泡核桃壳的化学成分研究

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摘　要：目的　研究泡核桃 *Juglans sigillata* 壳的化学成分。**方法**　采用硅胶、反相 RP_{18}、Sephadex LH-20、MCI 等色谱柱以及半制备 HPLC 柱及制备薄层等方法对泡核桃壳的化学成分进行分离纯化，根据理化性质与波谱数据对所分离到的化合物进行结构鉴定。**结果**　从泡核桃壳 95%乙醇提取物中共分离鉴定 15 个化合物，其中包括 7 个酚苷类化合物：它乔糖苷（**1**）、牡丹酚苷 A（**2**）、4-*O*-β-*D*-glucopyranosylvanillc acid（**3**）、breynioside A（**4**）、1-*O*-香草酰-β-*D*-葡萄糖苷（**5**）、6′-*O*-vanilloyltachioside（**6**）、6′-*O*-vanilloylisotachioside（**7**）；3 个苯丙酸类化合物：6-*O*-feruloyl-*D*-glucopyranose（**8**）、methyl-4-*O*-coumaroylquinate（**9**）、5-*p*-*cis*-coumaroylquinic acid（**10**）；2 个萘酮类化合物：胡桃苷 A（**11**）、胡桃苷 E（**12**）；1 个降倍半萜苷类化合物：长春花糖苷（**13**）；1 个黄酮类化合物：二氢槲皮素（**14**）；1 个脱落酸衍生物：二氢红花菜豆酸-4′-*O*-β-*D*-吡喃葡萄糖苷（**15**）。**结论**　除化合物 **14** 外，其他化合物均为首次从该植物中分离得到，其中化合物 **1**～**4**、**13**、**15** 为首次从该属植物中分离得到。

关键词：泡核桃；它乔糖苷；牡丹酚苷 A；胡桃苷 A；长春花糖苷；二氢红花菜豆酸-4′-*O*-β-*D*-吡喃葡萄糖苷

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Study on chemical constituents in shells of *Juglans sigillata*

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Abstract: Objective　To investigate the chemical constituents in the shells of *Juglans sigillata*. **Methods**　The chemical constituents were isolated by silica gel, RP_{18}, Sephadex LH-20, and MCI column chromatography and semi-preparative HPLC and so on. The structures were identified on the basis of spectroscopic analysis and chemical evidence. **Results**　Fifteen compounds were isolated and identified in the 70% ethanol extract from the shells of *J. sigillata* including seven phenolic glycosides: tachioside (**1**), mudanoside A (**2**), 4-*O*-β-*D*-glucopyranosylvanillc acid (**3**), breynioside A (**4**), 1-*O*-vanilloyl-β-*D*-glucose (**5**), 6′-*O*-vanilloyltachioside (**6**), and 6′-*O*-vanilloylisotachioside (**7**); three phenylpropanoide acid glycosides: 6-*O*-feruloyl-*D*-glucopyranose (**8**), methyl-4-*O*-coumaroylquinate (**9**), and 5-*p*-*cis*-coumaroylquinic acid (**10**); two tetralone glycosides: juglanin A (**11**) and juglanin E (**12**); one norsesquiterpenes glycoside: roseoside (**13**); one flavone: toxifolin (**14**); and one glucosylated abscisic acid derivate: (1′*R*, 3′*R*, 5′*R*, 8′*S*)-*epi*-dihydrophaseic acid β-*D*-glucoside (**15**). **Conclusion**　Except compound **14**, the other compounds are isolated from the shells of *J. sigillata* for the first time. And compounds **1**—**4**, **13**, and **15** are reported for the first time from the plants in genus of *Juglans* L.

