。

长叶马兜铃(*Aristolochia championii*)块根于 2014 年 8 月购于广西省玉林市药材市场,由中国医学科学院药物研究所马林副研究员鉴定为马兜铃科马兜铃属植物长叶马兜铃 *Aristolochia championii*,标本(ID-S-2566)存放于中国医学科学院药物研究所标本馆。

2　提取与分离

长叶马兜铃干燥块根 60 kg,粉碎,95% 乙醇回流提取(3 × 100 L),每次回流 1 h,合并提取液,减压浓缩得到浸膏(3 kg)。将浸膏用硅胶(100 ~ 200 目)拌样,装入色谱柱,依次用石油醚、二氯甲烷、乙酸乙酯、丙酮、甲醇快速洗脱。二氯甲烷部分(230 g)经硅胶柱色谱分离,以氯仿-甲醇(200∶1 ~ 10∶1)梯度洗脱,得到 B_1-B_7 七个组分;B_2 经硅胶柱层析、Sephadex LH-20 层析、制备液相纯化,得到化合物 **1**(137 mg),**6**(32 mg)。B_4 部分经中压液相色谱分离(甲醇:水 40∶60 ~ 100∶0),得到 6 个组分 B_{4-1}-B_{4-6};B_{4-1}经 Sephadex LH-20 析出化合物 **5**(121 mg);B_{4-2}经 Sephadex LH-20、制备液相纯化,得到化合物 **2**(32 mg)、**3**(41 mg)、**7**(23 mg);B_{4-3}经 Sephadex LH-20、制备液相纯化,得到化合物 **4**（17 mg)、**8**(91 mg)、**9**(35 mg);B_6 部分经中压液相色谱分离(甲醇:水 40∶60 ~ 100∶0),得到 12 个组分 B_{6-1}-B_{6-12};B_{6-2}经硅胶柱色谱、制备液相纯化得到化合物 **10**(27 mg);B_{6-3}经 Sephadex LH-20 层析、制备液相纯化得到化合物 **11**(19 mg)、**13**(21 mg)、**14**(14 mg);B_{6-7}经 Sephadex LH-20 层析、制备液相纯化得到化合物 **12**(22 mg)、**15**(11 mg)、**16**(13 mg)。

3　结构鉴定

化合物 1　白色固体;分子式 $C_{15}H_{22}O_2$;ESI-MS *m/z* 235 [M + H]$^+$;^{1}H NMR ($CDCl_3$,500 MHz):δ 5.82 (1H,s,H-1),4.28 (1H,dd,J = 4.0,2.2 Hz,H-9),2.26 (4H,m,H-3,4,8a),1.71 (1H,m,H-8b),1.45 (3H,s,H-14),1.09 (3H,d,J = 5.6 Hz,H-15),1.08 (3H,s,H-12),0.94 (3H,s,H-13),0.92 (1H,m,H-7),0.76 (1H,d,J = 9.3 Hz,H-6);^{13}C NMR ($CDCl_3$,125 MHz):δ 200.0 (C-2),170.4 (C-10),126.4 (C-1),72.6 (C-9),42.8 (C-3),37.5 (C-5),37.1 (C-6),31.9 (C-4),29.2 (C-14),28.0 (C-8),23.9 (C-13),19.1 (C-11),17.5 (C-12),16.4 (C-7),15.0 (C-15)。以上数据与文献[6]报道一致,因此确定化合物 **1** 为 debilon。

化合物 2　白色固体;分子式 $C_{15}H_{22}O_2$;ESI-MS *m/z* 235 [M + H]$^+$;^{1}H NMR ($CDCl_3$,500 MHz):δ 5.86 (1H,s,H-9),4.37 (1H,dd,J = 5.7,2.4,H-1),2.01 (1H,m,H-2β),1.89 (1H,m,H-3β),1.87 (1H,m,H-2α),1.79 (2H,m,H-4,7),1.40 (2H,H-3α,6),1.36 (3H,s,H-14),1.20 (3H,s,H-13),1.19 (3H,s,H-12),1.08 (3H,d,J = 6.5 Hz,H-15);^{13}C NMR ($CDCl_3$,125 MHz):δ 197.4 (C-8),165.4 (C-10),127.4 (C-9),73.3 (C-1),40.5 (C-6),39.2 (C-5),38.9 (C-4),36.6 (C-7),32.8 (C-2),29.9 (C-12),25.6 (C-13),25.0 (C-3),24.7 (C-15),16.3 (C-11),16.2 (C-14)。以上数据与文献[7]报道一致,因此确定化合物 **2** 为 1α-羟基-9-马兜铃稀-8-酮。

