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Two New Indole Alkaloids from *Evodia rutaecarpa*

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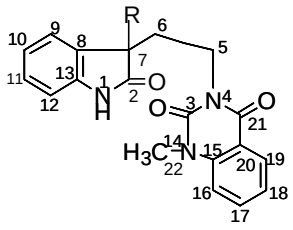
Abstract: Two new indole alkaloids, wuchuyuamide I and II were isolated from the fruits of *Evodia rutaecarpa* (Juss.) Benth and their structures were elucidated on the basis of spectral data.

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.



1 R=OH, **2** R=H

Wuchuyuamide I (**1**) , was isolated as colorless needles, m.p. 261-262^{o} C ($CHCl_3$-MeOH), $[\alpha]_D^{24}$ 0(c 0.24, C_5H_5N). Its molecular ion peak at *m/z* 351.1224 by HREIMS revealed the molecular formula $C_{19}H_{17}N_3O_4$(calcd. 351.1219). The ^{13}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 ($C_{11}H_{11}N_2O_2$), 146 ($C_8H_6NO_2$-2H, base peak) in EIMS spectrum supported this deduction. Thus the structure of **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 2DNMR spectra (^{1}H-^{1}H COSY, HMQC and HMBC) and comparison of the signals with those of the literature data[2,3].

Wuchuyuamide II (**2**) was obtained as needles, m.p. 199-200°C ($CHCl_3$-MeOH), $[\alpha]_D^{24}$ 0(c 0.24, $CHCl_3$), with the molecular formula $C_{19}H_{17}N_3O_3$ by HREIMS at *m/z* 335.1304 (calc. 335.1270). Its ^{13}CNMR (DEPT) spectrum also showed nineteen signals in accordance with those of **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 δ3.54 (1H, t, J=6.2Hz) supported this assignment. The UV spectrum showed similar absorption to those of **1**. IR absorption of an indolinone NH was observed at 3181cm^{-1}. Compared with compound **1**, the molecular ion peak *m/z* of **2** in EIMS was reduced by 16, suggested absence of hydroxyl group in **2**. All spectral evidence of **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 **1** and reported data[3-6].

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References and notes

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5. ^{1}HNMR data of compounds **1** and **2** (measured in $CDCl_3$ of **1** and C_5D_5N of **2,** δ in ppm). Compound **1**: δ 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=7.6Hz, H-18), 8.27 (1H, dd, J=6.4,1.6Hz, H-19), 3.40 (3H, s, H-22); Compound **2:** δ 4.18, 4.42 (each 1H, m, H-5), 2.26, 2.50 (each 1H, m, H-6), 3.54 (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 **1** and **2**. Compound **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 **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).

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