Two New Indole Alkaloids from *Evodia rutaecarpa*

Guo Ying ZUO\(^1\)\(^2\), Xiao Sheng YANG\(^1\), Xiao Jiang HAO\(^1\)\(^*\)

\(^1\)Laboratory of Phytochemistry, Kunming Institute of Botany, the Chinese Academy of Sciences, Kunming 650204
\(^2\)Kunming 43 Hospital, PLA, Kunming 650032

Abstract: Two new indole alkaloids, wuchuyuamide I and II were isolated from the fruits of *Evodia rutaecarpa* (Juss.) Benth and their structures were elucidated on the basis of spectral data.

Keywords: Rutaceae, *Evodia rutaecarpa* (Juss.) Benth, indolinone alkaloids, wuchuyuamides.

The fruit of *Evodia rutaecarpa* (Juss.) Benth is a Chinese traditional drug (Wu-Chu-Yu). The components of Wu-Chu-Yu have been studied by several groups, including indole alkaloids, quinolone alkaloids, limonoids and other kinds\(^1\). Further chemical investigation of this drug led us to isolate two new indole alkaloids 1 and 2. This is the first time to isolate indolinone alkaloids from this plant.

Wuchuyuamide I (1) , was isolated as colorless needles, m.p. 261-262\(^{\circ}\) C (CHCl3-MeOH), [\(\alpha\)]D\(^{25}\) 0 (c 0.24, C\(_5\)H\(_2\)N). Its molecular ion peak at \(m/z\) 351.1224 by HREIMS revealed the molecular formula C\(_{19}\)H\(_{17}\)N\(_3\)O\(_4\) (calcd. 351.1219). The \(^1\)CNMR (DEPT) spectrum showed nineteen signals of the indolequinazoline alkaloid (8C, 8CH, 2CH\(_2\) and one CH\(_3\)), including three carbonyl carbons at 180.6 (s, C\(_2=O\)), 161.6 (s, C\(_{21}=O\)), 151.0 (s, C\(_3=O\)), two methene carbons at 37.7 (t, C\(_5-CH_2\)), 36.4 (t, C\(_6-CH_2\)), one methyl carbon at 30.6 (q, N\(_4-CH_3\)) and one carbinol C-atom at 75.9 (s, C\(_7\)) \(^2\). Interestingly, the skeleton of this compound is indolinone instead of indoline. In the \(^1\)HNMR spectrum, an indolin-2-one N-H signal was observed at 11.65 (1H, s), and the signal of 5.25 (1H,br.) was designated to C\(_7\)-OH. The absorption at 3341 and 3190 (OH and NH), 1699 and 1658cm\(^{-1}\) (C=O) in IR and 246, 312, 319 nm in UV spectra, together
with typical fragments of \( m/z \) 335 (M\(^++1\)-OH\( \)), 203 (C\(_{11}\)H\(_{11}\)NO\(_{2}\)-2H, base peak) in EIMS spectrum supported this deduction. Thus the structure of \( \mathbf{1} \) was elucidated as 3-[2-(3-hydroxyindolin-2-onyl)ethyl]-1-methyl-2, 4-quinazolinedione. All proton\(^5\) and carbon\(^6\) resonances were assigned by analysis of 1D and 2D NMR spectra (\(^1\)H-\(^1\)H COSY, HMQC and HMBC) and comparison of the signals with those of the literature data\(^2\)\(^-\)\(^3\).

Wuchuyuamide II (\( \mathbf{2} \)) was obtained as needles, m.p. 199-200°C (CHCl\(_3\)-MeOH), \([\alpha]\)\(^D\)\( _{24} \) 0 (c 0.24, CHCl\(_3\)). Its \(^{13}\)CNMR (DEPT) spectrum also showed nineteen signals in accordance with those of \( \mathbf{1} \), except for the absence of a quaternary oxygenated C-atom and the increase of a tertiary C-atom which should be assigned to C\(_7\), the \(^1\)HNMR shift at \( \delta \)3.54 (1H, t, J=6.2Hz) supported this assignment. The UV spectrum showed similar absorption to those of \( \mathbf{1} \). IR absorption of an indolinone NH was observed at 3181cm\(^{-1}\).

