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红豆树茎枝中黄酮类成分及其抑菌活性研究

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摘　要:为了研究红豆树茎枝抑菌活性成分,采用色谱法分离纯化得到16个黄酮类化合物,通过理化性质及波谱技术分别鉴定为圆荚草双糖苷(**1**)、5,7-二羟基-4′-甲氧基异黄酮-7-*O*-*β*-D-葡萄糖苷(**2**)、4′,8-二甲氧基-7-*O*-*β*-D-葡萄糖基异黄酮(**3**)、芒柄花苷(**4**)、异樱黄素-7-*O*-*β*-D-葡萄糖苷(**5**)、芦丁(**6**)、山奈酚-3-*O*-*β*-D-芸香糖苷(**7**)、4′-甲氧基异黄酮-7-*O*-*β*-D-木糖(1→6)-*O*-*β*-D-吡喃葡萄糖苷(**8**)、4′-甲氧基异黄酮-7-*O*-*β*-D-芹糖(1→6)-*O*-*β*-D-吡喃葡萄糖苷(**9**)、染料木素(**10**)、异樱黄素(**11**)、2′,4′,5,7-四羟基异黄酮(**12**)、大豆素(**13**)、柚皮素(**14**)、二氢染料木素(**15**)、去甲基化美迪紫檀素(**16**)。其中化合物**1**~**16**为首次从红豆树植物中分离得到;化合物**1**、**3**、**4**、**6**~**9**、**12**、**15**、**16**首次从红豆属中分离得到;化合物**2**,**5**和**14**对禾谷镰刀菌、西瓜尖镰孢菌、茄病镰刀菌的菌丝生长显示出了中等强度的抑制作用。

关键词:红豆树;红豆属;黄酮;异黄酮;抑菌

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Flavonoids from the Twigs of *Ormosia hosiei* and Their Anti-fungal Activities

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Abstract:To investigate anti-fungal constituents from the twigs of *Ormosia hosiei*. Sixteen flavonoids were isolated and purified by column chromatography. Their structures were elucidated on the basis of physico-chemicial properties and spectral analysis as sphaerobioside (**1**),sissotrin (**2**),4′,8-dimethoxyl-7-*O*-*β*-D-glucopyranosyl isoflavone (**3**),ononin (**4**),isoprunetin-7-*O*-*β*-D-glucoside(**5**),rutin (**6**),kaempferol-3-*O*-*β*-D-rutinoside (**7**),kushenol O (**8**),7-hydroxy-4′-methoxylisoflavone-7-*O*-*β*-D-apiofuranosyl-(1→6)-*O*-*β*-D-glucopyranoside (**9**),genistein (**10**),isoprunetin (**11**),2′,4′,5,7-tetrahydroxyisoflavone (**12**),daidzein (**13**),naringenin (**14**),dihydrogenistein (**15**) and demethylmedicarpin (**16**). Compounds **1-16** are obtained from *O. hosiei* for the first time,and compounds **1**,**3**,**4**,**6-9**,**12**,**15**,**16** are obtained from the genus of *Ormosia* for the first time. Compounds **2**,**5**,and **14** showed moderate inhibitory activities to the mycelial growth of *Fusarium graminearum*,*Fusarium oxysporumf*,and *Fusarium solani*.

Key words:*Ormosia hosiei*;*Ormosia*;flavonoids;isoflavones;anti-fungi

红豆树(*Ormosia hosiei*)隶属于豆科(*Leguminosae*)红豆属(*Ormosia*),又称鄂西红豆树[1],主要分布在福建、浙江、江苏等地区,是国家Ⅱ级重点保护树种,具有较高的药用价值。其根、枝、叶和种子均可入药,具有理气、通经等功效,可用于治疗疝气、腹痛、血滞经闭等症状[2]。文献研究发现,红豆树的药用价值开发与利用几乎未见报道,化学成分研究方面仅报道了4个生物碱类成分[3]。

本课题组前期发现,红豆树枝条提取物对禾谷镰刀菌(*Fusarium graminearum*)、西瓜尖镰孢菌(*Fusarium oxysporumf*)、茄病镰刀菌(*Fusarium solani*)3种植物病原真菌有较好的抑制活性。为深入研究抑菌活性物质,我们对红豆树枝条提取物进行了系统的化学成分研究,并从中分离得到了16个黄酮类化合物,分别鉴定为圆荚草双糖苷(Sphaerobioside,**1**)、5,7-二羟基-4′-甲氧基异黄酮-7-*O*-*β*-D-葡萄糖苷

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(sissotrin,**2**)、4′,8-二甲氧基-7-*O*-*β*-D-葡萄糖基异黄酮(4′,8-dimethoxyl-7-*O*-*β*-D-glucopyranosyl isoflavone,**3**)、芒柄花苷(ononin,**4**)、异樱黄素-7-*O*-*β*-D-葡萄糖苷(isoprunetin-7-*O*-*β*-D-glucoside,**5**)、芦丁(rutin,**6**)、山柰酚-3-*O*-β-*D*-芸香糖苷(kaempferol-3-*O*-*β*-D-rutinoside,**7**)、4′-甲氧基异黄酮-7-*O*-*β*-D-木糖(1→6)-*O*-*β*-D-吡喃葡萄糖苷(Kushenol O,**8**)、4′-甲氧基异黄酮-7-*O*-*β*-D-芹糖(1→6)-*O*-*β*-D-吡喃葡萄糖苷(7-hydroxy-4′-methoxylisoflavone-7-*O*-*β*-D-apiofuranosyl-(1→6)-*O*-*β*-D-glucopyranoside,**9**)、染料木素(genistein,**10**)、异樱黄素(isoprunetin,**11**)、2′,4′,5,7-四羟基异黄酮(2′,4′,5,7-tetrahydroxyisoflavone,**12**)、大豆素(daidzein,**13**)、柚皮素(naringenin,**14**)、二氢染料木素(dihydrogenistein,**15**)、去甲基化美迪紫檀素(demethylmedicarpin,**16**),并对部分含量较大的化合物采用生长速率法进行抑菌活性评价。化合物**1**~**16**均为首次从该植物中分离得到,其中化合物**1**、**3**、**4**、**6**~**9**、**12**、**15**、**16**为首次从红豆属中分离得到。抑菌活性测试显示,化合物**2**、**5**和**14**对*F. graminearum*、*F. oxysporumf*、*F. solani*有较好的抑制作用。这将为红豆树后续的植物资源的开发与利用提供参考。