化合物 3　白色无定型粉末;分子式 $C_{15}H_{24}O_3$;ESI-MS *m/z* 253 [M + H]$^+$;^{1}H NMR ($CDCl_3$,500 MHz):δ 6.38 (1H,s,H-5),2.67 (1H,m,H-2a),2.42 (1H,m,H-2b),2.25 (3H,m,H-7,8β),2.09 (2H,m,H-3),2.08 (3H,s,H-14),1.90 (1H,m,H-8α),1.71 (1H,m,H-11),1.63 (1H,m,H-8b),1.44 (3H,s,H-15),0.88 (3H,d,J = 6.7 Hz,H-12),0.75 (3H,d,J = 6.7 Hz,H-13);^{13}C NMR ($CDCl_3$,125 MHz):δ209.4 (C-10),198.6 (C-1),150.1 (C-5),139.6 (C-6),69.0 (C-4),44.3 (C-7),42.2 (C-9),37.3 (C-3),35.4 (C-2),31.6 (C-

11),30.0 (C-14),27.8 (C-15),25.0 (C-8),20.9 (C-13),20.5 (C-12)。以上数据与文献[8]报道一致,因此确定化合物**3**为(4*S*)-4-hydroxyl-1,10-seco-muurol-5-ene-1,10-dione。

化合物4 白色无定型粉末;分子式 $C_{15}H_{26}O_2$;ESI-MS *m/z* 239 [M + H]$^+$;^{1}H NMR ($CDCl_3$,500 MHz):δ 5.06 (1H,d,*J* = 9.5 Hz,H-8),3.38 (1H,dd,*J* = 7.2,4.2,H-7),2.93 (1H,m,H-3),2.06 (1H,m,5β),1.79 (1H,m,5α),1.65 (6H,s,H-10,11),1.57 (1H,m,H-6α),1.41 (2H,m,H-1α,7b),1.27 (3H,m,H-1β,6β,2α),1.12 (3H,s,H-12),1.52 (3H,s,H-13),1.02 (1H,m,H-2β);^{13}C NMR ($CDCl_3$,125 MHz):δ 132.3 (C-8),128.8 (C-9),80.1 (C-7),71.8 (C-4),59.1 (C-7b),47.3 (C-7a),40.7 (C-5),38.7 (C-6),35.0 (C-3),30.8 (C-11),29.7 (C-2),28.1 (C-1),25.9 (C-10),18.2 (C-12),14.3 (C-13)。以上数据与文献[9]报道一致,因此确定化合物**4**为千年健醇 A。

化合物5 为无定型粉末;分子式为 $C_{11}H_{18}O_2N_2$;ESI-MS: *m/z* 211 [M + H]$^+$;^{1}H NMR ($CDCl_3$,500 MHz):δ 6.07 (1H,brs,NH),4.10 (1H,t,*J* = 7.8,H-6),4.00 (1H,dd,*J* = 8.3,4.0 Hz,H-9),3.55 (2H,m,H-3),3.32 (2H,m,H-5),2.13 (2H,m,H-4),1.87 (1H,m,H-11),1.72 (1H,m,H-10β),1.51 (1H,m,H-10α),0.97 (3H,d,*J* = 7.0 Hz,H-12),0.93 (3H,d,*J* = 7.0 Hz,H-13);^{13}C NMR ($CDCl_3$,125 MHz):δ 170.1 (C-1),166.2 (C-7),59.1 (C-6),53.3 (C-9),45.6 (C-3),38.7 (C-10),28.2 (C-5),24.8 (C-11),23.4 (C-4),22.8 (C-12),21.3 (C-13)。以上数据与文献[10]报道一致,因此确定化合物**5**为环-(*L*-亮氨酸-*L*-脯氨酸)。

