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鸡血藤中的酚酸类化合物

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摘要: 为了解鸡血藤(*Spatholobus suberectus* Dunn)的化学成分,从鸡血藤的 95% 乙醇提取物中分离出 15 个酚酸类单体成分,经波谱学分析分别鉴定为:没食子酸 (**1**)、tachioside (**2**)、isotachioside (**3**)、canthoside D (**4**)、3,5-二甲氧基-4-羟基苯基-1-*O*-β-D-吡喃葡萄糖苷 (**5**)、2,6-二甲氧基-4-羟基-苯酚-1-*O*-β-D-吡喃葡萄糖苷 (**6**)、4-羟甲基-2,6-二甲氧基苯基-β-D-吡喃葡萄糖苷 (**7**)、丁香酸葡萄糖苷 (**8**)、3-甲氧基苯乙醇-4-O-β-D-葡吡喃糖苷 (**9**)、2-(4-hydroxy-3,5-dimethoxyphenyl)ethyl-β-D-glucopyranoside (**10**)、4,6-二羟基-2-*O*-(β-D-吡喃葡萄糖苷)苯乙酮 (**11**)、松香 (**12**)、顺式紫丁香苷 (**13**)、(–)-(7*R*,8*S*)-guaiacylglycerol 8-*O*-β-D-glucopyranoside (**14**)和 l-*threo*-guaiacylglycerol-8-*O*-β-glucopyranoside (**15**)。其中 , 化合物 **2** ~ **8** 和 **10** ~ **15** 为首次从密花豆属植物中分离得到。

关键词: 鸡血藤; 酚酸类成分; 结构鉴定
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Phenolic Constituents from the Stems of *Spatholobus suberectus* Dunn

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Abstract: In order to understand the chemical constituents of *Spatholobus suberectus* Dunn, 15 phenolic constituents were obtained from 95% EtOH extract of *S. suberectus* stems by chromatographic separation methods. On the basis of spectral data, they were identified as gallic acid (**1**), tachioside (**2**), isotachioside (**3**), canthoside D (**4**), koaburaside (**5**), 2,6-dimethoxy-4-hydroxyphenol-1-*O*-β-D-glucopyranoside (**6**), 4-hydroxymethyl-2,6-dimethoxyphenyl-β-D-glucopyranoside (**7**), glucosyringic acid (**8**), 3-methoxyphenethyl alcohol-4-*O*-β-D-glucopyranoside (**9**), 2-(4-hydroxy-3,5-dimethoxyphenyl)ethyl-β-D-glucopyranoside (**10**), 4,6-dihydroxy-2-*O*-(β-D-glucopyranosyl)-acetophenone (**11**), rosin (**12**), *cis*-syringin (**13**), (–)-(7*R*,8*S*)-guaiacylglycerol 8-*O*-β-D-glucopyranoside (**14**), and l-*threo*-guaiacylglycerol-8-*O*-β-glucopyranoside (**15**). Among them, compounds **2** – **8** and **10** – **15** were isolated from the *Spatholobus* genus at first time.

Key words: *Spatholobus suberectus*; Phenolic constituent; Structure identification

鸡血藤为豆科(Leguminosae)密花豆属植物密花豆(*Spatholobus suberectus* Dunn)的干燥藤茎,又名大血藤、血藤、血风藤、三叶鸡血藤,广泛生长于我国南方地区,是补血活血的传统中药,具有行血补血,调经,舒经活络的功效;主治月经不调、血虚萎黄、麻木瘫痪、风湿痹痛等症[1]。主要含有黄酮、三萜、甾醇及酚类等化学成分。现代药理学证明,鸡血藤具有促进造血功能、抗肿瘤、抗病毒、免疫调节、对酪氨酸酶双向调节、抗炎、抗氧化、镇静催眠等药理作用[2–5]。在对鸡血藤的化学成分进行研

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究的过程中,我们利用色谱法与光谱法相结合的方法,从其95%乙醇提取物中分离鉴定出了15个酚酸类化合物。本文主要对其核磁共振波谱数据进行报道,为鸡血藤的活性成分研究提供科学依据。

1 材料和方法

1.1 材料

鸡血藤于2012年3月购自河北省安国药材市场,由天津中医药大学中药标本馆李天祥副教授鉴定为密花豆(*Spatholobus suberectus* Dunn)的干燥藤茎。植物凭证标本(No. 20120320)存放于天津中医药大学中医药研究院。

