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刺异叶花椒中的生物碱和香豆素类成分*

向 瑛 郑庆安 张灿奎 李 贞 屠治本**

(中国科学院武汉植物研究所 武汉 430074)

提 要 从刺异叶花椒根的木质部中分得 6 种生物碱, 分别为铁屎米-6-酮、乙氧基白屈菜红碱、N-去甲基白屈菜红碱、白蘞碱、勒楂碱、氧化勒楂碱, 以及 3 种香豆素类化合物, 滨蒿内酯、东莨菪内酯和异东莨菪内酯。利用化学方法和光谱数据证实了它们的结构。这些生物碱和香豆素类成分在广义花椒属的化学分类和应用研究中均具有重要意义。

关键词 刺异叶花椒, 生物碱, 香豆素, 化学分类

ALKALOIDS AND COUMARINS FROM *ZANTHOXYLUM DIMORPHOPHYLLUM* HEMSL. VAR. SPINIFOLIUM REHD. ET WILS.*

Xiang Ying Zheng Qing'an Zhang Cankui Li Zhen Tu Zhiben**

(*Wuhan Institute of Botany, The Chinese Academy of Sciences* Wuhan 430074)

Abstract Six alkaloids, canthin-6-one, ethoxychelerythrine, N-des-methylchelerythrine, dictamnine, avicine and oxyavicine as well as three coumarins, scoparone, scopoletin and isoscopoletin were isolated from the root xylem of *Zanthoxylum dimorphophyllum* var. *spinifolium*. Their structures were identified on the basis of spectral and chemical data. These alkaloids are significant to the chemotaxonomy of *Zanthoxylum* L. and have practical application.

Key words *Zanthoxylum dimorphophyllum* var. *spinifolium*, Alkaloids, Coumarins, Chemotaxonomy

The alkaloids of *Zanthoxylum* species possess several interesting biological activities, e.g., tumor and AIDS inhibitors[1]. It is a significant marker of chemotaxonomy on rutaceous plants which have strong arguments in morphological taxonomy. We have reported compounds isolated from *Zanthoxylum* species[2～8]. Especially, we have reported four alkaloids isolated from the root bark of *Z. dimorphophyllum* var. *spinifolium*. In continuation of our studies on the chemical constituents, we report the isolation and structural identification of six alkaloids and three coumarins from this plant. Bioassay shows that canthin-6-one has strong antibacterial activity and anti-arrhythmia effect. It has a light concentration both in the

收稿日: 1999-01-28, 修回日: 1999-04-22。第一作者: 女, 1974 年 2 月出生, 硕士研究生, 从事植物化学研究。
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** 通讯联系人。

root xylem and root bark. Benzophenanthridines and quinolins have been used as markers for chemotaxonomy. In molecular evolution views, tyrosin derived alkaloids e.g. benzophenanthridines are regarded as primary structure and anthranilic acid derived alkaloids e.g. quinolins are modern structure [6]. It is interesting that both of them are found in this plant. We will discuss it in other paper. Quinolin alkaloid dictamnine is isolated from this plant for the first time.

Experimental

General Mps are uncorrected. NMR spectra were measured on a Bruker AM-400 spectrometer using TMS as internal standard. EI-MS spectra were measured with VG-7070 E-HF (70ev) mass spectrometer. IR spectra were recorded in Perkin-Elmer 983 spectrometer (KBr).

Plant material Roots of *Z. dimorphophyllum* var. *spinifolium* were collected in August 1993 in Wufeng county of Hubei Province. A voucher specimen was identified by Prof. Li Hongjun and deposited in the Herbarium of Wuhan Institute of Botany.

Extraction and isolation Dried and powdered roots xylem (5.0 kg) were exhaustively extracted with 95% EtOH at 50℃. The ethanol solution was condensed under vacuum pressure to give a 1.5 kg extract. The extract was dissolved in 2 mol/L HCl and filtered. The acidic solution was extracted with chloroform to give fr. 1 (20 g). The aqueous phase was then basified with amonia liquor to pH 12 and partitioned with chloroform to give fr. 2 (30 g). These two parts were chromatographed on silica gel column eluting with $CHCl_3$ and $CHCl_3$-MeOH. Column chromatography of fr. 1 yielded compounds 1 (100 mg) and 2 (50 mg). Column chromatography of fr. 2 yielded compounds 3 (2 g), 4 (200 mg), 5 (200 mg), 6 (50 mg), 7 (40 mg), 8 (70 mg) and 9 (30 mg).

Canthin-6-one (1) pale yellow needles ($CHCl_3$), mp 160~161℃. IR υ_{max}^{KBr} (cm^{-1}): 1660. EI-MS (m/e, %): 220 (M^+, 100), 192 (85), 166 (10), 139 (18), 114 (13). ^{1}H-NMR ($CDCl_3$), δ(ppm): 6.95 (d, 1H, J = 10Hz), 7.95 (d, 1H, J = 10Hz), 8.75 (d, 1H, J = 5Hz), 7.80 (d, 1H, J = 5Hz), 8.60 (d, 1H), 7.30~8.00 (m, 3H).

Scoparone (2) white needles ($CHCl_3$-MeOH), mp 143~144℃. UV λ_{max}^{EtOH} (nm): 229, 294, 342. EI-MS (m/e, %): 206 (M^+, 100), 191 (51), 163 (38), 135 (30), 107 (20), 92 (16), 69 (21). ^{1}H-NMR ($CDCl_3$), δ(ppm): 3.87 (s, 3H), 3.89 (s, 3H), 6.22 (d, 1H, J = 9.7Hz), 6.78 (s, 1H), 6.79 (s, 1H), 7.57 (d, 1H, J = 9.7Hz).

