

## Chemical Constituents of *Piper aduncum* Linn (Piperaceae)

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### ABSTRAK

Kandungan kimia bagi daun *Piper aduncum* telah dikaji. Dua sebatian telah dipisahkan dan dikenalpasti secara spektroskopi. Komponen tidak berkutub telah dikenalpasti sebagai dillapiol atau 1-allyl-4, 5-metilenadioksi-2, 3-dimetoksibenzena, sementara komponen berkutub pula telah dikenalpasti sebagai 2, 6-dihidroksi-4-metoksidiidrochalkon.

### ABSTRACT

The leaves of *Piper aduncum* were studied for its chemical constituents. The non-polar component has been identified spectroscopically as dillapiole or 1-allyl-4, 5-methylenedioxy-2, 3-dimethoxybenzene while from the polar fraction 2, 6-dihydroxy-4-methoxydihydrochalcone has been isolated.

**Keywords:** *Piper aduncum*, Piperaceae, dillapiole, dihydrochalcone.

### INTRODUCTION

The genus *Piper* of the Piperaceae family comprises a large genus of herbs. It is categorized as woody climbers and sometimes shrubs and can be found widely in the tropical rain forests. Several species of *Piper* furnish pepper and other similar spices. *Piper aduncum* is used as a substitute for Indian long pepper in America (Burkhill 1966). *Piper aduncum* L and *Piper hispidum* are listed as remedies for colds and stomach aches and also as insect repellents (Burke and Nair 1986). The separation and structural elucidation of the chemical components present in the leaves of local *Piper aduncum* are reported.

### MATERIALS AND METHODS

Leaves of *P. aduncum* were collected from Hutan Simpanan Puchong. A voucher specimen is deposited at the herbarium of the Department of Biology, Universiti Pertanian Malaysia. The GC-MS was carried out on a Hewlett Packard GC-MS instrument using an SE30 capillary column with helium as the carrier gas. <sup>1</sup>H-NMR spectra were recorded on a Varian spectrometer operating at 60 MHz at room temperature. Samples were

dissolved in  $\text{CDCl}_3$  containing TMS as an internal standard. Infrared spectra were recorded on a Perkin Elmer FT-IR spectrophotometer. TLC were carried out on Merck pre-coated silica gel  $\text{F}_{254}$  plates, column chromatography was performed using TLC grade silica gel without binder.

#### Isolation and Identification of Components

The powdered air-dried leaves of *P. aduncum* (1.2 kg) were extracted with petroleum-ether (60-80°C) at room temperature for 24h and the solvent was evaporated under reduced pressure to give the crude extract (56.0g). The defatted air-dried leaves were then extracted with ethyl acetate at RT for 24h. Evaporation of solvent gave a crude extract (57.8g). The crude petroleum-ether extract (12.8g) was subjected to multiple column chromatography using petroleum-ether:acetone as eluent to afford compound (1). Vacuum column chromatography and multiple column chromatography (chloroform:ethyl acetate) on a portion of the crude ethyl acetate extract (7.4g) yielded compound (2).

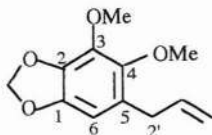
1-Allyl-4, 5-methylenedioxy-2, 3-dimethoxybenzene (1) was isolated as pale yellow liquid (0.062 g, 0.48%); IR  $\nu_{\text{max}}^{\text{film}} \text{ cm}^{-1}$  : 2935, 1626, 1480, 1463, 1082 and 1052;  $^1\text{H-NMR } \delta$  ( $\text{CDCl}_3$ ) : 3.3(2H, d,  $J=6$  Hz, benzylic  $\text{CH}_2$ ), 3.75(3H, s, -OMe), 4.10(3H, s, -OMe), 4.95(1H, m, H2'), 5.15(2H, m, vinylic  $\text{CH}_2$ ), 5.80(2H, s, methylenedioxy), 6.30(1H, s, H6); GC-MS :  $m/z$  222( $\text{M}^+$ ), 177, 149, 121, 106, 77 and 45.

2,6-Dihydroxy-4-methoxydihydrochalcone (2) was obtained as pale yellow crystals (0.014 g, 0.2%), m.p 163-165°C (Burke and Nair 1986, m.p. 164-165°C); IR  $\nu_{\text{max}}^{\text{KBR}} \text{ cm}^{-1}$  : 3261, 1646 and 1594;  $^1\text{H-NMR } \delta$  ( $\text{CDCl}_3$ ) : 3.05(2H, m, benzylic  $\text{CH}_2$ ), 3.38(2H, m,  $\text{COCH}_2$ ), 3.70(3H, s, -OMe), 5.92(2H, s, H3 and H5), 7.25(5H, s, Ph-), 11.80(1H, s, -OH); MS :  $m/z$  = 272( $\text{M}^+$ , 31.5%), 255(4%), 254(3%) and 167(100%).