1.2 仪器

Bruker 500 MHz NMR超导核磁共振波谱仪(TMS为内标,瑞士Bruker公司,Avance Ⅲ 500MR);安捷伦6500系列四级杆-飞行时间质谱仪;分析型高效液相色谱仪[Waters 600E (美国Waters),检测器:Waters 2487 (254 nm、230 nm双波长检测)、泵:600 Pump、控制器:600 controller、在线脱气装置:in-line Degasser AF)];制备型高效液相色谱仪[岛津(日本),LC-8A;SPD-20A (254 nm、230 nm双波长检测);CBM-20A;CTO-20A]。柱层析硅胶为青岛海洋化工厂生产的200 ~ 300目硅胶。薄层层析硅胶预板,高效硅胶GF_{254}为天津思利达科技有限公司生产;反相ODS, Chromatorex ODS MB 100 ~ 40/75 (Fuji Silisia Chemical, Ltd., Japan, 40 ~ 75 μM);Sephadex LH-20 (Ge Healthcare Bio-Sciences AB, made in Sweden);D101大孔吸附树脂是天津市海光化工有限公司生产(净品级);HPLC用分析柱以及制备柱型号分别为Cosmosil 5C18-MS-II (Nacalai Tesque Inc., 250 mm × 4.6 mm)以及(250 mm × 20 mm)。色谱纯及分析纯试剂购自天津市康科德科技有限公司。

1.3 提取和分离

取密花豆干燥藤茎8.0 kg, 用10倍量的95% EtOH溶液加热回流提取3次,减压回收溶剂,得浸膏860 g。浸膏经EtOAc-H_2O (1∶1, V/V,下同)萃取3次,得EtOAc和H_2O萃取物。H_2O萃取物经D101大孔吸附树脂处理(H_2O → 70% EtOH → 95% EtOH), 分别得到H_2O、70% EtOH和95% EtOH洗脱物。

取EtOAc萃取物72 g进行硅胶柱层析[$CHCl_3$-MeOH (100∶0 → 100∶3 → 100∶5 → 100∶7) → $CHCl_3$-MeOH-H_2O (10∶3∶1 → 6∶4∶1, 下层) → MeOH],得到14个组分(Fr. 1 ~ Fr. 14)。组分Fr. 10 (2.0 g)经ODS柱层析[MeOH-H_2O (10∶90 → 20∶80 → 30∶70 → 40∶60 → 50∶50 → 60∶40 → 70∶30 → 80∶20 → 90∶10 → 100∶0)], 得到6个组分(Fr. 10-1 ~ Fr. 10-6)。组分Fr. 10-1 (200.0 mg)经PHPLC分离制备[MeOH-H_2O (8∶92)], 得到化合物**1** (50.4 mg)。

取大孔吸附树脂70% EtOH洗脱物70 g, 经硅胶柱层析[$CHCl_3$-MeOH (100∶0 → 100∶5) → $CHCl_3$-MeOH-H_2O (20∶3∶1 → 10∶3∶1 → 7∶3∶1, 下层) → MeOH], 得到11个组分(Fr. 70-1 ~ Fr. 70-11)。组分Fr. 70-5 (3.0 g)经PHPLC分离制备[MeOH-H_2O (25∶75 → 35∶65 → 50∶50)], 共得到25个组分(Fr. 70-5-1 ~ Fr. 70-5-25)。组分Fr. 70-5-2 (101.1 mg)经PHPLC分离制备[MeOH-H_2O (5∶95)], 得到化合物**2** (17.0 mg)、**3** (22.8 mg)和**5** (40.2 mg)。组分Fr. 70-5-3 (251.3 mg)经PHPLC分离制备[MeOH-H_2O (10∶90)], 得到化合物**6** (96.1 mg)和**7** (45.3 mg)。组分Fr. 70-5-5 (101.1 mg)经PHPLC分离制备[MeOH-H_2O (12∶88)], 得到化合物**8** (17.0 mg)和**9** (22.8 mg)。组分Fr. 70-5-9 (76.4 mg)和组分Fr. 70-5-10 (21.5 mg)经PHPLC分离制备[MeOH-H_2O (20∶80)], 分别得到化合物**10** (31.1 mg)和**11** (8.5 mg)。组分Fr. 70-5-14 (436.6 mg)经PHPLC分离制备[CH_3CN-H_2O (12∶88)], 得到化合物**13** (7.1 mg)。组分Fr. 70-5-21 (73.2 mg)经PHPLC分离制备[MeOH-H_2O (35∶65)], 得到化合物**12** (16.7 mg)。组分Fr. 70-6 (2.0 g)经ODS柱层析[MeOH-H_2O (10∶90 → 20∶80 → 30∶70 → 40∶60 → 50∶50 → 60∶40 → 70∶30 → 100∶0)], 得到9个组分(Fr. 70-6-1 ~ Fr. 70-6-9)。组分Fr. 70-6-1 (200.0 mg)经PHPLC分离制备[MeOH-H_2O (10∶90)], 得到化合物**4** (17.9 mg)、**14** (5.3 mg)和**15** (9.8 mg)。组分Fr. 70-6-2 (388.3 mg)经PHPLC分离制备[MeOH-H_2O (13∶87)], 得到化合物**9** (112.3 mg)。

