仙茅的化学成分研究

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摘 要 从仙茅(*Curculigo orchioides* Gaertn.)根茎的乙醇提取物中分离鉴定了7个已知化合物,它们是:curculigoside Ⅰ(1),orcinol glucoside(2),3,3′,5,5′-tetramethoxy-7,9′:7′,9-diepoxy-lignan-4,4′-di-O-β-D-glucopyranoside(3),3-hydroxy-5-methyl-phenol-1-O-[β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside](4),2,3,4,7-tetramethoxyxanthone(5),1,3,7-trimethylxanthine(6),daucosterol(7)。其中化合物3~7均为首次从该植物中分离得到。

关键词 仙茅科;仙茅;化学成分

仙茅(*Curculigo orchioides* Gaertn.)为仙茅科仙茅属植物仙茅的根状茎。具温肾阳,壮筋骨,治阳痿精冷等功效[1]。鉴于仙茅具有耐缺氧,抗高温,抗炎,雄性激素样作用等药理作用[2],近年来人们对其进行了较为深入的化学研究。分离鉴定出多种化学成分[3~6]。在此基础上,我们继续对其根茎中的成分进行了系统的植化分离,从中分离鉴定的化合物类型有酚苷、木脂素苷、呫酮、黄嘌呤、甾体及其苷。其中酚苷为主要化学成分。

1 实验部分

1.1 实验仪器和材料

熔点用Kofler显微熔点仪测定(温度未校正);旋光由JASCO-20旋光仪测定;红外光谱(IR)用KBr压片法由Bio-Rad FTS-135红外分光光度仪测定;紫外光谱(UV)用UV-210A紫外分光光度仪测定;质谱(MS)用VG Autospec-3000型质谱仪测定,采用FAB技术测定;核磁共振谱(^{1}H NMR,^{13}C NMR,DEPT)用Bruker AM-400超导核磁仪测定,TMS内标,化学位移δ,单位ppm,偶合常数J,单位Hz;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

仙茅由云南省药材公司提供(2001年5月)。5.0 kg仙茅粗粉用80%乙醇加热回流提取3次,浓缩后,向乙醇提取物中加水至25.0 kg,水液经大孔树脂柱(D101)脱糖后,乙醇洗脱浓缩,得乙醇提取物50.0 g,经硅胶柱反复层析,共分离得到14个化合物,经各种波谱数据以及与参考文献对照的方法鉴定了其中7个化合物的结构(图1)。

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2 鉴定

2.1 curculigoside Ⅰ(1)

无色针晶(MeOH),mp. 158~160 ℃,分子式为:$C_{22}H_{26}O_{11}$,FAB$^-$-MS m/z:466[M]$^-$,302[M-glc.]$^-$,165[$C_9H_9O_3$]$^-$;^{1}H NMR(400 MHz,CD_3OD):δ 3.78(6 H,s,$OCH_3\times2$),4.76(1 H,d,J=7.65 Hz,glc. H-1),5.45(2 H,AB,$PhCH_2O-$),6.64(2 H,d,J=8.56 Hz,H-3′和H-5′),6.70(1 H,dd,J=8.84,3.04 Hz,H-4),6.91(1 H,d,J=3.04 Hz,H-6),7.07(1 H,d,J=8.84 Hz,H-3),7.31(1 H,t,J=8.56 Hz,H-4′)。^{13}C NMR(100 MHz,CD_3OD):δ128,8(s,C-1),153.9(s,C-2),116.2(d,C-3),118.9(d,C-4),149.6(s,C-5),116.4(d,C-6),56.5(q,$OCH_3\times2$),63.2(t,$PhCH_2O-$),168.5(s,C=O),114.2(s,C-1′),158.7(d,C-2′),105.2(d,C-3′),132.6(d,C-4′),105.2(d,C-5′),158.7(s,C-6′),104.3(d,C-1″),75.0(d,C-2″),78.1(d,C-3″),71.4(d,C-4″),78.0(d,C-5″),62.6(t,C-6″)。^{1}H NMR和^{13}C NMR数据与文献报道[3]一致。

2.2 orcinol glucoside(2)

白色无定形粉末,mp. 132~133 ℃,分子式为:$C_{13}H_{18}O_7$,FAB$^-$-MS(m/z):285[M-1]$^-$,123[M-1-glc.]$^-$;^{1}H NMR(400 MHz,CD_3OD):δ 2.04(3 H,s,CH_3),4.74(1 H,d,J=7.28 Hz,glc.H-1),6.32(1 H,s,H-2),6.28(1 H,s,H-4),6.18(1 H,s,H-6),3.33~3.80(5 H,m,glc-H),10.09(1 H,brs,

