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## Journal of Asian Natural Products Research

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713454007>

### **A new naphthoquinone from *Ceiba pentandra***

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Online publication date: 12 May 2010

**To cite this Article** Kishore, P. Hari , Reddy, M. Vijaya Bhaskar , Gunasekar, D. , Caux, Cristelle and Bodo, Bernard(2003) 'A new naphthoquinone from *Ceiba pentandra*', Journal of Asian Natural Products Research, 5: 3, 227 – 230

**To link to this Article:** DOI: 10.1080/1028602031000105812

**URL:** <http://dx.doi.org/10.1080/1028602031000105812>

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## A NEW NAPHTHOQUINONE FROM *CEIBA PENTANDRA*

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(Received 23 October 2002; Revised 5 January 2003; In final form 4 February 2003)

A new naphthoquinone, 2,7-dihydroxy-8-formyl-5-isopropyl-3-methyl-1,4-naphthoquinone (**1**) together with a known naphthoquinone, 8-formyl-7-hydroxy-5-isopropyl-2-methoxy-3-methyl-1,4-naphthoquinone (**2**), has been isolated from the heartwood of *Ceiba pentandra*. The structures of **1** and **2** have been elucidated by extensive 1D and 2D NMR experiments.

**Keywords:** *Ceiba pentandra*; Bombacaceae; Naphthoquinones

### INTRODUCTION

*Ceiba pentandra* L. Gaertn. (Bombacaceae) is a medium-sized deciduous tropical tree found throughout Western and Southern India [1]. In Asia, Oceania, Africa and Central America this species is used to treat various disorders, including diarrhea, fever, gonorrhoea and parasitic infections, and as a diuretic and an emollient [1,2]. Previous work on *Ceiba pentandra* has resulted in the isolation of several sesquiterpenoids [3] and isoflavones [4,5]. In our systematic search for active metabolites from Indian medicinal plants, we have investigated the heartwood of this plant and report here the isolation and characterization of a new naphthoquinone, 2,7-dihydroxy-8-formyl-5-isopropyl-3-methyl-1,4-naphthoquinone (**1**) together with 8-formyl-7-hydroxy-5-isopropyl-2-methoxy-3-methyl-1,4-naphthoquinone (**2**).

### RESULTS AND DISCUSSION

Compound (**1**), isolated as orange needles, showed a  $[M + H]^+$  peak at  $m/z$  275.0887 in its positive ESITOFMS, which is consistent with the molecular formula  $C_{15}H_{14}O_5$ . A positive response to sodium dithionite and the UV absorption maxima at 215, 254, 275, and 336 nm

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suggested that **1** could be a 1,4-naphthoquinone derivative [6]. It exhibited IR absorption bands at 3420, and 1710 and 1648  $\text{cm}^{-1}$  due to hydroxyl and carbonyl functions. The presence of three downfield carbon resonances at  $\delta$  193.3, 186.0 and 182.2 in its  $^{13}\text{C}$  NMR spectrum indicated an additional carbonyl function apart from the two quinonoid carbonyls.

The  $^1\text{H}$  NMR spectrum of **1** showed the presence of two chelated hydroxyl groups ( $\delta$  10.68 and 11.06), a formyl group ( $\delta$  10.16, s, 1H), an isopropyl group ( $\delta$  1.17, d, 6H,  $J = 6.8$  Hz; 4.31, sept, 1H,  $J = 6.8$  Hz) and a methyl group ( $\delta$  1.88, s, 3H). It also showed an aromatic proton singlet at  $\delta$  7.24. Compound **1** did not respond to Craven's test [7], which suggested that the 1,4-naphthoquinone ring in **1** is fully substituted.

