

虎杖的化学成分研究

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摘要 从虎杖(*Reynoutria Japonica* Houtt.)根茎中分离得到8个化合物,经波谱分析确定其结构分别为大黄素-6-甲醚(physcion 1),大黄素(emodin 2),fallacinol(3),大黄素-8-甲醚(questin 4),大黄素-8-O-β-D-葡萄糖吡喃糖甙(emodin-8-O-β-D-glucopyranoside 5),2-甲氧基-6-乙酰基-7-甲基胡桃醌(PC-1 6),白藜芦醇(resveratrol 7)和白藜芦醇甙(piceid 8)。另外,通过光学异构化,得到了相应的顺式白藜芦醇(9)和顺式白藜芦醇甙(10)。

关键词 虎杖;化学成分;异构化

虎杖(*Reynoutria Japonica* Houtt.)为我国的传统中药,主要分布于华东、中南及辽宁、陕西、甘肃、四川、贵州、云南等地。具活血定痛、清热利湿、止渴化痰作用^[1]。虎杖植物的化学成分研究已较为深入,迄今已从中分离到的化学成分主要有:蒽醌类、二苯乙烯类、萘醌类、黄酮类等^[2]。本文报道从滇虎杖中分离得到的8个化合物:大黄素-6-甲醚(physcion 1),大黄素(emodin 2),fallacinol(3),大黄素-8-甲醚(questin 4),大黄素-8-O-β-D-葡萄糖吡喃糖甙(emodin-8-O-β-D-glucopyranoside 5),2-甲氧基-6-乙酰基-7-甲基胡桃醌(PC-1 6),白藜芦醇(resveratrol 7)和藜芦醇甙(piceid 8)。这些成分在其他产地虎杖中均已报道^[2]。另外,化合物7和8分别通过光学异构化,得到了相应的顺式白藜芦醇(cis-resveratrol 9)和顺式白藜芦醇甙(cis-piceid 10)。

1 实验部分

1.1 仪器

MS用VG Autospec-300型测定;NMR用Brucker AM-400核磁共振仪测定,以TMS为内标;薄层层析硅胶和柱层析硅胶均为青岛海洋化工厂产品。

1.2 提取和分离

干燥虎杖根茎(10 kg)用80%丙酮室温浸提,减压回收溶剂,依次用石油醚、乙酸乙酯和正丁醇萃取。乙酸乙酯提取物通过反复硅胶、Sephadex LH-

20、聚酰胺柱层析,分离得到化合物1(200 mg),2(1.44 g),3(45 mg),4(800 mg),5(82 mg),6(60 mg),7(14 g)。正丁醇提取物经硅胶、聚酰胺柱层析分离,得到化合物8(9.5 g)。

1.3 光学异构化

Gamini等^[3]曾利用紫外光(365 nm)对反式resveratrol和piceid进行过异构化工作。我们把反式异构体分别置于表面皿中,用甲醇溶解,于紫外灯(λ254 nm)下照射24 h。照射后的溶液经半制备高效液相(λ=280 nm),甲醇-乙腈(25:75)洗脱液洗脱,制备得到顺式白藜芦醇(9)和顺式白藜芦醇甙(10)。转化率分别为55%和60.8%。

2 结构鉴定

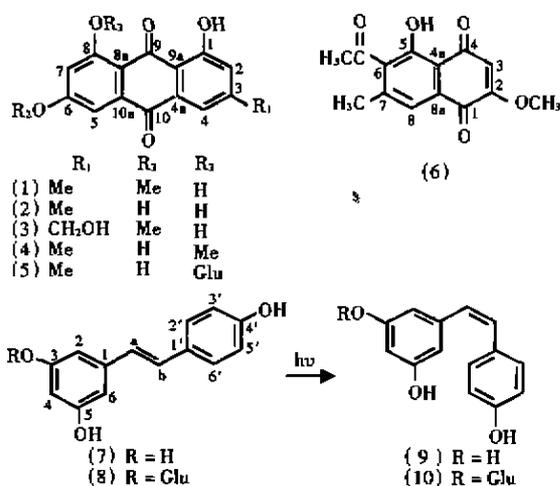
大黄素-6-甲醚(physcion 1):桔红色针晶(CHCl₃)。EI-MS m/z (%):284[M](100),255[M-CHO]⁺(33),241[M-CH₃CO]⁺(37);¹H NMR(CHCl₃)δ:6.99(1 H,s,H-2),7.54(1 H,s,H-4),7.25(1 H,d,J=2.5 Hz,H-5),6.60(1 H,d,J=2.5 Hz,H-7),2.42(3 H,s,CH₃),3.86(3 H,s,OCH₃),12.20,12.00(1 H each,s,OH);¹³C NMR(CDCl₃+DMSO)δ:164.87(C-1),120.84(C-2),148.11(C-3),124.09(C-4),107.87(C-5),162.14(C-6),106.37(C-7),166.26(C-8),190.46(C-9),181.49(C-10),132.91(C-4a),110.23(C-8a),113.15(C-9a),134.60(C-10a),21.74(CH₃),55.75(OCH₃)。以上氢谱数据与文献值相吻合^[4]。

