

- [9] 冯峰,文媛,优生,等.菝葜中黄酮和芪类成分的研究 [J].中国药科大学学报,2003,34(2):119.  
[10] 刘俊岭,热娜,堵年生.帕米尔红景天化学成分的研究 [J].天然产物研究与开发,2000,12(3):30.  
[11] 阮金兰,邹健,蔡亚玲.菝葜化学成分研究 [J].中药材,2005,28(1):24.  
[12] 邹建华,杨峻山.短瓣金莲花的化学成分研究 [J].中国药学杂志,2005,40(10):733.

## Studies on chemical constituents of rhizomes of Smilax china

XU Yan<sup>1,2</sup>, LIANG Jing-yu<sup>2</sup>, ZOU Zhong-mei<sup>1\*</sup>

(1) Institute of Medicinal Plant Development, Chinese Academy of Medical Sciences and Peking Union Medical College,  
Beijing 100193, China;

(2) Department of Natural Medicinal Chemistry, China Pharmaceutical University, Nanjing 210009, China)

**[Abstract]** **Objective:** To study the chemical constituents of the rhizomes of *Smilax china*. **Method:** The constituents of the rhizomes of *S. china* were isolated and purified by repeated silica gel and Sephadex LH - 20 chromatography, and their structures were elucidated on the basis of spectral analysis. **Result:** Thirteen compounds were obtained and identified as kaempferol-7-O-*D*-glucopyranoside (1), engeletin (2), isoengeletin (3), kaempferol (4), dihydrokaempferol (5), dihydrokaempferol-5-O-*D*-glucopyranoside (6), rutin (7), kaempferol-5-O-*D*-glucopyranoside (8), 3, 5, 4-trihydroxystibene (9), vanillic acid (10), 3, 5-dimethoxy-4-O-*D*-glucopyranosylcinnamic acid (11), *s*-sitosterol (12), and *d*-daucosterol (13), respectively. **Conclusion:** Compounds 1, 3, 7, 8, and 11 were isolated from this plant for the first time, and compounds 8 and 11 were isolated from the genus *Smilax* for the first time.

**[Key words]** *Smilax china*; flavonoids; phenolic acid; stilbene; sterols

[责任编辑 王亚君]

## 广东桑枝的化学成分研究

许延兰<sup>1</sup>, 李续娥<sup>1\*</sup>, 邹宇晓<sup>2</sup>, 陈纪军<sup>3</sup>

(1) 华南师范大学 广东省植物发育生物工程重点实验室, 广东 广州 510631;

2 广东省农业科学院, 广东 广州 510610;

3 中国科学院 昆明植物研究所 植物化学与西部植物资源持续利用国家重点实验室, 云南 昆明 650204)

**[摘要]** 目的:对桑科植物广东桑 *Morus atropurpurea* 桑枝的化学成分进行研究。方法:应用硅胶、聚酰胺、Sephadex LH - 20柱色谱技术进行分离纯化,并用 MS 和 NMR 分析鉴定化合物结构。结果:从 95%乙醇提取物中分离得到 11 个化合物,分别为 mulberrin (1), cyclomulberrin (2), 桑白皮素 (3), 环桑黄酮 (4), 2, 4, 4, 2-tetrahydroxy-3-[3-methylbut-3-enyl]-chalcone (5), mulberifran G (6), 东莨菪内酯 (7), moruchalcone A (8), 山柰酚 (9), 熊果酸 (10), 胡萝卜苷 (11)。结论:除 9, 11 外,其余化合物均首次从该植物中分离得到。

**[关键词]** 广东桑; 黄酮; 查耳酮; 三萜; 香豆素

**[中图分类号]** R 284.1 **[文献标识码]** A **[文章编号]** 1001-5302(2008)21-2499-04

[收稿日期] 2008-02-11

[基金项目] 广东省自然科学基金重点项目(05200575)

[通讯作者] \*李续娥, Tel: (020) 85211420, Fax: (020) 87596325, E-mail: liuxescnu@sohu.com

