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紫花列当水溶性成分的研究

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摘 要:采用大孔树脂、Sephadex LH-20等色谱方法,从列当科列当属植物紫花列当 *Orobanche coerulescens*中分离得到六个水溶性成分,通过波谱技术及理化手段分别鉴定为类叶升麻苷(**1**)、异类叶升麻苷(**2**)、crenatoside(**3**)、cistanoside F(**4**)、sinapoyl-4-O-β-D-glucoside(**5**)、腺苷(**6**)。其中化合物 **5**和 **6**为首次从该属植物中分离得到。

关键词:紫花列当;化学成分;苯乙醇苷

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Study on Water-soluble Constituents of *Orobanche coerulescens*

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Abstract: Six water-soluble constituents were isolated from *Orobanche coerulescens*, and their structures were determined on the basis of the physicochemical properties and spectral analysis as acteoside(**1**), isoacteoside(**2**), crenatoside(**3**), cistanoside F(**4**), sinapoyl-4-O-β-D-glucoside(**5**) and adenosine(**6**). Compounds **5** and **6** were isolated from *Orobanche* genus for the first time.

Key words: *Orobanche coerulescens*; chemical constituents; phenylethanoid glycosides

紫花列当(*Orobanche coerulescens* Steph)又名草苁蓉、独根草,为列当科列当属二年生或多年生寄生草本植物紫花列当的干燥带鳞叶的肉质茎,寄生在菊科蒿属(*Artemisia*)植物的根上,生长于干草原、沙丘、砾石沙地和戈壁之中,主产于我国的东北、西北、四川、河北、山东等地[1]。该药材性温、味甘,具有补肾,强筋之功效,民间用于肾虚、腰膝冷痛、阳痿遗精、神经官能症等疾病的治疗,收载于《中药大辞典》等医药文献中[2]。本文作者曾从紫花列当 95%乙醇提取物的乙酸乙酯部位得到六个化合物[3],现又从其正丁醇部位中分离得到六个水溶性化合物,并通过理化手段及波谱方法鉴定了它们的结构:类叶升麻苷(**1**)、异类叶升麻苷(**2**)、crenatoside(**3**)、cistanoside F(**4**)、sinapoyl-4-O-β-D-glucoside(**5**)、腺苷(**6**),其中 **5**和 **6**为首次从列当属植物中分离得到。

1 仪器与材料

WRS-1A数字显示熔点测定仪(温度未经校正);VARIAN NOVA 500型超导核磁共振仪;ZF-C型三用紫外分析仪;柱色谱及薄层色谱用硅胶(青岛海洋化工厂),Sephadex LH-20(Amersham Pharmacia Biotech AB公司),所用试剂均为国产分析纯。药材于 2006年 5月采自新疆吉木萨尔,由新疆药物研究所张彦福研究员鉴定为 *O. coerulescens*的干燥根茎,药材储存于新疆药物研究所维吾尔药研究开发重点实验室。

2 提取与分离

紫花列当干燥根茎 10.6 kg,95%乙醇回流提取 3次,每次 2 h,提取液合并后,放置过夜,过滤,滤液浓缩至浸膏,浸膏以水混悬后,分别以乙酸乙酯、饱

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和正丁醇萃取,萃取液减压浓缩至浸膏。取其中正丁醇部位 300 g,以水溶解后通过 AB-8型大孔吸附树脂柱,依次以水、30%、50%和 95%乙醇梯度洗脱,其中 30%洗脱部位上 Sephadex LH-20柱,分别以水、20%、40%、60%、80%甲醇和甲醇洗脱,再经 Sephadex LH-20柱 (60%甲醇)反复纯化,得到化合物 **1** (3.2 g)、**2** (116 mg)、**3** (87 mg)、**4** (9 mg)、**5** (18 mg)、**6** (30 mg)。

