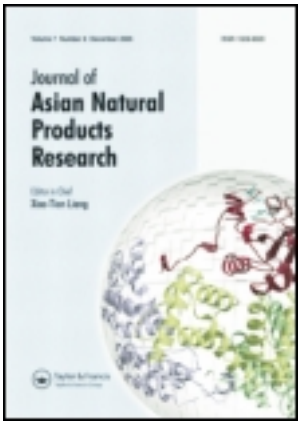

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A new carbazole alkaloid from the leaves of Malayan *Murraya koenigii*

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A new carbazole alkaloid from the leaves of Malayan *Murraya koenigii*

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New carbazole alkaloid, 7-hydroxymurrayazolinine (**1**), was isolated from the ethanol extract of the leaves of Malayan *Murraya koenigii*, together with five known carbazole alkaloids, mahanimbine (**2**), bicyclomahanimbine (**3**), girinimbine (**4**), koenimbine (**5**), and murrayamine-D (**6**). Their structures were elucidated on the basis of spectroscopic analysis.

Keywords: *Murraya koenigii*; Rutaceae; carbazole alkaloid

1. Introduction

Murraya koenigii (L.) Spreng., belonging to the family Rutaceae, is distributed throughout India, Bangladesh, Nepal, Sri Lanka, Malaysia, and Burma [1]. The leaves of this plant are well known as curry leaves. Traditionally, this plant is used for the treatment of dysentery, diarrhea, and insect bites [1]. Previous phytochemical investigations on this plant have resulted in the isolation of carbazole alkaloids [2–18]. In this paper, we would like to report the isolation and structural elucidation of carbazole alkaloids isolated from the leaves of Malayan *M. koenigii*.

2. Results and discussion

The ethanol extract of the leaves of Malayan *M. koenigii* furnished a new carbazole alkaloid, 7-hydroxymurrayazolinine (**1**), together with five known carbazole alkaloids, mahanimbine (**2**) [5], bicyclomahanimbine (**3**) [3], girinimbine (**4**) [5], koenimbine (**5**) [4], and murrayamine-D (**6**) [19]. Among the known alkaloids, murrayamine-D (**6**) is reported for the first time from *M. koenigii*.

7-hydroxymurrayazolinine (**1**) (Figure 1) was isolated as a colorless oil. The UV spectrum showed absorption maxima at 213, 239, 265, 289, 316, and 324 nm, indicating the presence of a 2,7-dioxygenated carbazole derivative [20], whereas the IR spectrum indicated the presence of absorption band at 3327 cm^{-1} (NH/OH). The EI-MS of **1** showed a molecular ion at *m/z* 365, and HR-EI-MS measurements (*m/z* 365.1999, cacld *m/z* 365.1991) established the molecular formula as $C_{23}H_{27}NO_3$, indicating 11 degrees of unsaturation. In addition, a peak due to the loss of H_2O was observed at *m/z* 347, indicating the presence of a hydroxyl group. The ^{13}C NMR spectrum showed a total of 23 separate carbon resonances (four methyl, three methylene, six methine, and ten quaternary carbons) in agreement with the molecular formula. The ^{1}H NMR spectrum showed the presence of an NH signal (δ 9.58), two hydroxyl groups (δ 8.27 and 3.62) and an ABX mutually coupled proton system at δ 6.67 (dd, $J = 8.0$,

