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Chemical constituents of *Ancistrocladus tectorius*

YI Bo[1,3]，CHEN Tao[2*]，FENG Shi-Xiu[2]，LI Qing-Hui[2,4]

(1. *Pharmacy Department*，*187 Hospital of PLA*，Haikou 571159，China; 2. *Key Laboratory of Southern Subtropical Plant Diversity*，*Shenzhen Fairy Lake Botanical Garden*，*Chinese Academy of Sciences*，Shenzhen 518004，China; 3. *South China Botanical Garden*，*Chinese Academy of Sciences*，Guangzhou 510650，China; 4. *College of Life Sciences*，*Shenzhen University*，Shenzhen 518060，China)

Abstract: The chemical constituents of the stems of *Ancistrocladus tectorius* were isolated by silica gel and Sephadex LH-20 column chromatography，and the structures were elucidated on the basis of spectral analysis. The results showed that five known dihydroflavoids(-)-epicatechin-3-gallate(**1**)，3，3′，5，5′，7-pentahydroxyflavan(**2**)，(-)-catechin(**3**)，(-)-Epicatechin(**4**)，(-)-epigallocatechin(**5**) and one known phenolic compound(3，5-dimethoxy-4-hydroxyphenol)-1-O-β-D-(6-O-galloyl) glucose(**6**) were obtained. Compounds **1**，**2**，**4**-**6** were reported for the first time from this species.

Key words: *Ancistrocladus tectorius*; chemical constituents; dihydroflavoids; phenolic compound

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钩枝藤化学成分研究

易　博[1,3]，陈　涛[2*]，冯世秀[2]，李庆辉[2,4]

(1. 解放军第187医院药剂科，海口 571159; 2. 深圳市中科院仙湖植物园 深圳市南亚热带植物多样性重点实验室，深圳 518004; 3. 中国科学院 华南植物园，广州 510650; 4. 深圳大学 生命科学学院，深圳 518060)

摘　要: 采用95%乙醇提取，石油醚、乙酸乙酯萃取分部，利用反复硅胶柱和凝胶柱色谱进行分离、纯化，根据波谱技术鉴定结构，研究钩枝藤茎中的化学成分。结果发现：分离得到5个已知二氢黄烷类化合物(-)-表儿茶素-3-没食子酸酯(1)、3，3′，5，5′，7-五羟基黄烷(2)、(-)-儿茶素(3)、(-)-表儿茶素(4)、(-)-表没食子酸儿茶素(5)和1个酚类化合物(3，5-二甲氧基-4-羟基苯酚)-1-O-β-D-(6-O-没食子酸)葡萄糖苷(6)。其中化合物1、2、4-6均为首次从该植物分离得到。

关键词: 钩枝藤; 化学成分; 二氢黄烷; 酚类

Ancistrocladus tectorius is a special tropical liana of the small palaeotropic families Ancistrocladaceae，with only one genus and one species distributes in southeast China. It was reported to be the only plant resource known to produce naphthylisoquinoline alkaloids，which possessed probable anti-infective activities against protozoic pathogens of the famous tropical diseases like malaria，trypanosomiasis and leishmaniasis，as well as anti-HIV and anti-tumor activities. Phytochemical investigations of this species by different groups in China reported the identification of over 20 novel anphthylisoquinoline alkaloids(Liu *et al.*，2008，Tang *et al.*，2010; Xu *et al.*，2010). However，other chemical constituents in this plant were nearly ignored with the only report of

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作者简介: 易博(1978-)，男，湖南湘阴县人，博士，主管药师，主要从事天然产物化学和医院药学研究，(E-mail) boyicn@126.com。

[*] **通讯作者:** 陈涛，博士，研究员，主要从事植物分类学研究，(E-mail) taochen.mobg@gmail.com。

several phenol and flavone compounds (Su *et al.*, 2007).

In our current work, the liposoluble fraction of the EtOH extract of *A. tectorius* was studied, as a result in the isolation of dihydroflavones and phenolic compound.

1 Materials and Methods

The ^1H(400 MHz), ^{13}C(100 MHz) and 2D NMR spectra were recorded on a Bruker DRX-600 instrument using TMS as internal standard. HRESI-MS data were obtained on a MAT 95XP Thermo mass spectrometer. Optical rotations were obtained on a Perkin-Elmer 341 polarimeter with MeOH as solvent. The UV spectrum was recorded in MeOH on a Perkin Elmer Lambda 25 UV-VIS Spectrophotometer. For column chromatography (CC), silica gel (200-300 mesh; Qingdao Puke Isolation Material Co.) and Sephadex LH-20 (Mitsubishi Chemical Holdings Co.) were used.

