枸杞根化学成分研究

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摘 要：目的 研究枸杞 *Lycium chinense* 根的化学成分。**方法** 采用硅胶柱色谱、ODS 开放柱色谱、Sephadex LH-20 葡聚糖凝胶柱色谱及制备高效液相色谱等方法对化合物进行分离纯化，根据其理化性质及波谱数据鉴定化合物结构。**结果** 从枸杞根部乙醇提取物的醋酸乙酯部位分离得到 12 个化合物，分别鉴定为大海米菊酰胺 K（**1**）、grossamide（**2**）、dihydrogrossamide（**3**）、大麻酰胺 H（**4**）、1,2-dihydro-6,8-dimethoxy-7-hydroxy-1-(3,4-dihydroxyphenyl)-N^1,N^2-bis [2-(4-hydroxyphenyl) ethyl]-2,3-naphthalene dicarboxamide（**5**）、大麻酰胺 D（**6**）、(1,2-*trans*)-N^3-(4-acetamidobutyl)-1-(3,4-dihydroxyphenyl)-7-hydroxy-N^2-(4-hydroxyphenethyl)-6,8-dimethoxy-1,2-dihydronaphthalene-2,3-dicarboxamide（**7**）、大麻酰胺 F（**8**）、(*E*)-2-(4,5-dihydroxy-2-{3-[(4-hydroxyphenethyl) amino]-3-oxopropyl} phenyl)-3-(4-hydroxy-3-methoxyphenyl)-*N*-(4-acetamidobutyl) acrylamide（**9**）、(*E*)-2-(4,5-dihydroxy-2-{3-[(4-hydroxyphenethyl) amino]-3-oxopropyl} phenyl)-3-(4-hydroxy-3,5-dimethoxyphenyl)-*N*-(4-hydroxyphenethyl) acrylamide（**10**）、(＋)-南烛木树脂酚-3α-*O*-β-*D*-葡萄糖（**11**）、(−)-南烛木树脂酚-3α-*O*-β-*D*-葡萄糖（**12**）。**结论** 化合物 **3** 为新天然产物，**1**、**2**、**4**～**8** 为首次从该植物中分离得到。

关键词：枸杞；大海米菊酰胺 K；dihydrogrossamide；大麻酰胺 H；大麻酰胺 F；(＋)-南烛木树脂酚-3α-*O*-β-*D*-葡萄糖

中图分类号：R284.1 **文献标志码：**A **文章编号：**0253 - 2670(2018)05 - 1007 - 06

DOI: 10.7501/j.issn.0253-2670.2018.05.003

Study on chemical constituents from roots of *Lycium chinense*

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Abstract: Objective To study the chemical constituents from the roots of *Lycium chinense*. **Methods** The compounds were isolated and purified by silica gel, ODS and Sephadex LH-20 chromatography in addition to preparative-HPLC. Their structures were elucidated on the basis of physicochemical properties and spectral analysis. **Results** Twelve compounds were isolated from the EtOAc fraction of the root of *Lycium chinense* and identified as grossamide K (**1**), grossamide (**2**), dihydrogrossamide (**3**), cannabisin H (**4**), 1,2-dihydro-6,8-dimethoxy-7-hydroxy-1-(3,4-dihydroxyphenyl)-N^1,N^2-bis [2-(4-hydroxyphenyl)ethyl]-2,3-naphthalene dicarboxamide (**5**), cannabisin D (**6**), (1,2-trans)-N^3-(4-acetamidobutyl)-1-(3,4-dihydroxyphenyl)-7-hydroxy-N^2-(4-hydroxyphenethyl)-6,8-dimethoxy-1,2-dihydronaphthalene-2,3-dicarboxamide (**7**), cannabisin F (**8**), (*E*)-2-(4,5-dihydroxy-2-{3-[(4-hydroxyphenethyl)amino]-3-oxopropyl} phenyl)-3-(4-hydroxy-3-methoxyphenyl)-*N*-(4-acetamidobutyl)acrylamide (**9**), (*E*)-2-(4,5-dihydroxy-2-{3-[(4-hydroxylphenethyl) amino]-3-oxopropyl}phenyl)-3-(4-hydroxy-3,5-dimethoxyphenyl)-*N*-(4-hydroxyphenethyl)acrylamide (**10**), (+)-lyoniresinol-3α-*O*-β-*D*-glucopyranoside (**11**), and (−)-lyoniresinol-3α-*O*-β-*D*-glucopyranoside (**12**). **Conclusion** Compound **3** is a new natural product. Compounds **1**, **2**, and **4**—**8** are isolated from this plant for the first time.

