

文章编号:1001-6880(2014)3-0348-03

长毛风车子的化学成分研究

刘兆花¹,王艳婷¹,刘寿柏²,钟惠民^{1*}¹青岛科技大学化学与分子工程学院,青岛 266042;²中国热带农业科学院热带生物技术研究所,海南省黎药资源天然产物研究与利用重点实验室,海口 571101

摘要:对采自海南三亚的长毛风车子(*Combretum pilosum Roxb.*)的化学成分进行研究。应用硅胶、Sephadex LH-20 等柱色谱技术进行分离纯化,并运用现代波谱技术(EI-MS,¹H NMR,¹³C NMR)进行结构鉴定。从长毛风车子中分离得到了7个化合物,分别为木栓酮(1)、常春藤皂苷元(2)、植物醇(3)、香荚兰醛(4)、 β -谷甾醇(5)、乌苏酸(6)、羽扇豆醇(7)。以上化合物均为首次从该植物中分离得到。

关键词:长毛风车子;化学成分;分离;结构鉴定

中图分类号:R284.2

文献标识码:A

Studies on the Chemical Constituents of *Combretum pilosum Roxb.*

LIU Zhao-hua¹, WANG Yan-ting¹, LIU Shou-bai², ZHONG Hui-min^{1*}¹College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China;²Hainan Key Laboratory for research and Development of Natural Products from Li Folk Medicine, Institute of Tropical Bioscience and biotechnology, Chinese Academy of Tropical Agriculture Sciences, Haikou 571101, China

Abstract: The current report studied the chemical constituents of *Combretum pilosum Roxb.* collected from Hainan Province in China. In order to study the chemical constituents from the *Combretum pilosum Roxb.*, Silica gel and Sephadex LH-20 column chromatography were used to isolate the chemical constituents, and the structures of compounds were identified by spectral analysis such as ¹H NMR, ¹³C NMR and EI-MS. Seven compounds were isolated and identified as: Friedelin(1)、Hederagenin(2)、Phytol(3)、Vanillin(4)、 β -sitosterol(5)、Ursolic acid(6)、Lupeol(7), which were isolated from *Combretum pilosum Roxb.* for the first time.

Key words: *Combretum pilosum Roxb.*; chemical constituents; isolate; structure identification

长毛风车子(*Combretum pilosum Roxb.*)为使君子科风车子属植物,使君子科植物主要为乔木、灌木,稀为木质藤本。主要产于热带,其中亚洲、非洲较多;亚热带地区也有分布,其中风车子属和榄仁树属为泛热带大属。使君子科植物大多为常用中药,在我国资源丰富,有悠久的临床应用历史。风车子属在我国主要分布在云南、海南等地,该属植物的根、茎、叶、花和种子均可作为药用部位,用于治疗麻风、肝炎、痢疾、呼吸道感染以及癌症等^[1]。目前,已从使君子科风车子属植物中得到了二苯乙烯类、黄酮类、五环三萜类、甾体类、生物碱类、大环内酯类、脂肪酸类等多种有效成分^[2]。目前未见有关长毛风车子化学成分研究的文献报道,为揭示长毛风车子的化学物质基础,对全草的化学成分进行了研

究,从石油醚提取部分中分离鉴定了7个单体化合物。

1 实验部分

1.1 仪器和材料

柱层析硅胶(200~300目)和薄层层析硅胶为青岛海洋化工厂产品,Sephadex LH-20为Merck公司产品。核磁共振仪,Bruker Avance500型,德国Bruker公司;旋转蒸发仪,E-52型,上海亚荣生化仪器厂;Buchi 中压制备色谱仪,653型,瑞士Buchi公司;循环水多用真空泵,SHB-3型,上海亚荣盛华仪器厂;显微熔点仪,SGW X-4型,上海精密仪器有限公司;质谱仪,Agilent Technology5975C。

溶剂均为分析纯。长毛风车子样品于2011年2月采自海南省昌江黎族自治县,经中国热带农业科学院热带生物技术研究所刘寿柏博士鉴定为使君子科风车子属长毛风车子。植物凭证标本