Key words: *Juglans sigillata* Dode; tachioside; mudanoside A; juglanoside A; roseoside; (1′*R*, 3′*R*, 5′*R*, 8′*S*)-*epi*-dihydrophaseic acid β-*D*-glucoside

泡核桃 *Juglans sigillata* Dode 系胡桃科胡桃属植物，又名漾濞核桃、茶核桃（云南）、铁核桃（四川、云南）等，落叶乔木，产于云南、贵州、四川西部、西藏雅鲁藏布江中下游地区[1]。云南大理漾濞县泡核桃树种植面积约有 700 km^2，年产泡核桃 3 万余吨，是当地农民的主要经济来源，但是这些核桃经过加工后，剩余核桃壳成了废弃物，没有得到充分利用；同时，胡桃属植物有很高的药用价值，其中泡核桃同属植物核桃楸的青果皮始载于《开宝本草》，古代诸家多以其清热解毒、祛风疗癣、止痛止痢等功效入药[2]，而泡核桃相关化学成分的研究还未见报道。为了对该植物的进一步开发利用研

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究提供科学依据，本实验对泡核桃壳的化学成分进行了研究，从中分离并鉴定了 15 个化合物，其中包括 7 个酚苷类化合物：它乔糖苷（tachioside，**1**）、牡丹酚苷 A（mudanoside A，**2**）、4-*O*-β-*D*-glucopyranosylvanillc acid（**3**）、breynioside A（**4**）、1-*O*-香草酰-β-*D*-葡萄糖苷（1-*O*-vanilloyl-β-*D*-glucose，**5**）、6′-*O*-vanilloyltachioside（**6**）和 6′-*O*-vanilloylisotachioside（**7**）；3 个苯丙酸类化合物：6-*O*-feruloyl-*D*-glucopyranose（**8**）、methyl-4-*O*-coumaroylquinate（**9**）、5-*p*-*cis*-coumaroylquinic acid（**10**）；2 个萘酮类化合物：胡桃苷 A（juglanoside A，**11**）、胡桃苷 E（juglanoside E，**12**）；1 个降倍半萜苷类化合物：长春花糖苷（roseoside，**13**）；1 个黄酮类化合物：二氢槲皮素（toxifolin，**14**）；1 个脱落酸衍生物：二氢红花菜豆酸-4′-*O*-β-*D*-吡喃葡萄糖苷 [(1′*R*, 3′*R*, 5′*R*, 8′*S*)-*epi*-dihydrophaseic acid β-*D*-glucoside，**15**]。除化合物 **14** 外，其余化合物均为首次从该植物中分离得到，其中化合物 **1**～**4**、**13**、**15** 为首次从该属植物中分离得到。

1 仪器及试剂

Bruker AV—600 型及 Bruker AV—400 型核磁共振仪（瑞士布鲁克公司）；VG Auto Sec—300 型质谱仪；柱色谱硅胶、硅胶 G、GF254 薄层色谱硅胶预制板（青岛海洋化工厂）；Sephadex LH-20（Pharmacia 公司）；MCI-gel CHP 20P（日本三菱化学公司）；实验用石油醚、氯仿、醋酸乙酯、丙酮、甲醇为工业试剂经重蒸后使用，其他试剂均为分析纯。

泡核桃壳采自云南省大理州漾濞县，由大理学院药学与化学学院生药教研室周浓副教授鉴定为胡桃科胡桃属植物泡核桃 *Juglans sigillata* Dode 的果壳。

2 提取与分离

干燥泡核桃壳 20 kg，粉碎后用 5 倍量 95%乙醇冷浸提取 3 次，每次浸泡 24 h，提取液经减压浓缩后得浸膏 651 g。取浸膏 645 g，经硅胶柱色谱，依次用石油醚、氯仿、醋酸乙酯、丙酮和甲醇洗脱，分别回收溶剂得到石油醚部位 87.3 g、氯仿部位 22.0 g、醋酸乙酯部位 132.5 g、丙酮部位 69.6 g、甲醇部位 100.0 g。取醋酸乙酯部位浸膏，先经硅胶柱色谱，石油醚-丙酮（0∶1→1∶1）梯度洗脱，收集各组分，经反复硅胶柱色谱、MCI 柱色谱、反相 RP_{18} 柱色谱、Sephadex LH-20 柱色谱以及制备薄层、半制备型高效液相等方法进行化合物的分离纯化，共得到 15 个化合物：化合物 **1**（32.8 mg）、**2**（46.9 mg）、**3**（15.2 mg）、**4**（31.2 mg）、**5**（5.1 mg）、**6**（38.1 mg）、**7**（22.7 mg）、**8**（12.7 mg）、**9**（7.0 mg）、**10**（60 mg）、**11**（4.5 mg）、**12**（63.5 mg）、**13**（15.0 mg）、**14**（56 mg）、**15**（4.9 mg）。