In the HMBC spectrum of **1** (Fig. 1) the correlations of the isopropyl methine proton at  $\delta$  4.31 with C-5 ( $\delta$  155.8), C-6 ( $\delta$  119.4) and C-10 ( $\delta$  121.2), and the aromatic proton signal at  $\delta$  7.24 with C-5 ( $\delta$  155.8), C-7 ( $\delta$  158.4), C-8 ( $\delta$  123.8), C-10 ( $\delta$  121.2) and C-12 ( $\delta$  28.3) indicated that the isopropyl group is at C-5 and the lone aromatic proton is at C-6. One of the chelated hydroxyl groups at  $\delta$  11.06 was placed at C-7 as it correlated with this carbon at  $\delta$  158.4, which in turn showed cross correlations with H-6 ( $\delta$  7.24) and the formyl proton ( $\delta$  10.16), suggesting the attachment of the formyl group at C-8. The presence of a formyl group at C-8 was further supported by  $^2J$  and  $^3J$  correlations of the formyl proton ( $\delta$  10.16) with C-8 and C-7, respectively. The placement of an isopropyl group at C-5, a lone aromatic

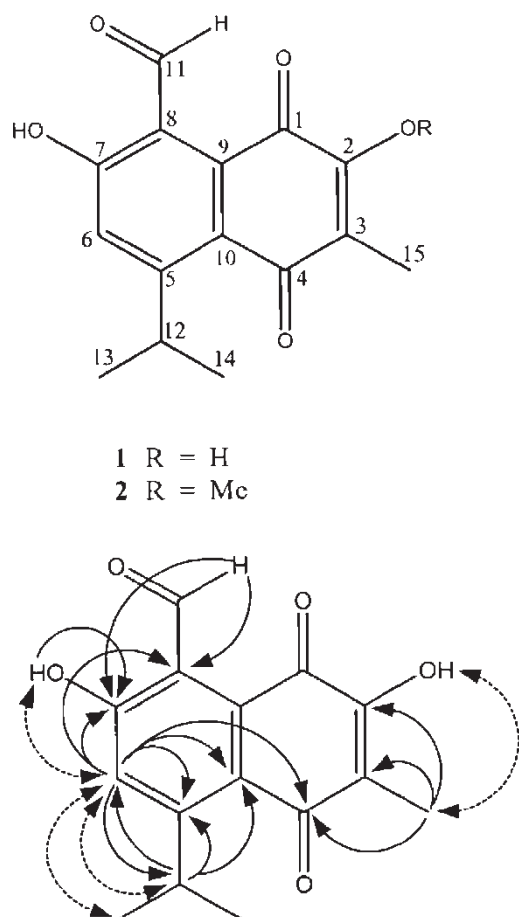


FIGURE 1 Selected HMBC ( $\rightarrow$ ) and NOESY ( $\leftrightarrow$ ) correlations of **1**.

proton at C-6 and a hydroxyl group at C-7 were further evidenced by strong NOE correlations between H-6 and OH-7; H-6 and 13-CH<sub>3</sub>; H-6 and H-12. The methyl group at  $\delta$  1.88 was located at C-3, based on the HMBC correlations of these protons with C-2 ( $\delta$  153.1), C-3 ( $\delta$  121.5) and C-4 ( $\delta$  186.0), and further corroborated by long-range ( $^4J$ ) correlation of H-6 ( $\delta$  7.24) with C-4 ( $\delta$  186.0), which showed cross correlation with methyl protons ( $\delta$  1.88) at C-3. Accordingly the second chelated hydroxyl ( $\delta$  10.68) should be at C-2. This was further supported by a strong NOE correlation of this hydroxyl proton with the methyl protons at C-3. Thus, compound **1** was characterized as 2,7-dihydroxy-8-formyl-5-isopropyl-3-methyl-1,4-naphthoquinone.

Compound **2** was identified as 8-formyl-7-hydroxy-5-isopropyl-2-methoxy-3-methyl-1,4-naphthoquinone by comparing its physical and spectral data with literature values [8].

## EXPERIMENTAL

### General Experimental Procedures

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. The UV spectra were recorded on a Shimadzu UV-240 double beam spectrophotometer, and IR spectra in KBr discs on a Perkin-Elmer 283 double beam spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were determined on Bruker Avance 400 and Bruker AC-300 spectrometers using CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> with TMS as internal standard. <sup>1</sup>H–<sup>1</sup>H COSY, HMQC, HMBC and NOESY spectra were recorded using standard pulse sequences. ESITOFMS and MS/MS were recorded on a API Q-STAR PULSA of Applied Bio-system. Column chromatography was performed on Acme silica gel (100–200 mesh).

