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灰毛豆叶片的化学成分研究

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摘要:从灰毛豆叶片中分离得到 10 个化合物,通过波谱数据和理化性质分别鉴定为:stigmast-1,5-dien-3 β -ol (1), clemaphenol A (2), 松脂醇 (3), 檉素 (4), 3-吲哚甲醛 (5), 色氨酸 (6), (S)-4-苄基-2-噁唑烷酮 (7), 4-羟基苯基丙酸 (8), buteaspermanol (9), bovatachalcone (10)。其中化合物 1, 2, 4, 5, 7, 8, 9 首次从该植物中分离得到。

关键词:灰毛豆叶片; 化学成分; 结构鉴定

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Chemical Constituents from the Leaves of *Tephrosia purpurea*

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Abstract: Ten compounds were isolated from the MeOH extracts of the *Tephrosia purpurea* leaves. The structures of the compounds were determined on the basis of spectroscopic data and physicochemical properties. Their structures were elucidated as stigmast-1,5-dien-3 β -ol (1), clemaphenol A (2), (+)-pinoresinol (3), eudesmin (4), indole-3-carbaldehyde (5), tryptophan (6), (S)-4-benzyl-2-oxazolidinone (7), 4-hydroxybenzene propanoic acid (8), buteaspermanol (9), bovatachalcone (10). Compounds 1, 2, 4, 5, 7, 8, 9 were isolated from the title plant for the first time.

Key words: *Tephrosia purpurea*; chemical compounds; structures identification

灰毛豆 *Tephrosia purpurea*, 又名山青、野蓝、野紫靛, 属于豆科 Leguminosae, 灰毛豆属 *Tephrosia*。该植物主要分布于热带及亚热带地区, 如越南、巴基斯坦和中国的广西、云南及湖南等地, 多生于低丘陵或平地草丛中或路旁及矿质土上^[1]。全株有毒, 其中以根部最毒, 中毒症状为腹泻等。民间多将其作为绿肥使用, 亦常作药用。据报道灰毛豆的整株植物具有治疗肿瘤、溃疡、麻风病、过敏症以及风湿、哮喘和支气管炎等药理作用^[2]。灰毛豆还具有杀虫活性, 除茎干木质部以外其它各部位包括种子、树皮、根皮、豆荚、枝条和树叶的甲醇提取物对白纹伊蚊幼虫、菜青虫幼虫、斜纹夜蛾幼虫和黄曲条跳甲成虫等都有杀虫活性^[3]。近年来的杀虫活性物质研究主要集中于灰毛豆的根、茎、种子等部位^[3], 灰毛

豆叶片尽管显示了一定的杀虫活性, 针对其化学成分的研究报道却很少, 其活性物质基础并不清楚。该植物目前处于野生状态、资源丰富。本文对灰毛豆叶片甲醇提取物的主要化学成分进行了研究, 分离得到 10 个化合物, 分别鉴定为 stigmast-1,5-dien-3 β -ol (1), clemaphenol A (2), 松脂醇 (3), 檉素 (4), 3-吲哚甲醛 (5), 色氨酸 (6), (S)-4-苄基-2-噁唑烷酮 (7), 4-羟基苯基丙酸 (8), buteaspermanol (9), bovatachalcone (10)。其中化合物 1, 2, 4, 5, 7, 8, 9 首次从该植物中分离报道。

1 仪器和材料

仪器: Bruker 400M 型核磁共振波谱仪 (¹H NMR 为 400 MHz, ¹³C NMR 为 100 MHz, TMS 为内标); 硅胶及 GF₂₅₄ 层析硅胶板(青岛海洋化工有限公司); GF₂₅₄ 厚制备薄层板(规格: 20 cm × 20 cm, 烟台江友硅胶开发有限公司); Sephadex LH-20 羟丙基葡聚糖(瑞士 Amersham 生物科学公司); 十八烷基

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甲硅烷基(ODS)(50目,YMC有限公司);Waters 1525(Waters 2414/2489检测器)高效液相色谱仪;EYELA N-1001型旋转蒸发仪(上海爱朗仪器有限公司);ZF-6型三用紫外线分析仪(上海嘉鹏科技有限公司);Z系列层析柱(上海沪西分析仪器厂有限公司)。

植物材料于2010年11月采自湖南省江永县,经广西林业科学院的钟业聪教授鉴定为豆科灰毛豆属植物灰毛豆(*Tephrosia purpurea*),标本(No. 200607)保存于湖南农业大学植保学院。