广东桑主要分布于华南地区,其同属植物白桑 *Monus abla* L. 为传统中药,树皮、枝、叶、果实均可入药,具有降压、抗菌、利尿、镇静等作用<sup>[1]</sup>。近 20 年来国内外对桑属植物作了大量研究,发现其中含有黄酮、二苯乙烯、苯骈呋喃等酚性化合物。国内外对白桑的研究较多,对广东桑化学成分的报道很少,仅见轧雾<sup>[2]</sup>等从种子中分到 10 个化合物。为促进桑树资源的综合利用,作者对广东桑桑枝的化学成分进行较系统的研究,从醋酸乙酯部分分离得到 11 个化合物,除化合物 9,10 外均首次从该植物中发现。

## 1 仪器与试药

VG Auto Spec 3000 型质谱仪,70 eV 电子轰击源,正离子电离源;Bruker AV - 400 MHz 和 DRX - 500 Hz 核磁共振仪,以 TMS 为内标测定。Sephadex LH - 20 为 Pharmacia 公司产品;柱色谱硅胶(200~300 目)和薄层硅胶 GF254 均为青岛美高有限公司生产。广东桑桑枝由广东农科院提供,经唐翠明副研究员鉴定为广东桑 *M. atropurpurea*。

## 2 提取与分离

广东桑干燥枝条(60 kg),粉碎后用 95% 的乙醇加热(50~70 ℃)浸泡 3 次,每次 2 d。提取液减压浓缩成浸膏后混悬于水中,依次用石油醚、醋酸乙酯、正丁醇萃取,回收溶剂得到石油醚部分(442 g)、醋酸乙酯部分(405 g)、正丁醇部分(474 g)、水部分(740 g)。醋酸乙酯萃取物经硅胶、聚酰胺、Sephadex LH - 20 柱色谱分离和纯化,得到 11 个化合物:化合物 1(1.147 g),2(239 mg),3(708 mg),4(83 mg),5(12 mg),6(16 mg),7(50 mg),8(180 mg),9(2 mg),10(620 mg),11(30 mg)。

## 3 结构鉴定

化合物 1 淡黄色粉末,ESI-MS  $m/z$  445 [M + Na]<sup>+</sup>,423 [M + H]<sup>+</sup>。<sup>1</sup>H-NMR(C<sub>5</sub>D<sub>5</sub>N,500 MHz): 13.88(1H,s,5-OH),12.26(2H,br s,-OH),7.58(1H,s,H-6),7.08(1H,d,J=2.1 Hz,H-3),6.95(1H,dd,J=7.3,2.1 Hz,H-5),6.76(1H,s,H-6),5.71(1H,t,J=7.2 Hz,H-17),5.6(1H,t,J=6.8 Hz,H-12),3.8(2H,d,J=7.2 Hz,H-16),3.6(1H,d,J=6.8 Hz,H-11),2.0(3H,s,H-20),1.81(3H,s,H-15),1.65(3H,s,H-19),1.63(3H,s,H-14)。<sup>13</sup>C-NMR(C<sub>5</sub>D<sub>5</sub>N,125 MHz): 158.5(C-2),120.8(C-3),183.2(C-4),156.4(C-5),98.8(C-6),162.8(C-7),106.9(C-8),162.7(C-9),105.0(C-10),25.0

(C-11),123.1(C-12),132.3(C-13),18.0(C-14),25.9(C-15),22.4(C-16),123.1(C-17),131.2(C-18),17.9(C-19),25.9(C-20),113.1(C-1),160.8(C-2),104.3(C-3),162.4(C-4),107.9(C-5),131.7(C-6)。以上数据与文献[3]一致,鉴定为 mulberrin。

