

## PHYTOCHEMICAL STUDIES ON *PIPER UMBELLATUM* L.

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### ABSTRACT

*Piper spp.* are widely used by the local communities living in the vicinities of Crocker Range Park Sabah for treating various diseases and also as natural insecticides. Chemical studies on *Piper umbellatum* L. resulted in the isolation of three pure compounds identified as isoasarone, 2-(4'-methoxyphenyl)-3-methyl-5-propenylbenzofuran and 2,3-dihydro-2-(4-hydrophenyl)-3-methyl-5-propenylbenzofuran. The chemical structures of these compounds were elucidated by spectral methods.

### INTRODUCTION

*Piper* spp are well known to the indigenous communities of Sabah because they are widely used as herbal medicines and food. Previous phytochemical studies of this genus have led to the isolation of a host of interesting chemical constituents which include lignans, amides, alkaloids and flavanoids. Furthermore some of these compounds have been reported to exhibit potentially beneficial insecticidal properties against a variety of medically important insect vectors and pests such as the house fly *Culex quinquefasciatus* larvae, *Ostrina nubilasis* and *Aedes atropalpus* (Duke 1985; Boff & De-Almeida 1996; Das et al. 1996; Pereda Miranda et al. 1997). In this short communication, we report the isolation, purification and structural elucidation of three compounds from *Piper umbellatum* collected from the forests of the Crocker Range National Park Sabah.

### MATERIALS AND METHODS

#### Plant Material

*Piper umbellatum* was collected from the forest sites of the Crocker Range National Park Sabah. A voucher specimen is deposited at UNIMAS Herbarium.

#### Extraction

The dried leaves of *Piper umbellatum* (500.0g) were extracted with methanol at room temperature for 3 days. The solvent was evaporated under pressure to give the crude extract (25.5g) which was then extracted 3 times with CHCl<sub>3</sub>. The CHCl<sub>3</sub> extract was combined (10.5g) and fractionated by column chromatography over silica gel (230-400 mesh) eluted with light petroleum ether: ether (100%, 9:1, 7:3, 1:1, 3:7 and 100%). Fractions with similar TLC profile were combined and further purified using preparative TLC (Silica gel 60F<sub>254</sub>, Hexane: EtOAc, 9:1). Using this combined techniques, 3 pure compounds were isolated: Compound 1 (42.5mg, 0.17%), compound 2 (55.4mg, 0.22%) and compound 3 (32.7mg, 0.13%).

**Compound 1.**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.25 (2H, dt,  $J = 1.5$  and  $5.5$  Hz, H9), 3.71, 3.76, 3.82 (9H, 3s, 3-OMe), 4.95 (1H, t,  $-\text{CH}_2$ ), 5.00 (1H, m,  $\text{CH}_2$ ), 5.92 (1H, m, H-8), 6.48 (1H, s, Ar, H-2), 6.64 (1H, Ar, H-5).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 33.1 (C-9), 58.4 (3-OMe), 98.7 (C-7), 114.8 (C-8), 115.7 (C-6), 120.7 (C1), 137.9 (C-3), 142.6 (C-2), 148.5 (C-4), 151.8 (C-5).

**Compound 2**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.91 (dd,  $J = 1.5, 6.8$  Hz, 3H, 10 Me), 2.42 (s, 3- Me), 3.86 (s, OMe), 6.26 (dq,  $J = 6.6, 15.9$ , 1H, H-9), 6.54 (dd,  $J = 1.5, 15.8$  Hz, 1H, H-8), 7.00 (2H, H-3' and H-5'), 7.25 (dd,  $J = 1.9, 8.5$  Hz, 1H, H-6), 7.36 (d,  $J = 8.5$ , 1H, H-7), 7.44 (d,  $J = 1.5$ , 1H, H-4), 7.74 (2H, H-2' & H-6).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 9.4 (Me-3), 18.5 (C10), 55.3 (OMe), 109.7 (C-3), 110.6 (C-7), 114.0 (C 3' & 5'), 116.0 (C4), 122.6 (C-6), 124.4 (C-9), 128.0 (C-2' & 6''), 131.0 (C-8), 131.5 (C3a), 132.7 (C-5), 133.0 (C-1'), 151.2 (C-2), 153.0 (C-7a), 159.4 (C-4).