3 结构鉴定

化合物 1 淡黄色无定形粉末,1%三氯化铁水溶液呈反应呈蓝黑色;^{1}H NMR (CD_3OD, 500 MHz) δ: ester moiety (E): 7.53 (1H, d, J = 16.0 Hz, E-H-7), 6.99 (1H, d, J = 2.0 Hz, E-H-2), 6.90 (1H, dd, J = 2.0, 8.0 Hz, E-H-6), 6.72 (1H, d, J = 8.0 Hz, E-H-5), 6.21 (1H, d, J = 16.0 Hz, E-H-8); aglycone (A): 6.63 (1H, dd, J = 2.0 Hz, A-H-2), 6.61 (1H, dd, J = 8.0 Hz, A-H-5), 6.50 (1H, dd, J = 2.0, 8.0 Hz, A-H-6), 2.73 (2H, m, A-H-7); sugar moiety: 5.13 (1H, brs, Rha-H-1), 4.31 (1H, d, J = 7.5 Hz, Glu-H-1), 1.03 (3H, d, J = 6.0 Hz, Rha-H-6); ^{13}C NMR (CD_3OD, 125 MHz) δ: 131.47 (C-A-1), 116.51 (C-A-2), 144.67 (C-A-3), 146.13 (C-A-4), 117.11 (C-A-5), 121.26 (C-A-6), 36.57 (C-A-7), 72.27 (C-A-8), 127.7 (C-E-1), 114.7 (C-E-2), 146.8 (C-E-3), 149.8 (C-E-4), 116.3 (C-E-5), 123.2 (C-E-6), 148.0 (C-E-7), 115.2 (C-E-8), 168.3 (CO), 104.2 (Glu-1), 76.0 (Glu-2), 81.6 (Glu-3), 70.4 (Glu-4), 76.2 (Glu-5), 62.4 (Glu-6), 103.0 (Rha-1), 72.3 (Rha-2), 72.1 (Rha-3), 73.8 (Rha-4), 70.6 (Rha-5), 18.5 (Rha-6)。以上波谱数据及理化特征与文献[4]报道一致,故推断该化合物为类叶升麻苷 (acteoside)。

化合物 2 淡黄色无定形粉末,1%三氯化铁水溶液反应呈蓝黑色;^{1}H NMR (DMSO-d_6, 500 MHz) δ: ester moiety (E): 7.46 (1H, d, J = 16.0 Hz, E-H-8), 7.04 (1H, d, J = 2.0 Hz, E-H-2), 6.96 (1H, dd, J = 2.0, 8.0 Hz, E-H-6), 6.73 (1H, d, J = 8.0 Hz, E-H-5), 6.28 (1H, d, J = 16.0 Hz, E-H-7); aglycone (A): 6.59 (1H, dd, J = 2.0 Hz, A-H-2), 6.57 (1H, dd, J = 8.0 Hz, A-H-5), 6.44 (1H, dd, J = 2.0, 8.0 Hz, A-H-6), 2.65 (2H, m, A-H-7); sugar moiety: 5.03 (1H, J = 5.5 Hz, Rha-H-1), 4.26 (1H, d, J = 8.0 Hz, Glu-H-1), 1.05 (3H, d, J = 6.0 Hz, Rha-H-6); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 129.1 (C-A-1), 115.8 (C-A-2), 143.5 (C-A-3), 144.9 (C-A-4), 116.3 (C-A-5), 119.5 (C-A-6), 35.1 (C-A-7), 70.6 (C-A-8), 125.5 (C-E-1), 113.8 (C-E-2), 145.4 (C-E-3), 148.4 (C-E-4), 115.4 (C-E-5), 121.4 (C-E-6), 145.5 (C-E-7), 114.9 (C-E-8), 166.5 (CO), 102.6 (Glu-1), 73.7 (Glu-2), 80.8 (Glu-3), 68.1 (Glu-4), 74.1 (Glu-5), 63.4 (Glu-6), 100.6 (Rha-1), 70.3 (Rha-2), 79.6 (Rha-3), 72.1 (Rha-4), 68.5 (Rha-5), 17.8 (Rha-6)。以上波谱数据及理化特征与文献[4]报道一致,故推断该化合物为异类叶升麻苷 (isoacteoside)。