Key words: *Lycium chinense* Mill.; grossamide K; dihydrogrossamide; cannabisin H; cannabisin F; (+)-lyoniresinol-3α-*O*-β-*D*-glucopyranoside

枸杞 *Lycium chinense* Mill. 为茄科（Solanaceae）枸杞属植物，主要分布在我国北部地区，是我国名贵的中药材，其味甘、性寒，归肺、肝、肾经，其果实具有滋补肝肾、润肺明目的作用，其根皮为中

收稿日期：2017-10-21

基金项目：国家自然科学基金面上项目（81573578）

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药地骨皮，主治肺结核低热、骨蒸盗汗、肺热咯血、高血压、糖尿病等症[1-2]。现代药理研究表明，枸杞具有抗氧化、抗肿瘤、抗炎、肝保护、神经保护、抑菌、降低血糖等作用[3-8]。为了进一步探索枸杞植物中活性成分，为其开发利用提供科学依据，本实验采用多种色谱分离技术，从枸杞根部乙醇提取物中分离得到 12 个化合物，分别鉴定为大海米菊酰胺 K（grossamide K，**1**）、grossamide（**2**）、dihydrogrossamide（**3**）、大麻酰胺 H（cannabisin H，**4**）、1,2-dihydro-6,8-dimethoxy-7-hydroxy-1-(3,4-dihydroxyphenyl)-N^1,N^2-bis [2-(4-hydroxyphenyl) ethyl]-2,3-naphthalene dicarboxamide（**5**）、大麻酰胺 D（cannabisin D，**6**）、(1,2-*trans*)-N^3-(4-acetamidobutyl)-1-(3,4-dihydroxyphenyl)-7-hydroxy-N^2-(4-hydroxyphenethyl)-6,8-dimethoxy-1,2-dihydronaphthalene-2,3-dicarboxamide（**7**）、大麻酰胺 F（cannabisin F，**8**）、(*E*)-2-(4,5-dihydroxy-2-{3-[(4-hydroxyphenethyl) amino]-3-oxopropyl} phenyl)-3-(4-hydroxy-3-methoxyphenyl)-*N*-(4-acetamidobutyl) acrylamide（**9**）、(*E*)-2-(4,5-dihydroxy-2-{3-[(4-hydroxyphenethyl) amino]-3-oxopropyl} phenyl)-3-(4-hydroxy-3,5-dimethoxyphenyl)-*N*-(4-hydroxyphenethyl) acrylamide（**10**）、(+)-南烛木树脂酚-3α-*O*-β-*D*-葡萄糖 [(+)-lyoniresinol-3α-*O*-β-*D*-glucopyranoside，**11**]、(−)-南烛木树脂酚-3α-*O*-β-*D*-葡萄糖 [(−)-lyoniresinol-3α-*O*-β-*D*-glucopyranoside **12**]。其中，化合物 **3** 为新天然产物，**1**、**2**、**4**～**8** 为首次从该植物中分离得到。

1 仪器与材料

Bruker AV-300 和 AV-600 型核磁共振仪（德国布鲁克公司）；LC-100 型液相色谱仪（上海伍丰科学仪器有限公司）；Agilent 6120 LC/MS TOF 质谱仪（美国安捷伦科技公司）；液相分析色谱柱为 Ultimate XB-C_{18}（250.0 mm×4.6 mm，5 μm，美国 Welch 公司）；半制备液相色谱柱为 Ultimate XB-C_{18}（250.0 mm×10.0 mm，5 μm，美国 Welch 公司）；Eyela 旋转蒸发仪；BP211D 电子天平（Sartorouius 公司）。TLC 预制板（青岛海洋化工厂）；Sephadex LH-20（Pharmacia 公司）；ODS（Silicycle 公司）；核磁用氘代试剂（Merck 公司）；色谱级甲醇（山东禹王公司）；液相用水（广东怡宝公司生产纯净水），其他试剂均为分析纯。

实验药材于 2015 年 11 月购自云南昆明植物研究所，采集于云南昆明市宜良县，由中国科学院昆明植物研究所刘恩德博士鉴定为茄科植物枸杞 *Lycium chinense* Mill. 的干燥根。

2 提取与分离

干燥的枸杞根 5.3 kg，粗粉碎后得到 5.0 kg 枸杞根粉末，用 9 倍量 95%乙醇热回流反复提取 3 次，80%乙醇热回流提取 1 次，每次 2 h，滤过，合并 4 次提取液，减压浓缩至无醇味，得到粗提取物浸膏。粗提取物浸膏加水混悬，依次用石油醚、醋酸乙酯、水萃取，萃取液分别减压浓缩，得到石油醚部位（75 g）、醋酸乙酯部位（49 g）、水部位（490 g）。醋酸乙酯部位经正相硅胶柱色谱分离，氯仿-甲醇（100∶0→0∶100）梯度洗脱，经薄层色谱检测，合并后得到 16 个组分 Fr. 1～16。取氯仿-甲醇（20∶1）洗脱部分 Fr. 8～9 样品 5.6 g，经过反复硅胶柱色谱（二氯甲烷-甲醇系统）、ODS 开放柱色谱（甲醇-水系统）、Sephadex LH-20 葡聚糖凝胶柱色谱及高效液相色谱分析制备纯化得到化合物 **1**（4.8 mg）、**3**（4 mg）、**5**（30 mg）、**6**（3 mg）、**7**（8 mg）、**9**（15 mg）、**10**（5 mg）；取氯仿-甲醇（10∶1）洗脱部分 Fr. 10～11 样品 4.7 g，经过反复 ODS 开放柱色谱（甲醇-水系统 20∶80→100∶0）、Sephadex LH-20 葡聚糖凝胶柱色谱及高效液相色谱分析制备纯化得到化合物 **2**（2 mg）、**4**（7 mg）、**8**（4 mg）、**11**（3.5 mg）、**12**（5 mg）。