The stems of *A. tectorius* were collected in Hainan Province of southern China in November, 2010, and identified by Professor Chen Tao (Shenzhen Fairy Lake Botanical Garden). A voucher specimen (20101109N) was deposited at the herbarium of Shenzhen Fairy Lake Botanical Garden.

2 Extraction and Isolation

The air dried material (10 kg) were powered and extracted with 95% EtOH at r. t. The combined extracts were concentrated to give a residue (730 g), which was suspended in H_2O and partitioned with petroleum ether (PE; 60-90 ℃), AcOEt and *n*-BuOH, successively, to give an EtOAc-soluble fraction (235 g).

The AcOEt soluble fraction (235 g) was subjected to a silica gel chromatography column (CC) and eluted with a gradient $CHCl_3$-MeOH (95∶5 to 60∶40) to yield fourteen fractions, Frs. 1-14. Fr. 3 (3.5 g) was repeatedly subjected to silica gel CC using $CHCl_3$-MeOH (92∶8) to obtained seven subfractions Frs. 3a-3g. Frs. 3c (310 mg) and 3d (260 mg) were purified by Sephadex LH-20 eluting with MeOH to get compound **2** (18 mg) and **3** (26 mg), respectively. Fr. 4 (2.8 g) was separated over Sephadex LH-20 CC using MeOH: $CHCl_3$ (1∶3) to yield ten subfractions Frs. 4a-4j. Frs. 4c (300 mg) was purified by silica gel CC using PE - acetone 3∶1 to afford compound **4** (41 mg). Frs. 4h (90 mg) was purified by PE-EtOAc (3∶1) to get compound **1** (20 mg). Fr. 5 (2.3 g) was submitted further to silica gel CC and eluted with $CHCl_3$-MeOH-H_2O (100∶11∶1), further purified by Sephadex LH-20 using MeOH to get compound **5** (18 mg). Fr. 6 (2.0 g) was subjected to repeated silica gel CC eluting with $CHCl_3$-MeOH-H_2O (100∶11∶1) to get compound **6** (32 mg).

3 Results and Analysis

(-)-Epicatechin-3-gallate (**1**)　White power. HR-ESI-MS *m/z* 441.0825 $[M-H]^-$ (calcd for $C_{22}H_{17}O_{10}$, Δ-0.45 ppm). ESI-MS *m/z* 443.1 $[M+H]^+$, 465.1 $[M+Na]^+$, 441.0 $[M-H]^-$, 883.0 $[2M-H]^-$. $[\alpha]^{20}_{D}$: -230° (*c* = 1.0, MeOH). UV/Vis λ_{max} (MeOH) nm (log ε): 204 (3.12), 277 (2.01). ^1H NMR (CD_3OD): δ 5.00 (1H, s, H-2), 5.51 (1H, m, H-3), 2.85 (1H, dd, *J* = 14.0, 2.4 Hz, H-4a), 2.96 (1H, dd, *J* = 14.0, 4.8 Hz, H-4b), 5.95 (1H, d, *J* = 2.0 Hz, H-6), 5.93 (1H, d, *J* = 2.0 Hz, H-8), 6.92, d (1H, d, *J* = 2.0 Hz, H-2′), 6.68 (1H, d, *J* = 8.0 Hz, H-5′), 6.79 (1H, dd, *J* = 2.0, 8.0 Hz, H-6′), 6.94 (2H, s, H-3″ and 5″); ^{13}C NMR (CD_3OD, 150 MHz): 77.2 (C-2), 68.6 (C-3), 25.5 (C-4), 156.4 (C-5), 96.5 (C-6), 156.4 (C-7), 94.0 (C-8), 155.8 (C-9), 98.0 (C-10), 130.0 (C-1′), 113.7 (C-2′), 144.5 (C-3′), 144.5 (C-4′), 114.7 (C-5′), 118.0 (C-6′), 120.0 (C-1″), 108.0 (C-2″ and C-6″), 144.9 (C-3″ and C-5″), 138.4 (C-6″), 166.2 (C-7″) (Li *et al.*, 2008).