1.4 结构鉴定

化合物1 白色粉末。Q-TOF-ESI-MS *m/z*: 169.0147 [M – H]$^-$, 分子式为$C_7H_6O_5$ (calcd for $C_7H_5O_5$, 169.0142)。^{1}H NMR (CD_3OD, 500 MHz): δ 7.10 (2H,

s, H-2,6)；^{13}C NMR (CD_3OD, 125 MHz)：δ 122.2 (C-1), 110.4 (C-2, 6), 146.4 (C-3, 5), 139.6 (C-4), 170.6 (C-7)。以上波谱数据与文献[6]报道基本一致，鉴定化合物 **1** 为没食子酸(gallic acid)。

化合物 2　白色粉末。Q-TOF-ESI-MS *m/z*：301.0933 [M – H]$^-$，分子式为 $C_{13}H_{18}O_8$ (calcd for $C_{13}H_{17}O_8$, 301.0929)。^{1}H NMR (CD_3OD, 500 MHz)：δ 6.80 (1H, d, *J* = 2.5 Hz, H-3), 6.58 (1H, dd, *J* = 2.5, 9.0 Hz, H-5), 6.69 (1H, d, *J* = 9.0 Hz, H-6), 4.74 (1H, d, *J* = 7.5 Hz, H-1′), 3.43 (1H, dd, *J* = 7.5, 9.0 Hz, H-2′), 3.44 (1H, dd, *J* = 9.0, 9.0 Hz, H-3′), 3.35 (1H, dd, *J* = 8.0, 9.0 Hz, H-4′), 3.38 (1H, m, H-5′), [3.68 (1H, dd, *J* = 5.5, 12.0 Hz), 3.89 (1H, dd, *J* = 2.0, 12.0 Hz), H_2-6′], 3.82 (3H, s, 3-OCH_3)；^{13}C NMR (CD_3OD, 125 MHz)：δ 143.0 (C-1), 149.3 (C-2), 103.84 (C-3), 152.9 (C-4), 110.0 (C-5), 116.1 (C-6), 103.81 (C-1′), 75.0 (C-2′), 78.1 (C-3′), 71.6 (C-4′), 78.2 (C-5′), 62.7 (C-6′), 56.4 (3-OCH_3)。以上波谱数据与文献[7]报道基本一致，鉴定化合物 **2** 为 tachioside。

化合物 3　白色粉末。Q-TOF-ESI-MS *m/z*：301.0927 [M – H]$^-$，分子式为 $C_{13}H_{18}O_8$ (calcd for $C_{13}H_{17}O_8$, 301.0929)。^{1}H NMR (CD_3OD, 500 MHz)：δ 6.47 (1H, d, *J* = 2.5 Hz, H-3), 6.30 (1H, dd, *J* = 2.5, 8.5 Hz, H-6), 7.01 (1H, d, *J* = 8.5 Hz, H-5), 4.70 (1H, d, *J* = 8.0 Hz, H-1′), 3.44 (1H, m, overlapped, H-2′), 3.44 (1H, m, overlapped, H-3′), 3.38 (1H, dd, *J* = 8.0, 8.0 Hz, H-4′), 3.30 (1H, m, overlapped, H-5′), [3.69 (1H, dd, *J* = 5.5, 12.0 Hz), 3.86 (1H, dd, *J* = 2.0, 12.0 Hz), H_2-6′], 3.81 (3H, s, 3-OCH_3)；^{13}C NMR (CD_3OD, 125 MHz)：δ 141.1 (C-1), 152.0 (C-2), 101.9 (C-3), 154.9 (C-4), 107.7 (C-5), 120.5 (C-6), 104.3 (C-1′), 75.1 (C-2′), 77.9 (C-3′), 71.4 (C-4′), 78.1 (C-5′), 62.7 (C-6′), 56.6 (2-OCH_3)。以上波谱数据与文献[8]报道基本一致，鉴定化合物 **3** 为 isotachioside。