3 结构鉴定

化合物 **1**：淡黄色粉末状（甲醇）。HR-ESI-MS *m*/*z*: 492.201 7 $[M+H]^+$，分子式 $C_{28}H_{29}NO_7$。^{1}H-NMR (600 MHz, CD_3OD) δ: 5.56 (1H, d, J = 6.4 Hz, H-2), 3.53 (1H, q, J = 6.2 Hz, H-3), 7.13 (1H, s, H-4), 7.08 (1H, s, H-6), 6.95 (1H, d, J = 2.0 Hz, H-2′), 6.78 (1H, d, J = 8.2 Hz, H-5′), 6.83 (1H, dd, J = 8.2, 2.0 Hz, H-6′), 3.81～3.86 (2H, m, H-1″), 7.47 (1H, d, J = 15.7 Hz, H-1‴), 6.43 (1H, J = 15.7 Hz, H-2‴), 3.45-3.49 (2H, m, H-1⁗), 2.75 (2H, t, J = 7.0 Hz, H-2⁗), 7.05 (2H, d, J = 8.5 Hz, H-2⁗′, 6⁗′), 6.72 (2H, d, J = 8.5 Hz, H-3⁗′, 5⁗′), 3.89 (3H, s, 7-OCH_3), 3.82 (3H, s, 3′-OCH_3); ^{13}C-NMR (150 MHz, CD_3OD) δ: 89.7 (C-2), 54.9 (C-3), 118.5 (C-4), 130.3 (C-5), 113.3 (C-6), 145.8 (C-7), 151.3 (C-8), 130.9 (C-9), 134.2 (C-1′), 110.6 (C-2′), 149.2 (C-3′), 147.7 (C-4′), 116.2 (C-5′), 119.2 (C-6′), 64.7 (C-1″), 142.0 (C-1‴), 119.8 (C-2‴), 42.6 (C-1⁗), 35.8 (C-2⁗), 131.3 (C-1⁗′), 130.7 (C-2⁗′, 6⁗′), 116.3 (C-3⁗′,

5′′′′′′), 156.9 (C-4′′′′′′), 169.1 (-CONH), 56.3 (3′-OCH_3), 56.7 (7-OCH_3)。以上数据与文献报道一致[9]，故鉴定化合物 **1** 为大海米菊酰胺 K。

化合物 **2**：淡黄色油状物（甲醇）。HR-ESI-MS *m*/*z*: 625.256 9 $[M+H]^+$，分子式 $C_{36}H_{36}N_2O_8$。^{1}H-NMR (600 MHz, DMSO-d_6) δ: 9.19 (3H, s, 4, 4″, 4‴-OH), 8.38 (1H, t, *J* = 5.6 Hz, 9″-NH), 8.05 (1H, t, *J* = 5.6 Hz, 9′-NH), 7.12 (1H, s, H-2), 6.88 (1H, s, H-6), 7.34 (1H, d, *J* = 15.7 Hz, H-7), 6.46 (1H, d, *J* = 15.7 Hz, H-8), 7.01 (2H, d, *J* = 8.4 Hz, H-2′, 6′), 6.68 (2H, d, *J* = 8.4 Hz, H-3′, 5′), 2.64 (2H, m, H-7′), 3.31 (2H, m, H-8′), 6.99 (2H, d, *J* = 8.4 Hz, H-2″, 6″), 6.67 (2H, d, *J* = 8.4 Hz, H-3″, 5″), 2.64 (2H, m, H-7″), 3.31 (2H, m, H-8″), 6.88 (1H, d, *J* = 2.0 Hz, H-2‴), 6.78 (1H, d, *J* = 8.1 Hz, H-5‴), 6.71 (1H, dd, *J* = 8.1, 2.0 Hz, H-6‴), 5.87 (1H, d, *J* = 8.0 Hz, H-7‴), 4.21 (1H, d, *J* = 8.0 Hz, H-8‴), 3.82 (3H, s, 3-OCH_3), 3.75 (3H, s, 3‴-OCH_3); ^{13}C-NMR (150 MHz, DMSO-d_6) δ: 128.6 (C-1), 111.7 (C-2), 144.1 (C-3), 148.7 (C-4), 128.5 (C-5), 116.0 (C-6), 138.7 (C-7), 119.6 (C-8), 129.5 (C-1′), 129.5 (C-2′, 6′), 115.2 (C-3′, 5′), 155.6 (C-4′), 34.4 (C-7′), 40.9 (C-8′), 165.2 (C-10′), 129.3 (C-1″), 129.4 (C-2″, 6″), 115.1 (C-3″, 5″), 155.6 (C-4″), 34.2 (C-7″), 40.7 (C-8″), 169.5 (C-10″), 130.6 (C-1‴), 110.4 (C-2‴), 147.7 (C-3‴), 146.9 (C-4‴), 115.5 (C-5‴), 118.8 (C-6‴), 87.7 (C-7‴), 55.9 (C-8‴), 55.8 (3-OCH_3), 55.7 (3‴-OCH_3)。以上数据与文献报道一致[10]，故鉴定化合物 **2** 为 grossamide。