1　仪器与材料

1.1　仪器

ZF-5 手提式紫外分析仪(上海嘉鹏科技有限公司);TQ-400Y 高速多功能粉碎机(永康市天祺盛世工贸有限公司);BS-100A 自动部份收集器(上海沪西分析仪器厂有限公司);BS-214D 电子天平(赛多利斯科学仪器北京有限公司);LC-20AP 制备型高效液相色谱仪(日本岛津有限公司);waters-2695-QDA 高效液相色谱-质谱联用仪(美国沃特世科技有限公司);Buchi Rotavapor Essential 旋转蒸发仪系列(瑞士步琦公司);HX-1050 恒温循环器(北京博医康实验仪器有限公司);Bruker AV-400III 型核磁共振仪(德国布鲁克公司)。

1.2　材料

GF_{254}薄层层析硅胶及柱色谱用硅胶(青岛海洋化工有限公司);D101 大孔吸附树脂、Sephadex LH-20 凝胶(美国通用电气公司);YMC-Pack ODS-A 反相色谱柱(250 mm×20 mm,5 μm),日本 YMC 公司;Diamonsil C_{18}分析型反相色谱柱(150 mm×4.6 mm,5 μm),北京迪马科技有限公司;SilGreen ODS 制备型色谱柱(250 mm×10 mm,5μm),北京绿百草科技发展有限公司;常用有机试剂甲醇、二氯甲烷、石油醚、乙酸乙酯等均为分析纯(国药集团化学试剂有限公司);HPLC 用色谱纯甲醇、乙腈(默克公司)。

红豆树枝条采自福建省福州市晋安区北峰村,经福建农林大学林学院邹小兴副教授鉴定为红豆树*Ormosia hosiei*枝条。

2　提取与分离

取干燥红豆树枝条 12.5 kg,经粉碎机粉碎至粗粉,用 125 L 的 70% 乙醇加热回流提取 2 次,每次 3 h,滤过,合并提取液,减压浓缩,得粗提取物浸膏 1.2 kg。加入 48 L 水溶解浸膏,将水溶物过 D101 大孔吸附树脂,以水-乙醇系统(100∶0、70∶30、40∶60、5∶95)梯度洗脱得到 4 个组分(A1-A4);A-4(160 g)经硅胶柱色谱,用二氯甲烷-乙醇系统(1∶0 ~ 0∶1)梯度洗脱,经合并后得到 17 个组分(B1-B17)。B-5(4.4 g)经 Sephadex LH-20 柱色谱,以[二氯甲烷-甲醇(1∶1)]洗脱分离,得到 5 个组分(C1-C5);C-3(291.8 mg)经硅胶柱色谱分离,用二氯甲烷-甲醇-水(5∶2∶0.2)等度洗脱,得到化合物**6**(45 mg)和**7**(16 mg);C-4(3.5 g)经制备 HPLC(C_{18},28% 乙腈,3.0 mL/min,检测波长 290 nm)纯化得到化合物**16**(t_R=29.241 min,6.4 mg)和**15**(t_R=35.789 min,3.3 mg);C-5(133 mg)经制备 HPLC(C_{18},55% 甲醇,8.0 mL/min,检测波长 210 nm)纯化得到化合物**10**(t_R=24.917 min,49.9 mg)和**14**(t_R=21.399 min,13.4 mg)。B-9(3.9 g)经 Sephadex LH-20 柱色谱,以甲醇洗脱分离,得到 12 个组分(D1-D12);D-3(450 mg)经制备 HPLC(C_{18},45% 甲醇,8.0 mL/min,检测波长 210 nm)纯化得到化合物**8**(t_R=21.648 min,56 mg)和**9**(t_R=23.957 min,33.8 mg);D-5(120 mg)经制备 HPLC(C_{18},34% 甲醇,8.0 mL/min,检测波长 210 nm)纯化得到化合物**5**(t_R=27.451 min,10.5 mg);D-6(149.5 mg)经制备 HPLC(C_{18},53% 甲醇,3.0 mL/min,检测波长 254 nm)纯化得到化合物**2**(t_R=22.928 min,15 mg);D-10(62.5 mg)经制备 HPLC(C_{18},53% 甲醇,8.0 mL/min,检测波长 210 nm)纯化得到化合物**1**(t_R=16.048 min,13 mg)。B-10(2.2 g)经 Sephadex LH-20 柱色谱,以甲醇洗脱分离,得到 10 个组分(E1-E10);E-4(85.9 mg)经制备 HPLC(C_{18},45% 甲醇,

