文章编号: 1001-6880(2009)04-0600-04

头花马先蒿和管花马先蒿的化学成分

杨佳倩[1],贺文军[2],谭宁华[2*],褚洪标[2],张玉梅[2],梅文莉[1],戴好富[1]

[1]中国热带农业科学院热带生物技术研究所,海口 571101;

[2]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,昆明 650204

摘 要:从头花马先蒿全草中发现 13个化合物,经波谱分析鉴定为:(±)松脂素(1)、金合欢素(2)、木犀草素(3)、7去氧栀子新苷(4)、yuheinoside(5)、euphroside(6)、mussaenosidic acid(7)、莫桑苷(8)、桃叶珊瑚苷(9)、角胡麻苷(10)、异角胡麻苷(11)、贞桐苷 A(12)和开德苷元(13)。从管花马先蒿全草中发现 4个化合物,经鉴定为:(+)-dehydrovomifoliol(14)、催吐萝芙木醇(15)、ω-hydroxypropioguaiacone(16)和 3-hydroxy-1-(4-hydroxy-3, 5-dimethoxyphenyl)-1-propanone(17)。所有化合物均为首次在该种中发现。

关键词:头花马先蒿;管花马先蒿;化学成分

中图分类号: Q946.91; R285 **文献标识码**: A

Chemical Constituents of *Pedicularis cephalantha* Franch and *P. siphonantha* Don

YANG Jia-qian[1], HE Wen-jun[2], TAN Ning-hua[2*], CHU Hong-biao[2], ZHANG Yu-mei[2], MEI Wen-li[1], DAI Hao-fu[1]

[1] *Institute of Tropical Bioscience and Biotechnology, Chinese Academy of Tropical Agriculture Sciences, Haikou 571101, China;* [2] *State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, China*

Abstract: Thirteen compounds were isolated from the whole plants of *Pedicularis cephalantha*, which were identified as (±)-pinoresinol(**1**), acacetin(**2**), luteolin(**3**), 7-deoxygardoside(**4**), yuheinoside(**5**), euphroside(**6**), mussaenosidic acid(**7**), mussaenoside(**8**), aucubin(**9**), martynoside(**10**), isomartynoside(**11**), clerodenoside A(**12**) and kidjolanin(**13**). Four compounds were isolated from the whole plants of *P. siphonantha*, which were identified as (+)-dehydrovomifoliol(**14**), vomifoliol(**15**), ω-hydroxypropioguaiacone(**16**) and 3-hydroxy-1-(4-hydroxy-3, 5-dimethoxyphenyl)-1-propanone(**17**).

Key words: *Pedicularis cephalantha; Pedicularis siphonantha*; chemical constituents

玄参科(Scorphulariaceae)马先蒿属(*Pedicularis*)植物有 600种以上,为双子叶植物中大属之一。我国有 329种,广泛分布于全国各省,西南部较多。马先蒿属药用种类繁多,应用历史悠久,疗效优良。我们曾从马先蒿属植物中分离发现黄酮、环烯醚萜、苯丙素等类型化合物[1-5],其中苯丙素类化合物[6]显示一定的抗氧化和抗肿瘤等生物活性[7]。为进一步研究马先蒿属植物的化学成分,本文对两种未报道化学成分的云南产马先蒿属植物:头花马先蒿(*Pedicularis cephalantha* Franch)全草和管花马先蒿(*P. siphonantha* Don)全草的化学成分进行了研究。从头花马先蒿全草中分离鉴定了 13个化合物:(±)松脂素(1),金合欢素(2),木犀草素(3),7去氧栀子新苷(4),yuheinoside(5),euphroside(6),mussaenosidic acid(7),莫桑苷(8),桃叶珊瑚苷(9),角胡麻苷(10),异角胡麻苷(11),贞桐苷 A(12)和开德苷元(13)。从管花马先蒿全草中分离鉴定了 4个化合物:(+)-dehydrovomifoliol(14),催吐萝芙木醇(15),ω-hydroxypropioguaiacone(16)和 3-hydroxy-1-(4-hydroxy-3, 5-dimethoxyphenyl)-1-propanone(17)。所有化合物均为首次在该种中发现,其结构类型包括环烯醚萜苷、苯丙素苷、黄酮、木脂素、C21甾体和降倍半萜;化合物 2, 3, 5, 6, 8~11我们先后从三色马先蒿(*P. tricolor*)[1]、长舟马先蒿(*P. dolichocymba*)[2-3]、大王马先蒿(*P. rex*)[4]、密穗马先蒿(*P. densispica*)[5]中报道过。

