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A NOVEL NAPHTHOQUINONE FROM *Plumbago zeylanica* ROOTS

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*A novel naphthoquinone (**1**) was isolated from the methanol extract of* P. zeylanica *roots in addition to a known compound plumbagin (**2**). Their structures were determined by UV, IR, MS, ^{1}H, and ^{13}C NMR spectroscopic analysis, including 2D NMR.*

Keywords: *Plumbago zeylanica*, Plumbaginaceae, 2-methyl-5-(3′-methyl-but-2′-enyloxy)-[1,4]naphthoquinone.

In the Indian system of medicine the plant *Plumbago zeylanica* (Plumbaginaceae) has been described as effective against rheumatic pain, sprains, scabies, skin diseases, wounds, ulcers, and inflammations [1–4]. Based on authentic literature reports, *P. zeylanica* serves as a rich source of naphthoquinones, binaphthoquinones, steroids, sugars, naphthalenones, alkanes, triterpenes, amino acids, flavones, and flavonoid glucosides [5, 6].

In a systematic phytochemical investigation, a novel naphthoquinone **1** was isolated from the methanol extract of *P. zeylanica* roots, together with a known compound plumbagin (**2**) [7]. In the present communication we describe the isolation and structure elucidation of novel 2-methyl-5-(3′-methyl-but-2′-enyloxy)-[1,4]naphthoquinone (**1**) on the basis of spectroscopic methods.

The UV spectrum of compound **1**, recorded in chloroform, exhibited maximum absorption (λ_{max}) at 266 and 415 nm characteristic of quinones. The infrared spectrum of the compound in KBr exhibited two absorption bands at 1656 and 1665 cm^{-1}, indicating the presence of two carbonyl groups [8]. Based on elemental analysis the molecular formula of compound **1** was established as $C_{16}H_{16}O_3$. In the mass spectrum a molecular ion peak was observed at *m/z* 256 (65%), corresponding to the molecular formula $C_{16}H_{16}O_3$. A base peak at *m/z* 187 (100%, corresponding to phenol after the loss of the isoprenyl moiety) confirmed the basic skeleton. An informative peak [M – CH_3] at *m/z* 241 (35%) was also observed in the mass spectrum.

A naphthoquinone skeleton was deduced on the basis of the mass spectrum. Sixteen carbon resonance signals appeared in the ^{13}C NMR spectrum, and four aromatic protons were observed in the ^{1}H NMR spectrum of compound **1**. DEPT pulse sequence analysis (e.g., DEPT 135 and DEPT 90) revealed the presence of seven quaternary, five tertiary, one oxymethylene (δ 70.4), and three methyl carbons. The ^{1}H NMR spectrum (300 MHz, $CDCl_3$) exhibited signals integrating for sixteen protons. Two aromatic signals corresponding to one proton each at δ 6.84 (q, J = 1.5 Hz) and δ 7.28 (dd, J = 7.8, 2.4 Hz) were identified for H-3 and for H-6 of the naphthoquinone skeleton. Two aromatic signals observed at δ 7.67 (1H, dd, J = 7.8, 2.4 Hz) and δ 7.63 (1H, td, J = 7.8 Hz) were identified for H-8 and H-7, while a three-proton doublet at δ 2.21 (J = 1.5 Hz) revealed the presence of an aryl-methyl group in compound **1**. The two singlets observed in the ^{1}H NMR spectrum of compound **1** at δ 1.79 (3H, s) and δ 1.78 (3H, s) were assigned to two terminal olefin methyl groups in the side chain. A signal for an olefin methine proton observed at δ 5.64 (1H, t, J = 7.0 Hz) and a downfield oxymethylene signal at δ 5.05 (2H, d, J = 7.0 Hz) confirmed that the side chain must be the isoprenyl moiety.