C_3-OH)。^{13}C NMR(100 MHz, CD_3OD): δ 160.0(s, C-1),102.1(d,C-2),159.1(s,C-3),109.7(d,C-4),141.2(s,C-5),111.2(d,C-6),102.0(d,C-1′),74.8(d,C-2′),77.8(d,C-3′),71.7(d,C-4′),78.3(d,C-5′),62.9(t,C-6′),22.1(q,C_1-CH_3)。^{1}H NMR 和^{13}C NMR 数据与文献报道[5]一致。

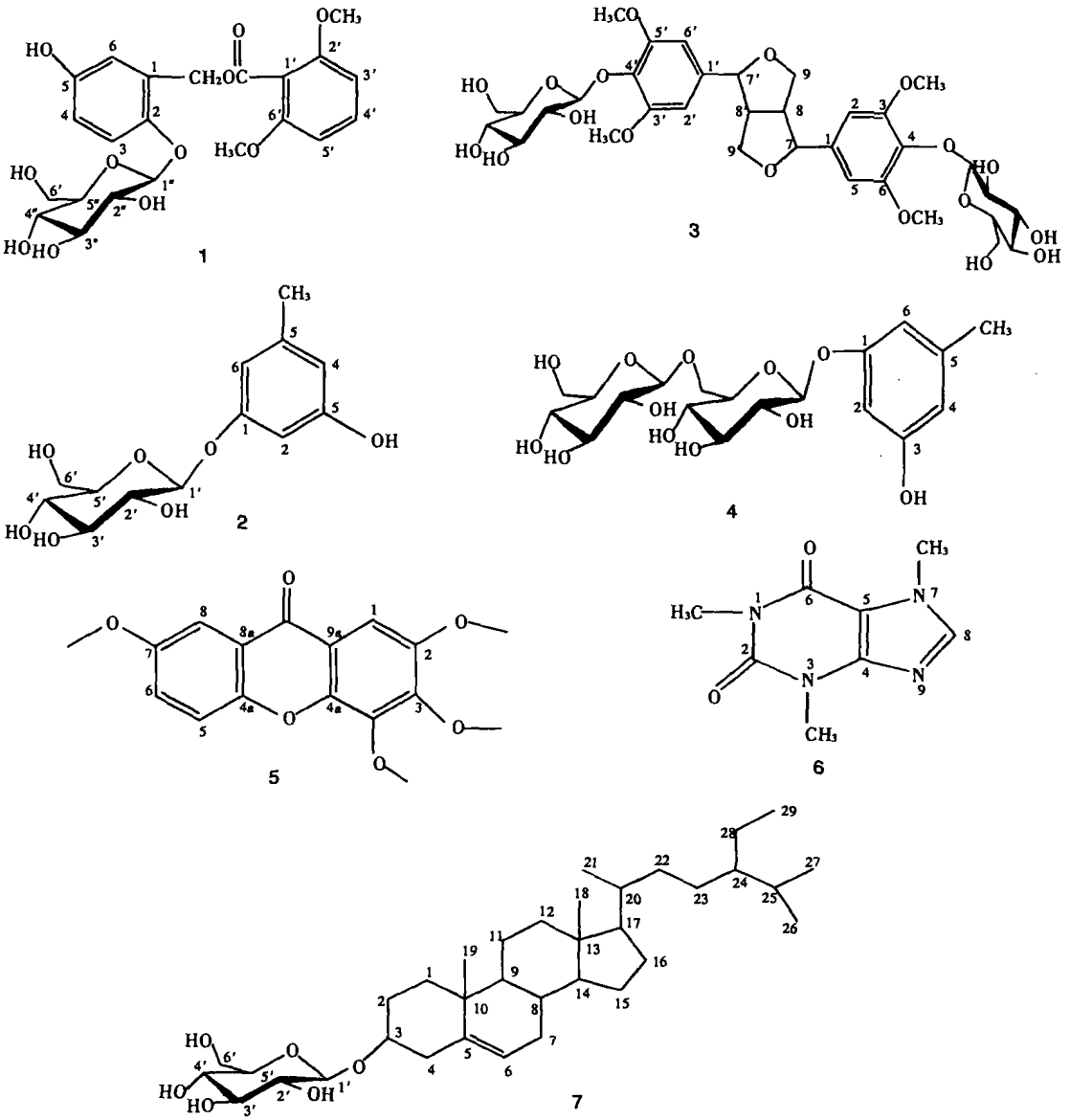

图 1 Fig.1

2.3 3,3′,5,5′-tetramethoxy-7,9′:7′,9-diepoxylignan-4,4′-di-O-β-D-glucopyranoside(3)