3, 3′, 5, 5′, 7-pentahydroxyflavan (**2**)　White power. $[\alpha]^{20}_{D}$: 0° (*c* = 1.0, MeOH). ESIMS: *m/z* 291.0 $[M+H]^+$, 313.1 $[M+Na]^+$, 288.8 $[M-H]^-$; ^1H NMR (DMSO-d_6, 600 MHz): δ 9.11 (1H, s, 5-OH), 8.90 (1H, s, 3′-OH), 8.81 (1H, s, 5′-OH), 8.72 (1H, s, 7-OH), 6.88 (1H, brd, *J* = 1.6 Hz, H-2′), 6.65 (1H, d, J = 1.6 Hz, H-6′), 6.65 (1H, brs, H-4′), 5.88 (1H, d, *J* = 2.0 Hz, H-8), 5.71 (1H, d, *J* = 2.0 Hz, H-6), 4.72 (1H, brs, H-2), 3.98 (1H, brs, H-3), 2.69 (1H, dd, *J* = 4.0, 4.4 Hz, H-4a), 2.44 (1H, dd, *J* = 4.0, 4.4 Hz, H-

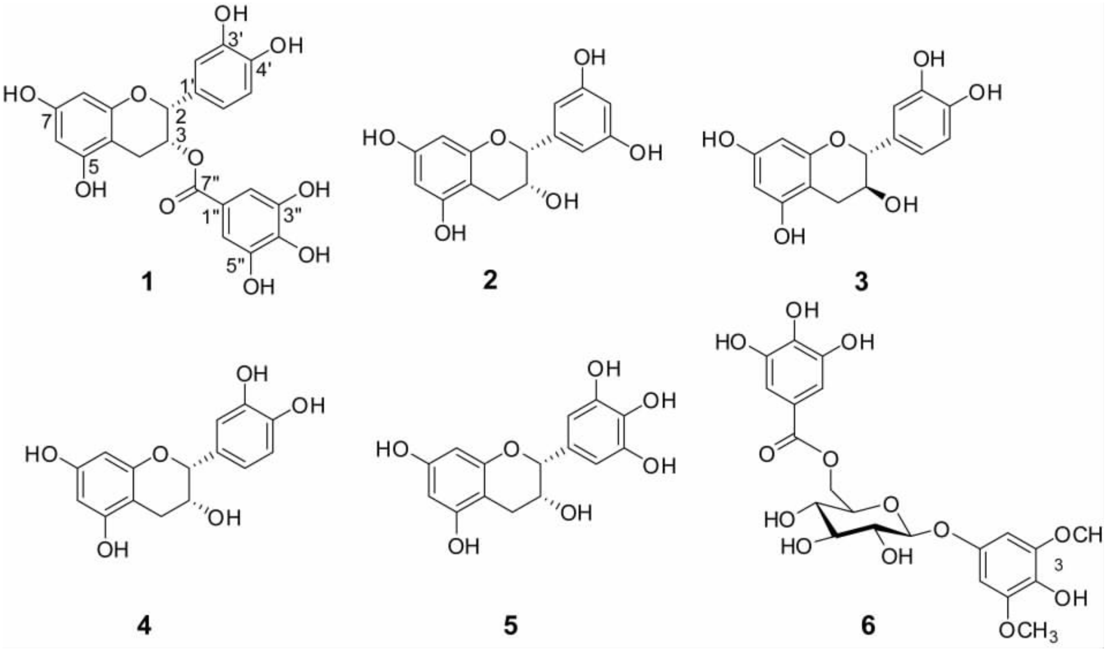

Fig. 1 Chemical structures of compounds **1-6**

4b); ^{13}C NMR(DMSO-d_6,150 MHz): δ 78.1(C-2),64.9(C-3),28.2(C-4),155.8(C-5),94.1(C-6),156.2(C-7),95.1(C-8),156.5(C-9),98.5(C-10),130.6(C-1′),114.8(C-2′),144.5(C-3′),118.0(C-4′),144.5(C-5′),114.9(C-6′)(Samaraweera *et al.*, 1983).

(-)-catechin(**3**) White power. [α]$^{20}_{\mathrm{D}}$: −23°(*c*=1.0,MeOH). ESIMS: *m/z* 288.8 [M-H]$^-$,579.1 [2M-H]$^-$,291.1 [M+H]$^+$,313.3 [M+Na]$^+$. ^{1}H NMR(DMSO-d_6,600 MHz): δ 6.88(1H,d,*J* =2.0 Hz,H-2′),6.75(1H,dd,*J*=8.0 and 2.0 Hz,H-6′),6.79(1H,d,*J*=8.0 Hz,H-5′),5.87(1H,d,*J*=2.0 Hz,H-6),6.01(1H,d,*J*=2.0 Hz,H-8),4.56(1H,d,*J*=7.5 Hz,H-2),3.98(1H,ddd,*J*=8.2,7.5,5.4 Hz,H-3),2.90(1H,dd,*J*=16.1,8.1 Hz,H-4a),2.51(1H,*J*=16.0,4.6 Hz,H-4b); ^{13}C NMR(150 MHz,DMSO-d_6):82.7(C-2),68.3(C-3),28.8(C-4),157.7(C-5),96.1(C-6),157.1(C-7),95.4(C-8),156.9(C-9),100.7(C-10),132.2(C-1′),115.7(C-2′),145.7(C-3′),145.6(C-4′),115.2(C-5′),120.1(C-6′)(Cai *et al.*,1991).

