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大叶紫珠苯丙素类衍生物研究

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摘　要:采用硅胶、Sephadex LH-20、ODS 柱层析等色谱技术,从大叶紫珠 70% 乙醇提取物的乙酸乙酯萃取部位分离得到 10 个苯丙素类衍生物。通过波谱分析并与文献数据对照方法,将其分别鉴定为蛇菰宁(**1**)、(7*R*,8*S*)-脱氢松柏醇-8,5′-脱氢松柏醛-9-*O*-*β*-D-吡喃葡萄糖苷(**2**)、连翘苷 B(**3**)、alyssonoside(**4**)、天人草甙 B(**5**)、阿克苷(**6**)、马蒂罗苷(**7**)、异阿克苷(**8**)、车前草甙 C(**9**)和异马蒂罗苷(**10**)。其中,化合物 **3** ~ **10** 均为首次从该植物中分离得到。

关键词:马鞭草科;大叶紫珠;苯丙素类衍生物;化学成分

中图分类号:R284.2　　**文献标识码**:A

Phenylpropanoid Derivatives Isolated from *Callicarpa macrophylla* Vahl

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Abstract: Ten phenylpropanoid derivatives were isolated and purified from EtOAc fraction of 70% ethanol extract of *Callicarpa macrophylla* Vahl by silica gel, Sephadex LH-20 and ODS column chromatography. On the basis of their physicochemical properties and spectroscopic data, these compounds were identified as balanophonin (**1**), (7*R*,8*S*)-dehydroconiferyl alcohol-8,5′-dehydroconiferyl aldehyde-9-*O*-*β*-D-glucopyranoside (**2**), forsythoside B (**3**), alyssonoside (**4**), leucosceptoside B (**5**), acteoside (**6**), martinoside (**7**), isoacteoside (**8**), plantainoside C (**9**), isomartynoside (**10**). Compounds **3-10** were isolated from this plant for the first time.

Key words: Verbenaceae; *Callicarpa macrophylla* Vahl; phenylpropanoid derivatives; chemical constituents

大叶紫珠(*Callicarpa macrophylla* Vahl)为马鞭草科紫珠属植物,以根和叶入药,其味苦、微辛、性平,具有散瘀止血、消肿止痛的功效,用于衄血、咯血、吐血、便血、外伤出血、跌打肿痛[1]。目前,对大叶紫珠化学成分的研究主要集中在三萜以及黄酮类成分。为了探讨大叶紫珠中的其它药用成分和镇痛活血等药效成分,本文作者对大叶紫珠乙酸乙酯萃取物化学成分进行了较系统的分离鉴定研究,从中分离得到 10 个苯丙素类衍生物,分别鉴定为蛇菰宁(**1**)、(7*R*,8*S*)-脱氢松柏醇-8,5′-脱氢松柏醛-9-*O*-*β*-D-吡喃葡萄糖苷[(7*R*,8*S*)-dehydroconiferyl alcohol-8,5′-dehydroconiferyl aldehyde-9-*O*-*β*-D-glucopyranoside,也即蛇菰宁吡喃葡萄糖苷,**2**]、连翘苷 B(**3**)、alyssonoside(**4**)、天人草甙 B(**5**)、阿克苷(acteoside,**6**)、马蒂罗苷(martinoside,**7**)、异阿克苷(isoacteoside,**8**)、车前草甙 C(plantainoside C,**9**)、异马蒂罗苷(isomartynoside,**10**)。其中,化合物 **3** ~ **10** 均为首次从该植物中分离得到。

1　实验部分

1.1　仪器与材料

Agilent 1200 型液相分析色谱仪(美国 Agilent 公司);Agilent 1200 型液相半制备色谱仪(美国 Agilent 公司);AV-300 MHz 超导核磁共振仪(德国 Bruker 公司);LCQ Advantage MAX 质谱仪(美国 Finnign 公司)。

Sephadex LH-20 柱层析材料(瑞典 Pharmacia 公司);ODS 柱层析材料(美国 Merck 公司);柱层析硅胶(青岛海洋化工厂产品);所用试剂均为分析纯或化学纯。实验所用大叶紫珠根药材于 2011 年夏采自广东省从化市流溪河区域,经暨南大学生药学教研室周光雄教授鉴定为马鞭草科紫珠属大叶紫珠干