大黄素(emodin 2):桔红色针晶(MeOH)。EI-MS m/z (%):270[M]⁺(100),214[M-2CO]⁺

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(25); ¹H NMR (CDCl₃ + DMSO) δ: 7.02 (1 H, s, H-2), 7.53 (1 H, s, H-4), 7.24 (1 H, d, J = 2.4 Hz, H-5), 6.61 (1 H, d, J = 2.4 Hz, H-7), 2.34 (3 H, s, CH₃), 12.10, 12.19 (1 H each, s, OH); ¹³C NMR (CDCl₃) δ: 164.66 (C-1), 120.19 (C-2), 147.33 (C-3), 123.57 (C-4), 109.09 (C-5), 161.62 (C-6), 107.83 (C-7), 165.29 (C-8), 189.73 (C-9), 181.34 (C-10), 132.62 (C-4a), 108.62 (C-8a), 113.04 (C-9a), 134.67 (C-10a), 21.37 (CH₃)。以上氢谱数据与文献值一致^[5]。

fallacinol (3): 桔黄色针晶 (MeOH)。EI-MS *m/z* (%): 300 [M]⁺ (100), 271 [M-CHO]⁺ (69), 243 [M-CHO-CO]⁺ (12); ¹H NMR (DMSO) δ: 7.22 (1 H, s, H-1), 7.60 (1 H, s, H-4), 7.10 (1 H, s, J = 2.0 Hz, H-5), 6.79 (1 H, d, 2.0 Hz, H-7), 3.89 (3 H, s, OCH₃), 4.58 (2 H, d, J = 5.5 Hz, OCH₂), 5.59 (1 H, t, J = 5.5 Hz, CH₂OH), 11.94, 12.10 (1 H each, s, OH); ¹³C NMR (DMSO) δ: 164.43 (C-1), 117.18 (C-2), 153.12 (C-3), 120.86 (C-4), 107.68 (C-5), 161.54 (C-6), 106.54 (C-7), 166.14 (C-8), 189.93 (C-9), 181.11 (C-10), 132.89 (C-4a), 109.83 (C-8a), 114.08 (C-9a), 134.79 (C-10a), 56.40 (OCH₃), 62.04 (OCH₂)。以上氢谱数据与文献值一致^[2]。

大黄素-8-甲醚 (questin 4): 桔黄色针晶 (MeOH)。EI-MS *m/z* (%): 284 [M]⁺ (100), 255 [M-CHO]⁺ (52); ¹H NMR (DMSO) δ: 7.10 (1 H, s, H-2), 7.40 (1 H, s, H-4), 7.18 (1 H, d, J = 2.0 Hz, H-5), 6.82 (1 H, d, J = 2.0 Hz, H-7), 2.36 (3 H, s, CH₃), 3.88 (3 H, s, OCH), 13.21 (1 H, s, OH); ¹³C NMR (DMSO) δ: 163.38 (C-1), 119.01 (C-2),

146.53 (C-3), 124.05 (C-4), 106.93 (C-5), 161.63 (C-6), 104.94 (C-7), 164.32 (C-8), 186.22 (C-9), 182.21 (C-10), 131.97 (C-4a), 112.67 (C-8a), 114.32 (C-9a), 136.75 (C-10a), 21.28 (CH₃), 56.28 (OCH₃)。以上氢谱数据与文献值一致^[2]。

