

Chemical Constituents of *Alpinia purpurata*

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ABSTRAK

Rizom bagi *Alpinia purpurata* yang dikumpul dari taman di Universiti Teknologi Malaysia Skudai mengandungi diterpena jenis labdana, labda-8(17), 12-dien-15, 16-dial yang tidak stabil dan alkaloid piperina. Struktur sebatian telah dikenalpasti secara kaedah spektroskopi. Ini merupakan laporan pertama pengasingan alkaloid piperina daripada spesies *Alpinia*.

ABSTRACT

The rhizomes of *Alpinia purpurata* collected in Universiti Teknologi Malaysia, Skudai contained an unstable labdane diterpene, labda-8(17),12-diene-15,16-dial and an alkaloid piperine. Their structures were established by spectroscopic methods. This is the first report on the isolation of a piperine alkaloid from an *Alpinia* species.

Keywords: *Alpinia purpurata*, Zingiberaceae, rhizome, labdane diterpene, piperine alkaloid

INTRODUCTION

The genus *Alpinia* (Zingiberaceae) with about 23 species, is distributed in lowland and hill forests of Peninsular Malaysia (Holttum 1950). Several species of *Alpinia* are used as flavouring agents, while several others are used as ingredients in traditional medicine formulations (Burkill 1966). *Alpinia purpurata* is one of the species cultivated in gardens for ornamental purposes for its attractive and long-lasting flowers.

Several papers have been published on the chemical constituents of *Alpinia* species, including *Alpinia galanga* (Mitsui *et al.* 1976; Scheffer *et al.* 1981; Nair *et al.* 1982; Janssen and Scheffer 1985; De Pooter *et al.* 1985; Itokawa *et al.* 1987; Morita and Itokawa 1988), *A. japonica* (Itokawa *et al.* 1980a), *A. speciosa* (Itokawa *et al.* 1980b, 1981a), *A. officinarum* (Itokawa *et al.* 1981b; Kuichi *et al.* 1982), *A. oxyphylla* (Itokawa *et al.* 1981c), and *A. formosana* (Itokawa *et al.* 1988). In the present communication we wish to report the isolation and identification of two constituents of *A. purpurata*.

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METHODS AND MATERIALS

The rhizomes of *A. purpurata* were collected from the Landscape Unit, Universiti Teknologi Malaysia, Skudai, Johor. A voucher specimen was deposited in the Herbarium of the Dept. of Biology, Universiti Pertanian Malaysia, Serdang, Selangor. Thin-layer chromatography was performed on Merck pre-coated plates silica gel F₂₅₄. Column chromatography was performed on silica gel (Merck 230-400 mesh). Infrared spectra were recorded on a Perkin Elmer 727B spectrophotometer and ¹H and ¹³C NMR were recorded on a Bruker AM 300 spectrometer in CDCl₃ with TMS as an internal standard.

Isolation and Identification of Constituents

Dried rhizome of *A. purpurata* (100g) was extracted with chloroform in a soxhlet apparatus for 24 h, and the solvent was evaporated under reduced pressure to give crude product (3.7 g). The crude extract was fractionated using dry short flash column chromatography (Clark-Still *et al.* 1978) using a linear petroleum ether-ether gradient system to give four fractions (A-D). Fraction A was subjected to silica gel column chromatography and chromatotron to give **1** (180 mg). Fraction B was subjected to silica gel column chromatography several times using petroleum ether - ether (3:1) followed by recrystallisation to give **2** (100 mg).

Labda-8(17),12-diene-15,16-dial (1)

Unstable oil; EI-MS : m/z (%), 302 (58), 273(10), 258(8), 177(11) and 137(100); HRMS: M⁺ Found 302.2246 C₂₀H₃₀O₂ requires 302.2238; IR ν_{max} cm⁻¹: 3070, 1645, 890 (exomethylene bands), 1730, 1690(C=O); ¹H NMR (CDCl₃)δ: 0.75, 0.85 and 0.90 (3H each, s, methyl H-18, 19 and 20), 1.45-2.50 (14H, m, CH and CH₂), 3.40 (2H, br. s, H-14), 4.40 (1H, br.s, H-17), 4.86 (1H, br.s, H-17), 6.76 (1H, t, J= 6.6Hz, H-12), 9.36 (1H,s,H-16) and 9.62 (1H, br.s, H-15); ¹³C NMR (CDCl₃) δ: 14.4(C-20), 19.3(C-2), 21.7(C-19), 24.1(C-6), 24.7(C-11), 33.6(C-18 and C-4), 37.8(C-14), 39.2(C-1), 39.3(C-7), 39.6(C-10), 42.0(C-3), 55.4(C-5), 56.5(C-9), 107.8(C-17), 134.7(C-13), 148.0(C-8), 159.8(C-12), 193.4(C-16), and 197.1(C-15).