### Plant Material

The heartwood of *Ceiba pentandra* was collected from Tirumala Hills, Andhra Pradesh, India in January 2001. The plant material was authenticated by Dr K. Madhava Chetty, Department of Botany, Sri Venkateswara University, Tirupati, India, where a voucher specimen (DG-011) was deposited.

### Extraction and Isolation

Dried and powdered heartwood (2 kg) of *Ceiba pentandra* was successively extracted with n-hexane, Me<sub>2</sub>CO and MeOH. The Me<sub>2</sub>CO extract was purified over a silica gel column using an n-hexane/EtOAc step gradient. A total of 70 fractions of 50 ml each were collected. Fractions 10–17 and 23–28 eluted with n-hexane/EtOAc, 7:3 and 1:1, respectively, yielded **2** (8 mg) and **1** (12 mg).

### 2,7-Dihydroxy-8-formyl-5-isopropyl-3-methyl-1,4-naphthoquinone (**1**)

Orange needles from CHCl<sub>3</sub>, 12 mg, mp 126–127°C; UV (MeOH)  $\lambda_{\max}$  (nm): (log  $\epsilon$ ) 215 (4.4), 254 (4.2), 275 (4.1), 336 (3.8); IR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>): 3420 (–OH), 1710 (>C=O), 1648 (>C=O), 1540, 1218, 772; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  11.06 (1H, s, OH-7), 10.68 (1H, s, OH-2), 10.16 (1H, s, H-11), 7.24 (1H, s, H-6), 4.31 (1H, sept, *J* = 6.8 Hz, H-12), 1.88 (3H, s, Me-3), 1.17 (6H, d, *J* = 6.8 Hz, Me-13 and 14); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz)  $\delta$  193.3 (C-11), 186.0 (C-4), 182.2 (C-1), 158.4 (C-7), 155.8 (C-5), 153.1 (C-2), 132.9 (C-9), 123.8 (C-8), 121.5 (C-3), 121.2 (C-10), 119.4 (C-6), 28.3 (C-12), 23.2

(C-13 and C-14), 8.9 (C-15); ESI-MS/MS (positive mode)  $m/z$  275.0 [M + H]<sup>+</sup> (26), 260.0 (84), 257.0 (8), 247.0 (6), 232.0 (19), 214.0 (95), 186.0 (100); ESITOFMS  $m/z$  275.0887 [M + H]<sup>+</sup> (calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>5</sub> + H, 275.0919).

### **8-Formyl-7-hydroxy-5-isopropyl-2-methoxy-3-methyl-1,4-naphthoquinone (2)**

Yellow needles from CHCl<sub>3</sub>, mp 82–83°C; UV, IR, and <sup>1</sup>H NMR data were in agreement with literature values [8]; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 197.0 (C-11), 186.0 (C-4), 183.0 (C-1), 165.0 (C-7), 161.0 (C-5), 156.5 (C-2), 135.0 (C-9), 131.5 (C-3), 124.0 (C-10), 121.2 (C-6), 117.0 (C-8), 60.0 (C-16), 30.0 (C-12), 23.8 (C-13 and 14), 9.0 (C-15); ESI-MS/MS (positive mode)  $m/z$  289.1 [M + H]<sup>+</sup> (48), 274.1 (68), 272.0 (1), 271.0 (14), 260.0 (22), 259.0 (100), 257.0 (15), 256.1 (27), 246.0 (15); ESITOFMS  $m/z$  289.1350 [M + H]<sup>+</sup> (calcd. for C<sub>16</sub>H<sub>16</sub>O<sub>5</sub> + H, 289.1071).

### **Acknowledgements**

The authors thank Dr J. P. Brouard, Laboratoire de Chimie des Substances Naturelles, MNHN, Paris, France, for providing mass spectral data.

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