



千里香化学成分的研究

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摘 要:千里香[*Murraya paniculata* (L.) Jack]枝叶晒干、甲醇浸泡提取,对乙酸乙酯萃取部分用硅胶柱层析、凝胶柱层析等分离手段进行分离。从千里香中分离得到6个化合物,经核磁共振波谱鉴定其结构为 indazole (1)、5,3'-dihydroxy-7,8,4'-trimethoxyflavone (2)、3,5,7,8,3',4',5'-heptamethoxyflavone (3)、5-hydroxy-3,7,8,3',4',5'-hexamethoxyflavone (4)、3,5,6,7,3',4',5'-heptamethoxyflavonol (5)、exoticin (6),其中化合物1和2从九里香属植物中首次分离得到。

关键词:千里香;分离;化合物

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Study on Chemical Compositions from *Murraya paniculata* (L.) Jack

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Abstract:The branches and leaves of *Murraya paniculata* were dried and extracted with methanol, and the ethyl acetate extracted part was separated by silica gel column chromatography, gel column chromatography and other separation means. Six compounds were isolated from *Murraya paniculata*, and their structures were identified by nuclear magnetic resonance spectroscopy as indazole (1), 5,3'-dihydroxy-7,8,4'-trimethoxyflavone (2), 3,5,7,8,3',4',5'-heptamethoxyflavone (3), 5-hydroxy-3,7,8,3',4',5'-hexamethoxyflavone (4), 3,5,6,7,3',4',5'-heptamethoxyflavonol (5), exoticin (6). Compound 1 and 2 were isolated from the *Murraya* genus for the first time.

Keywords:*Murraya paniculata*; isolation; compounds

千里香(*Murraya paniculata* (L.) Jack)属于芸香科九里香属植物^[1],是一种常绿灌木,原产于中国、印度、巴基斯坦和缅甸,我国主要分布在福建、广东、海南、云南等地^[2]。千里香是一种具有广泛药用价值的民间药物,可用于治疗胃痛、牙疼、瘰病等疾病,其根皮可用于治疗痛风、挫伤和骨痛,起到止痛剂或局部麻醉剂的效果^[3-4]。对千里香的化学成分诸多研究表明,千里香中主要含有香豆素、吲哚类生物碱、黄酮等成分,这些成分的生物活性具体表现为抗生育、抗炎抗菌、降血糖等作用^[5-7]。此外,该植物还具有较高的观赏及环境美化价值,可用于造型和绿篱。为进一步了解千里香的化学成分,从中寻找具有良好活性的化合物,提高该植物的利用率,本文对采自云南西双版纳的千里香枝叶进行了研究。将风干千里香枝叶的甲醇提取物用乙酸乙酯萃取多次,得到的浸膏经过硅胶柱层析、凝胶柱层析等手段分离纯化,得到6个成分。利用核磁共振波谱鉴定其结构分别为含氮化合物和黄酮类化合物。结构分别为:吲唑(indazole,1)、5,3'-dihydroxy-7,8,4'-trimethoxyflavone(2)、3,5,7,8,3',4',5'-heptamethoxyflavone(3)、5-hydroxy-3,7,8,3',4',5'-hexamethoxyflavone(4)、3,5,6,7,3',4',5'-heptamethoxyflavonol(5)、exoticin(6)。其中化合物1和2是首次从九里香属植物

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中分离得到。化合物结构见图1。

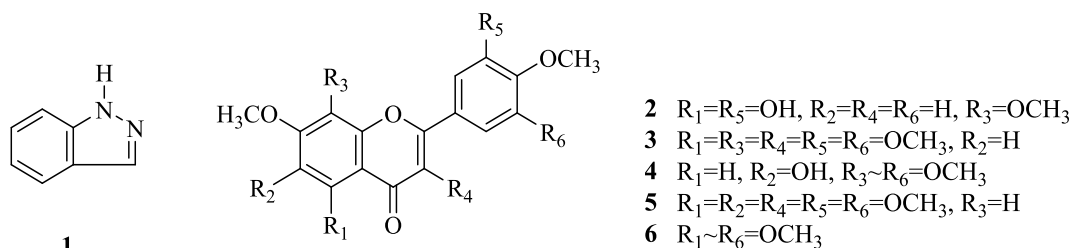


图1 千里香中的化学成分

Figure1 chemical composition from *Murraya paniculata* (L.) Jack

1 实验仪器、试剂与材料

1.1 实验仪器

超导核磁共振仪 DRX 500 MHz, 瑞士布鲁克公司; EYELA ROTARY EVAPORATOR N-1001, 东京理化器械独资工厂; ZF-2 型三用紫外仪, 上海安亭电子仪器厂。

