A new tetralone from *Diospyros cauliflora*

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1. **Subject and source**

*Diospyros* (common names ebony or persimmon) is a large genus of mainly tropical trees within Ebenaceae many of which possess considerable economic importance. The best known species is the Japanese persimmon, *Diospyros kaki* Thunb. The varied chemistry of many of its members was reviewed more than ten years ago (Mallavadhani et al., 1998) and many more articles have appeared in the literature since then. In the following we describe the results of our study of the roots of *Diospyros cauliflora* Blume from Southern Thailand, a species which has not been investigated previously.

Roots of *D. cauliflora* Blume were collected in Trang Province, Southern Thailand, in March 2007 and were identified by Mr. Chamlong Phengklai. A voucher specimen (BKF 143220) has been deposited at the Royal Forest Department, Paholyothin Road, Bangkok, Thailand.

2. **Previous work**

None

3. **Present study**

Dried powdered roots (4 kg) were extracted with hexane (3 × 10 L) at room temperature. The hexane solutions were combined and evaporated at reduced pressure to give a crude hexane extract (23 g) which was not investigated further. The
material remaining after the extraction with hexane was extracted with MeOH (3 × 10 L) at room temperature for seven days. The MeOH extracts were combined and evaporated at reduced pressure to give 130 g of crude extract which was dissolved with sonication in CHCl3 (3 × 2 L) at room temperature for seven days. The MeOH extracts were combined and evaporated at reduced pressure to give 26 g of crude extract which was chromatographed over Si gel (200 g) using mixtures of CHCl3-petrol and CHCl3-Me2O, 250 ml frs being collected as follows. Frs 1–12 (CHCl3-petrol, 2:3), 13–39 (CHCl3-petrol, 3:2), 40–63 (CHCl3-petrol, 4:1), 64–77 (CHCl3-petrol, 9:1) and 78–200 (CHCl3-Me2O, 9:1). Frs 19 and 20 were combined, chromatographed over a Si gel column and eluted with CHCl3-petrol, (3:2), 59 100 ml sfrs being collected. Sfr 5 (23 mg) on purification by TLC (Si gel, CHCl3-petrol-HCO2H, 95:5:0.1) gave lupeol (8.3 mg) identified by HRMS, 1H and 13C NMR spectrometry (Reynolds et al., 1986). Sfr 6 (54 mg) on purification by TLC (Si gel, CHCl3-Me2O-HCO2H, 90:10:0l) gave lupeol (4 mg) and betulinic acid (23 mg) identified by HRMS, 1H and 13C NMR spectrometry (Peng et al., 1998, Ullah et al., 2007). Sfrs 34–41 (238 mg) on purification by TLC (Si gel, CHCl3-Me2O-HCO2H, 85:15:0.1) furnished 124 mg of 7-hydroxy-4β,6-dimethoxyflavone (pratol) identified by HRMS, 1H and 13C NMR spectrometry (Park et al., 2007), 32 mg of 2,5-dimethyl-7-hydroxychromone identified by HRMS, 1H and 13C NMR spectrometry (Kashiwada et al., 1984) and 10 mg of vanillic acid. Frs 23–25 (123 mg) of the original chromatogram on purification by preparative TLC (Si gel, CHCl3-Me2O-HCO2H, 95:5:0.1) afforded vanillic acid (16 mg) and 29 mg of which is new to the chemical literature. Frs 119–143 were combined (186 mg) and purified by TLC (Si gel, CHCl3-MeOH-HCO2H, 90:10:0.1) to give 28 mg of nicotinamide, mp 130°C, identified by HRMS, 1H and 13C NMR spectrometry (Long et al., 1972; Charman et al., 1993; Singhal et al., 1998).

3,4-Dihydro-4β,6-dihydroxy-5-methoxy-2α-methyl-1(2H)-naphthalenone (1) was a yellow gum which resisted attempts at crystallization. FAB HRMS gave the molecular ion + H+ at 223.09664, calcd for C12 H15 O4 (M + H)+ 223.09666; [α]D 59.4° (c = 0.12 g/100 ml, CHCl3). Assignments of the 1H and 13C signals in DMSO-d6 at 300 resp. 75 MHz and the relative stereochemistry were based on COSY, HSQC, HMBC and NOESY experiments and are as follows: δ 2.98 (1 H, m, H-2β), 1.11 (3H, d, J = 6.8 Hz, 2-Me), 1.88 (1H, ddd, J = 13.4, 13.4, 2.8 Hz, H-3α), 2.15 (1H, ddd, J = 13.4, 4.4, 3 Hz, H-3β), 5.03 (1H, ddd, J = 5.8, 2.8, 2.8 Hz, H-4β), 5.24 (1H, d, J = 5.3 Hz, 4-OH), 3.81 (3H, s, 5-OMe), 6.92 (1 H, d, J = 8.5 Hz, H-7), 7.45 (1H, d, J = 8.5 Hz, H-8); δ 198.59 (C-1), 153.25 (C-2), 138.96 (C-4), 123.85 (C-1a), 60.68 (OMe). The assigned stereochemistry, with the aliphatic ring in a half chair conformation, could be derived from the strong NOESY interaction between axial H-2β and axial 4-OH.

4. Taxonomic significance

The secondary metabolites detected in the roots of D. cauliflora are on the whole relatively common natural products and not particularly characteristic of the species or the genus. The exception, the new dihydronaphthalenone 1 (absolute configuration undetermined), appears to have been formed by reduction of diomelquinone A (2-methyl-5-methoxy-6-hydroxy-1,4-naphthoquinone). The latter is a well-known representative of such naphthoquinones which are characteristic secondary metabolites within Diospyros species (Okuyama et al., 1999). However the occurrence of a compound of type 1 within this thoroughly investigated genus has no precedent.

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