化合物 4　白色粉末。Q-TOF-ESI-MS *m/z*：433.1366 [M – H]$^-$，分子式为 $C_{18}H_{26}O_{12}$ (calcd for $C_{18}H_{25}O_{12}$, 433.1351)。^{1}H NMR (CD_3OD, 500 MHz)：δ 6.76 (1H, d, *J* = 2.5 Hz, H-3), 6.60 (1H, dd, *J* = 2.5, 8.5 Hz, H-5), 6.72 (1H, d, *J* = 8.5 Hz, H-6), 4.72 (1H, d, *J* = 7.5 Hz, H-1′), 3.44 (1H, dd, *J* = 7.5, 8.0 Hz, H-2′), 3.46 (1H, dd, *J* = 8.0, 9.0 Hz, H-3′), 3.35 (1H, dd, *J* = 9.0, 9.0 Hz, H-4′), 3.54 (1H, m, H-5′), [3.62 (1H, dd, *J* = 6.5, 11.5 Hz), 4.01 (1H, dd, *J* = 1.5, 11.5 Hz), H_2-6′], 4.99 (1H, d, *J* = 2.0 Hz, H-1″), 3.91 (1H, d, *J* = 2.0 Hz, H-2″), [3.76 (1H, d, *J* = 10.0 Hz), 3.96 (1H, d, *J* = 10.0 Hz), H-4″], 3.58 (2H, s, H_2-5‴), 3.82 (3H, s, 2-OCH_3)；^{13}C NMR (CD_3OD, 125 MHz)：δ 152.7 (C-1), 149.2 (C-2), 103.7 (C-3), 143.0 (C-4), 110.1 (C-5), 116.1 (C-6), 104.0 (C-1′), 74.9 (C-2′), 77.9 (C-3′), 71.6 (C-4′), 76.8 (C-5′), 68.7 (C-6′), 110.9 (C-1″), 78.0 (C-2″), 80.5 (C-3″), 75.0 (C-4″), 65.6 (C-5″), 56.5 (2-OCH_3)。以上波谱数据与文献[9]报道基本一致，鉴定化合物 4 为 canthoside D。

化合物 5　白色粉末。Q-TOF-ESI-MS *m/z*：355.1010 [M + Na]$^+$，分子式为 $C_6H_5NO_2$ (calcd for $C_6H_5NO_2Na$, 355.1)。^{1}H NMR (DMSO-d_6, 500 MHz)：δ 6.38 (2H, s, H-2,6), 4.68 (1H, d, *J* = 7.5 Hz, H-1′), 3.19 (1H, dt, *J* = 5.0, 8.0 Hz, H-2′), 3.24 (1H, m, overlapped, H-3′), 3.10 (1H, dt, *J* = 5.0, 9.0 Hz, H-4′), 3.29 (1H, m, overlapped, H-5′), [3.42 (1H, dd, *J* = 6.0, 12.0 Hz), 3.77 (1H, m, overlapped), H_2-6′], 3.71 (6H, s, 3,5-OCH_3)；^{13}C NMR (DMSO-d_6, 125 MHz)：δ 150.2 (C-1), 94.9 (C-2,6), 148.0 (C-3,5), 130.3 (C-4), 101.6 (C-1′), 73.2 (C-2′), 76.7 (C-3′), 70.0 (C-4′), 77.1 (C-5′), 60.8 (C-6′), 55.7 (3,5-OCH_3)。以上波谱数据与文献[10]报道基本一致，故鉴定化合物 **5** 为 3,5-二甲氧基-4-羟基苯基-1-*O*-β-D-吡喃葡萄糖苷(koaburaside)。

化合物 6　白色粉末。Q-TOF-ESI-MS *m/z*：355.1012 [M + Na]$^+$，分子式为 $C_{13}H_{18}O_8$ (calcd for $C_{13}H_{18}O_8Na$, 355.1)。^{1}H NMR (CD_3OD, 500 MHz)：δ 6.13 (2H, s, H-3,5), 4.66 (1H, d, *J* = 7.5 Hz, H-1′), 3.45 (1H, dd, *J* = 7.5, 8.0 Hz, H-2′), 3.39 (1H, m, overlapped, H-3′), 3.39 (1H, m, overlapped, H-4′), 3.20 (1H, m, H-5′), [3.67 (1H, dd, *J* = 5.0, 12.0 Hz), 3.79 (1H, dd, *J* = 2.5, 12.0 Hz), H_2-6′], 3.79 (3H, s, 2,6-OCH_3)；^{13}C NMR (CD_3OD, 125 MHz)：δ 129.7 (C-1), 154.8 (C-2,6), 94.6 (C-3,5), 156.0 (C-4), 106.3 (C-1′), 75.8 (C-2′), 77.8 (C-3′), 71.4 (C-4′), 78.3 (C-5′), 62.7 (C-6′), 56.8 (2,6-OCH_3)。以上波谱数据与文献[11]报道基本一致，鉴定化合物 **6** 为 2,6-二甲氧基-4-羟基-苯酚-1-*O*-β-D-吡喃葡萄糖苷(2,6-dimethoxy-4-hydroxyphenol-1-*O*-β-D-glucopyranoside)。