收稿日期: 2008-01-23 接受日期: 2008-02-29

*通讯作者 E-mail: nhtan@mail.kib.ac.cn

1 实验部分

1.1 仪器与材料

SEPA-300旋光仪; VG Autospec-3000型质谱仪; Bruker AM-400和 DRX-500超导核磁共振仪, TMS为内标;薄层层析板和柱色谱硅胶(青岛海洋化工厂); Sephadex LH-20 (Pharmacia);反相填充材料 Lichroprep RP-18 (40～63 μm,德国默克公司); HPLC (Zorbax ODS-C_{18})为 Agilent 1100型。

1.2 提取与分离

头花马先蒿全草 4.5 kg(2004年 8月采集于云南省格山花卉公司附近,由中国科学院昆明植物研究所王红研究员鉴定)。经粉碎用 95%乙醇回流提取 3次,得浸膏 850 g。经硅胶柱以氯仿、氯仿/甲醇系统梯度洗脱,每 1000 mL为一馏份,共收集 180份。TLC薄层检测后合并相同部分,得 A～I共 9个分段部分。B部分经硅胶柱以氯仿/丙酮/氯仿/异丙醇洗脱,并用凝胶柱(氯仿/甲醇, 2∶1和甲醇系统)纯化得到化合物 **1** (4.8 mg), **2**[5] (5.2 mg), **3**[1,4] (4.8 mg), **13** (31.4 mg); C部分通过硅胶柱反复以氯仿/甲醇、乙酸乙酯/甲醇梯度洗脱,并经凝胶和 HPLC分离得化合物 **4** (22.3 mg), **5**[4] (7.2 mg), **6**[4] (106.0 mg), **7** (16.0 mg), **8**[4] (9.6 mg), **9**[2,4] (12.7 mg), **10**[3-5] (10.3 mg), **11**[4] (6.6 mg), **12** (20.3 mg)。

管花马先蒿全草 8 kg(2004年 8月采集于云南省格山花卉公司附近,由中国科学院昆明植物研究所王红研究员鉴定)的提取和分离方法同头花马先蒿,得总浸膏 2 kg,通过硅胶,凝胶,以及 HPLC分离得化合物 **14** (2 mg), **15** (5 mg), **16** (4 mg), **17** (3 mg)。

2 结构鉴定

化合物 1 $C_{20}H_{22}O_6$,为无色油状物,易溶于氯仿。$[\alpha]_D^{19}$ 0.0 °(*c* 0.06, $CHCl_3$)。FAB$^+$-MS *m/z*: 358 $[M]^+$。^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.74 (2H, d, *J* = 3.9 Hz, H-7, 7′), 3.11 (2H, m, H-8, 8′), 4.25 (2H, dd, *J* = 8.9, 6.7 Hz, H-9a, 9′a), 3.88 (2H, dd, *J* = 9.3, 3.4 Hz, H-9b, 9′b), 3.91 (6H, s, 3, 3′-OMe), 5.62 (2H, br s, OH), 6.81～6.90 (6H, m, H of arom); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.9 (s, C-1, 1′), 108.6 (d, C-2, 2′), 146.7 (s, C-3, 3′), 145.2 (s, C-4, 4′), 114.3 (d, C-5, 5′), 119.0 (d, C-6, 6′), 85.9 (d, C-7, 7′), 54.2 (d, C-8, 8′), 71.7 (t, C-9, 9′), 56.0 (q, 3, 3′-OMe)。以上波谱数据与文献[8]报道的一致,化合物鉴定为(±)-松脂素。

