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姜花中二芳基庚烷及黄酮成分的分离鉴定

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摘 要:姜花(*Hedychium coronarium* Koen)根茎用甲醇提取,利用硅胶柱层析、Sephadex LH-20柱层析、薄层层析及HPLC等手段对其化学成分进行分离纯化,得到5个化合物,经波谱解析和对其理化性质进行对比,鉴定为3个二芳基庚烷和2个黄酮,分别是gingerenone A (**1**), rel-(3*R*,5*S*)-3,5-dihydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(4-hydroxyphenyl)-heptane(**2**), hexahydrocurcumin (**3**), 3,5,7,4′-tetramethoxyflavone (**4**) 和5-hydroxy-3,7,4′-trimethoxyflavone (**5**)。化合物**1**~**4**为首次从姜花中分离得到。

关键词:姜花;二芳基庚烷;黄酮;结构鉴定
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Isolation and Identification of Diarylheptanoids and Flavonoids in *Hedychium coronarium* Koen

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Abstract: Five compounds were isolated from the methanol extract of the rhizomes of *Hedychium coronarium* Koen by silica gel column chromatography, Sephadex LH-20 chromatography, thin layer chromatography and high performance liquid chromatography. Their structures were identified by spectroscopic analysis combined with their physicochemical data. Three diarylheptanes and two flavonoids were identified as gingerenone A (**1**), rel-(3*R*,5*S*)-3,5-dihydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(4-hydroxyphenyl)-heptane (**2**), hexahydrocurcumin (**3**), 3,5,7,4′-tetramethoxyflavone (**4**) and 5-hydroxy-3,7,4′-trimethoxyflavone (**5**). Compounds **1** ~ **4** were isolated from this plant for the first time.

Keywords: *Hedychium coronarium* Koen; diarylheptanoids; flavonoids; structure identification

姜花(*Hedychium coronarium* Koen)为姜科姜花属植物,主要分布于我国云南、四川、广西等西南省区[1-2]。姜花的根茎又名土羌活,其果实和根茎在民间被用于祛风驱寒、治头痛、风湿等,同时姜花还可做观赏花卉和香料植物[3-4]。植物化学研究显示该植物主要含有二萜、倍半萜、黄酮等成分[4-6],其中部分二萜成分具有良好的细胞毒、抗氧化、降血糖等活性[7-9],因此我们对采自云南西双版纳的姜花根茎化学成分进行研究。采用各种层析技术包括硅胶柱层析、Sephadex LH-20柱层析、高效液相层析等分离得到5个化合物(图1)。波谱分析和理化性质分析鉴定结构分别为3个二芳基庚烷gingerenone A(**1**),rel-(3*R*,5*S*)-3,5-dihydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(4-hydroxyphenyl)-heptane(**2**), hexahydrocurcumin(**3**),2个黄酮3,5,7,4′-tetramethoxyflavone(**4**)和5-hydroxy-3,7,4′-trimethoxyflavone(**5**)。

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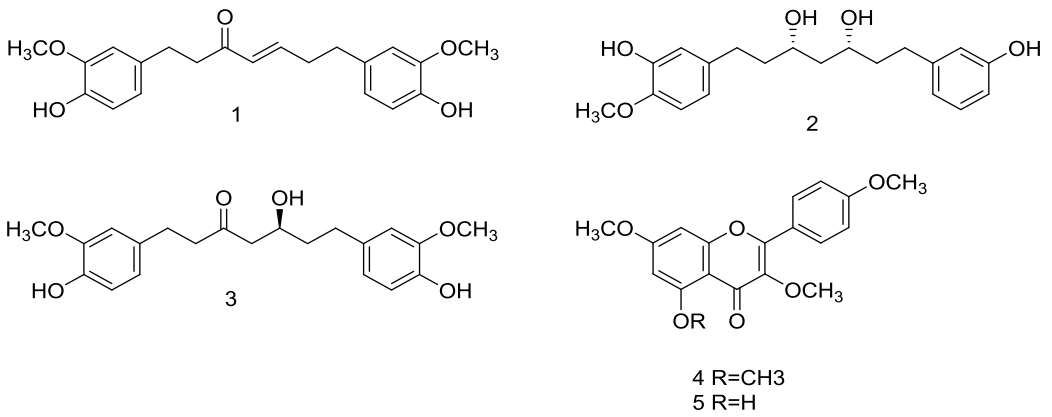