8.0 mL/min,检测波长 210 nm)纯化得到化合物 **4**(t_R = 34.469 min,3.3 mg)和 **3**(t_R = 46.983 min,12.8 mg);E-6(102.7 mg)经制备 HPLC(C_{18},50%甲醇,3.0 mL/min,检测波长 254 nm)纯化得到化合物 **11**(t_R = 20.272 min,40.9 mg);E-7(42.8 mg)经制备 HPLC(C_{18},46%甲醇,8.0 mL/min,检测波长 210 nm)纯化得到化合物 **12**(t_R = 21.520 min,7.6 mg)和 **13**(t_R = 29.396 min,3.5 mg)。

3 结构鉴定

化合物 1 白色粉末(甲醇),分子式为 $C_{27}H_{30}O_{14}$,mp. 216 ~ 218 ℃,ESI-MS:*m/z* 577.3 [M-H]$^-$,UV λ_{max}(MeOH-H_2O):259.2,327.0 nm;^{1}H NMR(400 MHz,DMSO-d_6) δ:12.88 (1H,s,5-OH),9.63 (1H,s,4′-OH),8.40 (1H,s,H-2),7.40 (2H,d,*J* = 8.4 Hz,H-2′,6′),6.83 (2H,d,*J* = 8.4 Hz,H-3′,5′),6.73 (1H,d,*J* = 2.0 Hz,H-8),6.44 (1H,d,*J* = 2.0 Hz,H-6),5.02 (1H,d,*J* = 7.2 Hz,H-1″),4.52 (1H,br s,H-1‴),1.10 (3H,d,*J* = 6.0 Hz,H-6‴);^{13}C NMR (100 MHz,DMSO-d_6) δ:180.5 (C-4),162.8 (C-4′),161.5 (C-7),157.5 (C-5),157.3 (C-9),154.8 (C-2),130.2 (C-2′,6′),122.5 (C-1′),121.1 (C-3),115.1 (C-3′,5′),106.2 (C-10),100.7 (C-1″),100.0 (C-1‴),99.7 (C-6),94.6 (C-8),76.5 (C-3″),75.6 (C-5″),73.1 (C-2″),72.2 (C-4‴),70.7 (C-3‴),70.3 (C-2‴),70.0 (C-4″),68.4 (C-5‴),66.4 (C-6″),17.9 (C-6‴)。以上数据与文献[4]报道一致,故鉴定化合物 **1** 为圆荚草双糖苷。

化合物 2 白色粉末(甲醇),分子式为 $C_{22}H_{22}O_{10}$,mp. 212 ~ 214 ℃,ESI-MS:*m/z* 447.2 [M + H]$^+$,UV λ_{max}(MeOH-H_2O):259.2,325.8 nm;^{1}H NMR(400 MHz,DMSO-d_6) δ:12.92 (1H,s,5-OH),8.48 (1H,s,H-2),7.53 (2H,d,*J* = 8.8 Hz,H-2′,6′),7.02 (2H,d,*J* = 8.8 Hz,H-3′,5′),6.73 (1H,d,*J* = 2.4 Hz,H-8),6.48 (1H,d,*J* = 2.4 Hz,H-6),5.07 (1H,d,*J* = 7.2 Hz,H-1″),3.16 ~ 3.70 (6H,m,H-2″,3″,4″,5″,6″),3.79 (3H,s,4′-OCH_3);^{13}C NMR (100 MHz,DMSO-d_6) δ:180.4 (C-4),163.1 (C-7),161.6 (C-5),159.2 (C-4′),157.2 (C-10),155.0 (C-2),130.2 (C-2′,6′),122.7 (C-1′),122.3 (C-3),113.8 (C-3′,5′),106.2 (C-9),99.8 (C-1″),99.6 (C-6),77.2 (C-5″),76.4 (C-3″),73.1 (C-2″),69.6 (C-4″),60.6 (C-6″),55.2 (4′-OCH_3)。以上数据与文献[5]报道一致,故鉴定化合物 **2** 为 5,7-二羟基-4′-甲氧基异黄酮-7-*O*-*β*-D-葡萄糖苷。

化合物 3 白色无定型粉末(甲醇),分子式为 $C_{23}H_{24}O_{10}$,mp. 216 ~ 218 ℃,ESI-MS:*m/z* 461.1 [M + H]$^+$,UV λ_{max}(MeOH-H_2O):253.3 nm;^{1}H NMR(400 MHz,DMSO-d_6) δ:8.49 (1H,s,H-2),7.80 (1H,d,*J* = 8.8 Hz,H-5),7.53 (1H,d,*J* = 8.8 Hz,H-2′,6′),7.36 (1H,d,*J* = 8.8 Hz,H-6),7.00 (1H,d,*J* = 8.8 Hz,H-3′,5′),5.10 (1H,d,*J* = 7.2 Hz,H-1″),3.94 (3H,s,8-OCH_3),3.79 (3H,s,4′-OCH_3),3.70 ~ 3.20 (6H,m,Glc-2″,3″,4″,5″,6″H);^{13}C NMR (100 MHz,DMSO-d_6) δ:174.8 (C-4),159.1 (C-4′),154.1 (C-7),153.7 (C-2),150.0 (C-9),136.8 (C-8),130.1 (C-2′,6′),124.0 (C-1′),123.1 (C-3),120.3 (C-5),119.3 (C-10),114.0 (C-6),113.7 (C-3′,5′),100.4 (C-1″),77.3 (C-5″),76.7 (C-3″),73.3 (C-2″),69.6 (C-4″),61.3 (8-OCH_3),60.6 (C-6″),55.2 (4′-OCH_3)。以上数据与文献[6]报道一致,故鉴定化合物 **3** 为 4′,8-二甲氧基-7-*O*-*β*-D-葡萄糖基异黄酮。