1.2 实验试剂

Sephadex LH-20 凝胶, GE Healthcare Bio-Sciences AB; 层析硅胶, 青岛海洋化工厂; 高效薄层层析硅胶板 GF25, 烟台化工研究院; 显色剂为硫酸乙醇溶液, 所用溶剂均为工业纯, 使用前重蒸; 其他为分析纯或化学纯试剂。

1.3 实验材料

千里香枝叶由中国医学科学院药用植物开发研究所云南分所彭朝中老师采集于云南西双版纳, 并鉴定为 *Murraya paniculata* (L.) Jack。

2 化合物的提取与分离

将风干后的千里香枝叶 (14.5 kg) 进行粉碎, 用甲醇 (50 L) 于室温下浸泡提取 6 次, 将得到的提取液进行减压浓缩合并, 得到甲醇粗提物 (2.7 kg)。再将甲醇粗提物溶于水中并用乙酸乙酯反复萃取 6 次后得萃取物 (1.1 kg), 将其用硅胶 (80 ~ 100 目) 进行拌样, 进行硅胶柱层析, 以石油醚/乙酸乙酯 (1:0 → 0:1) 进行梯度洗脱得到 A-H 8 个部分, 对 E 和 F 部分利用硅胶柱层析和 Sephadex LH-20 凝胶柱层析进行反复分离纯化得到 indazole (1)、5,3'-dihydroxy-7,8,4'-trimethoxyflavone (2)、3,5,7,8,3',4',5'-heptamethoxyflavone (3)、5-hydroxy-3,7,8,3',4',5'-hexamethoxyflavone (4)、3,5,6,7,3',4',5'-heptamethoxyflavonol (5)、exoticin (6)。

3 结构鉴定

化合物 1: 白色粉末, 在紫外 (254 nm) 有荧光, 10% 的硫酸乙醇溶液加热呈淡粉色, MF: $C_7H_6N_2$, MW: 118; 1H NMR (500 MHz, CD_3OCD_3): δ 8.05 (1H, s, H-9), 7.92 (1H, d, J = 8.8 Hz, H-7), 7.51 (1H, d, J = 6.7 Hz, H-4), 7.24-7.16 (1H, m, H-5), 6.93 (1H, d, J = 8.8 Hz, H-6)。 ^{13}C NMR (125 MHz, CD_3OCD_3): δ 137.5 (s, C-8), 132.8 (d, C-3), 127.4 (d, C-6), 123.3 (s, C-9), 122.1 (d, C-4), 121.9 (d, C-5), 112.8 (d, C-7)。与文献报道的 indazole 的 1H NMR 和 ^{13}C NMR 数据基本一致, 因此化合物 1 确定为 indazole^[8]。

化合物 2: 黄色粉末, 在紫外 (254 nm) 有荧光, 10% 的硫酸乙醇溶液加热呈黄色, MF: $C_{18}H_{16}O_7$, MW: 344; 1H NMR (500 MHz, DMSO- d_6): δ 12.61 (1H, s, 5-OH), 9.55 (1H, s, 3'-OH), 7.43 (1H, dd, J = 8.5, 2.2 Hz, H-6'), 7.34 (1H, d, J = 2.2 Hz, H-2'), 6.98 (1H, d, J = 8.6 Hz, H-5'), 6.68 (1H, s, H-3), 6.44

