

阿尔泰黄芪化学成分的研究

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摘要 阿尔泰黄芪 *Astragalus altaicus* 根部的甲醇提取物通过溶剂分配, 在正丁醇可溶部分得到3个环阿尔庭烷三萜甙化合物, 经FABMS、IR、 ^1H 、 ^{13}C NMR、DEPT、 ^1H - ^1H COSY、 ^1H - ^{13}C COSY及水解等方法鉴定为: 棉毛黄芪甙VI, IV, II, 这些化合物是首次从阿尔泰黄芪中报道。

关键词 阿尔泰黄芪 环阿尔庭烷三萜甙 棉毛黄芪甙

黄芪属豆科植物, 常用于利尿, 降压, 强身等, 并能提高人体免疫能力^[1], 仅在我国新疆自治区就产有200多种黄芪^[2]。从各种黄芪中分离鉴定了大量的环阿尔庭烷三萜甙及其它各种成分如黄酮、多糖等^[3], 但阿尔泰黄芪的成分研究尚未见报道。

1 材料与仪器

熔点用Buchi 535型熔点测定仪测定, 未作校正。旋光用Perkin-Elmer 241C型旋光仪测定, 以甲醇为溶剂。红外光谱通过压片法使用Shimadzu 440仪测定。FABMS用Finnigan 4021型仪测定。 ^1H , ^{13}C NMR, DEPT及2DNMR采用Bruker AMX-600型(对 ^1H 为600MHz)仪器测定, 用 CD_3OD 作溶剂, 溶剂峰3.30ppm作内标。元素分析由本所分析室测定。柱层析采用上海五四化工厂生产的硅胶(100~200目)或青岛海洋化工厂生产的微孔硅胶H。

2 提取与分离

阿尔泰黄芪采自新疆自治区阿尔泰地区, 取其根部自然风干, 磨成粉末(1.9kg), 用甲醇提取, 蒸除溶剂后的浸膏用水-正丁醇(1:1)分配, 正丁醇可溶部分(44.4g)进行硅胶柱(100~200目)层析, 氯仿-甲醇(7:3)洗脱, 所得低极性部分(16g)用微孔硅胶H重复纯化(氯仿-甲醇, 99:1~80:20), 得到化合物I, II及IV, 再分别进行重结晶得到纯品: I(432mg), II(607mg)及IV(1.2g)。

3 鉴定

化合物II: mp 271~273°C, $[\alpha]_{\text{D}} + 28.3$, FABMS显示m/z 819 ($\text{m}^+ + \text{Na}$)峰。元素分析表明II的分子式为 $\text{C}_{42}\text{H}_{68}\text{O}_{14}$, 600MHz ^1H NMR的高场处有7个叔甲基信号(0.88~1.25), 一个乙酰基甲基(2.08), 2个高场共振质子(0.23 d, 4.5Hz; 0.55, d, 4.5Hz)。红外显示有酰基及羟基存在(1740, 3410 cm^{-1})。因此该化合物应为一环阿尔庭烷三萜甙。COSY表明有2个五碳糖单元, 且均为 β -构型(4.28, d, 7.4Hz; 4.41, d, 7.9Hz), 而且乙酰基在其中之一糖单元的 C_2 位上(4.70, dd, 7.9, 9.4Hz)。在II的酸水解产物中检测到D-木糖。比较II与甙元^[5]的 ^1H 、 ^{13}C 化学位移可知2个D-木糖分别联接在 C_3 及 C_6 位。此外, 由于 C_3 位糖单元的异头碳(anomeric carbon)的共振在105.4(或105.7)ppm, 可以肯定在

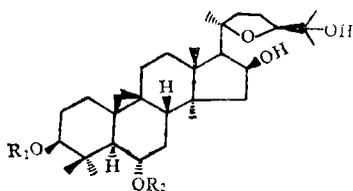
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该糖的C₂位带有一酰基取代基(δc75.98)^[6]。所以化合物I应为棉毛黄芪甙V^[7]。

化合物IV: mp 253~275°C, [α]_D+7.8, FABMS m/z显示861(M⁺+Na), 元素分析(C: 60.89, H: 8.25)表明分子式为C₄₄H₇₀O₁₆。IV的¹H NMR与I极为相似,但在2.01及2.03处有2个酰基甲基峰,比较两者的分子式及其它数据,可以推断化合物IV为I的乙酰化产物,在相同条件下(乙酸酐-吡啶,室温),两者给出完全相同的产物III〔FA-BMS, m/z 1071(M⁺+Na), ¹HNMR〕。化合物IV在较低场有2个dd裂分的质子,其化学位移及偶合常数分别为: 4.77, dd, 7.8, 9.4Hz; 4.97, dd, 9.4Hz。上述数据证明化合物IV的2个乙酰基在同一糖单元的C₂'及C₃'位。IV的异头氢共振分别在4.28(d, 7.2)、5.54(d, 7.8),其高场质子与化合物I中的C₆位D-木糖的异头氢完全一致,综合上述数据IV的结构如图所示,为棉毛黄芪甙I^[7]。

