

海南蕊木化学成分的研究

I. 根中单吲哚生物碱的分离与鉴定

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摘要 从海南蕊木 *Kopsia hainanensis* 根中分得8个化合物, 经理化常数和光谱分析鉴定为单吲哚生物碱: coronaridine(I), heyneanine(II), tabersonine(III), 11-methoxytabersonine(IV), scandine(V), N-methoxycarbonyl-11, 12-methylenedioxykopsinaline(VI), kopsinine(VII), N-methoxycarbonyl-12-methoxykopsinaline(VIII)。其中化合物 I~V 均系首次从该属植物中分得。

关键词 海南蕊木 吲哚生物碱

海南蕊木 *Kopsia hainanensis* Tsiang 为夹竹桃科蕊木属植物, 常绿灌木高2m左右, 产于海南崖县、保亭和万宁等地, 为我国特有品种, 为当地民间常用草药^[1]。我所药理实验表明, 海南蕊木根总生物碱部分具有明显的镇痛作用, 为此, 对其所含吲哚生物碱进行了系统的提取分离和鉴定。

我们用常规方法提取海南蕊木总生物碱部分, 通过Sephadex LH-20柱层将其粗分成单吲哚生物碱和双吲哚生物碱2个部分, 单吲哚部分再经硅胶层析和溶剂结晶法处理得到8个化合物, 根据理化常数和光谱分析分别鉴定为: coronaridine(I), heyneanine(II), tabersonine(III), 11-methoxytabersonine(IV), scandine(V), N-methoxycarbonyl-11, 12-methylenedioxykopsinaline(VI), kopsinine(VII), N-methoxycarbonyl-12-methoxykopsinaline(VIII)。生物碱V属于melosine型生物碱, 主要存在于夹竹桃科山橙属植物(*Melodinus*)中^[2], 蕊木中含有此碱还是首次发现; 生物碱I~IV分属bioga和vincadifformine型生物碱, 是首次从蕊木属植物得到的。

1 仪器和试剂

海南蕊木生药原料来自海南省兴隆县, 并由我所植物室陈毓享研究员对生药标本进行了鉴定。熔点用显微熔点测定仪测定, 未校正。紫外光谱用岛津UV-240; 红外光谱仪为Perkin-Elmer 683型; 质谱用ZAB-1F型; 核磁共振仪为WH-90(TMS为内标); 旋光用Perkin-Elmer 241旋光仪测定。制备薄层和旋转薄层用硅胶GF₂₅₄均为青岛海洋化工厂产品; 层析用氧化铝(中性, 160~200目)为上海五四农场产品; 显色剂为7%碳酸铈铵浓磷酸溶液; 展开剂为①二氯甲烷-己烷(9:1); ②乙酸乙酯-石油醚(2:8); ③乙酸乙酯-石油醚(17:3)。

2 提取和分离

海南蕊木根8kg粉碎后, 乙醇回流提取得乙醇提取物, 用2%盐酸研溶, 过滤, 滤液氨水碱化(pH=9~10)后, 分别用乙醚和氯仿萃取, 减压除去溶剂得总生物碱20g。20g总碱用少量氯仿-甲醇(1:1)溶解后进行Sephadex LH-20(200g)柱层析, 以氯仿-甲醇(1:6)洗

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脱, 每份收集10ml, 薄层检查, 第25~36份作为单呋喃生物碱部分(13g), 该部分进行硅胶柱层析, 乙醚洗脱每份收集100ml, 共收集42份。从第3~4份得固体物340mg, 进行旋转薄层分离, 展开剂①展开, 按荧光带收集。第1条蓝色荧光带洗脱物经乙醚-石油醚重结晶得生物碱Ⅰ(118mg); 第2条天蓝色荧光带洗脱物再经制备层析(展开剂①)得生物碱Ⅱ(29mg)。从第5~6份得固体物307mg经旋转薄层层析(展开剂②), 天蓝色荧光带洗脱物再经制备层析(展开剂②)得生物碱Ⅳ(79mg); 从第19份得洗脱固体物150mg, 经乙醚-己烷结晶得生物碱Ⅴ(120mg); 从第21份得固体物(70mg)用甲醇重结晶得生物碱Ⅵ(10mg); 从第22~42份得固体物4.44g, 进行氧化铝柱层析, 氯仿-甲醇梯度洗脱, 氯仿-甲醇(10:1)洗脱部分(782mg)再经氧化铝干柱层析, 己烷-乙醚(1:1)至乙醚梯度洗脱, 每份收集10ml, 薄层检查合并相似部分; 从第4'~6'部分经乙醚-己烷结晶得生物碱Ⅶ(30mg); 第9'~14'份经制备层析(展开剂③)得生物碱Ⅷ(5mg), 第18'~19'份经乙醚重结晶得生物碱Ⅸ(15mg)。