化合物 7　白色粉末。Q-TOF-ESI-MS *m/z*：381.0962 [M + Cl]$^-$，分子式为 $C_{15}H_{22}O_9$ (calcd for $C_{15}H_{22}O_9Cl$, 381.0958)。^{1}H NMR (CD_3OD, 500 MHz)：

δ 6.70 (2H, s, H-3,5), 4.54 (2H, s, H-7), 4.83 (1H, d, *J* = 7.5 Hz, H-1′), 3.48 (1H, dd, *J* = 7.5, 8.0 Hz, H-2′), 3.41 (1H, dd, *J* = 8.0, 8.5 Hz, H-3′), 3.43 (1H, dd, *J* = 8.5, 8.5 Hz, H-4′), 3.20 (1H, m, overlapped, H-5′), [3.66 (1H, dd, *J* = 5.0, 12.0 Hz), 3.76 (1H, dd, *J* = 2.0, 12.0 Hz), H_2-6′], 3.84 (6H, s, 2,6-OCH_3)；^{13}C NMR (CD_3OD, 125 MHz)：δ 135.3 (C-1), 154.2 (C-2,6), 105.6 (C-3,5), 139.7 (C-4), 65.1 (C-7), 105.5 (C-1′), 75.7 (C-2′), 77.8 (C-3′), 71.3 (C-4′), 78.3 (C-5′), 62.6 (C-6′), 57.0 (2,6-OCH_3)。以上波谱数据与文献[12]报道基本一致，鉴定化合物 **7** 为 4-羟甲基-2,6-二甲氧基苯基-β-D-吡喃葡萄糖苷(4-hydroxymethyl-2,6-dimethoxyphenyl-β-D-glucopyranoside)。

化合物 8 白色粉末。Q-TOF-ESI-MS *m/z*：359.0989 $[M - H]^-$，分子式为 $C_{15}H_{20}O_{10}$ (calcd for $C_{15}H_{19}O_{10}$, 359.0984)。^{1}H NMR (DMSO-d_6, 500 MHz)：δ 7.24 (2H, s, H-2,6), 5.13 (1H, d, *J* = 7.0 Hz, H-1′), 3.24 (1H, dd, *J* = 7.0, 8.5 Hz, H-2′), 3.22 (1H, dd, *J* = 8.5, 8.5 Hz, H-3′), 3.15 (1H, dd, *J* = 8.5, 8.5 Hz, H-4′), 3.08 (1H, m, overlapped, H-5′), [3.41 (1H, dd, *J* = 5.5, 11.5 Hz), 3.60 (1H, dd, *J* = 1.5, 11.5 Hz), H_2-6′], 3.61 (6H, s, 2,6-OCH_3)；^{13}C NMR (DMSO-d_6, 125 MHz)：δ 125.8 (C-1), 107.2 (C-2,6), 152.1 (C-3,5), 138.0 (C-4), 101.9 (C-1′), 74.1 (C-2′), 76.5 (C-3′), 69.8 (C-4′), 77.3 (C-5′), 60.7 (C-6′), 56.3 (3,5-OCH_3), 166.9 (1-COOH)。以上波谱数据与文献[13]报道基本一致，鉴定化合物 8 为丁香酸葡萄糖苷(glucosyringic acid)。

化合物 9 白色粉末。Q-TOF-ESI-MS *m/z*：353.1215 $[M + Na]^+$，分子式为 $C_{15}H_{22}O_8$ (calcd for $C_{15}H_{22}O_8Na$, 353.1207)。^{1}H NMR (CD_3OD, 500 MHz)：δ 6.88 (1H, d, *J* = 2.0 Hz, H-2), 7.08 (1H, d, *J* = 8.5 Hz, H-5), 6.76 (1H, dd, *J* = 2.0, 8.5 Hz, H-6), 2.76 (2H, t, *J* = 7.0 Hz, H-7), 3.73 (2H, t, *J* = 7.0 Hz, H-8), 4.85 (1H, d, *J* = 7.5 Hz, H-1′), 3.48 (1H, dd, *J* = 7.5, 9.0 Hz, H-2′), 3.45 (1H, dd, *J* = 9.0, 9.5 Hz, H-3′), 3.39 (1H, dd, *J* = 9.5, 9.5 Hz, H-4′), 3.38 (1H, m, H-5′), [3.68 (1H, dd, *J* = 5.0, 12.0 Hz), 3.86 (1H, dd, *J* = 2.0, 12.0 Hz), H_2-6′], 3.85 (3H, s, 3-OCH_3)；^{13}C NMR (CD_3OD, 125 MHz)：δ 135.6 (C-1), 114.7 (C-2), 150.8 (C-3), 146.5 (C-4), 118.4 (C-5), 122.6 (C-6), 39.9 (C-7), 64.3 (C-8), 103.2 (C-1′), 75.0 (C-2′), 77.9 (C-3′), 71.4 (C-4′), 78.2 (C-5′), 62.6 (C-6′), 56.8 (3-OCH_3)。以上波谱数据与文献[14]报道基本一致，鉴定化合物 **9** 为 3-甲氧基苯乙醇-4-*O*-β-D-葡吡喃糖苷(3-methoxyphenethyl alcohol-4-*O*-β-D-glucopyranoside)。