化合物I: mp 170~172°C. [α]_D+9.7, FABMS显示m/z 891(M⁺+Na), 分子式为C₄₅H₇₂O₁₆。I的¹HNMR与IV相近,均有2个乙酰甲基共振(2.01, 2.03)。但糖单元的质子共振(3.1~4.0ppm)稍有不同,此外I的酸水解产物中检测到D-木糖及D-葡萄糖,由于I与IV的乙酰基甲基及D-木糖部分的质子化学位移完全相同, I中的D-葡萄糖应联结在C₆位置,化合物与棉毛黄芪甙IV^[7]或astragaloside I一致。



I-R₁=2,3-O-diacetyl-β-D-xylopyranosyl;
R₂=β-D-glucopyranosyl
II-R₁=2-O-acetyl-β-D-xylopyranosyl;
R₂=β-D-xylopyranosyl
III-R₁=R₂=2,3,4-triacetyl-β-D-xylopyranosyl
IV-R₁=2,3-O-diacetyl-β-D-xylopyranosyl;
R₂=β-D-xylopyranosyl

图 化合物I~IV的化学结构式

化合物I, II及IV的非均相酸水解得一相同的甙元,其物理化学数据与棉毛黄芪甙元一致^[7],因此化合物应有如图所示的绝对立体化学。此外, I、II及IV还分别与cyclosiiversioside B, C及A一致^[8, 9]。后3个化合物最初报道时的构型为20S, 24R,但后来证明是不正确的^[10],应与棉毛黄芪甙元或黄芪甙元cycloastragenol^[5]一致,即为20R, 24S。

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(1993-05-05收稿)

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ABSTRACTS OF ORIGINAL ARTICLES

Studies on the Chemical Constituents of Aertaihuanqi (*Astragalus altaicus*)

Cheng Jiefei, Wu Jianfei, Azi Guli, et al

Three cycloaitesides were isolated for the first time from the n-BuOH extract of *Astragalus altaicus*. They were identified respectively as cyclosieversioside B, C and A, by FAB-MS, IR, ^1H , ^{13}C NMR, DEPT, ^1H - ^1H COSY, ^1H - ^{13}C COSY and hydrolysis.

(Original article on page 563)

Studies on the Chemical Constituents of Montane Spicebush (*Lindera reflexa*)

Zhang Junzeng, Fang Qicheng

Seven Compounds were isolated from dry Radix of *Lindera reflexa*. They were identified as launobine (I), lindcarpine (II), laulolitsine (III), \pm pinostrobin (IV), \pm pinoembrin (V), octacosanoic acid (VI) and β -sitosterol (VII) on the basis of chemical and spectral analyses.

(Original article on page 565)

Chemical Components of Mongolian Spirala (*Spiraea mongolica*)

Xie Haihui, Wei Xiaoyi, Wei Biyu

Six compounds were isolated for the first time from *Spiraea mongolica* Maxim. (*Rosaceae*) by means of chemical and spectral analysis and comparison with data of literature or authentic samples, 5 of them were identified as β -sitosterol (I), betulin (II), betulinic acid (III), betulinic acid 3, 5-dihydroxyl-cinnamate (IV) and daucosterol (VI).

(Original article on page 569)

Simultaneous Quantitative Determination of Ephedrine and Strychnine in Traditional Chinese Medicine "Joufensan" by HPLC

Chen Fakui, Yoshihiro Kano, et al

A rapid, simple and sensitive method was established for the evaluation of Chinese traditional medicine "Joufensan" by HPLC. Sample of "Joufensan" was extracted by solvent, and the extraction analysed by HPLC using an Inertsil ODS column with a solvent system, acetonitrile-water-phosphoric acid-sodium dodecyl sulfate (38:62:0.1:0.5) at 40°C and UV detector. The new method was reliable for the evaluation of ephedrine and strychnine in "Joufensan".

(Original article on page 571)

Quantitative Determination of paeonin in "Shuganzhitong Pian" by Macroporous Resin Preseparation-TLC Densitometry Method

Shou Guoxiang, Lu Guibao

A preliminary separation procedure of paeonin in "shuganzhitong pian" by macro-porous resin GDX-104 and its subsequent quantitative determination by double wavelength TLC scanning was developed. Through sample scanning, stability investigation and recovery tests, it reveals that the suggested method was precise and accurate, the results of determination