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燥根。

1.2 提取与分离

取干燥大叶紫珠根 12 kg 粉碎,70% 乙醇回流提取三次。减压浓缩后得浸膏 700 g,向浸膏中加入适量水悬浮,依次用石油醚、乙酸乙酯和正丁醇萃取,回收溶剂后得石油醚萃取物(45 g)、乙酸乙酯萃取物(80 g)、正丁醇萃取物(200 g)。将乙酸乙酯萃取物(80 g)经硅胶柱层析,以氯仿-甲醇梯度洗脱(100∶0 ~ 0∶100),共接收 200 个馏分,经 TLC 检测后合并成 A-T 共 20 个粗组分。其中,组分 Q 经反相 ODS 开放柱层析及 Sephadex LH-20 凝胶柱层析,分离得到化合物 **1**(10 mg)和 **2**(8 mg);组分 R 经硅胶柱层析,以氯仿-甲醇梯度洗脱(50∶1 ~ 0∶100),TLC 检测后合并得到 3 个组合馏分(Fr. R-1 ~ 3),Fr. R-1 经 Sephadex LH-20 凝胶柱层析,再经半制备 HPLC 纯化得到化合物 **7**(28 mg)和 **10**(17 mg)。Fr. R-2 经 ODS 开放柱层析,依次用 15%、30%、45% 甲醇水洗脱,得到子馏分再进行 Sephadex LH-20 凝胶柱层析,得到化合物 **5**(22 mg)、**6**(470 mg)、**8**(15 mg)和 **9**(50 mg)。Fr. R-3 经 Sephadex LH-20 凝胶柱层析,用 40% 甲醇水等度洗脱,得到化合物 **3**(500 mg)。

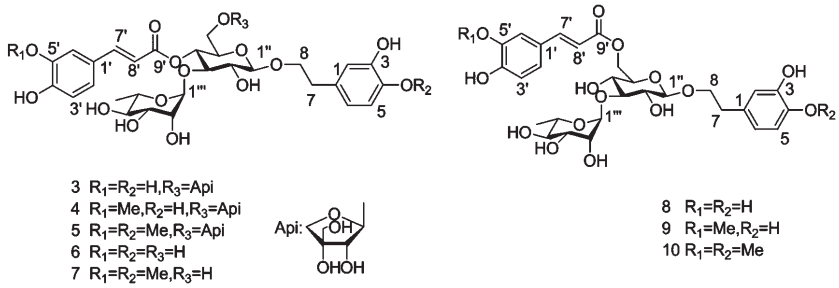

图 1 化合物 3 ~ 10 的化学结构

Fig. 1 Chemical structures of compounds **3-10**

2 结构鉴定

化合物 1 淡黄色粉末。ESI-MS *m/z* 379 [M + Na]$^+$,735 [2M + Na]$^+$,确定其相对分子质量为 356。^{1}H NMR (CD_3OD,300 MHz) δ:9.58 (1H,d,*J* = 7.8 Hz,H-9′),7.61 (1H,d,*J* = 15.7 Hz,H-7′),7.28 (1H,br s,H-6′),7.23 (1H,br s,*J* = 1.5 Hz,H-2′),6.95 (1H,d,*J* = 1.7 Hz,H-2),6.83 (1H,dd,*J* = 8.2,1.8 Hz,H-6),6.79 (1H,br s,H-5),6.68 (1H,dd,*J* = 15.7,7.9 Hz,H-8′),5.60 (1H,d,*J* = 6.4 Hz,H-7),3.91 (3H,s,3′-OCH_3),3.82 (3H,s,3-OCH_3),3.56 (1H,q,*J* = 6.1 Hz,H-8);^{13}C NMR (CD_3OD,75 MHz) δ:196.4 (C-9′),156.3 (C-7′),153.1 (C-4′),149.3 (C-3),148.0 (C-4),146.2 (C-3′),134.0 (C-1),131.4 (C-5′),129.7 (C-1′),127.2 (C-8′),120.1 (C-6′),120.0 (C-6),116.4 (C-5),114.3 (C-2′),110.7 (C-2),90.3 (C-7),64.7 (C-9),56.9 (3′-OCH_3),56.5 (3-OCH_3),54.6 (C-8)。上述数据与文献[2]一致,故将化合物 **1** 鉴定为蛇菰宁。