图1 化合物1-5的结构

Figure 1 Chemical structures of compounds **1-5**

1 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-1型三用紫外仪,上海安亭电子仪器厂。

1.2 实验试剂

层析硅胶,青岛海洋化工厂;SephadexLH-20凝胶,GE Healthcare Bio-Sciences AB;高效薄层层析硅胶板GF25,烟台化工研究院;显色剂为10%(*V*:*V*)浓硫酸/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

姜花根茎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于云南西双版纳采集,并鉴定为*Hedychium coronarium* Koen。

2 化合物的提取与分离

姜花根茎(6.5 kg)风干后粉碎,用甲醇(25 L)于室温下浸泡提取5次,将得到的提取液合并,进行减压浓缩,得到甲醇粗提物(400 g)。甲醇提取物分散于水中,用乙酸乙酯萃取10次,得到萃取物170 g,用硅胶(80~100目)拌样,进行硅胶柱层析,以石油醚/乙酸乙酯(0:1→1:0)进行梯度洗脱,合并后得到A-E5个部分,利用硅胶柱层析和Sephadex LH-20凝胶柱层析,RP-18及HPLC等手段对A和B部分进行反复分离纯化得到gingerenone A(**1**),rel-(3*R*,5*S*)-3,5-dihydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(4-hydroxyphenyl)-heptane(**2**),hexahydrocurcumin(**3**),3,5,7,4′-tetramethoxyflavone(**4**)和5-hydroxy-3,7,4′-trimethoxyflavone(**5**)。

3 结构鉴定

化合物**1**:无色油状,MF:$C_{21}H_{24}O_5$,MW:356;^{1}H NMR(500 MHz,$CDCl_3$):δ 2.65(2H,m,H-1),2.70(2H,m,H-7),2.81(4H,m,H-2,6),3.85(6H,s,H-3′,3"),6.10(1H,d,*J* = 16.0 Hz,H-4),6.91(3H,m,H-2′,5′,6′),6.70(3H,m,H-2",5",6"),6.80(1H,m,H-5)。^{13}C NMR(125 MHz,$CDCl_3$)δ 199.7(s,C-3),146.4(d,C-5),146.4(s,C-3′),146.3(s,C-3"),143.9(s,C-4"),143.8(s,C-4′),133.1(s,C-1"),132.5(s,C-1′),130.7(d,C-4),120.9(d,C-6"),120.7(d,C-6′),114.3(d,C-2"),114.3(d,C-2′),111.0(d,C-5"),110.8(d,C-5′),55.8(q,C-7′,C-7"),42.1(t,C-2),34.5(t,C-7),

34.1 (t, C-6), 29.8 (t, C-1)。与文献报道的gingerenone A的^{1}H NMR和^{13}C NMR数据基本一致,因此化合物**1**确定为gingerenone A[10]。

化合物**2**:无色油状,MF: $C_{20}H_{26}O_5$, MW: 346; ^{1}H NMR (500 MHz, CD_3OD) δ 7.06 (1H, d, *J* = 8.5 Hz, H-6"), 7.01 (1H, d, *J* = 8.5 Hz, H-2"), 6.78 (1H, d, *J* = 8.2 Hz, H-5′), 6.75 (1H, dd, *J* = 8.2 Hz, H-2′), 6.71 (1H, dd, *J* = 8.2, 3.8 Hz, H-6′), 6.65 (1H, d, *J* = 8.3 Hz, H-3"), 6.81 (1H, d, *J* = 8.5 Hz, H-5"), 3.84 (3H, s, OCH_3), 3.83 (1H, m, H-3), 3.78 (1H, m, H-5), 2.71 (2H, m, H-7), 2.58 (2H, m, H-1), 1.76 (2H, m, H-4), 1.73 (2H, m, H-6), 1.63 (2H, m, H-2)。^{13}C NMR (125 MHz, CD_3OD) δ 156.3 (s, C-4"), 148.8 (s, C-3′), 145.4 (s, C-4′), 135.2 (s, C-1′), 134.4 (s, C-1"), 130.3 (d, C-2"), 121.7 (d, C-6′), 116.2 (d, C-5"), 116.1 (d, C-5′), 113.1 (d, C-2′), 70.8 (d, C-3), 70.8 (d, C-5), 56.3 (q, OCH_3), 44.8 (t, C-4), 40.8 (t, C-6), 40.7 (t, C-2), 32.3 (t, C-1), 31.8 (t, C-7)。与文献报道的rel-(3*R*,5*S*)-3,5-dihydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(4-hydroxyphenyl)-heptane的^{1}H NMR和^{13}C NMR数据基本一致,因此化合物**2**确定为rel-(3*R*,5*S*)-3,5-dihydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(4-hydroxyphenyl)-hep-tane[11]。