大黄素-8-O-β-D-葡萄糖吡喃糖甙 (emodin-8-O-β-D-glucopyranoside 5): 桔红色针晶 (EtOH)。FAB-MS *m/z* (%): 431 [M-H]⁻ (100), 269 [431-162]⁻ (29); ¹H NMR (DMSO) δ: 7.09 (1 H, s, H-2), 7.38 (1 H, s, H-4), 7.23 (1 H, d, J = 2.0 Hz, H-5), 6.97 (1 H, d, J = 2.0 Hz, H-7), 2.35 (3 H, s, CH₃), 13.13 (1 H, s, OH), 5.03 (1 H, d, J = 7.6 Hz, sugar H-1); ¹³C NMR (DMSO) δ: 164.28 (C-1), 119.25 (C-2), 148.91 (C-3), 124.15 (C-4), 108.46 (C-5), 161.05 (C-6), 108.46 (C-7), 161.70 (C-8), 186.42 (C-9), 182.06 (C-10), 132.06 (C-4a), 113.39 (C-8a), 114.44 (C-9a), 136.49 (C-10a), 21.38 (CH₃), sugar C1~6 的 δ 值依次为: 101.02, 73.31, 76.37, 69.59, 77.32, 60.69。以上数据与文献值一致^[6]。

2-甲氧基-6-乙酰基-7-甲基胡桃醌 (PC-1 6): 桔红色针晶 (CHCl₃)。EI-MS *m/z* (%): 260 [M]⁺ (94), 245 [M-CH₃]⁺ (100), 217 [M-COCH₃]⁺ (58); ¹H NMR (CDCl₃) δ: 6.08 (1 H, s, H-3), 7.49 (1 H, s, H-8), 2.32 (3 H, s, CH₃), 3.90 (3 H, s, OCH₃), 2.56 (3 H, s, COCH₃), 12.48 (1 H, s, OH); ¹³C NMR (CDCl₃) δ: 179.50 (C-1), 161.13 (C-2), 109.61 (C-3), 190.33 (C-4), 158.23 (C-5), 130.62 (C-6), 143.54 (C-7), 121.65 (C-8), 136.75 (C-8a), 112.50 (C-4a), 19.95 (CH₃), 56.68 (OCH₃), 190.33 (COCH₃), 31.78 (COCH₃)。以上氢谱数据与文献值相吻合^[7]。

白藜芦醇 (resveratrol 7): 淡黄色针晶 (MeOH 水溶液)。EI-MS *m/z* (%): 228 [M]⁺ (100), 211 [M-OH]⁺ (10); ¹H NMR (Me₂CO) δ: 6.54 (d, J = 2.0 Hz, H-2), 6.27 (t, J = 2.0 Hz, H-4), 6.54 (d, J = 2.0 Hz, H-6), 7.40 (d, J = 8.5 Hz, H-2'), 6.83 (d, J = 8.5 Hz, H-3'), 6.83 (d, J = 8.5 Hz, H-5'), 7.40 (d, J = 8.5 Hz, H-6'), 6.88 (d, J = 16.3 Hz, H-a), 7.00 (d, J = 16.3 Hz, H-b); ¹³C NMR (Me₂CO) δ: 140.85 (C-1), 105.74 (C-2), 159.44 (C-3), 102.70 (C-4), 159.44 (C-5), 105.74 (C-6), 126.80 (C-a), 129.11 (C-b), 129.93 (C-1'), 128.66 (C-2'), 116.39