化合物 10 白色粉末。Q-TOF-ESI-MS *m/z*：359.1349 $[M - H]^-$，分子式为 $C_{16}H_{24}O_9$ (calcd for $C_{16}H_{23}O_9$, 359.1348)。^{1}H NMR (CD_3OD, 500 MHz)：δ 6.55 (2H, s, H-2,6), 4.30 (1H, d, *J* = 7.5 Hz, H-1′), 3.19 (1H, dd, *J* = 7.5, 8.5 Hz, H-2′), 3.36 (1H, dd, *J* = 8.5, 8.5 Hz, H-3′), 3.28 (1H, dd, *J* = 8.0, 8.5 Hz, H-4′), 3.27 (1H, m, H-5′), [3.66 (1H, dd, *J* = 5.0, 11.5 Hz), 3.86 (1H, dd, *J* = 1.5, 11.5 Hz), H_2-6′], 3.82 (6H, s, 3,5-OCH_3)；^{13}C NMR (CD_3OD, 125 MHz)：δ 134.9 (C-1), 107.3 (C-2,6), 149.2 (C-3,5), 131.0 (C-4), 37.2 (C-7), 71.9 (C-8), 104.3 (C-1′), 75.2 (C-2′), 78.2 (C-3′), 71.7 (C-4′), 78.0 (C-5′), 62.8 (C-6′), 56.8 (3,5-OCH_3)。以上波谱数据与文献[15]报道基本一致，鉴定化合物 **10** 为 2-(4-hydroxy-3,5-dimethoxyphenyl) ethyl-β-D-glucopyranoside。

化合物 11 白色粉末。Q-TOF-ESI-MS *m/z*：331.0982 $[M + H]^+$，分子式为 $C_{14}H_{18}O_9$ (calcd for $C_{14}H_{19}O_9$, 331.0956)。^{1}H NMR (CD_3OD, 500 MHz)：δ 6.18 (1H, br. s, H-3), 5.94 (1H, d, *J* = 7.5 Hz, H-5), 5.02 (1H, d, *J* = 7.5 Hz, H-1′), 3.54 (1H, dd, *J* = 8.5, 7.5 Hz, H-2′), 3.47 (1H, dd, *J* = 8.5, 8.5 Hz, H-3′), 3.43 (1H, dd, *J* = 8.5, 8.5 Hz, H-4′), 3.46 (1H, m, H-5′), [3.72 (1H, dd, *J* = 5.0, 12.0 Hz), 3.91 (1H, dd, *J* = 1.5, 12.0 Hz), H_2-6′], 2.69 (3H, s, H-8)；^{13}C NMR (CD_3OD, 125 MHz)：δ 106.8 (C-1), 162.7 (C-2), 95.5 (C-3), 166.4 (C-4), 98.2 (C-5), 167.7 (C-6), 204.9 (C-7), 33.5 (C-8), 102.0 (C-1′), 74.8 (C-2′), 78.5 (C-3′), 71.1 (C-4′), 78.4 (C-5′), 62.4 (C-6′)。以上波谱数据与文献[16]报道基本一致，鉴定化合物 **11** 为 4,6-二羟基-2-*O*-(β-D-吡喃葡萄糖苷)苯乙酮(4,6-dihydroxy-2-*O*-(β-D-glucopyranosyl)-acetophenone)。

化合物 12 白色粉末。Q-TOF-ESI-MS *m/z*：331.0962 $[M + Cl]^-$，分子式为 $C_{15}H_{20}O_6$ (calcd for $C_{15}H_{20}O_9Cl$, 331.0954)。^{1}H NMR (CD_3OD, 500 MHz)：δ 7.41(2H, br. d, *ca*. *J* = 8 Hz, H-2,6), 7.30 (2H, t like, *J* = 8 Hz, H-3,5), 7.21 (1H, br. t, *ca*. *J* = 8 Hz, H-4), 6.68 (1H, br. d, *ca*. *J* = 16 Hz, H-7), 6.37 (1H, dt, *J* = 6.5, 16.0 Hz, H-8), [4.38 (1H, ddd, *J* = 1.5, 6.5, 12.5 Hz), 4.53 (1H, ddd, *J* = 1.5, 6.5, 12.5 Hz), H_2-9], 4.37 (1H, d, *J* = 8.0 Hz, H-1′), 3.23 (1H, dd, *J* = 8.0、9.0 Hz,

