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兰香草的化学成分研究

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摘　要:研究兰香草(*C. incana*(Thunb.)Miq)的化学成分。利用 Sephadex LH-20,硅胶等柱色谱技术进行分离纯化,根据化合物的理化性质和光谱数据鉴定结构。分离并鉴定了 10 化合物的结构,分别为:香草酸(**1**),原儿茶酸(**2**),对羟基苯乙醇(**3**),木犀草素(**4**),落叶松脂醇(**5**),落叶松脂醇-4-*O*-β-D-葡萄糖苷(**6**),落叶松脂醇-9-*O*-β-D-葡萄糖苷(**7**),β-谷甾醇(**8**),硬脂酸(**9**),胡萝卜苷(**10**),以上化合物均为首次从该植物中分离得到。

关键词:马鞭草科;兰香草;化学成分;结构鉴定

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Chemical Constituents of *C. incana*(Thunb.)Miq

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Abstract:To investigate the chemical constituents of *C. incana*(Thunb.)Miq. The compounds were isolated with Sephadex LH-20,silica gel column chromatography. The structures of compounds were identified on the basis of physiochemical properties and spectral data. Ten compounds were isolated and identified as vanillic acid(**1**),protocatechuic acid(**2**),*p*-hydroxyphenylethyl alcohol(**3**),luteolin(**4**),lariciresinol(**5**),lariciresinol-4-O-β-D-glucopyranoside(**6**),lariciresinol-9-O-β-D-glucopyranoside(**7**),β-sitosterol(**8**),Stearic acid(**9**),daucosterol(**10**). All compounds were isolated from this plant for the first time.

Key words:Verbenaeeae; *C. incana*(Thunb.)Miq;chemical constituents;structure identification

兰香草(*C. incana*(Thunb.)Miq),亚灌木,为马鞭草科(Verbenaeeae)莸属(*Caryopteris* Bunge)植物。莸属植物全世界约 15 种,分布于亚洲中部和东部,我国有 13 种,2 变种及 1 变型[1],除东北地区之外,其他各省区均有分布[2]。兰香草主要分布于广东、广西、湖南、江西等地。资源丰富,为常用民间草药。现代药理学研究表明兰香草具有抗菌、止咳、抗炎消肿等药理作用,在临床上主要应用于治疗百日咳、慢性气管炎,肾盂肾炎等。全草含黄酮苷、生物碱、酚类、甾体、氨基酸、有机酸、鞣质等化学成分。目前对莸属植物兰香草的化学成分的研究比较少,因此对兰香草的 95% 乙醇提取物做了系统的化学成分研究,并从中分离鉴定了 10 个化合物,分别为:香草酸(**1**),原儿茶酸(**2**),对羟基苯乙醇(**3**),木犀草素(**4**),落叶松脂醇(**5**),落叶松脂醇-4-*O*-β-D-葡萄糖苷(**6**),落叶松脂醇-9-*O*-β-D-葡萄糖苷(**7**),β-谷甾醇(**8**),硬脂酸(**9**),胡萝卜苷(**10**)。以上化合物均为首次从该植物中分离得到。

1　仪器与试药

Bruker AVANCE Ⅲ 500 核磁共振仪(河南中医学院代测),TMS 为内标;N-1000 型旋转蒸发仪(上海爱朗仪器有限公司),RZ01C 旋转蒸发器、SHB-Ⅲ循环水式多用真空泵、HH-S 恒温水浴锅(郑州长城科技工贸有限公司),质谱仪(Mat-212 磁式(EI-MS)),Q-Tof micro(ESI-MS)。柱层析填充剂所用 Diaion HP-20,系日本三菱公司生产,硅胶(160-200 目)为青岛海洋化工厂生产;所用分析纯试剂为北京化工厂和天津第三化学试剂厂生产。

兰香草采自河南省太行山,经河南中医学院董诚明教授鉴定为马鞭草科植物兰香草(*C. incana*(Thunb.)Miq)。

2　提取与分离

兰香草干燥全草 5.5 kg,10 倍量 95% 乙醇加热

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回流 3 次,每次 2 h。提取液合并后低温减压回收乙醇,得稠膏 500 g。加适量水后,依次用石油醚、乙酸乙酯、正丁醇反复萃取,分别得到石油醚部位(97 g)、乙酸乙酯部位(78 g)、正丁醇部位(35 g)和水部位(166 g)。将各部分低温减压回收溶剂,浓缩,真空干燥后,乙酸乙酯部位和正丁醇部位利用 Diaion HP-20、Sephadex LH-20、Silica gel 等柱层析结合重结晶的方法,分离纯化,得到化合物 **1**(37 mg)、**2**(25 mg)、**3**(17 mg)、**4**(21 mg)、**5**(12 mg)、**6**(17 mg)、**7**(19 mg)、**8**(27 mg)、**9**(12 mg)、**10**(28 mg)。