2 提取分离

采集灰毛豆叶片18.8 kg 40 °C烘干粉碎,采用冷浸法用甲醇在室温浸提3次,合并滤液减压浓缩,得到灰毛豆叶片提取物浸膏414.4 g。

将提取物经硅胶柱层析,以石油醚-丙酮、乙酸乙酯-甲醇梯度洗脱,得24个组分(Fr. 1-24)。Fr. 4经正相硅胶柱色谱(石油醚-乙酸乙酯95:5),主点采用Sephadex LH-20层析柱(甲醇冲洗),及薄层制备得到化合物**10**(20 mg)。Fr. 6经正相硅胶柱色谱(石油醚-乙酸乙酯9:1)得到化合物**1**(100 mg)。Fr. 9经正相硅胶柱色谱(氯仿-甲醇98:2),采用Sephadex LH-20层析柱(甲醇冲洗),及薄层制备得到化合物**4**(19 mg),**5**(15 mg),**9**(17 mg)。Fr. 16经正相硅胶柱色谱(氯仿-甲醇98:2),采用Sephadex LH-20层析柱(甲醇冲洗)得到化合物**2**(30 mg),**3**(40 mg)。Fr. 22经反相ODS柱色谱,以甲醇-水(3:7-10:0)冲洗,然后采用Sephadex LH-20层析柱(甲醇冲洗)和半制备液相得到化合物**6**(32 mg),**7**(27 mg),**8**(39 mg)。

3 结构鉴定

化合物1为白色针状晶体,分子式为C₂₉H₄₈O,在UV下没吸收;¹H NMR(500 MHz, CDCl₃)δ: 5.35(1H,d,J=5.1 Hz,H-6),5.14(1H,d,J=8.4 Hz,H-1),5.02(1H,dd,J=8.4,8.4 Hz,H-2),3.52(1H,m,H-3),1.00(3H,br s,H-19),0.97(3H,d,J=6.6 Hz,H-21),0.88(3H,d,J=6.5 Hz,H-29),0.84(1H,d,J=6.0 Hz,H-26),0.82(3H,d,J=6.0 Hz,H-27),0.68(3H,br s,H-18);¹³C NMR(125 MHz, CDCl₃)δ:138.4(C-1),129.3(C-2),71.8(C-3),42.4(C-4),140.8(C-5),121.8(C-6),29.8(C-7),31.7(C-8),50.2(C-

9),36.2(C-10),21.1(C-11),37.3(C-12),39.8(C-13),56.9(C-14),24.3(C-15),28.3(C-16),56.1(C-17),11.9(C-18),19.4(C-19),34.0(C-20),18.8(C-21)。以上数据经与文献^[4]对照,鉴定此化合物为stigmast-1,5-dien-3β-ol。

化合物2为白色晶体,分子式为C₂₀H₂₂O₆,在UV₂₅₄下显暗斑;¹H NMR(400 MHz, CD₃OD)δ:3.01(2H,m,H-1,5),4.10(2H,d,J=4.1 Hz,H-2,6),4.07(1H,dd,J=8.8,3.3 Hz,H-4),4.11(1H,dd,J=8.8,6.6 Hz,H-8),6.86(2H,br s,H-2',2''),6.74(2H,d,J=8.2 Hz,H-5',5''),6.74(2H,dd,J=8.2,1.1 Hz,H-6',6''),4.59(3H,s,-OMe);¹³C NMR(100 MHz, CD₃OD)δ:54.0(C-1),54.0(C-5),85.7(C-2),85.7(C-6),71.1(C-4),71.1(C-8),132.5(C-1'),132.5(C-1''),110.7(C-2'),110.7(C-2''),145.8(C-3'),145.8(C-3''),148.0(C-4'),148.0(C-4''),115.5(C-5'),115.5(C-5''),118.9(C-6'),118.9(C-6''),55.6(-OMe)。以上数据经与文献^[5]对照,鉴定此化合物为clemaphenol A。