3 鉴定

生物碱Ⅰ(coronaridine): mp139~141°C(乙醚-石油醚), $[\alpha]_D^{20} - 26.4^\circ$ (c, 0.25, EtOH), UV $\lambda_{\text{max}}^{\text{EtOH}}$ (lg ϵ): 225(4.07), 283(3.62), 290(3.57), IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3400, 1724, 740; MS m/z: 1338(M⁺), 323, 309, 279, 253, 214, 208, 148, 136, 130, 124, 122; ¹H-NMR(CDCl₃, δ ppm): 7.78(1H, s), 7.0~7.5(4H, m), 3.71(3H, s), 0.89(3H, t, J=8Hz), 3.53(1H, s,) [3]。

生物碱Ⅱ(heyneanine): mp165°C(甲醇), $[\alpha]_D^{10} - 15.68^\circ$ (c, 0.22, CHCl₃), UV $\lambda_{\text{max}}^{\text{EtOH}}$ (lg ϵ): 224(4.06), 282(3.57), 290(3.50); IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3238, 3220, 1725, 740; MS m/z: 354(M⁺), 339, 336, 310, 295, 253, 214, 206, 195, 168, 154, 130; ¹H-NMR(CDCl₃, δ ppm): 7.82(1H, s), 7.0~7.5(4H, m), 6.34(1H bs), 3.75(3H, s), 1.10(3H, d, J=6Hz) [4]。

生物碱Ⅲ(tabersonine): 无定形粉末 $[\alpha]_D^{20} - 264.4^\circ$ (c, 0.32, EtOH), UV $\lambda_{\text{max}}^{\text{EtOH}}$ (lg ϵ): 223(3.71), 297(3.65), 328(3.81); IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3375, 1675, 1608; MS m/z: 336(M⁺), 229, 214, 170, 168, 154, 152, 135, 122, 121, 92; ¹H-NMR(CDCl₃, δ ppm): 8.88(1H, s), 7.18~6.40(4H, m), 5.70(2H, m), 3.73(3H, s)。 [5]

生物碱Ⅳ(11-methoxytabersonine): 无定形粉末, $[\alpha]_D^{20} - 347^\circ$ (c, 0.14, CHCl₃), UV $\lambda_{\text{max}}^{\text{EtOH}}$ (lg ϵ): 242(3.91), 324(3.99); IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3370, 1670, 1616; MS m/z: 385(M⁺) 35, 281, 259, 244, 200, 183, 153, 135, 122, 121, 109, 93; ¹H-NMR(CDCl₃, δ ppm): 8.88(1H, s), 7.04(1H, d, J=9Hz), 6.23(1H, d J=9Hz), 6.34(1H, s), 5.67(2H, m), 3.70(6H, s) [6]。

生物碱Ⅴ(scandine): mp198~199°C(乙醚-己烷), $[\alpha]_D^{10} + 255.7^\circ$ (c, 0.23, CHCl₃), UV $\lambda_{\text{max}}^{\text{EtOH}}$ (lg ϵ): 216(3.98), 256(3.61), 267(3.53), 285(3.12); IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3440, 1745, 1660, 1590, 1500; MS m/z: 350(M⁺), 335, 291, 263, 134, 120; ¹H-NMR(CDCl₃, δ ppm): 9.50(1H, s, -NH), 7.33(1H, dd, J₁=8Hz, J₂=2Hz), 7.06(2H, t, J₁=7Hz, J₂=2Hz), 6.74(1H, dd, J₁=8Hz, J₂=2Hz), 5.62(2H, s), 5.60(2H, dd, J₁=10Hz, J₂=10Hz), 4.90(1H, d, J=10Hz), 4.85(1H, d, J=18Hz), 3.56(3H, s)。 [2]

生物碱Ⅵ (N-methoxycarbonyl-11, 12-methylenedioxykopsinaline): mp 210~211°C (甲醇), $[\alpha]_D^{20} - 34.31^\circ$ (c, 0.33, CHCl₃)。UV $\lambda_{\text{max}}^{\text{EtOH}}$ (lg ϵ): 226 (4.14), 247 (3.76), 287 (3.65), 295 (3.05), IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3320, 1730, 1680; MS m/z: 456 (M⁺), 455, 438, 397, 365, 330, 309, 283, 273, 253, 109; ¹H-NMR (CDCl₃, δ ppm): 6.89 (1H, s), 6.75 (1H, d, J = 7 Hz), 6.46 (1H, d, J = 7 Hz), 5.89 (2H, s), 3.81 (3H, s), 3.78 (3H, s)。^[7]