化合物 **3**：淡黄色粉末（甲醇）。HR-ESI-MS *m*/*z*: 627.272 6 $[M+H]^+$，分子式 $C_{36}H_{38}N_2O_8$。^{1}H-NMR (600 MHz, CD_3OD) δ: 6.75 (1H, s, H-2), 6.41 (1H, s, H-6), 2.39 (2H, m, H-7), 2.80 (1H, m, H-8), 7.01 (2H, d, *J* = 8.5 Hz, H-2′, 6′), 6.69 (2H, d, *J* = 8.5 Hz, H-3′, 5′), 2.59 (2H, m, H-7′), 3.24～3.34 (2H, m, H-8′), 6.91 (2H, d, *J* = 8.5 Hz, H-2″, 6″), 6.71 (2H, d, *J* = 8.5 Hz, H-3″, 5″), 2.73 (2H, m, H-7″), 3.45 (2H, m, H-8″), 6.89 (1H, d, *J* = 1.9 Hz, H-2‴), 6.77 (1H, d, *J* = 8.1 Hz, H-5‴), 6.71 (1H, dd, *J* = 8.1, 1.9 Hz, H-6‴), 5.81 (1H, d, *J* = 8.0 Hz, H-7‴), 4.09 (1H, d, *J* = 8.0 Hz, H-8‴), 3.84 (3H, s, 3-OCH_3), 3.76 (3H, s, 3‴-OCH_3); ^{13}C-NMR (150 MHz, CD_3OD) δ: 130.6 (C-1), 114.4 (C-2), 145.5 (C-3), 147.9 (C-4), 128.7 (C-5), 117.3 (C-6), 32.9 (C-7), 39.5 (C-8), 131.3 (C-1′), 130.7 (C-2′, 6′), 116.3 (C-3′, 5′), 156.9 (C-4′), 35.8 (C-7′), 42.4 (C-8′), 175.2 (C-9′), 131.0 (C-1″), 131.0 (C-2″, 6″), 116.3 (C-3″, 5″), 156.9 (C-4″), 35.4 (C-7″), 42.3 (C-8″), 173.3 (C-9″), 132.9 (C-1‴), 110.4 (C-2‴), 149.3 (C-3‴), 148.1 (C-4‴), 116.3 (C-5‴), 120.0 (C-6‴), 89.4 (C-7‴), 59.4 (C-8‴), 56.7 (3-OCH_3), 56.3 (3‴-OCH_3)。以上数据与文献报道一致[11]，故确定化合物 **3** 为 dihydrogrossamide。

化合物 **4**：黄色油状物（甲醇）。HR-ESI-MS *m*/*z*: 532.194 9 $[M+Na]^+$，分子式为 $C_{28}H_{31}NO_8$。^{1}H-NMR (300 MHz, CD_3OD) δ: 4.90 (1H, brs, H-1), 4.39～4.43 (1H, m, H-2), 3.73～3.79, 3.51～3.54 (2H, m, H-3), 7.07 (1H, d, *J* = 1.9 Hz, H-2′), 6.75 (1H, d, *J* = 8.1 Hz, H-5′), 6.86 (1H, dd, *J* = 8.1, 1.9 Hz, H-6′), 7.16 (1H, d, *J* = 1.8 Hz, H-3″), 7.00～7.04 (1H, m, H-5″), 7.06 (1H, d, *J* = 8.6 Hz, H-6″), 7.44 (1H, d, *J* = 15.7 Hz, H-1‴), 6.45 (1H, *J* = 15.7 Hz, H-2‴), 3.44～3.54 (2H, m, H-1′′′′), 2.75 (2H, t, *J* = 7.3 Hz, H-2′′′′), 7.07 (2H, d, *J* = 8.4 Hz, H-2′′′′′, 6′′′′′), 6.73 (2H, d, *J* = 8.4 Hz, H-3′′′′′, 5′′′′′), 3.89 (3H, s, 2″-OCH_3), 3.81 (3H, s, 3′-OCH_3); ^{13}C-NMR (75 MHz, CD_3OD) δ: 73.9 (C-1), 86.5 (C-2), 62.0 (C-3), 133.7 (C-1′), 111.7 (C-2′), 148.8 (C-3′), 147.2 (C-4′), 115.8 (C-5′), 120.1 (C-6′), 151.3 (C-1″), 151.7 (C-2″), 112.2 (C-3″), 130.4 (C-4″), 122.8 (C-5″), 117.9 (C-6″), 141.5 (C-1‴), 120.7 (C-2‴), 42.5 (C-1′′′′), 35.8 (C-2′′′′), 131.3 (C-1′′′′′), 130.7 (C-2′′′′′, 6′′′′′), 116.3 (C-3′′′′′, 5′′′′′), 157.0 (C-4′′′′′), 168.9 (-CONH), 56.6 (3′-OCH_3), 56.3 (2″-OCH_3)。以上数据与文献报道一致[9]，故鉴定化合物 **4** 为大麻酰胺 H。