化合物 4 白色粉末(甲醇),分子式为 $C_{22}H_{22}O_9$,mp. 216 ℃,ESI-MS:*m/z* 431.2 [M + H]$^+$,UV λ_{max}(MeOH-H_2O):249.7 nm;^{1}H NMR(400 MHz,DMSO-d_6) δ:8.45 (1H,s,H-2),8.05 (1H,d,*J* = 8.8 Hz,H-5),7.53 (2H,d,*J* = 8.8 Hz,H-2′,6′),7.25 (1H,d,*J* = 2.4 Hz,H-8),7.15 (1H,dd,*J* = 2.4,8.8 Hz,H-6),7.00 (2H,d,*J* = 8.8 Hz,H-3′,5′),5.11 (1H,d,*J* = 7.6 Hz,H-1″),3.79 (3H,s,4′-OCH_3);^{13}C NMR (100 MHz,DMSO-d_6) δ:174.7 (C-4),161.5 (C-7),159.0 (C-4′),157.1 (C-9),153.7 (C-2),130.1 (C-2′,6′),127.0 (C-5),124.0 (C-1′),123.4 (C-3),118.5 (C-10),115.7 (C-6),113.6 (C-3′,5′),103.4 (C-8),100.0 (C-1″),77.2 (C-5″),76.5 (C-3″),73.1 (C-2″),69.6 (C-4″),60.6 (C-6″),55.2 (4′-OCH_3)。以上数据与文献[7]报道一致,故鉴定化合物 **4** 为芒柄花苷。

化合物 5 白色固体(甲醇),分子式为 $C_{22}H_{22}O_{10}$,ESI-MS:*m/z* 445.1 [M-H]$^-$,UV λ_{max}(MeOH-H_2O):255.7 nm;^{1}H NMR(400 MHz,DMSO-d_6) δ:8.16 (1H,s,H-2),7.31 (2H,d,*J* = 8.8 Hz,H-2′,

6′),6.78 (2H,d,*J* = 8.8 Hz,H-3′,5′),6.73 (1H,d,*J* = 2.0 Hz,H-8),6.59 (1H,d,*J* = 2.0 Hz,H-6),5.08 (1H,d,*J* = 7.2 Hz,H-1″),3.83 (3H,s,5-OCH_3),3.72 (1H,m,H-6″a),3.45 (2H,m,H-5″,6″b),3.30 (1H,m,H-3″),3.28 (1H,m,H-2″),3.16 (1H,m,H-4″);^{13}C NMR (100 MHz,DMSO-d_6) δ:173.9 (C-4),161.4 (C-7),160.8 (C-5),158.8 (C-9),157.1 (C-4′),150.9 (C-2),130.2 (C-2′,6′),124.9 (C-3),122.6 (C-1′),114.8 (C-3′,5′),109.6 (C-10),99.9 (C-1″),97.1 (C-6),95.6 (C-8),77.3 (C-5″),76.6 (C-3″),73.1 (C-2″),69.8 (C-4″),60.7 (C-6″),56.1 (5-OCH_3)。以上数据与文献[8]报道一致,故鉴定化合物**5** 为异樱黄素-7-*O*-β-D-葡萄糖苷。

化合物 6 黄色粉末(甲醇),分子式为 $C_{27}H_{30}O_{16}$,mp. 177 ~ 178 ℃,ESI-MS:*m/z* 609.2 [M-H]$^-$,UV λ_{max} (MeOH-H_2O):255.7,354.6 nm;^{1}H NMR (400 MHz,DMSO-d_6) δ:12.59 (1H,s,5-OH),7.55 (1H,d,*J* = 2.4 Hz,H-2′),7.53 (1H,dd,*J* = 8.4,2.4 Hz,H-6′),6.83 (1H,d,*J* = 8.4 Hz,H-5′),6.38 (1H,d,*J* = 2.0 Hz,H-8),6.18 (1H,d,*J* = 2.0 Hz,H-6),5.34 (1H,d,*J* = 7.2 Hz,H-1″),4.38 (1H,br s,H-1‴),0.98 (3H,d,*J* = 6.4 Hz,H-6‴);^{13}C NMR (100 MHz,DMSO-d_6) δ:177.4 (C-4),164.3 (C-7),161.2 (C-5),156.6 (C-9),156.5 (C-2),148.5 (C-4′),144.8 (C-3′),133.3 (C-3),121.6 (C-1′),121.2 (C-6′),116.3 (C-5′),115.3 (C-2′),103.9 (C-10),101.2 (C-1″),100.8 (C-1‴),98.8 (C-6),93.7 (C-8),76.5 (C-3″),75.9 (C-5″),74.1 (C-2″),71.9 (C-4‴),70.6 (C-3‴),70.4 (C-4″),70.0 (C-2‴),68.3 (C-5‴),67.0 (C-6″),17.8 (C-6‴)。以上数据与文献[9]报道一致,故鉴定化合物**6** 为芦丁。