化合物 2 淡黄色粉末,[ ]<sub>D</sub><sup>24.7</sup>-61.30 °(c 0.28,甲醇),FAB-MS  $m/z$  421 [M + H]<sup>+</sup>,405 [M - CH<sub>3</sub>]<sup>+</sup>。<sup>1</sup>H-NMR(DMSO-d<sub>6</sub>,400 MHz): 12.67(1H,s,5-OH),7.57(1H,d,J=8.6 Hz,H-6),6.55(1H,d,J=8.6 Hz,H-5),6.34(1H,d,J=1.6 Hz,H-3),6.25(1H,s,H-6),6.08(1H,d,J=9.4 Hz,H-11),5.35(1H,d,J=9.4 Hz,H-12),5.17(1H,t,J=6.5 Hz,H-17),3.34(2H,dd,J=14.6,6.8 Hz,H-16),1.85(3H,s,H-14),1.75(3H,s,H-15),1.62(3H,s,H-19 or 20),1.61(3H,s,H-20 or 19)。<sup>13</sup>C-NMR(DMSO-d<sub>6</sub>,100 MHz): 157.6(C-2),108.2(C-3),177.9(C-4),153.8(C-5),98.5(C-6),161.5(C-7),103.8(C-8),163.4(C-9),106.8(C-10),69.0(C-11),121.2(C-12),138.1(C-13),18.4(C-14),25.5(C-15),21.3(C-16),122.4(C-17),131.0(C-18),17.9(C-19),25.5(C-20),106.3(C-1),155.2(C-2),103.9(C-3),159.1(C-4),110.3(C-5),125.2(C-6)。以上数据与文献[4]一致,鉴定为 cyclo-mulberrin。

化合物 3 淡黄色粉末,ESI-MS  $m/z$  443 [M + Na]<sup>+</sup>,421 [M - H]<sup>+</sup>。<sup>1</sup>H-NMR(CDCl<sub>3</sub>,400 MHz): 7.16(1H,d,J=8.3 Hz,H-6),6.55(1H,d,J=10.0 Hz,H-16),6.53(1H,d,J=3.2 Hz,H-3),6.49(1H,d,J=2.1 Hz,H-5),6.17(1H,s,H-6),5.46(1H,d,J=10 Hz,H-17),5.09(1H,t,J=6.7 Hz,H-12),3.1(2H,dd,J=14.6,6.5 Hz,H-11),1.56(3H,s,H-14),1.40(3H,s,H-15),1.40(3H,s,19),1.38(3H,s,20)。<sup>13</sup>C-NMR(CDCl<sub>3</sub>,100 MHz): 155.3(C-2),121.3(C-3),182.4(C-4),161.1(C-5),99.8(C-6),155.3(C-7),101.2(C-8),152.2(C-9),104.9(C-10),24.3(C-11),120.8(C-12),131.6(C-13),17.6(C-14),25.6(C-15),114.7(C-16),127.1(C-17),78.1(C-18),28.1(C-19,20),112.3(C-1),159.4(C-2),103.8(C-3),160.3(C-4),108.3(C-5),133.2(C-6)。以上数据与文献[5]一致,鉴定为桑白皮素(morusin)。

**化合物4 黄色针晶(氯仿)**, ESI-MS  $m/z$  443 [M + Na]<sup>+</sup>。<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) : 12.84 (1H, s, 5-OH), 7.65 (1H, d,  $J$  = 8.5 Hz, H-6), 6.77 (1H, d,  $J$  = 10.0 Hz, H-16), 6.56 (1H, dd,  $J$  = 8.5 Hz, 1.4, H-5), 6.43 (1H, s, H-3), 6.26 (1H, s, H-6), 6.25 (1H, d,  $J$  = 6.7 Hz, H-11), 5.6 (1H, d,  $J$  = 10.0 Hz, H-15), 5.42 (1H, dd,  $J$  = 9.4, 3.8 Hz, H-12), 1.97 (3H, s, H-14), 1.70 (3H, s, H-15), 1.47 (6H, s, H-19, 20)。<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) : 158.1 (C-2), 108.8 (C-3), 178.6 (C-4), 155.0 (C-5), 100.2 (C-6), 161.7 (C-7), 104.6 (C-8), 160.9 (C-9), 101.4 (C-10), 69.8 (C-11), 120.9 (C-12), 139.5 (C-13), 18.7 (C-14), 25.9 (C-15), 114.8 (C-16), 127.6 (C-17), 77.9 (C-18), 28.1 (C-19), 28.2 (C-20), 109.6 (C-1), 151.1 (C-2), 105.5 (C-3) 159.1 (C-4), 109.8 (C-5), 125.2 (C-6)。以上数据与文献[4]一致, 鉴定为环桑黄酮(cyclomorusin)。

