

肉苁蓉鲜花序的化学成分研究[△]

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摘要 首次从列当科植物荒漠肉苁蓉*Cistanche deserticola* Ma新鲜花序的正丁醇萃取物中分离并鉴定了4个化合物,即6-去氧梓醇(6-deoxycatalpol, I)、黑立脂素甙(liriodendrin, II)、8-表马钱子酸葡萄糖甙(8-epiloganic acid, III)和半乳糖醇(IV),其成分与肉质茎基本相同,为肉苁蓉花序的开发利用提供了一定的依据。

关键词 肉苁蓉 列当科 环烯醚萜甙 木脂素甙

肉苁蓉为列当科寄生植物荒漠肉苁蓉*Cistanche deserticola* Ma去花序的肉质茎,具有补肾阳,益精血,润肠通便的功效。由于大量采挖,资源濒于枯竭,被国家列为二级保护植物。为了合理利用肉苁蓉资源,变废为宝,我们对肉苁蓉的花序进行了初步的化学成分研究。从正丁醇萃取部分分离鉴定了4个化合物,分别为6-去氧梓醇(6-deoxycatalpol, I)、黑立脂素甙(liriodendrin, II)、8-表马钱子酸葡萄糖甙(8-epiloganic acid, III)和半乳糖醇(IV),以上4种成分都是首次从该部位中分离得到。其化学成分与肉质茎基本一致^[1],可考虑作为肉苁蓉资源进行开发利用。

1 材料和仪器

肉苁蓉*C. deserticola* Ma的鲜花序系作者在内蒙古阿拉善左旗吉兰泰盐场附近向牧民收购并鉴定。

Kofler型熔点测定仪(未校正);红外光谱仪为:Perkin-Elmer 983G;核磁共振谱仪:¹H-NMR: Bruker 400MHz; ¹³C-NMR: JEOL FX-90Q, 22.5MHz;质谱仪为:ZAB-BS, FAB测定底物为S-GLY; GC-MS: GMS-3000。

2 提取和分离

肉苁蓉鲜花序15kg,切碎,水蒸气蒸馏,得蒸馏液5L(供GC-MS分析用)和水液8L,将水液浓缩到3000ml,用EtOAc萃取(1000ml×3),除去脂溶性成分,萃取后的水液再用BuOH萃取(1000ml×6),将BuOH回收至干,得BuOH萃取物40g。将BuOH萃取物经反复硅胶柱层析,用CHCl₃-MeOH(9:1)至CHCl₃-MeOH-H₂O(6:4:0.5)程序洗脱,得化合物I~IV。

3 鉴定

晶I: 无色方晶(MeOH), mp204~206°C; IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3400(OH), 1640; FAB-MS m/z: 347(M+1)⁺, 364(M+H₂O)⁺; ¹HNMR(300MHz, D₂O) δ ppm: 1.36~1.50(1H, m, C₆-H), 2.19(1H, m, C₅-H), 2.37(2H, m, C_{6,8}-H), 3.63(1H, C₇-H), 3.75, 4.19(2H, AB system, J=13Hz, C₁₀-H), 4.73(1H, d, J=8Hz, anomeric H), 4.9~5.0(2H, m, C₁, 4-H), 6.19(1H, d, J=6Hz, C₃-H); ¹³CNMR δ ppm: 141.9(C₃), 108.3(C₄), 101.1(C_{1'}), 96.9(C₁), 78.7(C_{3'}), 78.2(C_{6'}), 75.3(C_{2'}), 72.0(C_{4'}), 71.4(C₈),

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64.0 (C₇), 63.1 (C₁₀, δ'), 44.8 (C₉), 36.6 (C₈), 33.3 (C₅)。以上数据与文献^[2]中6-去氧梓醇的一致。

晶Ⅰ：白色粉末 (MeOH)，IR_v $\frac{\text{KBr}}{\text{max}}$ cm⁻¹: 3400 (OH), 1590, 1495; ¹³CNMR δ ppm: 153.5 (C₃', ε', ζ', ε''), 138.5 (C₄', ζ''), 134.3 (C₁', ι''), 104.9 (C₂', ε', ζ'', ε''), 103.8 (glu C₁), 86.1 (C₂', ε'), 77.8 (glu C₅), 77.2 (glu C₃), 75.2 (glu C₂), 72.4 (C₄, ζ), 70.6 (glu C₄), 61.8 (glu C₆), 54.6 (C₁, ε)。以上数据与文献^[3]中黑立脂素甙的一致。