(1H, s, H-6), 3.78 (3H, s, 4'-OCH₃), 3.74 (3H, s, 7-OCH₃), 3.71 (3H, s, 8-OCH₃)。 ¹³C NMR (125 MHz, DMSO-*d*₆): δ 182.2 (s, C-4), 163.8 (s, C-2), 158.5 (s, C-7), 156.8 (s, C-5), 151.4 (s, C-4'), 148.9 (s, C-9), 146.9 (s, C-3'), 128.6 (s, C-8), 123.1 (s, C-1'), 118.9 (d, C-6'), 113.0 (d, C-2'), 112.6 (d, C-5'), 104.0 (s, C-10), 103.4 (d, C-3), 96.1 (d, C-6), 61.3 (q, 8-OCH₃), 56.6 (q, 7-OCH₃), 55.9 (q, 4'-OCH₃)。与文献报道的5,3'-dihydroxy-7,8,4'-trimethoxyflavone的¹H NMR和¹³C NMR数据基本一致,因此化合物2确定为5,3'-dihydroxy-7,8,4'-trimethoxyflavone^[9]。

化合物3:黄色晶体,在紫外(254 nm)有荧光,10%的硫酸乙醇溶液加热呈黄色,MF: C₂₂H₂₄O₉, MW: 432; ¹H NMR (500 MHz, CDCl₃): δ 7.53 (1H, s, H-3), 6.41 (1H, s, H-1', H-6'), 4.00 (3H, s, 5-OCH₃), 3.99 (3H, s, 7-OCH₃), 3.96 (3H, s, 3'-OCH₃), 3.93 (3H, s, 5'-OCH₃), 3.93 (3H, s, 8-OCH₃), 3.90 (3H, s, 4'-OCH₃)。 ¹³C NMR (125 MHz, CDCl₃): δ 174.4 (s, C-4), 156.5 (s, C-7), 156.5 (s, C-2), 153.2 (s, C-3'), 152.1 (s, C-5'), 151.0 (s, C-5), 150.9 (s, C-9), 141.4 (s, C-4'), 140.1 (s, C-3), 130.4 (s, C-8), 126.2 (s, C-1'), 109.3 (s, C-10), 105.7 (d, C-6'), 104.8 (d, C-2'), 92.2 (d, C-6), 61.5 (q, 5-OCH₃), 61.1 (q, 8-OCH₃), 60.1 (q, 3-OCH₃), 56.7 (q, 7-OCH₃), 56.5 (q, 3'-OCH₃), 56.2 (q, 4'-OCH₃), 56.2 (q, 5'-OCH₃)。与文献报道的3,5,7,8,3',4',5'-heptamethoxyflavone的¹H NMR和¹³C NMR数据基本一致,因此化合物3确定为3,5,7,8,3',4',5'-heptamethoxyflavone^[10]。

化合物4:黄色粉末,在紫外(254 nm)有荧光,10%的硫酸乙醇溶液加热呈黄色,MF: C₂₁H₂₂O₉, MW: 418; ¹H NMR (500 MHz, CDCl₃): δ 12.39 (1H, s, 5-OH), 7.51 (2H, s, H-2', H-6'), 6.42 (1H, s, H-6), 3.97 (3H, s, 8-OCH₃), 3.95 (3H, s, 7-OCH₃), 3.94 (3H, s, 3'-OCH₃), 3.92 (3H, s, 3-OCH₃), 3.90 (3H, s, 4'-OCH₃, 5'-OCH₃)。 ¹³C NMR (125 MHz, CDCl₃): δ 179.2 (s, C-4), 158.7 (s, C-5), 157.6 (s, C-7), 155.4 (s, C-2), 153.3 (s, C-3', C-5'), 148.5 (s, C-9), 140.7 (s, C-4'), 139.3 (s, C-3), 128.8 (s, C-8), 125.8 (s, C-1'), 105.9 (d, C-2'), 105.5 (s, C-10), 95.6 (d, C-6), 61.4 (q, 8-OCH₃), 61.2 (q, 7-OCH₃), 60.5 (q, 3-OCH₃), 56.5 (q, 3'-OCH₃), 56.4 (q, 4'-OCH₃), 56.3 (q, 5'-OCH₃)。与文献报道的5-hydroxy-3,7,8,3',4',5'-hexamethoxyflavone的¹H NMR和¹³C NMR数据基本一致,因此化合物4确定为5-hydroxy-3,7,8,3',4',5'-hexamethoxyflavone^[10]。

