热带亚热带植物学报 2009,17(6):617~620
Journal of Tropical and Subtropical Botany

何首乌的酚类成分研究

李续娥[1*], 刘金珠[1], 廖森泰[2], 徐良雄[3], 魏孝义[3]
(1. 华南师范大学 广东省植物发育生物工程重点实验室,广州 510631; 2. 广东省农业科学院, 广州 510640;
3. 中国科学院华南植物园, 广州 510650)

摘要: 运用多种色谱学方法对德庆产何首乌(*Polygonum multiflorum* Thunb.)块茎的化学成分进行了分离,根据波谱数据鉴定了 8 个化合物,分别为 physcion-8-β-D-(6′-*O*-acetyl) glucoside (**1**),大黄素-3-甲醚-8-β-D-葡萄糖苷(**2**),大黄素(**3**),表儿茶素(**4**),决明酮-8-*O*-β-D-吡喃葡萄糖苷(**5**),2,3,5,4′-tetrahydroxystilbene 2-*O*-β-D-glucopyranoside (**6**),对羟基苯甲醛(**7**)和 5-羧甲基-7-羟基-2-甲基色原酮(**8**)。化合物 **1**, **7** 和 **8** 均为首次从何首乌中分离得到。

关键词:何首乌; 化学成分; 蒽醌
中图分类号:Q946 **文献标识码**:A **文章编号**:1005-3395(2009)06-0617-04

Chemical Constituents from Tubers of *Polygonum multiflorum* Thunb.

LI Xu-e[1*], LIU Jin-zhu[1], LIAO Sen-tai[2], XU Liang-xiong[3], WEI Xiao-yi[3]
(1. *Key laboratory of Biotechnology for Plant Development of Guangdong Province, South China Normal University,* Guangzhou 510631, China; 2. *Guangdong Academy of Agricultural Sciences,* Guangzhou 510640, China;
3. *South China Botanical Garden, Chinese Academy of Sciences,* Guangzhou 510650, China)

Abstract: The chemical constituents extracted from tubers of *Polygonum multiflorum* Thunb. originated from Deqing of Guangdong Province were isolated by using chromatographic techniques. On the basis of spectral data, eight phenolic components were identified, such as physcion-8-β-D-(6′-*O*-acetyl)glucoside (**1**), physcionin (**2**), emodin (**3**), epicatechin (**4**), torachrysone 8-*O*-β-D-glucopyranoside (**5**), 2,3,5,4'-tetrahydroxystilbene 2-*O*-β-D-glucopyranoside (**6**), 4-hydroxybenzaldehyde (**7**), 5-carboxymethyl-7-hydroxy-2-methylchromone (**8**). Compounds **1**, **7** and **8** were isolated from this plant for the first time.

Key words: *Polygonum multiflorum*; Chemical constituents; Anthraquinones

Radix Polygoni Multiflori was firstly recorded in Kaiyuan Materia Medica of Song Dynasty. It comes from the dry tubers of *Polygonum multiflorum* Thunb., which is neutral in nature, sweet and bitter in taste, and attributive to the meridians of the heart, liver and large intestine, and it has the actions of checking malaria and removing toxins, moistening the bowls and promoting defection. While Radix Polygoni Multiflori is slightly warm in nature, sweet and astringent in taste, and attributive to the meridians of the liver and kidney, which has the actions of tonifying meridians and blood, strengthening kidney and blacking hair. Recent pharmacological research indicated that Radix Polygoni Multiflori has antibacterial and hematopoietic effects, and also can counteract aging, enhance immunity and promote cardiovascular function. The main chemical constituents of Radix Polygoni Multiflori are anthraquinones, diphenyl ethylene glycosides, and polyproanthocyanidins. In addition, it also includes large amount of lecithin and various kinds of trace elements. Till now, it was reported that different kinds of compounds had been isolated from the tubers of *P. multiflorum*[1]. In this study, in order to supply

Received:2008-12-16 **Accepted**:2009-03-16
Foundation item: Financially supported by the Natural Science Foundation (05100575) of Guangdong Province
* Corresponding author

evidence for the advanced development of medicinal material from the south of five ridges in China, a further analysis of chemical constituents of tubers of *P. multiflorum* from Deqing of Guangdong Province was carried out. Eight phenolic components have been isolated and identified, and compounds **1**, **7** and **8** were isolated from this plant for the first time.