化合物**3**:无色油状, MF: $C_{21}H_{26}O_6$, MW: 374; ^{1}H NMR (500 MHz, CD_3OD) δ 6.76 (2H, t, *J* = 1.6 Hz, H-2′, 2"), 6.69 (2H, dd, *J* = 8.0, 1.6 Hz, H-6′, 6"), 6.61 (1H, t, *J* = 1.6 Hz, H-2′), 6.60 (1H, t, *J* = 1.6 Hz, H-2"), 4.02 (1H, m, H-5), 3.82 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 2.69-2.50 (8H, m, H-1, 4, 6, 7), 1.68 (2H, m, H-2)。^{13}C NMR (125 MHz, CD_3OD) δ 212.0 (s, C-3), 148.9 (s, C-3′), 148.8 (s, C-4′), 145.6 (s, C-3"), 145.5 (s, C-4"), 134.9 (s, C-1′), 134.0 (s, C-1"), 121.8 (d, C-6′), 121.7 (d, C-6"), 116.1 (d, C-5′), 116.0 (d, C-5"), 113.1 (d, C-2′), 113.0 (d, C-2"), 68.2 (d, C-5), 56.3 (q, OCH_3), 56.2 (q, OCH_3), 51.3 (q, C-4), 46.4 (t, C-2), 40.5 (t, C-6), 32.4 (t, C-7), 30.3 (t, C-1)。与文献报道的hexahydrocurcumin的^{1}H NMR和^{13}C NMR数据基本一致,因此化合物**3**确定为hexahydrocurcumin[12]。

化合物**4**:黄色晶体, MF: $C_{19}H_{18}O_6$, MW: 342; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (2H, d, *J* = 8.9 Hz, H-2′, 6′), 7.03 (2H, d, *J* = 8.9 Hz, H-3′, 5′), 6.53 (1H, d, *J* = 2.1 Hz, H-8), 6.36 (1H, d, *J* = 2.1 Hz, H-6), 3.98 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 3.89 (3H, s, OCH_3)。^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1 (s, C-4), 163.8 (s, C-7), 161.1 (s, C-4′), 158.8 (s, C-9), 152.7 (s, C-2), 141.1 (s, C-3), 129.8 (d, C-2′), 123.2 (s, C-1′), 113.9 (d, C-3′, 5′), 109.5 (s, C-10), 95.7 (d, C-6), 92.4 (d, C-8), 59.9 (q, OCH_3), 56.4 (q, OCH_3), 55.8 (q, OCH_3), 55.4 (q, OCH_3)。与文献报道的3,5,7,4′-tetramethoxyflavone的^{1}H NMR和^{13}C NMR数据基本一致,因此化合物**4**确定为3,5,7,4′-tetramethoxyflavone[13]。

化合物**5**:黄色晶体,MF: $C_{18}H_{16}O_6$, MW: 328; ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.66 (1H, s, 5-OH), 8.08 (2H, d, *J* = 9.1 Hz, H-2′, 6′), 7.02 (2H, d, *J* = 9.1 Hz, H-3′, 5′), 6.45 (1H, d, *J* = 2.2 Hz, H-8), 6.36 (1H, d, *J* = 2.2 Hz, H-6), 3.90 (3H, s, OCH_3), 3.87 (3H, s, OCH_3), 3.85 (3H, s, OCH_3)。^{13}C NMR (125 MHz, $CDCl_3$) δ 178.8 (s, C-4), 165.4 (s, C-7), 162.0 (s, C-4′), 161.7 (s, C-5), 156.8 (d, C-9), 156.0 (s, C-2), 138.9 (s, C-3), 130.1 (d, C-2′, 6′), 122.8 (s, C-1′), 114.1 (d, C-3′, 5′), 106.1 (s, C-10), 97.8 (d, C-6), 92.2 (d, C-8), 60.2 (q, OCH_3), 55.8 (q, OCH_3), 55.5 (q, OCH_3)。与文献报道的5-hydroxy-3,7,4′-trimethoxyflavone的^{1}H NMR和^{13}C NMR数据基本一致,因此化合物**5**确定为5-hydroxy-3,7,4′-trimethoxyflavone[13]。