(CN2011023)存放于中国热带农业科学院热带生物技术研究所。

1.2 提取和分离

长毛风车子枝叶(20 kg)用95%工业乙醇浸提3次,每次7 d。减压回收乙醇至无醇味,得乙醇提取物,然后用水分散成悬浊液后,依次用石油醚,乙酸乙酯,正丁醇各萃取3次,分别浓缩得浸膏。将石油醚提取的浸膏(98 g)经反复硅胶柱层析(石油醚-乙酸乙酯,体积比80:1→5:1),得到10个流份(I、II、III、IV、V、VI、VII、VIII、IX、X);流份III(18 g)依次经Sephadex LH-20凝胶色谱(95%乙醇)和硅胶柱色谱(石油醚-乙酸乙酯,体积比为50:1→20:1)分离,得到化合物1(20.6 mg)、2(19.8 mg)、5(14.7 mg);流份IX(20 g),依次经Sephadex LH-20凝胶(95%乙醇)和硅胶柱色谱(石油醚-丙酮,体积比为40:1→10:1)分离,得到化合物3(10.3 mg)、4(14.5 mg)、6(16.8 mg)、7(15.9 mg)。

2 结构鉴定

化合物1 白色针状晶体,mp. 260~265 °C,分子式 $C_{30}H_{50}O$,¹H NMR(500 MHz, CDCl₃, δ): 0.88(3H, s, H-23), 0.72(3H, s, H-24), 0.87(3H, s, H-25), 1.05(3H, s, H-26), 1.01(3H, s, H-27), 1.17(3H, s, H-28), 1.00(3H, s, H-29), 1.88(3H, s, H-30), 2.21~2.30(2H, m, H-2), 2.35~2.41(1H, m, H-4);¹³C NMR(125 MHz, CDCl₃, δ): 22.4(C-1), 41.5(C-2), 212.9(C-3), 58.2(C-4), 42.2(C-5), 41.4(C-6), 18.3(C-7), 53.1(C-8), 37.5(C-9), 59.6(C-10), 35.6(C-11), 30.5(C-12), 39.7(C-13), 38.3(C-14), 32.5(C-15), 36.1(C-16), 30.0(C-17), 42.9(C-18), 35.4(C-19), 28.2(C-20), 32.9(C-21), 39.2(C-22), 6.80(C-23), 14.7(C-24), 18.0(C-25), 18.7(C-26), 20.3(C-27), 32.1(C-28), 31.8(C-29), 35.0(C-30)。以上数据与文献数据^[3]报道基本一致,故鉴定化合物1为木栓酮。

化合物2 白色针状晶体,mp. 290~300 °C, EI-MS m/z : 472[M]⁺。¹H NMR(500 MHz, DMSO, δ): 0.66, 0.85, 0.88, 0.93, 1.03, 1.12(each 3H, s, 6×CH₃); 5.14(1H, brs, H-12);¹³C NMR(125 MHz, DMSO, δ): 38.5(C-1), 27.7(C-2), 71.0(C-3), 42.4(C-4), 47.6(C-5), 18.1(C-6), 33.3(C-7), 39.4(C-8), 47.1(C-9), 36.8(C-10), 23.8(C-11), 122.1(C-12), 144.5(C-13), 41.9(C-14), 27.5(C-15), 23.4

(C-16), 46.2(C-17), 41.5(C-18), 46.0(C-19), 30.8(C-20), 34.0(C-21), 32.7(C-22), 65.2(C-23), 13.1(C-24), 15.9(C-25), 17.4(C-26), 26.2(C-27), 179.0(C-28), 32.6(C-29), 23.2(C-30)。以上数据与文献数据^[4]报道基本一致,故鉴定化合物2为常春藤皂苷元。