化合物 4 $C_{16}H_{22}O_9$,为无色油状物,易溶于甲醇。FAB$^-$-MS *m/z*: 357 $[M-H]^-$。^{1}H NMR (400 MHz, CD_3OD) δ: 5.46 (1H, d, *J* = 4.6 Hz, H-1), 7.42 (1H, s, H-3), 2.75 (1H, m, H-5), 1.82～2.30 (4H, m, H-6, 7), 2.97 (1H, dd, *J* = 12.6, 6.4 Hz, H-9), 5.08 (1H, d, *J* = 1.6 Hz, H-10a), 5.04 (1H, d, *J* = 1.5 Hz, H-10b), 4.70 (1H, d, *J* = 7.8 Hz, H-1′), 3.21～3.43 (4H, m, H-2′, 3′, 4′, 5′), 3.84 (1H, dd, *J* = 11.0, 1.7 Hz, H-6′a), 3.64 (1H, dd, *J* = 11.6, 4.8 Hz, H-6′b); ^{13}C NMR (100 MHz, CD_3OD) δ: 95.6 (d, C-1), 152.9 (d, C-3), 110.6 (s, C-4), 34.8 (d, C-5), 30.8 (t, C-6), 31.5 (t, C-7), 150.1 (s, C-8), 46.0 (d, C-9), 109.4 (t, C-10), 99.5 (d, C-1′), 74.4 (d, C-2′), 77.6 (d, C-3′), 71.4 (d, C-4′), 77.9 (d, C-5′), 62.7 (t, C-6′)。其波谱数据与文献[9]报道一致,化合物鉴定为 7-去氧栀子新苷。

化合物 7 $C_{16}H_{24}O_{10}$,为无色油状物,易溶于甲醇。FAB$^-$-MS *m/z*: 375 $[M-H]^-$。^{1}H NMR (400 MHz, CD_3OD) δ: 5.45 (1H, d, *J* = 4.1 Hz, H-1), 7.40 (1H, s, H-3), 1.45～2.29 (6H, m, H-5, 6, 7, 9), 1.32 (1H, s, H-10), 4.68 (1H, d, *J* = 7.9 Hz, H-1′), 3.13～3.40 (4H, m, H-2′, 3′, 4′, 5′), 3.89 (1H, br d, *J* = 11.8 Hz, H-6′a), 3.64 (1H, dd, *J* = 11.9, 6.2 Hz, H-6′b); ^{13}C NMR (100 MHz, CD_3OD) δ: 95.3 (d, C-1), 152.0 (d, C-3), 113.5 (s, C-4), 32.0 (d, C-5), 30.7 (t, C-6), 40.7 (t, C-7), 80.5 (s, C-8), 52.3 (d, C-9), 24.6 (q, C-10), 170.8 (s, CO), 99.7 (d, C-1′), 74.7 (d, C-2′), 77.9 (d, C-3′), 71.7 (d, C-4′), 78.3 (d, C-5′), 62.9 (t, C-6′)。其波谱数据与文献[10]报道一致,化合物鉴定为 mussaenosidic acid。

化合物 12 $C_{35}H_{44}O_{17}$,无色油状,易溶于甲醇。FAB$^-$-MS *m/z*: 735 $[M-H]^-$。^{1}H NMR (400 MHz, CD_3COCD_3) δ: 2.78 (2H, t, *J* = 7.3 Hz, H-7), 3.47-3.99 (2H, m, H-8), 3.78 (3H, s, -OMe in aglycone), 6.68～7.33 (6H, m, H of arom), 7.65 (1H, d, *J* = 15.9Hz, H-7′), 6.41 (1H, d, *J* = 15.9 Hz, H-8′), 3.90 (3H, s, -OMe in acyl), 4.43 (1H, d, *J* = 7.8 Hz, H-1″of Glc), 3.47～3.99 (10H, m, H of Glu and Rha), 5.25 (1H, d, *J* = 1.5 Hz, H-1‴of Rha), 1.17 (3H, d, *J* = 6.2 Hz, H-6‴of Rha), 2.08 (3H, s, H-2‴