1 Experiment

1.1 Equipment and regents

The ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were obtained on a Bruker DRX-400 instrument with TMS as internal standard. ESIMS was performed on a MDS SCIEX API 2000 LC/MS/MS instrument. For column chromatography, silica gel 60 (100 ~ 200 mesh, Qingdao Marine Chemical Ltd., Qingdao, China), polyamide (100 ~ 200 mesh, Sijia Biochemical Plastic Company, Taizhou, Zhejiang), Develosil ODS (10 μm, Nomura Chemical Co. Ltd., Japan), and Sephadex LH-20 were used.

1.2 Plant materials

The tubers of *P. multiflorum* were collected from Deqing, Guangdong in July 2005, and authenticated by Prof. LI Ying-li, College of Pharmaceutical Sciences, Xi'an Jiaotong University.

1.3 Extraction and isolation

The air-dried and powdered tubers of *P. multiflorum* (1.5 kg) were extracted with 95% EtOH three times at room temperature. The EtOH solutions were combined and concentrated in vacuo. The residue was sequentially extracted with petroleum ether, $CHCl_3$ and EtOAc. The combined EtOAc solution, upon evaporation, yielded the dark-brown syrup (52.5 g). This syrup was subjected to SiO_2 column chromatography (CC) eluted with $CHCl_3$-MeOH mixtures of increasing polarities (95: 5 to 80: 20), and then five fractions (I ~ V) were obtained. Further separation by SiO_2 CC eluted with petroleum ether-acetone (75: 25) followed by recrystallization to afford **3** (187 mg) and **1** (10 mg) from fraction II. Fraction III was further chromatographed on a SiO_2 CC eluted with $CHCl_3$-MeOH (95: 5 to 75: 25) followed by purification with polyamide CC eluted with MeOH-H_2O (1: 2) to afford **8** (8 mg), **2** (12 mg) and **5** (60 mg). Fraction IV, which was further separated by SiO_2 CC eluted with petroleum ether-acetone mixtures of increasing polarities (95: 5 to 50: 50) followed by purification with Sephadex LH-20 CC eluted with MeOH, afforded **4** (180 mg), **6** (113 mg), and afford **7** (12 mg) by purification with HPLC eluted with MeOH-H_2O (3: 2).

1.4 Structure identification

Physcion-8-β-D-(6′-*O*-acetyl) glucoside (1) Yellow needles, ESIMS *m/z* 489 $[M+H]^+$. ^1H NMR (400 MHz, pyridine-d_5), δ 7.69 (1H, br s, H-5), 7.67 (1H, d, J = 2.2 Hz, H-4), 7.50 (1H, br s, H-7), 7.12 (1H, d, J = 2.2 Hz, H-2), 5.73 (1H, d, J = 7.7 Hz, H-1'), 4.30 ~ 5.05 (6H, m, H-2' ~ 6'), 3.84 (3H, s, 3-OCH_3), 2.20 (3H, s, 6-CH_3), 2.01 (3H, s, 6'-OCOCH_3); ^{13}C NMR (100 MHz, pyridine-d_5): δ 187.4 (C-9), 182.3 (C-10), 170.8 (6'-O*C*OCH$_3$), 165.3 (C-3), 163.0 (C-8), 161.5 (C-1), 147.3 (C-6), 132.8 (C-4a), 124.8 (C-10a), 123.0 (C-7), 120.1 (C-5), 116.2 (C-9a), 115.4 (C-8a), 109.0 (C-2), 106.5 (C-4), 102.9 (C-1'), 78.2 (C-2'), 75.8 (C-5'), 74.8 (C-3'), 71.2 (C-4'), 64.7 (C-6'), 56.0 (3-O*C*H$_3$), 21.4 (6-*C*H$_3$), 20.7 (6'-OCO*C*H$_3$). All these data are consistent with those reported in literature [2].

Physcionin (2) Yellow needles, ESIMS *m/z* 445 $[M-H]^-$. ^1H NMR (400 MHz, pyridine-d_5), δ 7.68 (1H, br s, H-5), 7.64 (1H, d, J = 2.2 Hz, H-4), 7.60 (1H, br s, H-7), 7.14 (1H, d, J = 2.2 Hz, H-2), 5.78 (1H, d, J = 6.1 Hz, H-1'), 4.22 ~ 4.65 (6H, m, H-2' ~ 6'), 3.81 (3H, s, 3-OCH_3); ^{13}C NMR (100 MHz, pyridine-d_5): δ 187.4 (C-9), 182.3 (C-10), 165.3 (C-3), 162.8 (C-8), 161.7 (C-1), 147.1 (C-6), 132.8 (C-4a), 124.5 (C-10a), 122.9 (C-7), 119.8 (C-5), 115.6 (C-9a), 115.2 (C-8a), 108.1 (C-2), 107.3 (C-4), 103.0 (C-1'), 79.3 (C-2'), 78.1 (C-5'), 74.7 (C-3'), 71.2 (C-4'), 62.4 (C-6'), 55.8 (3-O*C*H$_3$), 21.4 (6-*C*H$_3$). All these data are consistent with those reported in literature [3].