化合物6 为无定型粉末;分子式为 $C_{17}H_{24}O_4$;ESI-MS:*m/z* 293 [M + H]$^+$;^{1}H NMR (DMSO,500 MHz):δ 9.64 (1H,s,OH),6.25 (1H,d,*J* = 1.2 Hz,H-14),6.20 (1H,d,*J* = 1.2 Hz,H-12),5.03 (1H,m,H-3),3.67 (3H,s,H-18),2.46 (2H,m,H-9),1.81 (1H,m,H-4β),1.52 (5H,m,H-4α,5,10),1.33 (4H,m,H-6,7),1.20 (3H,d,*J* = 6.4 Hz,H-17),1.17 (2H,m,H-8);^{13}C NMR (DMSO,125 MHz):δ 168.2 (C-1),159.5 (C-13),157.7 (C-15),142.1 (C-11),116.3 (C-16),108.3 (C-12),97.3 (C-14),71.5 (C-3),56.0 (C-18),32.2 (C-4),30.2 (C-10),29.9 (C-9),26.6 (C-6),25.2 (C-8),24.3 (C-7),20.9 (C-5),19.7 (C-17)。以上数据与文献[11]报道一致,因此确定化合物**6**为 lasiodiplodin。

化合物7 白色固体;分子式 $C_{14}H_{22}O_3$;ESI-MS:*m/z* 239 [M + H]$^+$;^{1}H NMR ($CDCl_3$,500 MHz):δ 4.16 (1H,s,H-4),2.63 (1H,m,H-6),2.50 (2H,m,H-1β,8β),2.30 (4H,m,H-1α,8α,11),1.95 (2H,m,H-7),1.75 (1H,m,H-2β),1.65 (1H,m,H-2α),1.22 (3H,s,H-14),1.05 (3H,d,*J* = 6.8 Hz,H-12),0.90 (3H,d,*J* = 6.8 Hz,H-13);^{13}C NMR ($CDCl_3$,125 MHz):δ 199.8 (C-9),157.5 (C-5),132.6 (C-10),75.2 (C-4),72.3 (C-3),40.2 (C-6),35.1 (C-8),32.3 (C-2),29.9 (C-11),22.4 (C-14),22.0 (C-7),21.7 (C-1),21.6 (C-12)。以上数据与文献[12]报道一致,因此确定化合物**7**为 oxyphyllenodiol A。

化合物8 白色固体;分子式为 $C_{15}H_{22}O_2$;ESI-MS:*m/z* 235 [M + H]$^+$;^{1}H NMR ($CDCl_3$,500 MHz):δ 6.98 (1H,s,H-5),6.70 (1H,s,H-8),3.50 (1H,m,H-2),2.87 (1H,m,H-4),2.60 (1H,m,H-1),2.38 (1H,m,H-11),2.21 (3H,s,H-15),2.04 (1H,m,H-3α),1.49 (1H,m,H-3β),1.30 (3H,d,*J* = 6.7 Hz,H-14),1.02 (3H,d,*J* = 6.7 Hz,H-12),0.65 (3H,d,*J* = 6.7 Hz,H-13);^{13}C NMR ($CDCl_3$,125 MHz):δ 152.0 (C-7),139.6 (C-9),131.0 (C-10),129.3 (C-5),121.5 (C-15),113.0 (C-8),42.4 (C-4),41.6 (C-1),31.8 (C-3),31.0 (C-11),20.9 (C-13),16.9 (C-14),15.9 (C-15),15.7 (C-12)。以上数据与文献[13]报道一致,因此确定化合物**8**为(7*R*,9*R*,10*R*)-3,9-di-hydroxycalameneno。