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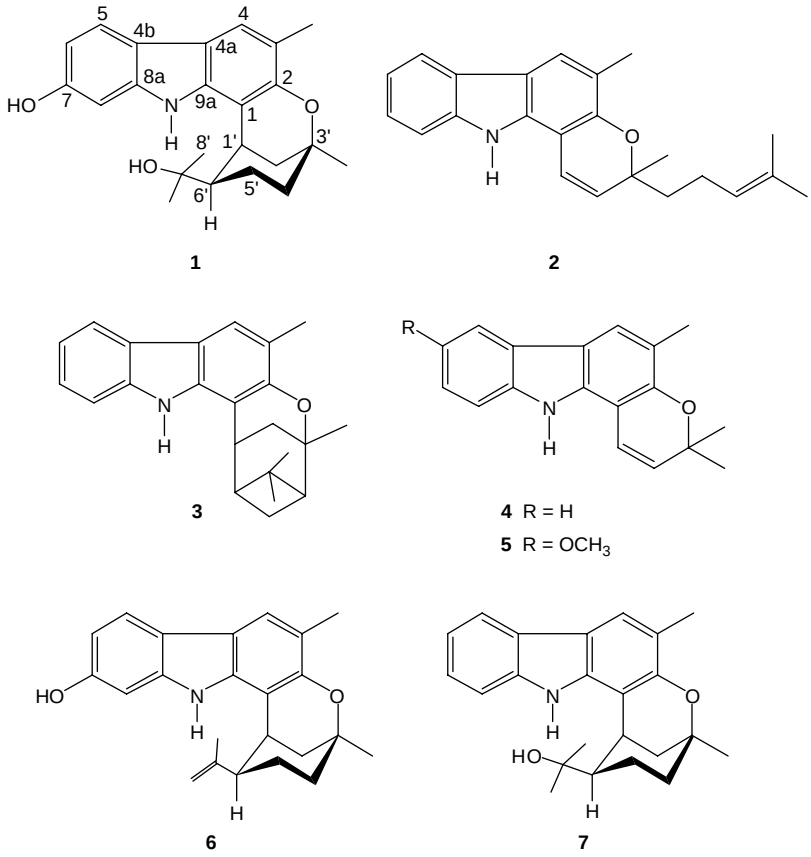

Figure 1. Structures of compounds **1**–**7.**

1.8 Hz), 6.85 (d, $J = 1.8$ Hz), and 7.68 (d, $J = 8.0$ Hz), indicating a monosubstituted ring A. The chemical shifts and multiplicity of these three aromatic protons are agreed with the placement of a hydroxyl group at C-7 in ring A [19]. A downfield shift singlet at δ 7.52 (1H), together with a three-proton singlet at δ 2.31, is due to H-4 and 3-Me of the carbazole skeleton. The remaining characteristic signals at δ 0.51 (3H) and 1.25 (3H) for the *gem*-dimethyl group, another methyl singlet at δ 1.40 for tertiary methyl (3′-Me), a benzylic proton (H-1′) at δ 3.70, and three methylene protons between δ 1.38–2.06 and one methine proton at δ 1.87 were attributed to a 10-carbon bicyclic moiety similar to that of murrayazolinine (**7**) [7,10]. In the HMBC spectrum, important long-range correlations were observed between C-1 (δ 106.2) and H-6′ (δ 1.87); C-2 (δ 152.7) and H-4 (δ 7.52) and H-1′ (δ 3.70); C-4*a* (δ 114.9) and H-5 (δ 7.68); C-9*a* (δ 138.8) and H-4 (δ 7.52) and H-1′ (δ 3.70); C-2′ (δ 38.4) and H-4′ (δ 1.58 and 2.06) and H-6′ (δ 1.87); C-3′ (δ 74.3) and H-1′ (δ 3.70) and H-5′ (δ 1.38); C-8′ (δ 23.0) and H-6′ (δ 1.87); C-9′ (δ 32.8) and H-6′ (δ 1.87). Consequently, compound **1** is therefore elucidated as 7-hydroxymurrayazolinine.

3. Experimental

3.1 General experimental procedures

The UV spectra were obtained on a Perkin-Elmer Lambda 35 UV/VIS spectropho-

tometer, whereas the IR spectra were recorded on a Perkin-Elmer Spectrum RX1 FT-IR spectrophotometer. EI-MS and HR-EI-MS were obtained on a Finnigan MAT95XL-T mass spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (Merck, Darmstadt, Germany) using TMS as an internal standard on a JEOL ECX-400 spectrometer at 400 and 100 MHz, respectively. Centrifugal TLC was performed on a chromatotron model 7924T over silica gel Merck 7749. Silica gel Merck 9385 was used for vacuum column chromatography. Silica gel $60F_{254}$ Merck was used for TLC. Spots on TLC plates were visualized by exposure to iodine vapors and UV radiation. All solvents were distilled before use.