晶Ⅱ：无色针晶 (MeOH)，mp 146~149°C，IR_v $\frac{\text{KBr}}{\text{max}}$ cm⁻¹: 3400 (OH), 2080~2500, 1680, 1640, 1430; FAB-MS m/z: 377 (M+1)⁺; ¹HNMR, (300MHz, C₅D₅N) δ ppm: 1.16 (3H, d, J=7.2Hz, CH₃), 2.25~2.40 (2H, m, C₆-H), 2.26 (1H, m, C₈-H), 3.06 (1H, s, C₃-H); ¹³CNMR δ ppm: 169.6 (C₁₁), 150.6 (C₃), 114.5 (C₄), 100.4 (C₁'), 95.7 (C₁), 78.6 (C₇, ε', ε'), 74.7 (C₂'), 71.4 (C₄'), 62.8 (C₆'), 44.7 (C₉), 42.3 (C₈), 41.3 (C₈), 30.5 (C₅), 74.3 (C₁₀)。以上数据与文献^[4]中8-表马钱子酸葡萄糖甙的一致。

晶Ⅳ：无色针晶 (MeOH)，mp 169~171°C，IR_v $\frac{\text{KBr}}{\text{max}}$ cm⁻¹: 3280 (OH), 1440, 1075, 1010; ¹HNMR (300MHz, C₅D₅N) δ ppm: 3.68 (2H, q, C₂, ε-H), 3.71~3.82 (4H, m, C₁, ε-H), 3.87 (2H, dd, J=11.5, 2.7Hz, C₃, ζ-H); ¹³CNMR δ ppm: 70.8 (C₃, ζ), 69.2 (C₂, ε), 63.2 (C₁, ε)。以上数据与文献^[5~7]中半乳糖醇的一致。

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翼首草中的三萜皂甙

Wu F E, et al. Phytochem, 1993, 32(6): 1535

翼首草属川续断科，为多年生草本，盛产于我国云南、四川和西藏地区，具有清热解暑，祛风湿等功能。其化学成分尚未见报道。作者等在研究该属植物匙叶翼首花 *Pterocephalus hookeri* (Clarke) Hock中，分得4个新皂甙定名为hookeroside A、B、C和D，从裂叶翼首花 *P. bretschneideri* (Batal) Pritz中分到2个皂甙，定名为bretschoside A和B。酸水剂都得到同样的糖甙配基石竹素 (oleanolic acid)。hookeroside A, C₅₂H₈₄O₁₀, [α]_D²² -22.50° (c,

0.405, MeOH)。hookeroside B, C₅₇H₉₂O₁₄, [α]_D²² -27.14° (c, 0.715, MeOH)。hookeroside C, C₆₃H₁₀₂O₁₈, [α]_D²² -95.25° (c, 0.420, MeOH)。hookeroside D, [α]_D²² -32.23° (c, 0.402, MeOH)。bretschoside A, C₅₂H₈₄O₁₀, [α]_D²² -39.64° (c, 0.312, MeOH)。bretschoside B, C₅₂H₈₄O₁₀, [α]_D²² -26.67° (c, 0.305, MeOH)。

(史玉俊 摘译)

ABSTRACTS OF ORIGINAL ARTICLES

Studies on the Chemical Constituents of the Fresh Inflorescences of Desertliving Cistanche (*Cistanche deserticola*)

Tu Pengfei, He Yanping and Lou Zhicen

Four known compounds are isolated from the butanol fraction of the fresh inflorescences of *Cistanche deserticola* Ma (*Orobanchaceae*) for the first time. They are identified as 6-deoxycatalpol (I), liriiodendrin (II), 3-epiloganic acid (III) and galactitol (IV). These constituents are similar to the main constituents of the dried fleshy stem. It is suggested that the inflorescence may be exploited as a substitute for herb *C. deserticola* Ma.

(Original article on page 451)

Studies on the Alkaloids of shezushishan (*Huperzia serrata*)

Yuan Shanqin, Feng Rui and Gu Guoming

Three alkaloids were isolated from *Huperzia serrata* (Thunb.) Trev. Their structure were identified as 8-deoxyserratinine (I), lycodine (II) and phlegmariurine B (III) by means of spectral analysis (UV, IR, NMR, MS). Compound II and III were isolated for the first time from this species.

(Original article on page 453)

Studies on the Chemical Constituents of Common Leafy Flower (*Phyllanthus urinaria*)

Wan Zhenxian, Zhou Guoping and Yi Yanghua

Six compounds were isolated from the whole herb of *Phyllanthus urinaria* L. They were identified as ellagic acid (I), 3, 3', 4-tri-O-methylellagic acid (II), succinic acid (III), ferulic (IV), β -sitosterol-glucoside (V) and gallic acid (VI) by means of spectral analysis and chemical reaction. Compound II, III, IV, and V were isolated for the first time from this plant.

(Original article on page 455)

Studies on the Quality Standard of Shenrongsanshen Medicinal Wine

Yang Guohong

Quality standard of Shenrongsanshen medicinal wine was discussed. A TLC method was used in the identification of the chemical constituents of some of the medicinal herbs used in the wine, such as, fruit of *Lycium chinense* Mill. fruit of *Psoralea corylifolia* L., rhizome of *Vladimiria souliei* (Franch.) Ling. A HPLC method was used in the determination of icariine. The average recovery was 99.87%, RSD=0.04% (n=5).

(Original article on page 457)

High Performance Liquid Chromatographic Assay of Tetramethylpyrazine in "Fubidou Granule"

Jiang Zhirong