化合物 2 淡黄色粉末。ESI-MS *m/z* 541 [M + Na]$^+$,确定其相对分子质量为 518。^{1}H NMR (DMSO-d_6,300 MHz) δ:9.60 (1H,d,*J* = 7.8 Hz,H-9′),9.10 (1H,s,Ar-OH),7.64 (1H,d,*J* = 15.8 Hz,H-7′),7.52 (1H,br s,H-6),7.33 (1H,br s,H-2),7.00 (2H,br s,H-2′,6′),6.76 (1H,d,*J* = 8.0 Hz,H-5),5.55 (1H,d,*J* = 7.4 Hz,H-7),4.25 (1H,d,*J* = 7.8 Hz,H-1),4.04 (1H,br s,H-9),3.84 (3H,s,3′-OCH_3),3.76 (3H,s,3-OCH_3);^{13}C NMR (DMSO-d_6,75 MHz) δ:194.1 (C-9),154.1 (C-7′),150.5 (C-4′),147.6 (C-4),146.7 (C-3),144.1 (C-3′),130.9 (C-1),130.3 (C-5′),127.9 (C-1′),126.2 (C-8′),119.2 (C-6′),119.0 (C-6),115.3 (C-5),113.0 (C-2′),110.7 (C-2),103.0 (C-1″),87.9 (C-7),76.9 (C-3″),76.7 (C-5″),73.5 (C-2″),70.1 (C-9),70.0 (C-4″),61.1 (C-6″),55.9 (3-OCH_3),55.6 (3′-OCH_3),49.8 (C-8)。上述数据与文献[3]一致,故将化合物 **2** 鉴定为 (7*R*,8*S*)-dehydroconiferyl alcohol-8,5′-dehydroconiferyl aldehyde-9-*O*-β-D-glucopyranoside。

化合物 3 白色无定型粉末。ESI-MS *m/z* 779 [M + Na]$^+$,755 [M-H]$^-$,确定其相对分子质量为 756。^{1}H NMR (CD_3OD,300 MHz) δ:7.63 (1H,d,*J* = 15.8 Hz,H-8′),7.11 (1H,br s,H-2′),6.98 (1H,

d, J = 8.2 Hz, H-6′), 6.83 (1H, d, J = 8.1 Hz, H-5′), 6.75 (2H, br s, H-2, 5), 6.59 (1H, d, J = 8.0 Hz, H-6), 6.32 (1H, d, J = 15.8 Hz, H-7′), 4.38 (1H, d, J = 7.6 Hz, H-1″), 2.8 (2H, br s, H-7), 1.12 (3H, d, J = 6.0 Hz, H-6‴); ^{13}C NMR (CD_3OD, 75 MHz) 数据见表 1。以上数据与文献[4]一致,故将化合物 **3** 鉴定为连翘苷 B。

化合物 4　白色无定型粉末。ESI-MS m/z 793 $[M+Na]^+$, 769 $[M-H]^-$, 确定其相对分子质量为 770。^{1}H NMR (CD_3OD, 300 MHz) δ: 7.61 (1H, d, J = 15.9 Hz, H-8′), 6.32 (1H, d, J = 15.9 Hz, H-7′), 5.14 (1H, br s, H-1⁗), 4.85 (1H, d, J = 2.3 Hz, H-1⁗), 4.30 (1H, d, J = 7.9 Hz, H-1″), 3.82 (3H, s, 5′-OCH_3), 2.73 (2H, t, J = 7.1 Hz, H-7), 1.04 (3H, d, J = 6.1 Hz, H-6‴); ^{13}C NMR (CD_3OD, 75 MHz) 数据见表 1。以上数据与文献[4]一致,故将化合物 **4** 鉴定为 alyssonoside。

化合物 5　白色无定型粉末。ESI-MS m/z 807 $[M+Na]^+$, 783 $[M-H]^-$, 确定其相对分子质量为 784。^{1}H NMR (CD_3OD, 300 MHz) δ: 7.59 (1H, d, J = 15.8 Hz, H-8′), 7.09 (1H, br s, H-2′), 7.00 (1H, d, J = 8.2 Hz, H-6′), 6.66 (1H, d, J = 1.3 Hz, H-2), 6.59 (1H, d, J = 8.2 Hz, H-6), 6.31 (1H, d, J = 15.9 Hz, H-7′), 5.13 (1H, br s, H-1⁗), 4.28 (1H, d, J = 7.7 Hz, H-1″), 3.78 (3H, s, 5′-OCH_3), 3.70 (3H, s, 4-OCH_3), 2.72 (2H, t, J = 6.7 Hz, H-7), 1.03 (3H, d, J = 6.0 Hz, H-6⁗); ^{13}C NMR (CD_3OD, 75 MHz) 数据见表 1。以上数据与文献[4]一致,故将化合物 **5** 鉴定为 leucosceptoside B。

