Three new dammarane triterpenes, cereotagaloperoxide (1), cereotagal A (2), and cereotagal B (3), together with four known dammarane triterpenes, an oleanane triterpene, and 13 known lupane triterpenes were isolated from the hypocotyls and fruits of Ceriops tagal. The structures of 1–3 were characterized on the basis of their spectroscopic data.

Ceriops tagal (Perr.) C. B. Rob is a mangrove plant belonging to the Rhizophoraceae family. The bark of this plant has been used for the treatment of infected wounds in Thailand and for obstetric and hemorrhagic conditions in the Philippines. As part of our continuing chemical studies on Thai medicinal mangrove plants, we report herein the isolation and structural elucidation of three new dammarane triterpenoids (1–3) along with 18 known compounds from the hypocotyls and fruits of C. tagal.

All compounds were obtained from n-hexane and dichloromethane extracts of the air-dried powdered hypocotyls and fruits of C. tagal, as described in the Experimental Section. Identifications of the known compounds were achieved by comparison with previously reported spectroscopic data and characterized as dammarane triterpenoids: isofouquierol (4),2 fouquierol (5),2 dammarenediol II,2 and ocotillol II.4 The stereochemistry at C-20 of all isolated dammaranes was characterized as S configured by comparison of the carbon chemical shifts at C-17, C-20, and C-21 with the corresponding reported dammaranes.5,18 The other isolates were characterized as oleanolic acid,5 3β-E-feruloylupeol,6 3β-Z-feruloylupeol,6 3β-E-feruloylbetulin,5 3β-E-feruloylbetulinic acid (6),4 3β-E-cafeoylbetulinic acid,3 3β-E-cafeoylbetulonic acid,3 3β-E-comaroylupellic acid,10 3β-α-betulinic acid,11 betulinic acid,12 betulonic acid,14 3α-betulonic acid,15 3β-betulonic acid,14 and lupeol.15 The 13C NMR spectroscopic data of isofouquierol and fouquierol are shown here as the first complete report (Table 2).

The ESITOFMS of 1 revealed a pseudomolecular ion peak at m/z 499.3754 [M + Na]++, corresponding to the molecular formula C_{30}H_{52}O_{4} (calcd for C_{30}H_{52}O_{4}Na m/z 499.3763). The EIMS showed fragment peaks at m/z 317 [M–side chain]+, 299 [M–side chain – H_{2}O]+, 207 [side chain + ring D – HO_{2}]+, and 125 [side chain – H_{2}O]+. The IR spectrum displayed absorption bands at 3450 and 1655 cm^{-1} for hydroxyl and double-bond functionalities, respectively. In the 13C NMR spectrum (Table 2), compound 1 showed 30 carbon resonances, of which the signals of C-1 to C-19 and C-28 to C-30 agreed well with those of compounds 4 and 5 (Table 1). Therefore, compound 1 was suggested to be a dammarane triterpenoid derivative. Characteristic for a tetracyclic dammarane, five methyl singlets at δ 0.78 (Me-29), 0.85 (Me-19), 0.87 (Me-30), 0.96 (Me-18), and 0.97 (Me-28) appeared in the 1H NMR spectrum of 1. The oxymethine proton (H-3) resonated at δ 3.20 (dd, J = 11.1, 5.7 Hz), showing J values consistent with an axial orientation.16 The 13C NMR spectrum and DEPT experiments revealed the side chain (C-20 to C-27) as having two methyls (δ 17.1, 24.6), three methylenes (δ 24.6, 36.5, 113.7), one oxymethine carbon (δ 89.5), and two quaternary carbons (δ 75.1, 144.1). The terminal olefinic methylene protons at δ 5.02 (2H, m) at C-26 (δ 113.7) showed the HMBC correlations with the C-27 vinyl methyl carbon (δ 17.1), the C-25 olefinic carbon (δ 144.1), and the C-24 carbon (δ 89.5). An oxymethine proton at δ 4.31 (t, J
The presence of a hydroperoxy group at C-24 was supported structurally as \(20(16.3 \text{ Hz})\) at C-24 (Table 1). The IR spectrum showed the same pattern as that of \(1\). The NMR spectroscopic data of the side chain (C-20 to C-27) of \(2\) agreed well with those of fouquierol (5) (Table 2). Thus, compound \(2\) (cereotagalol A) was identified as 20(S)-3β,20,24,28-tetrahydroxydammar-24-ene.