化合物 **5**：白色粉末（甲醇）。HR-ESI-MS *m*/*z*: 641.251 1 $[M+H]^+$，分子式为 $C_{36}H_{36}N_2O_9$。^{1}H-NMR (300 MHz, CD_3OD) δ: 4.81 (1H, brs, H-1), 3.66 (1H, d, *J* = 1.3 Hz, H-2), 7.26 (1H, s, H-4), 6.75 (1H, s, H-5), 6.45 (1H, d, *J* = 2.1 Hz, H-2′), 6.59 (1H, d, *J* = 8.0 Hz, H-5′), 6.40 (1H, dd, *J* = 8.0, 2.1 Hz, H-6′), 6.81 (2H, d, *J* = 8.5 Hz, H-2″, 6″), 6.63 (2H, d, *J* = 8.5 Hz, H-3″, 5″), 2.67 (2H, t, *J* = 7.3 Hz, H-7″), 3.36 (2H, m, H-8″), 6.95 (2H, d, *J* = 8.5 Hz, H-2‴, 6‴), 6.67 (2H, d, *J* = 8.5 Hz, H-3‴, 5‴), 2.52 (2H, t, *J* = 6.8 Hz, H-7‴), 3.20 (2H, m, H-8‴), 3.91 (3H, s, 6-OCH_3), 3.55 (3H, s, 8-OCH_3); ^{13}C-NMR (75 MHz, CD_3OD) δ: 41.0 (C-1), 50.4 (C-2), 126.9 (C-3), 135.3

(C-4), 109.2 (C-5), 149.1 (C-6), 143.1 (C-7), 146.9 (C-8), 124.3 (C-4a), 125.5 (C-8a), 174.0 (C-2a), 170.1 (C-3a), 136.1 (C-1′), 116.2 (C-2′), 144.8 (C-3′), 145.9 (C-4′), 115.9 (C-5′), 119.9 (C-6′), 131.1 (C-1″), 130.7 (C-2″, 6″), 116.2 (C-3″, 5″), 156.7 (C-4″), 35.5 (C-7″), 42.4 (C-8″), 131.4 (C-1‴), 130.8 (C-2‴, 6‴), 116.2 (C-3‴, 5‴), 156.8 (C-4‴), 35.6 (C-7‴), 42.8 (C-8‴), 56.8 (6-OCH_3), 60.8 (8-OCH_3)。以上数据与文献报道一致[12]，故鉴定化合物 **5** 为 1,2-dihydro-6,8-dimethoxy-7-hydroxy-1-(3,4-dihydroxyphenyl)-N^1, N^2-bis [2-(4-hydroxyphenyl) ethyl]-2,3-naphthalene dicarboxamide。

化合物 **6**：白色不定型粉末（甲醇）。HR-ESI-MS *m*/*z*: 625.254 8 $[M+H]^+$，分子式为 $C_{36}H_{36}N_2O_8$。^{1}H-NMR (600 MHz, CD_3OD) δ: 4.34 (1H, d, *J* = 4.0 Hz, H-1), 3.68 (1H, d, *J* = 4.0 Hz, H-2), 7.20 (1H, s, H-4), 6.88 (1H, s, H-5), 6.52 (1H, s, H-8), 6.70 (1H, d, *J* = 2.1 Hz, H-2′), 6.64 (1H, d, *J* = 8.1 Hz, H-5′), 6.41 (1H, dd, *J* = 8.1, 2.1 Hz, H-6′), 6.82 (2H, d, *J* = 8.5 Hz, H-2″, 6″), 6.65 (2H, d, *J* = 8.5 Hz, H-3″, 5″), 2.48 (2H, m, H-7″), 3.23 (2H, m, H-8″), 6.98 (2H, d, *J* = 8.5 Hz, H-2‴, 6‴), 6.68 (2H, d, *J* = 8.5 Hz, H-3‴, 5‴), 2.70 (2H, t, *J* = 7.3 Hz, H-7‴), 3.40 (1H, t, *J* = 7.3 Hz, H-8‴) 3.35 (1H, t, *J* = 7.3 Hz, H-8‴), 3.89 (3H, s, 6-OCH_3), 3.75 (3H, s, 3′-OCH_3)；^{13}C-NMR (150 MHz, CD_3OD) δ: 47.7 (C-1), 51.0 (C-2), 127.6 (C-3), 134.7 (C-4), 113.2 (C-5), 149.7 (C-6), 148.2 (C-7), 115.9 (C-8), 124.9 (C-4a), 132.6 (C-8a), 174.5 (C-2a), 170.4 (C-3a), 135.9 (C-1′), 112.5 (C-2′), 148.8 (C-3′), 146.2 (C-4′), 117.2 (C-5′), 121.4 (C-6′), 131.2 (C-1″), 130.7 (C-2″, 6″), 116.2 (C-3″, 5″), 156.8 (C-4″), 35.5 (C-7″), 42.4 (C-8″), 131.4 (C-1‴), 130.8 (C-2‴, 6‴), 116.2 (C-3‴, 5‴), 156.9 (C-4‴), 35.7 (C-7‴), 42.7 (C-8‴), 56.6 (3′-OCH_3), 56.3 (6-OCH_3)。以上数据与文献报道一致[13]，故鉴定化合物 **6** 为大麻酰胺 D。