化合物9 白色固体;分子式为 $C_{15}H_{26}O_2$;ESI-MS:*m/z* 239 [M + H]$^+$;^{1}H NMR ($CDCl_3$,500 MHz):δ 5.57 (1H,d,*J* = 3.2 Hz,H-6),3.32 (1H,dd,*J* = 3.4,11.4 Hz,H-1),2.45 (1H,m,H-4),2.05 (1H,m,H-7),1.99 (3H,s,H-12),1.66 (1H,m,H-3β),1.63 (4H,m,H-3α,8,9β),1.56 (3H,m,H-2,9α),1.21 (3H,s,H-13),1.15 (3H,d,*J* = 7.6 Hz,H-15),1.09 (3H,s,H-14);^{13}C NMR ($CDCl_3$,125 MHz):δ 149.1 (C-5),123.6 (C-6),78.5 (C-1),73.5 (C-11),45.6 (C-7),40.1 (C-10),38.7 (C-4),34.9 (C-9),30.9 (C-2),28.1 (C-13),27.3 (C-12),26.6 (C-3),22.4 (C-15),20.8 (C-14),20.2 (C-8)。以上数据与文献[14]报道一致,因此确

定化合物 **9** 为 1β,11-2 羟基-5-桉叶稀。

化合物 10　白色油状固体;分子式为 $C_{13}H_{20}O_3$;ESI-MS:*m/z* 225 [M + H]$^+$;^{1}H NMR ($CDCl_3$, 500 MHz):δ 5.82 (1H,d,*J* = 16.0 Hz,H-7),5.75 (1H,dd,*J* = 16.0,5.0 Hz,H-8),5.62 (1H,s,H-2),4.40 (1H,m,H-9),2.96 (1H,d,*J* = 12.0 Hz,H-6β),2.09 (1H,d,*J* = 12.0 Hz,H-6α),1.90 (3H,s,H-13),1.30 (3H,d,*J* = 7.0 Hz,H-10),0.95 (3H,s,H-11),0.90 (3H,s,H-12);^{13}C NMR ($CDCl_3$,125 MHz):δ 197.9 (C-1),162.7 (C-3),135.9 (C-8),129.1 (C-7),127.1 (C-2),79.2 (C-4),68.1 (C-9),49.9 (C-6),41.3 (C-5),24.2 (C-13),23.9 (C-11),23.0 (C-12),19.0 (C-10)。以上数据与文献[15]报道一致,因此确定化合物 **10** 为吐叶醇。

化合物 11　白色固体;分子式为 $C_{19}H_{24}O_6$;ESI-MS:*m/z* 349 [M + H]$^+$;^{1}H NMR ($CDCl_3$, 500 MHz):δ 6.85 (1H,d,*J* = 8.0 Hz,H-5′),6.83 (1H,d,*J* = 8.0 Hz,H-5″),6.67 (1H,dd,*J* = 8.0,2.0 Hz,H-6′),6.65 (1H,dd,*J* = 8.0,2.0 Hz,H-6″),6.57 (1H,d,*J* = 2.0 Hz,H-2′),6.55 (1H,d,*J* = 2.0 Hz,H-2″),5.54 (1H,d,*J* = 6.0 Hz,H-3),3.87 (1H,m,H-1β),3.80 (3H,s,OMe),3.76 (3H,s,OMe),3.74 (1H,m,H-1α),3.42 (1H,m,H-1‴β),3.27 (1H,m,H-1‴α),3.11 (1H,m,H-2);^{13}C NMR ($CDCl_3$,125 MHz):δ 146.4 (C-3′),146.2 (C-3″),145.2 (C-4″),144.5 (C-4‴),131.9 (C-1′),130.9 (C-1″),121.9 (C-6′),120.7 (C-6″),114.1 (C-5′),113.7 (C-5″),112.1 (C-2″),109.7 (C-2′),83.6 (C-3),64.5 (C-1),64.4 (C-1‴),55.9 (C-OMe),54.2 (C-2),15.4 (C-2‴)。以上数据与文献[16]报道一致,因此确定化合物 **11** 为苏式-2,3-双-(4-羟基-3-甲氧基苯基)-3-乙氧基丙烷-1-醇。