化合物 7 黄色粉末(甲醇),分子式为 $C_{27}H_{30}O_{15}$,mp. 223 ~ 225 ℃,ESI-MS:*m/z* 617.3 [M + Na]$^+$,UV λ_{max} (MeCN-H_2O):265.1,347.4 nm;^{1}H NMR (400 MHz,DMSO-d_6) δ:12.56 (1H,s,5-OH),10.18 (1H,s,7-OH),7.98 (2H,d,*J* = 8.8 Hz,H-2′,6′),6.87 (2H,d,*J* = 8.8 Hz,H-3′,5′),6.41 (1H,d,*J* = 2.0 Hz,H-8),6.20 (1H,d,*J* = 2.0 Hz,H-6),5.31 (1H,d,*J* = 7.2 Hz,H-1″),4.37 (1H,br s,H-1‴),0.98 (1H,d,*J* = 6.4 Hz,H-6‴);^{13}C NMR (100 MHz,DMSO-d_6) δ:177.4 (C-4),164.3 (C-7),161.2 (C-5),159.9 (C-4′),156.9 (C-2),156.5 (C-9),133.2 (C-3),130.9 (C-2′,6′),120.9 (C-1′),115.1 (C-3′,5′),104.0 (C-10),101.4 (C-1″),100.8 (C-1‴),98.8 (C-6),93.8 (C-8),76.4 (C-3″),75.8 (C-5″),74.2 (C-2″),71.8 (C-4‴),70.6 (C-3‴),70.4 (C-2‴),69.9 (C-4″),68.3 (C-5‴),66.9 (C-6″),17.8 (C-6‴)。以上数据与文献[10]报道一致,故鉴定化合物**7** 为山柰酚-3-*O*-β-D-芸香糖苷。

化合物 8 白色无定型粉末(甲醇),分子式为 $C_{27}H_{30}O_{13}$,ESI-MS:*m/z* 563.3 [M + H]$^+$,UV λ_{max} (MeOH-H_2O):249.7 nm;^{1}H NMR (400 MHz,DMSO-d_6) δ:8.40 (1H,s,H-2),8.07 (1H,d,*J* = 8.8 Hz,H-5),7.53 (2H,d,*J* = 8.8 Hz,H-2′,6′),7.28 (1H,d,*J* = 2.4 Hz,H-8),7.19 (1H,dd,*J* = 8.8,2.4 Hz,H-6),7.00 (2H,d,*J* = 8.8 Hz,H-3′,5′),5.04 (1H,d,*J* = 6.8 Hz,H-1″),4.18 (1H,d,*J* = 7.2 Hz,H-1‴),3.79 (3H,s,4′-OCH_3);^{13}C NMR (100 MHz,DMSO-d_6) δ:174.7 (C-4),161.4 (C-7),159.0 (C-4′),157.0 (C-9),153.7 (C-2),130.1 (C-2′,6′),127.1 (C-5),124.1 (C-3),123.4 (C-1′),118.5 (C-10),115.5 (C-6),113.7 (C-3′,5′),104.1 (C-1‴),103.7 (C-8),100.1 (C-1″),76.5 (C-5″),76.4 (C-3‴),75.8 (C-3″),73.5 (C-2‴),73.1 (C-2″),69.7 (C-4″),69.5 (C-4‴),68.6 (C-6″),65.7 (C-5‴),55.2 (4′-OCH_3)。以上数据与文献[11]报道一致,故鉴定化合物**8** 为4′-甲氧基异黄酮-7-*O*-β-D-木糖(1→6)-*O*-β-D-吡喃葡萄糖苷。

化合物 9 白色无定型粉末(甲醇),分子式为 $C_{27}H_{30}O_{13}$,ESI-MS:*m/z* 563.1 [M + H]$^+$,UV λ_{max} (MeOH-H_2O):249.7 nm;^{1}H NMR (400 MHz,DMSO-d_6) δ:8.39 (1H,s,H-2),8.07 (1H,d,*J* = 8.8 Hz,H-5),7.53 (2H,d,*J* = 8.8 Hz,H-2′,6′),7.25 (1H,d,*J* = 2.4 Hz,H-8),7.16 (1H,dd,*J* = 8.8,2.4 Hz,H-6),7.00 (2H,d,*J* = 8.8 Hz,H-3′,5′),5.07 (1H,d,*J* = 7.6 Hz,H-1″),4.82 (1H,d,*J* = 3.2 Hz,H-1‴),3.79 (3H,s,4′-OCH_3);^{13}C NMR (100 MHz,DMSO-d_6) δ:174.7 (C-4),161.4 (C-7),159.0 (C-4′),157.1 (C-9),153.7 (C-2),130.1 (C-2′,6′),127.1 (C-5),124.1 (C-3),123.4 (C-1′),118.5 (C-10),115.5 (C-6),113.7 (C-3′,5′),109.4 (C-1‴),103.7 (C-8),100.0 (C-1″),78.7

(C-3‴),76.5 (C-5″),75.9 (C-2‴),75.7 (C-3″),73.3 (C-4‴),73.1 (C-2″),70.0 (C-4″),67.8 (C-6″),63.1 (C-5‴),55.2 (4′-OCH_3)。以上数据与文献[11]报道一致,故鉴定化合物 **9** 为 4′-甲氧基异黄酮-7-*O*-*β*-D-芹糖(1→6)-*O*-*β*-D-吡喃葡萄糖苷。

化合物 10 浅黄色粉末(甲醇),分子式为 $C_{15}H_{10}O_5$, mp. 303 ~ 304 ℃, ESI-MS: *m/z* 269.2 [M-H]$^-$, UV λ_{max} (MeOH-H_2O): 260.4 nm; ^{1}H NMR (400 MHz, DMSO-d_6) *δ*: 12.96 (1H, s, 5-OH), 10.88 (1H, s, 7-OH), 9.59 (1H, s, 4′-OH), 8.32 (1H, s, H-2), 7.37 (2H, d, *J* = 8.8 Hz, H-2′,6′), 6.82 (2H, d, *J* = 8.8 Hz, H-3′,5′), 6.38 (1H, d, *J* = 2.0 Hz, H-8), 6.22 (1H, d, *J* = 2.0 Hz, H-6); ^{13}C NMR (100 MHz, DMSO-d_6) *δ*: 180.2 (C-4), 164.3 (C-7), 162.0 (C-5), 157.6 (C-4′), 157.4 (C-9), 154.0 (C-2), 130.2 (C-2′,6′), 122.3 (C-1′), 121.2 (C-3), 115.1 (C-3′,5′), 104.5 (C-10), 99.0 (C-6), 93.7 (C-8)。以上数据与文献[12]报道一致,故鉴定化合物 **10** 为染料木素。