Piperine (2)

Pale yellow crystals, mp. 132-134°C, (lit. m.p. 128°C) (Agarwal 1975); EI-MS: m/z (%) 285(73), 261(100), 173(29), 143(17), 115(56) and 84(22), HRMS: M⁺ Found 285.1365 C₁₇H₁₉NO₃ requires 285.1360; IR ν_{max} (nujol) cm⁻¹: 1640 (C=O), 1595 and 1500 (C=C); ¹H NMR (CDCl₃)δ: 1.6(6H, m, 3x CH₂), 3.6 (4H,m, 2x CH₂N), 5.98 (2H, s, methylenedioxy group), 6.44 (1H,d, J= 14.7 Hz, H-2), 6.74-6.78 (3H, m, overlapping peaks of H-4, H-5 and H-5'), 6.90 (1H, dd, J= 8.0, and 1.6 Hz, H-6'), 6.99 (1H,d, J= 1.6 Hz, H-2') and 7.44 (1H, ddd, J= 14.7, 8.0 and 2.3 Hz, H-3); ¹³C NMR (CDCl₃) δ: 24.6(CH₂),

25.6(CH₂), 26.7(CH₂), 43.2(CH₂), 101.2(OCH₂O), 105.6(C-2'), 108.5(C-5'), 120.0(C-6'), 122.5(C-2), 125.3(C-5), 131.0(C-1'), 138.2(C-4), 142.5(C-3), 148.1(C-3' and C-4') and 165.4 (C=O).

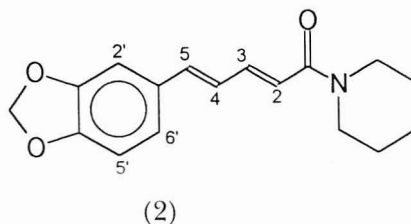
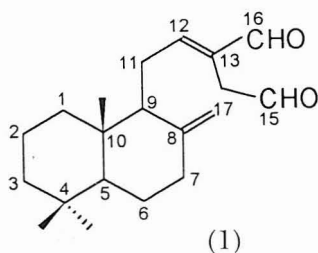
RESULTS AND DISCUSSION

The rhizome extractives of *A. purpurata* yielded two components. The structures were elucidated by spectroscopic methods. The major constituent was a labdane-type diterpene labda-8(17),12-diene-15-16-dial (**1**) while the minor constituent was an alkaloid piperine (**2**).

Compound (**1**) had the molecular formula C₂₀H₃₀O₂ by high resolution MS (M⁺ at m/z 302) and appeared as an unstable oil. Its IR spectrum showed two strong carbonyl absorptions at 1730 and 1690 cm⁻¹, and an exomethylene absorption at 1645 and 890 cm⁻¹.

The ¹H NMR spectrum indicated the presence of two aldehydic protons [δ 9.62 and 9.36]. A one-proton triplet [δ 6.76, J = 6.6 Hz] was consistent with an olefinic β-proton (H-12) of an αβ-unsaturated carbonyl group. Signals for the exomethylene protons of H-17 [δ 4.40 and 4.86] and the three methyl groups [δ 0.75, 0.85 and 0.90] are typical of labdane diterpene. This was supported by the appearance of a characteristic mass fragment at m/z 137 (100%) in the mass spectrum (Budzikiewicz *et al.* 1964). Thus compound (**1**) was concluded to be labda-8(17),12-diene-15,16-dial by comparison with the spectral data of the compound isolated from *A. speciosa* (Itokawa *et al.* 1980b). The structure was also supported by the ¹³C NMR data as shown in the experimental section.

Compound (**2**), which was isolated as a minor component, had the molecular formula C₁₇H₁₉NO₃ by high resolution MS (M⁺ at m/z 285) and appeared as pale yellow crystals. The IR spectrum showed the carbonyl amide absorption at 1640 and carbon-carbon double bond absorption at 1595 and 1500 cm⁻¹. The ¹H NMR spectrum showed the presence of a methylenedioxy group [δ 5.98], a piperidine ring [δ 1.6 and 3.6], an αβ-unsaturated carbonyl grouping [δ 6.44, d, J = 14.7 Hz for H - 2 and 7.44, ddd, J = 14.7, 8 and 2.3 Hz for H - 3], three aromatic protons [δ 6.78, d, J = 8.0 Hz, H-5', 6.90, dd, J = 8.0 and 1.6 Hz, H-6' and 6.99, d, J = 1.6 Hz, H-2'], and two other olefinic protons [δ 6.74-6.78, m, H-4 and H-5, overlapping with H-5']. Compound (**2**) was identified as piperine alkaloid by direct comparison with



an authentic sample isolated from *Piper nigrum* (Agarwal 1975). The structure of piperine (**2**) was also in agreement with the ^{13}C NMR data summarized in the experimental section. This work represents the first report on the chemical constituents of *A. purpurata* and the isolation of piperine from the genus.

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