A New Indole Alkaloid from *Limonia Crenulata*

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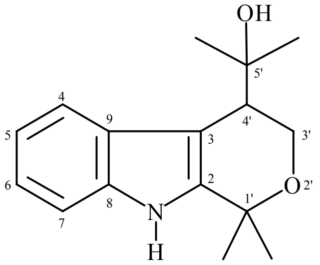
Abstract: A new indole alkaloid, crenulatine **1**, was isolated from the stems of *Limonia Crenulata*. The structure was identified by spectral means.

Keywords: *Limonia Crenulata*, *Rutaceae*, alkaloids, indole alkaloid, crenulatine.

Limonia crenulata Roxb. (*Rutaceae*), a small tree widely distributed in dry warm regions of southeastern Asia, has been reported to have antiepileptic, purgative and sudorific effects and is used for colic trouble and cardialgia[1]. Various parts of this plant have been employed in indigenous medicine. Our investigation on its stems led to the isolation of one new alkaloid, crenulatine **1**, together with three known ones, 4-methoxy-6- hydroxy-1-methyl-2-quinolone[2], N-benzoyltyramine methyl ether[2], tembamid[2]. Their structures have been determined by spectral analysis, especially by 1D and 2D NMR spectroscopy.

Figure 1 The structure of **1**



Compound **1,** obtained as white amorphous powder, showing a molecular ion peak at *m/z* 259, has a molecular formula of $C_{16}H_{21}NO_2$ based on HREIMS (found 259.1543, calcd. 259.1572) and ^1H and ^{13}C NMR spectra. The presence of four aromatic protons at δ 7.62 (1H, d, 8.0), 7.00 (1H, m), 7.02 (1H, m), and 7.28 (1H, d, 8.0) and one NH proton at δ 10.18 (1H, brs) in ^1H NMR spectrum[3], in association with the exhibition of four methines at δ 121.6, 121.1, 119.6 and 111.7, and four quaternary carbons at δ 141.5, 137.6, 129.0 and 107.7 in the lowfield of ^{13}C NMR spectrum[4], suggested that **1** possessed a 2,3-disubstituted indole alkaloid skeleton, which was confirmed by its UV [λ_{max} (logε)

223.5 (4.54), 281 (3.87), 289 (3.79) nm] spectrum[1]. The relationships of H-4/H-5/H-6/H-7 were established by a ^{1}H-^{1}H COSY experiment. In addition, four methyls in the highfield of ^{13}C NMR spectrum were divided into two groups of *gem*-methyls, which were connected with two oxy-quaternary carbons respectively. The results were supported by HMBC spectrum. Further, the cross-peaks between the oxy-methylene protons at δ 4.30 (1H, d, 12.1) and 3.82 (1H, dd, 12.1, 3.6) and the methine proton at δ 2.76 (1H, d, 3.6) in ^{1}H-^{1}H COSY spectrum, combined with the long-range correlations of one group of *gem*-methyls at δ 1.29 and 1.34 with the methine carbon at δ 45.6 (d, C-4′), and of the oxy-methylene protons with the two oxy-quaternary carbons at δ 74.1 (s, C-5′) and 72.7 (s, C-1′) in HMBC spectrum, determined the structure of this compound as **1** (**Figure 1**). The formation of the third ring was also supported by the 7 degrees of unsaturation of its molecular formula. The stereochemistry of C-4' still remains unknown.

References and Notes

1. B. M. Ratnayake Bandara, A. A. Leslie Gunatilaka, E. M. Kithsiri Wijeratne, and N. K. B. Adikaram, *Planta Medica*, **1988**, *54*, 374.
2. Musa H. Abu Zarga, *J. Nat. Prod.* **1986**, *49*, 901.
3. ^{1}H NMR data of **1** (CD_3COCD_3, 500 MHz, δ in ppm, J in Hz): 10.18 (brs, 1-NH), 7.62 (1H, d, J = 8.0 Hz , H-4), 7.00 (1H, m, H-5), 7.02 (1H, m, H-6), 7.28 (1H, d, J = 8.0 Hz, H-7), 4.30 (1H, d, J = 12.1 Hz, H-3′a), 3.82 (1H, dd, J = 12.1, 3.6 Hz, H-3′b), 2.76 (1H, d, J = 3.6 Hz, H-4'); 1'-CH_3: 1.57 (s), 1.47 (s); 5'-CH_3: 1.34 (s), 1.29 (s).
4. ^{13}C NMR data of **1** (CD_3COCD_3, 125 MHz, δ in ppm): 141.5 (s, C-2), 107.7 (s, C-3), 121.1 (d, C-4), 119.6 (d, C-5), 121.6 (d, C-6), 111.7 (d, C-7), 137.6 (s, C-8), 129.0 (s, C-9), 72.7 (s, C-1'), 62.9 (t, C-3'), 45.6 (d, C-4'), 74.1 (s, C-5'); 1'-CH_3: 29.2 (q), 26.5 (q); 5'-CH_3: 30.7 (q), 28.6 (q).

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