化合物 11 白色粉末(甲醇),分子式为 $C_{16}H_{12}O_5$, mp. 287 ℃, ESI-MS: *m/z* 285.1 [M + H]$^+$, UV λ_{max} (MeOH-H_2O): 255.7 nm; ^{1}H NMR (400 MHz, DMSO-d_6) *δ*: 10.74 (1H, s, 7-OH), 9.51 (1H, s, 4′-OH), 8.06 (1H, s, H-2), 7.29 (2H, d, *J* = 8.8 Hz, H-2′,6′), 6.77 (2H, d, *J* = 8.8 Hz, H-3′,5′), 6.39 (1H, d, *J* = 2.0 Hz, H-8), 6.37 (1H, d, *J* = 2.0 Hz, H-6), 3.79 (3H, s, 5-OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6) *δ*: 173.8 (C-4), 162.4 (C-7), 161.2 (C-5), 159.1 (C-4′), 157.0 (C-9), 150.4 (C-2), 130.2 (C-2′,6′), 124.7 (C-3), 122.8 (C-1′), 114.8 (C-3′,5′), 107.9 (C-10), 96.5 (C-6), 94.8 (C-8), 55.9 (5-OCH_3)。以上数据与文献[13]报道一致,故鉴定化合物 **11** 为异樱黄素。

化合物 12 浅黄色固体(甲醇),分子式为 $C_{15}H_{10}O_6$, mp. 271 ~ 273 ℃, ESI-MS: *m/z* 285.1 [M-H]$^-$, UV λ_{max} (MeOH-H_2O): 258 nm; ^{1}H NMR (400 MHz, DMSO-d_6) *δ*: 12.97 (1H, s, 5-OH), 9.35 (2H, br s, 2′,4′-OH), 8.13 (1H, s, H-2), 6.96 (1H, d, *J* = 8.0 Hz, H-6′), 6.35 (1H, d, *J* = 2.0 Hz, H-8), 6.34 (1H, d, *J* = 2.4 Hz, H-3′), 6.26 (1H, dd, *J* = 8.4, 2.4 Hz, H-5′), 6.19 (1H, d, *J* = 2.0 Hz, H-6); ^{13}C NMR (100 MHz, DMSO-d_6) *δ*: 180.4 (C-4), 164.5 (C-7), 161.9 (C-5), 158.6 (C-4′), 157.7 (C-9), 156.5 (C-2′), 155.3 (C-2), 132.2 (C-6′), 120.5 (C-3), 108.7 (C-1′), 106.2 (C-5′), 104.4 (C-10), 102.6 (C-3′), 99.0 (C-6), 93.7 (C-8)。以上数据与文献[14]报道一致,故鉴定化合物 **12** 为 2′,4′,5,7-四羟基异黄酮。

化合物 13 浅黄色粉末(甲醇),分子式为 $C_{15}H_{10}O_4$, mp. 170 ~ 172 ℃, ESI-MS: *m/z* 253.4 [M-H]$^-$, UV λ_{max} (MeOH-H_2O): 248.6, 302.0 nm; ^{1}H NMR (400 MHz, DMSO-d_6) *δ*: 10.80 (1H, s, 7-OH), 9.55 (1H, s, 4′-OH), 8.29 (1H, s, H-2), 7.96 (1H, d, *J* = 8.8 Hz, H-5), 7.38 (2H, d, *J* = 8.4 Hz, H-2′,6′), 6.93 (1H, dd, *J* = 2.0, 8.8 Hz, H-6), 6.86 (1H, d, *J* = 2.0 Hz, H-8), 6.80 (2H, d, *J* = 8.4 Hz, H-3′,5′); ^{13}C NMR (100 MHz, DMSO-d_6) *δ*: 174.7 (C-4), 162.6 (C-7), 157.4 (C-9), 157.2 (C-4′), 152.9 (C-2), 130.1 (C-2′,6′), 127.3 (C-5), 123.5 (C-3), 122.6 (C-1′), 116.6 (C-10), 115.2 (C-6), 115.0 (C-3′,5′), 102.1 (C-8)。以上数据与文献[15]报道一致,故鉴定化合物 **13** 为大豆素。

化合物 14 无色针状结晶(甲醇),分子式为 $C_{15}H_{12}O_5$, mp. 247 ~ 249 ℃, ESI-MS: *m/z* 271.1 [M-H]$^-$, UV λ_{max} (MeOH-H_2O): 212.0, 291.3, 324.7 nm; ^{1}H NMR (400 MHz, DMSO-d_6) *δ*: 12.15 (1H, s, 5-OH), 9.63 (1H, s, 4′-OH), 7.31 (2H, d, *J* = 8.8 Hz, H-2′,6′), 6.79 (2H, d, *J* = 8.8 Hz, H-3′,5′), 5.87 (2H, s, H-6,8), 5.43 (1H, dd, *J* = 12.8, 3.2 Hz, H-2), 3.26 (1H, dd, *J* = 17.0, 12.8 Hz, H-3a), 2.67 (1H, dd, *J* = 17.0, 3.2 Hz, H-3b); ^{13}C NMR (100 MHz, DMSO-d_6) *δ*: 196.3 (C-4), 166.8 (C-7), 163.5 (C-5), 162.9 (C-9), 157.7 (C-4′), 128.9 (C-1′), 128.4 (C-2′,6′), 115.2 (C-3′,5′), 101.7 (C-10), 95.8 (C-6), 95.0 (C-8), 78.4 (C-2), 42.0 (C-3)。以上数据与文献[16]报道一致,故鉴定化合物 **14** 为柚皮素。