Emodin (3) Yellow needles, ESIMS *m/z* 269 $[M-H]^-$. ^1H NMR (400 MHz, DMSO-d_6), δ 7.40 (1H, br s, H-5), 7.14 (1H, d, J = 2.0 Hz, H-4), 7.09

(1H, br s, H-7), 6.66 (1H, d, J = 2.0 Hz, H-2), 2.46 (3H, s, 6-CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 191.6 (C-9), 182.1 (C-10), 166.4 (C-3), 166.2(C-1), 163.2 (C-8), 149.5 (C-6), 136.5 (C-10a), 134.1 (C-4a), 124.5 (C-7), 121.4 (C-5), 114.4 (C-9a), 110.4 (C-8a), 109.6 (C-4), 108.8 (C-2), 22.0 (6-CH_3). All these data are consistent with those reported in literature [4].

Epicatechin (**4**)　Brown solid, ESIMS m/z 291.3 $[M+H]^+$. ^{1}H NMR (400 MHz, acetone-d_6), δ 6.88 (1H, d, J = 2.0 Hz, H-2'), 6.78 (1H, dd, J = 7.6, 1.8 Hz, H-5'), 6.75 (1H, d, J = 8.0 Hz, H-6'), 6.01 (1H, d, J = 1.8 Hz, H-8), 5.86 (1H, d, J = 1.8 Hz, H-6), 4.54 (1H, d, J = 7.6 Hz, H-2), 3.99 (1H, m, H-3), 2.90 (1H, dd, J = 16.4, 5.6 Hz, H-4a), 2.51 (1H, m, H-4b); ^{13}C NMR (100 MHz, acetone-d_6): δ 157.6 (C-5), 157.1 (C-7), 156.7 (C-9), 145.6(C-3'), 145.6 (C-4'), 131.9 (C-1'), 119.9 (C-6'), 115.6(C-2'), 115.1 (C-5'), 100.5 (C-10), 96.1 (C-6), 95.3 (C-8), 82.5 (C-2), 68.2 (C-3), 28.7 (C-4). All these data are consistent with those reported in literature [5].

Torachrysone 8-*O*-β-*D*-glucopyranoside (**5**)　Yellow needles, ESIMS m/z 409.3 $[M+H]^+$. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.02 (1H, s, H-4), 7.00 (1H, d, J = 2.3 Hz, H-7), 6.85 (1H, d, J = 2.3 Hz, H-5), 5.18 (1H, d, J = 7.2 Hz, H-1'), 3.52~3.98 (6H, m, H-2'~6'), 3.86 (3H, s, 6-OCH_3), 2.51(3H, s, 2-COCH_3), 2.26(3H, s, 3-CH_3); ^{13}C NMR (100 MHz, acetone-d_6): δ 204.9 (2-COCH$_3$), 159.6 (C-6), 156.7 (C-8), 153.0 (C-1), 138.3 (C-4a), 135.1 (C-3), 124.0 (C-2), 119.8 (C-4), 109.9 (C-8a), 103.9 (C-7), 103.8 (C-5), 102.0 (C-1'), 78.3 (C-5'), 77.7 (C-3'), 74.5 (C-2'), 71.1 (C-4'), 62.3 (C-6'), 55.7 (6-OCH$_3$), 32.4 (2-COCH$_3$), 20.1 (3-CH$_3$). All these data are consistent with those reported in literature [6].

2,3,5,4′-Tetrahydroxystilbene 2-*O*-β-D-glucopyranoside (**6**)　Yellow needles, ESIMS m/z 407 $[M+H]^+$. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.67 (1H, d, J = 16.5 Hz, H-1β), 7.41 (2H, d, J = 8.6 Hz, H-2', 6'), 6.96 (1H, d, J = 16.5 Hz, H-1α), 6.82 (1H, d, J = 6.8 Hz, H-3', 5'), 6.66 (1H, d, J = 2.8 Hz, H-6), 6.28 (1H, d, J = 2.8 Hz, H-4), 4.61 (1H, d, J = 7.4 Hz, H-1''), 3.89 (1H, t, J = 10.4 Hz, H-6''a), 3.79 (1H, dd, J = 10.5, 5.3 Hz, H-6''b), 3.45~3.72 (3H, m, H-2'', H-3'', H-4''), 3.35 (1H, m, H-5''a); ^{13}C NMR (100 MHz, acetone-d_6): δ 158.1 (C-4'), 155.9 (C-5), 151.9 (C-3), 137.6 (C-2), 133.2 (C-1), 129.4 (C-1β, 1'), 128.8 (C-3', 5'), 121.8 (C-1α), 116.3 (C-2', 6'), 108.0 (C-6), 103.4 (C-4), 102.1 (C-1''), 77.8 (C-5''), 76.3(C-3''), 74.7(C-2''), 68.5(C-4''), 62.5 (C-6''). All these data are consistent with those reported in literature [7].