3 结构鉴定

化合物 **1**：无色针晶（氯仿-甲醇），ESI-MS *m*/*z*: 302，分子式为 $C_{13}H_{18}O_8$。^{1}H-NMR (400 MHz, CD_3OD) δ: 9.01 (1H, s, Ph-OH), 6.59 (1H, d, J = 8.6 Hz, H-3), 6.47 (1H, d, J = 2.6 Hz, H-5), 6.70 (1H, d, J = 2.6 Hz, H-6), 4.63 (1H, d, J = 7.2 Hz, H-1′), 4.81 (1H, d, J = 4.6 Hz, 2′-OH), 4.63 (1H, d, J = 4.7 Hz, 3′-OH), 4.68 (1H, d, J = 4.6 Hz, 4′-OH), 3.20～3.21 (3H, m, H-2′～4′), 4.45 (1H, t, J = 5.8 Hz, 6′-OH), 3.64～3.42 (2H, m, H-6′), 3.72 (3H, s, 2-OCH_3)；^{13}C-NMR (100 MHz, CD_3OD) δ: 142.8 (C-1), 149.3 (C-2), 103.7 (C-3), 152.8 (C-4), 109.9 (C-5), 115.9 (C-6), 103.7 (C-1′), 74.9 (C-2′), 78.1 (C-3′), 71.5 (C-4′), 78.0 (C-5′), 62.6 (C-6′), 56.3 (2-OCH_3)。上述数据与文献报道基本一致[3]，故鉴定化合物 **1** 为它乔糖苷。

化合物 **2**：淡黄色粉末，ESI-MS *m*/*z*: 330，分子式为 $C_{14}H_{18}O_9$。^{1}H-NMR (400 MHz, CD_3OD) δ: 7.88 (1H, dd, J = 8.6, 1.6 Hz, H-6), 7.60 (1H, d, J = 1.6 Hz, H-2), 6.84 (1H, d, J = 1.6 Hz, H-5), 5.72 (1H, d, J = 3.28 Hz, H-1′β), 5.15 (1H, d, J = 8.2 Hz, H-1′α), 4.90 (2H, d, J = 12.1 Hz, H-6′β), 4.83 (1H, d, J = 5.0 Hz, H-6′α), 4.59 (1H, d, J = 8.2 Hz, H-5′α), 4.54 (1H, d, J = 8.2 Hz, H-3′α), 4.42 (1H, d, J = 8.2 Hz, H-3′β), 4.41 (1H, d, J = 8.2 Hz, H-5′β), 4.40 (1H, d, J = 8.0, 3.6 Hz, H-2′α), 4.39 (1H, d, J = 8.2 Hz, H-4′α), 4.39 (1H, d, J = 8.2 Hz, H-4′β), 4.38 (1H, d, J = 8.2 Hz, H-2′β), 3.88 (3H, s, 3-OCH_3)；^{13}C-NMR (100 MHz, CD_3OD) δ: 168.1 (C-7), 152.8 (C-4), 148.7 (C-3), 125.2 (C-6), 122.5 (C-1), 116.2 (C-5), 113.4 (C-2), 98.2 (C-1′β), 94.0 (C-1′α), 77.9 (C-3′β), 76.2 (C-2′β), 75.5 (C-2′α), 74.8 (C-3α), 73.8 (C-5′β), 72.1 (C-4′α), 71.8 (C-4′β), 65.2 (C-6′α), 65.1 (C-6′β), 56.5 (3-OMe)。该化合物苷元与糖所连接的位置为葡萄糖的 6 位，因此葡萄糖在溶液中以 α 和 β 两种构型存在。以上数据与文献报道基本一致[4]，故鉴定化合物 **2** 为牡丹酚苷 A。