化合物3 透明油状物,5%硫酸-乙醇溶液反应显紫色。EI-MS m/z : 319[M+Na]⁺。¹H NMR(500 MHz, CDCl₃, δ): 5.41(1H, d, J =7.2 Hz, H-2), 4.16(2H, d, J =7.2 Hz, H-1), 2.00(2H, d, J =6.8 Hz, H-4), 1.67(3H, s, H-20), 1.60~1.00(19H, m), 1.01~0.87(12H, brs);¹³C NMR(125 MHz, CDCl₃, δ): 59.4(C-1), 123.1(C-2), 140.3(C-3), 39.8(C-4), 25.1(C-5), 36.7(C-6), 32.7(C-7), 37.4(C-8), 24.4(C-9), 37.4(C-10), 32.6(C-11), 37.3(C-12), 24.8(C-13), 39.3(C-14), 27.9(C-15), 22.7, 22.6(C-16, 17), 19.7, 19.7(C-18, 19), 16.2(C-20)。以上数据与文献数据^[5]报道基本一致,故鉴定化合物3为植物醇。

化合物4 白色针晶,mp. 80~82 °C, EI-MS m/z : 152[M]⁺。¹H NMR(500 MHz, CDCl₃, δ): 9.83(1H, s), 7.43(2H, m, 6-H, H-2), 7.04(1H, d, J =9.0 Hz, H-5), 6.40(1H, brs, -OH), 3.96(3H, s, -OCH₃)。¹³C NMR(125 MHz, CDCl₃, δ): 190.79(-CHO), 151.81(C-4), 147.26(C-3), 129.88(C-6), 127.42(C-1), 114.45(C-2), 108.80(C-5), 56.11(-OCH₃)。以上数据与文献数据^[6]报道基本一致,故鉴定化合物4为香茅兰醛。

化合物5 白色针状结晶,mp. 136~138 °C。¹H NMR(500 MHz, CDCl₃, δ): 5.35(1H, d, H-6), 3.54(1H, m, H-3), 2.26(2H, m, H-4), 2.00(2H, t, H-7), 1.66(1H, m, 3-OH);¹³C NMR(125 MHz, CDCl₃, δ): 37.1(C-1), 31.5(C-2), 72.0(C-3), 42.0(C-4), 140.9(C-5), 120.8(C-6), 31.6(C-7), 31.9(C-8), 49.9(C-9), 36.0(C-10), 20.8(C-11), 38.9(C-12), 41.8(C-13), 56.7(C-14), 24.0(C-15), 27.6(C-16), 55.8(C-17), 11.9(C-18), 19.5(C-19), 39.5(C-20), 21.1(C-21), 31.0(C-22), 23.0(C-23), 29.3(C-24), 29.8(C-25), 20.0(C-26), 19.1(C-27), 23.3(C-28), 12.0(C-29)。以上数据与文献数据^[7]报道基本一致,故鉴定化合物5为β-谷甾醇。

化合物6 白色粉末,mp. 230~238 °C,硫酸-

乙醇显红色。EI-MS m/z : 456 [M]⁺。¹H NMR (CDCl₃, 500 MHz) δ: 2.08 (1H, d, H-18), 3.11 (1H, t, H-3), 5.24 (1H, t, H-12), 0.80 (3H, d, J = 7.4 Hz, H-29), 0.70 (3H, d, J = 7.4 Hz, H-30), 1.24, 1.08, 0.87, 0.84, 0.75 (5 × 3H, s); ¹³C NMR (CDCl₃, 125 MHz) δ: 38.5 (C-1), 27.1 (C-2), 79.0 (C-3), 38.6 (C-4), 55.1 (C-5), 18.5 (C-6), 33.0 (C-7), 39.4 (C-8), 47.8 (C-9), 37.2 (C-10), 23.2 (C-11), 125.6 (C-12), 138.0 (C-13), 42.3 (C-14), 28.1 (C-15), 24.2 (C-16), 47.9 (C-17), 52.6 (C-18), 39.1 (C-19), 38.7 (C-20), 30.9 (C-21), 36.4 (C-22), 28.0 (C-23), 15.7 (C-24), 15.6 (C-25), 17.0 (C-26), 23.5 (C-27), 181.0 (C-28), 17.3 (C-29), 21.2 (C-30)。以上数据与文献数据^[8]报道基本一致,故鉴定化合物6为乌苏酸。