生物碱Ⅶ (kopsinine): mp 102~104°C (乙醚-己烷) $[\alpha]_D^{20} - 74.02^\circ$ (c, 0.46, CHCl₃); UV $\lambda_{\text{max}}^{\text{EtOH}}$ (lg ϵ): 207 (3.86), 242 (3.53), 292 (3.05); IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3350, 1725; MS m/z: 338 (M⁺), 310, 129, 109。

生物碱Ⅷ (N-methoxycarbonyl-12-methoxykopsinaline): mp 228~229°C (乙醚-己烷); $[\alpha]_D^{10} - 5.3^\circ$ (c, 1.3, CHCl₃); UV $\lambda_{\text{max}}^{\text{EtOH}}$ (lg ϵ): 224 (4.35), 257 (4.07), 283 (3.26); IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3357, 1730, 1675; MS m/z: 442 (M⁺), 441, 427, 383, 351, 339, 295, 259, 109; ¹H-NMR (CDCl₃, δ ppm): 6.87 (1H, d), 7.08 (1H, t), 6.75 (1H, d), 7.01 (1H, bs), 3.94 (3H, s), 3.89 (3H, s), 3.81 (3H, s)。^[7]

致谢: 本所仪器分析室代测各种光谱。

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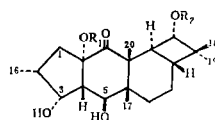
(1992-10-14 收稿)

Euphorbia micractina 中的双萜类化合物

贾忠建, 等. Phytochem, 1993, 32 (1): 208

Euphorbia micractina 为多年生草药, 盛产于我国西南和西北地区, 其化学成分尚未见报道。本文报道从其全草分得 2 个双萜类化合物, 命名为 euphoractine A 和 B。

euphoractine A, C₂₀ H₃₈ O₆, mp 208~210°C, $[\alpha]_D^{24} + 64.8^\circ$ (C, 0.50, CHCl₃), R₁ = 肉桂酰, R₂ = H



euphoractine B, C₂₀ H₃₈ O₆, $[\alpha]_D^{24} + 11.63^\circ$ (C, 0.92, CHCl₃), R₁ = H, R₂ = 肉桂酰

(史玉俊 摘译)

ABSTRACTS OF ORIGINAL ARTICLES

Studies on the Chemical Components of Veined *Rabdosia*

(*Rabdosia nervosa*)

Wang Xianrong, Wang Suqing, et al

Neorabdosin (I), odonicin (II), effusanin A (III), nervosanin A (IV) and effusanin E (V) were isolated from *Rabdosia nervosa*, IV proved to be a new natural compound.

(Original article on page 115)

Studies on the Chemical Components of Hainanruimu

(*Kopsia hainanensis*)

I. Isolation and Identification of Monomeric Indole Alkaloids from Its Root

Yun Wenhui, Chen Yuwu and Feng Xiaozhang

From the total alkaloids of the root of *Kopsia hainanensis* Tsiang, eight compounds were isolated and identified as coronaridine (I), heyneanine (II), tabersonine (III), 11-methoxytabersonine (IV), scandine (V), N-methoxycarbonyl-11, 12-methylenedioxykopsinaline (VI), kopsinine (VII) and N-methoxycarbonyl-12-methoxykopsinaline (VIII) by means of physical constants and spectral analysis.

(Original article on page 118)

Preliminary Study of Extracting Chinese Traditional Medicine with Cellulase

Ma Tiantian

The yield of berberine can be increased by pre-treating *Phellodendron amurense* with cellulase before extracting. It is suggested that the use of cellulase for the extraction of other natural products may be worth consideration.

(Original article on page 123)

A New Method for the Extraction of Tea-Polyphenols

Ge Yizhang and Jin Hong

A new method for the extraction of tea-polyphenols (TP) from tea using $AlCl_3$ as precipitating agents was proposed. Compared with the traditional extraction method using organic solvents, it is shown that the new method is simple and can be operated easily. The extraction rate of TP by the new method could reach 10.5% and the content of the effective ingredients of TP could reach over 99.5%.

(Original article on page 124)