化合物 **3**：白色针状结晶（氯仿-甲醇），ESI-MS

m/*z*: 330，分子式为 $C_{14}H_{18}O_9$。^{1}H-NMR (400 MHz, CD_3OD) *δ*: 7.61 (1H, d, *J* = 1.8 Hz, H-2), 7.64 (1H, dd, *J* = 8.4, 1.8 Hz, H-6), 7.19 (1H, d, *J* = 8.4 Hz, H-2), 5.02 (1H, d, *J* = 7.4 Hz, H-1′), 3.88 (1H, dd, *J* = 9.7, 7.4 Hz, H-6′), 3.54 (1H, d, *J* = 9.7, 7.4 Hz, H-2′), 3.47 (1H, dd, *J* = 9.7, 7.4 Hz, H-3′), 3.46 (1H, ddd, *J* = 9.7, 7.4, 2.0 Hz, H-5′), 3.43 (1H, dd, *J* = 9.7, 7.4 Hz, H-4′)；^{13}C-NMR (100 MHz, CD_3OD) *δ*: 170.0 (C-7) 152.0 (C-4), 150.3 (C-3), 126.0 (C-1), 124.7 (C-6), 116.3 (C-5), 114.3 (C-2), 101.9 (C-1′β), 78.2 (C-3′), 77.8 (C-5′), 74.7 (C-2′), 71.2 (C-4′), 56.6 (3-OCH_3)。以上数据与文献报道基本一致[5]，故鉴定化合物 **3** 为 4-*O*-β-*D*-glucopyranosylvanillc acid。

化合物 **4**：白色粉末，ESI-MS *m*/*z*: 392，分子式为 $C_{19}H_{20}O_9$。^{1}H-NMR (400 MHz, CD_3OD) *δ*: 7.89 (2H, d, *J* = 8.7 Hz, H-2″, 6″), 6.92 (2H, d, *J* = 8.8 Hz, H-2, 6), 6.84 (2H, d, *J* = 8.7 Hz, H-3″, 5″), 6.59 (2H, d, *J* = 8.7 Hz, H-3, 5), 4.72 (1H, d, *J* = 7.2 Hz, H-1′), 4.65 (1H, dd, *J* = 10.1, 1.6 Hz, H-6′β), 4.33 (1H, d, *J* = 7.6 Hz, H-6′α), 3.69 (1H, ddd, *J* = 10.1, 8.7, 2.0 Hz, H-5′), 3.39 (2H, s, H-2′, 3′)；^{13}C-NMR (100 MHz, CD_3OD) *δ*: 167.9 (C-7′), 163.6 (C-4′), 153.8 (C-4), 152.2 (C-1), 132.9 (C-2″, 6″), 122.1 (C-1″), 119.4 (C-2, 6), 116.5 (C-3, 5), 116.2 (C-3″, 5″), 103.5 (C-1′), 77.9 (C-3′), 75.5 (C-5′), 74.9 (C-2′), 72.0 (C-4′), 65.0 (C-6′)。以上数据与文献报道基本一致[6]，故鉴定化合物 **4** 为 breynioside A。

化合物 **5**：黄色粉末，ESI-MS *m*/*z*: 330，分子式为 $C_{14}H_{18}O_9$。^{1}H-NMR (400 MHz, CD_3OD) *δ*: 7.65 (1H, dd, *J* = 8.0, 2.2 Hz, H-6), 7.64 (1H, d, *J* = 2.2 Hz, H-2), 6.90 (1H, d, *J* = 8.0 Hz, H-5), 4.89 (1H, d, *J* = 7.2 Hz, H-1′), 3.92 (3H, s, 3-OCH_3), 3.86 (1H, dd, *J* = 10.1, 1.6 Hz, H-6′β), 3.73 (1H, dd, *J* = 10.1, 1.6 Hz, H-6′α), 3.45 (4H, overlapped, H-2′ ～ 5′)；^{13}C-NMR (100 MHz, CD_3OD) *δ*: 166.8 (C-7), 153.4 (C-4), 148.8 (C-3), 125.7 (C-6), 121.9 (C-1), 116 (C-5), 114.1 (C-2), 101.9 (C-1′), 78.8 (C-3′), 78.1 (C-5′), 74.0 (C-2′), 71.1 (C-4′), 56.5 (3-OCH_3)。以上数据与文献报道基本一致[7]，故鉴定化合物 **5** 为 1-*O*-香草酰-β-*D*-葡萄糖苷。