化合物 **7**：黄色油状物（甲醇）。HR-ESI-MS *m*/*z*: 634.275 6 $[M+H]^+$，分子式为 $C_{34}H_{39}N_3O_9$。^{1}H-NMR (300 MHz, CD_3OD) δ: 6.79 (1H, s, H-6), 7.34 (1H, s, H-7), 6.46 (1H, d, *J* = 1.9 Hz, H-2′), 6.59 (1H, d, *J* = 8.1 Hz, H-5′), 6.40 (1H, dd, *J* = 8.1, 1.9 Hz, H-6′), 4.82 (1H, s, H-7′), 3.70 (1H, s, H-8′), 6.84 (2H, d, *J* = 8.1 Hz, H-2″, 6″), 6.65 (2H, d, *J* = 8.1 Hz, H-3″, 5″), 2.55 (2H, t, *J* = 6.1 Hz, H-7″), 3.23 (2H, m, H-8″), 3.15 (2H, m, H-1‴), 1.48 (4H, m, H-2‴, 3‴), 3.19 (2H, m, H-4‴), 1.91 (3H, s, -CH_3), 3.57 (3H, s, 3-OCH_3), 3.92 (3H, s, 5-OCH_3)；^{13}C-NMR (75MHz, CD_3OD) δ: 126.9 (C-1), 125.4 (C-2), 146.9 (C-3), 143.0 (C-4), 149.1 (C-5), 109.2 (C-6), 135.2 (C-7), 131.1 (C-8), 170.1 (C-9), 136.1 (C-1′), 115.9 (C-2′), 145.9 (C-3′), 144.8 (C-4′), 116.1 (C-5′), 119.9 (C-6′), 41.0 (C-7′), 50.3 (C-8′), 174.1 (C-9′), 124.3 (C-1″), 130.7 (C-2″, 6″), 116.2 (C-3″, 5″), 156.7 (C-4″), 35.5 (C-7″), 42.4 (C-8″), 40.1 (C-1‴), 27.7 (C-2‴), 27.7 (C-3‴), 40.4 (C-4‴), 173.3 (*N*-$COCH_3$), 22.5 (-CH_3), 60.8 (3-OCH_3), 56.8 (5-OCH_3)。以上数据与文献报道一致[14]，故鉴定化合物 **7** 为 (1,2-trans)-N^3-(4-acetamidobutyl)-1-(3,4-dihydroxyphenyl)-7-hydroxy-N^2-(4-hydroxyphenethyl)-6,8-dimethoxy-1,2-dihydro-naphthalene-2,3-dicarboxamide。

化合物 **8**：不定形粉末（甲醇）。HR-ESI-MS *m*/*z*: 625.254 2 $[M+H]^+$，分子式为 $C_{36}H_{36}N_2O_8$。^{1}H-NMR (600 MHz, CD_3OD) δ: 7.27 (1H, d, *J* = 2.0 Hz, H-2), 6.70 (1H, d, *J* = 8.5 Hz, H-5), 7.01 (1H, dd, *J* = 8.5, 2.0 Hz, H-6), 7.24 (1H, s, H-7), 7.23 (1H, s, H-2′), 6.71 (1H, d, *J* = 8.4 Hz, H-5′), 7.03 (1H, d, *J* = 8.4 Hz, H-6′), 7.46 (1H, d, *J* = 15.7 Hz, H-7′), 6.49 (1H, *J* = 15.7 Hz, H-8′), 7.05 (2H, d, *J* = 8.4 Hz, H-2″, 6″), 6.59 (2H, d, *J* = 8.4 Hz, H-3″, 5″), 3.45 (1H, t, *J* = 6.9 Hz, H-7″), 2.64 (1H, t, *J* = 6.9 Hz, H-8″), 6.84 (2H, d, *J* = 8.4 Hz, H-2‴, 6‴), 6.72 (2H, d, *J* = 8.4 Hz, H-3‴, 5‴), 3.47 (1H, *J* = 7.3 Hz, H-7‴), 2.75 (1H, *J* = 7.3 Hz, H-8‴), 3.91 (3H, s, 3′-OCH_3), 3.65 (1H, s, 3-OCH_3)；^{13}C-NMR (150 MHz, CD_3OD) δ: 125.0 (C-1), 112.5 (C-2), 149.2 (C-3), 147.5 (C-4), 115.2 (C-5), 121.0 (C-6), 125.5 (C-7), 141.2 (C-8), 168.8 (C-9), 131.8 (C-1′), 113.6 (C-2′), 150.5 (C-3′), 150.4 (C-4′), 116.4 (C-5′), 126.4 (C-6′), 141, 1 (C-7′), 122.3 (C-8′), 165.5 (C-9′), 130.8 (C-1″), 130.7 (C-2″, 6″), 116.3 (C-3″, 5″), 156.9 (C-4″), 35.5 (C-7″), 42.2 (C-8″), 131.2 (C-1‴), 130.7 (C-2‴, 6‴), 116.3 (C-3‴, 5‴), 156.8 (C-4‴), 35.7 (C-7‴), 42.6 (C-8‴), 56.4 (3′-OCH_3), 56.0 (3-OCH_3)。以上数据与文献报道一致[15]，故鉴定化合物 **8** 为大麻酰胺 F。