Me), 2.02 (3H, s, H-3″-Me); ^{13}C NMR (100 MHz, CD_3COCD_3) δ: 133.0 (s, C-1), 112.9 (d, C-2), 147.4 (s, C-3), 147.2 (s, C-4), 117.1 (d, C-5), 121.1 (d, C-6), 36.6 (t, C-7), 71.8 (t, C-8), 56.7 (q, -OMe), 127.7 (s, C-1′), 111.7 (d, C-2′), 149.2 (s, C-3′), 150.7 (s, C-4′), 116.5 (d, C-5′), 124.6 (d, C-6′), 147.6 (d, C-7′), 115.4 (d, C-8′), 167.5 (s, CO), 56.7 (q, -OMe), 104.1 (d, C-1″), 76.3 (d, C-2″), 80.7 (d, C-3″), 71.1 (d, C-4″), 76.3 (d, C-5″), 62.7 (t, C-6″), 99.9 (d, C-1‴), 73.2 (d, C-2‴), 71.0 (d, C-3‴), 70.5 (d, C-4‴), 70.1 (d, C-5‴), 18.8 (q, C-6‴), 170.9 (s, 2‴-CO), 21.2 (q, 2‴-Me), 170.7 (s, 3‴-CO), 21.1 (q, 3‴-Me)。其波谱数据与文献[11]报道基本一致,化合物鉴定为贞桐苷 A。

化合物 13 $C_{30}H_{38}O_7$,白色粉末,易溶于丙酮。FAB$^+$-MS *m/z*: 511 [M + H]$^+$。[α]$_D^{19}$ + 11.8 °(*c* 1.15, CH_3COCH_3)。^{1}H NMR (400 MHz, CD_3COCD_3) δ: 1.15 (1H, m, H-1a), 1.77 (1H, m, H-1b), 1.57 (1H, m, H-2a), 2.05 (1H, m, H-2b), 3.43 (1H, m, H-3), 2.25 (2H, m, H-4), 5.27 (1H, m, H-6), 2.18 (2H, m, H-7), 1.57 (1H, m, H-9), 2.05 (1H, m, H-11a), 1.90 (1H, m, H-11b), 4.61 (1H, dd, *J* = 11.6, 4.4 Hz, H-12), 2.19 (1H, m, H-15a), 2.05 (1H, m, H-15b), 1.77 (1H, m, H-16a), 2.87 (1H, m, H-16b), 1.59 (3H, s, H-18), 1.15 (3H, s, H-19), 2.19 (3H, s, H-21), 7.42 (2H, m, H-3′, 5′), 7.68 (2H, m, H-2′, 6′), 7.42 (1H, m, H-4′), 7.60 (1H, d, *J* = 16.1 Hz, H-7′), 6.47 (1H, d, *J* = 16.0 Hz, H-8′); ^{13}C NMR (100 MHz, CD_3COCD_3) δ: 39.3 (t, C-1), 31.7 (t, C-2), 71.9 (d, C-3), 43.0 (t, C-4), 140.6 (s, C-5), 118.4 (d, C-6), 34.8 (t, C-7), 74.7 (s, C-8), 44.4 (d, C-9), 37.6 (s, C-10), 24.9 (t, C-11), 73.5 (d, C-12), 58.1 (s, C-13), 89.6 (s, C-14), 33.8 (t, C-15), 32.8 (t, C-16), 92.6 (s, C-17), 10.3 (q, C-18), 18.4 (q, C-19), 209.4 (s, C-20), 27.5 (q, C-21), 135.3 (s, C-1′), 128.9 (d, C-2′, 6′), 129.7 (d, C-3′, 5′), 131.1 (d, C-4′), 145.0 (d, C-7′), 119.2 (d, C-8′), 165.6 (s, C-9′)。其波谱数据与文献[12]报道一致,化合物鉴定为开德苷元。

化合物 14 $C_{13}H_{18}O_3$,为无色油状物,易溶于甲醇。[α]$_D^{20}$ + 74.9 °(*c* 0.12, CH_3OH)。^{1}H NMR (400 MHz, CD_3OD) δ: 2.61 (1H, d, *J* = 17.1 Hz, H-2a), 2.27 (1H, d, *J* = 17.2 Hz, H-2b), 5.94 (1H, s, H-4), 7.00 (1H, d, *J* = 15.8 Hz, H-7), 6.43 (1H, d, *J* = 15.8 Hz, H-8), 2.31 (3H, s, H-10), 1.06 (3H, s, H-11), 1.01 (3H, s, H-12), 1.89 (3H, d, *J* = 1.1 Hz, H-13); ^{13}C NMR (100 MHz, CD_3OD) δ: 42.7 (s, C-1), 50.5 (t, C-2), 128.1 (d, C-4), 148.4 (d, C-7), 131.7 (d, C-8), 27.7 (q, C-10), 23.5 (q, C-11), 24.8 (q, C-12), 19.2 (q, C-13)。其波谱数据与文献[13]报道一致,化合物鉴定为 (+)-dehydrovomifoliol。