化合物 **6**：淡黄色粉末，ESI-MS *m*/*z*: 452，分子式为 $C_{21}H_{24}O_{11}$。^{1}H-NMR (400 MHz, CD_3OD) *δ*: 7.58 (1H, dd, *J* = 8.3, 2.0 Hz, H-6″), 7.56 (1H, d, *J* = 1.9 Hz, H-2″), 6.87 (1H, d, *J* = 8.3 Hz, H-5″), 6.71 (1H, d, *J* = 2.0 Hz, H-2), 6.57 (1H, dd, *J* = 8.3, 2.0 Hz, H-6), 6.57 (1H, d, *J* = 2.0 Hz, H-2), 4.79 (1H, d, *J* = 7.4 Hz, H-1′), 4.73 (1H, dd, *J* = 11.8, 2.0 Hz, H-6′), 4.39 (1H, dd, *J* = 11.8, 2.0 Hz, 4′-OH), 3.77 (1H, dd, *J* = 10.1, 1.6 Hz, H-6′α), 3.65 (1H, dd, *J* = 10.1, 1.6 Hz, H-6′β), 3.85 (3H, s, 3′-OCH_3), 3.46～3.42 (3H, overlapped, H-2′ ～ 4′), 3.70 (3H, s, 3″-OCH_3)；^{13}C-NMR (100 MHz, CD_3OD) *δ*: 167.9 (C-6″), 152.5 (C-4″), 152.9 (C-1), 149.2 (C-3″), 148.7 (C-3), 143 (C-4), 125.3 (C-5″), 122.4 (C-1″), 116.0 (C-5), 115.9 (C-4″), 113.7 (C-2″), 110.0 (C-2), 104.9 (C-1′), 103.6 (C-6), 77.9 (C-3′), 75.6 (C-2′), 74.9 (C-4′), 72.5 (C-5′), 72.5 (C-5′), 56.5 (3-OCH_3), 56.3 (3″-OCH_3)。以上数据与文献报道基本一致[8]，故鉴定化合物 **6** 为 6′-*O*-vanilloyltachioside。

化合物 **7**：无色固体，ESI-MS *m*/*z*: 480，分子式为 $C_{21}H_{24}O_{11}$。^{1}H-NMR (400 MHz, CD_3OD) *δ*: 7.55 (1H, dd, *J* = 8.5, 1.9 Hz, H-6″), 7.52 (1H, d, *J* = 1.9 Hz, H-3), 7.51 (1H, d, *J* = 1.9 Hz, H-2″), 7.39 (1H, d, *J* = 8.5 Hz, H-5), 7.08 (1H, d, *J* = 7.4 Hz, H-6), 6.82 (1H, d, *J* = 7.4 Hz, H-5″), 5.01 (1H, d, *J* = 7.3 Hz, H-1′), 4.64 (1H, dd, *J* = 11.8, 1.8 Hz, H-6′), 4.28 (3H, s, 3-OCH_3), 3.85 (1H, s, 3″-OCH_3), 3.81 (1H, m, H-5′), 3.50 (1H, dd, *J* = 9.1, 9.1 Hz, H-6′), 3.40 (1H, dd, *J* = 11.8, 1.8 Hz, H-3′), 3.38 (1H, dd, *J* = 11.8, 1.8 Hz, H-4′)；^{13}C-NMR (100 MHz, CD_3OD) *δ*: 167.9 (C-7″), 153.1 (C-4″), 151.1 (C-1), 150.3 (C-2), 148.6 (C-3″), 127.9 (C-4), 125.2 (C-6″), 124.4 (C-5), 122.4 (C-1″), 116.6 (C-5″), 113.9 (C-2″), 102.0 (C-1′), 77.8 (C-3′), 75.8 (C-5′), 74.8 (C-2′), 72.5 (C-4′), 65.1 (C-6′), 56.7 (3-OCH_3), 56.6 (3″-OCH_3)。以上数据与文献报道基本一致[5]，故鉴定化合物 **7** 为 6′-*O*-vanilloylisotachioside。

