

Alkenylamides from *Piper maingayi* Hk. F

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ABSTRAK

Dua amida tak-tepu, *N*-isobutil-9-fenil-2*E*,4*E*,8*E*-nonatrienamida dan *N*-isobutil-7-(3',4'-metilenadioksifenil)-2*E*, 6*E*-heptadienamida, telah dapat diasingkan daripada daun *Piper maingayi*. Kedua-dua amida ini telah dicirikan secara spektroskopi.

ABSTRACT

Two unsaturated amides, *N*-isobutyl-9-phenyl-2*E*,4*E*,8*E*-nonatrienamide and *N*-isobutyl-7(3', 4'-methylenedioxyphenyl)-2*E*,6*E*-heptadienamide, were isolated from the leaves of *Piper maingayi*. Both amides were characterized by spectral studies.

Keywords: *Piper maingayi*, Piperaceae, isobutyl amides, 2D NMR

INTRODUCTION

Many species of the genus *Piper* have been shown to possess antifungal, insecticidal, anthelmintic and antitumour properties (Boll *et al.* 1992). Presently we are investigating the constituents of Malaysian *Piper* species as part of a research programme seeking potent insecticides. *Piper maingayi* Hk. F (Piperaceae) is a climber with a green inflorescence. There is no record of folkloric medicinal use of this plant; nor do there appear to be any reported chemical studies. We now report the isolation and structure elucidation of two alkenylamides from the leaves of *Piper maingayi*.

EXPERIMENTAL

Mps: uncorr. IR (in KBr pellets). UV (EtOH) ^1H NMR spectra were recorded at 300 MHz while the ^{13}C NMR spectra were taken at 75.7 MHz. The mass spectra were determined at 70 eV. VLC and CC were carried out using silica gel (230-400 and 70-230 mesh).

Plant Material

The leaves of *P. maingayi* were collected from the Fernarium plot, UKM campus, Bangi, Selangor. A voucher specimen (AZ 4476) is deposited at the herbarium of the Botany Department, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia.

Extraction and Isolation

The powdered air-dried leaves of *P. maingayi* (200 g) were extracted with ether at room temperature for 24 h and the solvent was evaporated under reduced pressure to give the crude extract (14.0 g). The crude extract was then subjected to vacuum liquid chromatography followed by multiple column chromatography using light petroleum : ether as eluent to afford *N*-isobutyl-9-phenyl-2*E*, 4*E*, 8*E*-nonatrienamide (10.7 mg, 0.07%) and *N*-isobutyl-7-(3',4'-methylenedioxyphenyl)-2*E*, 6*E* - heptadienamide (16.5 mg, 0.11%).

N-isobutyl-9-phenyl-2*E*,4*E*,8*E*-nonatrienamide **1**

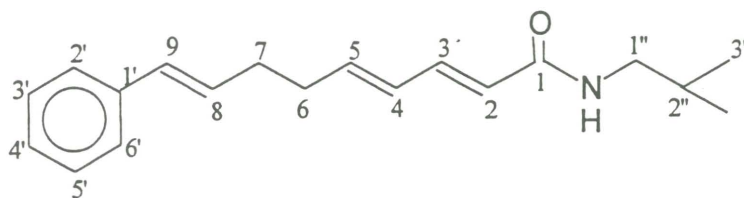
IR $\nu_{\text{max}}^{\text{KBR}}$ cm^{-1} : 3297, 2963, 1655, 1626, 1543, 1262, 1166, 995, 960 and 739; MS m/z (rel int): 283(M^+ , 14.7), 117(100), 115(10.6), 91(7.0), 66(2.8) and 57(2.7).

N-isobutyl-7-(3',4'-methylenedioxyphenyl)-2*E*,6*E*-heptadienamide **2**

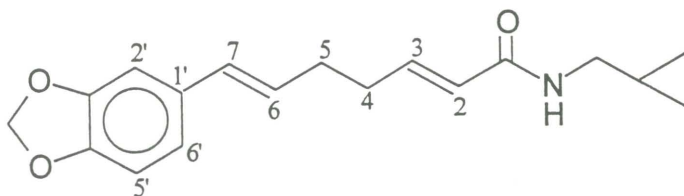
IR $\nu_{\text{max}}^{\text{KBR}}$ cm^{-1} : 3435, 3302, 2958, 1669, 1626, 1559, 1493, 1256, 1044 and 968; MS m/z (rel int) : 301(M^+ , 28.8), 161(72.5), 131(100), 103(25.0), 84(32.0) and 77(8.3).

RESULTS AND DISCUSSION

Compound 1 was a white solid which analysed as $\text{C}_{19}\text{H}_{25}\text{NO}$ ($[\text{M}^+]$ m/z 283) mp 134-137°C. The UV spectrum showed maxima at 262, 210 nm. Its IR spectrum (KBr) exhibited a band for an -NH function (3295 cm^{-1}) which was incorporated in a dienamide grouping (1655, 1626 and 995 cm^{-1}). The ^{13}C NMR spectrum (Table 1) showed the presence of 19 carbons. In the ^1H NMR spectrum, signals attributed to an *N*-isobutyl moiety were observed at δ 0.93 (6H, d, $J = 6.6 \text{ Hz}$), 1.79 (1H, m), 3.16 (2H, $J = 6.5 \text{ Hz}$) and 5.50 (1H, b s). In addition, it showed signals for 6 olefinic protons. Two of them appeared at δ 5.76 (1H, d, $J = 15 \text{ Hz}$) and