Compared with compound \( \mathbf{1} \), the molecular ion peak \( m/z \) of \( \mathbf{2} \) in EIMS was reduced by 16, suggested absence of hydroxyl group in \( \mathbf{2} \). All spectral evidence of \( \mathbf{2} \) enable to elucidate its structure as 3-[2-(3-indolin-2-onyl)ethyl]-1-methyl-2,4-quinazolinedione. The \(^1\)H and \(^{13}\)C chemical shifts were also assigned completely by direct comparison with \( \mathbf{1} \) and reported data\(^3\)\(^-\)\(^6\).

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References and notes


5. \(^1\)HNMR data of compounds \( \mathbf{1} \) and \( \mathbf{2} \) (measured in CDCl\(_3\) of \( \mathbf{1} \) and C\(_5\)D\(_5\)N of \( \mathbf{2} \), \( \delta \) in ppm). Compound \( \mathbf{1} \): \( \delta \) 11.65 (1H, s, 1-N-H), 4.72, 4.84 (each 1H, m, H-5), 2.81, 2.92 (each 1H, m, H-6), 5.25 (1H, br, 7-O-H), 7.79 (1H, d, J=7.2Hz, H-9), 7.04 (1H, t, J=7.4Hz, H-10), 7.21 (1H, m, H-11), 6.97 (1H, d, J=8.0Hz, H-12), 7.09 (1H, d, J=8.4Hz, H-16), 7.58 (1H, m, H-17), 7.15 (1H, t, J=6.6Hz, H-18), 8.27 (1H, dd, J=4.6,1.6Hz, H-19), 3.40 (3H, s, H-22); Compound \( \mathbf{2} \): \( \delta \) 4.18, 4.42 (each 1H, m, H-5), 2.26, 2.50 (each 1H, m, H-6), 5.34 (1H, t, J=6.2Hz, H-7), 7.62 (1H, m, H-9), 6.88 (1H, t, J=7.5Hz, H-10), 7.21 (1H, m, H-11), 6.81 (1H, d, J=7.7Hz, H-12), 7.07 (1H, d, J=7.6Hz, H-16), 7.31 (1H, d, J=7.4Hz, H-17), 7.11 (1H, d, J=8.3Hz, H-18), 8.14 (1H, dd, J=6.2,1.6, H-19), 3.51 (3H, s, H-22).

6. \(^{13}\)CNMR data of compounds \( \mathbf{1} \) and \( \mathbf{2} \). Compound \( \mathbf{1} \): 180.6 (s, C-2), 151.0 (s, C-3), 37.7 (t, C-5), 36.4 (t, C-6), 75.9 (s, C-7), 133.4 (s, C-8), 124.9 (d, C-9), 122.3 (d, C-10), 129.5 (d, C-11), 110.4 (d, C-12), 143.0 (s, C-13), 141.0 (s, C-15), 114.3 (d, C-16), 135.2 (d, C-17), 122.8 (d, C-18), 128.7 (d, C-19), 116.1 (s, C-20), 161.6 (s,C-21), 30.6 (q, C-22); Compound \( \mathbf{2} \): 179.4 (s, C-2), 150.8 (s, C-3), 39.2 (t, C-5), 28.0 (t, C-6), 44.2 (d, C-7), 129.1 (s, C-8), 124.0 (d, C-9), 122.1 (d, C-10), 127.8 (d, C-11), 109.6 (d, C-12), 141.6 (s, C-13), 140.5 (s, C-15), 113.4 (d, C-16), 134.9 (d, C-17), 122.8 (d,C-18), 128.9 (d, C-19), 115.5 (s, C-20), 161.7 (s, C-21), 30.6 (q, C-22).