3 结构鉴定

化合物 1 白色结晶(甲醇)。^{1}H NMR(500 MHz,MeOD)δ:7.58(1H,dd,J =1.9,8.0 Hz,H-6),7.57(1H,d,J =1.9 Hz,H-2),6.99(1H,d,J =8.0 Hz,H-5),3.88(3H,s,-OCH_3);^{13}C NMR(125 MHz,MeOD)δ:126.5(C-1),115.4(C-2),151.0(C-3),148.3(C-4),114.3(C-5),123.2(C-6),171.4(C-7),56.2(-OCH_3)。以上数据与文献[3]报道的香草酸(vanillic acid)基本一致。

化合物 2 白色粉末(甲醇)。^{1}H NMR(500 MHz,MeOD)δ:7.29(1H,d, J =1.8 Hz,H-2),6.75(1H,dd,J =1.8,8.0 Hz,H-6),6.60(1H,d,J =1.8 Hz,H-5);^{13}C NMR(125 MHz,MeOD)δ:121.4(C-1),117.0(C-2),149.7(C-3),150.0(C-4),117.1(C-5),121.5(C-6),170.1(1-COOH)。以上数据与文献[4]报道的原儿茶酸(protocatechuic acid)基本一致。

化合物 3 无色结晶(甲醇)。^{1}H NMR(500 MHz,acetone-d_6)δ:7.15(2H,d,J =8.0 Hz,H-2,6),6.78(2H,d,J =8.0 Hz,H-3,5),3.69(2H,m,J =7.4 Hz,H-8),2.77(2H,m,J =7.2 Hz,H-7);^{13}C NMR(125 MHz,acetone-d_6)δ:132.8(C-1),131.0(C-2,6),115.7(C-3,5),157.4(C-4),49.9(C-7),64.5(C-8)。以上数据与文献[5]报道的对羟基苯乙醇(p-hydroxyphenylethyl alcohol)基本一致。

化合物 4 黄色粉末(甲醇)。^{1}H NMR(500 MHz,DMSO-d_6)δ:7.27(1H,d,J =2.0,8.3 Hz,H-6′),7.16(1H,d,J =2.0 Hz,H-2′),6.55(1H,d,J =8.3 Hz,H-5′),6.21(1H,s,H-3),5.97(1H,m,H-8),5.79(1H,m,H-6);^{13}C NMR(100 MHz,DMSO-d_6)δ:166.3(C-2),102.7(C-3),181.7(C-4),159.9(C-5),100.9(C-6),163.9(C-7),95.2(C-8),163.3(C-9),105.7(C-10),117.9(C-1′),112.1(C-2′),150.0(C-3′),152.0(C-4′),116.3(C-5′),126.3(C-6′)。以上数据与文献[6]报道的木犀草素(luteolin)基本一致。

化合物 5 白色粉末(甲醇)。^{1}H NMR(500 MHz,$CDCl_3$)δ:6.99(1H,d,J =8.0 Hz,H-5),6.88(1H,d,J =2.1 Hz,H-2),6.79(1H,d,J =1.7 Hz,H-2′),6.73(1H,d,J =7.9 Hz,H-5′),6.71(1H,d,J =2.1,8.0 Hz,H-6),6.64(1H,d,J =1.7,7.9 Hz,H-6′),4.74(1H,d, J =6.9 Hz H-7),3.87(1H,t,H-9′),3.84(3H,s,-OCH_3),3.83(3H,s,-OCH_3),3.65(1H,t,H-9′),3.75(1H,d,H-9),3.62(1H,m,H-9),2.92(1H,m,H-7′a),2.74(1H,m,H-8′),2.51(1H,m,H-7′b),2.33(1H,m,H-8);^{13}C NMR(125 MHz,$CDCl_3$)δ:135.4(C-1),110.5(C-2),149.0(C-3),147.1(C-4),116.0(C-5),119.7(C-6),83.8(C-7),54.1(C-8),60.4(C-9),133.2(C-1′),113.4(C-2′),149.9(C-3′),145.9(C-4′),116.3(C-5′),122.3(C-6′),33.8(C-7′),43.8(C-8′),73.4(C-9′),56.3(3,3′-OCH_3)。以上数据与文献[7]报道的落叶松脂醇(lariciresinol)基本一致。

