

Cyripediquinone A, a new phenanthraquinone from *Cyripedium macranthum* (Orchidaceae)

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Abstract: A new phenanthraquinone, cyripediquinone A, was isolated from the rhizome of *Cyripedium macranthum* (Orchidaceae) and its structure was established as 2,4,7-trimethoxy-9,10-phenanthraquinone mainly by spectroscopic analysis.

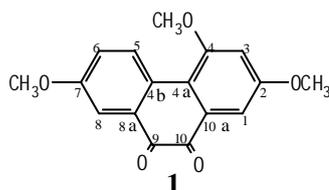
Key words: *Cyripedium macranthum*, cyripediquinone A.

Cyripedium macranthum SW. is widely distributed in northeast and southwest of China. As a Chinese folk herb medicine, its rhizome and the whole plant are used to treat edema, bacillary dysentery, headache and epilepsy. No phytochemical investigation of this species has so far been reported. During the course of our study on the constituents of this plant in order to obtain a more comprehensive understanding of its effective constituents, a new 9,10-phenanthraquinone **1**, was isolated from the CHCl₃ extract of the dried rhizome of *Cyripedium macranthum*.

Cyripediquinone A (**1**) was obtained as deep violet needles (CHCl₃-MeOH), mp. 196–198°C. Its UV-VIS spectrum exhibited absorption bands at $\lambda_{\text{max}}^{\text{MeOH}}$ 204, 266, 532 nm (log ϵ 4.15, 4.04, 3.38), indicating that **1** had a phenanthraquinone skeleton¹. The IR spectrum of **1** showed a band at 1660 cm⁻¹ (quinone carbonyl) and 1595, 1485 cm⁻¹ (aromatic ring). The EI-MS spectrum gave the peak of molecular ion at m/z 298(100) as well as the ions at m/z 270 (M-CO,70), 255 (M-CO-CH₃,80), 227 (M-CO-CH₃-CO,35), 212 (10), 184 (25), 156 (15), which suggested **1** was a phenanthraquinone. The combination of EI-MS, ¹H and ¹³CNMR (Table 1) spectrum revealed the molecular formula of **1** to be C₁₇H₁₄O₅.

The ¹HNMR spectrum of **1** showed signals for three aromatic methoxyl groups [δ 3.85 (6H,s), 3.91(3H,s)], and five aromatic protons [δ 8.58 (1H, d, J=9.1Hz), 7.07 (1H, dd, J₁=9.1, J₂=3.0Hz), 7.51 (1H, d, J=3.0Hz), 7.21(1H, d, J=2.3Hz) and 6.71(1H,d, J=2.3Hz)]. The lowest field aromatic proton signal at δ 8.58 of **1** appeared essentially at the same position as that of H-5 and H-4 of the parent phenanthraquinone (δ 8.25). If the above signal is assigned to H-5 of **1**, C-4 must be substituted by one of the methoxyl groups^{1,2}. Further, the appearance of this signal as a clear doublet corresponding to coupling with an *ortho* aromatic proton implies that while C-6 of **1** must be unsubstituted, another methoxyl group must be attached to C-7. Thus, the signal at δ 7.07 of **1** may be assigned to H-6 which couples with both H-5 and H-8. The signal at δ 7.51 thus corresponds to H-8 which shows *meta* coupling with H-6. The splitting pattern of the remaining two aromatic proton signals of **1** at δ 7.21 and 6.71 (each 1H, d, J=2.3Hz) corresponded to two *meta*-coupled protons, which could then be attributed to H-1 and

H-3, respectively, flanked by its third aromatic methoxyl group at C-2. The above spectral data for **1** are thus intelligible in terms of a 2,4,7-trimethoxy-9,10-phenanthraquinone formulation for the compound.



The ^{13}C NMR spectral data also coincide with the proposed structure. Seventeen carbon signals were observed in the ^{13}C NMR spectrum, of which twelve were aromatic carbons including three oxygenated aromatic carbons (δ 159.9, 159.0, 158.8). The two quinone carbonyl carbons of **1** appeared at δ 181.5 and 181.1, which were in good agreement with a 9,10-phenanthraquinone skeleton. Three methoxyl groups that appeared at δ 55.5, 55.7 and 56.1 can be easily discerned.

More convincing evidence in support of the structure **1** for cypripediquinone A was provided by its 2D NMR spectral analysis. The ^{13}C - ^1H cosy spectrum of **1** showed strong one-bond correlations between H-5 (δ 8.58) and C-5 (δ 130.8), H-6 (δ 7.07) and C-6 (δ 122.8), H-8 (δ 7.51) and C-8 (δ 113.0), H-1 (δ 7.21) and C-1 (δ 105.4) and H-3 (δ 6.71) and C-3 (δ 107.7). Another one-bond correlations were also observed between the methoxyl protons at δ 3.91, 3.85 (6H, s) with the methoxyl carbons at δ 56.1, 55.7 and 55.5 respectively. An HMBC experiment was performed and enabled complete assignment of all carbon signals (**Table 1**). These results have now enabled us to establish unambiguously the structure of cypripediquinone A as 2,4,7-trimethoxy-9,10-phenanthraquinone.

Table 1. ^1H (500MHz) and ^{13}C (125MHz) NMR for **1** in CDCl_3

C	δ_c	^1H - ^{13}C connectivity δ_H (J in Hz)	HMBC correlations C correlates with (observed)
1	105.4	H-1, 7.21(2.3)	H-3(6.71)
2	159.9		H-1(7.21), H-3(6.71), 2-OCH ₃ (3.85)
3	107.7	H-3, 6.71(2.3)	H-1(7.21)
4	159.0		H-3(6.71), 4-OCH ₃ (3.91)
4a	119.1		H-1(7.21), H-3(6.71), H-5(8.58)
4b	129.4		H-6(7.07), H-8(7.51)
5	130.8	H-5, 8.58(9.1)	
6	122.8	H-6, 7.07(9.1, 3.0)	H-8(7.51)
7	158.8		H-5(8.58), H-6(7.07), H-8(7.51), 7-OCH ₃ (3.85)
8	113.0	H-8, 7.51(3.0)	H-6(7.07)
8a	132.6		H-5(8.58)
9	181.1		H-8(7.51)
10	181.5		H-1(7.21)
10a	131.3		
2-OCH ₃	55.7	3.85	
4-OCH ₃	56.1	3.91	
7-OCH ₃	55.5	3.85	

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