The HMQC spectrum verified that the signal at δ 5.63 belongs to an olefin methine proton attached to the heteronuclear carbon at δ 120.0. The position of the side chain was evidenced by HMBC correlations in which H-1′ at δ 5.02 showed HMBC correlation to C-5, placing the isoprenyl moiety at the C-5 position (Fig. 1). Also, multiple correlations from H-1′ to C-2′ and C-3′ and H-2′ to C-4′ and C-5′ were observed for the isoprenyl moiety. Based on the above spectral analysis, the structure of compound **1** was determined as 2-methyl-5-(3′-methyl-but-2′-enyloxy)-[1,4]naphthoquinone.

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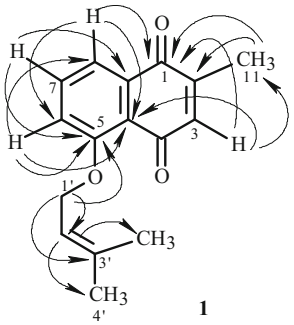

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Fig. 1. Key HMBC correlations of compound **1**.

EXPERIMENTAL

General Experimental Procedures. Melting points were measured in open capillary tubes on a Buchi 530 apparatus and are uncorrected. NMR spectra were obtained on a JEOL AL300 FTNMR spectrometer in $CDCl_3$ with TMS as an internal reference. The mass spectrum was recorded on a JEOL SX-102(EI-CI-FAB) mass spectrometer, SAIF, CDRI, Lucknow. Infrared spectra were recorded as KBr pelletes on a Perkin–Elmer RX-1 spectrometer. Elemental analysis was performed on a Perkin–Elmer 2400 C, H, N analyzer.

Plant Materials. The roots of *Plumbago zeylanica* L. were purchased from the suburb of Varanasi, India. Identification of roots was verified by Prof. N. K. Dubey, Department of Botany, Faculty of Science, Banaras Hindu University, Varanasi, India. A specimen sample of plant material (Code: PZX1RN1) has been preserved in the Natural Product Laboratory (No. 39), Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi, India.

Extraction and Isolation. Dried and finely powdered roots of *P. zeylanica* (1 kg) were extracted with methanol (5 L) for 24 h at 60–70°C using a Soxhlet extractor. The methanol extract was concentrated under reduced pressure, and the residue (117 g) was fractionated with petroleum ether (3 L × 2), $CHCl_3$ (2 L × 2), EtOAc (3 L × 2), and *n*-BuOH (1 L × 2). The petroleum ether fraction (17 g) was chromatographed on silica gel (200–300 mesh) and eluted with mixtures of hexane, benzene, and ethyl acetate. Fractions eluted with benzene afforded compound **1**, which was recrystallized with benzene–MeOH (90:1) into yellow needles (25 mg, mp 70–72°C).

Compound 1. Yellow needles, mp 70–72°C. UV ($CHCl_3$, λ_{max} nm): 266, 415. IR (KBr, cm^{-1}): 2932, 2860, 1656, 1665, 1468, 1370, 1051, 788, 676, 470. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 7.67 (1H, dd, J = 7.8, 2.4, H-8), 7.63 (1H, J = 7.5, H-7), 7.28 (1H, dd, J = 7.8, 2.4, H-6), 6.84 (1H, q, J = 1.5, H-3), 5.64 (1H, t, J = 7.0, H-2′), 5.05 (2H, d, J = 7.0, H-1′), 2.21 (3H, d, J = 1.5, Me-2), 1.79 (3H, s, Me-4′), 1.78 (3H, s, Me-5′). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 184.9 (C-l), 149.5 (C-2), 135.2 (C-3), 190.4 (C-4), 161.2 (C-5), 124.1 (C-6), 136.0 (C-7), 120.2 (C-8), 132.4 (C-9), 114.8 (C-10), 16.8 (C-11), 70.0 (C-1′), 120.0 (C-2′), 132.6 (C-3′), 18.2 (C-4′), 25.8 (C-5′). MS *m/z* (I_{rel}, %): 256 [M^+, 65], 201 (26), 187 (100), 241 (34), 120 (22), 69 (47). Found, %: C 74.95; H 6.32, calcd, %: C 74.98; H 6.29. $C_{16}H_{16}O_3$.

Plumbagin (2). Yellow needles, mp 78–80°C (benzene–EtOAc 9:1) [7].

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