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A 1,4-ANTHRAQUINONE DERIVATIVE FROM *TECTONA GRANDIS**

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Key Word Index—*Tectona grandis*, Verbenaceae, naphthoquinones, anthraquinones

Abstract—A petrol extract of the heartwood of *Tectona grandis* afforded a new 9,10-dimethoxy-2-methyl anthra-1,4-quinone along with tecomaquinone I and several known naptho- and anthra-quinone derivatives The structure of the new quinone was elucidated by high field ^{1}H NMR and NOE studies.

INTRODUCTION

In continuation of our earlier work on *Tectona grandis* [1], we have re-examined a Sawai Madhopur collection of this plant and report the isolation of a 1,4-anthraquinone derivative (**1**) in addition to earlier isolated tectoquinone, lapachol, dehydro-α-lapachone, tecomaquinone I and some unidentified anthraquinones Previous work on this plant led to the isolation of a number of naphthoquinone and anthraquinone derivatives as well as steroidal compounds, squalene, polyisoprene, σ-tolylmethyl ether, betulinic acid, etc. [2–8]

RESULTS AND DISCUSSION

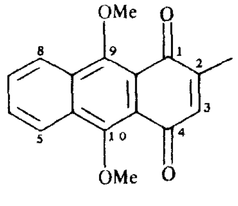
Anthraquinone (**1**), $C_{17}H_{14}O_4$(M^+, m/z 282 089) showed an IR absorption band at 1660 cm^{-1} for cross conjugated carbonyls. Its UV spectrum displayed peaks at 215, 248 (sh), 270, 298 and 400 nm The ^{1}H NMR spectrum established the presence of two methoxy groups (δ4 06 and 4.08, each *s*) and a methyl group (δ2 19, *d*, J = 1.5 Hz). A quinonoid H-3 proton signal appeared as a quartet at δ6 80 (J = 1 5 Hz) and showed coupling with the C-2 methyl group Aromatic proton signals for H-5 and H-8 appeared as double doublets at δ8 38 and 8 40 (J = 7, 1 Hz, each) and those for H-6 and H-7 as triplets at δ7.73 and 7 76 (J = 7 Hz, each respectively The *peri* position of the methoxyl groups was ascertained by NOE difference spectroscopy There were clear NOEs between OMe-9 and H-8 (5%), OMe-10 and H-5 (5%), Me-2 and H-3 (20%) The sequence of the protons was established by spin decoupling experiments The mass spectrum showed a molecular ion peak at m/z 282 089 (100) corresponding to the molecular composition $C_{17}H_{14}O_4$ Other important peaks were at m/z 267 $[M-Me]^+$, 254 $[M-CO]^+$, 253 $[M-CHO]^+$, 239 $[254-Me]^+$, 211 $[239-CO]^+$ and 210 $[239-CHO]^+$ The quinone was identified as 9,10-dimethoxy-2-methylanthra-1,4-quinone.

The structures of known compounds were established by comparison with authentic samples or by comparing the ^{1}H NMR data with literature

EXPERIMENTAL

The air-dried and coarsely powdered heartwood shavings (5 kg, collected from Sawai Madhopur district of Rajasthan) were extracted with petrol (60–80°) on a water bath for 3 × 12 hr Evapn of the solvent at red pres. furnished a reddish brown semisolid mass which was taken up in Et_2O and fractionated into acidic and neutral parts by extraction with 1 M Na_2CO_3 The Na_2CO_3-soluble part was neutralized with 6 M HCl and furnished 15 mg lapachol as bright yellow crystals, mp 139–140° The Na_2CO_3-insoluble part (neutral fraction) was chromatographed over neutral alumina (deactivated with 10% aq AcOH) to give fraction 1 (petrol), fraction 2 (petrol–C_6H_6, 1 1), fraction 3 (C_6H_6), fraction 4 (C_6H_6–EtOAc, 9 1), fraction 5 (C_6H_6–EtOAc, 3 1), fraction 6 (C_6H_6–EtOAc, 1 1) and fraction 7 (EtOAc) Fraction 1 gave a single spot on TLC and afforded 500 mg tectoquinone, mp 174–176° Fraction 2 was a dark blue green semi-solid which on crystallization (MeOH) gave 50 mg tecomaquinone I, mp 198–199° Fraction 3 on prep. TLC ($CHCl_3$) yielded 45 mg of red needles of dehydro-α-lapachone, mp 143–144° Fraction 4 yielded 12 mg of the anthraquinone **1** Fractions 5–7 gave yellow crystals in very small amounts which could not be identified due to the paucity of the material