**化合物5 淡黄色粉末**, ESI-MS  $m/z$  363 [M + Na]<sup>+</sup>。<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 400 MHz) : 14.06 (1H, s, 2-OH), 8.02 (1H, d,  $J$  = 8.8 Hz, H-6), 7.76~7.73 (4H, m, H-1, 2, 6), 6.83 (2H,  $J$  = 7.6 Hz, H-3, 5), 6.44 (1H, d,  $J$  = 8.8 Hz, H-5), 4.62, 4.58 (each 1H, br s, H-4), 4.27 (1H, t,  $J$  = 6.4 Hz, H-2), 2.81 (1H, dd,  $J$  = 12.8, 6.8 Hz, H-1), 2.72 (1H, dd,  $J$  = 12.8, 6.8 Hz, H-1), 1.73 (3H, s, H-5)。<sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, 100 MHz) : 191.8 (C=O), 164.3 (C-2), 163.2 (C-4), 160.2 (C-4), 148.1 (C-3), 144.1 (C-1), 131.2 (C-2, 6), 130.1 (C-6) 125.8 (C-1), 117.4 (C-1), 115.9 (C-3, 5), 112.5 (C-1), 112.5 (C-3), 109.8 (C-4), 107.5 (C-5), 73.4 (C-2), 29.0 (C-1), 17.3 (C-5)。以上数据与文献[6]一致, 鉴定为2,4,4,2-tetrahydroxy-3-{3-methylbut-3-enyl}-chalcone。

**化合物6 褐色结晶(甲醇)**, <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 400 MHz) : 7.98 (1H, d,  $J$  = 8.6 Hz, H-4), 7.56 (1H, d,  $J$  = 8.6 Hz, H-19), 7.52 (1H, br s, H-11), 7.42 (1H, s, H-14), 7.40 (1H, s, H-20), 7.37 (1H, d,  $J$  = 8.4 Hz, H-13), 7.21 (1H, d,  $J$  = 1.9 Hz, H-7), 7.19 (1H, s, H-17), 7.08 (1H, d,  $J$  = 2.0 Hz, H-6), 7.06 (1H, d,  $J$  = 0.6 Hz, H-3), 7.01 (1H, d,  $J$  = 2.0 Hz, H-2), 6.65 (1H, dd,  $J$  = 8.6, 2.0 Hz, H-5), 2.77 (1H, dd,  $J$  = 17.0, 5.2 Hz, H-6), 2.24 (1H, dd,

$J$  = 16.0, 11.2 Hz, H-6), 1.83 (3H, s, H-7)。以上数据与文献[7]一致, TLC与mulberrofran G标准品对照(甲醇 氯仿 15:85)R<sub>f</sub>值一致, 故鉴定为mulberrofran G。

**化合物7 无色针晶(氯仿 甲醇)** ESI-MS  $m/z$  215 [M + Na]<sup>+</sup>, 193 [M + H]<sup>+</sup>。<sup>1</sup>H-NMR (C<sub>5</sub>D<sub>5</sub>N, 400 MHz) : 7.70 (1H, d,  $J$  = 9.6 Hz, H-4), 7.12 (1H, s, H-5), 7.05 (1H, s, H-8), 6.32 (1H, dd,  $J$  = 9.2, 0.8 Hz, H-3), 3.78 (3H, s, 6-OCH<sub>3</sub>)。<sup>13</sup>C-NMR (C<sub>5</sub>D<sub>5</sub>N, 100 MHz) : 161.6 (C-2), 153.1 (C-7), 151.1 (C-9), 146.3 (C-6), 144.2 (C-4), 112.4 (C-5), 111.2 (C-10), 109.5 (C-3), 104.2 (C-8), 56.3 (-OCH<sub>3</sub>)。以上数据与文献[8]一致, 故鉴定为东莨菪内酯。