白色无定形粉末,分子式为:$C_{34}H_{46}O_{18}$,FAB$^+$-MS(m/z):743[M+1]$^+$,579[M−1−glc.]$^+$,418[M−2glc.]$^+$;^{1}H NMR(400 MHz, C_5D_5N): δ 3.81(3 H,s,CH_3),6.86(1 H,d,J=6.86 Hz,glc.H-1),6.96(4 H,s,H-2,H-6,H-2′和 H-6′)。^{13}C NMR(100 MHz,C_5D_5N): δ 138.4(s,C-1 和 C-1′),105.2(d,C-2 和 C-2′),154.0(s,C-3 和 C-3′),135.5(s,C-4 和 C-4′),154.0(s,C-5 和 C-5′),105.2(d,C-6 和 C-6′),86.2(d,C-7 和 C-7′),54.8(d,C-8 和 C-8′),72.3(t,C-9 和 C-9′),105.1(d,glc.C-1),76.1(d,glc.C-2),78.4(d,glc.C-3),71.8(d,glc.C-4),78.6(d,glc.C-5),62.8(t,glc.C-6)。^{1}H NMR 和^{13}C NMR 数据与文献报道[7,8]一致。

2.4 3-hydroxy-5-methylphenol-1-O-[β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside](4)

白色无定形粉末,mp. 117～119 ℃,分子式为:

$C_{19}C_{28}O_{12}$, FAB$^-$-MS(m/z):447[M−1]$^-$, 123[M-1-2glc.]$^-$; ^{1}H NMR(400 MHz, CD_3OD): δ 7.15(br s, H-2), 6.68(br s, H-4), 6.72(br s, H-6), 2.15(s, H-7), 5.44(d, J = 7.52 Hz, H-1′), 5.05(d, J = 7.54 Hz, H-1″); ^{13}C NMR(100 MHz, CD_3OD): δ 159.8(s, C-1), 101.9(d, C-2), 159.1(s, C-3), 111.1(d, C-4), 141.1(s, C-5), 109.7(d, C-6), 21.5(q, C-7), 101.9(d, C-1′), 74.7(d, C-2′), 77.6(d, C-3′), 71.2(d, C-4′), 77.3(d, C-5′), 69.4(t, C-6′), 104.4(d, C-1″), 75.1(d, C-2″), 77.3(d, C-3″), 71.4(d, C-4″), 77.6(d, C-5″), 62.5(t, C-6″)。^{1}H NMR 和 ^{13}C NMR 数据与文献报道[9]一致。

2.5 **2,3,4,7-tetramethoxyxanthone(5)**

白色无定形粉末，分子式为：$C_{17}H_{16}O_6$, EI-MS(m/z):316[M]$^+$; ^{1}H NMR(400 MHz, DMSO-d_6): δ 3.75(3 H, s, C_2-OCH_3), δ 3.92(3 H, s, C_3-OCH_3), δ 3.82(3 H, s, C_4-OCH_3), δ 3.82(3 H, s, C_7-OCH_3), δ 6.94(1 H, s, H-1), δ 7.43(1 H, d, J = 8.70 Hz, H-5), δ 7.34(1 H, dd, J = 8.70, 2.75 Hz, H-6), δ 7.45(1 H, d, J = 2.75 Hz, H-8)。^{13}C NMR(100 MHz, DMSO-d_6): δ 96.7(d, C-1), 139.0(s, C-2), 158.6(s, C-3), 152.6(s, C-4), 118.9(d, C-5), 123.4(C-6), 155.6(s, C-7), 105.9(d, C-8), 173.6(s, C-9), 154.0(s, C-4a), 149.1(s, C-4b), 122.1(s, C-8a), 109.4(s, C-9a), 61.0(q, C_2-OCH_3), 56.5(q, C_3-OCH_3), 55.6(q, C_4-OCH_3), 61.76(q, C_7-OCH_3)。^{1}H NMR 和 ^{13}C NMR 数据与文献报道[10]一致。