Compound \(3\) was obtained as a colorless gum. This compound also exhibited a pseudomolecular ion peak [M + Na\(^+\)] at m/z 499.3754 in the ESITOFMS. The \(^1H\) and \(^{13}C\) NMR spectra for the tetracyclic moiety of \(3\) (Tables 1 and 2) were similar to those of \(2\), with signals for the hydroxymethylene protons at \(\delta 3.72\) and \(3.43\) and \(\delta 1.33\) and Me-27 and 28. The \(^1H\) NMR spectroscopic data of the side chain (C-20 to C-27) of \(3\) agreed well with those of isofouquierol (4) and isofouquierol. Thus, compound \(3\) (cereotagalol B) was identified as 20(S)-3β,20,25,28-tetrahydroxydammar-23-ene.

Most isolates from \(C. tagal\) were tested for cytotoxic activity. Only 3β-E-feruloylbeutelinic acid (6) exhibited potend.
cytotoxic activity for KB, BC, and NIC-H187 cell lines, with IC_{50} values of 3.8, 3.0, and 1.8 µg/mL, respectively.

**Experimental Section**

**General Experimental Procedures.** Melting points were determined on a Electrothermal melting point apparatus model IA6301 and were uncorrected. Optical rotations were measured on an Autopol II automatic polarimeter. UV spectra were determined on a Shimazu UV 160A spectrophotometer. The IR spectra were recorded on a Nicolet Magna IR 560 spectrophotometer and a Perkin-Elmer 2000 spectrophotometer. 1D and 2D NMR spectra were recorded on a Bruker Avance-300 spectrometer, operating at 300 MHz for proton and 75 MHz for carbon. Chemical shifts (δ) were expressed in ppm with reference to internal TMS in CDCl₃. The EIMS was performed using a Thermofinnigan MAT 95 XL mass spectrometer. The ESITOFMS were obtained on a Micromass LCT mass spectrometer. Quick column chromatography and column chromatography were carried out on silica gel 60 F254 and silica gel 100, respectively. Precoated plates of silica gel 60 GF254 were used for analytical purposes.

**Plant Material.** The hypoxocots and fruits of *C. tagal* were collected at the Mangrove Research Station in Nakhon Si Thammarat Province, Thailand, in November 2002. The plant was identified by Prof. Puangpen Sirirugs, Department of Biology, Faculty of Science, Prince of Songkla University, Songkhla, Thailand, and a voucher specimen (No. FSU 0012581) has been deposited at the same institute.

**Extraction and Isolation.** Dried milled hypocotyls of *C. tagal* (5.3 kg) were extracted with hexane and CH₂Cl₂, successively. Evaporation resulted in the crude extracts of hexane (6.0 g) and CH₂Cl₂ (6.1 g) extracts. The combined dried crude hexane and CH₂Cl₂ extracts (12.1 g) was subjected to quick column chromatography using gradient elution by a mixture of hexane and ethyl acetate (10:0–7:3) to afford 10 fractions (C01–C10) on the basis of TLC analysis. Fraction C06 (443 mg) was subjected to quick column chromatography using hexane–ethyl acetate (9:1) as eluting solvent, to afford dammarenediol II (31 mg) and compound I (40 mg), the latter after crystallization from acetone. Fraction C07 (717 mg) was subjected to quick column chromatography using gradient elution of a hexane and acetone mixture with increasing polarity (9:1–8:2) to afford oleanolic acid (30 mg), ocolitoll II (6 mg), fougleriol (12 mg), and isofuquiferol (6 mg).

**Bioassay.** The cytotoxicity assay employed the colorimetric method. The reference substances, ellipticine, exhibited activities toward human oral epidermoid carcinoma (BC), human breast cancer (KB), and human small cell lung cancer (NCI-H187) cell lines in the IC_{50} range of 0.3–0.6 µg/mL.

**Cereotagalolperoxide (1):** an amorphous powder; mp 183–185 °C; [α]_D²⁷ +54.1 (c 0.4, MeOH); IR (KBr) ν_max 3450, 1655, 1460, 1375 cm⁻¹; ¹H NMR data, see Table 1; ¹³C NMR data, see Table 2; ESITOFMS m/z 476 [M⁺] (0.5), 317 (5), 299 (10), 207 (60), 125 (100); ESITOFMS m/z 499.3754 (calculated for C₂₉H₆₁O₅Na, 499.3763).  

**Cereotagalol A (2):** colorless gum; [α]_D²⁷ +52.6 (c 0.02, MeOH); IR (KBr) ν_max 3390, 1660, 1380 cm⁻¹; ¹H NMR data, see Table 1; ¹³C NMR data, see Table 2; ESITOFMS m/z 497.3677 (calculated for C₂₉H₆₀O₅Na, 497.3673).

**Cereotagalol B (3):** colorless gum; [α]_D²⁷ +55.6 (c 0.02, MeOH); IR (KBr) ν_max 3480 cm⁻¹; ¹H NMR data, see Table 1; ¹³C NMR data, see Table 2; ESITOFMS m/z 499.3754 (calculated for C₂₉H₆₁O₅Na, 499.3763).

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**References and Notes**


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