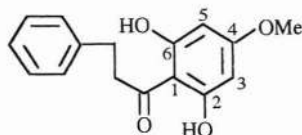
### DISCUSSION

Air-dried leaves of *P. aduncum* were ground and extracted with cold petroleum ether. A green viscous syrup was afforded upon removal of the solvent. The syrup was then subjected to multiple vacuum column chromatography followed by column chromatography to yield compound (1). Ethyl acetate extraction of the defatted leaf residue gave (2).

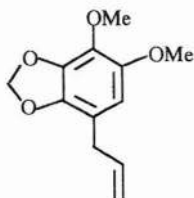
The GC-MS analysis of (1) confirms it to be dillapiole or 1-allyl-4, 5-methylenedioxy-2, 3-dimethoxybenzene with a molecular ion peak  $\text{M}^+$  at  $m/z$  222 which suggests a molecular formula of  $\text{C}_{12}\text{H}_{14}\text{O}_4$ . The IR spectrum of (1) shows absorption bands at 2935  $\text{cm}^{-1}$  and 1626  $\text{cm}^{-1}$  are due to the C-H and C=C stretchings of the allyl group. Bands at 1480  $\text{cm}^{-1}$  and 1463  $\text{cm}^{-1}$  are due to the aromatic skeleton and bands due to the C-O-C stretching are also observed at 1082  $\text{cm}^{-1}$  and 1052  $\text{cm}^{-1}$ . The integration of the  $^1\text{H-NMR}$  spectrum supported the presence of 14 protons in the



(1)



(2)



(3)

compound with the presence of two methoxyl groups at  $\delta$  3.75 and  $\delta$  4.01. Resonances due to vinylic protons are observed at  $\delta$  4.95 (1H, -CH=) and  $\delta$  5.15 (2H, =CH<sub>2</sub>) respectively. A singlet at  $\delta$  5.80 is due to the methylenedioxy group and the signal due to an aromatic proton is seen at  $\delta$  6.30 as a singlet. These data are in agreement with dillapiole which was isolated previously from *Erigeron pappochroma* (Sorensen and Sorensen 1969).

The naturally-occurring dillapiole belongs to the phenylpropanoid class of compounds and contributes to the volatile flavour and odour of the plant (Harborne 1984). Dillapiole was recognized as the major component of the leaf oil of Fijian *P. aduncum* (Smith and Hashim 1979). Pseudo-dillapiole (3) or 1-allyl-4, 5-dimethoxy-2, 3-methylenedioxybenzene was isolated previously from the fruits of *Piper aduncum* (Burke and Nair 1986) and the compound showed an antimicrobial activity against *Xanthomonas campestris* and *X. carotae* (Nair and Burke 1990).

Compound (2) was isolated as pale yellowish crystals with m.p. 163-165°C (EtOAc-MeOH). The compound was identified spectroscopically as 2, 6-dihydroxy-4-methoxydihydrochalcone.

The EI-MS spectrum of (2) shows a molecular ion peak at m/z 272 which suggests a molecular formula of C<sub>16</sub>H<sub>16</sub>O<sub>4</sub>. A base peak is observed at m/e 167 which indicated the loss of the Ar-CH<sub>2</sub>-CH<sub>2</sub> group from the

molecule. Compound (2) shows a medium-intensity broad band at 3216  $\text{cm}^{-1}$  which is due to the presence of O-H stretching in the molecule while bands at 1646  $\text{cm}^{-1}$  and 1594  $\text{cm}^{-1}$  are due to C=O and C=C stretchings. The  $^1\text{H-NMR}$  spectrum shows a triplet centred at  $\delta$  3.05 which is attributed to the benzylic protons. A split triplet signal centred at  $\delta$  3.38 due to the methylene protons adjacent to the carbonyl group is also observed. A singlet at  $\delta$  3.70 which integrates for three protons is assigned to the methoxyl group. The singlet at  $\delta$  5.92 is assigned to the two aromatic protons at C3 and C5 positions and another singlet due to an isolated five phenyl protons is observed at  $\delta$  7.25. The phenolic proton at C6 position is observed at  $\delta$  9.45 as a singlet and a signal which resonated as a singlet at  $\delta$  11.50 is attributed to the hydroxyl proton at C2 position.

Chalcone (2) was previously isolated from petroleum-ether extract of the fruits of Jamaican *P. aduncum* (Burke and Nair 1986).

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