化合物 15 $C_{13}H_{20}O_3$,为无色油状物,易溶于甲醇。ESI-MS *m/z*: 223 [M-H]$^-$。[α]$_D^{20}$ + 105.3 °(*c* 0.25, CH_3OH)。^{1}H NMR (400 MHz, CD_3OD) δ: 1.01 (3H, s, H-12), 1.03 (3H, s, H-11), 1.23 (3H, d, *J* = 6.4 Hz, H-10), 1.91 (3H, d, *J* = 0.8 Hz, H-13), 2.15 (1H, d, *J* = 16.9 Hz, H-2b), 2.48 (1H, d, *J* = 17.0 Hz, H-2a), 4.31 (1H, m, H-9); ^{13}C NMR (100 MHz, CD_3OD) δ: 42.4 (s, C-1), 50.7 (t, C-2), 201.4 (s, C-3), 127.1 (d, C-4), 136.9 (d, C-7), 129.9 (d, C-8), 68.6 (d, C-9), 23.4 (q, C-10), 23.8 (q, C-11), 24.5 (q, C-12), 19.6 (q, C-13)。其波谱数据与文献[14]报道一致,化合物鉴定为催吐萝芙木醇。

化合物 16 $C_{10}H_{12}O_4$,为无色油状物,易溶于甲醇。^{1}H NMR (500 MHz, CD_3OD) δ: 7.52 (1H, d, *J* = 1.6 Hz, H-2), 6.84 (1H, d, *J* = 8.2 Hz, H-5), 7.55 (1H, dd, *J* = 8.3, 1.8 Hz, H-6), 3.14 (2H, t, *J* = 6.2 Hz, H-8), 3.92 (2H, t, *J* = 6.2 Hz, H-9), 3.88 (3H, s, -OMe); ^{13}C NMR (125 MHz, CD_3OD) δ: 130.5 (s, C-1), 111.8 (d, C-2), 153.5 (s, C-3), 149.1 (s, C-4), 115.8 (d, C-5), 124.8 (d, C-6), 199.6 (s, C-7), 41.6 (t, C-8), 58.9 (t, C-9), 56.3 (q, -OMe)。其波谱数据基本与文献[15]一致,化合物鉴定为 ω-hydroxypropioguaiacone。

化合物 17 $C_{11}H_{14}O_5$,为无色油状物,易溶于甲醇。ESI-MS *m/z*: 226 [M]$^+$。^{1}H NMR (500 MHz, CD_3OD) δ: 7.30 (2H, s, H-2, 6), 3.93 (2H, t, *J* = 6.1 Hz, H-9), 3.88 (6H, s, -OMe), 3.16 (2H, t, *J* = 6.1 Hz, H-8); ^{13}C NMR (125 MHz, CD_3OD) δ: 149.1 (s, C-3, 5), 107.3 (d, C-2, 6), 199.6 (s, C-7), 59.0 (t, C-8), 41.6 (t, C-9), 56.8 (q, -OMe)。其波谱数据与文献[16]报道一致,化合物鉴定为 3-hydroxy-1-(4-hydroxy-3, 5-dimethoxyphenyl)-1-propanone。

致谢:MS和 NMR由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分析测试中心测定。

参考文献

1 Yang LR, Xiong J, Tan NH, *et al* Chemical constituents of *Pedicularis tricolor* (Scrophulariaceae). *Acta Botanica Yunnanica*, 2006, 28: 553-557.

2 Chu HB, Tan NH. Iridoid glycosides from *Pedicularis dolichocymba* Hand.-Mass. *J Integr Plant Biol*, 2006, 48: 1250-1253.