(-)-Epicatechin(**4**) White power. [α]$^{20}_{\mathrm{D}}$: -58°(*c*=1.0,MeOH). ESIMS: *m/z* 288.6 [M-H]$^-$,291.1 [M+H]$^+$,313.1 [M+Na]$^+$. ^{1}H NMR(DMSO-d_6,600 MHz): δ 6.90(1H,d,*J* =2.0 Hz,H-2′),6.75(1H,dd,*J*=8.0 and 2.0 Hz,H-6′),6.70(1H,d,*J*=8.0 Hz,H-5′),5.86(1H,d,*J*=2.0 Hz,H-6),5.88(1H,d,*J*=2.0 Hz,H-8),4.76(1H,brs,H-2),4.11(1H,m,H-3),2.82(1H,dd,*J*=16.1,5.6 Hz,H-4a),2.70(1H,*J*=16.1,4.4 Hz,H-4b); ^{13}C NMR(DMSO-d_6,150 MHz,): δ 79.9(C-2),67.5(C-3),29.2(C-4),158.0(C-5),96.4(C-6),157.7(C-7),95.9(C-8),157.4(C-9),100.0(C-10),132.3(C-1′),115.9(C-2′),145.9(C-3′),145.8(C-4′),115.3(C-5′),119.4(C-6′)(Cui *et al.*,2005).

(-)-epigallocatechin (**5**) White power. [α]$^{20}_{\mathrm{D}}$: -28°(*c*=1.0,MeOH). ESIMS: *m/z* 304.8 [M-H]$^-$,307.1 [M+H]$^+$,329.1 [M+Na]$^+$. ^{1}H NMR(CD$_3$OD,600 MHz,): δ 6.39(2H,d,*J* =2.0 Hz,H-2′ and H-6′),5.90(1H,d,*J*=2.0 Hz,H-6),5.84(1H,d,*J*=2.0 Hz,H-8),4.74(1H,brs,H-2),4.15(1H,m,H-3),2.82(1H,dd,*J*=16.1,5.0 Hz,H-4a),2.72(1H,*J*=16.1,4.6 Hz,H-4b); ^{13}C NMR(CD$_3$OD,150 MHz): δ78.4(C-2),66.1(C-3),27.7(C-4),155.9(C-5),94.9(C-6),156.5(C-7),94.4(C-8),156.6(C-9),98.6(C-10),130.1(C-1′),105.7(C-2′),145.2(C-3′),132.1(C-4′),145.2(C-5′),105.7(C-6′)(Li *et al.*,2008).

(3,5-dimethoxy-4-hydroxyphenol)-1-O-β-d-(6-O-galloyl) glucose (**6**) Yellow power. ^{1}H NMR (600 MHz, CD_3OD, δ, ppm, J/Hz): 6.40 (2H, brs, H-3 and H-5), 7.05 (2H, brs, H-2″ and 6″), 3.64 (6H, s, 2-OCH_3 and 6-OCH_3), 4.72 (1H, d, $J = 7.5$, H-1′), 3.72 (1H, m, H-2), 3.38-3.50 (3H, m, H-3, 4 and 5), 4.59 (1H, d, J = 12.0 Hz), 4.41 (1H, dd, $J = 11.8$, 4.8 Hz). ^{13}C NMR (CD_3OD, 150 MHz): 150.9 (C-1), 95.5 (C-2 and 6), 147.9 (C-3 and 5), 131.0 (C-4), 102.6 (C-1′), 102.6 (C-1′), 73.5 (C-2′), 76.2 (C-3′), 70.3 (C-4′), 74.3 (C-5′), 63.7 (C-6′), 119.0 (C-1″), 108.7 (C-2″ and 6″), 145.1 (C-3″ and 5″), 138.5 (C-4″), 166.8 (C-7″), 55.2 (3-OCH_3 and 5-OCH_3) (Lampire *et al.*, 1998).

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