化合物 12　白色固体;分子式为 $C_{14}H_{18}O_7$;ESI-MS:*m/z* 299 [M + H]$^+$;^{1}H NMR (DMSO, 500 MHz):δ 7.18 (1H,d,*J* = 1.5 Hz,H-8),6.51 (1H,d,*J* = 3.5 Hz,H-4′),5.30 (1H,d,*J* = 3.5 Hz,H-3′),4.98 (H,s,H-2),4.46 (2H,s,H-6′),3.77 (2H,m,H-6,9β),3.59 (1H,m,H-9α),3.48 (2H,m,H-7),1.15 (3H,t,*J* = 7.0 Hz);^{13}C NMR ($CDCl_3$,125 MHz):δ 197.1 (C-3),160.5 (C-5′),149.4 (C-2′),126.8 (C-4),121.7 (C-8),121.4 (C-3′),110.3 (C-4′),97.9 (C-2),80.8 (C-5),74.4 (C-6),63.9 (C-9),62.2 (C-7),56.0 (C-6′),15.0 (C-10)。以上数据与文献[17]报道一致,因此确定化合物 **12** 为 pollenfuran A。

化合物 13　白色固体;分子式为 $C_{19}H_{21}O_5N$;ESI-MS:*m/z* 344 [M + H]$^+$;^{1}H NMR (DMSO,500 MHz):δ 9.15 (1H,s,7-OH),8.74 (1H,s,4′-OH),7.94 (1H,br.s,NH),7.28 (1H,d,*J* = 15.6 Hz,H-3),6.99 (2H,d,*J* = 7.5 Hz,H-2′,6′),6.82 (2H,s,H-5,9),6.66 (2H,d,*J* = 7.5 Hz,H-3′,5′),6.44 (1H,d,*J* = 15.6 Hz,H-2),3.77 (6H,s,6,9-OMe),3.31 (2H,t,*J* = 7.3 Hz,H-α),2.62 (2H,t,*J* = 7.3 Hz,H-β);^{13}C NMR ($CDCl_3$,125 MHz):δ 165.2 (C-1),155.7 (C-4′),148.0 (C-6,8),139.2 (C-3),137.2 (C-7),129.6 (C-1′),129.5 (C-2′,6′),125.3 (C-4),119.4 (C-2),115.1 (C-3′,5′),105.2 (C-5,9),55.9 (C-OMe),40.7 (C-α),34.4 (C-β)。以上数据与文献[18]报道一致,因此确定化合物 **13** 为 N-芥子酰基酪胺。

化合物 14　白色固体;分子式为 $C_{18}H_{19}O_4N$;ESI-MS:*m/z* 314 [M + H]$^+$;^{1}H NMR (DMSO,500 MHz):δ 9.14 (1H,s,OH),7.94 (1H,s,NH),7.28 (1H,d,*J* = 15.7 Hz,H-3),7.09 (1H,d,*J* = 1.5 Hz,H-5),6.98 (2H,d,*J* = 7.5 Hz,H-2′,6′),6.95 (1H,dd,*J* = 7.1,1.5 Hz,H-9),6.76 (1H,d,*J* = 7.1 Hz,H-8),6.65 (2H,d,*J* = 7.5 Hz,H-3′,5′),6.40 (1H,d,*J* = 15.7 Hz,H-2),3.77 (3H,s,7-OMe),3.31 (2H,t,*J* = 7.3 Hz,H-α),2.62 (2H,t,*J* = 7.3 Hz,H-β);^{13}C NMR ($CDCl_3$,125 MHz):δ 165.3 (C-1),155.6 (C-4′),148.0 (C-6),147.8 (C-7),138.8 (C-3),129.6 (C-1′),129.5 (C-2′,6′),126.6 (C-9),121.5 (C-4),119.0 (C-2),115.6 (C-8),115.1 (C-3′,5′),105.2 (C-5,9),55.5 (C-OMe),40.7 (C-α),34.4 (C-β)。以上数据与文献[18]报道一致,因此确定化合物 **14** 为 N-阿魏酰基酪胺。