化合物 15 黄色粉末(甲醇),分子式为 $C_{15}H_{12}O_5$, mp. 216 ~ 218 ℃, ESI-MS: *m/z* 273.1 [M + H]$^+$, UV λ_{max} (MeOH-H_2O): 213.2, 291.3 nm; ^{1}H NMR (400 MHz, DMSO-d_6) *δ*: 12.19 (1H, s, 5-OH), 9.43 (1H, s, 4′-OH), 7.07 (2H, d, *J* = 8.4 Hz, H-2′,6′), 6.72 (2H, d, *J* = 8.4 Hz, H-3′,5′), 5.89 (1H, d, *J* = 2.0 Hz, H-8), 5.87 (1H, d, *J* = 2.0 Hz, H-6),

4.53 (2H,d,J = 6.4 Hz,H-2),4.00 (1H,t,J = 6.4 Hz,H-3);^{13}C NMR (100 MHz,DMSO-d_6) δ:196.9 (C-4),166.9 (C-7),163.9 (C-5),162.9 (C-9),156.7 (C-4′),129.7 (C-2′,6′),125.7 (C-1′),115.3 (C-3′,5′),101.7 (C-10),96.0 (C-6),94.8 (C-8).70.8 (C-2),49.3 (C-3)。以上数据与文献[17]报道一致,故鉴定化合物 **15** 为二氢染料木素。

化合物 16　白色粉末(甲醇),分子式为 $C_{15}H_{12}O_4$,ESI-MS:m/z 257.2 $[M+H]^+$,UV λ_{max}(MeOH-H_2O):285.3 nm;^{1}H NMR (400 MHz,DMSO-d_6) δ:9.63 (1H,s,3-OH),9.36 (1H,s,9-OH),7.25 (1H,d,J = 8.4 Hz,H-1),7.09 (1H,d,J = 8.0 Hz,H-7),6.46 (1H,dd,J = 8.4,2.4 Hz,H-2),6.28 (1H,dd,J = 8.0,2.0 Hz,H-8),6.25 (1H,d,J = 2.4 Hz,H-4),6.20 (1H,d,J = 2.0 Hz,H-10),5.47 (1H,d,J = 6.0 Hz,H-11a),4.20 (1H,m,H-6),3.52(2H,m,H-6a,6);^{13}C NMR (100 MHz,DMSO-d_6) δ:160.2 (C-10a),158.7 (C-3),158.5 (C-9),156.3 (C-4a),132.1 (C-1),125.1 (C-7),117.6 (C-6b),111.3 (C-11b),109.6 (C-2),107.3 (C-8),102.8 (C-4),97.5 (C-10),77.8 (C-11a),66.0 (C-6),38.8 (C-6a)。以上数据与文献[18]报道一致,故鉴定化合物 **16** 为去甲基化美迪紫檀素。

4　活性测定

采用菌丝生长速率法测定化合物 **1 ~ 5**、**10 ~ 16** 对 *F. graminearum*、*F. oxysporumf*、*F. solani*3 种植物病原真菌的抑制活性。将上述化合物用 *V* 甲醇:*V* 水(50:50)溶解,药液最终浓度 150 mg/L。活性测定及计算方法参照文献[19,20]。化合物 **2**、**5** 和 **14** 对 3 种植物病原真菌显示中等抑制活性,实验数据见表 1,未列出的化合物其抑制率均低于 30%。

表 1　部分化合物对 3 种植物病原真菌的抑制活性

Table 1　Inhibitory activity of some compounds on three plant pathogenic fungi

化合物 Compound	抑制率 ± SE Inhibition ratio ± SE (%)		
	禾谷镰刀菌 *F. graminearum*	西瓜尖镰孢菌 *F. oxysporumf*	茄病镰刀菌 *F. solani*
2	33.64 ± 4.40	25.08 ± 1.34	24.65 ± 4.02
5	33.64 ± 4.40	39.81 ± 1.34	34.30 ± 1.52
14	31.95 ± 1.47	32.83 ± 2.69	30.79 ± 0.00

5　结论

本次研究从红豆树茎枝中分离并鉴定了 16 个黄酮类化合物,其中,化合物 **1**、**3**、**4**、**6 ~ 9**、**12**、**15**、**16** 为首次从红豆属中分离得到,化合物 **1 ~ 16** 为首次从红豆树中分离得到。抑菌活性研究提示化合物 **2**,**5** 和 **14** 对禾谷镰刀菌、西瓜尖镰孢菌、茄病镰刀菌的菌丝生长显示出了中等强度的抑制作用。

参考文献

1　Flora of China Editorial Committee(中国科学院中国植物志编辑委员会). Flora reipublicae popularis sinicae,40(中国植物志)[M]. Beijing:Science Press,1994:28.

2　Sichuan Institute of Chinese materia medica(四川省中药研究所). Common Chinese herbal medicine in Sichuan(四川常用中草药)[M]. Sichuan:Renmin Press,1971.

3　Pouny I,Batut M,Vendier L,*et al*. Cytisine-like alkaloids from *Ormosia hosiei* Hemsl. & E. H. Wilson[J]. *Phytochemistry*,2014,107:97-101.