化合物 3 淡黄色无定形粉末,1%三氯化铁水溶液反应呈蓝黑色;^{1}H NMR (DMSO-d_6, 500 MHz) δ: ester moiety (E): 7.47 (1H, d, J = 16.0 Hz, E-H-8), 7.01 (1H, d, J = 2.0 Hz, E-H-2), 6.96 (1H, dd, J = 2.0, 8.0 Hz, E-H-6), 6.75 (1H, d, J = 8.0 Hz, E-H-5), 6.18 (1H, d, J = 16.0 Hz, E-H-7); aglycone (A): 6.73 (1H, dd, J = 2.0 Hz, A-H-2), 6.68 (1H, dd, J = 8.0 Hz, A-H-5), 6.60 (1H, dd, J = 2.0, 8.0 Hz, A-H-6), 4.56 (1H, d, J = 7.5 Hz, A-H-7), 4.02 (1H, d, J = 9.5 Hz, A-H-8), 3.70 (1H, m, A-H-8); sugar moiety: 5.02 (1H, brs, Rha-H-1), 4.53 (1H, d, J = 7.5 Hz, Glu-H-1), 1.01 (3H, d, J = 6.50 Hz, Rha-H-6); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 128.0 (C-A-1), 113.5 (C-A-2), 145.1 (C-A-3), 145.1 (C-A-4), 115.2 (C-A-5), 117.1 (C-A-6), 76.1 (C-A-7), 71.4 (C-A-8), 125.5 (C-E-1), 113.3 (C-E-2), 145.9 (C-E-3), 148.5 (C-E-4), 115.7 (C-E-5), 121.5 (C-E-6), 145.5 (C-E-7), 114.7 (C-E-8), 165.4 (CO), 96.9 (Glu-1), 80.4 (Glu-2), 74.3 (Glu-3), 68.7 (Glu-4), 76.1 (Glu-5), 60.4 (Glu-6), 100.3 (Rha-1), 70.9 (Rha-2), 70.4 (Rha-3), 71.4 (Rha-4), 70.2 (Rha-5), 17.4 (Rha-6)。以上波谱数据及理化特征与文献[5]报道一致,故推断该化合物为 (Crenatoside)。

化合物 4 白色无定形粉末,1%三氯化铁水溶液反应呈蓝黑色;^{1}H NMR (DMSO-d_6, 500 MHz) δ: ester moiety (E): 7.44 (1H, d, J = 16.0 Hz, E-H-7), 7.01 (1H, d, J = 2.0 Hz, E-H-2), 6.97 (1H, dd, J = 2.0, 8.0 Hz, E-H-6), 6.75 (1H, d, J = 8.0 Hz, E-H-5), 6.18 (1H, d, J = 16.0 Hz, E-H-8), sugar moiety:

5.18(1H, brs, rha-H-1), 4.71(1H, overlapped), 1.08(3H, d, J = 6.0 Hz, rha-H-6); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 125.5 (C-E-1), 114.7 (C-E-2), 145.5 (C-E-3), 148.4 (C-E-4), 115.7 (C-E-5), 121.5 (C-E-6), 145.5 (C-E-7), 113.6 (C-E-8), 165.7 (CO), 96.5/92.2 (Glu-1), 74.4/70.4 (Glu-2), 81.3/79.0 (Glu-3), 68.7 (Glu-4), 75.9 (Glu-5), 60.9 (Glu-6), 100.9 (Rha-1), 70.5 (Rha-2), 71.6 (Rha-3), 73.2 (Rha-4), 69.4 (Rha-5), 18.1 (Rha-6)。**以上波谱数据及理化特征与文献**[4]**报道一致,故推断该化合物为** Cistanoside F。

化合物 5 **白色粉末**, mp. 172～175 ℃, ESHMS m/z: 387.9 $[M+H]^+$; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 7.50 (1H, d, J = 15.6 Hz, H-β), 7.02 (2H, s, H-2, 6), 6.50 (1H, d, J = 15.6 Hz, H-α), 3.80 (6H, s, 3, 5-OMe), 5.02 (1H, d, J = 6.8 Hz, H-1′); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 129.9 (C-1), 106.8 (C-2, 6), 152.9 (C-3, 5), 136.4 (C-4), 118.2 (C-α), 144.2 (C-β), 167.9 (C=O), 56.7 (3, 5-OMe), 102.4 (C-1′), 74.9 (C-2′), 76.8 (C-3′), 70.1 (C-4′), 77.5 (C-5′), 61.1 (C-6′)。**以上波谱数据及理化特征与文献**[6]**相对照一致,故推断该化合物为** sinapoyl-4-O-β-*D*-glucoside。

化合物 6 **白色粉末**, mp. 230～232 ℃; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 3.58 (1H, d, J = 10.8 Hz, H-5′), 3.67 (1H, d, J = 11.4 Hz, H-5′), 5.88 (1H, d, J = 9.6 Hz, H-1′), 7.33 (2H, brs, J = 1.0 Hz, NH_2), 8.14 (1H, s, H-8), 8.34 (1H, s, H-2); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 152.3 (C-2), 149.0 (C-4), 119.3 (C-5), 156.1 (C-6), 139.9 (C-8), 87.9 (C-1′), 73.4 (C-2′), 70.6 (C-3′), 85.8 (C-4′), 61.6 (C-5′), 156.1 (C-6′),**以上波谱数据及理化特征与文献**[7]**报道一致,故鉴定该化合物为腺苷** (adenosine)。

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