1



2

7.18 (1H, dd, $J = 15$ Hz and 6.7 Hz) and were attributed to protons H-2 and H-3 of an α,β -unsaturated carbonyl system. The assignments of these protons were also established by ^1H - ^1H COSY experiments. Signals were also observed at δ 6.21 (1H, dd, $J = 15$ Hz and 8.0 Hz) and δ 6.10 (1H, dt, $J = 15$ Hz and 6.1 Hz) and were assigned to protons in a *trans* relationship on a second double bond that was conjugated to the first. Signals at δ 6.40 (1H, d, $J = 15.7$ Hz) and δ 6.15 (1H, dt, $J = 15.7$ Hz and 9.6 Hz) were attributed to the olefinic protons (H-9 and H-8) on the third double bond that was conjugated to the aromatic ring of the molecule. In addition, signals resonating at δ 7.23-7.35 (5H, m) were attributed to the phenyl protons of the molecule. The mass spectrum showed a base peak at m/z 117 (C_9H_9^+) which supported the presence of an arylalkenyl moiety. Signals attributed to two methylene groups were observed at δ 2.33 – 2.35 (4H, m) in the ^1H NMR spectrum. The complete assignment for the ^1H NMR was further substantiated by the ^1H - ^1H COSY experiments. Correlation cross-peaks were observed for the olefinic proton H-8 at δ 6.15 and the methylene protons at δ 2.33 – 2.35, which in turn showed cross-peaks to the olefinic proton H-5 at δ 6.10. Based on these spectroscopic data, compound **1** is proposed as *N*-isobutyl-9-phenyl-2*E*, 4*E*, 8*E*-nonatrienamamide. Compound **1** is not known naturally but has been synthesized [CA, 101: 210764g] for its pesticidal properties.

Compound **2**, $\text{C}_{18}\text{H}_{23}\text{NO}_3$ ($[\text{M}^+]$ m/z 301) was obtained as an amorphous solid with mp 123.6-126.9°C. The UV spectrum ($\lambda_{\text{max}}^{\text{EtOH}}$

TABLE 1
¹H NMR (300 MHz, CDCl₃) and ¹³C NMR (75.5 MHz, CDCl₃) of
 Compound **1** and Compound **2**

C	1				2			
	¹³ C	¹ H	Multiplicity and <i>J</i> in Hz	COSY-correlation with	¹³ C	¹ H	Multiplicity and <i>J</i> in Hz	COSY-correlations with
1	166.25				165.8			
2	122.20	5.76	d(15)	H-3	124.16	5.76	d(15.31)	H-3
3	141.74	7.18	dd(15,6,7)	H-2, H-4	141.01	6.83-6.90	m	H-2, H-4, H-5
4	128.50	6.21	dd(15,8)	H-3, H-6, H-7	31.96	2.34	n m	H-3, H-6
5	141.02	6.10	dt(15,6.1)	H-3, H-6, H-7	31.57	2.34		H-3, H-6
6	32.77	2.33 - 2.35	n m	H-4, H-5, H-7, H-8	130.32	5.96 - 6.06	m	H-7, H-4, H-5
7	32.28	2.33 - 2.35	n m	H-4, H-5, H-6, H-8	127.41	6.32	d(15.8)	H-6, H-4, H-5
8	128.82	6.15	dt(15.7, 9.6)	H-7, H-6, H-9				
9	129.43	6.40	d(15.7)	H-8				
1'	128.50				132.00			
2'	127.02				105.44	6.88	s	
3'	126.00	7.23 - 7.35	m		147.94			
4'	130.65				146.76			
5'	126.00				108.22	6.73	d (8.0)	
6'	127.02				120.40	6.75	d(8.1)	
1''	46.93	3.16	t (6.5)	H-2'', N-H	46.80	3.15	dd (6.7, 6.7)	
2''	28.62	1.79	9 line multiplet	H-1'', H-3''	28.57	1.80	9 line m (6.7)	H-2'', N-H
3'' & 4''	20.12	0.93	d (6.6)	H-2''	20.12	0.92	d (6.7)	
NH		5.50	b s	H-1'', H-2''		5.45	b s	H-1''
O-CH ₂ -O					100.90	5.93	s	

214, 261 and 305 nm) showed a similar pattern to that of compound **1**. The IR spectrum displayed strong absorption bands at 3435, 1669 and 1626 cm^{-1} due to the presence of an unsaturated amide moiety. In addition, bands for a methylenedioxy group (1256, 1044 and 968 cm^{-1}) were also present. The ^1H NMR spectrum of compound **2** also showed signals for an *N*-isobutylamide skeleton. The spectrum contained signals for olefinic protons of an α , β -unsaturated carbonyl system at δ 5.79 (1H, d, $J = 15.3$ Hz) and 6.83 – 6.90 (1H, m). Signals at δ 6.32 (1H, d, $J = 15.8$ Hz) and δ 5.96-6.06 (1H, m) were assigned to the olefinic protons in a *trans* relationship of a second bond that was conjugated to the aromatic ring system. The aromatic proton, H-2' appeared as a singlet at δ 6.88 while a set of two *ortho* coupled aromatic protons (δ 6.73, 1H, d, $J = 8.0$ Hz; 6.75, 1H, br d, $J = 8.1$ Hz) were assigned to H-5' and H-6' respectively. The assignments of these protons were further substantiated by a ^1H - ^1H COSY spectrum (Table 1). Thus, signals for methylene protons (δ 2.34) were coupled to the olefinic proton at H-6 (δ 5.96 – 6.06) and to H-3 (δ 6.83 – 6.90). The ^{13}C NMR of compound **2** showed the presence of 18 carbons with a carbonyl carbon (δ 165.80) and 3 quaternary carbons (δ 132.00, 147.94 and 146.76). Based on these spectroscopic results compound **2** is assigned as *N*-isobutyl-7-(3,4-methylenedioxyphenyl)-2*E*, 6*E*-heptadienamide which is also known as futoamide (Takahashi *et al.* 1969).

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