**化合物8 黄色粉末**, ESI-MS  $m/z$  363 [M + Na]<sup>+</sup>, 341 [M + H]<sup>+</sup>。<sup>1</sup>H-NMR (C<sub>5</sub>D<sub>5</sub>N, 400 MHz) : 15.2 (1H, br s, H-2), 8.96 (1H, d,  $J$  = 15.2 Hz, H-1), 8.28 (1H, d,  $J$  = 15.2 Hz, H-1), 8.11 (1H, d,  $J$  = 8.8 Hz, H-6), 7.89 (1H, d,  $J$  = 8.4 Hz, H-6), 6.94 (1H, s, H-3), 6.86 (1H, d,  $J$  = 8.4 Hz, H-5), 6.75 (1H, d,  $J$  = 8.4 Hz, H-5), 5.78 (1H, t,  $J$  = 6.8 Hz, C-8), 3.90 (2H, d,  $J$  = 6.8 Hz, C-7), 1.94 (3H, s, H-5), 1.69 (3H, s, H-4)。<sup>13</sup>C-NMR (C<sub>5</sub>D<sub>5</sub>N, 100 MHz) : 193.4 (C=O), 165.3 (C-2), 163.7 (C-4), 163.5 (C-4), 161.5 (C-2), 141.8 (C-1), 132.4 (C-2), 132.4 (C-6), 129.9 (C-6), 131.3 (C-3), 124.0 (C-2), 117.3 (C-1), 116.4 (C-1), 115.3 (C-3), 114.3 (C-1), 108.0 (C-5), 104.0 (C-3), 26.1 (C-5), 22.8 (C-1), 18.2 (C-4)。以上数据与参考文献[9]一致, 鉴定为moruchalcone A。

**化合物9 淡黄色粉末**, ESI-MS (+)  $m/z$  286 [M]<sup>+</sup>。<sup>1</sup>H-NMR (C<sub>5</sub>D<sub>5</sub>N, 400 MHz) : 13.36 (1H, s, 5-OH), 8.54 (1H, d,  $J$  = 8.8 Hz, H-3, 5), 7.33 (1H, d,  $J$  = 8.8 Hz, H-2, 6), 6.87 (1H, d,  $J$  = 2.0 Hz, H-6), 6.77 (1H, d,  $J$  = 2.0 Hz, H-8)。<sup>13</sup>C-NMR (C<sub>5</sub>D<sub>5</sub>N, 100 MHz) : 137.9 (C-2), 147.6 (C-3), 177.4 (C-4), 162.5 (C-5), 99.3 (C-6), 165.6 (C-7), 94.4 (C-8), 157.5 (C-9), 104 (C-10), 130.6 (C-2, 6), 160.8 (C-4), 116.4 (C-3, 5)。以上数据与文献[2]一致, 鉴定为山柰酚(kaempferol)。

**化合物10 白色粉末**, ESI-MS  $m/z$  455 [M - H]<sup>-</sup>。<sup>1</sup>H-NMR (C<sub>5</sub>D<sub>5</sub>N, 500 MHz) 与<sup>13</sup>C-NMR (C<sub>5</sub>D<sub>5</sub>N, 125 MHz)。以上数据与文献[2]一致, 鉴