H-2′), 3.36 (1H, dd, *J* = 9.0, 9.0 Hz, H-3′), 3.29 (1H, m, overlapped, H-4′), 3.28 (1H, m, overlapped, H-5′), [3.68 (1H, dd, *J* = 5.5, 12.0 Hz), 3.88 (1H, dd, *J* = 2.0, 12.0 Hz), H_2-6′]；^{13}C NMR (CD_3OD, 125 MHz)：δ 138.3 (C-1), 127.6 (C-2,6), 129.6 (C-3,5), 128.7 (C-4), 133.8 (C-7), 126.7 (C-8), 70.8 (C-9), 103.4 (C-1′), 75.2 (C-2′), 78.2 (C-3′), 71.7 (C-4′), 78.0 (C-5′), 62.9 (C-6′)。以上波谱数据与文献[17]报道基本一致，鉴定化合物 **12** 为松香(rosin)。

化合物 13　白色粉末。Q-TOF-ESI-MS *m/z*：417.1425 [M + COOH]$^-$, 分子式为 $C_{17}H_{24}O_9$ (calcd for $C_{18}H_{25}O_{11}$, 417.1402)。^{1}H NMR (CD_3OD, 500 MHz)：δ 6.58 (2H, s, H-2,6), 6.50 (1H, br. d, *ca*. *J* = 12.0 Hz, H-7), 5.82 (1H, dt, *J* = 6.5, 12.0 Hz, H-8), 4.35 (2H, d, *J* = 6.5 Hz, H-9), 4.89 (1H, d, *J* = 7.5 Hz, H-1′), 3.48 (1H, dd, *J* = 7.5, 9.0 Hz, H-2′), 3.42 (1H, m, overlapped, H-3′), 3.42 (1H, m, overlapped, H-4′), 3.22 (1H, m, overlapped, H-5′), 3.67 (1H, dd, *J* = 5.0, 12.0 Hz, H-6′), 3.78 (1H, dd, *J* = 2.0, 12.0 Hz, H-6′), 3.85 (6H, s, 3,5-OCH_3)；^{13}C NMR (CD_3OD, 125 MHz)：δ 134.8 (C-1), 108.1 (C-2,6), 154.1 (C-3,5), 135.6 (C-4), 131.5 (C-7), 132.6 (C-8), 59.8 (C-9), 105.3 (C-1′), 75.8 (C-2′), 77.9 (C-3′), 71.4 (C-4′), 78.4 (C-5′), 62.6 (C-6′), 57.1 (3,5-OCH_3)。以上波谱数据与文献[18]报道基本一致，鉴定化合物 **13** 为顺式紫丁香苷(*cis*-syringin)。

化合物 14　白色粉末。Q-TOF-ESI-MS *m/z*：375.1292 [M – H]$^-$, 分子式为 $C_{16}H_{24}O_{10}$ (calcd for $C_{16}H_{23}O_{10}$, 375.1297)。$[\alpha]_D^{25}$：–18.5°, MeOH。^{1}H NMR (CD_3OD, 500 MHz)：δ 7.05 (1H, d, *J* = 2.0 Hz, H-2), 6.77 (1H, d, *J* = 8.0 Hz, H-5), 6.84 (1H, dd, *J* = 2.0, 8.0 Hz, H-6), 4.79 (1H, d, *J* = 4.5 Hz, H-7), 3.92 (1H, m, H-8), [3.57 (1H, dd, *J* = 3.5, 12.0 Hz), 3.61 (1H, dd, *J* = 5.0, 12.0 Hz), H_2-9], 4.36 (1H, d, *J* = 7.5 Hz, H-1′), 3.26 (1H, dd, *J* = 7.5, 8.0 Hz, H-2′), 3.35 (1H, dd, *J* = 8.0, 8.0 Hz, H-3′), 3.29 (1H, dd, *J* = 8.0, 8.0 Hz, H-4′), 3.28 (1H, m, H-5′), 3.85 (1H, br. d, *ca*. *J* = 12 Hz), 3.65 (1H, dd, *J* = 5.5, 2.0 Hz), H_2-6′], 3.86 (3H, s, 3-OCH_3)；^{13}C NMR (CD_3OD, 125 MHz)：δ 133.7 (C-1), 111.8 (C-2), 148.9 (C-3), 147.0 (C-4), 115.9 (C-5), 120.7 (C-6), 74.5 (C-7), 85.8 (C-8), 62.7 (C-9), 104.1 (C-1′), 75.3 (C-2′), 77.8 (C-3′), 71.5 (C-4′), 78.0 (C-5′), 62.6 (C-6′), 56.5 (3-OCH_3), 以上波谱数据与文献[19]报道基本一致，鉴定化合物 **14** 为 (–)-(7*R*,8*S*)-guaiacylglycerol 8-*O*-β-D-glucopyranoside。