9,10-*Dimethoxy-2-methylanthra*-1,4-*quinone* (**1**) Yellow crystalline solid, UV $\lambda_{\max}^{Et_2O}$ 215, 248 (sh), 270, 298 and 400 nm, IR $\nu_{\max}^{CCl_4}$ 2860–2820, 1660 (C=C–C=O), 1340, 1320 and 1230 cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$) δ2 19 *d* (J = 1 5 Hz, Me), 4 06 *s*, 4 08 *s* (2 × OMe), 6 80 *q* (J = 1 5 Hz, H-3), 7 73 *t* and 7 76 *t* (J = 7 Hz each H-6 and H-7), 8 38 *dd* and 8 40 *dd* (J = 7,



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1 Hz each, H-5, H-8), MS *m/z* (rel. int) 282 0890 $[M]^+$ (100) (Calc for $C_{17}H_{14}O_4$ 282.0890), 267 $[M-Me]^+$ (20), 254 $[M-CO]^+$ (60), 253 $[M-CHO]^+$ (44), 239 $[254-Me]^+$ (24), 211 $[239-CO]^+$ (12), 210 $[239-CHO]^+$ (13), 57 (98)

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ANGUSTIFOLENONE, A KETONE FROM *BACKHOUSIA ANGUSTIFOLIA*

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Key Word Index—*Backhousia angustifolia*, Myrtaceae; cyclohexenone, NMR GC/MS

Abstract—Angustifolenone, 2-ethyl-4,6,6-trimethylcyclohex-2-ene-1-one, has been identified in 25% yield from the steam volatile leaf oil of *Backhousia angustifolia*

INTRODUCTION

Backhousia angustifolia F Muell. is a shrub or small tree reaching 6–8 m in height. The species is endemic to Queensland where it occurs in depauperate rainforests mainly in central and south-eastern areas of the state, between Blackdown Tableland and the Bunya Mountains. Two disjunct populations have been recorded north of this range, one in the Eungella area west of Mackay and the other near Wando Vale, *ca* 75 km south of Greenvale. A southern outlying occurrence south west of Stanthorpe at present referred to as *B. angustifolia* may prove on further study to warrant recognition as a distinct taxon.

Backhousia angustifolia was first investigated by Penfold in 1923 [1]. He isolated the two β-triketones angustione (**1**) and dehydroangustione (**2**), and in some cases the chromone angustifolionol (**3**), together with some monoterpenes, from the steam volatile leaf oil. The structures of the two β-triketones were finally elucidated by Birch [2, 3], and proved by synthesis [4, 5], while the structure of the chromone was also deduced by Birch *et al.* [6] Some years later Cannon and Corbett demonstrated the existence of physiological forms in this species [7]

RESULTS AND DISCUSSION

During an investigation of tropical oil bearing Australian plants we found that the leaf oil from several specimens of *Backhousia angustifolia* contained, as well as the two β-triketones, **1** and **2**, a significant amount of 1,8-cineole and *ca* 25% of a compound of M_r 166. This compound had GLC Linear Retention indices (LRI) of 1422 on FFAP and 1157 on OV1 respectively. To facilitate identification, the compound was isolated by preparative GLC

^{13}C NMR spectroscopy, using the DEPT procedure, revealed a carbonyl (δ 204 4) plus olefinic CH and C