化合物 **9**：黄色油状物（甲醇）。HR-ESI-MS *m*/*z*: 628.264 8 $[M+Na]^+$，分子式为 $C_{33}H_{39}N_3O_8$。^{1}H-NMR

(600 MHz, CD_3OD) δ: 6.39 (1H, d, J = 1.8 Hz, H-2), 6.66 (1H, d, J = 8.3 Hz, H-5), 6.74 (1H, dd, J = 8.3, 1.8 Hz, H-6), 7.59 (1H, s, H-7), 6.84 (1H, s, H-2′), 6.58 (1H, s, H-5′), 2.53 (2H, m, H-7′), 2.23 (2H, m, H-8′), 6.95 (2H, d, J = 8.4 Hz, H-2″, 6″), 6.68 (2H, d, J = 8.4 Hz, H-3″, 5″), 2.60 (2H, m, H-7″), 3.20 (2H, m, H-8″), 3.15 (2H, m, H-1‴), 1.47 (2H, m, H-2‴), 1.47 (2H, m, H-3‴), 3.24 (2H, m, H-4‴), 1.91 (3H, s, -CH_3), 3.45 (3H, s, 3′-OCH_3); ^{13}C-NMR (150 MHz, CD_3OD) δ: 128.2 (C-1), 113.1 (C-2), 148.5 (C-3), 149.2 (C-4), 116.0 (C-5), 127.0 (C-6), 138.3 (C-7), 131.7 (C-8), 170.7 (C-9), 132.5 (C-1′), 118.2 (C-2′), 147.4 (C-3′), 146.3 (C-4′), 118.3 (C-5′), 127.2 (C-6′), 29.9 (C-7′), 37.7 (C-8′), 175.0 (C-9″), 131.2 (C-1″), 130.7 (C-2″, 6″), 116.2 (C-3″, 5″), 156.8 (C-4″), 35.6 (C-7″), 42.3 (C-8″), 40.2 (C-1‴), 27.7 (C-2‴), 28.0 (C-3‴), 40.6 (C-4‴), 55.7 (3′-OCH_3), 173.3 (N-$COCH_3$), 22.6 (-CH_3)。以上数据与文献报道一致[14]，故鉴定化合物 **9** 为 (*E*)-2-(4,5-dihydroxy-2-{3-[(4-hydroxyphenethyl) amino]-3-oxopropyl}phenyl)-3-(4-hydroxy-3-methoxyphenyl)-*N*-(4-acetamidobutyl) acrylamide。

化合物 **10**：黄色油状物（甲醇）。HR-ESI-MS *m*/*z*: 665.247 0 $[M+Na]^+$，分子式为 $C_{36}H_{38}N_2O_9$。^{1}H-NMR (300 MHz, CD_3OD) δ: 6.36 (2H, s, H-2, 6), 7.57 (1H, s, H-7), 6.80 (1H, s, H-2′), 6.53 (1H, s, H-5′), 2.46 (2H, m, H-7′), 2.15 (2H, m, H-8′), 6.90 (2H, d, J = 8.5 Hz, H-2″, 6″), 6.66 (2H, d, J = 8.5 Hz, H-3″, 5″), 2.67 (2H, m, H-7″), 3.42 (2H, m, H-8″), 6.94 (2H, d, J = 8.5 Hz, H-2‴, 6‴), 6.69 (2H, d, J = 8.5 Hz, H-3‴, 5‴), 2.58 (2H, t, J = 7.4 Hz, H-7‴), 3.21 (2H, m, H-8‴), 3.58 (6H, s, 3′, 5′-OCH_3); ^{13}C-NMR (75 MHz, CD_3OD) δ: 126.7 (C-1), 109.1 (C-2), 148.9 (C-3), 138.4 (C-4), 148.9 (C-5), 109.1 (C-6), 138.7 (C-7), 131.9 (C-8), 170.4 (C-9), 132.2 (C-1′), 118.2 (C-2′), 147.9 (C-3′), 146.8 (C-4′), 118.2 (C-5′), 126.7 (C-6′), 29.9 (C-7′), 37.8 (C-8′), 130.9 (C-1″), 130.7 (C-2″, 6″), 116.2 (C-3″, 5″), 157.0 (C-4″), 35.5 (C-7″), 42.8 (C-8″), 131.2 (C-1‴), 130.7 (C-2‴, 6‴), 116.4 (C-3‴, 5‴), 156.9 (C-4‴), 35.6 (C-7‴), 42.3 (C-8‴), 56.3 (3′, 5′-OCH_3)。以上数据与文献报道一致[14]，故鉴定化合物 **10** 为 (*E*)-2-(4,5-dihydroxy-2-{3-[(4-hydroxyphenethyl) amino]-3-oxopropyl}phenyl)-3-(4-hydroxy-3,5-dimethoxyphenyl)-*N*-(4-hydroxyphenethyl) acrylamide。