化合物3为白色晶体,分子式为C₂₀H₂₂O₆,在UV₂₅₄下显暗斑;¹H NMR(400 MHz, CD₃OD)δ:2.92(2H,m,H-1,5),4.08(2H,d,J=4.6 Hz,H-2,6),4.04(1H,dd,J=9.2,3.8 Hz,H-4),4.06(H,dd,J=9.2,7.0 Hz,H-8),6.85(2H,d,J=2.2 Hz,H-2',2''),6.83(2H,d,J=8.5 Hz,H-5',5''),6.72(2H,dd,J=8.5,2.2 Hz,H-6',6''),4.54(3H,s,-OMe);¹³C NMR(100 MHz, CD₃OD)δ:54.0(C-1),54.0(C-5),85.2(C-2),85.2(C-6),71.1(C-4),71.1(C-8),134.1(C-1'),134.1(C-1''),112.5(C-2'),112.5(C-2''),147.3(C-3'),146.6(C-4'),146.6(C-4''),113.8(C-5'),113.8(C-5''),117.2(C-6'),117.2(C-6''),55.8(-OMe)。以上数据经与文献^[5]对照,鉴定此化合物为松脂醇((+)-pinoresinol)。

化合物4为无定型粉末,分子式为C₂₂H₂₆O₆,在UV₂₅₄下显暗斑;¹H NMR(400 MHz, DMSO)δ:3.75(6H,s,3,3'-OMe),3.73(6H,s,4,4'-OMe),3.05(2H,m,H-3,5),3.78(2H,m,H-4),4.15(2H,dd,J=9.0,6.9 Hz,H-8),6.90~6.93(6H,m,H-6'',6',5'',5',2'',2')4.65(2H,d,J=4.8 Hz,H-6,2);¹³C NMR(100 MHz, DMSO)δ:54.0(C-1),54.0(C-5),85.3(C-2),85.3(C-6),71.4

(C-4), 71.4 (C-8), 134.3 (C-1'), 134.3 (C-1''), 110.2 (C-2'), 110.2 (C-2''), 148.5 (C-3'), 148.5 (C-3''), 149.2 (C-4'), 149.2 (C-4''), 111.9 (C-5'), 111.9 (C-5''), 118.4 (C-6'), 118.4 (C-6''), 55.9 (4 \times -OMe)。以上数据经与文献^[6]对照, 鉴定此化合物为桉素(eudesmin)。

化合物5 为白色晶体, 分子式为 C₉H₇NO, 在 UV₂₅₄ 下显暗斑; ¹H NMR (400 MHz, DMSO) δ : 9.93 (1H, s, -CHO), 8.27 (1H, s, -NH), 8.09 (1H, dd, J = 5.0, 7.4 Hz, H-4), 7.52 (1H, d, J = 7.5 Hz, H-7), 7.25 (2H, m, H-5, 6); ¹³C NMR (100 MHz, DMSO) δ : 185.4 (-CHO), 138.8 (C-7a), 124.3 (C-4a), 121.2 (C-6), 122.7 (C-5), 112.9 (C-7), 118.6 (C-3), 123.7 (C-4), 137.5 (C-2)。以上数据经与文献^[7]对照, 鉴定此化合物为 3-吲哚甲醛(indole-3-carbaldehyde)。

化合物6 为白色晶体, 分子式为 C₁₁H₁₂N₂O₂, 在 UV₂₅₄ 下显暗斑; ¹H NMR (400 MHz, CD₃OD) δ : 7.70 (1H, d, J = 8.0 Hz, H-5), 7.37 (1H, d, J = 8.0 Hz, H-6), 7.21 (1H, s, H-2), 7.11 (1H, dd, J = 11.8, 6.2 Hz, H-7), 7.04 (1H, dd, J = 11.8, 5.8 Hz, H-4), 3.86 (1H, br s, H-NH₂), 3.52 (1H, dd, J = 10.7, 6.8 Hz, H-2'), 3.15 (1H, dd, J = 6.8, 4.3 Hz, H-1'); ¹³C NMR (100 MHz, CD₃OD) δ : 176.0 (C-3'), 136.9 (C-3), 127.0 (C-4), 123.6 (C-9), 121.3 (C-8), 118.7 (C-6), 117.9 (C-7), 111.1 (C-5), 108.1 (C-2), 55.3 (C-2'), 27.0 (C-1')。以上数据经与文献^[8]对照, 鉴定此化合物为色氨酸(tryptophan)。

化合物7 为白色晶体, 分子式为 C₁₀H₁₀NO₂, 在 UV 下没吸收, $[\alpha]_D^{18}$ + 64 (c 1.0, CHCl₃); ¹H NMR (400 MHz, CD₃OD) δ : 7.25-7.34 (5H, m, H-2, 3, 4, 5, 6), 4.40 (1H, t, J = 7.5 Hz, H-2'), 4.20 (1H, s, NH), 4.15 (2H, m, H-2''), 2.87 (1H, dd, J = 6.1, 12.2 Hz, H-1'), 2.90 (1H, dd, J = 6.1, 12.2 Hz, H-1'); ¹³C NMR (100 MHz, CD₃OD) δ : 136.3 (C-1), 128.3 (C-2), 129.0 (C-3), 126.4 (C-4), 129.0 (C-5), 128.3 (C-6), 40.5 (C-1'), 53.5 (C-2'), 69.2 (C-3'), 160.5 (C-4')。以上数据经与文献^[9]对照, 鉴定此化合物为 (S)-4-苄基-2-噁唑烷酮((S)-4-benzyl-2-oxazolidinone)。