4　Xiang C(向诚),Cheng J(成军),Liang H(梁鸿),*et al*. Isoflavones from *Millettia nitida* var. hirsutissima[J]. *Acta Pharm Sin*(药学学报),2009,44:158-161.

5　Fu MQ,Deng D,Feng SX,*et al*. Chemical constituents from roots of *Flemingia philippinensis*[J]. *Chin Herbal Med*,2012,4(1):8-11.

6　Wang YZ(王彦志),Feng WS(冯卫生),Shi RB(石任兵),*et al*. A new chemical component of *Pueraria lobata* (Willd) ohwi[J]. *Acta Pharm Sin*(药学学报),2007,42:964-967.

7　Cui BL,Nakamura M,Kinjo J,*et al*. Chemical constituents of *Astragali Semen*[J]. *Chem Pharm Bull*,1993,41:178-182.

8　Ichige M,Fukuda E,Miida S,*et al*. Novel isoflavone glucosides in groundnut(*Apios americana* Medik) and their anti-androgenic activities[J]. *J Agric Food Chem*,2013,61:2183-2187.

9 Wang PP(王培培), Luo J(罗俊), Yang MH(杨鸣华), *et al*. Chemical constituents of *Lobelia chinensis*[J]. *Chin Tradit Herbal Drugs*(中草药), 2013, 44: 794-797.

10 Wu D(吴笛), Zhang M(张勉), Zhang CF(张朝凤), *et al*. Flavonoids and phenolic acid derivatives from *Flos Farfarae*[J]. *Chin J Chin Mater Med*(中国中药杂志), 2010, 35: 1142-1144.

11 Li X(黎雄), Li JF(李剑芳), Wang D(王东), *et al*. Isoflavone glycosides from the bark of *Maackia amurensis*[J]. *Acta Pharm Sin*(药学学报), 2009, 44(1): 63-68.

12 Zhang QH(张庆贺), Bai JC(柏金辰), Sun BX(孙冰雪), *et al*. Chemical constituents and their anti-osteoporosis activities of *Fructus sophorae*[J]. *Nat Prod Res Dev*(天然产物研究与开发), 2017, 29: 1517-1522.

13 Young HS, Park JH, Park HJ, *et al*. Chemical study on the stem of *Cudrania tricuspidata*[J]. *Arch Pharm Res*, 1989, 12(1): 39-41.

14 Yin T(尹婷), Liu H(刘桦), Wang B(王邠), *et al*. Chemical constituents from *Spatholobus sinensis*[J]. *Acta Pharm Sin*(药学学报), 2008, 43(1): 67-70.

15 Luan L(栾兰), Wang GL(王钢力), Yu JP(郁建平), *et al*. Studies on chemical constituents of *Phyllporia ribis*[J]. *Chin Tradit Herb Drugs*(中草药), 2007, 38: 825-826.

16 Xu RL(徐瑞兰), Shi YP(师彦平). Chemical constituents from *Artemisiae anomalae* Herba[J]. *Chin Tradit Herb Drugs*(中草药), 2014, 45: 1521-1525.

17 Soidinsalo O, Wähälä K. Synthesis of phytoestrogenic isoflavonoid disulfates[J]. *Phytochemistry*, 2004, 69: 613-616.

18 Fu MQ, Xiao GS, Xu YJ, *et al*. Chemical constituents from roots of *Millettia speciosa*[J]. *Chin Herbal Med*, 2016, 8: 385-389.

19 Lei SN(雷绍南), Ni L(倪林), Wu XQ(吴晓芹), *et al*. Study on antifungal constituents of *Pogonatherum crinitum*[J]. *Chin J Pestic Sci*(农药学学报), 2017, 19: 119-124.

20 Niu R(牛蓉), Qiu YT(邱亚铁), Ni L(倪林), *et al*. Study on the antifungal effect and chemical constituents from the extract of *Bauhinia purpurea* bark[J]. *Agrochemicals*(农药), 2018, 57: 184-188.

(上接第 2103 页)

11 Xiao J(肖娟), Wang Y(王莹), Wang XH(王新宏), *et al*. Advances in the intestinal bacteria metabolic of Chemincal composition from Chinese medicine[J]. *Chin J Exp Tradit Med Form*(中国实验方剂学杂志), 2012, 18: 247-251.

12 Shi TR(史同瑞), Liu N(刘宁), Wang S(王爽), *et al*. The interaction of intestinal microflora and metabolism of effective ingredients from Chinese herbal medica[J]. *Chin J Microecol*(中国微生态学杂志), 2014, 26: 479-482.

13 Lai RZ(赖睿智), Zhao YM(赵益铭), Li YH(李怡宏), *et al*. Recent research progress on metabolism of traditional Chinese medicine by intestinal flora[J]. *J Heilongjiang Med*(黑龙江医药), 2016, 29: 415-419.

14 Ji FQ(季凤清), Li BH(李宝红), Sun HM(孙海梅), *et al*. Effective of quercetin on the expression of caspase-3 in AMI rat[J]. *J Capit Med Univ*(首都医科大学学报), 2004, 25: 435-437.

15 Zhou MJ(周明杰), Liu LQ(刘立群). Effects of kaempferol against myocardial ischemia-reperfusion injury in rat heart[J]. *Acta Academiae Med Weifang*(潍坊医学院学报), 2015, 3: 168-170.

16 Bu LM(卜丽梅), Guan FY(关凤英), Qiao P(乔萍), *et al*. Protective effect of gallic acid on apoptosis after myocardial ischemia-reperfusion in rats and its mechanism[J]. *Chin J Lab Diag*(中国实验诊断学), 2010, 14: 1693-1697.