定为熊果酸 (ursolic acid)。

化合物 11 白色无定形粉末 , 经硅胶 TLC 与胡萝卜苷标准品对照 ( 甲醇 氯仿 10:90) Rf 值一致 , 混合熔点不下降 , 鉴定为 胡萝卜苷。

#### 4 讨论

分离得到的化合物除化合物 5 外 , 其他化合物均可以在白桑中找到。由此可见广东桑枝与桑白皮的化合物种类及结构相近 , 黄酮类化合物均具有异戊烯基 , 两者具有一定的替代性。但是广东桑中化合物譬如化合物 5 (2,4,4,2'-tetrahydroxy-3-{3-methylbut-3-enyl}-chalcone) 的异戊烯基具有更多的变化 , 这一点有待于进一步研究。另外 , 广东桑枝中的化合物种类和含量都有别于其种子。

#### [参考文献]

- [1] 国家中医药管理局中华本草编委会 . 中华本草 . 第 2 卷 [M]. 上海 : 上海科学出版社 , 1999: 525.
- [2] 车 霖 , 张小琦 , 叶文才 , 等 . 广东桑种子的化学成分研究 [J]. 中国药科大学学报 , 2006, 37(4): 301.

- [3] Nomura T, Fukai T, Katayanagi M, Kuwanon A, B, C and oxydihydromorusin, four new flavones from the root bark of the cultivated mulberry tree (*Morus alba* L.) [J]. Chem Pharm Bull, 1977, 25: 529.
- [4] Chen Chienchin, Huang Yulin, Ou Junchin Three new prenylflavones from *Artocarpus altilis* [J]. J Nat Prod, 1993, 56: 1594.
- [5] Nomura T, Fukai T, Yamada S, et al Phenolic constituents of the cultivated mulberry tree (*Morus alba* L.) [J]. Chem Pharm Bull, 1976, 24(11): 2898.
- [6] Elsohly H N, Joshi A S, Nimbard A C, et al Antifungal chalcones from *Maclura tinctoria* [J]. Planta Med, 2001, 67: 87.
- [7] Fukai T, Hano Y, Hirakura K, et al Structures of two natural hypotensive Diels-Alder type adducts, mulberrofuran F and G from the cultivated mulberry tree (*Morus thom Koidz*) [J]. Chem Pharm Bull, 1985, 33(8): 3195.
- [8] 张光浓 , 张朝凤 , 罗英 , 等 . 球花石斛的化学成分 ( ) [J]. 中国天然药物 , 2005, 3(5): 287.
- [9] Monache G D, Rosa M C D, Scurria S, et al Comparison between metabolite productions in cell culture and in whole plant of *Maclura pomifera* [J]. Phytochemistry, 1995, 39(3): 575.

## Studies on chemical constituents from twigs of *Morus atropurpurea*

XU Yan-lan<sup>1</sup>, LI Xu-e<sup>1\*</sup>, ZOU Yu-xiao<sup>2</sup>, CHEN Ji-jun<sup>3</sup>

(1. Guangdong Provincial Key Lab of Biotechnology for Plant Development, South China Normal University,

Guangzhou 510631, China; 2. Guangdong Academy of Agricultural Sciences, Guangzhou 510610, China

3. State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, China)

**[Abstract]** **Objective:** To study the chemical constituents of the twigs of *Morus atropurpurea*. **Method:** The compounds of the EOAc fraction were isolated and purified by column chromatography on silica gel, polyamide, Sephadex LH - 20, and their structures were elucidated on the basis of spectroscopic evidence (MS, NMR). **Result:** Eleven compounds were identified as mulberrin (1), cyclomulberrin (2), morusin (3), cyclomorusin (4), 2,4,4,2'-tetrahydroxy-3-{3-methylbut-3-enyl}-chalcone (5), mulberrofran G (6), scopoletin (7), moruchalcone A (8), kaempferol (9), ursolic acid (10), daucosterol (11). **Conclusion:** Except compounds 9 and 11, all the other compounds were obtained from *M. atropurpurea* for the first time.

**[Key words]** *Morus atropurpurea*; flavonoids; chalcones; triterpenoid; coumarin

[责任编辑 王亚君 ]

投稿请登录《中国中药杂志》网站：  
[www.cjcm.com.cn](http://www.cjcm.com.cn); [www.chinajcm.com](http://www.chinajcm.com)