2.6 **1,3,7-trimethylxanthine(6)**

白色无定形粉末，分子式为：$C_8H_{10}N_4O_2$, EI-MS(m/z):194[M]$^+$。^{1}H NMR(400 MHz, $CDCl_3$): δ 3.36(3 H, s, N_7-CH_3), δ 3.78(3 H, s, N_1-CH_3), δ 4.14(3H, s, N_3-CH_3), δ 7.48(1 H, s, H-8)。^{13}C NMR(100 MHz, $CDCl_3$): δ 152.1(s, C-2), 148.8(s, C-4), 108.0(s, C-5), 155.7(s, C-6), 142.5(d, C-8), 29.9(q, N_1-CH_3), 33.8(q, N_3-CH_3), 28.1(q, N_7-CH_3)。TCL 与其标准品一致。

2.7 **daucosterol(7)**

白色无定形粉末，分子式为：$C_{35}H_{60}O_6$; $[\alpha]_D^{25}$ −38.5°(c 0.20, C_5H_5N); IR(KBr) υ_{max}(cm^{-1}): 3395, 2930, 2855, 1620, 1465, 1378, 1167, 1075, 1024; FAB$^-$-MS m/z: 576[M]$^-$, EI-MS m/z(%): 414[M-162]$^+$(5), 396(100), 382(27), 231(10), 187(7), 147(24)。^{1}H NMR(400 MHz, C_5D_5N): δ 5.34(1 H, br d, J = 4.8 Hz, H-6), 3.98(1 H, m, αH-3), 5.06(1 H, d, J = 7.7 Hz, H-1′)。^{13}C NMR(100 MHz, C_5D_5N): δ 37.6(t, C-1), 30.4(t, C-2), 78,8(d, C-3), 39.5(t, C-4), 141.1(s, C-5), 121.1(d, C-6), 32.3(t, C-7), 32.2(d, C-8), 50.5(d, C-9), 37.1(s, C-10), 21.4(t, C-11), 40.1(t, C-12), 42.6(s, C-13), 56.4(d, C-14), 26.6(t, C-15), 28.7(t, C-16), 57.0(d, C-17), 12.3(q, C-18), 19.2(q, C-19), 36.5(d, C-20), 19.4(q, C-21), 34.4(t, C-22), 24.7(t, C-23), 46.2(d, C-24), 29.6(d, C-25), 20.1(q, C-26), 19.6(q, C-27), 23.6(t, C-28), 12.1(q, C-29), 102.7(d, C-1′), 75.5(d, C-2′), 78.6(d, C-3′), 71.9(d, C-4′), 78.3(d, C-5′), 63.0(t, C-6′)。IR 图谱、氢谱和质谱与文献[11]一致。

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STUDY ON THE CHEMICAL CONSTITUENTS OF *CURCULIGO ORCHIOIDES*

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Abstract Eight known compounds, curculigoside Ⅰ(1), orcinol glucoside(2) 3,3′,5,5′-tetramethoxy-7,9′:7′,9-diepoxylignan-4, 4′-di-O-β-D-glucopyranoside (3), 3-hydroxy-5-methylphenol-1-O-[β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside](4), 2,3,4,7-tetramethoxyxanthone(5), 1,3,7-trimethylxanthine(6), daucosterol(7) were isolated from rhizomes of *Curculigo orchioides*. Their structures were elucidated by spectral evidence.

Key words hypoxidaceae; *Curculigo orchioides*; chemical constituents

(上接第 205 页)

FLAVONOIDS AND BIOACTIVITY OF *SAGERETIA GRACILIS*

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Abstract From the rhizomes of *Sageretia gracilis* six flavonoids were isolated and determined as maesopsin (1), maesopsin-6-O-β-D-glucopyranoside (2), 5,7,4′-trihydroxy dihydroflavonol (3), 5,7,4′-trihydroxy dihydroflavonol-3-O-α-L-arabinofuranoside (4), 5,7,4′-trihydroxy dihydroflavonol-3-O-α-L-rhamnopyranoside (5), 5,7,4′-trihydroxy flavonol (6) together with octadecoic acid, methyl triacontanoic acid and daucosterol based on spetral data, in which compound 4 is a new compound. The EtOH extracts, H_2O extracts, petroleum ether fractions, EtOAc fractions, n-butanol fractions, compound 1, 5 and 6 were tested on PEPT, YNG, CDC25, CAT-B, CA-II and PAI bioassays respectively for finding some samples with anti-bacterium, anti-fungus, anti-cancer, anti-osteoporosis, anti-thrombus activities. The results indicated that only the n-butanol fractions and H_2O extracts showed anti-bacterium and anti-fungus activities with the IC_{50} of 74.9 and 13.8 μg/ml, respectively.

Key words *Sageretia gracilis*; Rhamnaceae; 5,7,4′-trihydroxy dihydroflavonol-3-O-α-L-arabinofuranoside; flavonoids; bioactivity