4-Hydroxybenzaldehyde (**7**)　Colorless needles, ESIMS m/z 123 $[M+H]^+$. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.84 (1H, s, 1-CHO), 7.79 (2H, d, J = 8.6 Hz, H-2, 6), 6.96 (1H, d, J = 8.6 Hz, H-3, 5); ^{13}C NMR (100 MHz, acetone-d_6) :δ 190.9 (1-CHO), 163.9 (C-4), 132.8 (C-2, 6), 130.4 (C-1), 116.6 (C-3, 5). All these data are consistent with those reported in literature [8].

5-Carboxymethyl-7-hydroxy-2-methylchromone (**8**)　Yellow needles, ESIMS m/z 235 $[M+H]^+$. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.20 (1H, s, H-6), 7.00 (1H, s, H-8), 6.08 (1H, s, H-3), 4.72 (2H, s, 5-CH_2COOH), 1.99 (3H, s, 2-CH_3); ^{13}C NMR (100 MHz, acetone-d_6) δ 179.1 (C-4), 173.8 (5- CH$_2$$C$OOH), 163.9 (C-2), 162.7 (C-7), 160.7(C-8a), 139.5 (C-5), 118.9 (C-6), 115.7 (C-4a), 111.5 (C-3), 102.5 (C-8), 41.7 (5-CH$_2$COOH), 19.4 (2-CH$_3$). All these data are consistent with those reported in literature [9].

2 Discussion

In this study, compounds **1**, **7** and **8** were first isolated from the tubers of *P. multiflorum*. Compounds **3** and **5** had ever been isolated from Radix Polygoni Multiflori originated from Deqing of Guangdong. Compound **6** has preventive and therapeutic effects on hepatic injury, counteracts lipid peroxidation and monoamine oxidase, and inhibits the increase of vascular endothelial growth factor (VEGF) and VEGF165 mRNA expression induced by lysophosphatidylcholine (LPC)[1]. The amount of compound **6** arrived 113 mg $(1.5\ kg)^{-1}$, which is highest in the eight compounds obtained in the research, indicating that *P. multiflorum* originated from Deqing of Guangdong has a bright future for the

prevetion and treatmetnent of atherosclerosis.

References

[1] Wu X Q. General review on chemical constituents and pharmacological effects of Radix Plygoni Multiflori [J]. Li Shi Zhen Med Mat Med Res, 2009, 20(1): 146-147.(in Chinese)

[2] Qi H Y, Zhang C F, Zhang M, et al. Three new anthraquinones from *Polygonum cillinerve* [J]. Chin Chem Lett, 2005, 16(8): 1050-1052.

[3] Kubo I, Murai Y, Soediro I, et al. Cytotoxic anthraquinones from *Rheum pulmatum* [J]. Phytochemistry, 1992, 31(3): 1063-1065.

[4] Hua Y, Zhou J Y, Ni W, et al. Studies on the constituents of *Reynoutria japonica* Houtt [J]. Nat Prod Res Dev, 2001, 13(6): 16-18.(in Chinese)

[5] Hu J M, Chen J J, Zhao Y X, et al. Chemical constituents from hulls of *Garcinia mangostana* [J]. Acta Bot Yunnan, 2006, 28(3): 319-322.

[6] Yuan Y, Chen W S, Zheng S Q, et al. Studies on chemical constituents in root of *Rumex patientia* L. [J]. Chin J Chin Mat Med, 2001, 26(4): 256-258.(in Chinese)

[7] Yang X W, Gu Z M, Ma C M, et al. A new indole derivative isolated from the root of tuber fleece flower (*Polygonum multiflorum*) [J]. Chin Trad Herb Drugs, 1998, 29(1): 5-11.

[8] Beistel D W, Edwards W D. The internal chemical shift-a key to bonding in aromatic molecules. 2. Substituent effects on the carbon-13 magnetic resonance spectra of the 1,4-disubstituted benzenes [J]. J Phys Chem, 1976, 80(18): 2023-2027.

[9] Liu X Q, Wu L J, Song G F, et al. Study on chemical constituents of *Polygonum cuspidatum* Sieb [J]. J Shenyang Pharm Univ, 1999, 16(Suppl.): 17-20.(in Chinese)