化合物 15　白色固体;分子式为 $C_{38}H_{40}O_{10}N_2$;ESI-MS:*m/z* 685 [M + H]$^+$;^{1}H NMR (CD_3OD,500 MHz):δ 7.28 (1H,s,H-4),6.95 (2H,d,*J* = 7.1 Hz,H-2″,6″),6.82 (2H,d,*J* = 7.1 Hz,H-2‴,6‴),6.78 (1H,s,H-5),6.64 (4H,m,H-3″,5″,3‴,5‴),6.33 (2H,s,H-2′,6′),3.92 (3H,s,6-OMe),3.82 (1H,br.s,H-1),3.70 (6H,s,3′,5′-OMe),3.58 (3H,s,8-OMe),3.32 (4H,m,H-α,α′),3.21 (1H,

br. s,H-2),2.68 (2H,t,J = 7.3 Hz,H-β),2.54 (2H,t,J = 7.3 Hz,H-β');^{13}C NMR (CD_3OD,125 MHz):δ 174.0 (C-2a),170.0 (C-3a),156.8 (C-4″),156.7 (C-4‴),149.2 (C-6),149.0 (C-3′,5′),146.8 (C-8),143.1 (C-7),135.3 (C-1′),135.1 (C-4′),135.0 (C-4),131.3 (C-1‴),131.1 (C-1″),130.8 (C-2‴,6‴),130.7 (C-2″,6″),127.1 (C-3),125.2 (C-8a),124.3 (C-4a),116.2 (C-3″,5″),116.1 (C-3‴,5‴),109.1 (C-5),106.0 (C-2′,6′),60.8 (8-OMe),56.8 (6-OMe),56.7 (3′,5′-OMe),49.2 (C-2),42.8 (C-α'),42.4 (C-α),41.6 (C-1),35.6 (C-β'),35.4 (C-β)。以上数据与文献[18]报道一致,因此确定化合物 **15** 为 1,2-二氢-6,8-二甲氧基-7-羟基-1-(3,5 - 二甲氧基-4-羟苯基)-N^1,N^2-双-[2-(4-羟苯基]-2,3-萘酰胺。

化合物 16 白色固体;分子式为 $C_{36}H_{36}O_8N_2$;ESI-MS:m/z 625 $[M+H]^+$;^{1}H NMR (DMSO,500 MHz):δ 7.32 (1H,d,J = 15.6 Hz,H-1′′′′),7.13 (1H,s,H-6),7.02 (2H,d,J = 8.3 Hz,H-2⁗,6⁗),6.99 (2H,d,J = 8.3 Hz,H-2‴,6‴),6.89 (1H,s,H-2′),6.89 (2H,d,J = 8.3 Hz,H-3⁗,5⁗),6.88 (1H,s,H-4),6.78 (1H,d,J = 8.1 Hz,H-5′),6.71 (1H,dd,J = 8.1,2.1 Hz,H-6′),6.66 (2H,d,J = 8.3 Hz,H-3‴,5 ‴),6.46 (1H,d,J = 15.6 Hz,H-2′′′′),5.87 (1H,d,J = 8.0 Hz,H-2),4.21 (1H,d,J = 8.0 Hz,H-3),3.83 (3H,s,7-OMe),3.76 (3H,s,3′-OMe),3.32 (4H,m,H-1″,1′′′′′),2.65 (4H,m,H-2″,2′′′′′);^{13}C NMR (DMSO,125 MHz):δ 170.3 (3-CONR),167.4 (2′′′′-CONR),156.7 (C-4⁗),156.5 (C-4‴),150.4 (C-8),148.3 (C-3′),147.5 (C-4′),145.4 (C-7),141.2 (C-1′′′′′),132.3 (C-1′),130.7 (C-1⁗),130.5 (C-2‴,6‴),130.4 (C-1‴),130.3 (C-2⁗,6⁗),129.4 (C-5),129.0 (C-9),119.7 (C-6′),119.0 (C-4),118.8 (C-2′′′′),116.7 (C-3‴,5‴),115.9 (C-3⁗,5⁗),115.7 (C-5′),111.0 (C-6),110.4 (C-2′),88.8 (C-2),57.6 (C-3),56.2 (7,3′-OMe),42.0 (C-1),41.4 (C-1″),35.4 (C-2′′′′′),34.5 (C-2″)。以上数据与文献[19]报道一致,因此确定化合物 **16** 为克罗酰胺。

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