Huperzine W, a Novel 14 Carbons Lycopodium Alkaloid from Huperzia serrata

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Abstract: Huperzine W, a novel 14 carbons Lycopodium alkaloid, was isolated from the whole plant of *Huperzia serrata*, and its stucture was determined by spectroscopic analysis.

Keyword: Huperzine W, Huperzia serrata, Lycopodium alkaloids.

Lycopodium plants have long been studied and many alkaloids have been reported thus far. Most of the compounds reported have a common formula of $C_{16}N^1$. During the course of chemical investigation on *Huperzia serrata*, we gained huperzine W (1, 25 mg from 10 kg dry whole plant), a novel compound which possessed a unique structure among Lycopodium alkaloids, along with a known compound, alopecuridine (2)². In present paper, we report on the isolation and structural elucidation of 1.



Huperzine W (1), obtained as yellowish oil, showed a positive effect on Dragendorff's reagent and was attributed to the molecular formula $C_{14}H_{21}NO_2$ from HR-EIMS analysis in which the M⁺ appeared at m/z 235.1569 (calculated for $C_{14}H_{21}NO_2$ 235.1572). The ¹³C NMR spectrum (**Table 1**) displayed 14 carbon signals, which were resolved into one methyl, eight methylene, two methine and three quarternary carbons through DEPT experiments. As shown in **Figure 1**, its ¹H-¹H COSY and HMQC spectra indicated the presence of three isolated segments and HMBC spectrum exhibited links among the three segments *via* a lactam group ($\delta_C 138.39$, $\delta_C 145.38$, and $\delta_C 199.65$), respectively. On account of the coupling

constants of the protons of 14-CH₂ (dd, J=15.1, 11.5 and ddd, J=15.1, 3.0, 1.6), we concluded H-15 as axial orientation. Therefore, the structure of huperzine W was decided as **1**.





Table 1 ¹H and ¹³C assignments for compound 1^{a} (δ ppm)

Site	$\delta_{\rm H} (J \text{ in Hz})$	δ_{C}	Site	$\delta_{\rm H} (J \text{ in Hz})$	$\delta_{\rm C}$
1	3.38 t (7.1) 2H	46.99 t	10	1.61 qui (7.4) 2H	26.22 t
2	2.00 qui (7.6) 2H	17.93 t	11	2.15 t (7.6) 2H	26.96 t
3	2.37 t (8.1) 2H	31.12 t	12		138.39 s
4		174.99 s	13		199.65 s
7	6.73 dd (5.6, 2.6)	145.38 d	14α (ax)	2.08 dd (15.1,11.5)	46.65 t
8α (ax)	2.02 ^b ;	34.36 t	β (eq)	2.47 ddd (15.1, 3.0, 1.6)	
β (eq)	2.40 br.d (14.9)		15 (ax)	2.16 m	30.62 d
9	3.25 t (7.2) 2H	42.04 t	16 (eq)	1.03 d (6.3)	21.13 q

a. Solution in CDCl₃, δ values referenced to CHCl₃ residue at δ_H 7.26 and δ_C 77.30, respectively. b. Overlapping signal.

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