化合物 6 白色粉末(甲醇)。^{1}H NMR(500 MHz,MeOD)δ:7.13(1H,d,J =8.1 Hz,H-5),6.98(1H,d,J =1.9 Hz s,H-2),6.84(1H,dd,J =1.9,8.1 Hz,H-6),6.80(1H,d,J =2.0 Hz,H-2′),6.75(1H,dd,J =2.0,8.5 Hz,H-6),6.73(1H,d,J =8.0 Hz,H-5),4.95(1H,d,J =8.0,H-1′′′),4.74(1H,d,H-7),3.99(1H,t,H-9′),3.87(3H,s,-OCH_3),3.81(3H,s,-OCH_3),4.80(1H,d,H-7′),3.76(1H,d,H-9),3.74(1H,m H-9′),3.70(1H,d,H-9),2.75(1H,m,H-8′),2.46(1H,m,H-7′),2.37(1H,m,H-8);^{13}C NMR(125 MHz,MeOD)δ:139.4(C-1),111.0(C-2),149.9(C-3),147.3(C-4),118.3(C-5),119.6(C-6),83.9(C-7),54.1(C-8),60.5(C-9),133.5(C-1′),113.3(C-2′),149.9(C-3′),145.4(C-4′),117.0(C-5′),122.1(C-6′),33.6(C-7′),43.8(C-8′),73.5(C-9′),102.9(C-1′′),74.9(C-2′′),77.6(C-3′′),71.6(C-4′′),78.3(C-5′′),62.5(C-6′′),56.4(3′-OCH_3),56.7(3-OCH_3)。以上数据与文献[8]报道的落叶松脂醇-4-O-β-D-葡萄糖苷(lariciresinol-4-O-β-D-glucopyranoside)基本一致。

化合物 7 白色粉末(甲醇)。^{1}H NMR(500

MHz, MeOD): δ6.94 (1H, d, J = 1.9 Hz, H-2), 6.80 (1H, d, J = 1.8 Hz, H-2′), 6.83 (1H, dd, J = 1.9, 7.9 Hz, H-6), 6.70 (1H, d, J = 7.9 Hz, H-5), 6.71 (1H, d, J = 8.1 Hz, H-5′), 6.67 (1H, dd, J = 1.8, 8.1 Hz, H-6′), 4.83 (1H, m, H-7), 4.28 (1H, d, J = 7.8 Hz, H-1′′), 4.24 (1H, m, H-9a), 3.91 (1H, m, H-9′a), 3.84 (1H, m, H-6′′a), 3.75 (1H, m, H-9′b), 3.64 (1H, m, H-6′′b), 3.59 (1H, m, H-9b), 2.99 (1H, m, H-7′a), 2.76 (1H, m, H-8′), 2.52 (1H, m, H-7′b), 2.48 (1H, m, H-8), 3.84 (3H, s, 3-OCH_3), 3.81 (3H, s, 3′-OCH_3); ^{1}C NMR (125 MHz, MeOD): δ135.6 (C-1), 110.2 (C-2), 149.2 (C-3), 147.3 (C-4), 116.5 (C-5), 119.6 (C-6), 84.1 (C-7), 51.7 (C-8), 68.5 (C-9), 133.9 (C-1′), 113.7 (C-2′), 148.9 (C-3′), 145.8 (C-4′), 116.0 (C-5′), 122.6 (C-6′), 33.8 (C-7′), 44.5 (C-8′), 73.8 (C-9′), 56.6 (3-OCH_3), 56.3 (3′-OCH_3); glu′: 104.7 (C-1′′), 75.2 (C-2′′), 78.3 (C-3′′), 71.6 (C-4′′), 78.4 (C-5′′), 62.0 (C-6′′)。以上数据与文献[9]报道的落叶松脂醇-9-*O*-β-D-葡萄糖苷(lariciresinol-9-*O*-β-D-glucopyranoside)基本一致。

化合物 8 白色结晶(氯仿)。^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.50 (1H, m, H-3), 5.32 (1H, br. s, H-6); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 37.2 (C-1), 31.6 (C-2), 71.8 (C-3), 42.3 (C-4), 140.7 (C-5), 121.7 (C-6), 31.9 (C-7), 31.9 (C-8), 50.2 (C-9), 36.2 (C-10), 21.1 (C-11), 30.8 (C-12), 42.4 (C-13), 56.4 (C-14), 24.3 (C-15), 39.9 (C-16), 56.8 (C-17), 12.0 (C-18), 19.4 (C-19), 37.5 (C-20), 18.8 (C-21), 38.4 (C-22), 26.2 (C-23), 51.2 (C-24), 30.9 (C-25), 19.2 (C-26), 19.5 (C-27), 23.4 (C-28), 12.8 (C-29)。以上数据与文献[10]报道的β-谷甾醇(β-sitosterol)基本一致。

化合物 9 白色粉末(氯仿)。ESI-MS m/z: 290.0677 [M-H]$^-$; ^{1}H NMR (500 MHz, $CDCl_3$), δ: 2.52 (2H, t, J = 7.2 Hz, H-2), 1.547 (2H, m, H-3), 1.254 (n × CH_2), 0.88 (3H, t, -CH_3)。以上数据与文献[11]报道的硬脂酸(Stearic acid)基本一致。

化合物 10 无色针晶(甲醇),茴香醛-硫酸喷雾显紫红色(105 ℃),与胡萝卜苷对照品共薄层 R_f 值相同,与β-谷甾醇对照品混合,熔点不下降,故确定该化合物为胡萝卜苷(Daucosterol)。

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