化合物 **8**：淡黄色粉末，ESI-MS *m*/*z*: 356，分子式为 $C_{16}H_{20}O_9$。^{1}H-NMR (400 MHz, CD_3OD) *δ*: 7.62 (1H, d, *J* = 15.8 Hz, H-7), 7.18 (1H, s, H-2), 7.06 (1H, d, *J* = 8.0 Hz, H-6), 8.14 (1H, d, *J* = 8.0 Hz, H-5), 6.35 (1H, d, *J* = 11.5 Hz, H-8), 5.1 (1H, d, *J* = 3.6 Hz, H-1′α), 4.5 (1H, d, *J* = 7.9 Hz, H-1′β), 4.46 (1H, dd, *J* = 12.0, 1.8 Hz, H-6′α), 4.44 (1H, dd, *J* = 12.0, 6.2 Hz, H-6′β), 4.32 (1H, d, *J* = 7.3 Hz, H-1′β), 4.29 (1H, d, *J* = 3.6 Hz, H-6′α), 4.02 (1H, t, *J* = 9.1

Hz, H-4′β), 3.88 (3H, s, 3-OCH_3), 3.69 (1H, t, *J* = 9.1 Hz, H-3′α), 3.53 (1H, m, H-5′β), 3.38 (5H, overlapped, H-4′α, 2′α, 3′β, 5′α, 2′β)；^{13}C-NMR (100 MHz, CD_3OD) *δ*: 169.0 (C-9), 152.7 (C-4), 149.3 (C-3), 147.1 (C-7), 127.6 (C-1), 124.1 (C-6), 116.8 (C-5), 115.2 (C-8), 111.6 (C-2), 98.3 (C-1′β), 94.0 (C-1′α), 77.9 (C-3′β), 76.2 (C-2′β), 75.4 (C-5′), 74.7 (C-3′α), 73.7 (C-2′α), 72.0 (C-5′α), 71.7 (C-4′α), 70.77 (C-4′β), 64.8 (C-6′β), 64.8 (C-6′α), 56.4 (3-OCH_3)。以上数据与文献报道基本一致[9]，故鉴定化合物 **8** 为 6-*O*-feruloyl-*D*-glucopyranose。

化合物 **9**：无色固体，ESI-MS *m*/*z*: 352，分子式为 $C_{17}H_{20}O_8$。^{1}H-NMR (400 MHz, CD_3OD) *δ*: 7.71 (1H, d, *J* = 15.9 Hz, H-7), 7.46 (2H, d, *J* = 8.5 Hz, H-2, 6), 6.80 (2H, d, *J* = 12.8 Hz, H-3, 4), 6.42 (1H, d, *J* = 15.9 Hz, H-7), 5.10 (1H, d, *J* = 15.9 Hz, H-8), 5.02 (1H, s, 1′-OH), 4.78 (1H, dd, *J* = 8.7, 2.7 Hz, 5′-OH), 4.3 (1H, d, *J* = 5.6 Hz, 3′-OH), 4.28 (2H, m, H-3′, 4′), 4.22 (1H, d, *J* = 4.5 Hz, 4′-OH), 3.72 (3H, s, 7′-OCH_3), 2.14 (1H, dd, *J* = 12.5, 2.1 Hz, H-6′eq), 2.05 (2H, m, H-2′), 1.99 (1H, dd, *J* = 12.5, 2.1 Hz, H-6′ax)；^{13}C-NMR (100 MHz, CD_3OD) *δ*: 175.7 (C-7′), 168.9 (C-9), 161.4 (C-4), 146.7 (C-7), 131.1 (C-2, 6), 127.2 (C-1), 116.6 (C-3, 5), 115.3 (C-2), 78.5 (C-5′), 76.4 (C-1′), 68.9 (C-3′), 65.7 (C-4′), 52.8 (7′-OCH_3), 42.1 (C-6′), 38.4 (C-2′)。以上数据与文献报道基本一致[10]，故鉴定化合物 **9** 为 methyl-4-*O*-comaroylquinate。

化合物 **10**：无色固体，ESI-MS *m*/*z*: 338，分子式为 $C_{16}H_{18}O_8$。^{1}H-NMR (400 MHz, CD_3OD) *δ*: 7.69 (1H, d, *J* = 15.9 Hz, H-7), 7.50 (2H, d, *J* = 8.5 Hz, H-2, 6), 6.81 (2H, d, *J* = 12.8 Hz, H-3, 5), 6.33 (1H, d, *J* = 15.9 Hz, H-8), 4.32 (1H, m, H-4′), 4.3 (1H, d, *J* = 5.6 Hz, 3′-OH), 4.28 (2H, m, H-3′, 5′)；^{13}C-NMR (100 MHz, CD_3OD) *δ*: 179.2 (C-7′), 168.3 (C-9), 161.2 (C-4), 147.4 (C-7), 131.4 (C-2, 6), 127.2 (C-1), 116.6 (C-3, 5), 114.7 (C-8), 77.8 (C-5′), 75.3 (C-1′), 70.2 (C-3′), 64.8 (C-4′), 37.8 (C-6′), 36.8 (C-2′)。以上数据与文献报道基本一致[11]，故鉴定化合物 **10** 为 5-*p*-*cis*-coumaroylquinic acid。