化合物8 为白色晶体, 分子式为 C₉H₁₀O₃, 在 UV₂₅₄ 下显暗斑; ¹H NMR (400 MHz, CD₃OD) δ : 6.77

(2H, d, J = 8.0 Hz, H-2, 6), 7.10 (2H, d, J = 8.0 Hz, H-3, 5), 3.10 (2H, t, J = 8.4 Hz, H-1'); ¹³C NMR (100 MHz, CD₃OD) δ : 126.9 (C-1), 129.4 (C-2), 115.2 (C-3), 136.2 (C-4), 115.1 (C-5), 129.4 (C-6), 32.5 (C-1'), 40.8 (C-2'), 156.0 (C-3')。以上数据经与文献^[10]对照, 鉴定此化合物为 4-羟基苯基丙酸(4-hydroxybenzene propanoic acid)。

化合物9 为白色晶体, 分子式为 C₁₆H₁₄O₈, 在 UV₂₅₄ 下显暗斑; ¹H NMR (400 MHz, CD₃OD) δ : 5.01 (1H, d, J = 11.6 Hz, H-2), 4.52 (1H, dd, J = 3.7, 11.6 Hz, H-3), 7.20 (1H, s, H-5), 6.32 (1H, s, H-8), 7.47 (1H, m, H-2', 6'), 7.33 (3H, m, H-3', 5'), 7.82 (1H, m, H-4'), 4.98 (1H, br d, 3-OH), 3.78 (3H, s, 7-OMe); ¹³C NMR (100 MHz, CD₃OD) δ : 73.3 (C-2), 84.4 (C-3), 192.6 (C-4), 106.7 (C-5), 137.3 (C-6), 103.1 (C-8), 128.5 (C-2'), 128.1 (C-3'), 127.5 (C-4'), 128.1 (C-5'), 128.1 (C-6'), 55.3 (7-OMe)。以上数据经与文献^[11]对照, 鉴定此化合物为 buteaspermanol。

化合物10 为黄色晶体, 分子式为 C₂₁H₂₀O₄, 在 UV₂₅₄ 下显暗斑; ¹H NMR (500 MHz, CDCl₃) δ : 14.52 (1H, s, -OH), 7.87 (1H, d, J = 15.5 Hz, H-7), 7.77 (1H, d, J = 15.5 Hz, H-8), 7.60 (2H, m, H-2, 6) 7.41-7.38 (3H, m, H-3, 4, 5), 6.68 (1H, d, J = 10.0 Hz, H-4'), 5.93 (1H, s, H-8'), 5.46 (1H, d, J = 10 Hz, H-5'), 3.92 (3H, s, -OMe), 1.45 (6H, s, CH₃-10', 11'); ¹³C NMR (125 MHz, CDCl₃) δ : 192.7 (C-9), 162.6 (C-7'), 162.5 (C-9'), 160.4 (C-2'), 142.2 (C-7), 135.6 (C-1), 130.0 (C-4), 128.9 (C-3, 5), 128.4 (C-5'), 127.7 (C-8), 125.4 (C-2, 6), 116.1 (C-4'), 106.1 (C-1'), 103.0 (C-3'), 91.6 (C-8'), 78.0 (C-6'), 55.9 (-OMe), 28.6 (2 \times CH₃)。以上数据经与文献^[12]对照, 鉴定此化合物为 obovatachalcone。

4 讨论

本文针对灰毛豆(*T. purpurea*)叶片甲醇提取物的化学成分进行了研究, 从中分离得到 10 个化合物: 为 stigmast-1, 5-dien-3 β -ol (1), clemaphenol A (2), 松脂醇(3), 桉素(4), 3-吲哚甲醛(5), 色氨酸(6), (S)-4-苄基-2-噁唑烷酮(7), 4-羟基苯基丙酸(8), buteaspermanol (9), bovatachalcone (10), 其中

化合物**1、2、4、5、7、8、9**首次从该植物中分离得到。以上化学成分为灰毛豆叶片的深入研究和开发利用提供了化学物质基础。

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