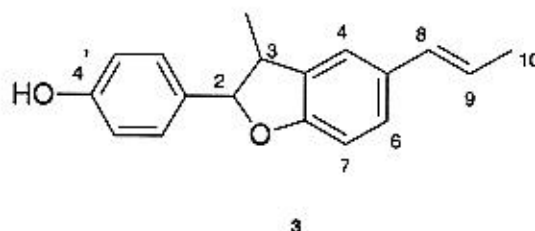
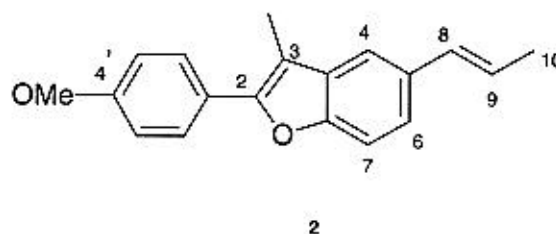
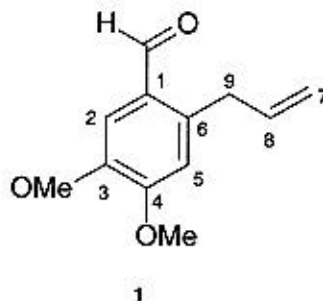
**Compound 3.**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.39 (d,  $J = 6.9$ , 3H, Me-3), 1.86 (dd,  $J = 1.5, 6.8$  Hz, 3H, H-10), 3.41 (m, 1H, H-3), 4.91 (s, OH), 5.10 (d,  $J = 9.0$ , 1H, H-2), 6.10 (dq,  $J = 6.8, 15.8$ , 1H, H-9), 6.35 (d,  $J = 15.8$ , 1H, H-8), 6.75 (d,  $J = 8.2$ , 1H, H-7), 6.83 (2H, H-3' & 5'), 7.12 (m, 2H, H-4 & H-6), 7.30 (2H, H-2' & 6'). C-NMR ( $\text{CDCl}_3$ )  $\delta$ : 17.8 (Me-3), 18.5 (C10), 45.2 (C-3), 92.6 (C-2), 110.0 (C-7), 123.4 (C-9), 120.7.0 (C-4), 126.3 (C-6), 27.9 (C 2'' & 6''), 130.5 (C-8), 131.2 (C-5), 132.4 (C-1), 132.9 (C-3a), 155.4 (C 3' & 5), 155.7 (C-7a), 158.2 (C-4).

## RESULTS AND DISCUSSION

Three pure compounds were isolated and characterised based on  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$ , mass spectroscopy and infrared information. Compound 1, was obtained as amorphous solid with a molecular ion peak at  $m/z$  208 consistent to molecular formula  $\text{C}_{12}\text{H}_{16}\text{O}_3$ . Based on spectroscopic information compound 1 was assigned as isoasarone. This compound has been previously isolated from *Piper sormentosum* (Satariah et al. 1999). Compound 2 was obtained as a white solid with a molecular ion peak at  $m/z$  278 which corresponded to the molecular formula  $\text{C}_{19}\text{H}_{18}\text{O}_2$ . The NMR spectrum of compound 2 showed signals corresponding to propenyl moiety at  $\delta$  1.91, 6.26 and 6.54. Signal at  $\delta$  7.00 and 7.74 were assigned for para disubstituted benzene, while siglet at  $\delta$  2.42 and 3.86 were assigned to methyl at C-3 and methoxy at C-4' respectively.  $^{13}\text{C-NMR}$  data showed the presence of 19 carbons with 7 quaternary carbon. Based on spectroscopic information compound 2 was assigned as 2-(4'-methoxyphenyl)-3-methyl-5-propenylbenzofuran.

Compound 3 was obtained as a white crystal with a molecular ion peak at  $m/z$  266 which corresponded to molecular formula  $\text{C}_{18}\text{H}_{18}\text{O}_2$ .  $^1\text{H-NMR}$  showed signal for the propenyl moiety similar to compound 2 at  $\delta$  1.86, 6.10 and 6.35; and the presence of a para disubstituted benzene at  $\delta$  6.83 and 7.30.  $^{13}\text{C-NMR}$  for compound 3 showed the presence of 18 carbon. Based on the spectroscopic information compound 3 was assigned as 2,3-dihydro-2-(4-hydrophenyl)-3-methyl-5-propenylbenzofuran. Both lignan (compounds 2 and 3) have been isolated previously from the leaves of *Piper magnibacum* (Farediah et al. 1999).

Biological activity studies on isoasarone showed that the compound is capable of causing immediate hyperexcitation and complete inhibition of the cockroach cercal nerve activity (Satariah et al. 1999). A few other compounds are also present in *Piper umbellatum* which are currently being investigated with respect to their biological activities against termites, bacteria and fungi in our laboratory at UNIMAS.



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