3.2 Plant material

The leaves of *M. koenigii* used in this study were collected in Kuala Lumpur, Malaysia (May, 2007) and identified by Meng-Cheu Chuah, Universiti Tunku Abdul Rahman. A voucher specimen (M-2007-05) is deposited at the Herbarium of the Department of Chemical Science, Universiti Tunku Abdul Rahman, Malaysia.

3.3 Extraction and isolation

The dried leaves (4 kg) were grounded and extracted with 95% EtOH (15 liters × 3, 7 days each) at room temperature. After filtration and evaporation, the concentrated ethanol extract was partitioned in distilled water (1 liter). The mixture was then extracted successively with chloroform (2 liters × 3). Evaporation of the chloroform gave a dark green oil (80 g). The chloroform crude extract was separated by initial vacuum column chromatography on silica gel with $CHCl_3$ with increasing proportions of MeOH, followed by rechromatography of appropriated partial fractions by centrifugal TLC. Initial vacuum column chromatography of the chloroform crude extract provided 10 main fractions. Rechromatography of fractions 2 (0.95 g) and 3 (0.57 g) with $CHCl_3$, followed by centrifugal TLC (*n*-hexane–chloroform 25:1) gave compounds **2** (50 mg), **3** (24 mg), and **4** (32 mg). Compound **5** (28 mg) was isolated from fraction 4 (0.48 g) by centrifugal TLC using *n*-hexane–chloroform (15:1) as eluent. Rechromatography of fractions 5 (0.62 g) and 6 (0.98 g) with $CHCl_3$–MeOH, followed by centrifugal TLC (*n*-hexane–acetone, 4:1), gave compounds **1** (65 mg) and **6** (120 mg).

3.3.1 7-Hydroxymurrayazolinine (*1*)

Colorless oil; UV (EtOH) λ_{max} (log ε): 213 (3.45), 239 (3.67), 265 (3.26), 289 (2.90), 316 (3.15), and 324 (3.18) nm. IR (dry film) ν_{max}: 3327, 2971, 2929, 1608, 1448,

Table 1. ^{1}H and ^{13}C NMR spectral data of compound **1** (400 MHz for ^{1}H, 100 MHz for ^{13}C, $CDCl_3$).

Position	δ_C	δ_H
1	106.2	
2	152.7	
3	117.0	
4	118.6	7.52 s
4a	114.9	
4b	117.0	
5	119.6	7.68 d (8.0)
6	107.7	6.67 dd (8.0, 1.8)
7	153.8	
8	97.0	6.85 d (1.8)
8a	141.1	
9a	138.8	
1′	29.3	3.70 m
2′	38.4	1.80 m
3′	74.3	
4′	40.5	1.58 td (13.0, 6.0); 2.06 brd (13.0)
5′	22.8	1.38 m
6′	52.6	1.87 m
7′	73.6	
8′	23.0	0.51 s
9′	32.8	1.25 s
3-Me	16.8	2.31 s
3′-Me	28.9	1.40 s
NH		9.58 s
7-OH		3.62 s
7′-OH		8.27 s

1212, 1158, 755 cm^{-1}. ^{1}H and ^{13}C NMR spectral data, see Table 1; EI-MS *m/z* (rel. int.): 365 $[M]^+$(100), 347 (29), 332 (16), 304 (12), 279 (10), 264 (81), 250 (13), 226 (16); HR-EI-MS: *m/z* 365.1999 $[M]^+$ (calcd for $C_{23}H_{27}NO_3$, 365.1991).

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