化合物 6　白色无定型粉末。ESI-MS m/z 647 $[M+Na]^+$, 623 $[M-H]^-$, 确定其相对分子质量为 624。^{1}H NMR (CD_3OD, 300 MHz) δ: 7.60 (1H, d, J = 15.8 Hz, H-8′), 7.08 (1H, br s, H-2′), 6.93 (1H, d, J = 8.1 Hz, H-6′), 6.79 (1H, d, J = 8.1 Hz, H-5′), 6.70 (1H, d, J = 7.8 Hz, H-5), 6.54 (1H, d, J = 8.0 Hz, H-6), 6.28 (1H, d, J = 15.9 Hz, H-7′), 4.94 (1H, br s, H-4″), 4.36 (1H, d, J = 7.6 Hz, H-1″), 3.82 (1H, t, J = 9.1 Hz, H-3″), 2.76 (2H, d, J = 6.5 Hz, H-7), 1.10 (3H, d, J = 5.8 Hz, H-6‴); ^{13}C NMR (CD_3OD, 75 MHz) 数据见表 1。以上数据与文献[5]一致,故将化合物 **6** 鉴定为 acteoside。

化合物 7　白色无定型粉末。ESI-MS m/z 675 $[M+Na]^+$, 1327 $[2M+Na]^+$, 确定其相对分子质量为 652。^{1}H NMR (CD_3OD, 300 MHz) δ: 7.59 (1H, d, J = 15.8 Hz, H-8′), 7.09 (1H, d, J = 1.3 Hz, H-2′), 6.59 (1H, dd, J = 8.2, 1.7 Hz, H-6), 6.30 (1H, d, J = 15.9 Hz, H-7′), 4.29 (1H, d, J = 7.9 Hz, H-1″), 3.78 (3H, s, 5′-OCH_3), 3.70 (3H, s, 4-OCH_3), 3.27 (2H, d, J = 4.1 Hz, H-6′), 2.73 (2H, t, J = 7.2 Hz, H-7), 1.04 (3H, d, J = 6.1 Hz, H-6‴); ^{13}C NMR (CD_3OD, 75 MHz) 数据见表 1。以上数据与文献[6]一致,故将化合物 **7** 鉴定为 martinoside。

化合物 8　白色无定型粉末。ESI-MS m/z 647 $[M+Na]^+$, 623 $[M-H]^-$, 确定其相对分子质量为 624。^{1}H NMR (CD_3OD, 300 MHz) δ: 7.57 (1H, d, J = 15.9 Hz, H-8′), 7.05 (1H, d, J = 1.9 Hz, H-2′), 6.90 (1H, dd, J = 8.3, 1.9 Hz, H-6′), 6.78 (1H, d, J = 8.2 Hz, H-5′), 6.69 (1H, d, J = 1.9 Hz, H-2), 6.66 (1H, d, J = 8.0 Hz, H-5), 6.54 (1H, dd, J = 8.1, 1.9 Hz, H-6), 6.30 (1H, d, J = 15.9 Hz, H-7′), 5.21 (1H, d, J = 1.3 Hz, H-1″), 2.79 (2H, t, J = 7.4 Hz, H-7), 1.27 (3H, d, J = 6.2 Hz, H-6‴); ^{13}C NMR (CD_3OD, 75 MHz) 数据见表 1。以上数据与文献[7]一致,故将化合物 **8** 鉴定为 isoacteoside。

化合物 9　白色无定型粉末。ESI-MS m/z 661 $[M+Na]^+$, 637 $[M-H]^-$, 确定其相对分子质量为 638。^{1}H NMR (CD_3OD, 300 MHz) δ: 7.63 (1H, d, J = 15.9 Hz, H-8′), 7.09 (1H, d, J = 1.6 Hz, H-2′), 6.98 (1H, dd, J = 8.2, 1.7 Hz, H-6′), 6.76 (1H, d, J = 1.9 Hz, H-2), 6.31 (1H, d, J = 15.9 Hz, H-7′), 5.22 (1H, br s, H-1″), 3.83 (3H, s, 5′-OCH_3), 2.84 (2H, t, J = 7.4 Hz, 7-H), 1.13 (3H, d, J = 6.2 Hz, H-6‴); ^{13}C NMR (CD_3OD, 75 MHz) 数据见表 1。以上数据与文献[8]一致,故将化合物 **9** 鉴定为 plantainoside C。