化合物5:黄色粉末,在紫外(254 nm)有荧光,10%的硫酸乙醇溶液加热呈黄色,MF: C₂₂H₂₄O₉, MW: 432; ¹H NMR (500 MHz, CDCl₃): δ 7.34 (1H, s, H-3), 6.74 (2H, s, H-2', H-6'), 6.74 (1H, s, H-8), 4.00 (3H, s, 5-OCH₃), 3.98 (3H, s, 7-OCH₃), 3.94 (3H, s, 3'-OCH₃), 3.93 (3H, s, 4'-OCH₃, 5'-OCH₃), 3.91 (3H, s, 3-OCH₃), 3.87 (3H, s, 6-OCH₃)。 ¹³C-NMR (125 MHz, CDCl₃): δ 173.8 (s, C-4), 157.9 (s, C-7), 157.9 (s, C-2), 153.7 (s, C-5), 153.2 (s, C-3'), 153.2 (s, C-5'), 152.5 (s, C-9), 141.3 (s, C-4'), 140.3 (s, C-6), 140.2 (s, C-3), 126.0 (s, C-1'), 113.2 (s, C-10), 105.9 (d, C-6'), 96.1 (d, C-8), 62.3 (q, 5-OCH₃), 61.7 (q, 7-OCH₃), 61.1 (q, 6-OCH₃), 60.2 (q, 3-OCH₃), 56.6 (q, 3'-OCH₃), 56.5 (q, 4'-OCH₃, 5'-OCH₃)。与文献报道的3,5,6,7,3',4',5'-heptamethoxyflavonol的¹H NMR和¹³C NMR数据基本一致,因此化合物5确定为3,5,6,7,3',4',5'-heptamethoxyflavonol^[10]。

化合物6:黄色粉末,在紫外(254 nm)有荧光,10%的硫酸乙醇溶液加热呈黄色,MF: C₂₃H₂₆O₁₀, MW: 462; ¹H NMR (500 MHz, CDCl₃): δ 7.50 (2H, s, H-2', H-6'), 4.08 (3H, s, 7-OCH₃), 3.98 (3H, s, 8-OCH₃), 3.95 (3H, s, 5-OCH₃), 3.92 (12H, s, 6-OCH₃, 3'-OCH₃, 4'-OCH₃, 5'-OCH₃), 3.88 (3H, s, 3-OCH₃)。 ¹³C NMR (125 MHz, CDCl₃): δ 173.9 (s, C-4), 153.2 (s, C-3), 152.8 (s, C-3', C-5'), 151.5 (d, C-2), 148.3 (s, C-5), 146.8 (s, C-9), 143.9 (s, C-6), 140.2 (s, C-4'), 137.9 (s, C-8), 126.1 (s, C-1'), 115.1 (s, C-10), 105.7 (d, C-2', C-6'), 62.4 (q, 5-OCH₃), 62.0 (q, 6-OCH₃), 61.9 (q, 8-OCH₃), 61.8 (q, 7-OCH₃), 61.1 (q, 4'-OCH₃), 60.0 (q, 3-OCH₃), 56.2 (q, 3'-OCH₃, 5'-OCH₃)。与文献报道的exoticin

的¹H NMR和¹³C NMR数据基本一致,因此化合物**6**确定为exoticin^[11]。

4 结论

对千里香枝叶的化学成分进行了研究,从中分离得到6个化学成分,分别为:indazole (**1**)、5,3'-dihydroxy-7,8,4'-trimethoxyflavone (**2**)、3,5,7,8,3',4',5'-heptamethoxyflavone(**3**)、5-hydroxy-3,7,8,3',4',5'-hexamethoxyflavone (**4**)、3,5,6,7,3',4',5'-heptamethoxyflavonol (**5**)、exoticin (**6**),其中化合物**1**和**2**是首次从九里香属植物中分离得到。

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