4 结论

对采自西双版纳的姜花根茎甲醇浸提物的乙酸乙酯萃取部分分离得到**5**个化合物,经波谱解析和对其理化性质进行对比,将结构鉴定为gingerenone A (**1**, 3.4 mg), rel-(3*R*,5*S*)-3,5-dihydroxy-1-(4-hydroxy-

3-methoxyphenyl)-7-(4-hydroxyphenyl)-heptane (**2**, 3.3 mg), hexahydrocurcumin (**3**, 3.5 mg), 3,5,7,4′-tetramethoxyflavone (**4**, 5.0 mg)和5-hydroxy-3,7,4′-trimethoxyflavone (**5**, 6.2 mg)。化合物**1**~**4**为首次从姜花中分离得到。

参考文献:

[1] 中国科学院中国植物志编辑委员会. 中国植物志[M]. 北京:科学出版社,1981,16(2):24.

[2] 中国科学院昆明植物所. 云南植物志[M]. 北京:科学出版社,1997,8:549-560.

[3] NAKATANI N,KIKUZAKI H,YAMAJI H,et al. Labdane diterpenes from rhizomes of *Hedychium coronarium*[J]. Phytochemistry,1994,37(5):1383-1388.

[4] CHAN E W C,WONG S K. Phytochemistry and pharmacology of ornamental gingers, *Hedychium coronarium* and *Alpinia purpurata*: a review[J]. Journal of Integrative Medicine,2015,13(6):368-379.

[5] SURESH G,REDDY P P,BABU K S,et al. Two new cytotoxic labdane diterpenes from the rhizomes of *Hedychium coronarium*[J]. Bioorganic & Medicinal Chemistry Letters,2010,20(24):7544-7548.

[6] CHEN L C,WEN Z H,SUNG P J,et al. New labdane-type diterpenoid and cytotoxic constituents of *Hedychium coronarium*[J]. Chemistry of Natural Compounds,2017,53(1):72-76.

[7] PANIGRAHY S K,KUMAR A,BHATT R. *Hedychium coronarium* rhizomes: promising antidiabetic and natural inhibitor of α-amylase and α-glucosidase[J]. Journal of Dietary Supplements,2020,17(1):81-87.

[8] ZHAN Z J,WEN Y T,REN F Y,et al. Diterpenoids and a diarylheptanoid from *Hedychium coronarium* with significant anti-angiogenic and cytotoxic activities[J]. Chemistry & Biodiversity,2012,9(12):2754-2760.

[9] PANIGRAHY S K,KUMAR A,BHATT R. Antioxidant potentials of successive solvent extracts from the unexplored Hedhychium coronarium rhizome[J]. Journal of Food Science and Technology,2017,54(10):3297-3306.

[10] ENDO K,KANNO E,OSHIMA Y. Structures of antifungal diarylheptenones, gingerenones A, B, C and isogingerenone B, isolated from the rhizomes of *Zingiber officinale*[J]. Phytochemistry,1990,29(3):797-799.

[11] LI J,LIAO C R,WEI J Q,et al. Diarylheptanoids from *Curcuma kwangsiensis* and their inhibitory activity on nitric oxide production in lipopolysaccharide-activated macrophages[J]. Bioorganic & Medicinal Chemistry Letters,2011,21(18):5363-5369

[12] MURATA T,SHINOHARA M,MIYAMOTO M. Isolation of hexahydrocurcumin, dihydrogingerol and two additional pungent principles from ginger[J]. Chemical and Pharmaceutical Bulletin,1972,20(10):2291-2292.

[13] SUTTHANUT K,SRIPANIDKULCHAI B,YENJAI C,et al. Simultaneous identification and quantitation of 11 flavonoid constituents in *Kaempferia parviflora* by gas chromatography[J]. Journal of Chromatography A,2007,1143(1/2):227-233.

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