化合物7 白色粉末,硫酸-乙醇显紫色,mp. 200~210 °C。EI-MS m/z : 427 [M + H]⁺。¹H NMR (CDCl₃, 500 MHz) δ: 0.74, 0.80, 0.81, 0.95, 0.98, 1.02, 1.66 (each 3H, s, Me-23, 24, 25, 26, 27, 28, 30), 3.14 (1H, dd, J = 5.2, 10.6 Hz, H-3), 4.57 (1H, brs, H-29β), 4.65 (1H, d, J = 1.7 Hz, H-29α); ¹³C NMR (CDCl₃, 125 MHz) δ: 38.6 (C-1), 27.7 (C-2), 78.0 (C-3), 38.8 (C-4), 55.3 (C-5), 18.2 (C-6), 34.5 (C-7), 41.0 (C-8), 50.3 (C-9), 37.1 (C-10), 21.1 (C-11), 25.0 (C-12), 38.1 (C-13), 43.0 (C-14), 27.2 (C-15), 35.5 (C-16), 43.2 (C-17), 48.3 (C-18), 48.0 (C-19), 150.7 (C-20), 29.8 (C-21), 40.1 (C-22), 27.8 (C-23), 15.3 (C-24), 16.2 (C-25), 15.6 (C-26), 14.3 (C-27), 18.0 (C-28), 109.1 (C-29), 19.5 (C-30)。以上数据与文献数据^[9]报道基本一

致,故鉴定化合物7为羽扇豆醇。

参考文献

- Banskota AH, Tezuka Yasuhiro, Phung L K, et al. Cytotoxic cycloartane-type triterpenes from *combretem quadrangulare*. *Bioorganic & Medicinal Chemistry Letters*, 1998, 8: 3519-3524.
- Wu XP(吴晓鹏), Chen GY(陈光英), Jiang CW(蒋才武), et al. Research advances in the chemical constituents and pharmacological functions of *Combretem*. *J Hainan Normal Univ*(海南师范大学学报), 2007, 20: 63-66.
- SR anjanyulu, et al. New nor-tmterpenes from *elaeodendron glaucum*. *Phytochemistry*, 1980, 19: 1163-1169.
- Ktzu H, Hirabyasht S, Sumkt M, et al. Studies on the Constituents of *Hedeea rhombea* Bean. IV. On the Hederagenin Glycosides(2). *Chem Pharm Bull*, 1985, 33: 3474.
- Brown G. Phytene-1,2-diol from *Artenisia annua*. *Phytochemistry*, 1994, 36: 1553.
- Liu YM(刘玉明), Liang GY(梁广义), Zhang JX(张建新), et al. Studies on chemical constituents of *Dichondra repens*. *Chin Pharm J*(中国药学杂志), 2002, 37: 577-579.
- Chi X(迟祥), Guo ML(郭美丽), Song H(宋慧) et al. Study on chemical constituents of *Celosia cristata* seed. *J Jilin Agric Univ*(吉林农业大学学报), 2010, 32: 657-660.
- Zhang J(张洁), Yu R(喻蓉), Wu X(吴霞), et al. Studies on the chemical constituents of *Ilex cornuta*. *Nat Prod Res Dev*(天然产物研究与开发), 2008, 20: 821-823.
- Huang XJ(黄晓君), Yin ZQ(殷志琦), Ye WC(叶文才), et al. Chemical constituents from fruits of *Ligustrum lucidum*. *China J Chin Mater Med*(中国中药杂志), 2010, 35: 861-864.

(上接第353页)

- Chang TS. Two potent suicide substrates of mushroom tyrosinase: 7,8,4'-trihydroxyisoflavone and 5,7,8,4'-tetrahydroxyisoflavone. *J Agric Food Chem*, 2007, 55: 2010-2015.
- Hayashi T, Thomson R. Isoflavones from *Dipteryx Odorata*. *Phyto*, 1974, 13: 1943-1946.
- Naim M, Gestetneer B, Zilkah S, et al. Soybean isoflavones characterization, determination, and antifungal activity. *J Ag-*

ric Food Chem, 1974, 22: 806-810.

- Ji GE. Stucture-function analysis of transfromed phytochemical glycosides. *FASEB J*, 2009, 23: 111.
- Theil C, Brises V, Gerber B, et al. The efects of different lignans and isofavones, tested as aglycones and glycosides, on hormone receptor-positive and negative breast carcinoma cells in vitro. *Arch Gynecol Obstet*, 2011, 284: 459-465.