3 Chu HB, Tan NH, Xiong J, *et al* Chemical constituents of *Pedicularis dolichocymba* Hand.-Mass. *Nat Prod Res Dev* (天然产物研究与开发), 2007, 19: 584-587.

4 Chu HB, Tan NH, Zhang YM. Chemical constituents from *Pedicularis rex* C. B. Clarke. *Z Naturforsch*, 2007, 62b: 1465-1470.

5 Chu HB, Tan NH, Zhang YM, *et al* Chemical constituents of *Pedicularis densispica* Franch. *J Integr Plant Biol*, 2008, accepted.

6 Wu Z, Li FR, Yang JX. Researches in *Pedicularis* L.. *Lishizhen Med Materia Med Res*, 2002, 13: 305-307.

7 Yang JX, Tian JW, Li FR. Influence on antioxidative ability of Taibaishen in mice. *Northwest Pharm J*, 2001, 16: 209-211.

8 Guz NR, Sternitz FR. Spectral comparisons of coniferyl and cinnamyl alcohol epoxide derivatives with a purported cis-epoxyconiferyl alcohol isolate. *Phytochemistry*, 2000, 54: 897-899.

9 Bianco A, Passacantilli P, Righi G, *et al* 7-deoxygardoside, a new acid iridoid glucoside from *Argylia radiata*. *Gazzetta Chimica Italiana*, 1986, 116: 67-68.

10 Damtoft S, Hansen SB, Jacobsen B, *et al* Iridoid glucosides from *Melampyrum*. *Phytochemistry*, 1984, 23: 2387-2389.

11 Tian J, Sun HD. Chemical constituents from *Clerodendrum japonicum*. *Acta Botanica Yunnanica*, 1995, 17: 103-108.

12 Yoshikawa K, Okada N, Kan Y, *et al* Steroidal glycosides from the fresh stem of *Stephanotis lutchuensis* var. *japonica* (Asclepiadaceae). Chemical structures of stephanosides K-Q. *Chem Pharm Bull*, 1996, 44: 2243-2248.

13 Kai H, Baba M, Okuyama T. Two new megastigmanes from the leaves of *Cucumis sativus*. *Chem Pharm Bull*, 2007, 55: 133-136.

14 Yamano Y, Ito M. Synthesis of optically active vomifoliol and roseoside stereoisomers. *Chem Pharm Bull*, 2005, 53: 541-546.

15 Achenbach H, Stocker M, Constenla MA. Flavonoid and other constituents of *Bauhinia manca*. *Phytochemistry*, 1988, 27: 1835-1841.

16 Nakasone Y, Takara K, Wada K, *et al* Antioxidative compounds isolated from kokuto, non-centrifugal cane sugar. *Biosci Biotech Biochem*, 1996, 60: 1714-1716.

(上接第 569页)

10 Wen J (文镜), He SH (贺素华), Yang YY (杨育颖), *et al* The *in vitro* experimental methods and principles for the elimination of free radicals by health functional foods. *Food Sci* (食品科学), 2004, 25 (1): 190-195.

11 Hu Y (胡野), Ling ZQ (凌志强). Molecular Medicine About Apoptosis (细胞凋亡的分子医学). Beijing: Military Medical Science Publishing House, 2001. 50-53.

12 Ma AG (马爱国), Liu SC (刘四朝), Du W (杜卫), *et al* Effect of nucleosides supplementation on the repair of DNA oxidative damage in lymphocytes. *Acta Nutrim Sinica* (营养学报), 2000, 22: 40-42.

13 Yang M (杨敏). Protection of Hsian-tsao (*Mesona procumbens* Hemsl) on H_2O_2-induced DNA damage of primarily cultured mice spleen lymphocytes. *J Zhejiang Univ, Med Sci* (浙江大学学报, 医学版), 2006, 35: 34-38.

14 Doerfler W, Hohlweg U, Müller K, *et al* Foreign DNA interaction-perturbations of the genome-oncogenesis. *Annals New York Acad Sci*, 2001, 945: 276-288.

15 Wang LF (王兰芳), Le GW (乐国伟), Dai QP (戴秋萍). Effect of exogenous nucleotides on repair of damaged DNA in mouse thymocyte. *J Fourth Mil Med Univ* (第四军医大学学报), 2007, 28: 613-615.