Dictamnine (3) white needles ($CHCl_3$), mp 137℃. UV λ_{max}^{EtOH} (nm): 236, 293, 310, 330. EI-MS (m/e, %): 199 (M^+, 100), 184 (85), 156 (74), 128 (30), 130 (17), 101 (39), 76 (3). ^{1}H-NMR ($CDCl_3$), δ(ppm): 4.35 (s, 3H), 8.01 (d, 1H, J = 8.5Hz), 8.23 (d, 1H, J = 8.5Hz), 7.02 (d, 1H, J = 2.8Hz), 7.59 (d, 1H, J = 2.8Hz), 7.43 (t, 1H), 7.67 (t, 1H).

N-des-methylchelerythrine (4) pale yellow or colorless needles ($CHCl_3$), mp 212~215℃. UV λ_{max}^{EtOH} (nm): 240, 254, 273, 322. IR υ_{max}^{KBr} (cm^{-1}): 1600, 1581, 1526, 1465, 1285, 1195, 1046, 946, 853. EI-MS (m/e, %): 333 (M^+, 100), 318 (16), 304 (5), 290 (40), 275 (17), 232 (7), 217 (8), 201 (2), 188 (9). ^{1}H-NMR ($CDCl_3$), δ(ppm): 9.75 (s, 1H), 8.72 (s, 1H), 8.36 (d, 1H, J = 9.2Hz), 8.34 (d, 1H, J = 8.7Hz), 7.85 (d, 1H, J = 9.2Hz), 7.60

(d, 1H, J= 8.7Hz), 7.26(s, 1H), 6.14(s, 2H), 4.13(s, 3H), 4.06(s, 3H).

Ethoxychelerythrine (5) white crystals ($CHCl_3$), mp 203～204℃. UV λ_{max}^{EtOH} (nm): 228, 283, 320. IR υ_{max}^{KBr} (cm^{-1}): 935, 2830. EI-MS (m/e, %): 393 (M^+, 18), 348 (100), 333 (11), 332 (8), 316 (6), 305 (1), 304 (4), 290 (8). ^{1}H-NMR ($CDCl_3$), δ(ppm): 1.10 (t, 3H, J = 7Hz), 3.90 (m, 2H), 2.80 (s, 3H), 3.95 (s, 3H), 3.97 (s, 3H), 5.55 (s, 1H), 6.09 (s, 2H), 7.10 (s, 1H), 7.70 (s, 1H), 7.06 (d, 1H), 7.62 (s, 1H), 7.46 (d, 1H), 7.77 (d, 1H).

Scopoletine (6) light yellow crystals ($CHCl_3$), mp 203～205℃. UV λ_{max}^{EtOH} (nm): 253, 300, 349. IR υ_{max}^{KBr} (cm^{-1}): 3321, 1690, 1600, 1558, 1510, 1435, 1280, 1130. EI-MS (m/e, %): 192 (M^+, 100), 177 (68), 164 (43), 149 (75), 121 (32). ^{1}H-NMR ($CDCl_3$), δ(ppm): 6.26 (d, 1H), 7.60 (d, 1H), 6.90 (s, 1H), 6.38 (s, 1H), 6.11 (s, 1H), 3.69 (s, 3H).

Isoscopoletine (7) light yellow needles ($CHCl_3$-Me_2CO), mp 205～206℃. UV λ_{max}^{EtOH} (nm): 253, 300, 349. IR υ_{max}^{KBr} (cm^{-1}): 3321, 1690, 1600, 1558, 1510, 1435, 1280, 1130. EI-MS (m/e, %): 192 (M^+, 100), 177 (68), 164 (43), 149 (75), 121 (32). ^{1}H-NMR ($CDCl_3$), δ (ppm): 6.26 (d, 1H), 7.60 (d, 1H), 6.90 (s, 1H), 6.38 (s, 1H), 6.11 (s, 1H), 3.69 (s, 3H).

Avicine (8) yellow crystals ($CHCl_3$-MeOH), mp more than 310℃. IR υ_{max}^{KBr} (cm^{-1}): 930. EI-MS (m/e, %): 332 (M^+, 6.6), 317 (100), 316 (14.7), 288 (5.5), 287 (3.5), 260 (9.8), 259 (14), 201 (24). ^{1}H-NMR (CF_3COOH), δ(ppm): 5.05 (s, 3H), 6.35 (s, 2H), 6.50 (s, 2H), 7.60 (s, 1H), 7.70 (s, 1H), 8.20 (s, 1H), 8.25 (s, 1H), 8.25 (d, 1H, J= 9Hz), 8.55 (d, 1H, J= 9Hz), 9.40 (s, 1H).

Oxyavicine (9) colorless crystals ($CHCl_3$-MeOH), mp 272～274℃. UV λ_{max}^{EtOH} (nm): 250, 280, 285, 322, 335. IR υ_{max}^{KBr} (cm^{-1}): 930, 1640. EI-MS (m/e, %): 347 (M^+). ^{1}H-NMR ($CDCl_3$), δ(ppm): 4.10 (s, 3H), 6.28 (s, 2H), 6.30 (s, 2H), 7.40 (s, 1H), 7.82 (s, 1H), 7.85 (s, 1H), 8.17 (s, 1H), 7.85 (d, 1H, J= 9Hz), 8.15 (d, 1H, J= 9Hz).

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