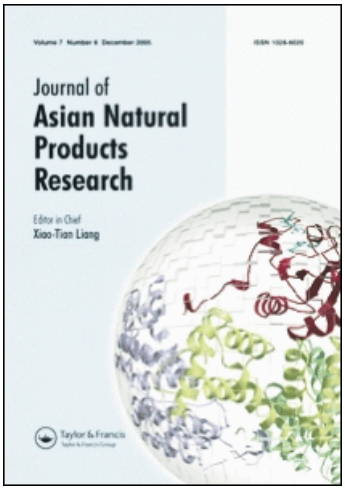

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A novel alkaloid from *Huperzia crispate*

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A novel alkaloid from *Huperzia crispate*

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A novel alkaloid, hupcrispatine (**1**), has been isolated from the unique Chinese species *Huperzia crispate* Ching. The structure of hupcrispatine has been elucidated as 9-amino-6-methyl-3-quinolone on the basis of spectral evidence.

Keywords: *Huperzia crispate*; alkaloid; quinolone; hupcrispatine

1. Introduction

Huperzia crispate Ching is a unique species in China. It is mainly distributed in the South of China, limited to the damp areas under the trees at an altitude of 900 ~ 2600 m above sea level [1]. It has been used as a Chinese folk medicine to treat fracture. Serratenediol-3-acetate, serratenediol, *n*-triacontanol, and β-sitosterol had been previously isolated from this plant [2]. The investigation on the alkaloid part of this plant led to the isolation of a novel alkaloid, hupcrispatine (**1**).

2. Results and discussion

Hupcrispatine (**1**) was obtained as a white solid, whose molecular formula was determined to be $C_{10}H_{10}N_2O$ by HR-EI-MS at *m/z* 174.0767 $[M]^+$. The IR spectrum indicated absorption bands of amino (3376, 3279 cm^{-1}), carbonyl (1696 cm^{-1}), double C=N bond (1662 cm^{-1}), double C=C bond (1529 cm^{-1}), and methyl (1375 cm^{-1}) groups. The ^1H NMR spectral data of **1** (Table 1) showed the presence of two pyridine protons at δ 8.52 and 8.80, three alkene protons at δ 7.04, 7.12, and 7.51, amino at δ 3.65, and methyl protons at δ 2.12. The ^{13}C NMR spectral data of **1** (Table 1) exhibited 10 carbon signals including one carbonyl (δ 169.7), seven alkene carbons (δ 114.3, 114.7, 124.6, 130.2, 136.4, 137.7, and 152.4), one quaternary carbon (δ 51.6), and one methyl carbon (δ 17.0). Its HMBC spectrum indicated that the methyl group was located at C-6 and the amino group was attached to C-9 by showing correlations from ^3J coupling to C_8 and C_{10} (Figure 1), confirmed by the fragment peaks at *m/z* 147 (M^+-HCN) and 146 (M^+-CO) in the EI-MS spectrum. Thus, the structure of **1** was determined as 9-amino-6-methyl-3-quinolone named hupcrispatine.

3. Experimental

3.1 General experimental procedures

Melting point was determined on a Fisher–Johns hot-stage apparatus and is uncorrected. The optical rotation was measured using a Perkin–Elmer 241 MC polarimeter in MeOH. IR spectrum was measured on Nicolet Magna 750 FTIR (KBr) spectrophotometer. ^1H, ^{13}C NMR, and HMBC spectra were recorded on an INOVA–300 spectrometer, using DMSO-d_6 as solvent and TMS as internal standard.

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Table 1. ^{1}H and ^{13}C NMR spectral data of compound **1** in DMSO-d_6 (J in Hz).

Position	δ_H (300 MHz)	δ_C (75 MHz)
1		124.6
2	7.51 (d, 2.4)	130.2
3		169.7
4	7.12 (dd, 8.4,2.4)	137.7
5	7.04 (d, 8.4)	136.4
6		51.6
7		
8	8.80 (s)	114.7
9		152.4
10	8.52 (s)	114.3
11	2.12 (s)	17.0
NH_2	3.65 (s)	

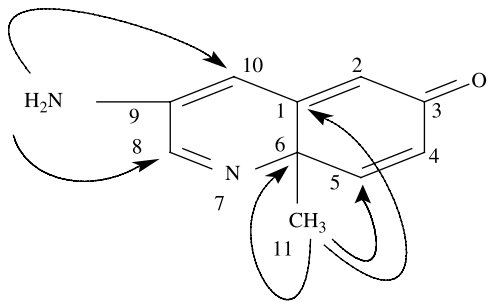

Figure 1. Key HMBC correlations of compound **1**.

EI-MS and HR-EI-MS were recorded on MAT-95 and MAT-711 mass spectrometer, respectively. The spots on TLC were detected by iodine vapor.

3.2 Plant material

Huperzia crispate was collected in October 2001 in Sangzhi county, Hunan province, China and identified by Dr Dao-Song Jiang, Hunan Agricultural University, China. A voucher specimen has been deposited in School of Science, Hunan Agricultural University (SIMM 01–79).

3.3 Extraction and isolation

The total crude alkaloids (42 g) from 5 kg of dried *H. crispate*, obtained as previously described [3], were chromatographed over silica gel (600 g) with gradient eluents ($CHCl_3$, 2000 ml; 1%–3% Me_2CO in $CHCl_3$, each 2000 ml) to afford fractions A–D. Fraction A (6.7 g) was chromatographed on silica gel column eluting with EtOAc (1800 ml) to afford four fractions: A_1–A_4. Fraction A_1 (2.5 g) was subjected to silica gel column eluting with $CHCl_3$:MeOH (20:1, 2000 ml), collected in 15 ml aliquots and detected using TLC (silica gel G, isopropanol:acetone:water 7:3:1, iodine vapor for detection) to yield **1** (25 mg).

Hupcrispatine (1). A white solid (MeOH), mp 124–127°**C**, $[\alpha]_D^{23}$ − 2.875 (*c* 0.012, MeOH). IR (KBr) cm^{-1}: 3376, 3279, 2949, 1696, 1662, 1603, 1530, 1431, 1375, 1255, 1068, 820. ^{1}H and ^{13}C NMR (DMSO) spectral data, see Table 1. HR-EI-MS**:** *m/z* 174.0767 $[M]^+$ (calcd for $C_{10}H_{10}N_2O$, 174.0793). EI-MS: *m/z* (%) 174 (38), 147 (100), 146 (25), 132 (12), 120 (13), 92 (23), 77 (24), 59 (44), 29 (25).

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References

[1] L.B. Zhang and H.S. Kung, *Acta Phytotaxon. Sin.* **36**, 610 (1998).
[2] G. Pei, P.H. Zhou, G.X. He, F.L. Du, and D.S. Jiang, *Nat. Prod. R&D* **16**, 213 (2004).
[3] D.Y. Zhu, M.F. Huang, B.D. Wang, X.M. Kong, and Y.Q. Yang, *Chin. J. Appl. Envion. Bio.* **2**, 352 (1996).