化合物 **11**：黄色油状物（甲醇）。HR-ESI-MS *m*/*z*: 605.220 6 $[M+Na]^+$，分子式为 $C_{28}H_{38}O_{13}$。^{1}H-NMR (300 MHz, CD_3OD) δ: 2.72 (1H, dd, J = 15.0, 5.0 Hz, H-1), 2.61 (1H, dd, J = 15.0, 11.2 Hz, H-1), 1.72 (1H, m, H-2), 2.09 (1H, m, H-3), 6.58 (1H, s, H-8), 3.63 (1H, dd, J = 11.0, 5.0 Hz, H-2a), 3.54 (1H, dd, J = 11.0, 5.4 Hz, H-2a), 3.89 (1H, dd, J = 9.9, 5.5 Hz, H-3a), 3.45 (1H, dd, J = 9.9, 4.5 Hz, H-3a), 4.42 (1H, d, J = 6.1 Hz, H-4), 6.58 (1H, s, H-8), 6.43 (2H, s, H-2′, 6′), 4.28 (1H, d, J = 7.9 Hz, H-1″), 3.23 (1H, m, H-2″), 3.38 (1H, m, H-3″), 3.27 (1H, m, H-4″), 3.27 (1H, m, H-5″), 3.82 (1H, dd, J = 12.0, 1.9 Hz, H-6″), 3.67 (1H, dd, J = 12.0, 6.8 Hz, H-6″), 3.35 (3H, s, 5-OCH_3), 3.86 (3H, s, 7-OCH_3), 3.75 (6H, s, 3′, 5′-OCH_3); ^{13}C-NMR (75 MHz, CD_3OD) δ: 33.9 (C-1), 40.6 (C-2), 46.7 (C-3), 66.2 (C-2a), 71.4 (C-3a), 42.8 (C-4), 147.6 (C-5), 138.9 (C-6), 148.6 (C-7), 130.2 (C-9), 126.4 (C-10), 139.3 (C-1′), 106.9 (C-2′), 149.0 (C-3′), 134.4 (C-4′), 149.0 (C-5′), 106.9 (C-6′), 104.8 (C-1″), 75.2 (C-2″), 78.0 (C-3″), 71.7 (C-4″), 78.2 (C-5″), 62.8 (C-6″), 60.2 (5-OCH_3), 56.6 (7-OCH_3), 56.9 (3′, 5′-OCH_3)。以上数据与文献报道一致[16-17]，故鉴定化合物 **11** 为 (+)-南烛木树脂酚-3α-*O*-β-*D*-葡萄糖。

化合物 **12**：黄色油状物（甲醇）。HR-ESI-MS *m*/*z*: 605.220 3 $[M+Na]^+$，分子式为 $C_{28}H_{38}O_{13}$。^{1}H-NMR (300 MHz, CD_3OD) δ: 2.67 (2H, d, J = 7.8 Hz, H-1), 1.69 (1H, m, H-2), 2.13 (1H, m, H-3), 3.87 (1H, m, H-3a), 3.55～3.63 (3H, m, H-2a, 3a), 4.23 (1H, d, J = 6.5 Hz, H-4), 6.58 (1H, s, H-8), 6.41 (2H, s, H-2′, 6′), 4.13 (1H, d, J = 7.7 Hz, H-1″), 3.15～3.33 (4H, m, H-2″～5″), 3.81 (1H, dd, J = 2.4, 12.0 Hz, H-6″), 3.69 (1H, dd, J = 12.0, 5.3 Hz, H-6″), 3.32 (3H, s, 5-OCH_3), 3.86 (3H, s, 7-OCH_3), 3.75 (6H, s, 3′, 5′-OCH_3); ^{13}C-NMR (75 MHz, CD_3OD) δ: 33.8 (C-1), 41.2 (C-2), 46.6 (C-3), 66.2 (C-2a), 72.0 (C-3a), 43.3 (C-4), 147.5 (C-5), 139.5 (C-6), 148.7 (C-7), 107.7 (C-8), 130.2 (C-9), 126.2 (C-10), 134.6 (C-1′), 107.0 (C-2′), 149.0 (C-3′), 138.9 (C-4′), 149.0 (C-5′), 107.0 (C-6′), 104.3 (C-1″), 75.1 (C-2″), 78.2 (C-3″), 71.5 (C-4″), 78.0 (C-5″), 62.7 (C-6″), 60.1 (5-OCH_3), 56.6

(7-OCH_3), 56.9 (3′, 5′-OCH_3)。以上数据与文献报道一致[16-17]，故鉴定化合物 **12** 为 (−)-南烛木树脂酚-3α-*O*-β-*D*-葡萄糖。

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