化合物 10　白色无定型粉末。ESI-MS m/z 675 $[M+Na]^+$, 1327 $[2M+Na]^+$, 确定其相对分子质量为 652。^{1}H NMR (CD_3OD, 300 MHz) δ: 7.62 (1H, d, J = 15.9 Hz, H-8′), 7.14 (1H, br s, H-2), 7.01 (1H, d, J = 8.3 Hz, H-6), 6.79 (1H, d, J = 8.2 Hz, H-5), 6.69 (1H, d, J = 1.7 Hz, H-2″), 6.65 (1H, br s, H-5′), 6.62 (1H, br s, H-6′), 6.38 (1H, d, J = 15.9 Hz, H-7′), 5.18 (1H, d, J = 1.3 Hz, H-1‴), 4.50 (1H, dd, J = 11.8, 1.9 Hz, H-6″), 4.37 (1H, dd, J = 19.4, 7.0 Hz, H-6″), 3.85 (3H, s, 5′-OCH_3), 3.74 (3H, s, 4-OCH_3), 2.80 (3H, t, J = 7.6

Hz,H-7),1.25 (3H,d,J = 6.2 Hz,H-6′′′);^{13}C NMR (CD_3OD,75 MHz) 数据见表 1。以上数据与文献[4]一致,故将化合物 **10** 鉴定为 isomartynoside。

表 1 化合物 3 ~ 10 的^{13}C NMR 数据(CD_3OD)

Table 1 ^{13}C NMR data of compounds **3-10**(CD_3OD)

No.	3	4	5	6	7	8	9	10
1	131.4	131.5	132.7	131.4	132.8	131.4	132.9	132.8
2	116.6	116.5	112.8	116.4	117.1	117.8	117.1	112.9
3	144.4	144.7	147.1	145.8	147.3	146.1	146.9	147.6
4	145.8	146.2	147.4	144.4	147.5	144.7	147.4	147.4
5	117.8	117.2	117.1	117.2	112.9	116.5	112.8	117.1
6	121.4	121.4	121.3	121.4	121.3	121.4	121.3	121.3
7	36.4	36.7	36.5	36.3	36.5	36.7	36.6	36.9
8	72.2	72.5	72.2	71.9	72.1	72.5	72.1	72.5
1′	127.5	127.7	127.6	127.5	127.6	127.7	127.7	127.6
2′	114.6	111.9	111.7	115.3	111.8	115.2	115.3	111.7
3′	146.5	150.9	150.6	146.5	149.6	146.8	147.6	149.6
4′	149.5	149.5	149.3	149.5	150.8	149.7	149.9	151.1
5′	116.4	116.6	116.6	116.6	116.6	116.6	116.6	116.7
6′	123.6	124.5	124.4	123.4	124.4	123.3	123.4	124.5
7′	148.1	148.1	148.0	148.1	148.0	147.4	148.1	147.3
8′	115.3	115.2	115.1	114.6	115.1	114.9	114.7	115.2
9′	168.2	168.3	168.1	168.4	168.4	169.3	168.4	169.3
Glc-1	103.9	104.3	104.1	103.9	104.2	104.4	104.2	104.5
2	75.0	76.2	74.4	76.0	76.2	75.8	76.2	75.8
3	81.7	81.6	81.6	81.7	81.6	83.9	81.8	84.1
4	70.3	70.5	70.4	70.3	70.6	70.4	70.5	70.7
5	75.9	74.6	76.0	75.6	75.9	75.4	76.0	75.5
6	68.2	68.6	68.4	62.2	62.4	64.7	62.4	64.8
Rha-1	102.9	103.1	103.0	102.9	103.0	102.8	103.1	102.9
2	71.9	72.1	72	72.2	72.3	72.4	72.4	72.5
3	72.2	72.2	72.2	72	72.1	72.3	72.2	72.4
4	73.6	73.8	73.7	73.7	73.8	74.0	73.8	74.1
5	70.7	71.0	70.8	70.0	70.4	70.1	70.6	70.2
6	18.4	18.6	18.5	18.5	18.6	18.0	18.6	18.0
Api-1	110.8	111.1	110.9					
2	78.1	78.2	78.1					
3	80.6	80.7	80.7					
4	74.2	75.2	75.1					
5	65.6	65.8	65.7					
R_1		56.4	56.5		56.5		56.5	56.5
R_2			56.5		56.6			56.5

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