化合物 **11**：白色粉末，ESI-MS *m*/*z*: 324，分子式为 $C_{16}H_{20}O_7$。^{1}H-NMR (400 MHz, CD_3OD) *δ*: 7.98 (1H, d, *J* = 15.9 Hz, H-8), 7.71 (H, d, *J* = 8.5 Hz, H-5), 7.64 (1H, t, *J* = 7.2 Hz, H-6), 7.49 (1H, t, *J* = 7.5 Hz, H-7), 5.10 (1H, d, *J* = 2.1 Hz, H-4), 4.36 (1H, d, *J* = 7.9 Hz, H-1′), 3.94 (1H, dd, *J* = 8.7, 2.7 Hz, H-6′), 3.71 (1H, d, *J* = 5.6 Hz, H-6′), 3.22～3.33 (3H, overlapped, H-3′～5′), 3.04 (1H, m, H-2ax), 2.60 (1H, m, H-2eq), 2.44 (1H, m, H-3ax), 2.36 (1H, m, H-3eq)；^{13}C-NMR (100 MHz, CD_3OD) *δ*: 200.2 (C-1), 143.7 (C-10), 134.8 (C-6), 132.9 (C-9), 130.2 (C-5), 129.8 (C-7), 127.9 (C-8), 103.1, C-1′), 78.1 (C-3′), 78.0 (C-5′), 75.2 (C-4), 74.8 (C-2′), 71.7 (C-4′), 62.9 (C-6′), 35.3 (C-2′), 31.4 (C-3′)。以上数据与文献报道基本一致[12]，故鉴定化合物 **11** 为胡桃苷 A。

化合物 **12**：白色粉末，ESI-MS *m*/*z*: 356，分子式为 $C_{16}H_{20}O_9$。^{1}H-NMR (400 MHz, CD_3OD) *δ*: 7.50 (1H, d, *J* = 9.1 Hz, H-6), 6.84 (2H, d, *J* = 9.1 Hz, H-7), 4.80 (1H, t, *J* = 3.2 Hz, H-4), 4.77 (1H, d, *J* = 7.9 Hz, H-1′), 3.85 (1H, dd, *J* = 8.7, 2.8 Hz, H-6′), 3.67 (1H, d, *J* = 5.6 Hz, H-6′), 3.50 (1H, overlapped, H-3′), 3.43 (1H, d, *J* = 5.6 Hz, H-4′), 3.03 (1H, m, H-2ax), 3.52 (1H, m, H-2eq), 2.22 (1H, m, H-3ax), 2.18 (1H, m, H-3eq)；^{13}C-NMR (100 MHz, CD_3OD) *δ*: 206.5 (C-1), 159.1 (C-10), 134.8 (C-5, C-10), 128.5 (C-6), 119.0 (C-7), 114.8 (C-9), 104.7, (C-1′), 78.4 (C-5′), 78.0 (C-3′), 75.4 (C-2′), 71.4 (C-4′), 62.6 (C-6′), 61.4 (C-4), 33.6 (C-2′), 30.3 (C-3′)。以上数据与文献报道基本一致[12]，故鉴定化合物 **12** 为胡桃苷 E。