(C-3'), 158.02 (C-4'), 140.85 (C-5'), 105.74 (C-6')。上述氢谱数据与文献值一致^[3]。

白藜芦醇甙(piceid)(8):白色针晶(MeOH水溶液)。FAB-MS m/z (%): 389 [M-H]⁻ (100), 227 [389-162]⁻ (32); ¹H NMR (Me₂CO) δ : 6.83 (t, J = 2.0 Hz, H-2), 6.47 (t, J = 2.0 Hz, H-4), 6.67 (t, J = 2.0 Hz, H-6), 7.41 (d, J = 8.5 Hz, H-2'), 6.84 (d, J = 8.5 Hz, H-3'), 6.84 (d, J = 8.5 Hz, H-5'), 7.41 (d, J = 8.5 Hz, H-6'), 6.90 (d, J = 16.3 Hz, H-a), 7.08 (d, J = 16.3 Hz, H-b), 4.94 (d, J = 7.7 Hz, sugar H-1); ¹³C NMR (Me₂CO) δ : 140.91 (C-1), 106.76 (C-2), 160.29 (C-3), 104.03 (C-4), 159.42 (C-5), 108.29 (C-6), 126.56 (C-a), 129.73 (C-b), 129.95 (C-1'), 128.84 (C-2'), 116.48 (C-3'), 158.29 (C-4'), 116.48 (C-5'), 128.81 (C-6'), sugar C1~6 的 δ 值依次为: 102.16, 74.81, 78.53, 71.59, 77.81, 62.86。上述氢谱数据与文献值一致^[3]。

顺式白藜芦醇(9):白色粉末。¹H NMR (Me₂CO) δ : 6.30 (d, J = 2.0 Hz, H-2), 6.24 (t, J = 2.0 Hz, H-4), 6.30 (d, J = 2.0 Hz, H-6), 7.15 (d, J = 8.5 Hz, H-2'), 6.71 (d, J = 8.5 Hz, H-3'), 6.71 (d, J = 8.5 Hz, H-5'), 7.16 (d, J = 8.5 Hz, H-6'), 6.35 (d, J = 12.0 Hz, H-a), 6.41 (d, J = 12.0 Hz, H-b); ¹³C NMR (Me₂CO) δ : 140.62 (C-1), 107.81 (C-2), 159.46 (C-3), 102.40 (C-4), 159.81 (C-5), 107.50 (C-6), 128.86 (C-a), 129.42 (C-b), 129.23 (C-1'), 130.85 (C-2'), 115.92 (C-3'), 157.54 (C-4'), 115.05 (C-5'), 130.83 (C-6')。以上氢谱数据中 H_a、H_b 的 J_{a,b} 值为 12.0 Hz, 显示其为顺式产物, 其余波谱数据与 resveratrol 基本一致。

顺式白藜芦醇甙(10):白色粉末。¹H NMR (Me₂CO) δ : 6.46 (t, J = 2.0 Hz, H-2), 6.44 (t, J = 2.0 Hz, H-4), 6.52 (s, H-6'), 7.15 (d, J = 8.5 Hz, H-

2'), 6.74 (d, J = 8.5 Hz, H-3'), 6.74 (d, J = 8.5 Hz, H-5'), 7.15 (d, J = 8.5 Hz, H-6'), 6.37 (d, J = 12.0 Hz, H-a), 6.44 (d, J = 12.0 Hz, H-b), 4.76 (d, J = 8.0 Hz, sugar H-1); ¹³C NMR (Me₂CO) δ : 140.25 (C-1), 108.52 (C-2), 161.00 (C-3), 103.94 (C-4), 159.32 (C-5), 110.38 (C-6), 129.45 (C-a), 130.56 (C-b), 129.45 (C-1'), 131.50 (C-2'), 116.00 (C-3'), 157.23 (C-4'), 115.82 (C-5'), 128.97 (C-6'), sugar C1~6 的 δ 值依次为: 102.11, 74.63, 78.24, 71.25, 77.60, 62.54。氢谱数据中 H_a、H_b 的 J_{a,b} 值为 12.0 Hz, 显示其为顺式产物, 其余波谱数据与 piceid 基本一致。

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STUDIES ON THE CONSTITUENTS OF *REYNOUTRIA JAPONICA* HOUTT.

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Abstract Eight known compounds, physcion (1), emodin (2), fallacinol (3), questin (4), emodin-8-O- β -D-glucopyranoside (5), 2-methoxy-6-acetyl-7-methyljuglone (PC-1, 6), resveratrol (7), piceid (8) were isolated from the dry roots of *Reynoutria Japonica* Houtt. Besides, two cis-stilbenes, cis-resveratrol (9) and cis-piceid (10) were obtained through phytochemical isomerization.

Key words *Reynoutria Japonica* Houtt.; chemical constituents; isomerization