化合物 15　白色粉末。Q-TOF-ESI-MS *m/z*：375.1312 [M – H]$^-$, 分子式为 $C_{16}H_{24}O_{10}$ (calcd for $C_{16}H_{23}O_{10}$, 375.1297)。$[\alpha]_D^{25}$：+10.8°, MeOH。^{1}H NMR (CD_3OD, 500 MHz)：δ 7.01 (1H, d, *J* = 1.5 Hz, H-2), 6.78 (1H, d, *J* = 8.5 Hz, H-5), 6.82 (1H, dd, *J* = 1.5, 8.5 Hz, H-6), 4.68 (1H, d, *J* = 7.5 Hz, H-7), 3.82 (1H, m, H-8), [3.54 (1H, dd, *J* = 3.5, 12.0 Hz), 3.39 (1H, dd, *J* = 6.0, 12.0 Hz), H_2-9], 4.42 (1H, d, *J* = 7.5 Hz, H-1′), 3.33 (1H, m, H-2′), 3.37 (1H, m, H-3′), 3.35 (1H, m, H-4′), 3.27 (1H, m, H-5′), [3.66 (1H, dd, *J* = 5.5, 12.0 Hz), 3.84 (1H, dd, *J* = 2.0, 12.0 Hz), H_2-6′], 3.86 (3H, s, 3-OCH_3)。^{13}C NMR (CD_3OD, 125 MHz)：δ 133.5 (C-1), 111.6 (C-2), 149.0 (C-3), 147.4 (C-4), 116.1 (C-5), 120.9 (C-6), 75.0 (C-7), 87.7 (C-8), 63.2 (C-9), 105.3 (C-1′), 75.5 (C-2′), 77.9 (C-3′), 71.4 (C-4′), 78.0 (C-5′), 62.5 (C-6′), 56.5 (3-OCH_3), 以上波谱数据与文献[20]报道基本一致，鉴定化合物 **15** 为 l-*threo*-guaiacylglycerol-8-*O*-β-glucopyranoside。

2 结果和讨论

为了扩大对鸡血藤的资源开发，笔者结合色谱法与光谱法，对鸡血藤 95% 乙醇提取物的化学成分进行了初步研究，从中分离鉴定了 15 个酚酸类化合物，分别为：没食子酸 (**1**)、tachioside (**2**)、isotachioside (**3**)、canthoside D (**4**)、3,5-二甲氧基-4-羟基苯基-1-*O*-β-D-吡喃葡萄糖苷 (**5**)、2,6-二甲氧基-4-羟基-苯酚-1-*O*-β-D-吡喃葡萄糖苷 (**6**)、4-羟甲基-2,6-二甲氧基苯基-β-D-吡喃葡萄糖苷 (**7**)、丁香酸葡萄糖苷 (**8**)、3-甲氧基苯乙醇-4-*O*-β-D-葡吡喃糖苷 (**9**)、2-(4-hydroxy-3,5-dimethoxyphenyl) ethyl-β-D-glucopyranoside (**10**)、4,6-二羟基-2-*O*-(β-D-吡喃葡萄糖苷)苯乙酮 (**11**)、松香 (**12**)、顺式紫丁香苷 (**13**)、(–)-(*7R,8S*)-guaiacylglycerol 8-*O*-β-D-glucopyranoside (**14**)及 l-*threo*-guaiacylglycerol-8-*O*-β-glucopyranoside (**15**)。除化合物 **1** 和 **9** 之外，其它化合物均是首次从密花豆属植物中分离得到。

作为鸡血藤中的主要成分，酚酸化合物具有很强的抗氧化活性及清除活性氧的能力，并具有预防、治疗心血管疾病、延缓衰老和抗癌等药理作用。

这与之前所述的“鸡血藤具有促进造血功能、抗肿瘤、抗病毒、免疫调节、抗炎、抗氧化等药理作用”相吻合。提示我们可以在化学成分研究的基础上从抗氧化、抗肿瘤等多个方面对鸡血藤的药理活性进行深入研究，寻找相应的药效物质。

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