化合物 **13**：白色粉末，ESI-MS *m*/*z*: 386，分子式为 $C_{19}H_{30}O_8$。^{1}H-NMR (400 MHz, CD_3OD) *δ*: 5.83～5.91 (3H, overlapped, H-4, 7, 8), 4.43 (1H, m, H-9), 4.35 (1H, d, *J* = 7.9 Hz, H-1′), 3.84 (1H, dd, *J* = 8.7, 2.6 Hz, H-6′), 3.62 (1H, d, *J* = 5.6 Hz, H-6′), 3.35 (1H, overlapped, H-3′), 3.32 (1H, d, *J* = 5.6 Hz, H-4′), 3.25 (1H, d, *J* = 5.6 Hz, H-5′), 3.19 (1H, d, *J* = 5.61 Hz, H-2′), 1.94 (3H, s, 13-CH_3), 1.50 (3H, s, 11-CH_3), 1.31 (3H, s, 10-CH_3), 1.05 (3H, s, 12-CH_3)；^{13}C-NMR (100 MHz, CD_3OD) *δ*: 201.1 (C-3), 167.2 (C-5), 135.3 (C-8), 131.5 (C-7), 127.1 (C-4), 102.7 (C-1′), 80 (C-6), 78.1 (C-5′), 78.0 (C-3′), 77.0 (C-9), 75.2 (C-2′), 71.6 (C-4′), 62.8 (C-6′), 50.7 (C-2), 42.4 (C-1), 24.7 (C-12), 21.2 (C-12), 19.5 (C-12)。以上数据与文献报道基本一致[13]，故鉴定化合物 **13** 为长春花糖苷。

化合物 **14**：白色粉末，ESI-MS *m*/*z*: 304，分子

式为 $C_{15}H_{12}O_7$。^{1}H-NMR (400 MHz, CD_3OD) δ: 11.73 (1H, Ph-OH), 6.87 (1H, d, J = 8.2 Hz, H-6′), 6.82 (1H, d, J = 8.2 Hz, H-5′), 5.92 (1H, d, J = 2.0 Hz, H-8), 5.85 (3H, d, J = 8.1 Hz, H-6), 5.75 (1H, d, J = 5.6 Hz, 3-OH), 4.94 (1H, overlapped, H-2), 4.51 (1H, d, J = 11.5 Hz, H-3)；^{13}C-NMR (100 MHz, CD_3OD) δ: 198.4 (C-4), 168.7 (C-7), 165.2 (C-5), 164.5 (C-9), 147.1 (C-4′), 146.3 (C-3′), 129.9 (C-1′), 120.9 (C-6′), 116.1 (C-2′), 115.9 (C-5′), 101.8 (C-10), 97.3 (C-6), 96.3 (C-8), 85.1 (C-2), 73.68 (C-3)。以上数据与文献报道基本一致[14]，故鉴定化合物 **14** 为二氢槲皮素。

化合物 **15**：白色粉末，ESI-MS m/z: 444，分子式为 $C_{21}H_{32}O_{10}$。^{1}H-NMR (400 MHz, CD_3OD) δ: 7.95 (1H, d, J = 16.0 Hz, H-4), 6.45 (1H, d, J = 16.0 Hz, H-5), 6.58 (1H, s, H-2), 4.37 (1H, overlapped, H-1″), 4.24 (1H, m, H-3′), 3.97 (1H, d, J = 11.8 Hz, H-6″), 3.79 (1H, dd, J = 13.9, 6.6 Hz, H-3″), 3.75 (1H, m, H-7′), 3.29 (3H, overlapped, H-1′, 4″, 5″), 3.79 (1H, dd, J = 13.9, 6.6 Hz, H-3″), 3.10 (1H, t, J = 8.2 Hz, H-2″), 2.17 (1H, m, H-4′), 2.05 (3H, s, 6-CH_3), 1.90 (1H, m, H-2′), 1.18 (3H, s, 9′-CH_3), 0.95 (3H, s, 10′-CH_3)；^{13}C-NMR (100 MHz, CD_3OD) δ: 148.3 (C-3), 133.6 (C-5), 132.3 (C-4), 122.0 (C-2), 103.1 (C-1″), 87.7 (C-5′), 83.2 (C-8′), 78.1 (C-5″), 78.0 (C-3″), 77.1 (C-7′), 75.1 (C-7′), 74.0 (C-3′), 71.7 (C-4″), 62.8 (C-6″), 49.3 (C-1′), 42.9 (C-4′), 42.1 (C-2′), 21.1 (6-CH_3), 19.7 (9′-CH_3), 16.3 (10′-CH_3)。以上数据与文献报道基本一致[15]，故鉴定化合物 **15** 为二氢红花菜豆酸-4′-*O*-β-*D*-吡喃葡萄糖苷。

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